CHAPTER IV
POLYBENZOXAZINE-BASED MEMBRANE FOR ETHANOL—WATER SEPERATION VIA PERVAPORATION

4.1 Abstract

Cardanol-modified polybenzoxazine membrane has been successfully prepared by mixing cardanol into benzoxazine prepolymer to prevent membrane swelling during ethanol-water separation. The maximum cardanol content was 5 wt% because at higher concentrations, cardanol could not mix homogeneously with the benzoxazine precursor. The total permeation flux of this membrane with a 200 µm thickness was 0.33 kg/m^{2}h and the separation factor was higher than 10,000 when 50 wt% of ethanol was used as a feed. Additionally, an increase in permeation flux was achieved by adding NaA into the system since more water could pass through the membrane owing to the increased porosity of the membranes increase as increasing NaA content. However, the separation factor was not affected because the pore size of NaA allowed only water molecules to pass through. When NaA was incorporated (up to 5 wt%), the total permeation flux was increased to 0.98 kg/m^{2}h, while the seperation factor was still higher than 10,000.

Keywords: Cardanol, Polybenzoxazine, NaA zeolite, Ethanol-Water seperation, Pervaporation

4.2 Introduction

Nowadays, the alternative renewable energy becomes an attractive choice of fuel due to the increasing in price of fuel, a serious shortage of fossil resources and environmental concerns, particularly greenhouse gas emissions. One of the interested renewable energy is biofuels and the most common renewable biofuel today is bioethanol or otherwise, is also known as "gasohol" [1]. Generally, ethanol used in gasohol is derived from the distillation process that requires high energy consumption and high operating cost. Therefore, more efficient ethanol/water separation techniques are preferred in order to reduce the gasohol production cost [2-3].

Pervaporation (PV) is especially attractive separation technique that utilizes the concept of partial vaporization of liquid through a membrane that derived from the two-step of the process. Firstly, liquid permeates through a membrane and then it evaporates into the vapor phase [4]. Pervaporation technique continues receiving an increase attention due to its higher separation efficiency and potential savings in capital and energy consumption [5]. Furthermore, a polymeric membrane has great design flexibility to improve the membrane selectivity and permeability.

Polybenzoxazine (PBZ) was selected as a membrane due to its excellent characteristics such as high heat resistant, good flame resistant, chemical resistant and electrical properties. Moreover it also shows low absorption of water, low shrinkage upon polymerization, no need of catalyst for polymerization, no by-product or volatile generation and excellent molecular design flexibility [6]. In this study, polybenzoxazine was prepared by using hexamethylenediamine as a precursor due to in the previous work of our group showed this type of membrane can separate between ethanol and water via pervaporation with permeation flux and seperation factor were 1.52 kg/m^{2}h and 10,000, respectively [8].

The aims of this research was to prepare a new kind of polybenzoxazine-based membranes for ethanol/water separation via pervaporation technique by mixing cardanol into benzoxazine prepolymer and adding NaA zeolite prior to the membrane fabrication process. The effect of cardanol contents on the swelling behaviors of the membrane was investigated. Moreover, the effects of feed concentration and NaA zeolite contents on the permeation flux and separation factor were also studied.

4.3 Experimental

4.3.1 Materials

Bisphenol–A (BA, $C_{15}H_{16}O_2$) was purchased from Aldrich, Germany. Formaldehyde (CH_2O, analytical grade) was purchased from Merck, Germany. Hexamethylene diamine (hda, $C_6H_{16}N_2$) was purchased from Fluka, Switzerland. Cardanol was purchased from Satya Cashew Chemicals Pvt.Ltd., India. 1,4- Dioxane ($C_4H_8O_2$) was purchased from Labscan, Ireland. All chemicals were used without further purification to synthesize cardanol-modified polybenzoxazine membrane. And NaA zeolites with a pore size of 0.2 μm were supported by senior in our group [7].

4.3.2 Characterizations

The structural characteristics of benzoxazine precursor were measured by using Proton Nuclear Magnetic Resonance (^1H NMR). The thermal stability of membranes was investigated by using Thermogravimetric analysis (TGA). The polymerization process and the glass transition temperature (T_g) were measured by using Differential scanning calorimetry (DSC). The chemical structure and sorption behavior of membrane were investigated by using Attenuated Total Reflectance Infrared Spectrometer (ATR–IR). The membrane morphology was investigated using field emission scanning electron microscope (FE-SEM). The mechanical properties of the membranes were investigated by using Lloyd/LRX Universal Testing Machine. The quantities of ethanol and water were determined by using a gas chromategraph (GC) and the permeation flux and separation factor were investigated by using prevaporation apparatus.

4.3.3 Methodology

4.3.3.1 Synthesis of Polybenzoxazine Precursor

The polybenzoxazine precursor was synthesized by using bisphenol–A (BPA, $C_{15}H_{16}O_2$), formaldehyde (CH_2O), and 1,6–hexanediamine (hda, $C_6H_{16}N_2$), as reactants with a molar ratio of 1:4:1, respectively. Firstly, bisphenol–A (3.42 g) was dissolved in 1,4 dioxane (5 g) in a glass bottle and stirred until the clear solution was obtained. Then formaldehyde solution (4.87 g) was added into the bisphenol–A solution and stirred continuously for approximately 20 min. The reaction was cooled and temperature was kept under 10°C by using an ice bath. After that aliphatic diamine was added dropwise into the mixture while continuously stirred for approximately 1 hour until transparent yellow viscous liquid was obtained.

4.3.3.2 Preparation of Cardanol-modified Polybenzoxazine Membrane

Cardanol was added into the mixture at 80 °C and stirred continuously for 1 hour. The amounts of cardanol were varied. After that, the mixtures were left to cool down and then cast on a glass plate which was wrapped with aluminum foil with a thickness of approximately 300 µm by using Elcometer 3580 casting knife film applicator from elcometer/inspection equipment. The membranes were dried at room temperature in air for one day yielding transparent yellowish membranes. Then, the membranes were placed in an air-circulating oven at 80°C for 24 hours to remove excess solvent. Cardanol contents in polybenzoxazine were varied from 1, 3, 5, 7 and 10 wt%, respectively.

4.3.3.3 Preparation of Zeolite-filled Cardanol-modified Polybenzoxazine Membrane

Various contents of NaA zeolite were disperse in 1,4-Dioxane and stirred for 3 hours and sonicated for 10 minutes in order to improve the dispersion of NaA zeolite particles in the solution. Then, NaA zeolite particles were primed by adding approximately 5wt% of total amount of cardanol-modified polybenzoxazine, to increase the compatibility between NaA zeolite and polymer and also to minimize the aggregation of NaA zeolite particles. After that, the mixture was stirred and sonicated to enhance the homogeneity. Then, the remaining cardanol-modified polybenzoxazine was added, the mixture was furtherly stirred for 6 hours before cast on a glass plate by using Elcometer 3580 casting knife film applicator. Finally, the membranes were placed in an air-circulating oven at 80°C for 24. NaA zeolite contents in cardanol-modified polybenzoxazine were varied from 1, 3, 5, and 10 wt%, respectively

4.3.3.4 Characterization of Swelling behaviors of Membrane

Cardanol-modified polybenzoxazine membranes and Zeolite-filled cardanol-modified polybenzoxazine membrane (approximately 200 μm thick and 25 mm × 25 mm in size) were placed in the solvents: ethanol, water, and various mixtures of ethanol-water (20, 40, 60, 80 % by volume of ethanol), for 8 h at room temperature to ensure the attainment of swelling equilibrium. At the specific time, the membranes were removed from the mixture and blotted with a tissue to remove excess liquid before weighing and replacing into them back. The procedure was repeated until a constant weight for each sample was obtained and sorption behaviors of membrane were investigated by using Attenuated Total Reflectance Infrared Spectrometer (ATR–IR). The degree of swelling, D_s was defined by the following equation.

$$D_s = ((W_t - W_0)/W_0) \times 100\% \tag{4.1}$$

Where W_t = The weight of the swollen membrane (g)

W_0 = The initial weight of the membrane (g)

The results obtained from each condition were the average of 3 tested membrane samples.

4.3.3.5 Pervaporation System

A schematic diagram of the system used to carry out the ethanol-water mixture separation experiments was shown in Fig 4.1. The membrane was placed in a stainless steel module. The feed temperature was maintained at 70°C in the cell while the flow rate of 900 ml/min was used to circulate the mixture from the feed reservoir to a permeation cell. The ethanol contents in feed solution were varied from 10, 20, 40, 50, 60, 80, and 90 wt%, respectively. Moreover, The effects of NaA zeolite contents on the permeation flux and seperation factor were investigated.

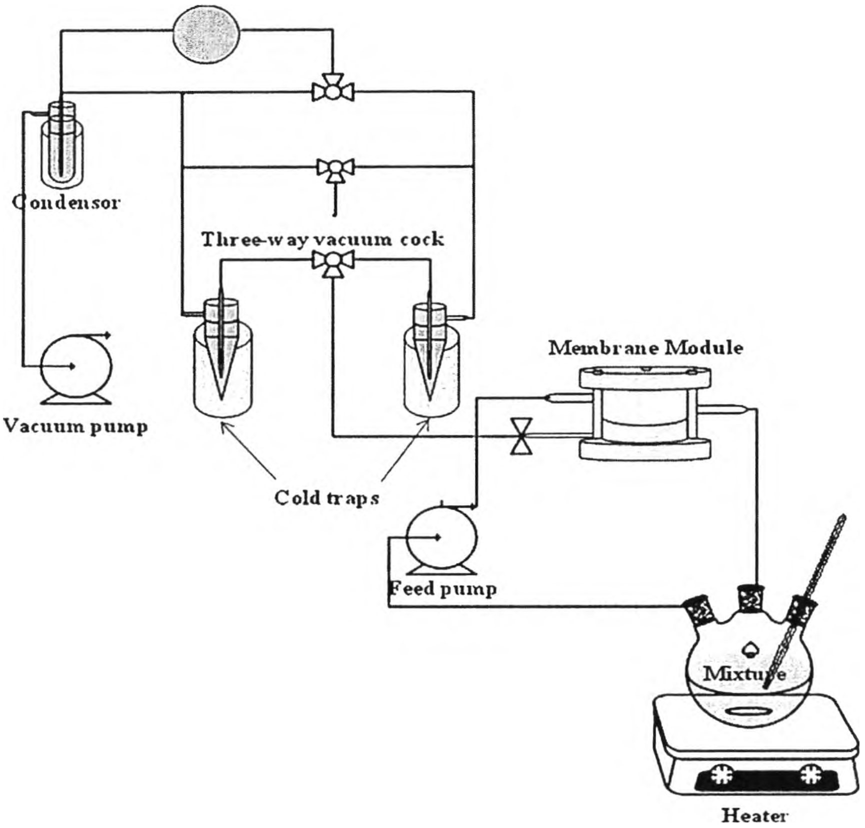

Figure 4.1 Experimental set up for pervaporation apparatus.

A Teflon gasket was also applied on the membrane to avoid leaking. The capacity of the upper cell compartment was approximately 100 ml while the area of the membrane in contact with the liquid was 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 vapor was condense and collected in a cold trap immersed in liquid nitrogen.

The performances of the membranes were determined by measuring % ethanol in the permeate side to calculate the permeation flux of water

(g/cm^2h) and the separation factor of the ethanol/water mixture. The quantities of ethanol and water were determined by using gas chromatography (GC).

4.3.3.5.1 Pervaporation Analysis

The permeation flux of water (g/cm^2h) and the separation factor of the ethanol/water mixture were determined by using the quantities of ethanol and water obtained from GC, as follows;

Permeation flux of water (J, kg/m^2h) can be calculate from equation 4.2

$$J = M/At \qquad (4.2)$$

Where M = Permeate weight (kg)
A = Effective membrane surface area (m^2)
t = Pervaporation time (h)

Seperation factor ($\alpha_{water/ethanol}$) was calculated from equation 4.3

$$\alpha_{water/ethanol} = (Y_{water}/Y_{ethanol})/(X_{water}/X_{ethanol}) \qquad (4.3)$$

Where Y_{water} = the weight fraction of water in the permeate side
$Y_{ethanol}$ = the weight fraction of ethanol in the permeate side
X_{water} = the weight fraction of water in the feed
$X_{ethanol}$ = the weight fraction of ethanol in the feed

4.4 Results and Discussion

4.4.1 Polybenzoxazine Membrane Characterizations

The synthesis of polybenzoxazine precursor was based on the reaction of bisphenol-A, 1,6–hexadiamine and formaldehyde at the molar ratio of 1:4:1 by using “a quasi-solventless method”. The reaction was carried out within an hour and small amount of 1,4-Dioxane was used as a solvent to help the mixing of all reactants.

4.4.1.1 Proton Nuclear Magnetic Resonance (^{1}H NMR)

The synthesis process of polybenzoxazine precursor was confirmed by ^{1}H-NMR. Fig 4.2 showed ^{1}H-NMR spectra of polybenzoxazine precursors. The spectra showed the characteristic peaks assigned to the methylene protons of $O-CH_2-N$ and $Ar-CH_2-N$ of the ring-closed benzoxazine ring at 4.80 and 3.90 ppm, respectively. The methyl protons of bisphenol-A were observed at 1.57 ppm. The methylene protons of the ring-opened benzoxazine were observed at 2.85 ppm. These results strongly agree with the results reported by Takeichi *et al.* [7] and Pakkethati *et al.* [8].

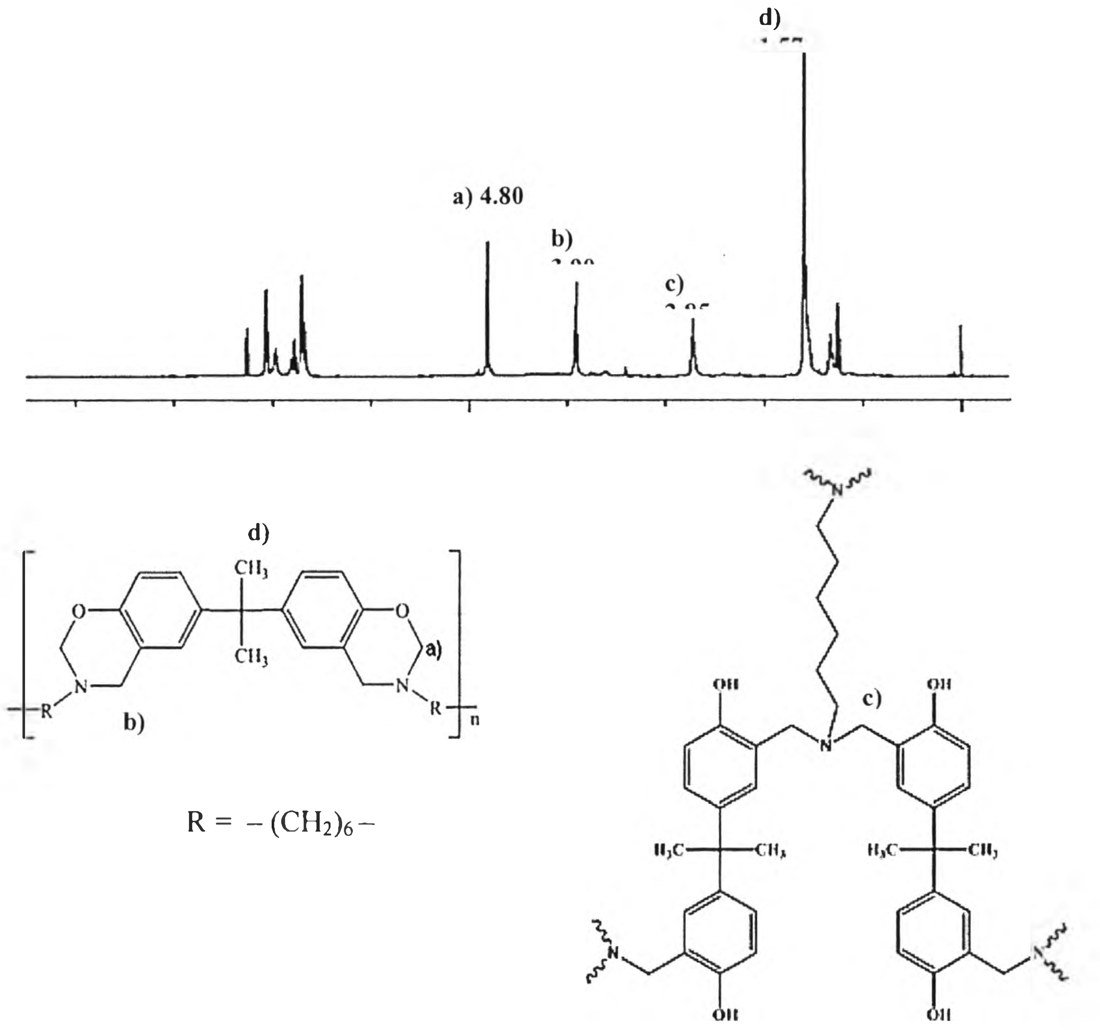

Figure 4.2 ^{1}H NMR spectra of polybenzoxazine precursors.

4.4.1.2 Preparation of Polybenzoxazine Membrane

The precursor was cast on a glass plate which was wrapped with aluminum foil and then dried at 80° C for 24 hours yielding the membrane with the thickness around 200 μm ± 10 μm. The characteristic of polybenzoxazine membrane (P(BA-hda) was shown in Figure 4.5.

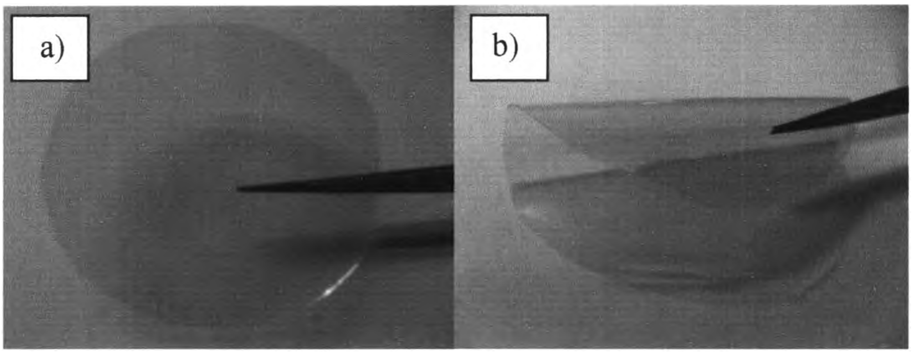

Figure 4.3 Appearance of polybenzoxazine membrane.

4.4.1.3 Scanning Electron Microscopy (SEM)

The polybenzoxazine membrane used in this study was a dense polymeric membrane, as can be seen from the SEM micrograph in Fig 4.4.

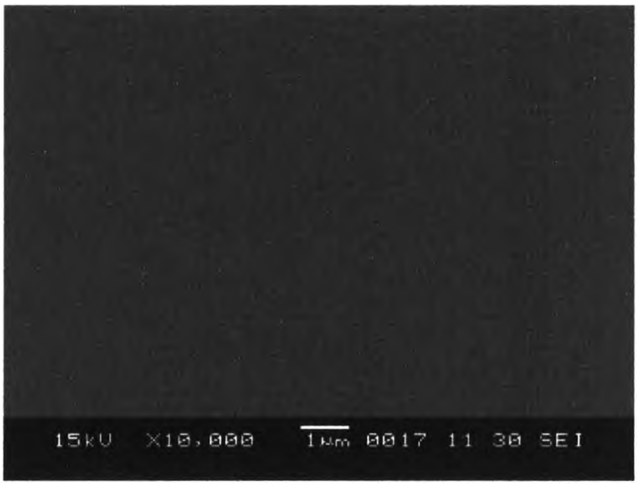

Figure 4.4 SEM micrograph of polybenzoxazine membrane.

4.4.1.4 Fourier Transform Infrared Spectrometer (FT–IR)

The chemical structure of polybenzoxazine membrane was examined by FTIR spectra as shown in Fig. 4.5. The characteristics absorption bands at 1228 cm^{-1} (asymmetric stretching of C-O-C of oxazine), 1175 cm^{-1} (asymmetric stretch of C-N-C) and 1129 cm^{-1} (CH_2 wagging of oxazine) were observed. Moreover, the characteristic absorption bands related to trisubstituted benzene ring at 1495 cm^{-1} and out of plane bending vibrations of C–H at 929 cm^{-1} were observed also. These IR results were in agreement with the study of Takeichi *et al.* [7] and Pakkethati *et al.* [8].

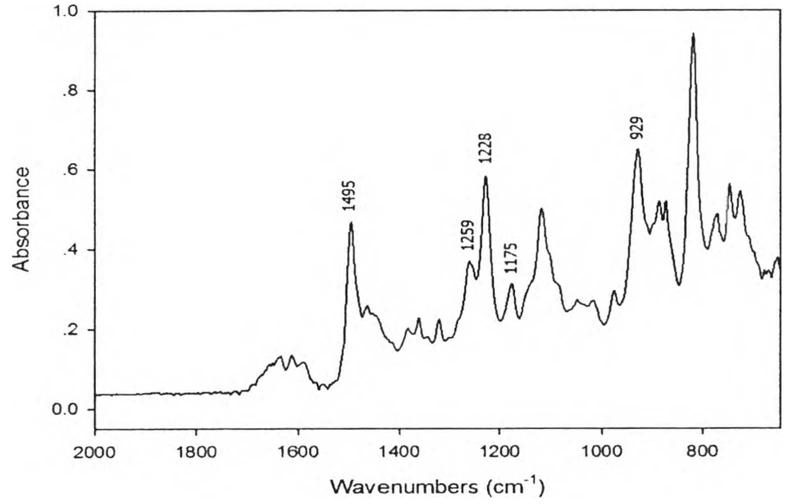

Figure 4.5 FTIR spectra of polybenzoxazine membrane.

4.4.2 Characterization of Cardanol-modified Polybenzoxazine Membrane

4.4.2.1 Preparation of Cardanol-modified Polybenzoxazine Membrane

Various contents of cardanol (1, 3, 5, 7, and 10 wt.%) were added into the polybenzoxazine solution and cast on a glass plate. The membranes were dried at 80° C for 24 hours yielding the cardanol-modified polybenzoxazine membrane with the thickness around 200 μm±10 μm and a testing diameter of 6.5 cm for the pervaporation study. The characteristics of cardanol-modified polybenzoxazine membranes were shown in Fig 4.6.

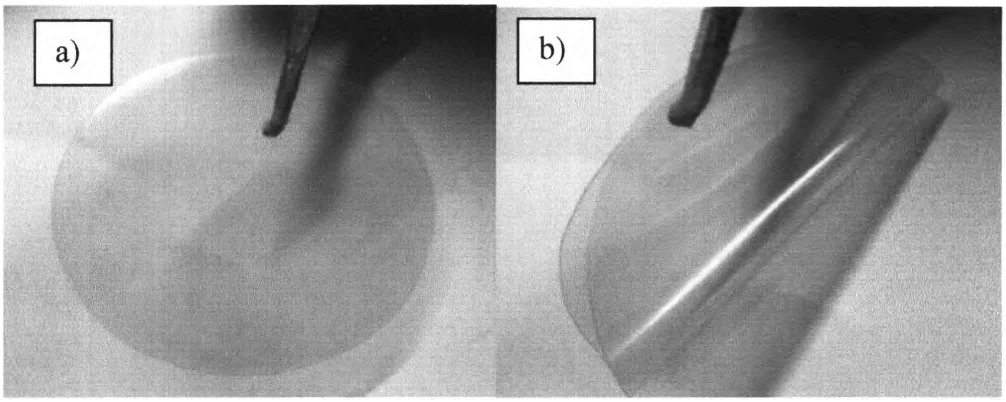

Figure 4.6 Appearance of cardanol-modified polybenzoxazine membrane.

4.4.2.2 Swelling behaviors of Cardanol-modified Polybenzoxazine Membrane

Degree of swelling of cardanol-modified polybenzoxazine membrane decreased as cardanol content increased (Fig 2). Since when cardanol was added in the system, the amount of crosslink density in the system was lower. Moreover, aliphatic chains in cardanol could absorb ethanol and water molecule, so the amount of ethanol and water that absorbed on the aliphatic diamine chains lossened the degree of swelling.When compare between the effect of ethanol and water on the degree of swelling of the membrane, the result showed that, ethanol affected to the degree of swelling of membranes higher than water. It may be due to the fact that cardanol-modified polybenzoxazine consisted of very long aliphatic hydrocarbon that provided hydrophobicity of the membrane; therefore, membrane preferred to absorb ethanol more than water leading to the degree of swelling of membrane in ethanol higher than in water. A similar swelling behavior was observed by chuang *et al.* [9].

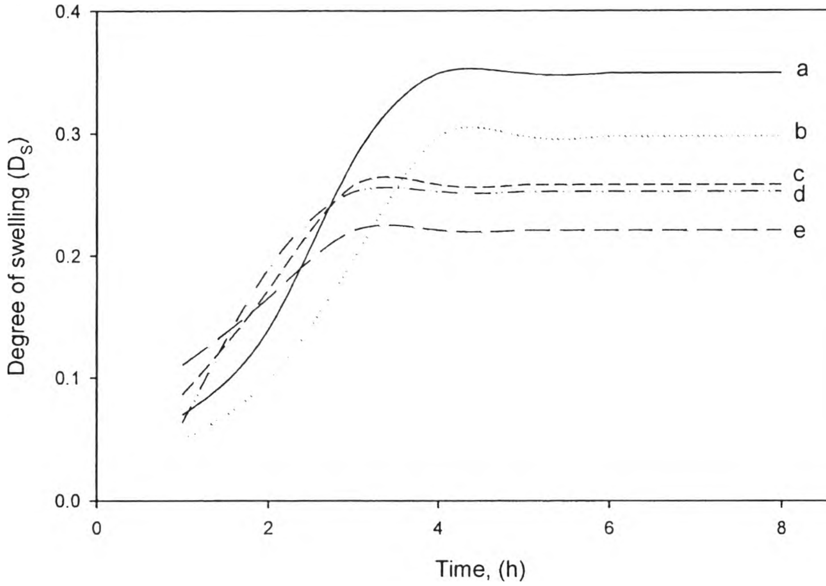

Figure 4.7 Swelling degrees of cardanol-modified polybenzoxazine with (a) 1, (b) 3, (c) 5, (d) 7, and 10 wt% of cardanol in water.

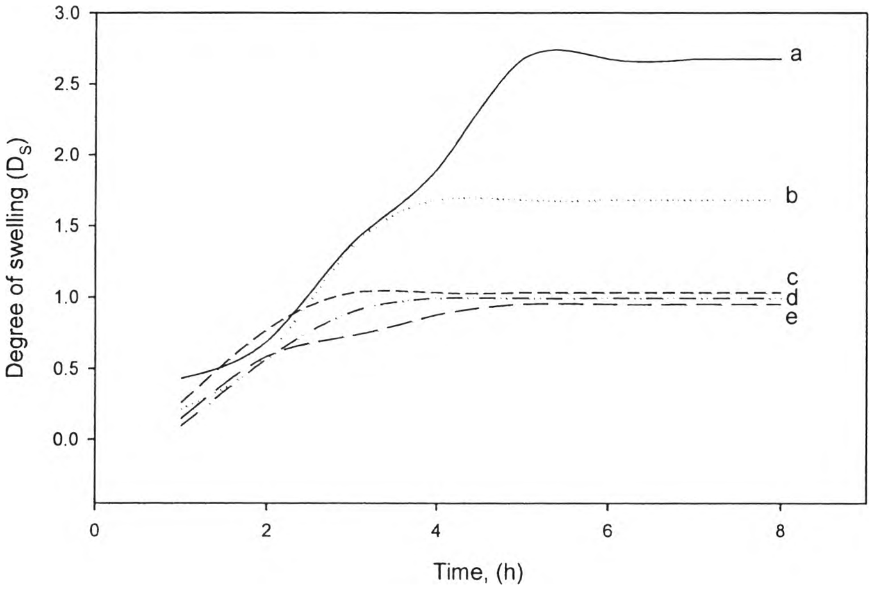

Figure 4.8 Swelling degrees of cardanol-modified polybenzoxazine with (a) 1, (b) 3, (c) 5, (d) 7, and 10 wt% of cardanol in ethanol.

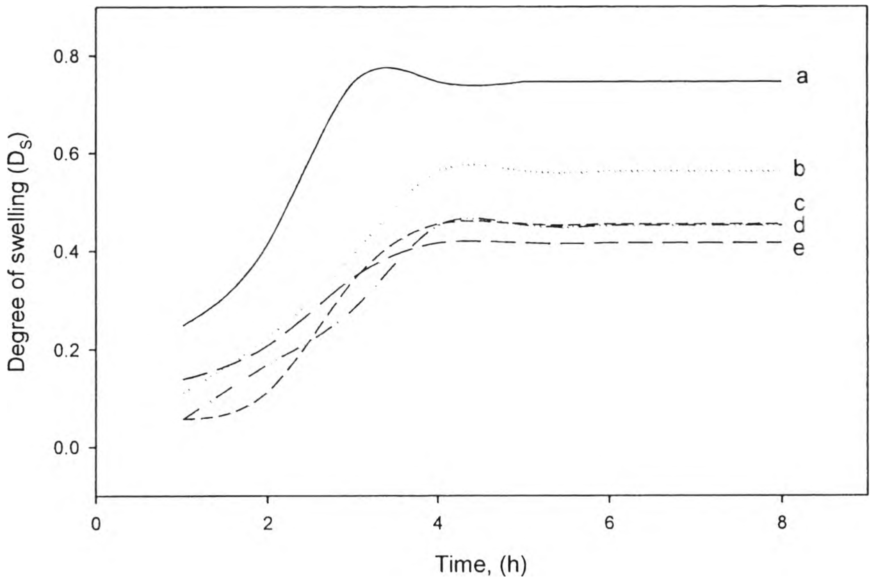

Figure 4.9 Swelling degrees of cardanol-modified polybenzoxazine with (a) 1, (b) 3, (c) 5, (d) 7, and 10 wt% of cardanol in ethanol-water mixture.

From the degree of swelling results, we found that, the most suitable cardanol content added to benzoxazine precursor was 5%wt cardanol due to degree of swelling of membrane at this content much lower than 1%wt and 3%wt. Moreover, when the contents of cardanol added to the benzoxazine precursor higher than 5 wt%, the degree of swelling was not significantly changed and cardanol could not mixed homogeneously with benzoxazine precursor. Therefore, crack surface was formed that affected to the performance of the membrane.

4.4.2.3 Sorption behaviors of Cardanol-modified Polybenzoxazine Membranes

ATR-IR was used to study the sorption behavior of cardanol-modified polybenzoxazine membrane that prepared by adding 5%wt cardanol to benzoxazine prepolymer in various ethanol–water concentrations. The results were shown in Fig 4.10 and Fig 4.11. The characteristic peaks of ethanol and water were identified at 2972 cm^{-1} and 1639 cm^{-1}, respectively. When the ethanol concentrations increased, the sorption of the cardanol-modified polybenzoxazine membrane also increased, as can be seen from the increasing of intensity of the characteristic peaks of ethanol (Fig 4.10). Similarly, the intensity of the characteristic peak of water decreased with the decrease of water concentration in the mixture as shown in Fig 4.11, indicating that both ethanol and water can penetrate the matrix of the cardanol-modified polybenzoxazine membrane. These results strongly agree with the results reported by Pereira *et al.*, who founded the peak intensity of the water and ethanol sorption increased upon an increase in the water and ethanol concentrations [10].

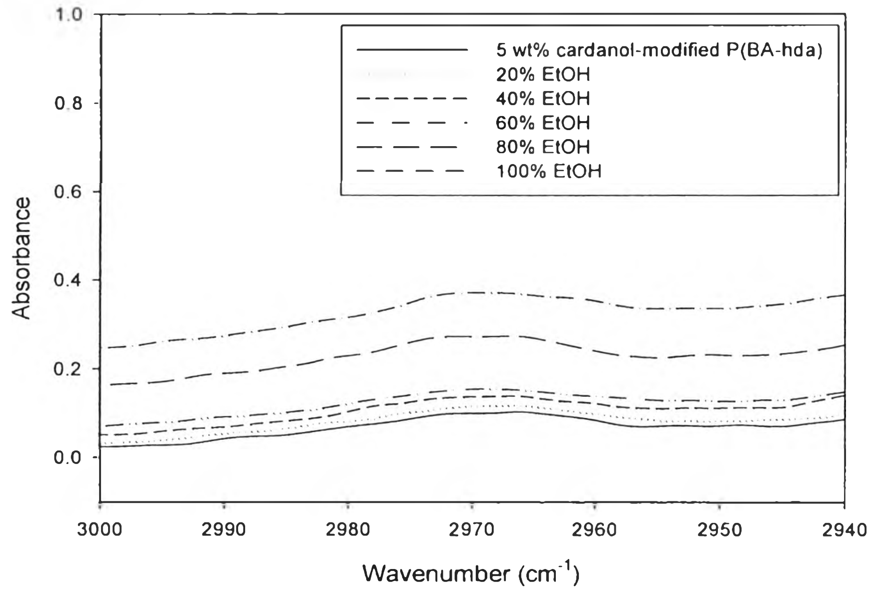

Figure 4.10 ATR-IR spectra of the cardanol-modified polybenzoxazine membrane immersed in the ethanol – water mixtures and the characteristic peaks of ethanol.

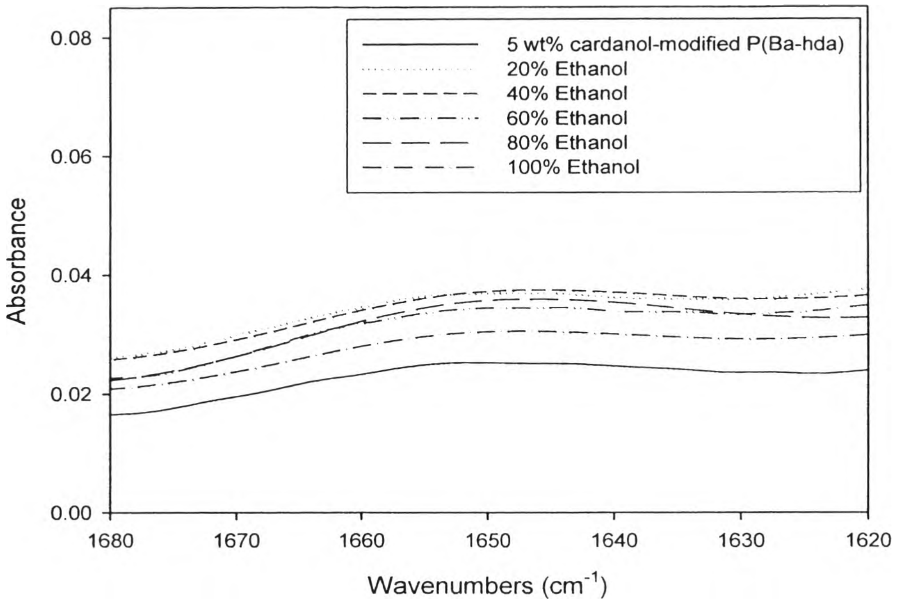

Figure 4.11 ATR-IR spectra of the cardanol-modified polybenzoxazine membrane immersed in the ethanol – water mixtures and the characteristic peaks of water.

4.4.2.4 Morphology of Cardanol-modified Polybenzoxazine Membrane

SEM micrograph (Fig 4.12a) shows the densed membranes without any void when 5 wt% of cardanol was added into the system. However, the cracked membrane was obtained when the cardanol content was increased to 10 wt% (Fig 4.12b).

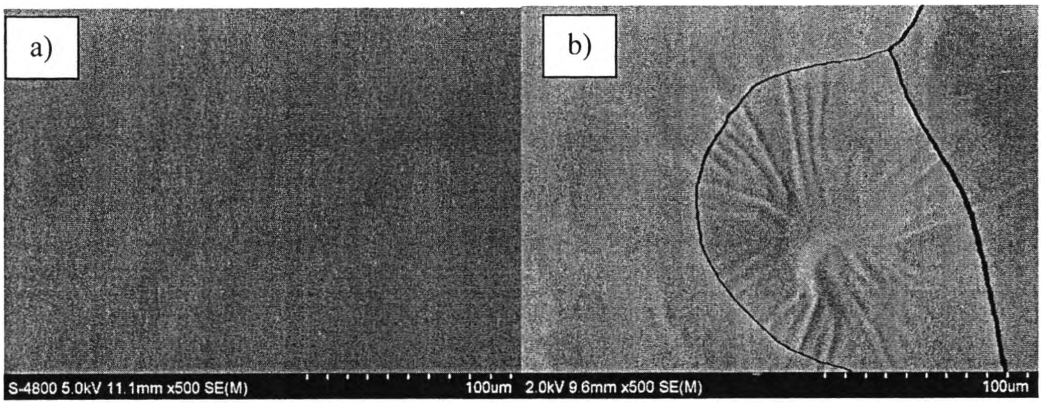

Figure 4.12 SEM surface image of cardanol-modified polybenzoxazine membrane with (a) 5, and (b) 10 wt% of cardanol.

4.4.2.5 Thermal properties of Cardanol-modified Polybenzoxazine Membrane

The progress of the ring-opening polymerization of the polybenzoxazine membranes was monitored by DSC (Fig 4.13). The DSC thermogram of partially-cured polybenzoxazine showed an exothermic peak starting from 165 °C with a maximum at 240 °C, while cardanol-modified polybenzoxazine showed an exothermic peak starting from 145 °C with a maximum at 233 °C, attributed to the benzoxazine ring-opening polymerization. In the case of cardanol-modified polybenzoxazine membrane, the peak exotherms were found to be lower than those of polybenzoxazine membrane may be due to the presence of phenolic compounds of cardanol can act as initiator for the ring opening of benzoxazine compounds. Similar results were found by Kasemsiri P. *et al.*, who study the effect of cashew nut shell liquid on gelation, cure kinetics, and thermomechanical properties of benzoxazine resin [11]. After the precursor was fully cured, the exothermic peak disappeared, while the transitions of base line were showed assigned to the glass transition temperature of membranes (Fig 4.14).

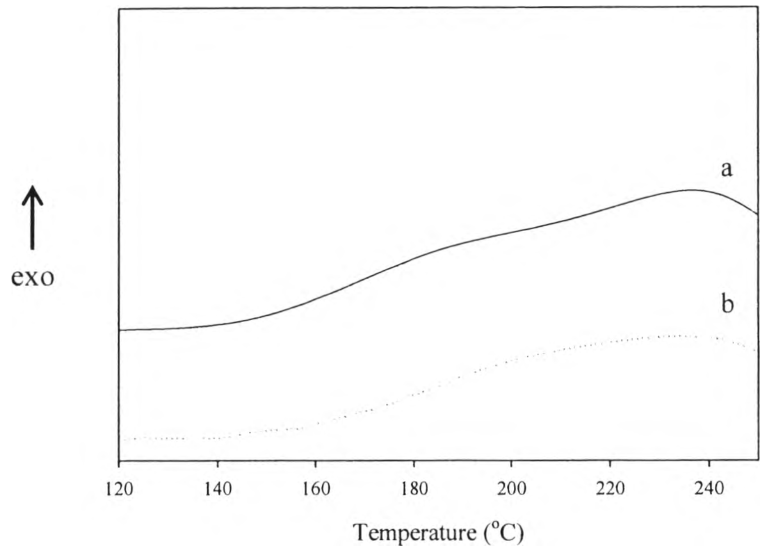

Figure 4.13 DSC Thermogram of fully-cured of polybenzoxazine membrane (a) and cardanol-modified polybenzoxazine membrane (b).

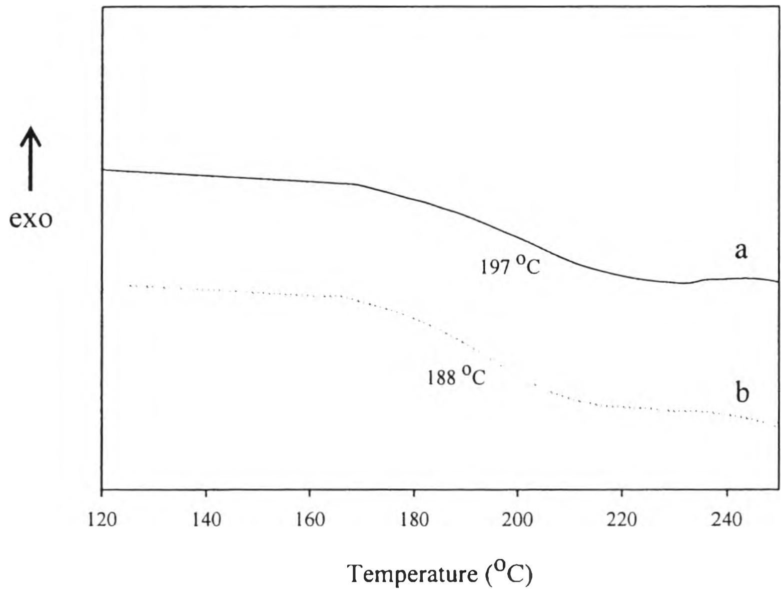

Figure 4.14 DSC Thermogram of partially-cured of polybenzoxazine membrane (a) and cardanol-modified polybenzoxazine membrane (b).

Glass transition temperature of the polybenzoxazine and cardanol- modified polybenzoxazine membranes were also monitored by DSC. The DSC thermogram of fully-cured polybenzoxazine and cardanol-modified polybenzoxazine shows a transition at 197 °C and 188 °C, respectively (Fig 4.14). When compared between polybenzoxazine membrane and cardanol-modified polybenzoxazine membrane, cardanol that mixed with benzoxazine prepolymer has very long alkyl side chain in their structure affected to rotational motions of polymer molecule segments occurred easily, leading to the shift of the glass transition temperature to lower temperatures [12].

Thermogravimetric analysis of the cured sample was conducted under a nitrogen atmosphere and the thermogram of fully-cured polybenzoxazine and cardanol-modified polybenzoxazine were given in Fig 4.15. Cardanol-modified polybenzoxazine start to decompose at lower temperature than polybenzoxazine and char yield of cardanol-modified polybenzoxazine was lower than polybenzoxazine due to the overall number of aromatic per unit mass decreased with the amount of cardanol that has long alkyl side chain in its structure increased. The char yield of polybenzoxazine was in the same trend as Pakkethati *et al.* [8] and the char yield of cardanol-modified polybenzoxazine was similar to Rao B.S. *et al.*, that study the thermal stability of cardanol benzoxazine [13-14].

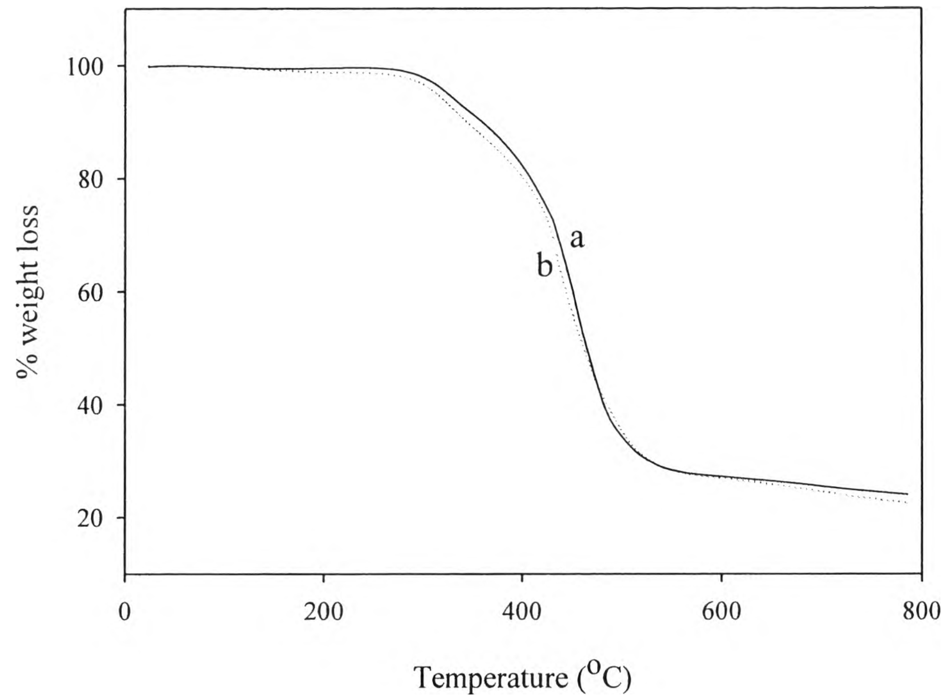

Figure 4.15 TGA Thermogram of fully-cured polybenzoxazine membrane (a) and fully-cured cardanol-modified polybenzoxazine membrane (b).

4.4.2.6 Mechanical properties of Cardanol-modified Polybenzoxazine Membrane

The mechanical properties of membranes were studied using tensile testing. (The tensile modulus, tensile strength, and elongation at break values are summarized in Table 4.1) Both types of membranes showed similar modulus (E). The tensile strength (σ_b) and elongation at break (ε_b) of the cardanol-modified polybenzoxazine membrane higher than that of polybenzoxazine membrane which is reported by Pakkethati *et al.*, A higher elongation at break indicates greater flexibility [8].

Table 4.1 Tensile modulus, tensile strength, and elongation at break values of polybenzoxazine and cardanol-modified polybenzoxazine

Membrane	E (GPa)	σ_b (MPa)	ε_b (%)	References
P(BA-hda)	1.78 ± 0.14	42.58 ± 6.03	3.96 ± 0.67	[13]
Cardanol-modified polybenzoxazine membrane	1.72 ± 0.04	68.01 ± 2.86	7.84 ± 0.52	This study

The increasing of the tensile strength (σ_b) might be due to the alkyl chain of cardanol hinders the movement of the polymer chain and the increasing of elongation at break (ε_b) when cardanol was added into the system were likely from the structure of cardanol that have long aliphatic chain that provide the flexibility of the membrane, respectively. The same trend was found by Campaner P. *et al.*, who study the mechanical properties of cardanol benzoxazine [12].

4.4.3 Characterization of Zeolite-filled Cardanol-modified Polybenzoxazine Membrane

4.4.3.1 Preparation of Zeolite-filled Cardanol-modified Polybenzoxazine Membrane

Various contents of zeolite (1, 3, 5 and 10 wt%) were added into the cardanol-modified polybenzoxazine solution and cast on a glass plate. The membranes were dried at 80° C for 24 hours yielding the zeolite-filled cardanol-modified polybenzoxazine membrane with the thickness around 200 μm±10 μm and a testing diameter of 6.5 cm for the pervaporation study. The characteristics of zeolite-filled cardanol-modified polybenzoxazine membrane membranes are shown in Fig 4.16.

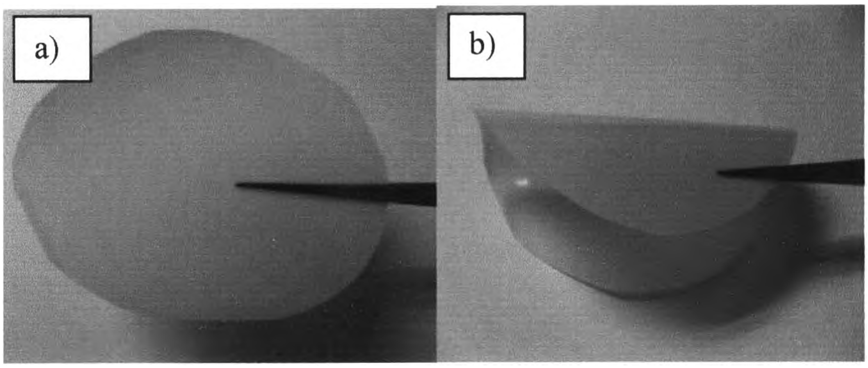

Figure 4.16 Appearance of zeolite-filled cardanol-modified polybenzoxazine membrane.

4.4.3.2 X-ray Diffraction (XRD) Analysis

X-ray diffraction analysis (XRD) was used to confirm the identity of NaA zeolite that used in this study. Fig 4.17 shows the XRD crystallogram for NaA zeolite and zeolite filled cardanol-modified polybenzoxazine membrane. From the crystallogram, major peaks for NaA zeolite structure were detected at 2theta 7.08°, 2theta 10.08°, 2theta 12.36°, 2theta 15.98°, 2theta 21.58°, 2theta 23.9°, 2theta 27.02°, 2theta 29.86 and 2theta 34.06° as the same angle that Ling W.S. *et al.* founded confirming that the sample has NaA zeolite structure [15].

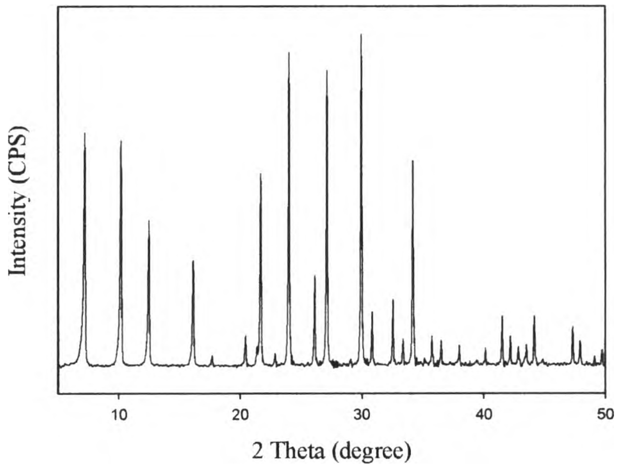

Figure 4.17 XRD crystallogram of NaA zeolite.

4.4.3.3 Swelling behaviors of Zeolite-filled Cardanol-modified Polybenzoxazine Membrane

The membrane swelling in the liquid mixture depends on the extent of crosslinking, morphology of the polymer and the free volume available within the polymer matrix [16]. In pervaporation study, degree of swelling of the membrane was an important factor that controls the transport of permeating molecules through the membrane. Fig 4.18- Fig 4.20 shows the degree of swelling of zeolite-filled cardanol-modified polybenzoxazine membrane in water, ethanol and ethanol-water, respectively. We found that, when the polymer matrix was filled with NaA zeolite, the degree of swelling in water increased more than that of cardanol-modified polybenzoxazine membrane. This may be due to the fact that NaA zeolite has cationic particles in their cages, which tend to increase a greater electrostatic force of attraction between the water molecules and membranes. Therefore, adsorption of water molecules increases remarkably with an increase of zeolite content in the membrane that affected to swelling of the membranes as the same result as Kariduraganavar *et al.* work [17]. On the other hand, when ethanol was used as a media, degree of swelling of the membrane decrease as the zeolite content in the membrane increased resulting from NaA zeolite preferred to adsorb water molecule only; so, the area of the membrane that can adsorb ethanol decrease leading to the degree of swelling of membrane in ethanol decrease as increasing zeolite content.

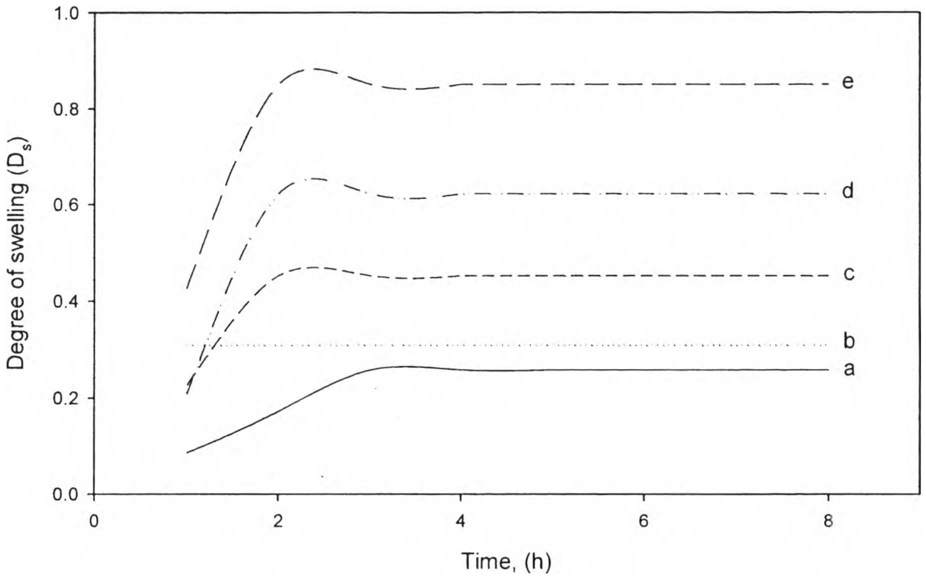

Figure 4.18 Swelling degrees of cardanol-modified polybenzoxazine membranes with and without zeolite: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 10 wt% in water.

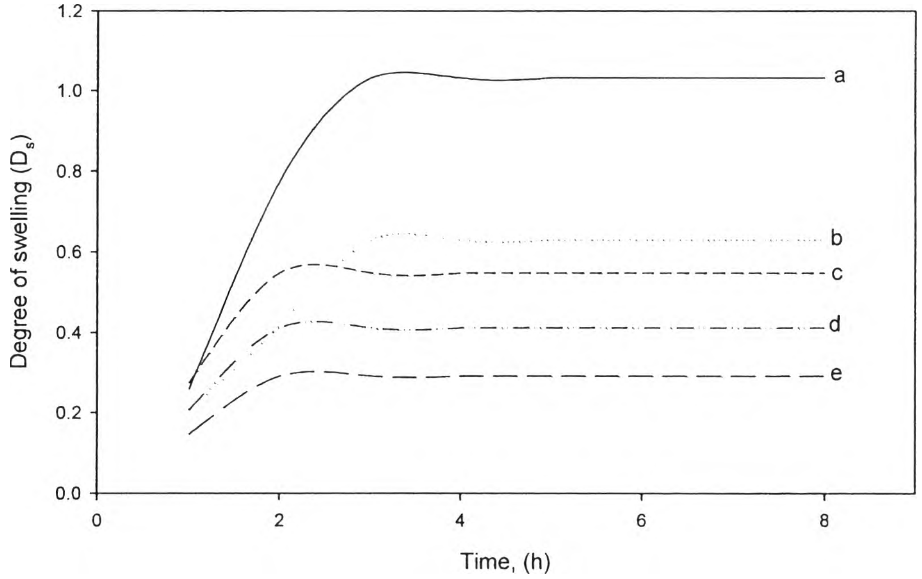

Figure 4.19 Swelling degrees of cardanol-modified polybenzoxazine membranes with and without zeolite: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 10 wt% in ethanol.

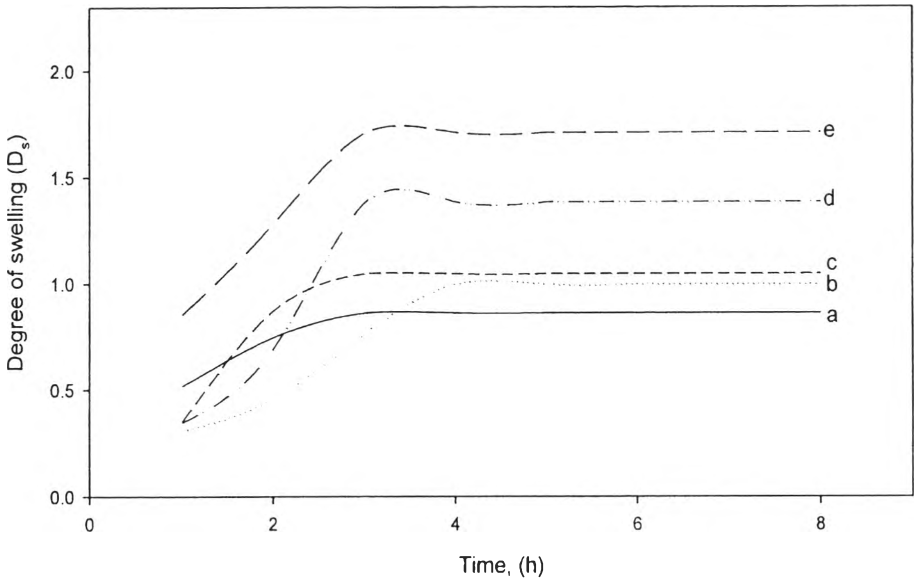

Figure 4.20 Swelling degrees of cardanol-modified polybenzoxazine membranes with and without zeolite: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 10 wt% in ethanol-water mixture.

4.4.3.4 Morphology of Zeolite-filled Cardanol-Modified Polybenzoxazine Membrane

Zeolite-filled cardanol-modified polybenzoxazine membranes with different zeolite loadings were examined by SEM to determine the NaA zeolite particles distribution in cardanol-modified polybenzoxazine matrix.

The SEM micrographs of zeolite-filled membranes are shown in Fig 4.21, where the cubic particles are NaA zeolite, and the continuous phase is cardanol-modified polybenzoxazine. When added 1 wt% of zeolite into the system, zeolite particles are uniformly distributed without any void. However, particles aggregration and voids are observed when increasing the zeolite loading, due to poor interfacial adhesion since cardanol-modified polbenzoxazine is considered to be more hydrophobic while zeolite is hydrophilic [18].

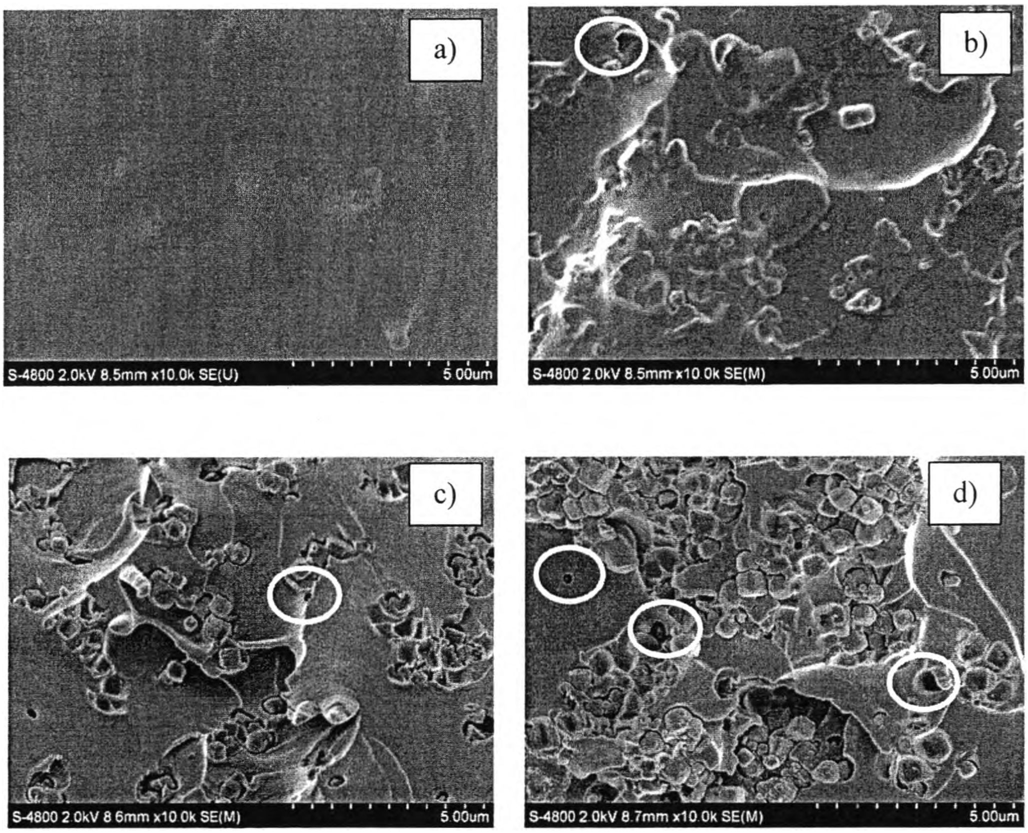

Figure 4.21 Cross–section SEM image of zeolite filled cardanol-modified polybenzoxazine with (a) 1, (b) 3, (c) 5, and (d) 10 wt% of NaA zeolite loading.

4.4.4 Ethanol-Water Seperation via Pervaporation

According to the swelling and sorption results, the content of cardanol on cardanol-modified polybenzoxazine membrane was an important factor in the performance of the membranes. In this study, the optimum cardanol content added to benzoxazine prepolymer to prepared cardanol-modified polybenzoxazine membrane based on swelling study was 5%wt cardanol. The feed temperature was kept at 70 °C, while a thickness of 200 μm was used in order to study the permeation flux and separation factor of each membrane compared with our group previous study [8].

4.4.4.1. Effect of ethanol concentration in feed on the permeation flux and separation factor

By varying the ethanol concentration up to 50 wt%, we found that the separation factor was higher than 10,000. However, as the ethanol content was furtherly increased, the separation factor decreased, while the permeation flux increased. This may be due to the sorption of ethanol in membrane owing to the increased of degree of swelling as a results, both ethanol and water could pass through the membrane, leading to the increase of permeation flux, while separation factor decreased (Fig 5a) [19].

In our study, cardanol-modified polybenzoxazine could be used to separate ethanol-water mixture at higher ethanol content in feed than prestine polybenzoxazine that our group has been done before (could use this type of membrane only at 10wt% ethanol). Moreover, only water molecules could penetrated and moved across the membrane until 50wt% ethanol in feed was used, suggesting that the longer aliphatic chain length in cardanol could help to absorb more ethanol and reduce degree of swelling of membrane, so it allowed only water molecules to pass through, resulting in the separation factor at 50wt% ethanol in feed higher than 10,000 with the highest permeation flux of 0.33 kg/m^{2}h at 70 °C.

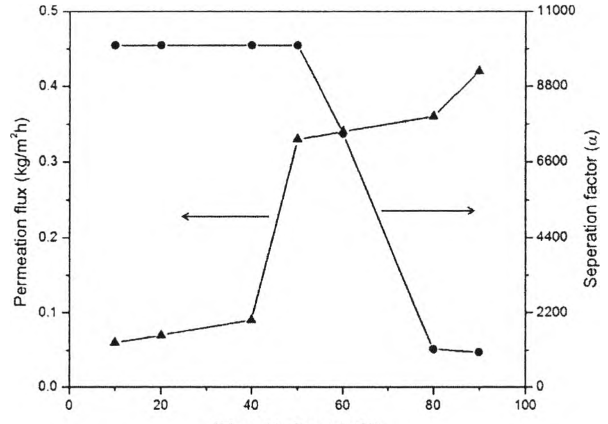

Figure 4.22 Permeation flux and separation factor of the cardanol-modified polybenzoxazine membrane as a function of ethanol in feed (wt%).

4.4.4.2 *Effect of zeolite contents incorporated to Cardanol-modified Polybenzoxazine Membrane on the permeation flux and separation factor*

NaA zeolite was suitable for ethanol-water separation since it has a nominal pore size of 0.4 nm, which is larger than the kinetic diameter of water molecule (0.264 nm) but smaller than the kinetic diameter of ethanol molecule (0.430 nm) [20]. In order to improve the permeation flux, zeolite was incorporated into the membrane. It was found that the permeation flux increased with the increase of zeolite content up to 5 wt%, while separation factor was still higher than 10,000 since more water could pass through the membrane owing to the molecular sieve effect of NaA zeolite. However the separation factor was not affected because the pore size of NaA allowed only water molecules to pass through. Nevertheless, when more than 5 wt% of zeolite was incorporated, the separation factor decreased drastically which might probably resulted from the poor interfacial adhesion between membrane matrix and zeolite as discussed earlier (Fig 4.23) [21].

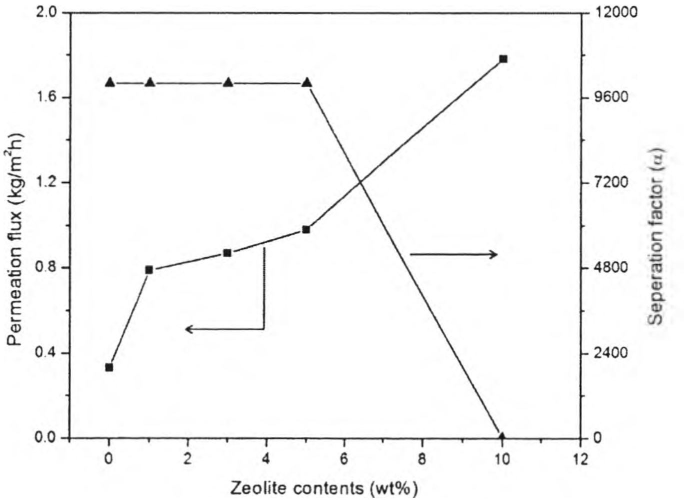

Figure 4.23 Permeation flux and separation factor of the zeolite-filled cardanol-modified polybenzoxazine membrane as a function of zeolite content (wt%).

4.5 Conclusion

From the results, we clearly showed that cardanol could reduce the membrane swelling. The optimum cardanol content was 5 wt%. Additionally, an increased in permeation flux was achieved by adding NaA into the system. When NaA was incorporated up to 5 wt%, the total permeation flux was increased to 0.98 kg/m^{2}h, while the seperation factor was still higher than 10,000. However, the suitable NaA content was 1 wt% since at higher zeolite loading, the zeolite particles agglomerated and some voids were observed from the SEM micrographs.

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4.7 References

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