CHAPTER IV
DEVELOPMENT OF POLYBENZOXAZINE MEMBRANES
FOR ETHANOL/WATER SEPARATION

4.1 Abstract

Gasohol has been widely used in recent years because it has many advantages when compared with normal gasoline. However, high purity of ethanol is required for gasohol to mix with gasoline. Pervaporation is the new technique for separation of the close boiling point azeotropic mixture. For this technique, the membrane is very important because it provides selectivity and permeability to separate the mixtures.

Polybenzoxazine (PBZ) membrane have been prepared from bisphenol-A, formaldehyde, and two difference type of diamines, 1,6-hexanediamine (hda) and ethylenediamine (eda) to use as pervaporation membranes. Both poly (BA-hda) and poly (BA-eda) membrane were suitable for ethanol/water separation by using pervaporation at the feeding temperature of 70 °C, and membrane thickness of 200 μm. However, poly (BA-hda) membrane provided high permeation flux and separation factor with increasing ethanol concentration while the continuous increasing of ethanol concentration showed insignificant effect on permeation flux and separation factor.

Keywords: Gasohol, Azeotropic Pervaporation, Polybenzoxazine

4.2 Introduction

The development of alternative renewable energy has been one of the main research focus due to the energy crisis and environmental concern related to fossil fuels. One of these clean forms of renewable energy is biofuel that includes biodiesel, bioethanol, biomethanol, biogas, etc. These fuels are produced from agricultural and industries waste which are a very low prime cost by fermentation process [1]. Bioethanol is focused as it can be mixed with gasolineto form "Gasohol" which obtains many advantages including higher octane number and better antiknock properties than gasoline and very low cost compared with traditional petroleum based fuel. Moreover, it burns more slowly and dissipate less heat, its combustion process is complete resulting in reduced emission of some pollutants. However, the products from this process contain not only ethanol but also other by-products such as water. Therefore, in order to acquire bioethanol from fermentation process, the separation of bioethanol from other by-products is essentially.

Several separation techniques to achieve ethanol have been studied including liquid-liquid extraction, carbon absorption, air stripping and particularly distillation process which is a common technology used in the petrochemical industry [2]. However, these techniques require high operating cost, high energy and have some limitations to make them unattractive for azeotropic isomeric mixtures separation so they are not suitable for industrial applications [3]. Therefore, new technique was invented to solve these problems. The pervaporation (PV) technique is an interesting candidate for ethanol/water separation whichalso has several advantages over traditional distillation process such as reduced energy consumption and simple equipment since only a vacuum pump is needed to create a driving force leading to lower capital cost. The pervaporation technique utilizes the concept of partial vaporization of a liquid through a dense membrane. This separation technique using polymer membranes, which is the basis for separating, has received much attention due to the design flexibility in order to improve the selectivity and permeability [4]. Many polymer types have used to study the separation performance in pervaporation process including polybenzoxazine (PBZ) whichis a class of

phenolic resin providing many advantages such as high glass-transition temperature (T_g), high thermal stability, low shrinkage, no need of catalyst for polymerization, no by-product or volatile generation, excellent dimensional stability, low water absorption and rich molecular design flexiblility. The polybenzoxazine precursors have been synthesized from various aromatic/aliphatic amines, mono/diphenols, and formaldehyde [5].One approach is to synthesize polybenzoxazine from low molecular weight monomer by using monofunctional amine, phenol, and formaldehyde as reactants. However, polybenzoxazines obtained via this approach usually suffers from brittleness. Another method is to prepare polybenzoxazine from high molecular weight oligomers from diamine, bisphenol-A, and formaldehyde [6,7]. The properties of polybenzoxazines derived from this approachare greatly improved in flexibility when compared with cured films from the typical low molecular weight precursors. Hence, polybenzoxazine can be tailored as desired which makes it a great candidate for membrane separation [8,9,10]. The performance and stability of these membranes should be concerned withmixed solvents media due to the sorption and swelling of the membrane matrix influence to the mixture separation. As a result, it is important to study the suitable condition in order to receivethe high separation performance. In order to use polybenzoxazine membrane in the pervaporation process, the permeate water flux and separation factor of the ethanol and water mixture are investigated.

The objective of this work is to study the effect of chemical structure, temperature of the mixture and mixture content on the ethanol/water separation efficiency.

4.3 Experimental

4.3.1 Materials

1,4-Dioxane (Lab-Scan), bisphenol-A (97% purity) (Aldrich), ethanol (99.9% purity) (J.T. Baker; White Group), formaldehyde (37%wt. in water) (Merck),

1,6-Hexanediamine (had, 98% purity) (Aldrich) and ethylenediamine (99%purity) (Fluka) were used without treatment.

4.3.2 Measurements

Polybenzoxazine precursors obtained from the reactions were characterized by using Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded ona Varian Mercury 300 (300 MHz) instrument. To identify chemical composition was characterized in the range of 1-5 ppm. The prepared polybenzoxazine precursors were dissolved in deuterated chloroform ($CDCl_3$) for 24 h prior to use. Attenuated Total Reflectance Infrared Spectrometer (ATR-IR) spectra of membranes were obtained from a Thermo Nicolet Nexus 670 by using ZnSe 45° (flat plate) with scans at a scanning resolution of 4 cm^{-1}. The morphology was investigated using Scanning Electron Microscopy (SEM) (JEOL model JSM-5410LV). This technique was done at a faculty of Dentist, Chulalongkorn University. Thermogravimetric Analyzer (TGA) was used to carried out by using a Perkin-Elmer Pyris Diamond with heating rate of 20°C/min under a N_2 flow. The thermogravimetric data was recorded from 25 to 750 °C.
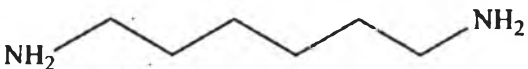
4.3.3 Methodology

4.3.3.1 Synthesis of Polybenzoxazine Precursors

Polybenzoxazine precursors were prepared by using bisphenol-A, formaldehyde and two types of diamines as shown in table 4.1., with mole ratio of 1:4:1, respectively [19]. To synthesizing poly (BA-1,6-hexadiamine) and poly(BA-ethylenediamine) membranes, bisphenol-A 6.84 gand 4.56 g were dissolved in a 1,4-dioxane (15 ml) in 50 ml glass bottle, respectively, and then stired until the clear solution was obtained. Formaldehyde solution at 9.73 g and 6.5 g were added into the

bisphenol- A solution, consecutively. The temperature was kept under 10°C using an ice bath. After that diamine was added dropwise into the mixture and stirred continuously for approximately 1 hour until transparent yellow viscous liquid was obtained [11]. Next, the mixture was heated at 100°C and stirred continuously until transparent yellowish viscous liquid was obtained. The products was then purified filtering, washing once with 0.1 M NaHCO₃ aqueous solution 200 ml, and drying under vacuum afforded as white powder. The purified benzoxazine precursors were then characterized by using ^1H NMR .

Table 4.1 The chemical structure of diamines.

Diamines	Chemical structures
1,6-hexanediamine (hda)	
Ethylenediamine (eda)	

4.3.3.2 Preparation of Polybenzoxazine Membranes

Two polybenzoxazine precursors obtained from the reactions were cast on the glass plate at room temperature with thickness of approximately 100, 200 and 300 μm using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membranes were dried at room temperature in air for one day yielding the yellow transparent membranes. The membranes were then further dried at 80°C in an air-circulating oven for 24 h. Figure 4.1 depicts the chemical structure of polybenzoxzine membranes [12,13].
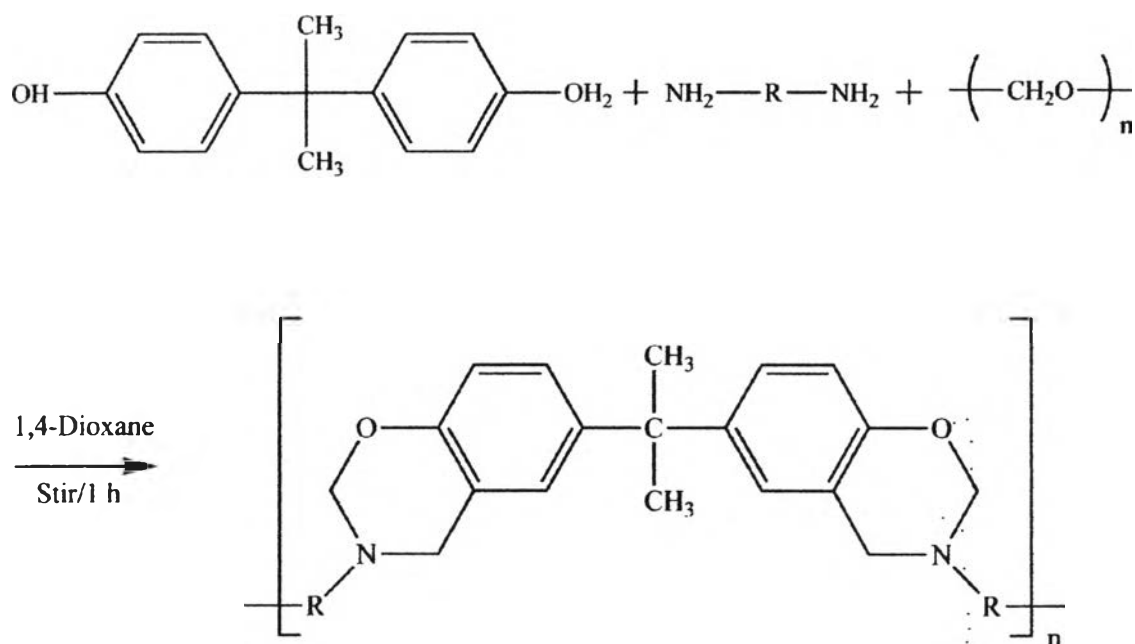
$$OH-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH_2 + NH_2-R-NH_2 + \left(CH_2O\right)_n$$

1,4-Dioxane
$\xrightarrow{\text{Stir/1 h}}$

$$\left[\begin{array}{c} O\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}O \\ N-R R-N \end{array}\right]_n$$

Figure 4.1 The chemical structure of polybenzoxazine membranes.

4.3.3.3 Pervaporation System

A schematic diagram of the system used to carry out the pervaporation experiments is shown in Figure 4.2. The membrane is supported on a stainless steel disc which separated the cell into two compartments. The feed was studied at 40, 50, 60 and 70°C in the cell. The ethanol content of the mixture including 5, 10, 15 and 20 % by volume were used as the feed solution. The flow rate of 900 ml/min was used to circulate the mixtures from the feed reservoir to a permeation cell [14].

A Teflon gasket was applied on the membrane. After the membrane was placed in the chamber, then the two compartments were fixed together to prohibit the leakage. The capacity of the upper cell compartment is approximately 100 ml, while the area of the membrane in contact with the liquid is 22.07 cm^2. A hot plate was used to control the feed solution temperature. The mixtures were stirred continuously during the experiments. Vacuum was applied to the permeate side of the membrane, and the permeate vapor was condensed and collected in a cold trap immersed in liquid nitrogen [15].

The performances of membranes were determined by measuring % ethanol in permeate side to calculate the total water flux (kg/m^2hr) and the separation factor of ethanol/water mixture. The quantities of ethanol and water were determined using gas chromatography on an Agilent GC-6890. A ZEBRON-WAX (30 m x 0.25 mm I.D.). Samples of 0.5 μL were injected under the following conditions: the carrier gas was helium and set at 55 kPa for TCD were maintained. The isothermal oven temperature was set at 200°C, while the injector and detectortemperatures were set at 200°C and 250°C, respectively.
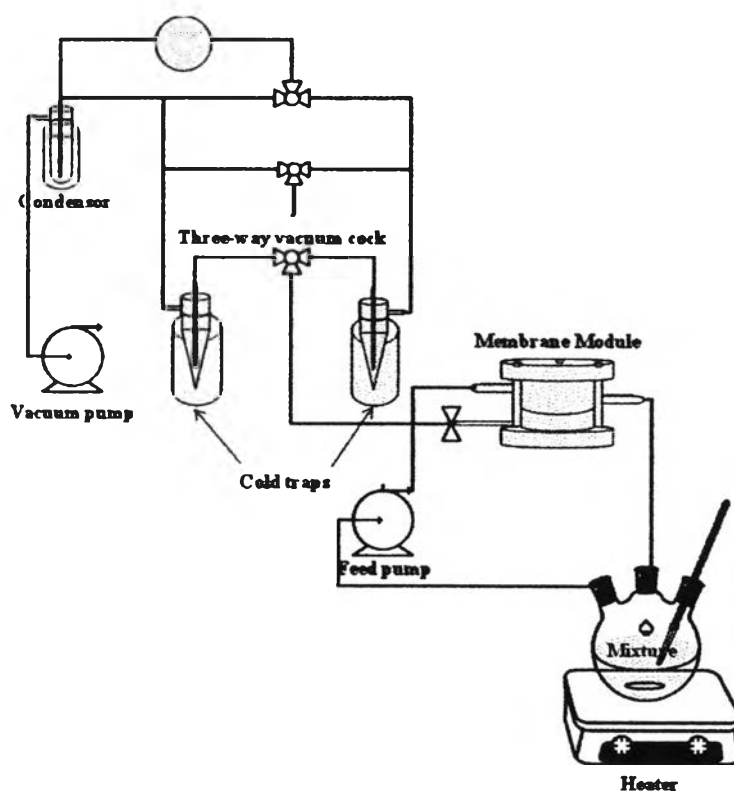

Figure 4.2 Experimental set up for the pervaporation apparatus.

4.4 Results and Discussion

4.4.1 Characterization of Polybenzoxazine Precursors

Polybenzoxazine precursors, abbreviated as Poly(BA-hda) and Poly(BA-eda) were derived from the reaction of diamine, bisphenol-A and formaldehyde at the

molar ratio of 1:1:4 via quasi-solventless approach in which 1,4-Dioxane was added with all reactants in order to adjust the viscosity of the mixtures.

4.4.1.1 Proton Nuclear Magnetic Resonance (^1H NMR)

The ^{1}H NMR measurement was conducted to confirm the chemical structure of the obtained precursor.

The ^{1}H NMR spectra are shown in Figure 4.3. In case of membranes derived from Poly (BA-1,6 hexadiamine), the characteristic peaks assigned to the methylene protons of ($O-CH_2-N$) and ($Ar-CH_2-N$) of oxazine ring were observed at 4.80 and 3.90 ppm, respectively. The methyl protons of bisphenol-A and ethylene protons of 1,6-hexadiamine show the peaks at 1.57 and 2.85 ppm, respectively. For the ^{1}H-NMR spectrum of Poly (BA-ethylenediamine), the characteristic peaks assigned to the methylene protons of ($O-CH_2-N$) and ($Ar-CH_2-N$) of oxazine ring were observed at 4.85 and 3.98 ppm, respectively. The methyl protons of bisphenol-A and ethylene protons of ethylenediamine show the peaks at 1.56 and 2.95 ppm, respectively. These results are strongly ageed with the results reported by Takeichi et al. [16,17].
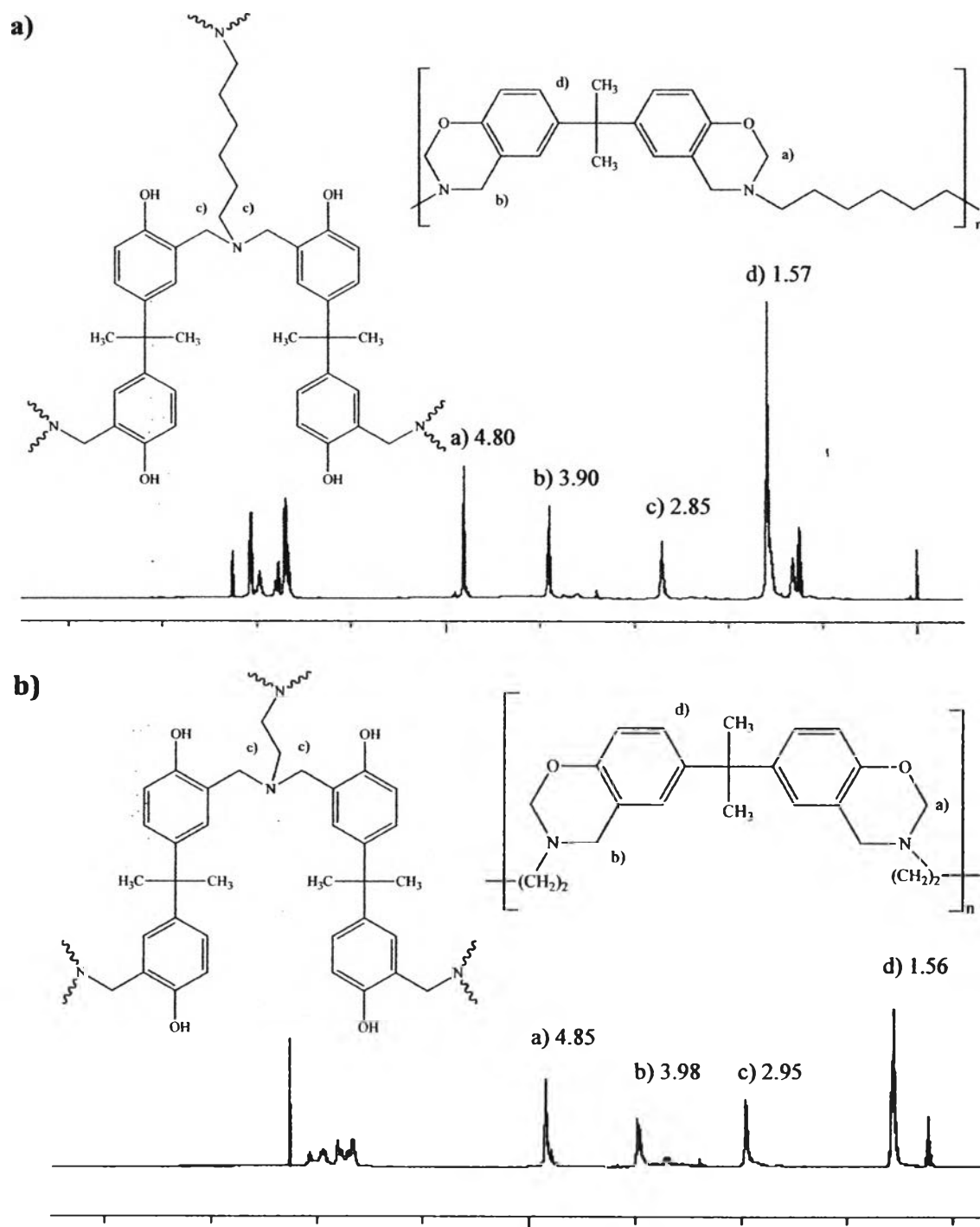
Figure 4.3 ¹H NMR spectra of polybenzoxazine precursors: Poly(BA-hda) (a) and Poly(BA-eda) (b).

4.4.2 Polybenzoxazine Membrane Characterizations

4.4.2.1 Attenuated Total Reflectance Infrared Spectrometer (ATR-IR)

The chemical structure of the prepared polybenzoxazine membranes were confirmed by using ATR-IR, as shown in Figure 4.4
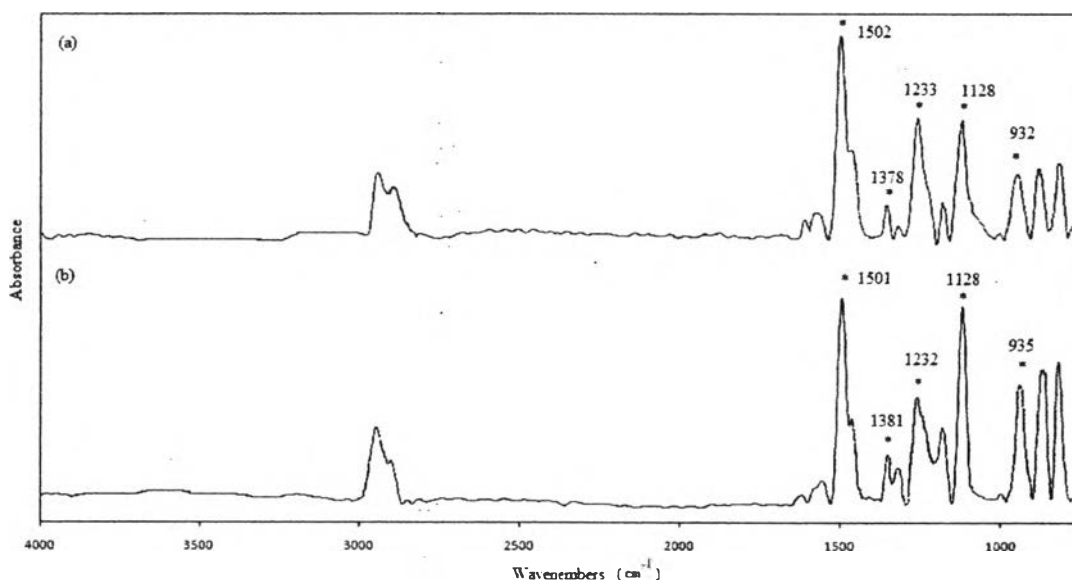

Figure 4.4 ATR-IR spectra of poybenzoxazine membranes: Poly(BA-hda) (a) and Poly(BA-eda) (b).

Poly(BA-hda) membrane shows the band at 1502 cm^{-1} representing the stretching of trisubstituted benzene ring. The – out - of plane bending vibration of C–H was observed at 932 cm^{-1}. In addition, the band assigned to the asymmetric stretching of C–O–C and C–N–C were found at 1233 and 1128 cm^{-1}, respectively. Furthermore, the CH$_2$ wagging of oxazine ring was also observed at 1378 cm^{-1}. For poly(BA-eda) membrane, the band at 1501 cm^{-1} represents the stretching of trisubstituted benzene ring and the - out - of plane bending vibration of C–H was observed at 935 cm^{-1}. The bands assigned to asymmetric stretching of C–O–C and C–N–C were found at 1232 and 1128 cm^{-1}, respectively. Moreover, the CH$_2$ wagging of oxazine ring was also observed at 1381 cm^{-1}.

4.4.2.2 Scanning Electron Microscopy (SEM)

Two types of polybenzoxazine membranes used in this study are dense polymeric membranes, as can be seen from the SEM micrographs in Figure 4.5 (a) and 4.5 (b).
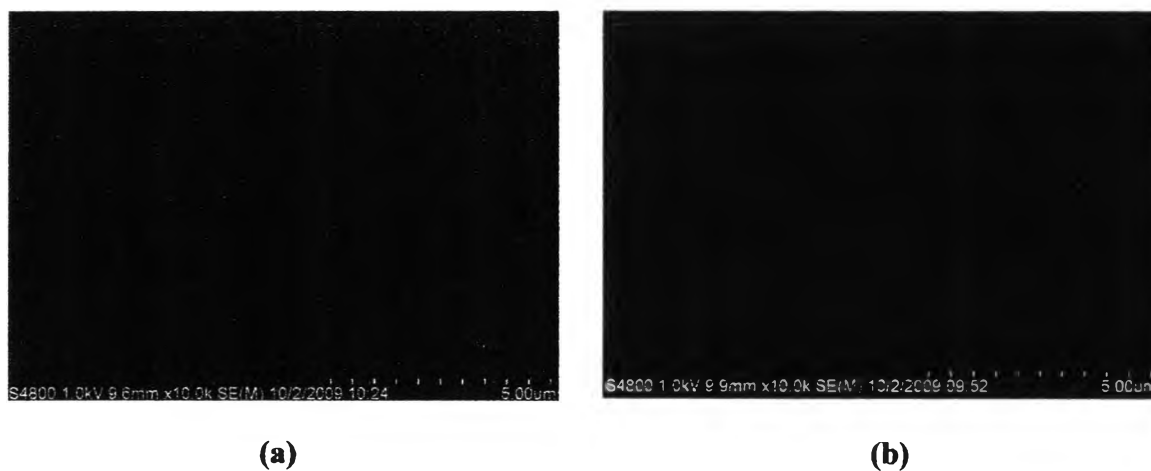

(a)   (b)

Figure 4.5 the SEM micrographs of poybenzoxazine membranes: Poly(BA-hda) (a) and Poly(BA-eda) (b).

4.4.2.3 Thermogravimetric Analyses (TGA)

The thermal stability of polybenzoxazine membranes was investigated by TGA as shown in Figure 4.6 The values of 5 and 10% weight loss temperatures and the char yield are summarized in Table 4.2 The polybenzoxazine membranes obtained from both prepolymers started to degrade around 250°C and the char yield was in the following order: Poly(BA-eda) > Poly(BA-hda). Poly (BA-hda) showed lower the thermal stability and char yield than those of poly(BA-eda) because of its high aliphatic content. These results agree with the results of Takeichi and Agag [11] that the thermal stability of poly(BA-hda) and Poly(BA-eda) began to degrade around 240 °C and char yield was around 25 %and 31%, respectively. In addition, the fully cured Poly (BA-hda) also showed $T_{-5\%}$ and $T_{-10\%}$ of 301 °C and 338 °C, respectively.
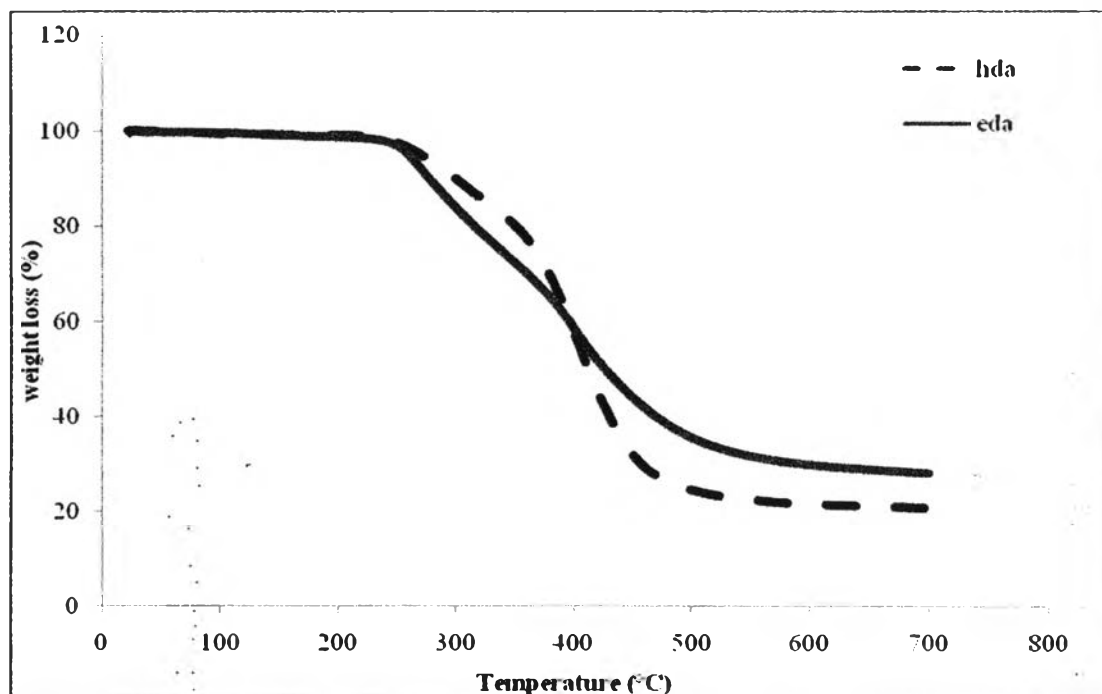
Figure 4.6 The thermal stability of Poly(BA-hda) and Poly(BA-eda) membranes.

Table 4.2 Heat resistance of both polybenzoxazine membranes

Membranes	$T_{-5\%}$ (°C)	$T_{-10\%}$ (°C)	% Char yield
Poly(BA-eda)	260	277	27
Poly(BA-hda)	270	290	20

4.4.3 *Pervaporation Analysis*

4.4.3.1 Effect of temperature

From our previous study, it was found that poly (BA-hda) membrane provided the highest permeation flux of 1.52 kg/m² at the thickness of 200 μm and testing temperature of 70°C. Thus, in this study, the effect of the feed temperature

(40-70 °C), the membrane thickness (100-300 μm) and the mixture content (5-20 % by volume of ethanol) were further investigated.
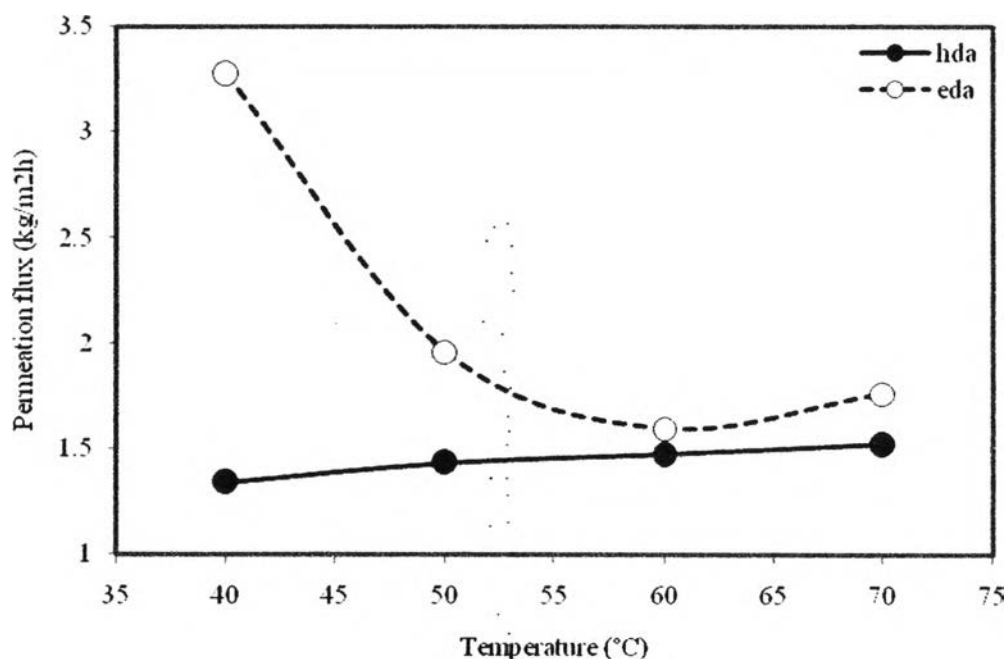

Figure 4.7 Comparison of the permeation flux between poly(BA-hda) and poly(BA-eda) membrane as a function of feeding temperature.

Table 4.3 Comparison of the separation factor of the pervaporation process between poly(BA-hda) and poly(BA-eda) membrane as a function of feeding temperature.

Temperature (°C)	Separation Factor	
	BZ-hda	BZ-eda
40	> 10, 000	1.25
50	> 10, 000	20.55
60	> 10, 000	> 10, 000
70	> 10, 000	> 10, 000

Poly (BA-eda) membranes showed high permeation flux and low separation factor at low temperature (40-50 ° C) as shown in fig. 4.7 and table 4.3 because the feed solution was still in the liquid phase in the permeate side but at high temperature (60-70 °C), only vapor phase was obtained resulting in lower permeation flux and high separation factor. However, poly (BA-hda) membranes showed high permeation flux with increasing temperature because it provided only vapor phase.

The effect of pervaporation temperature was investigated by Huang and Yeom [18] who suggested that the apparent activation energy was a function of permeate concentrations because of the plasticizing effect of the permeants and the interaction between the permeants and the polymer. In order to investigate the effect of temperature on the flux and separation factor, the Arrhenius-type equation was used to explain the relationship between temperature and permeation flux which agree with the explanation of Qunhui et al. [19]

$$J = J_o \exp\left(\frac{-Ep}{RT}\right) \tag{1}$$

Where J_o is permeation rate constant, R is gas constant, T is temperature in terms of Kelvin, and Ep is activation energy for permeation which can be obtained from the slope of curve plotted between ln J and 1/T. The activation energy shows the amount of energy in excess of the average energy level required to permeate through the membrane.

From the principle of pervaporation, the permeate component will undergo a liquid-vapor phase change when it passes through a dense polymeric membrane and finally, only vapor phase pass through the permeate side. Therefore, the separation performance and the activation energy are generally determined from vapor phase of the permeated side. In case of poly(BA-hda) membrane, we found that the activation energy can be calculated at every testing temperature(3.74 kJ/mol). However, in case of poly(BA-eda) membrane, the vapor phase appeared at only high testing temperature (60-70 °C). Therefore, the energy activation of both poly(BA-hda) and poly(BA-eda) membrane could be compared at only high testing temperature. The

activation energy of poly(BA-hda) was 3.18 kJ/mol while that of poly(BA-eda) membrane was 9.40 kJ/mol meaning that at high temperature poly(BA-eda) membrane have the exceed energy for water molecules to permeate through membrane more than poly(BA-hda) membrane resulting in poly (BA-eda) membrane showed higher permeation flux than that of poly (BA-hda) membrane. Moreover, at high temperature, both membranes showed high permeation flux and high separation factor which agrees with the explanation of Quihui *et al.* [19] that at high temperature the interactions of the permeated such as those between water-water, water-ethanol and ethanol-ethanol became weaker but the interaction between permeates and membrane was restored so more water could pass through the membrane. In addition, the solubility parameters which is the ratio of molar attraction constant and molar volume constant can also be used to support the affinity of membranes to ethanol. From this calculation, the solubility of water, ethanol, poly(BA-hda) and poly(BA-eda) membrane were 18.63, 8.33, 11.11 and 12.65 $(cal)^{0.5}/ (cm)^{1.5}$, respectively. We can see that the solubility of both poly(BA-hda) and poly(BA-eda) membranes have better affinity to ethanol more than that of water leading to more water permeated to passed through.

However, at low temperature, poly (BA-eda) membrane showed high permeation flux and low separation factor because it have shorter aliphatic chain length leading to less ethanol absorption, then both ethanol and water to passed through and finally, they condensed into liquid phase which is ethanol/water mixture. Moreover, Quihui *et al.* [19] also suggested that at low temperature the interactions of the permeates became stronger and the interaction between permeates and membrane became weaker so both water and ethanol could pass through the membrane. However, poly (BA-hda) membrane which have longer aliphatic chain length could absorb more ethanol content so it provided only water molecules to pass through resulting in low permeation flux and high separation factor.

4.4.3.2 Effect of membrane thickness

After the appropriate temperature of 70°C, which provided highest permeation flux and high separation factor, was acquired, the membrane thicknesses of 100 μm, 200 μm and 300 μm were investigated under the mixture ratio of ethanol and water equal to 1: 9.
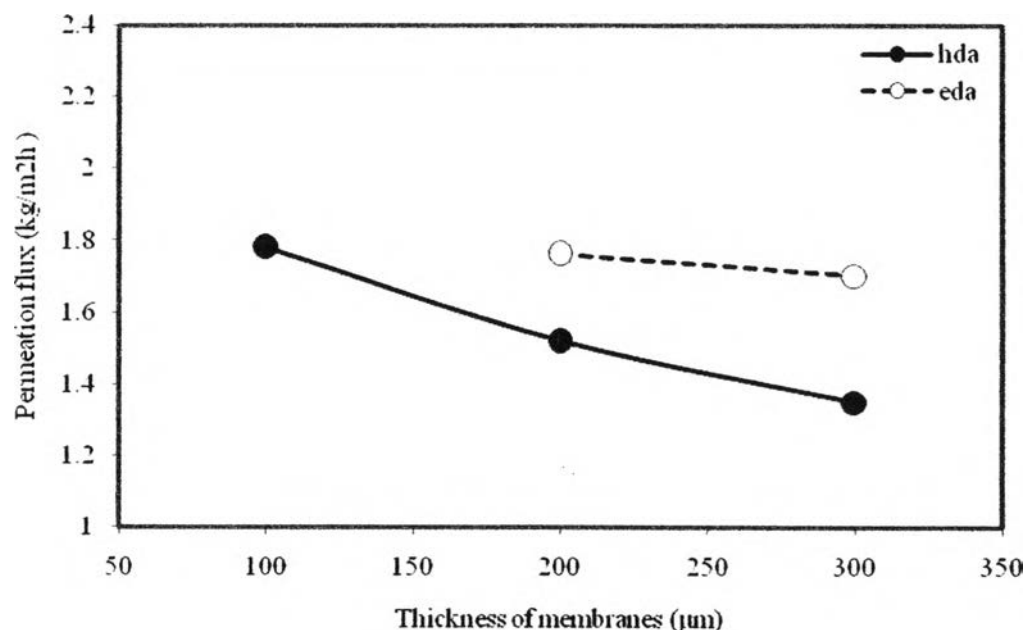

Figure 4.8 Comparison of the permeation flux between poly(BA-hda) and poly(BA-eda) membrane as a function of membrane thickness.

Table 4.4 Comparison of the separation factor of the pervaporation process between poly(BA-hda) and poly(BA-eda) membrane as a function of membrane thickness.

Thickness (μm)	Separation Factor	
	BZ-hda	BZ-eda
100	76.59	0
200	> 10, 000	> 10, 000
300	> 10, 000	> 10, 000

Figure 4.8 and table 4.4 show the permeate water flux and separation factor of pervaporation process using poly(BA-hda) and poly(BA-eda) membrane as a function of the membrane thickness. The tendency of permeation fluxes of both membranes were decreased with increasing the thickness. This results agree with the report of Qunhui *et al.* [19] whose studied the effect of various thickness of the multi-layered membrane to the permeation flux. They found that the swelling profile in the membrane was a function of the thickness and the swelling profile decreased with increasing the amount of layers or increasing the distance between feed part and permeate part. Therefore, the average concentration of the permeates in a thicker membrane can be predicted to be lower than that of a thinner membrane. In our study, at the lowest thickness (100 μm), poly (BA-hda) membrane presented very large amount of the total permeation flux because of high degree of the membrane swelling. Meanwhile, some ethanol molecules were also adsorbed in aliphatic chains of polybenzoxazine membrane resulted in some ethanol molecules passed through the membrane. Nevertheless, the permeation flux of the thinnest poly(BA-eda) membrane (100 μm) could not be obtained since this membrane was more rigid causing the membrane to be brittle and more easily to damage after swelling resulting in the separation factor was not available.

At the thickness of 200 μm, the permeation flux of both membranes was decreased because the degree of swelling was less or has more sorption of ethanol onto the membrane resulted in the separation factor to be more than 10,000. However, poly (BA-eda) membrane presented the permeation flux more than poly(BA-hda) membrane as its short aliphatic chain length provides larger free volume.

The small amount of permeation flux was achieved when membranes with the thickness of 300 μm was used since more water molecules were adsorbed onto the membrane. This result is also in agreement with J.P.G. Villaluenga and co-worker's work [20] whose reported that the permeate flux through membranes decreased with increasing the membrane thickness.

4.4.3.3 Effect of ethanol content

Various ethanol concentrations such as 5, 10, 15, and 20 % by volume were studies. The permeate water flux and separation factor of pervaporation process using poly(BA-hda) and poly(BA-eda) membrane as a function of the ethanol concentration are shown in fig. 4.7 and table 4.4, respectively.
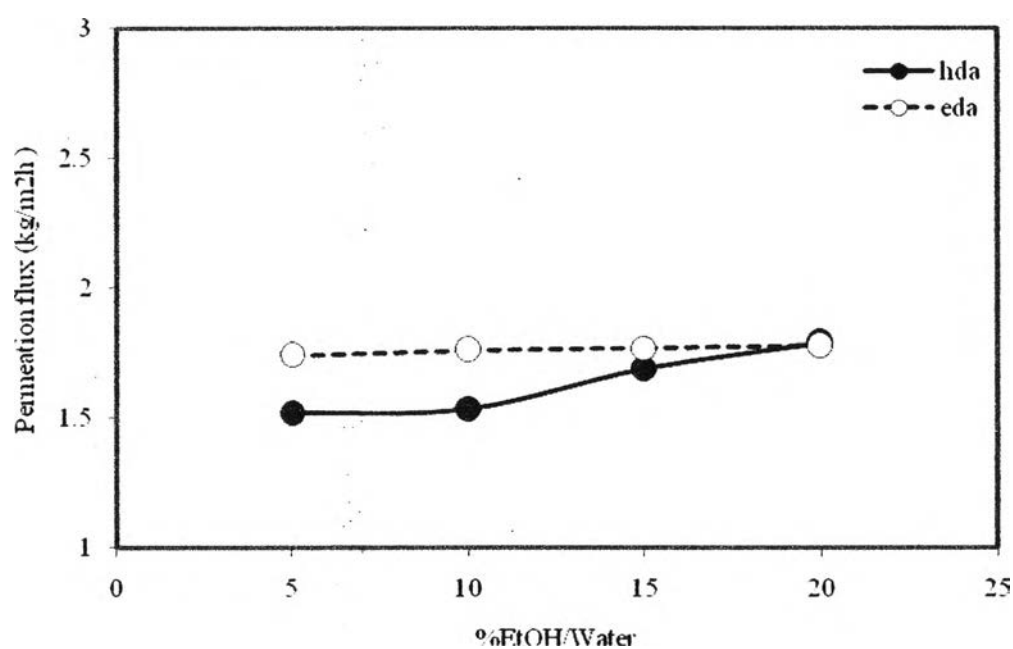

Figure 4.9 Comparison of the permeation flux between poly(BA-hda) and poly(BA-eda) membrane as a function of ethanol content.

Table 4.5 Comparison of the separation factor of the pervaporation process between poly (BA-hda) and poly(BA-eda) membrane as a function of ethanol content.

Ethanol concentration	Separation Factor	
(% by volume)	BZ-hda	BZ-eda
5	> 10, 000	> 10, 000
10	> 10, 000	> 10, 000
15	> 10, 000	> 10, 000
20	> 10, 000	> 10, 000

Huang *et al.* [21] studied the effect of ethanol concentration to the separation of polyphosphazene with three different pendant groups. They concluded that increasing of ethanol content enhanced ethanol sorption into the membrane, and as a result, the membrane swelled more. This results are similar to the results from our study in which both membranes showed high permeation flux and separation factor when ethanol concentration was increased. In case of poly(BA-hda) membrane, the permeation flux increased when the ethanol concentration was increased because of more ethanol absorption due to longer aliphatic chain length resulting in greater swelling ability that allow more water molecules to pass through. However, poly (BA-eda) membrane showed similar permeation flux for each ethanol content (fig.4.9). This is because poly(BA-eda) membrane has less ethanol absorption capacity.

4.5 Conclusions

Polybenzoxazine (PBZ) membranes were successfully synthesized from bisphenol-A, formaldehyde, and two types of diamines, hexamethylenediamine (hda) and ethylenediamine (eda). It was found that both poly(BA-hda) and poly(BA-eda) membranes were suitable for ethanol/water separation at the thickness of 200 μm with the feeding temperature of 70 °C. However, poly(BA-hda) membrane provided high permeation flux and separation factor with increasing ethanol concentration while increasing ethanol concentration showed insignificant effect on permeation flux and separation factor.

4.6 Acknowledgements

4.7 References

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