Natural Rubber/Poly(acrylic acid) Semi-Interpenetrating Polymer Network Membranes for the Pervaporation of Water–Ethanol Mixtures

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ABSTRACT: Pervaporation membranes for the dehydration of water–ethanol mixtures were prepared from a semi-interpenetrating polymer network (semi-IPN) of natural rubber (NR) and crosslinked poly(acrylic acid) (PAA). The swelling studies revealed that hydrophilic PAA present in the semi-IPN membranes caused the membranes to swell greatly in water. The swelling degree of the membranes in water was significantly affected by the amount ratio between the hydrophobic NR and the hydrophilic PAA. The sorption experiments of the NR/PAA membranes in various concentrations of water–ethanol mixtures suggested the preferential sorption to water. However, for the membrane with high PAA content, the water sorption selectivity decreased considerably at high water concentration of water–ethanol mixtures because the membrane was in the highly swollen state. Pervaporation separations of water–ethanol mixtures using NR/PAA membranes were performed and it was found that at low water concentrations of feed mixtures, increasing the PAA content of the membrane can enhance both water permeation flux and selectivity. Additionally, under low feed water concentration, increasing the feed temperature would increase the water flux with the decreasing of the ethanol flux. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3501–3509, 2009

Key words: hydrophilic polymers; membrane; natural rubber; semi-IPN; pervaporation

INTRODUCTION

Pervaporation is an attractive separation process for azeotropic mixtures, close-boiling point components, and heat-sensitive mixtures. Pervaporation is a membrane separation process in which feed liquid mixture is fractionated by the selective membrane, and the separated component will selectively absorb and pass through the membrane as vapor on the permeate side where the vacuum is applied. In evaluating the pervaporation performance, the permeate flux and the separation factor of the membranes are considered and they are dependent upon the solubility and diffusivity of the separated component on the membrane.

For the dehydration of organic–water mixtures, pervaporation membranes are usually made of crosslinked hydrophilic polymers, for example, poly(vinyl alcohol) (PVA)[1,2] or poly(acrylic acid) (PAA),[3] to enhance the water permeation flux and selectivity because these hydrophilic polymers possess the functional groups that can interact specifically with water molecules.[4] At high water content of the liquid mixtures, the hydrophilic membrane may be in a highly swollen state, which reduces the membrane selectivity and sometimes leads to the loss of membrane integrity. To limit the excessive swelling of the hydrophilic membranes, they require crosslinking[5] or blending with less water-swelling (hydrophobic) polymer.[6] Practically, blend membranes consist of the hydrophilic polymer that provides active interactions with water molecules and the elastomeric polymer that restraints the membrane swelling as well as improves the integrity of the membrane. Because blending of hydrophilic and hydrophobic polymers forms a heterogeneous phase, to prepare the hydrophilic–hydrophobic blended membranes, the dispersed phase of the membrane should swell well in the component for which the membrane should be selective, whereas the continuous phase is the polymer which does not swell in either of the components of the liquid mixtures.[7]

Pervaporation membranes made of natural rubber (NR) were suitably applied for the separation of organic mixtures because of its hydrophobic nature.[8,9] Although there has been previous attempts to employ NR as a selective pervaporation membranes for removing the trace organic from its aqueous

mixtures,[10] it has been shown to have a poor organic selectivity in the aqueous system because a water molecule diffuses through the membrane faster than does the organic molecule due to the large molecular size of most organics when compared with the size of a water molecule. Therefore, instead of attempting to separate an organic component from its aqueous mixtures, it is more interesting to study the separation of water from organic–water mixtures using the membrane comprising NR. In this investigation, the dehydration of water–ethanol mixtures using NR-based membrane was performed by a pervaporation process. The NR-based pervaporation membranes were prepared from the NR and crosslinked-PAA which forms the semi-interpenetrating polymer network membranes (semi-IPN). PAA is very hydrophilic because of the presence of carboxylic groups along the polymer chains, which makes PAA suitable for the separation of aqueous mixtures. Hydrophobic NR is the elastomer with a low glass transition temperature ($T_g \sim -70$ °C) available in latex form that allows the fabrication into a thin membrane without requiring polymer dissolution. The water swelling of the NR/PAA semi-IPN membrane can be maintained depending upon the amount of NR in the membrane because NR does not swell in either ethanol or water. More importantly, the performance of pervaporation separation should be altered for different water–ethanol feed compositions by adjusting the amount ratio of hydrophilic PAA and hydrophobic NR.

EXPERIMENTAL

Materials

Concentrated natural rubber latex (NR) with approximately 60% w/w dry rubber content was purchased from Thai Hua Rubber, Udonthani, Thailand. The NR latex was cleaned by centrifugation at 6000 rpm for 20 min and redispersed in 7% w/w NH_4OH solution. The NR cleaning process was performed twice. PAA with $M_w \sim 1,000,000$ g/mol was obtained from Sigma-Aldrich (St. Louis, USA). Surfactant Triton X-100 was supplied from Sigma-Aldrich. Ethylene glycol (EG) used as a crosslink agent for PAA was obtained from Carlo Erba Reagenti (Milan, Italy). Absolute ethanol (99.9% v/v AR grade) and NH_4OH solution (30% w/w) were purchased from Merck (Darmstadt, Germany). Water used in these experiments was distilled and deionized (DI water).

Membrane preparation

Dry PAA powder was stirred in 30% w/w NH_4OH aqueous solution using a mechanical stirrer until the clear solution was obtained. The PAA solution was then mixed with NR latex. Before mixing NR latex

TABLE I
Weight Compositions of Chemicals Used for Preparation of NR/PAA Semi-IPN Membranes

Membrane	% w/w PAA in membrane	NR latex[a] (g)	PAA (g)	EG (g)	Triton X-100 (g)
5P	5	6.00	0.18	0.08	0.20
10P	10	6.00	0.36	0.15	0.20
20P	20	6.00	0.72	0.31	0.20
30P	30	6.00	1.08	0.46	0.20

[a] NR latex has approximately 60% dry rubber content.

with PAA solution, Triton X-100 was added to the latex to prevent the premature coagulation of the NR latex. After that, EG was added into the NR dispersion to initiate the crosslinking of PAA. PAA per dry NR was varied from 5 to 30% w/w as shown in Table I, together with the weight compositions of all materials. The mixture was stirred for 3 h at 70°C under nitrogen atmosphere. Then, the dispersion was cast on a glass plate and dried at 70°C for 24 h in the oven where PAA was allowed to crosslink in the immediate presence of NR yielding the semi-IPN structure. The resultant dry membrane was carefully peeled off from a glass plate and placed on a porous ceramic support to be used in the pervaporation separation. The membrane thicknesses were in the range of 200 ± 10 μm measured in five different points using the micrometer (Mitutoyo).

Membrane characterizations

Fourier-transform infrared spectra (FTIR) of NR/PAA membranes were obtained using PerkinElmer FTIR spectrometer (Spectrum One) measuring in the range of 4000–450 cm^{-1}.

Thermal gravimetric analysis (TGA) of the membranes was conducted by Perkin–Elmer Pyris Diamond TG/DTA analysis in the temperatures up to 600°C with the heating rate of 10°C/min under nitrogen atmosphere.

Swelling experiments of the membranes were performed as follows. Dry membrane W_d was weighted and immersed in pure solvents, i.e., water or ethanol or water–ethanol mixtures of various concentrations. The membrane was left in the liquid for 48 h. After that the swollen membrane was taken out and blotted with filter paper to remove excess liquid on the membrane surface and then weighted W_s. The swelling degree of the membrane was calculated from the following equation:

$$\text{Swelling degree} = \frac{W_s - W_d}{W_d} \qquad (1)$$

The states of water in the swollen membrane were examined using differential scanning calorimetry

(DSC) (Perkin–Elmer Pyris 1). A water-swollen sample sealed in an aluminum pan was cooled to −50°C and remained at this temperature for 15 min before being heated to 50°C with a heating rate of 5°C/min under nitrogen atmosphere.

Membrane sorption

A dry membrane was immersed in the water–ethanol solutions for 48 h. The membrane was then removed from the solution and quickly wiped out with filter paper to remove the liquid on the membrane surface. Next, the membrane was placed in the dry flask, which was connected to a cold trap and a vacuum pump. The flask was heated to 100°C to evaporate the liquid retained inside the membrane. The vapor was condensed in the cold trap by cooling with liquid nitrogen. The condensed liquid was then analyzed with the refractive index detector (Waters model 2414), and the water concentration was evaluated using the calibration curve constructed from the plot between the compositions of water–ethanol mixtures (% w/w) and their refractive indices. The water sorption selectivity of the membrane (α_s) was defined by

$$\alpha_s = \frac{C_{H_2O}/C_{EtOH}}{X_{H_2O}/X_{EtOH}} \qquad (2)$$

where C and X are the weight fractions of either of water (H_2O) or ethanol (EtOH) in the membrane and water–ethanol solution, respectively.

Pervaporation

A laboratory-scale pervaporation process was employed as schematically depicted in Figure 1. The membrane module consists of the 100-cm^3 feed compartment and a porous support with the effective membrane area of 19.6 cm^2. The permeate side was subjected to the pressure of 1 kPa generated by the vacuum pump. The feed solution temperature was controlled by the oil-bath heater. The permeate vapor was collected in cold traps cooling with liquid nitrogen. Feed solution was circulated to the feed compartment of the membrane module for 2 h before the vacuum was applied to allow the solution to swell the membrane. The pervaporation process was operated for 2 h after which the vacuum was terminated, and the condensed permeate was removed from the cold traps and weighed. The amount of permeate collected during the pervaporation was small when compared with the amount of liquid mixtures in a feed reservoir, hence the composition of the feed can be assumed constant throughout the experiment. The composition of the permeate was determined using the calibration curve of the solution compositions versus their refractive indices. The total permeate flux (J) and the water separation factor (α_P) were calculated by the following equations:

$$J = \frac{W}{A \times t} \qquad (3)$$

$$\alpha_P = \frac{Y_{H_2O}/Y_{EtOH}}{X_{H_2O}/X_{EtOH}} \qquad (4)$$

where W, A, and t represent the weight of permeate (g), the effective membrane area (m^2), and the operating time (h), respectively. Y and X are the weight fractions of water or ethanol in the permeate and feed, respectively. For the partial flux of each constituent in the permeation, it was estimated from the equation:

$$J_i = Y_i \times J \qquad (5)$$

where index i represents water or ethanol.

RESULTS AND DISCUSSION

FTIR spectroscopy

The crosslink of PAA was confirmed by FTIR spectra as displayed in Figure 2. The carbonyl absorption
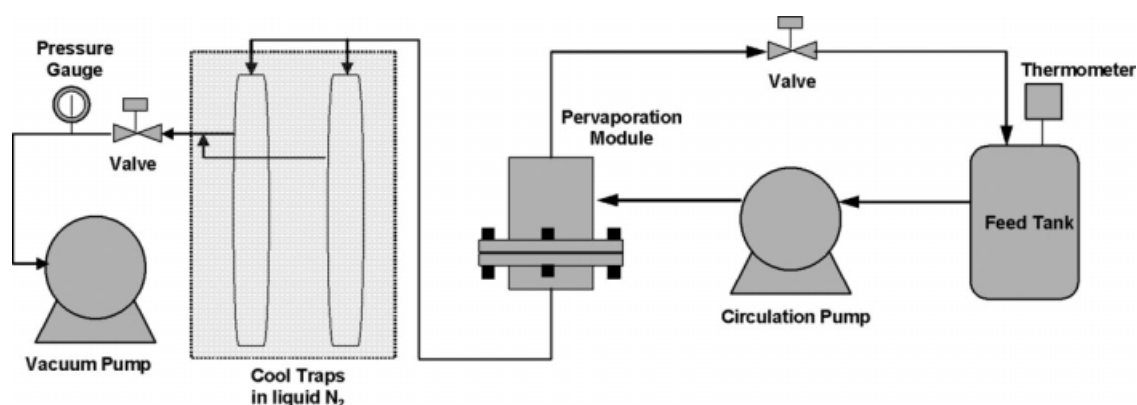

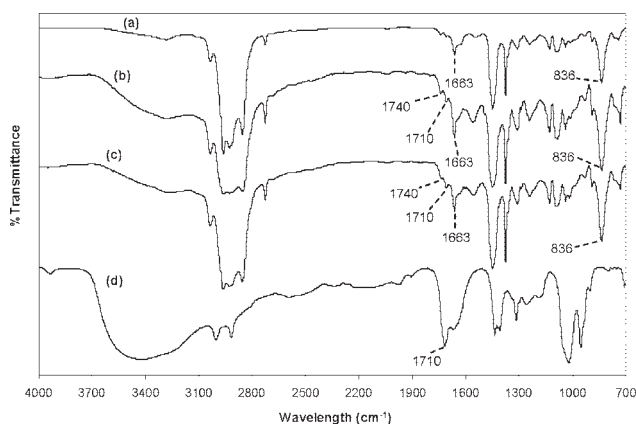**Figure 1** Schematic diagram of a pervaporation system.

Figure 2 FTIR spectra of (a) NR, (b) 30P NR/PAA, (c) 20P NR/PAA, and (d) uncrosslinked PAA.

band at 1710 cm^{-1} represents the carboxylic groups of PAA, which was clearly evident for uncrosslinked PAA, whereas the absorption bands at 1740 cm^{-1} can be observed for NR/PAA membranes, which corresponds to the ester linkage arising from the crosslink reaction of PAA carboxylic groups and EG hydroxyl groups. The 30P NR/PAA spectrum exhibited the stronger absorption peak at 1740 cm^{-1} when compared with the 20P NR/PAA spectrum implying the higher degree of crosslinking. For NR spectrum, the peaks at 836 and 1663 cm^{-1} attributed to the C=C bending and stretching of the isoprene unit.

Thermal analysis

Figure 3 shows the TG curves for NR, crosslinked PAA, and NR/PAA membranes. It can be seen that NR exhibited a single weight loss around 350–400 °C, whereas the crosslinked PAA showed the two-stage weight loss around 170–230°C and 350–

450°C. The first weight loss is attributed to the breakage of crosslink bonds (—CO—O), and the second weight loss was due to the decomposition of the main chain PAA. For NR/PAA membranes, the three-stage weight loss was observed corresponding to the disintegration of crosslink sites of PAA networks at around 170–230°C followed by the decomposition of NR molecules, and finally, the decomposition of PAA molecules at temperature > 400°C. The amount of weight loss at the crosslink-breakage temperature range increased with the amount of PAA indicating that the number of crosslink sites would increase as increasing the PAA content in the membrane. Note that the weight loss of crosslinked PAA at the temperature 50–150°C corresponded to the loss of absorbed water molecules, which exist in the bound state because of their interactions with the carboxylic groups of PAA.[11]

Swelling of NR/PAA membranes

The swelling behaviors of the membranes can infer the ability of a membrane to specifically absorb the liquid, henceforth the swelling degrees of the NR/PAA membranes in either pure water or pure ethanol were measured as shown in Figure 4. For all compositions of PAA, the membranes swelled negligibly in pure ethanol when compared with the swelling in water. This indicates that the membranes have more affinity to water, which is due to the presence of the hydrophilic PAA. Moreover, the water swelling was promoted as the PAA content in the membranes was increased suggesting that the water swelling of the membranes could be regulated by adjusting the amount ratio between the hydrophobic NR and the hydrophilic PAA.

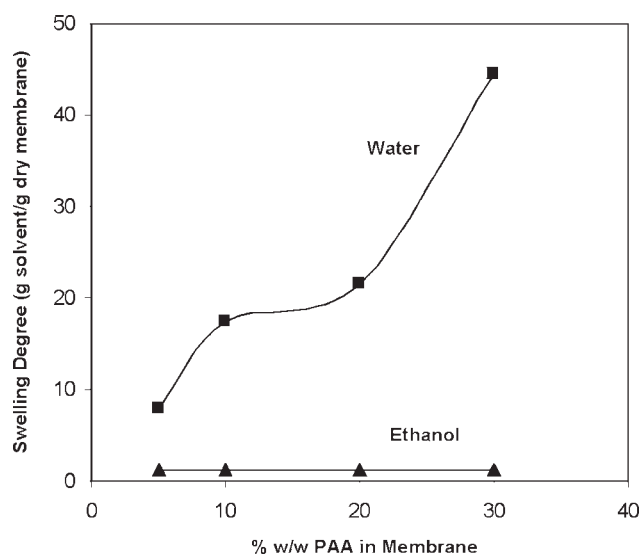**Figure 3** TG curves of (a) NR, (b) 5P NR/PAA, (c) 10P NR/PAA, (d) 20P NR/PAA, and (e) crosslinked PAA.

Figure 4 Swelling degree in pure water and pure ethanol of NR/PAA membranes.

TABLE II
Estimated Interaction Parameters of NR/PAA Membranes with
Pure Water $\chi_{water/membrane}$ and Pure Ethanol $\chi_{EtOH/membrane}$

Membrane	Weight ratio EG : PAA (g/g)	Swelling degree in water	$\chi_{water/membrane}$	Swelling degree in ethanol	$\chi_{EtOH/membrane}$
5P	0.44/1.00	7.90	0.55	1.20	1.42
10P	0.42/1.00	17.4	0.52	1.10	1.53
20P	0.43/1.00	21.5	0.52	1.10	1.50
30P	0.43/1.00	44.6	0.51	1.20	1.28

The affinity between the polymer and solvent can be expressed by the interaction parameter χ. For equilibrium sorption of pure solvent in polymer, the χ can be estimated from the simplified Flory-Huggins equation for a binary system[12]:

$$\chi = -\frac{\ln(1 - \phi_P) + \phi_P}{\phi_P^2} \quad (6)$$

where ϕ_p is a volume fraction of polymer. The estimated interaction parameters for water/membrane ($\chi_{water/membrane}$) and ethanol/membrane ($\chi_{EtOH/membrane}$) are tabulated in Table II. The estimated $\chi_{water/membrane}$ was about 0.5 and nearly the same for all NR/PAA membranes, whereas the $\chi_{EtOH/membrane}$ was found to be higher ($\sim$1.3–1.5). The lower $\chi_{water/membrane}$ means higher affinity of water toward the membrane. The $\chi_{water/membrane}$ was almost equal to the interaction parameter of PAA in water[13] affirming that the swelling in water of NR/PAA membranes occurred because of the interactions between water molecules and the carboxylic groups of PAA.

The swelling of NR/PAA membranes can be maintained not only by increasing the amount of NR but also by decreasing the chain mobility and the number of water-active carboxylic groups of PAA molecules. These can be accomplished by increasing the amount of crosslinker for the PAA crosslinking. Table III shows the effect of crosslink agent (EG) on the swelling of the 10P NR/PAA membrane in water. Evidently, the swelling degree was suppressed by increasing the amount of EG because the increase in the degree of crosslinking could limit the polymer chain mobility. Accordingly, this caused the polymer network to be more compact and rigid, in addition to the reduced number of active carbox-

ylic groups by crosslink reaction, which resulted in a decrease in the free volume that is accessible to water molecules.[14]

Figure 5 shows the effect of water concentration in the water–ethanol mixtures on the swelling of NR/PAA membranes. All membranes showed the maximum degree of swelling in pure water and the swelling degree declined with reducing of water concentration in the liquid mixtures. Finally, the membranes showed indistinguishable swelling at about 70% w/w of ethanol. As shown earlier, the NR/PAA membranes were swollen highly in water but not in ethanol. Therefore, adding more ethanol in the solution mixtures lowers the chance of water molecules to interact with PAA resulting in the decrease in the swelling degree.[15] More specifically, under high ethanol concentration ($>$70% w/w), the carboxylic groups of PAA are unassociated; therefore the intra and intermolecular H-bonding among PAA chains are realized apart from the crosslinking leading to more compact networks. As a consequence, intruding of ethanol and water molecules into the membrane structure will be difficult. Although the H-bonding between water molecules and the carboxylic groups may occur, due to the very less amount of water in the mixtures, its presence cannot counterpart
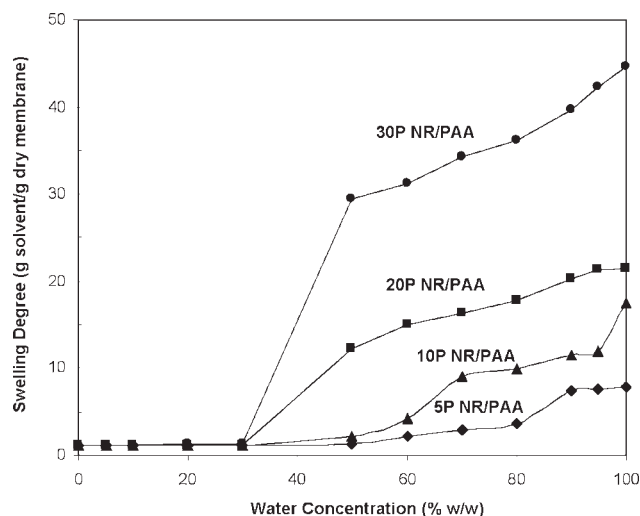
TABLE III
Effect of Crosslink Agent (EG) on Water Swelling
of 10P NR/PAA Membrane

Weight ratio EG : PAA (g/g)	Swelling degree in water
0.150/0.36	17.4
0.075/0.36	35.5
0.037/0.36	44.6

Figure 5 Swelling degree of NR/PAA membranes in water–ethanol mixtures.

the interactions among PAA chains. At high water content of the liquid mixtures, on the contrary, the pendant ─COOH groups on PAA are ionized producing more ─COO⁻. Having the ionized groups on the PAA chains, the repulsion between the ionized groups causes the PAA networks to expand allowing more intruding molecules. In addition, these ionized groups interact strongly with water molecules via the ion–dipole interaction, which promotes the penetrating of water molecules into the membranes.[4] Expectedly, the swelling degree of NR/PAA membranes increased with the weight content of PAA because the carboxylic groups on PAA chains are more attainable to attract water molecules into the membranes.

States of water in NR/PAA membranes

There are three states of water associated with the swollen hydrophilic membrane: free water, freezing, and nonfreezing bound water.[16] Free water is defined as water that has the same phase transition temperature as bulk water at 0°C, whereas freezing bound water has phase transition temperature lower than 0°C occurring due to the interactions of water clusters with polymer. Nonfreezing bound water is defined as water that possess no detectable phase transition peak for the temperature lower than the freezing point of pure water.[17] This nonfreezing bound water arises from the strong interaction between water molecules and polymer. The states of water in the water-swollen NR/PAA membranes have been examined as revealed by DSC thermograms in Figure 6. For all membranes, significant melting peaks appeared around 0°C. These peaks are believed to be the transition peak of free water, which corresponds to the melting transition of bulk water (water clusters). The phase transition peak was
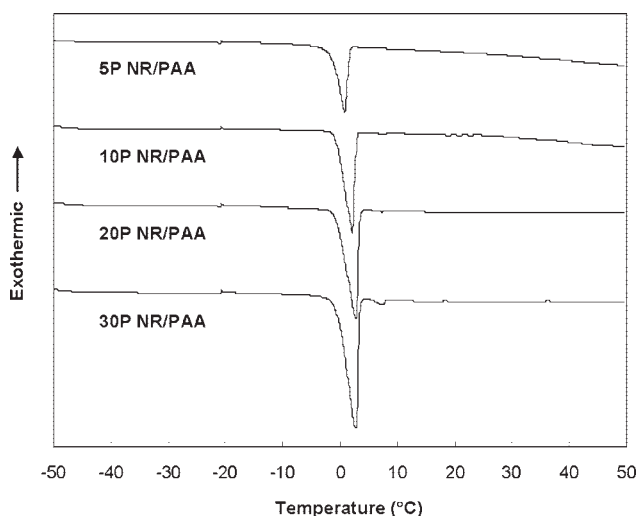
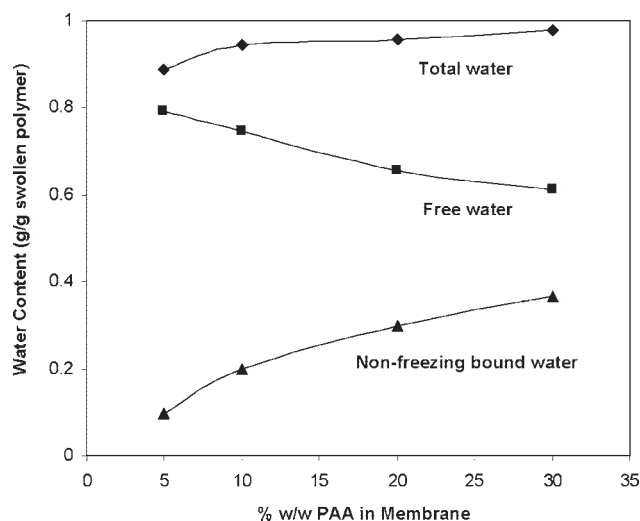**Figure 6** DSC melting curves of water-swollen NR/PAA membranes.

Figure 7 Water content corresponding to total, free, and nonfreezing bound water as a function of % w/w PAA in the NR/PAA membranes.

not observed at temperature below 0 to −50°C, and hence, it can be assumed that the freezing bound water did not exist and there was no interaction between water clusters and the PAA molecules.[18] The weight of free water m_{free} in the membrane was determined using the following equation:

$$m_{free} = \frac{\Delta H_{free}}{Q_{melting}} \qquad (7)$$

where ΔH_{free} is the heat of melting obtained from the peak area of DSC thermogram, and $Q_{melting}$ is the heat of melting of pure water which is equal to 334 J/g.[19] The amount of bound water arising from the interaction between the carboxylic groups of PAA and water molecules was estimated from the difference between the free water and the total water, which is calculated from the swelling degree of the membranes in water. Figure 7 shows the water content as a function of PAA weight fraction in the membranes. It is observed that the amount of nonfreezing-bound water increased with the amount of PAA while the free water showed the opposite trend. This suggests that the water molecules are strongly bound to the polar sites of PAA molecules preventing the aggregation of water molecules to form the water clusters. As the amount of PAA decreased, the probability of PAA to interact with water molecules has declined, thus, allowing the water molecules, which are in close contact, attract each other and form ice crystals.[20]

Membrane sorption selectivity

The permeability of the pervaporation membrane depends partly upon the solubility of the separated-liquid component in the membrane which can be revealed not only by the swelling behavior but also
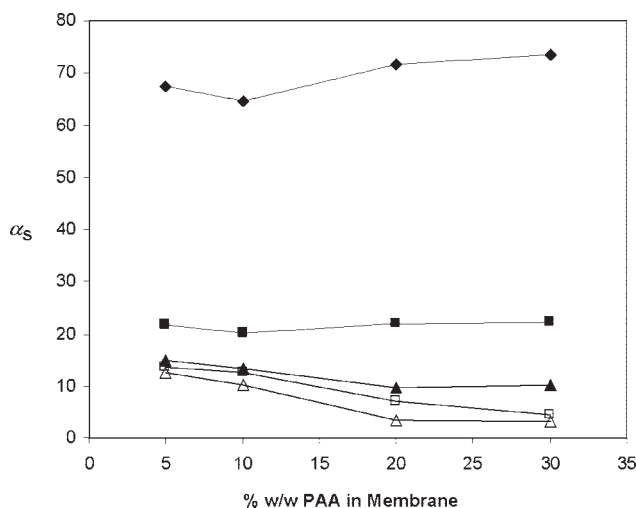
Figure 8 Water sorption selectivities (α_S) versus % w/w PAA in NR/PAA membranes at water concentration in water–ethanol liquid mixtures of 5 % w/w ($\blacklozenge$), 15 % w/w ($\blacksquare$), 30 % w/w ($\blacktriangle$), 50 % w/w ($\square$), and 90 % w/w ($\triangle$).

the sorption selectivity of the membrane. Therefore, the sorption experiment was conducted to evaluate the water sorption selectivity (α_S) of NR/PAA membranes at different water–ethanol compositions as demonstrated in Figure 8. The membranes showed the preferential sorption of water for all liquid mixture compositions as indicated by the α_S values higher than 1.0. For water concentration of 5% w/w, increasing the PAA in the membranes resulted in the increase in α_S because the hydrophilicity of the membranes was enhanced giving more attractions between water molecules and the membranes. Additionally, the lean-water surrounding (5 and 15% w/w water) yielded a more compact structure to the membranes, which could hinder the transport of larger ethanol molecules through the membranes. For water concentration at 30, 50, and 90% w/w, the α_S decreased with increasing amount of PAA. This decreasing of α_S at water-rich conditions was in agreement with the membrane swelling (see Fig. 5), which started to swell noticeably at water concentration higher than 30% w/w. High water content in the liquid mixtures caused the membranes to swell excessively resulting in the loose structure of the PAA chain networks. Accordingly, the ethanol molecules will readily permeate through the membranes together with water molecules.[21,22]

Pervaporation

Effect of feed compositions

The partial fluxes of permeated water (J_W) and ethanol (J_E) through the NR/PAA membranes in pervaporation separation of water–ethanol mixtures are illustrated in Figure 9. The partial water fluxes were significantly higher than the partial ethanol fluxes

indicating the preferential permeation of water to ethanol. The water permeated increasingly through the membrane when the water content in feed mixtures was increased. However, the increasing of the ethanol fluxes with feed water concentrations was obviously less. The permeation of water and ethanol molecules takes place more likely through the hydrophilic channels of PAA in the membranes. Water molecules can interact with functional groups of PAA by H-bonding and ion–dipole interaction where such interactions allow the water molecule to be able to attract other water molecules. Consequently, water clusters are formed in the membranes. These water clusters hinder the penetrating of ethanol molecules resulting in the less permeation rate of ethanol.[9] Increasing PAA content in the membranes generates more hydrophilic paths for water molecules to pass through the membrane, thus, giving rise to the enhancement of the water permeation.

At high feed water concentrations, the water fluxes were augmented because more water molecules are available to interact with PAA. Nonetheless, under this condition, the membranes could swell considerably at 30% w/w PAA. As a result, the polymer chains are more flexible and the activation energy for diffusive transport will be lower facilitating the permeating through the membranes of both components.[21,23] Evidently, this caused both partial water flux and ethanol flux for 30% w/w PAA membrane to increase.

Figure 10 revealed the effect of feed water concentration on the water separation factor (α_P) of NR/PAA membranes. The membranes showed high α_P at water content of feed mixtures less than 30% w/w; and increasing the PAA content in the membranes resulted in the water separation factor to
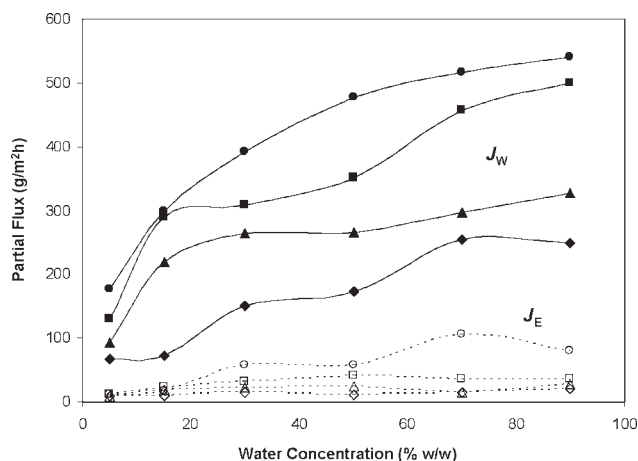

Figure 9 Effect of water concentration (% w/w) of feed water–ethanol mixtures on J_W and J_E for PAA content in the NR/PAA membranes of 5 % w/w ($\blacklozenge$, $\diamondsuit$), 10 % w/w ($\blacktriangle$, $\triangle$), 20 % w/w ($\blacksquare$, $\square$), and 30 % w/w ($\bullet$, $\circ$); feed temperature was 30°C.
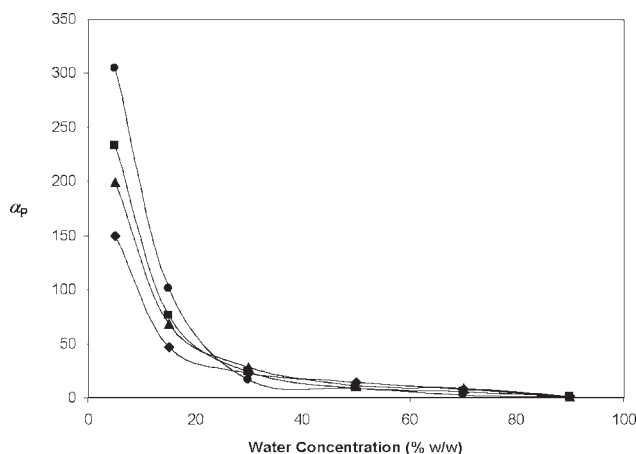
Figure 10 Effect of water concentration (% w/w) of feed water–ethanol mixtures on water separation factor (α_P) for NR/PAA membranes with PAA content of 5% w/w ($\blacklozenge$), 10% w/w ($\blacktriangle$), 20% w/w ($\blacksquare$), and 30% w/w ($\bullet$); feed temperature was 30°C.

increase. Nevertheless the α_P dropped substantially for higher water concentrations. The low α_P indicates that more ethanol molecules can penetrate through the membranes along with the water molecules, which takes place because the membranes have swelled excessively (see Fig. 5). In swollen membranes, the polymer chains are less restricted and hence both water and ethanol molecules can transport readily through the membranes.

Effect of feed temperature

The effect of feed temperature on the permeate flux through NR/PAA membranes was revealed in Figure 11 for low (5% w/w) and high (90% w/w) feed water concentrations. Evidently, for high water content in the feed, both J_W and J_E showed increasing trend with
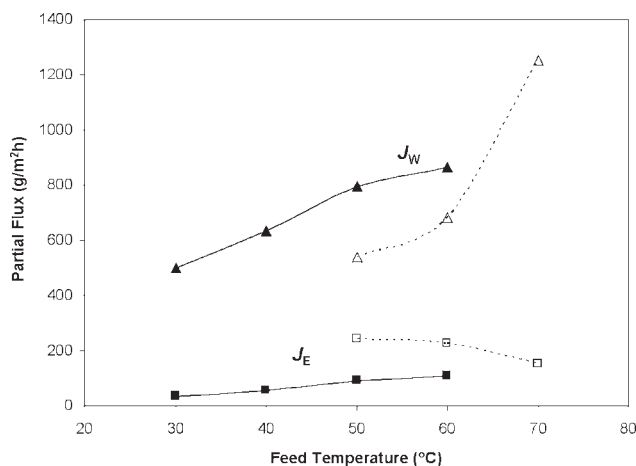
elevating feed temperature by which J_W increased more significantly than J_E. The flux enhancement with the feed temperature is the result of the increasing mobility of polymer chains at elevated temperatures that promotes the diffusion of penetrating molecules.[24,25] Moreover, under the water-rich conditions, the polymer networks will be less compact because the membranes could swell considerably which provides a less restricted permeation of both water and ethanol molecules through the membranes. For low feed water concentration, despite the pronounced enhancing of J_W with the feed temperature, J_E responded oppositely as increasing the temperature of feed liquids. Since the membrane swelling is less influential at high concentration of ethanol, the temperature rise tends to be more profound in agitating PAA chains while they were entrapped in NR matrix. This resembles to the polymer in a pore-confinement which impedes the passage of the permeants through a membrane.[26,27] However, with the specific interactions of water molecules with the PAA, the water diffusion will be more susceptible to the temperature than the diffusion of ethanol molecules yielding the water flux enhancement with the depression of the ethanol flux.

It will be clearer if the temperature dependence of permeation fluxes is described by the Arrhenius type relationship as follows[28]:

$$J_W = J_{OW} \exp(-E_{JW}/RT) \tag{8}$$

$$J_E = J_{OE} \exp(-E_{JE}/RT) \tag{9}$$

where E_J is the activation energy for permeation, J_O is the pre-exponential term, and RT is the thermal energy. Figure 12 shows the plot between ln J and
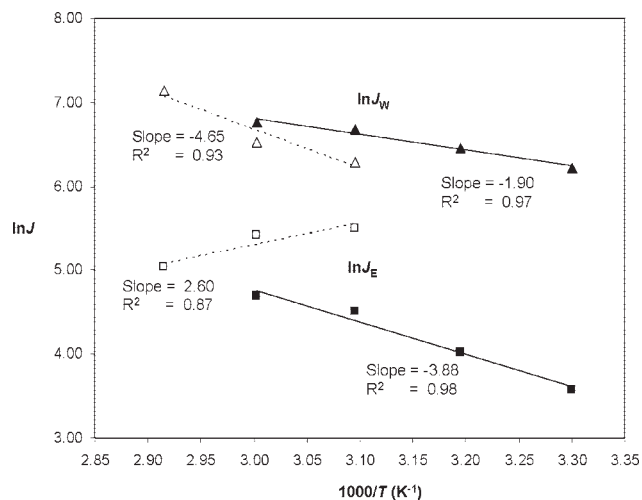

Figure 11 Effect of feed temperature on a partial water flux (J_W) and a partial ethanol flux (J_E) through 20P NR/PAA with 90% w/w feed water (closed symbols) and 30P NR/PAA with 5% w/w feed water (opened symbols).

Figure 12 Plot of ln J versus $1000/T$ for a partial water flux (J_W) and a partial ethanol flux (J_E) through 20P NR/PAA with 90% w/w feed water (closed symbols) and 30P NR/PAA with 5% w/w feed water (opened symbols).

$1000/T$ of the partial permeation fluxes of water and ethanol through NR/PAA membranes for 5 and 90% w/w of feed water concentrations. As can be seen, the linear relationships were obtained confirming the Arrhenius relationships of the permeation through NR/PAA membranes. For 20P NR/PAA with 90% w/w feed water, the activation energies were estimated as 15.8 and 32.2 kJ/mol for the permeation of water and ethanol, respectively. Because of the lower E_{JW}, water molecules can penetrate through the membrane more easily than ethanol. For 30P NR/PAA with 5% w/w feed water, the estimated E_{JW} was 38.67 kJ/mol suggesting more impeded transport of water molecules because of the less membrane swelling. For the ethanol permeation, the activation energy changed from 32.2 to -21.60 kJ/mol, which indicates that increasing feed temperature poses unfavorable transport of ethanol molecules through the membrane.

CONCLUSIONS

The hydrophobic–hydrophilic pervaporation membranes were fabricated from NR and PAA, which was crosslinked by EG. The use of NR allowed the formation of membranes from latex without the necessity of dissolving polymer which required organic solvent. The membranes were used in the pervaporation dehydration of water–ethanol mixtures. The swelling of the membranes revealed more extensive swelling in pure water when compared with the swelling in pure ethanol, which is mainly due to the presence of hydrophilic PAA. Therefore, an increase in the ethanol concentration in the liquid mixtures will result in the decrease of the membrane swelling degree. Furthermore, the water swelling was affected by the amount ratio of the hydrophobic NR and the hydrophilic PAA as well as the amount of EG crosslinker. The states of water absorbed by the membranes were examined by DSC. It was found that as the PAA content in the membranes was increased, more water molecules were strongly bound to the functional groups of PAA molecules and appeared as nonfreezing-bound water. Although NR/PAA membranes showed the preferential sorption to water, high fraction of water in the water–ethanol mixtures caused the excessive swelling of the membranes resulting in the decrease of the water sorption selectivity. Pervaporation separation of water–ethanol mixtures was performed, and the results showed that for low water concentration of feed mixtures (<30% w/w), increasing PAA content of the membrane could improve both water permeation flux and separation factor. However, if the water concentration in the feed was increased further, even though both water and ethanol permea-

tion fluxes have increased, the water separation factor would be reduced. This is because at high water content, the membrane swelled substantially and causes the loose structure of the polymer networks, which allows the water and ethanol molecules to transport through the membrane more easily. Increasing feed mixture temperature at high feed water concentration was found to affect the permeation flux in the similar manner as increasing water concentration of the feed mixtures. On the other hand, for low feed water concentration where the membrane swelling was less extensive, the temperature rise caused the increase of water flux with the decrease of ethanol flux.

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