

Comparative Behavior of PVA/PAN and PVA/PES Composite Pervaporation Membranes in the Pervaporative Dehydration of Caprolactam

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ABSTRACT: Flat-sheet composite membranes were developed by the traditional phase inversion technique using poly(vinyl alcohol) (PVA). PVA composite pervaporation (PV) membranes were prepared with crosslinked PVA selective layer and porous polyacrylonitrile (PAN) and polyether sulfone (PES) substrate layer material as supports for separating heat sensitivity substance ϵ -caprolactam (CPL) from CPL/water mixtures. Glutaraldehyde was used as crosslinking agent. The effect of the composition of glutaraldehyde on membrane stability and structure were investigated. The operating parameters, such as feed concentration and operating temperature, remarkably affected PV performance of the com-

posite membranes. The composite membranes with PVA casted on PAN (PVA/PAN) showed superior PV performance than that casted on PES (PVA/PES). This study has also shown that the type of porous support plays an important role in the PV performance. As a result, this work has presented the information needed of the behavior of PV membranes for dehydration applications of industrial caprolactam. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 4005–4011, 2007

Key words: composite pervaporation membranes; separate; glutaraldehyde; CPL/water mixtures; PVA/PES; PVA/PAN; pervaporation performance

INTRODUCTION

ϵ -Caprolactam (CPL) is an important organic chemical material widely used in the manufacture of high quality nylon 6 fibers and resins, whose structure is shown in Figure 1. Since CPL is highly heat sensitive, water as the most important impurity in the final CPL purification creates further difficulties. To prevent decomposition, CPL is usually crystallized from CPL–water mixtures under a reduced pressure distillation through triple-effect evaporation sets, for water has a higher volatility than CPL. But this process has some disadvantages such as low heat transfer coefficient, a large amount of middle pressure steam consumption, and coagulation from steam containing considerable CPL. Therefore, a high-efficiency dehydration process operation for the concentrate of CPL/water mixtures is required.

Pervaporation (PV) is considered to be an energy efficient alternative and eco-friendly clean technology. Moreover, PV can be operated at lower temperatures than other separation methods such as distillation, which makes it possible to utilize waste-heat as the heat of vaporization to separate volatile organic compounds (VOCs) from water in the chemical industry.¹ It often has the advantages for the separation of constant-boiling azeotropes, close boiling, isomeric, and

also used for the dehydration of organic solvents and the removal of organics from aqueous mixtures.^{1–21}

PV composite membranes are often widely used in industry. The thinner skin layer is coated on a porous support layer to achieve a higher permeation rate and sufficient mechanical strength. Poly(vinyl alcohol) (PVA) can readily form thin films showing high permselectivity to water and chemical resistance, which makes it an attractive polymer to be used as a PV membrane for the dehydration of aqueous–organic mixtures.^{2–16} However, in adopting PVA polymeric membranes to separate organic–liquid mixtures, there is a problem of membrane swelling, which reduces selectivity because of its plasticization effect. Therefore, suppressing membrane swelling is important to obtain good permselectivity. Some methods have been used to improve the structural stability, including the crosslinking treatment,^{2,6–8,15,16} graft,^{4,12} heat treatment,^{2,6,9} and so on to improve the chemical and thermal stability of the membrane in aqueous solutions. Crosslinking can suppress the degree of swelling by reducing the mobility of polymer chains; the resulting composite membranes show high permeabilities and high permselectivities in PV of organic–liquid mixtures. Here, we developed asymmetric membranes with a PVA as “active layer” and two different types of membrane materials—porous polyacrylonitrile (PAN) ultrafiltration (UF) membranes and polyether sulfone (PES) UF membranes as support layers have been selected for separating CPL/water

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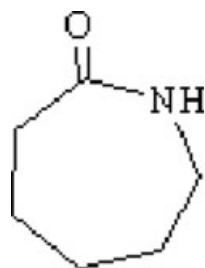


Figure 1 The structure of CPL.

mixtures and the PV performances were compared for this purpose: PAN UF membranes, owing to its hydrophilic character, are widely used for dehydration applications in PV technology^{3,10,19}; PES UF membranes, due to its excellent chemical resistance, good thermal stability, and mechanical properties and are widely used for development of asymmetric composite membranes.^{6,15}

EXPERIMENTAL

Materials

ϵ -Caprolactam (CPL) (chemical pure) was supplied by Baling Petrochemical Co. (SINOPEC, China); Poly(vinyl alcohol) (PVA) (hydrolyzed 99%, with average $M_w = 89,000$ – $98,000$) and glutaraldehyde (GA, 25 wt % in water) were obtained from Aldrich Chemicals (USA). Porous ultrafiltration membranes (UF) of polyacrylonitrile (PAN) (cut-off MW 5×10^4) and polyether sulfone (PES) (cut-off MW 5×10^4) were supplied by the Development Center of Water Treatment Technology (China). All the chemicals were used without further purification. Deionized water was used in preparing the aqueous feed solutions for the PV experiments.

Preparation of dense membrane and composite membrane

Membranes were prepared by crosslinking technique in a laboratory. The casting procedure is as follows⁹: Firstly, PVA was dissolved in water by refluxing and stirring for 6 h at 100°C . Homogeneous solution of 10 wt % polymer in water was obtained. To this solution, HCl as a catalyst, a certain amount of crosslinking agent (glutaraldehyde) was added and the reaction was started. Continue to slowly stir the solution at room temperature for 20 h, then, the reaction was stopped by neutralization with sodium hydroxide solution. The solution was degassed and any bubbles in the solutions were removed and then the cooled and degassed homogeneous solution was cast on a clean Plexiglas using a casting knife. The gelatination state was allowed to evaporate slowly and dried at room temperature. Finally, the crosslinked membranes were treated in an air-circulating oven at temperature 120 – 150°C for 1 h for thermal crosslinking.

Phase inversion is the usual procedure for fabrication of asymmetric PES and PAN flat-sheet membranes. The dry coated membranes, which had been treated with 4 wt % 1N sodium hydroxide solution for 24 h, were washed and rinsed by about 4 wt % 1N hydrogen chloride solution and deionized water till neutrality and air-dried. Then, the prepared solution was cast for a desired thickness on the porous PAN and PES substrate membranes held on a glass plate with the aid of a casting knife made in our laboratory. The composite membranes in the gelatination state were allowed to evaporate slowly till dry at room temperature. Finally, the composite membranes were treated in an air-circulating oven at temperature 120 – 150°C for 1 h for thermal crosslinking.^{9,15}

Characterization

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to study the morphology of the various composite membranes. The air-dried composite membranes were frozen in liquid nitrogen and broken and the membrane samples were then coated with a conductive layer of sputtered gold. The morphologies of the PVA composite membranes were observed with SEM (FEI Quanta 200, FEI, Holland).

Fourier transform infrared spectroscopy

The crosslinking reaction of PVA with GA was confirmed by the Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of uncrosslinked and crosslinked membranes were scanned using Nicolet AVATAR 360 FTIR spectrometer (Nicolet AVATAR 360, Nicolet, USA).

Thermogravimetric analysis

The thermal stability of the PVA active layer was performed in a Setaram SETSYS Evolution 16 thermogravimetric analyzer (SETSYS Evolution 16 SETARAM-France). Samples (2–5 mg) were heated at the rate of $20^\circ\text{C min}^{-1}$ from ambient temperature to 650°C . Nitrogen was used as the purge gas at a flow rate of 20 mL min^{-1} .

PV performance

The procedure used in PV experiments were described earlier and shown in Figure 2.¹³ The liquid feed was circulated through the PV cell from a feed tank by a pump with a rate of 200 L/h. The pressure at the downstream side was kept about 10 mbar within ± 1 mbar by a vacuum pump. Permeate was condensed in liquid nitrogen traps. PV flux was determined by weighing a penetrant collected by a liquid nitrogen trap during a given amount of time. Steady

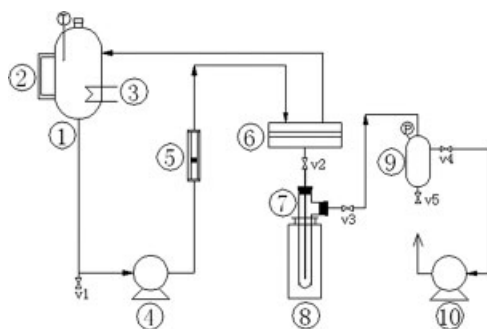


Figure 2 Schematic diagram of pervaporation apparatus, 1: feed tank; 2: liquid level meter; 3: heater; 4: circulation pump; 5: rotor flow meter; 6: membrane cell; 7: collecting bottle; 8: liquid nitrogen cold trap; 9: buffer vessel; 10: vacuum pump; V1–5: valves; T: temperature control; P: vacuum pressure gauge.

state was obtained after 2 h throughout the experiments. The feed solution temperature maintained in the range of 30–60°C and the membrane with an effective area of 72.35 cm² was supported by a porous titanium plate. The composition of the liquid feed mixture was analyzed by measuring the refractive index of the permeate within an accuracy of ± 0.0001 units using high-precision Abbe Refractometer (Atago NAR-3T, Japan) and using standard graph of refractive index versus known compositions of CPL–water mixtures. The refractometer prisms were maintained at 20°C \pm 0.1°C. The results from refractive index measurements can compare well with those from gas chromatography; for all tested membranes the variation of flux and selectivity of samples from different batches was less than 10%.¹⁶ The vapor penetrant collected mixture was determined by a SP3400 gas chromatography with a FID detector (made in China) under the following conditions: PEG-20M capillary column, 2 m \times 6 mm i.d., temperature: 170°C, carrier gas: nitrogen, flow rate: 30 mL min⁻¹.

The permeation flux (J) (in g/m² h) and the separation factor (α), and the PV separation index (PSI) were calculated by the following equations, respectively:

$$J = \frac{W}{A \times t} \quad (1)$$

$$\alpha = \frac{Y_{\text{water}}/Y_{\text{CPL}}}{X_{\text{water}}/X_{\text{CPL}}} \quad (2)$$

$$PSI = J \times (\alpha - 1) \quad (3)$$

where W is the weight of the permeate (g) collected in a time interval t (h), and A the effective membrane area (m²); X_{water} , X_{CPL} and Y_{water} , Y_{CPL} are the weight fraction of water and CPL in the feed and permeate, respectively.

RESULTS AND DISCUSSION

SEM analysis

Scanning electron micrographs of the crosslinked PVA composite membranes are shown in Figure 3. The SEM micrographs indicate the typical asymmetric structure with a very thin and compact layer on the top (skin layer) and a porous and thicker layer as a support. Figure 3(a) shows the crosslinked PVA thin dense layer coating on composite membranes. PVA/PAN and PVA/PES composite membranes are shown in Figures 3(b) and 3(c). It can be obviously seen from the pictures that the composite membrane was composed of three layers: a coating layer, a supported porous membrane, and a nonwoven fabric. The thicknesses of PES and PAN porous supports were 100 \pm 5 and 95 \pm 5 μ m, respectively, and the total thicknesses of dry composite membranes PVA/PES and PVA/PAN were found to be about 110 \pm 5 and 105 \pm 5 μ m from SEM images, respectively. Therefore, the thickness of the active layer was almost the same about 10–15 μ m.

FTIR analysis

Un-crosslinked and crosslinked PVA coating layer was determined using FTIR spectroscopy and its results are compared with Figure 4. Related studies, PVA with GA via an acetal reaction,^{6,7,22} have already been well documented. Results have already shown that the intensity of the O–H bands observed in membranes decreases considerably with the GA contents increasing in the crosslinking agent. It can be seen from these spectra that the main characteristic absorption peaks are: one distinct broad absorption

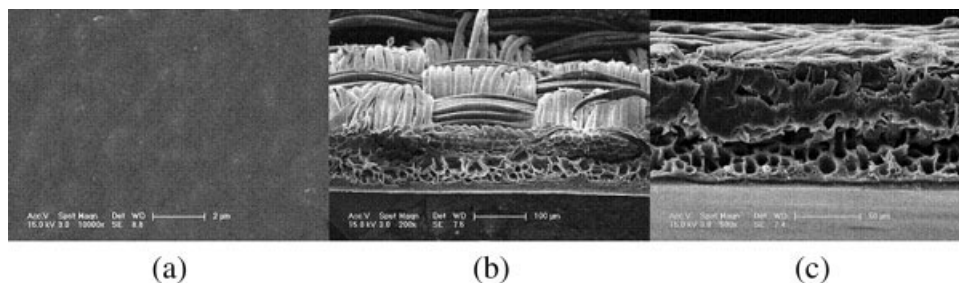


Figure 3 The morphology of PVA composite membranes (a) top surface, (b) PVA/PES, and (c) PVA/PAN.

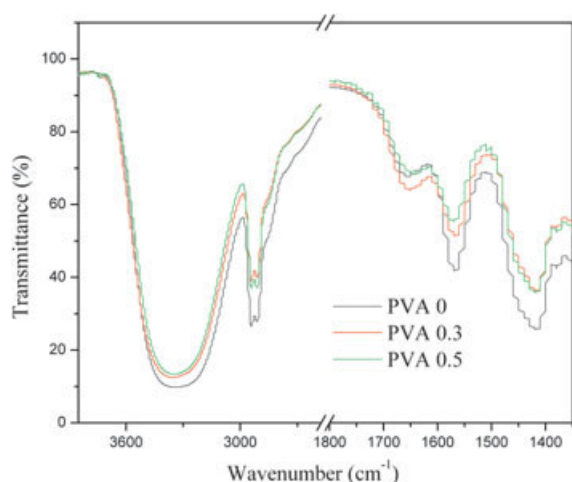


Figure 4 FTIR spectra of PVA composite membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bands at 3000–3600 cm^{-1} , which is attributed to stretching of the O–H hydroxyl group; the two sharp band at 2900 cm^{-1} corresponding to asymmetric and symmetric stretching of the CH; 1720 cm^{-1} , corresponding to stretching of C=O group of aldehyde; 1350–1480 cm^{-1} , maybe corresponding to variable deformation vibrations of the CH₂ or C–H groups. The similar trend was observed that the relative intensity of the O–H group gradually weakened with GA content in the FTIR spectra, which means that the degree of crosslinking in the PVA coating layer on the supports increased with increasing GA content.^{13,15}

Thermal analysis

Figure 5 compares the thermal stability and decomposition curves of uncrosslinked and crosslinked PVA

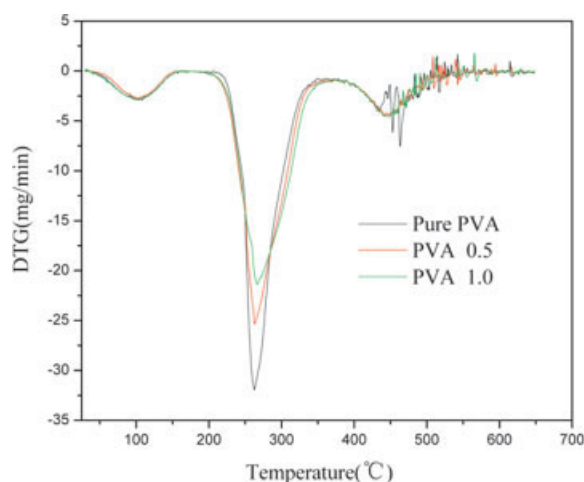


Figure 5 TGA thermograms of PVA composite membranes crosslinked at different GA contents in the crosslinking agents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composite membranes, respectively. A weight loss before 220 °C was observed for all samples. This weight loss was considered to be corresponding to the absorbed water in the membranes. The recorded thermograms for all samples showed two degradation steps: PVA membranes decomposition starts to decompose at 230 °C and decomposes completely around 530 °C. Compared with uncrosslinked PVA membranes (Pure PVA), less weight loss is observed for the crosslinked PVA membranes (PVA 0.5/1.0), this implies that the more formation of acetal rings and ether linkages complex would have higher thermal stability.

Using wide angle X-ray diffraction, we found that the relative intensity of typical diffraction peak at $2\theta = 20^\circ$ decreased. The crystallinity decreased from 34.39 to 26.43% with increasing GA contents from pure PVA to PVA crosslinked with 0.7 wt % GA contents in the crosslinking agents. The result also implies that the increase in the crosslinking of the PVA membrane decreases the crystallinity of the membrane, which results in a compression of the amorphous region.¹³

Effect of operating temperature on PV properties

In general, the effect of temperature on flux is positive. This is due to the increased thermal motion of the chain with increasing temperature that accelerates the diffusion of the permeants.¹⁷ The effect of operating temperature on PV performances of PVA composite membranes for 60 wt % of CPL–water mixtures in the feed was studied and the results are shown in Figures 6 and 7. As is reflected from the plot, when the temperature increases, both permeation flux increase, but separation factors represent differently. The separa-

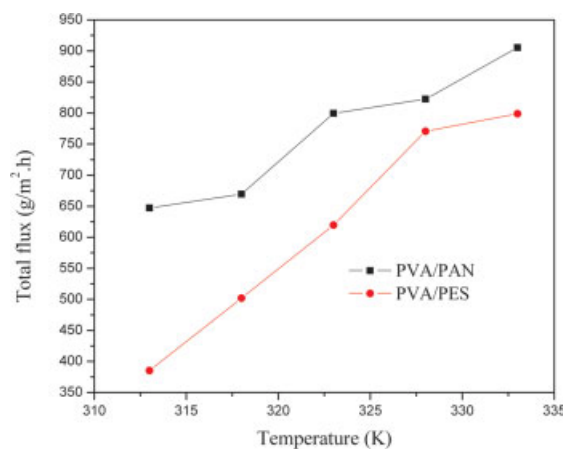


Figure 6 Effect of the operating temperature on total flux of CPL–water mixtures through PVA composite membranes crosslinked with 0.6 wt % GA contents in the crosslinking agent at 60 wt % CPL feed concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

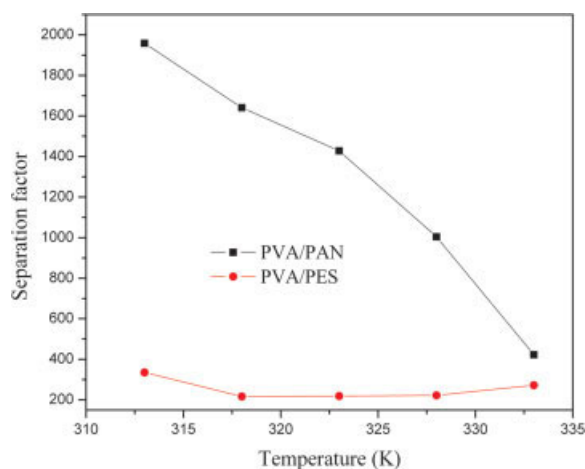


Figure 7 Effect of the operating temperature on the separation factor of CPL–water mixtures through PVA composite membranes crosslinked with 0.6 wt % GA contents in the crosslinking agent at 60 wt % CPL feed concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ration factor of PVA/PAN composite membrane decreases significantly as the temperature increases; however, the separation factor of PVA/PES composite membrane stays comparatively constant. Perhaps this is due to the characters of different substrate membrane materials. According to the free volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature increases, the frequency and amplitude of chain jumping increase and the free volume in the selective layer will be enlarged. At the same time, increase in temperature also reduces the interaction between CPL and water molecules and diffusing substance will have greater kinetic energies, so that the diffusion rate of individual permeating molecules and associated permeating molecules are high, thus the total flux could be higher and separation factor lower.

The temperature dependence of the permeation rate J can be expressed by an Arrhenius-type relationship:

$$J = A_0 \exp(-E_0/RT) \quad (4)$$

where A_0 is the pre-exponential factor; E_0 , the apparent activation energy of permeation; and T , the operating temperature. Arrhenius plots for composite PVA/PES and PVA/PAN are shown in Figure 8. The relationship between fluxes and the reciprocal of temperature indicated a good linearity in the given temperature range and the behavior of these membranes followed Arrhenius law. The apparent activation energies of CPL/water mixtures through PVA composite membranes calculated from the slopes of Arrhenius plots are 15.27 and 32.49 kJ/mol with CPL 60 wt % in the feed, respectively. The apparent activation ener-

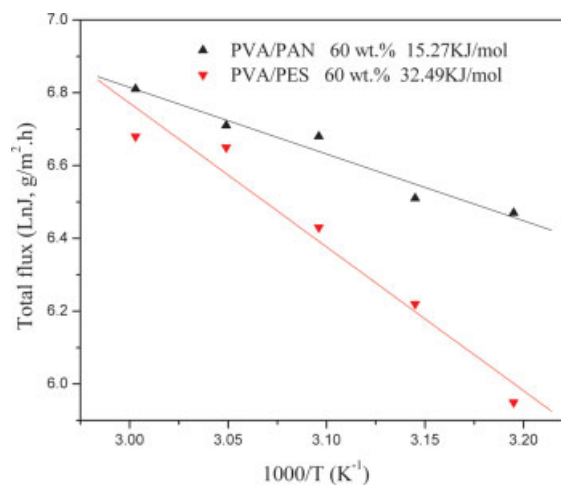


Figure 8 The plots between the total flux of the composite membranes and the feed temperature reciprocal. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

gies of CPL/water through PVA/PAN composite membrane was lower than that of PVA/PES composite membrane indicating that the permeation of CPL/water through PVA/PAN composite membrane was easier and required less energy than PVA/PES composite membrane.

Effect of the feed composition on PV properties

At 55°C, the total flux and separation factor characteristics of CPL/water mixtures in the concentration range of 30–70 wt % through the two crosslinked PVA composite membrane are compared in Figures 9 and 10. It is observed that both the two composite membranes exhibit an increase in the total flux, while the

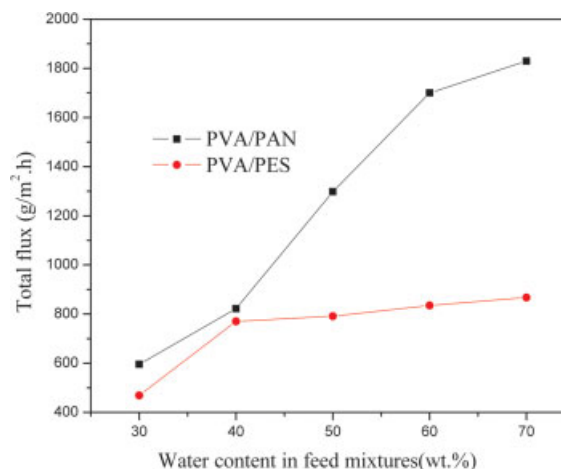


Figure 9 Effect of the feed concentration on total flux of CPL–water mixtures through PVA composite membranes crosslinked with 0.6 wt % GA contents in the crosslinking agent at 55°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

separation factor decreases distinctly with the weight fraction of water in the feed increasing. This is due to the combined internal plasticizing and coupling effects occurring between the transports of different penetrant and the membrane.² With higher water concentration in the feed mixture, more water molecules can be sorbed into the membrane and the amorphous regions of the membrane are more swollen, as a consequence, the polymer chains become more flexible. This makes both water and CPL molecules require less energy for diffusion through voids of the membranes, thus the total flux increases and the separation factor decreases. Such behavior is consistent with the previous reports in the dehydration of aqueous organic mixture through hydrophilic polymeric membranes.^{12,16}

Influence of the support layer on PV properties of composite membranes

The PV properties of composite membranes with different supports for separating CPL/water mixtures are shown in Figures 6, 7, 9, and 10. The composite membrane prepared with the hydrolyzed PAN porous membrane gives a higher separation factor and total flux for CPL/water mixtures than that of PES. When comparing the overall and intrinsic permeabilities for each composite membrane, the largest difference of PV properties between the two composite membranes is the supports layer. Total fluxes of the composite membranes with the same active layer (PVA) but with different supports (PES and PAN) varied in different ways. This may be due to different hydrophilic–hydrophobic properties of PES and PAN.¹⁸ Since the thickness and the crosslinking density of the active layers of the both membranes were almost the same, one major reason for this high total

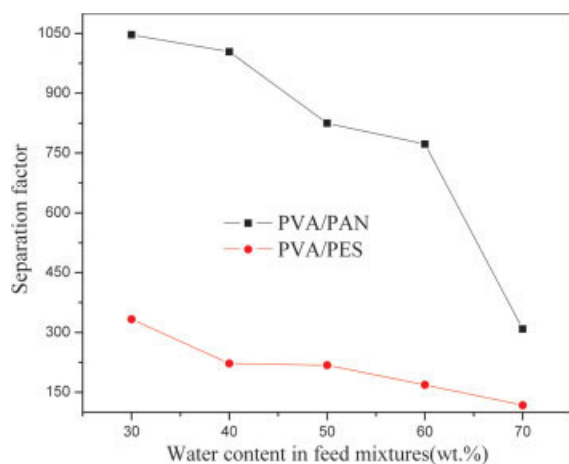


Figure 10 Effect of the feed concentration on the separation factor of CPL–water mixtures through PVA composite membranes crosslinked with 0.6 wt % GA contents in the crosslinking agent at 55°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

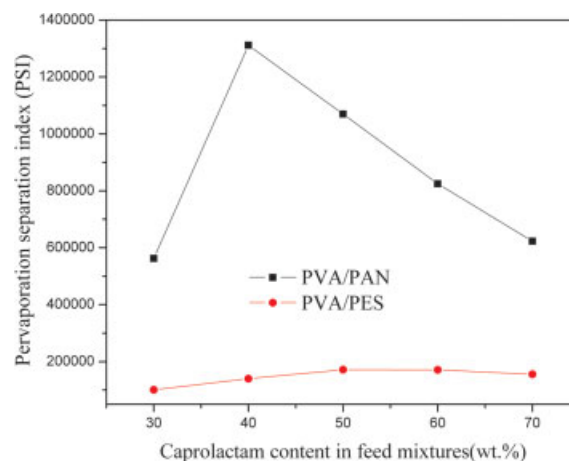


Figure 11 Comparisons of pervaporation separation index (PSI) with the two different composite pervaporation membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

flux and separation factor of the membranes with the PAN support could be that PAN was more hydrophilic than PES. Because part hydrolysis of PAN porous membrane using aqueous sodium hydroxide made some $-\text{CN}$ groups into $-\text{COOH}$ on its surface that increased the affinity between PAN and water molecules.¹⁹ Lower total flux and separation factor of PVA/PES compared to that of PVA/PAN can be explained from the viewpoint that PES, even though the active layer can interact permselectively with water but due to the hydrophobic properties of PES caused a significant decrease of the polymer dehydration capacity, thus there is a decrease in total flux and separation factor. Hence, we can come to a conclusion that the type of porous support has significant effects on PV performance. Similar results have been reported in the literature.^{20,21} The PSI in Figure 11 confirmed that composite PVA/PAN membrane had superior performance.

CONCLUSIONS

Two types of PV composite membranes developed from PVA using PES and PAN as porous supports for separation of CPL/water mixtures were investigated in this article. Crosslinked PVA active layer decreases the hydrophilicity of the membranes and has higher thermal stability than the uncrosslinked membrane. The results of dehydration of CPL using PV composite membranes show that the PVA composite membranes are good PV membrane for dehydration of CPL. The type of porous support layer plays an important role in the PV performance. By comparison, PV performance of PVA/PAN composite membrane is superior to that of PVA/PES for separating CPL–water mixtures. It has the better performance in terms of dehydration capacity removing most of water from CPL/water mixtures. This kind of permeation behavior of

PV composite membranes is very useful to obtain information for industrial applications in future.

References

1. Feng, X. S.; Huang, R. Y. M. *J Membr Sci* 1996, 116, 67.
2. Yeom, C. K.; Lee, S. H.; Lee, J. M. *J Appl Polym Sci* 2001, 79, 703.
3. Qiao, X. Y.; Chung, T.-S.; Guo, W. F.; Matsuura, T.; Teoh, M. M. *J Membr Sci* 2005, 252, 37.
4. Chiang, W.-Y.; Chen, C.-L. *Polymer* 1998, 39, 2227.
5. Nam, S. Y.; Chun, H. J.; Lee, Y. M. *J Appl Polym Sci* 1999, 72, 241.
6. Chen, F. R.; Chen, H. F. *J Membr Sci* 1996, 109, 247.
7. Yeom, C. K.; Lee, K.-H. *J Membr Sci* 1996, 109, 257.
8. Kusumocahyo, S. P.; Sano, K.; Sudoh, M.; Kensaka, M. *Sep Purif Technol* 2000, 18, 141.
9. Cai, B. X.; Yu, L.; Ye, H. L.; Gao, C. J. *J Membr Sci* 2001, 194, 151.
10. Li, J. D.; Chen, C. X.; Han, B. B.; Peng, Y.; Zou, J.; Jiang, W. J. *J Membr Sci* 2002, 203, 127.
11. Upadhyay, D. J.; Bhat, N. V. *J Membr Sci* 2005, 255, 181.
12. Alghazawi, N.; Sanly, O.; Aras, L.; Asman, G. *Chem Eng Process* 2005, 44, 51.
13. Zhang, L.; Yu, P.; Luo, Y. B. *Sep Purif Technol*, to appear.
14. Wei, Y. M.; Xu, Z. L.; Qusay, F. A.; Wu, K.; *J Appl Polym Sci* 2005, 98, 247.
15. Ahn, S. M.; Ha, J. W.; Kim, J. H.; Lee, Y. T.; Lee, S. B. *J Membr Sci* 2005, 247, 51.
16. Kariduraganavar, M. Y.; Kulkarni, S. S.; Kittur, A. A. *J Membr Sci* 2005, 246, 83.
17. Huang, R. Y. M.; Pal, R.; Moon, G. Y. *J Membr Sci* 1999, 160, 17.
18. Jiraratananon, R.; Sampranpiboon, P.; Uttapap, D.; Huang, R. Y. M. *J Membr Sci* 2002, 210, 389.
19. Wang, X. P.; Feng, Y. F.; Shen, Z. Q. *J Appl Polym Sci* 2000, 75, 740.
20. de Bruijn, F. T.; Sun, L.; Olujić, Ž.; Jansens, P. J.; Kapteijn, F. *J Membr Sci* 2003, 223, 141.
21. Trifunović, O.; Trägårdh, G. *J Membr Sci* 2005, 259, 122.
22. de Azevedo, W. M.; de Souza, J. M.; de Melo, J. V. *Synth Met* 1999, 100, 241.