CHAPTER IV
DEVELOPMENT OF POLYBENZOXAZINE MEMBRANES FOR ETHANOL/WATER SEPARATION

4.1 Abstract

Fermentation is an attractive process for producing feedstock chemicals from renewable biomass. However, the low concentration of the fermentative products creates cost-intensive product separation. The separation of the alcohol from dilute aqueous solutions by distillation is unfavorable since the energy consumption required for purification exceeds the energy content of the alcohol recovered. To make the fermentation process economically attractive, a more efficient alcohol recovery process is preferred. The pervaporation (PV) technique is, especially, attractive for applications such as separation of close-boiling-point liquids or azeotropes, e.g. ethanol/water mixture, which cannot be separated by the standard distillation process; and dense membranes are usually used for the PV. In this study, polybenzoxazine (PBZ) membranes, are successfully synthesized from bisphenol-A, formaldehyde, and three different types of diamines and characterized by ATR-IR and ^{1}H-NMR to confirm the chemical composition. They are effectively used in the PV system for the ethanol/water (12:88 wt%) separation. Poly(BA-hda) membrane shows the best service time. The average of the permeate water flux is found around 0.008–0.01 kg/m^{2}hr and the separation factor is increased to higher than 10,000 with the separation time.

Keywords: Gasohol, Azeotropic, Pervaporation, Polybenzoxazine

4.2 Introduction

Due to the substantial increase in the price of fuels and the global warming concern, the development of alternative renewable energy has been one of the main research focuses. One of these clean forms of renewable energy is biofuel that includes biodiesel, bioethanol, biomethanol, biogas, etc. These fuels are produced from agricultural and industrial waste with a very low prime cost [1]. Gasohol, which is a mixture of gasoline and ethanol, has higher octane number and better antiknock properties than gasoline. Furthermore, it burns slower and dissipates less heat. Its combustion process is complete, resulting in reduced emission of some pollutants. Generally, ethanol used in gasohol is derived from the distillation process which is the common ethanol/water separation technology used in the petrochemical industry [2]. Other techniques, such as liquid-liquid extraction, carbon absorption and air stripping, etc., require high operating costs and in some cases have some limitations that make them unattractive for industrial applications [3].

Pervaporation is an interesting candidate for ethanol/water separation. This technique utilizes the concept of partial vaporization of a liquid through a dense polymeric membrane. The separation technique using polymer membranes has received much attention due to the design flexibility to improve the selectivity and permeability [4, 5].

Polybenzoxazine precursors have been synthesized from various aromatic/aliphatic amines, mono/diphenols, and formaldehyde [6–8]. One approach is to synthesize polybenzoxazine from low molecular weight monomers with monofunctional amine, phenol, and formaldehyde. However, polybenzoxazines obtained via this approach usually suffers from brittleness. Another method is to prepare polybenzoxazine from high molecular weight oligomers with diamine, bisphenol-A, and formaldehyde [7, 8]. The properties of polybenzoxazines derived from this approach, especially brittleness, are greatly improved, as compared with cured film from the typical low molecular weight precursors. This will enable polybenzoxazine to be the candidate material for flexible membrane applications [9–11]. The purpose of this work, thus, involves the study of the synthesis and the characteristic properties of polybenzoxazine membranes for ethanol/water separation using pervaporation technique.

4.3 Experimental

4.3.1 Materials

1,4-Dioxane (analytical grade) was purchased from Labscan, Ireland. Bisphenol-A (BPA, 97% purity) and hexa-methylenediamine (hda, 98% purity) were purchased from Aldrich, Germany. Ethanol (99.9% purity) was purchased from J.T. Baker; White Group, Malyasia. Formaldehyde (analytical grade, 37%wt. in water) was purchased from Merck, Germany. Tetraethylenepentamine (TEPA, 85% purity) and tetraethylenetriamine (TETA, 85% purity) were purchased from Fluka, Switzerland.

4.3.2 Measurements

Polybenzoxazine precursors obtained were characterized by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR, Varian Mercury 300), using deuterated chloroform ($CDCl_3$) as solvent. Differential scanning calorimeter (DSC7, Perkin-Elmer) was used to study the polymerization process, using a heating rate of 10 °C/min under N_2 flow. Attenuated total reflectance infrared spectrometer (ATR-IR, Thermo Nicolet Nexus 670) was employed for structural study, using ZnSe 45° (flat plate) with a scanning resolution of 4 cm^{-1}. The membrane morphology was investigated using scanning electron microscopy (SEM, JEOL model JSM-5410LV). Thermogravimetric analyzer (TGA, Perkin-Elmer Pyris Diamond) was used to investigate the thermal stability of membranes, using a heating rate of 20 °C/min under a N_2 flow.

4.3.3 Methodology

4.3.3.1 Synthesis of Polybenzoxazine Precursors

Polybenzoxazine precursors were prepared using bisphenol-A, formaldehyde, and three types of diamines, whose structures are shown in Table 4.1, with a mole ratio of 1:1:4, respectively. Firstly, bisphenol-A (6.84 g, 30 mmol) was dissolved in 15 ml of 1,4-dioxane in a 50 ml glass bottle and stirred until obtaining a clear solution. Formaldehyde solution (9.73 g, 324 mmol) was then added to bisphenol-A solution. The temperature was kept under 10 °C by using an ice bath.

Diamine was then added dropwise into the mixture with continuously stirring for approximately 1 hour. Transparent yellow viscous liquid was obtained [12]. However, when hda was used as the reactant, the mixture needed heat treatment, 100 °C, to drive the reaction go with stirring continuously until transparent yellowish viscous liquid was obtained, implying that hda has lower reactivity than those of TEPA and TETA. Benzoxazine precursors were then purified by washing with 200 ml of 0.1 M NaHCO₃ solution before removing solvent by evaporation and drying under vacuum. The purified benzoxazine precursors were then characterized using ¹H-NMR [6].

Table 4.1 The chemical structures of diamines

Diamine	Chemical structure
Tetraethylenepentamine (TEPA)	(chemical structure)
Triethylenetetramine (TETA)	(chemical structure)
hexamethylenediamine (hda)	(chemical structure)
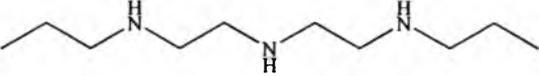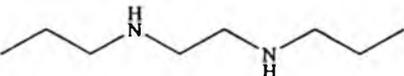
4.3.3.2 Preparation of Polybenzoxazine Membranes

Polybenzoxazine precursors obtained from the reactions were cast on a glass plate at room temperature with the thickness of approximately 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 hours to remove excess solvent. Figure 4.1 depicts the synthesis of polybenzoxzine membranes [7, 8].

4.3.3.3 Pervaporation System

A schematic diagram of pervaporation experiment is shown in Figure 4.2. The membrane was equipped in a stainless steel module. The feed was

maintained at 70 °C in the cell. The mixture of ethanol and water (1:9) was used as the feed solution. The flow rate of 900 ml/min was used to circulate the mixture from the feed reservoir to a permeation cell. This condition was similar to the work done by Hsueh et al. [13], carrying out the experiment using different of the ethanol/ water ratios.
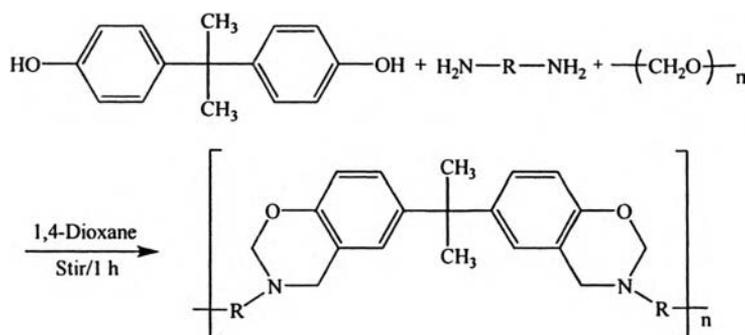

Figure 4.1 The synthesis of polybenzoxazine.

A Teflon gasket was also applied on the membrane to avoid leaking. The capacity of the upper cell compartment is approximately 100 ml while the area of the membrane in contact with the liquid is 22.1 cm^2. A water bath on a hot plate was used to control the feed solution temperature. The mixture was stirred continuously during the experiments. Vacuum was applied to the permeate side of the membrane, and the permeate vapour was condensed and collected in a cold trap immersed in liquid nitrogen. [14].

The performances of the membranes were determined by measuring % ethanol in the permeate side to calculate the permeate water flux (kg/m^2hr) and the separation factor of the ethanol/water mixture. The quantities of ethanol and water were determined using gas chromatography (GC) on an Agilent GC-6890. Samples of 0.5 μL were injected under the following conditions: the carrier gas was helium and the pressure was set at 55 kPa for TCD. The isothermal oven temperature was set at 200 °C while the injector and detector temperatures were set at 200 °C and 250 °C, respectively.
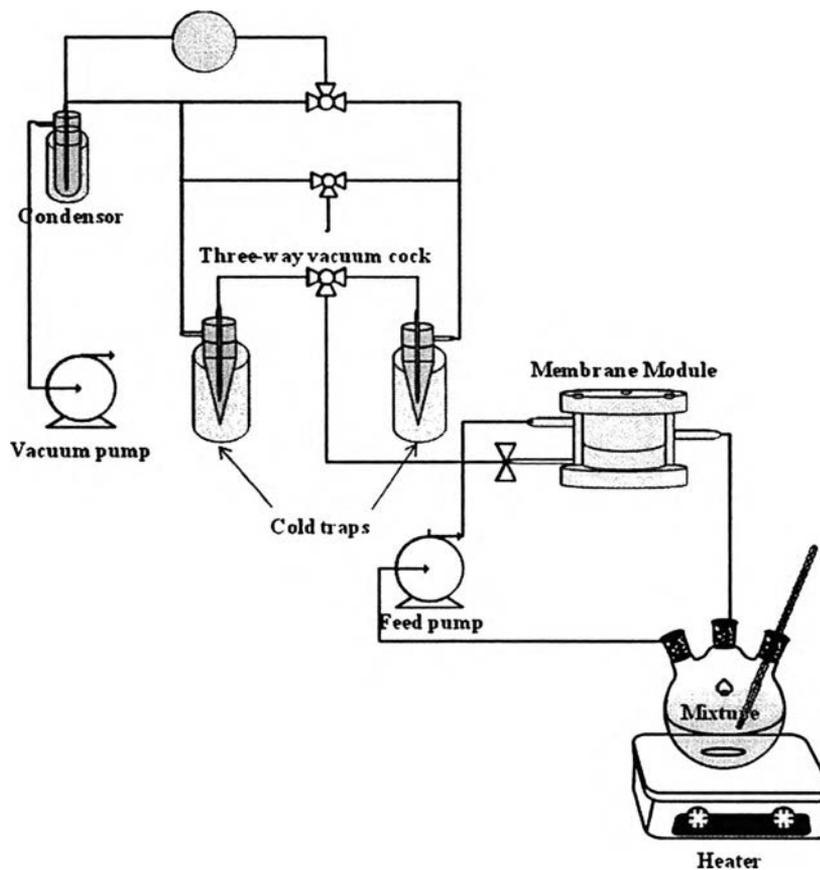
Figure 4.2 Experimental set up for the pervaporation apparatus.

4.3.3.4 Pervaporation Analysis

The permeate water flux (kg/m^2hr) and the separation factor of the ethanol/water mixture (88:12 % by volume) are determine using the quantities of ethanol and water obtained from GC, as follows;

4.3.3.4.1 Permeate Water Flux $(J, kg/m^2hr)$

The J can be calculated from equation 4.1:

$$J = M/At \qquad\qquad (4.1)$$

where   M =   permeate weight (kg)

A =   effective membrane surface area (m^2)

t   =   pervaporation time (hr)

4.3.3.4.2 Separartion Factor ($\alpha_{water/ethanol}$)

The $\alpha_{water/ethanol}$ was calculated from equation 4.2:

$$\alpha_{water/ethanol} = (Y_{water}/Y_{ethanol})/X_{water}/X_{ethanol}) \tag{4.2}$$

where Y_{water} =   the weight fraction of water in the permeate

                  $Y_{ethanol}$ =   the weight fraction of ethanol in the permeate

                  X_{water} =   the weight fraction of water in the the feed

                  $X_{ethanol}$ =   the weight fraction of ethanol in the feed

4.4 Results and Discussion

4.4.1 Characterization of Polybenzoxazine Precursors

Polybenzoxazine precursors, abbreviated as poly(BA-hda), poly(BA-TETA), and poly(BA-TEPA), were derived from the reaction of diamine, bisphenol-A, and formaldehyde at the molar ratio of 1:1:4 via quasi-solventless approach. The quasi-solventless method is our first recovery to employ dioxane for only helping mixing. The reaction takes place within 1 hours at low temperature, unlike the traditional method requiring solvent and long reaction at high temperature, as first described by Takeichi et al. 2007 [7].

The ^{1}H-NMR measurement was conducted to confirm the synthesis process. The ^{1}H-NMR spectra are shown in Figure 4.3. In case of membranes derived from poly(BA-TETA) and poly(BA-TEPA), the characteristic peaks assigned to the methylene protons of $O-CH_2-N$ and $Ar-CH_2-N$ of in the ring-closed benzoxazine ring were observed at around 4.82 and 3.94 ppm, respectively. The methyl protons of bisphenol-A were observed at 1.55 ppm. The methylene protons of the ring-opened benzoxazine in TETA and TEPA showed the peaks around 2.86 ppm. For poly(BA-hda), the characteristic peaks assigned to the methylene protons of $O-CH_2-N$ and $Ar-CH_2-N$ of in the ring-closed benzoxazine ring were observed at 4.80 and 3.90 ppm, respectively. In addition, methyl protons of bisphenol-A and methylene protons of the ring-opened benzoxazine in hda were observed at 1.57 and 2.85 ppm, respectively. These results are strongly agreed with the results reported by Takeichi

et al. [6, 7] who also found that the characteristic peaks corresponding to methylene protons of $O-CH_2-N$ and $Ar-CH_2-N$ in the ring-closed benzoxazine structure were at 4.86 and 3.97 ppm, respectively. Additionally, the methylene protons of the ring-opened benzoxazine of $Ar-CH_2-N$ also showed at 2.85 ppm, and the methyl protons of bisphenol-A showed peaks at 1.58 ppm.
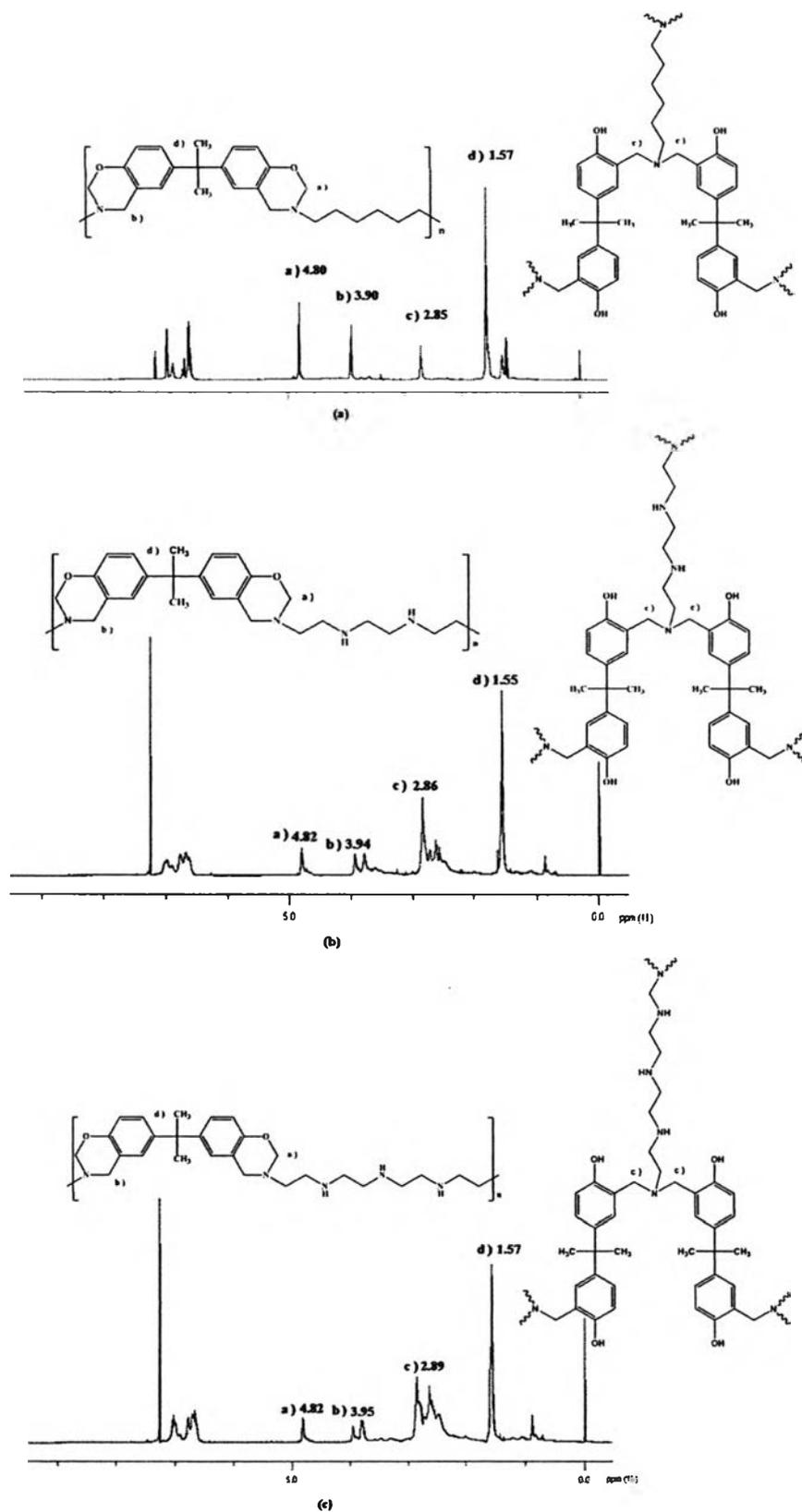
Figure 4.3 ¹H-NMR spectra of polybenzoxazine precursors: poly(BA-hda) (a), poly(BA-TETA) (b), and poly(BA-TEPA) (c).

4.4.2 Polybenzoxazine Membrane Characterizations

The precursors were dissolved in 1,4-dioxane and cast on a glass plate with a thickness around 300 μm. The obtained membranes after being dried at 80 °C for 24 hours gave the thickness around 200 μm, and were characterized as follows;

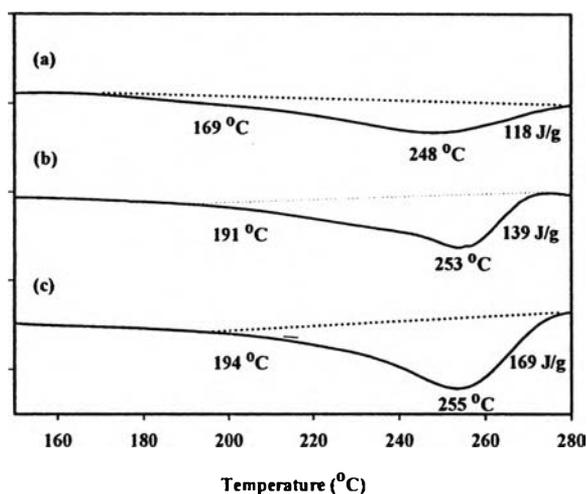DSC thermograms of polybenzoxazine membranes are shown in Figure 4.4.

Figure 4.4 DSC thermograms of polybenzoxazine membranes: poly(BA-hda) (a), poly(BA-TETA) (b), and poly(BA-TEPA) (c).

The progress of ring-opening polymerization of the polybenzoxazine membranes were monitored by DSC. The DSC thermograms of partially-cured poly(BA-hda) showed the exotherm peak, starting from 169 °C with a maximum at 248 °C, attributed to the benzoxazine ring-opening polymerization. After the precursor was fully cured, the exothermal peak disappeared. This result is similar to Agag and Takeichi' study [8], who reported that poly(BA-hda) showed the exotherm onset at 171 °C with a maximum at 244 °C. When comparing with poly(BA-hda), poly(BA-TEPA) and poly(BA-TETA) have higher nitrogen atoms in the molecule, resulting in stronger H-bonding. Therefore, a larger amount of energy was required.

The chemical structure of the prepared polybenzoxazine membranes were confirmed using ATR-IR, as shown in Figure 4.5.
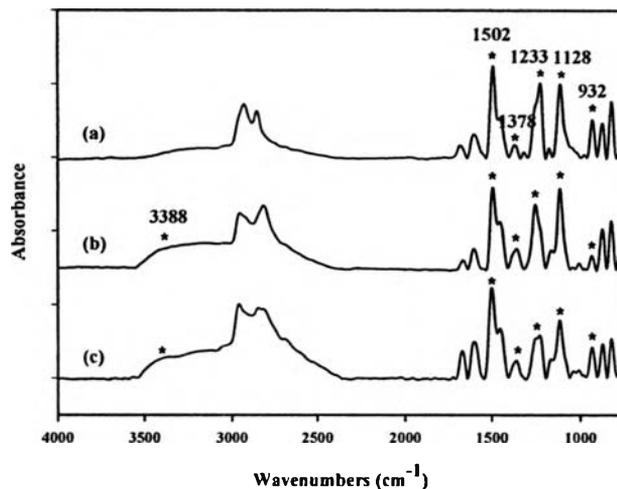
Figure 4.5 ATR-IR spectra of poybenzoxazine membranes: poly(BA-hda) (a), poly(BA-TETA) (b), and poly(BA-TEPA) (c).

The band of N–H stretching of TETA and TEPA was observed around 3400 cm^{-1}. The band at 1502 cm^{-1} represents 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 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}. This FTIR results are in agreement with the study of Ning and Ishida [5], reporting that the asymmetric stretching of C–O–C (1234cm^{-1}), the asymmetric stretching of C–N–C (1180-1187 cm^{-1}) and CH$_2$ wagging of oxazine (1325-1328 cm^{-1}) were observed. Additionally, the characteristic absorptions assigned to trisubstituted benzene ring at 1502-1511 cm^{-1} and out of plane bending vibrations of C–H at 1502-1511 cm^{-1} and 937-943 cm^{-1} were observed, respectively.

Three types of polybenzoxazine membranes used in this study were dense polymeric membranes, as can be seen from the SEM micrographs in Figure 4.6.
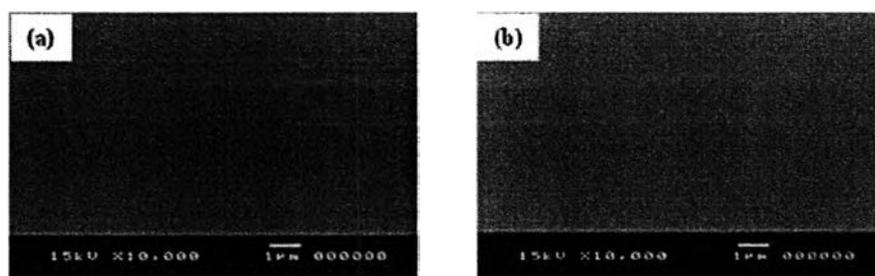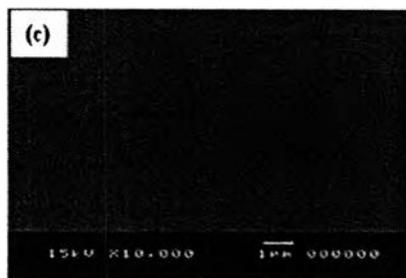
Figure 4.6 SEM micrographs of poly(BA-hda) (a), poly(BA-TETA) (b), and poly(BA-TEPA) (c).

The thermal stability of polybenzoxazine membranes was investigated by TGA, and the results are shown in Figure 4.7.
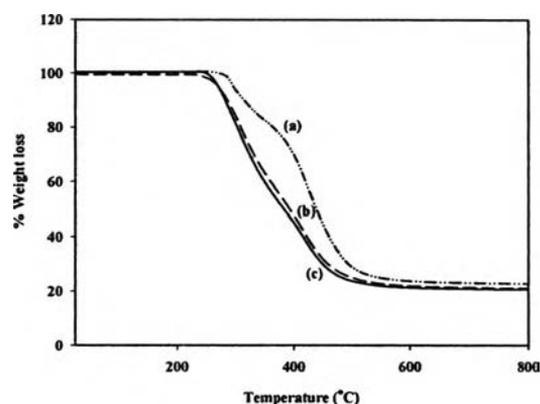

Figure 4.7 TGA thermograms of polybenzoxazine membranes: poly(BA-hda) (a), poly(BA-TETA) (b), and poly(BA-TEPA) (c).

The decomposition temperatures at 5 and 10% weight loss and the char yield were summarized in Table 4.2. Polybenzoxazine membranes obtained from all three prepolymers started to degrade around 240 °C. The char yield of these membranes are in the following order: poly(BA-hda) > poly(BA-TETA) > poly(BA-TEPA). Poly(BA-TEPA) has the lowest char yield due to its high aliphatic content resulting in lower thermal stability. This TGA result is in agreement with the study of Takeichi and Agag [12] who reported that poly(BA-hda) began to degrade around 240 °C and char yield was around 25%.

Table 4.2 Heat resistance of polybenzoxazine membranes

Membrane	$T_{d-5\%}$ (°C)	$T_{d-10\%}$ (°C)	% Char yield
Poly(BA-hda)	295	313	23
Poly(BA-TETA)	269	285	21
Poly(BA-TEPA)	269	281	20

4.4.3 Pervaporation Analysis

The pervaporation analysis of polybenzoxazine membranes is illustrated in Figures 4.8–4.10.
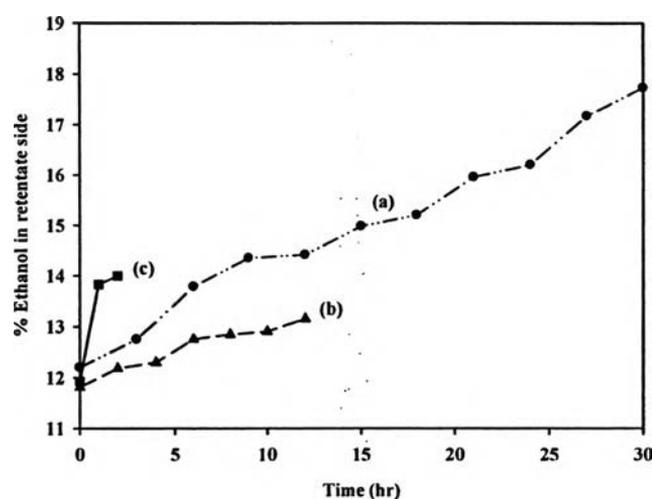

Figure 4.8 % Ethanol in retentate side of pervaporation process as a function of the operating time of poly(BA-hda) (a), poly(BA-TETA) (b), and poly(BA-TEPA) (c) membranes.

Since to make the fermentation process economically attractive, more efficient ethanol recovery process needed [16], in this work we are, thus, concentrating on dilute ethanol in water. The mixture of ethanol and water (12: 88 % by volume) was used as the feed solution. Figure 4.8 shows % ethanol in retentate side, analyzed by GC, as a function of the operating time. Compared with the membranes prepared from poly(BA-TETA) and poly(BA-TEPA), those prepared from poly(BA-hda) showed better physical integrity even after 120 hours. On the other hand, the service time for poly(BA-TETA) and poly(BA-TEPA) membranes

were approximately 12 and 3 hours, respectively. This might be due to the fact that poly(BA-hda) consisted of a long aliphatic chain in the structure, hence, poly(BA-hda) was more flexible whereas poly(BA-TEPA) had nitrogen atoms in the structure which can form H-bonding, leading to swelling and finally damage. Kim and Ishida [17] also described that both intermolecular and intramolecular H-bonding took place in the molecule.

Hsueh *et al.* [13] studied the ethanol/water separation using poly(acrylonitrile-co-acrylic) for pervaporation. They found that water molecules permeated within the membrane by interacting with carboxyl groups of acrylic acid by H-bonding, enabling it to form H-bonds with other free water molecules. Water clusters are, thus, formed in the polymer membrane accordingly. The clustered water shields most penetrating alcohol molecules as they passed through the membrane. Considering our case of using polybenzoxazine membrane, during the pervaporation process (70°C) the water vapor has permeated through polybenzoxazine membranes. This could be due to the vapor pressure of water (31 kPa) is lower than ethanol (72.2 kPa), making water become gas which is easier to permeate through the membrane.

Since poly(BA-hda) membrane showed the best service time, it was chosen for further investigation.

4.4.3.1 Permeate Water Flux using Poly(BA-hda) Membrane

Figure 4.9 shows the permeate water flux of pervaporation process using poly(BA-hda) membrane as a function of the operating time.
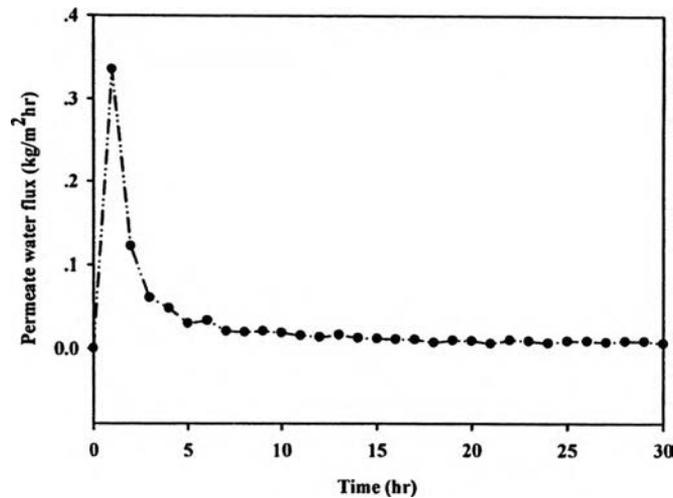
Figure 4.9 Permeate water flux of pervaporation process using poly(BA-hda) membrane as a function of the operating time.

At the beginning, the permeate water flux was the highest, and dramatically decreased. This could be due to the fact that during the pervaporation process, penetrating molecules diffused through free volumes of the membranes in amorphous regions. As a result, at the initial stage, water molecular can pass through free volume and after 2 hours the free volume was then blocked by mixture clusters [13]. The average of the permeate water flux was found around 0.008–0.01 kg/m^{2}hr, and it decreased slowly when increasing time, in agreement with Kurdi and Tremblay [18]. It is owing to the decrease of the amount of water in the retentate while keeping on going of the pervaporation process, resulting in a decrease of the permeate water flux of the system (Ahn *et al.*, 2006, Kuanchertchoo *et al.*, 2007 and Zhang *et al.*, 2004 [19–21]).

4.4.3.2 Separation Factor using Poly(BA-hda) Membrane

Figure 4.10 shows the separation factor of the pervaporation process using poly(BA-hda) membrane as a function of the operating time.
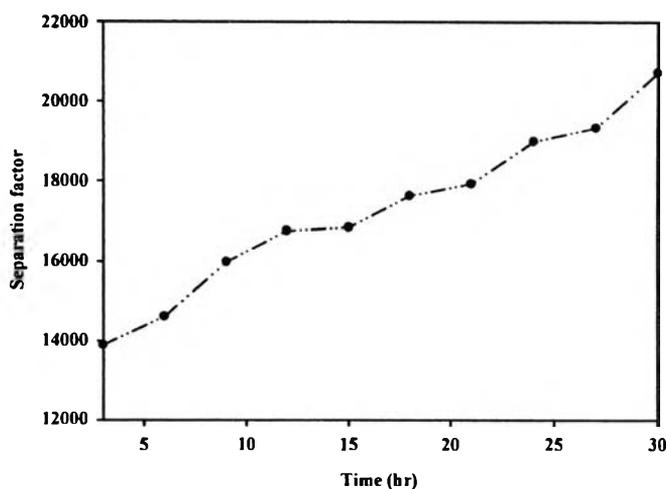
Figure 4.10 Separation factor of the pervaporation process using poly(BA-hda) membrane as a function of the operating time.

The separation factor was increased to higher than 10,000 with the separation time. As mentioned in Kita and coworkers' study [22], the membrane selectivity can be characterized by the separation factor which was increased when % water in the retentate decreased.

4.5 Conclusions

Polybenzoxazine (PBZ) membranes were successfully synthesized from bisphenol-A, formaldehyde, and different types of diamines, including hexa-methylenediamine (hda), tetraethylenepentamine (TEPA) and triethylenetetramine (TETA). It was found that polybenzoxazine membranes were suitable for ethanol/water separation of dilute ethanol in water. Poly(BA-hda) showed the longest service time when comparing with poly(BA-TETA) and poly(BA-TEPA). The total water flux (kg/m^2hr) of poly(BA-hda) membrane for the ethanol/water separation was found around 0.008–0.01 kg/m^2hr and decreased with time due to the free volume in membranes blocked by mixture clusters after 2 hours. The separation factor of poly(BA-hda) membranes for the ethanol/water separation was increased to higher than 10,000.

4.6 Acknowledgements

4.7 References

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