

# Preparation and Characterization of CMCS/PVA Blend Membranes and Its Sorption and Pervaporation Performance (I)

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**ABSTRACT:** Novel pervaporation (PV) membranes for ethanol dehydration were prepared by blend poly(vinyl alcohol) (PVA) and carboxymethyl chitosan (CMCS), followed by the crosslinking reaction with glutaraldehyde; the structure and miscibility of the blend membranes were characterized by Fourier transform infrared, X-ray diffraction, and differential scanning calorimetry; the results indicated that the blends were miscible. The effect of feed concentration, operation temperature, crosslinking agent content, etc. on sorption performance and PV per-

formance of the blend membrane is investigated. The membrane of CMCS/PVA blend ratio of 8 : 2 exhibited a high separation factor of 2959 with a reasonably high water flux value of  $0.14 \text{ kg m}^{-2} \text{ h}^{-1}$  at the azeotropic feed composition (95 wt % of ethanol) at a temperature of 45°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3369–3378, 2009

**Key words:** CMCS/PVA; blend membrane; crosslinking; pervaporation; sorption

## INTRODUCTION

Among many separation and purification technologies available in the literature, pervaporation (PV) is considered to be one of the simplest unit operations to separate azeotropic mixtures, closely boiling liquid mixtures, heat-sensitive biochemicals, liquid-liquid isomers, etc.<sup>1–5</sup> PV is an energy saving and eco-friendly method when compared with other separation techniques including conventional distillation.

Natural polysaccharides are among the most widely used biopolymers for various applications and also in developing membranes for PV separation applications.<sup>6</sup> Chitosan (CS) is the widely studied membrane material in PV separation and particularly in dehydrating industrial solvents, such as ethanol, isopropanol, and THF. Usually, carboxymethylation of polysaccharides provides solubility in water. For example, carboxymethyl cellulose and carboxymethyl chitin or CS are all soluble in water.<sup>7</sup>

However, to our knowledge, few research results on membranes prepared by carboxymethyl chitosan (CMCS) were reported. Uragami et al.<sup>8,9</sup> investigated the CMCS membrane crosslinked with glutaraldehyde (GA) for evaporation of the aqueous alcoholic solutions. They found that a control in both chemical and physical structure was very important in the permeation and separation through the membranes. Zhang et al.<sup>10</sup> also prepared the blend membranes from CMCS/alginate for separation of alcohol/water mixture. In previous studies, we<sup>11</sup> also prepared CMCS membrane and GA crosslinked hollow fiber composite membranes for PV dehydration of aqueous isopropanol mixtures.

PVA is an aliphatic polymer containing hydroxyl groups and can be crosslinked by GA and multicomponent carboxylic acids, and its membranes also have been widely used in various PV dehydration applications in industries, such as dehydrations of alcohols, esters, acids, and volatile organic compounds.<sup>12,13</sup> However, PVA is a crystalline polymer, which gives a low flux for water. Nam et al.<sup>14</sup> prepared carboxymethylated poly(vinyl alcohol) (CMPVA) composite membranes for PV separation of water-isopropanol mixture, CMPVA composite membrane having 16% substitution efficiency, PV permeation flux is  $831 \text{ g m}^{-2} \text{ h}^{-1}$ , and separation factor is 362.

Blended polymer membranes are widely studied for PV dehydration.<sup>15–17</sup> The blend properties of

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polymer possess the intrinsic chemical, physical, mechanic, and morphological properties of each polymer. The advantages from each polymer can be combined by blending two polymers. In this study, novel PV membranes for ethanol dehydration were prepared by blend PVA and CMCS followed by the crosslinking reaction with GA, and the effect of operating parameters on sorption performance and PV performance of the blend membrane is investigated.

## EXPERIMENTAL

### Materials

Chitosan with an N-deacetylation degree of 90% was supplied by Yuhuan ocean Biochemistry in Zhejiang province (China). CMCS was prepared according to the methods described by Muzzarelli et al.<sup>18</sup> and Liu et al.<sup>19</sup> PVA with degree of polymerization of  $1750 \pm 50$  and degree of hydrolysis of 98% and glutaraldehyde (25 wt % in water) were purchased from Shanghai Chemical Reagent. The polyacrylonitrile (PAN) UF membrane (MWCO: 30,000) was supplied by Hangzhou Water Treatment Center (China). Alcohol was obtained from Shanghai Chemical Reagent and used directly without further purification. Deionized water (conductivity  $\approx 0.02 \mu\text{S cm}^{-1}$ ) was generated in our own laboratory. All other reagents and chemicals were of analytical grade.

### Membrane preparation

Tsai et al.<sup>20</sup> reported that the treated PAN support membrane will enhance the PV performance of the membrane. In this study, the PAN membrane was treated by introducing PAN flat membrane into 5 wt % aqueous NaOH solution at 40°C for 3 h. Then, the NaOH-hydrolyzed PAN flat membrane was washed using deionized water. A 8 wt % of PVA solution was prepared in deionized water at 100°C. A 4 wt % solution of CMCS was prepared and the solution was filtered to remove any undissolved suspend matters. Then the mixtures of CMCS and PVA solution were stirred in different ratios. The cast solution used for casting the membranes was defoamed at the vacuum. The composite membrane was prepared by casting the polymer solution on the PAN ultrafiltration membrane (MWCO 30,000), followed by drying at room temperature and crosslinked with GA up to 4 h. After crosslinking, the membrane was washed with distilled water to remove the traces of residual solvents and dried in a dust-free atmosphere. The membrane thickness was adjusted by varying the amount of solution cast on the support membrane with the same surface area. The thickness in the dry state was

determined with a micrometer. To minimize experimental error, at least six thicknesses were averaged on a membrane to get a reliable value. The thickness of the membrane in the current paper was about 30  $\mu\text{m}$ .

### Membrane characterization

Pure CS, CMCS, and CMCS/PVA, crosslinked CMCS/PVA blend membrane samples were scanned in the range of 400–4000  $\text{cm}^{-1}$  wave numbers using Mattson 1000 Fourier transform infrared (FTIR) spectrophotometer. The occurrence of crosslinking was proved by FTIR. X-ray scattering experiments were carried out for studying the miscible of the PVA and CMCS. The angle of diffraction ( $2\theta$ ) was varied from 0° to 65°. Differential scanning calorimetry (DSC) thermograms of CMCS/PVA blend membranes were obtained on a Perkin-Elmer DSC-7. Thermograms were recorded from 30 to 300°C at a heating rate of 10°C  $\text{min}^{-1}$  in a nitrogen atmosphere.

### Swelling measurements

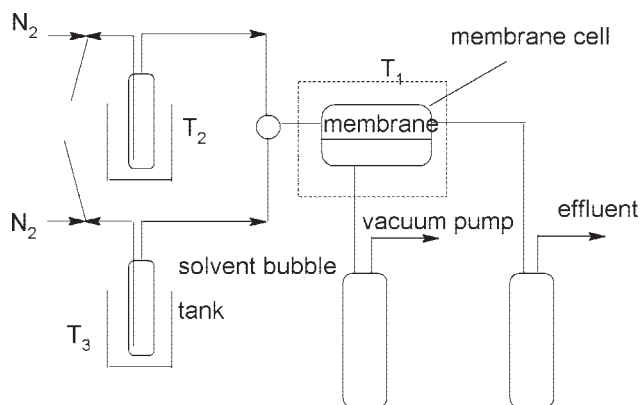
The degree of swelling of membrane at a given time is defined by the following equation:

$$A_{\tau}(\text{g/g}) = \frac{(m_{\tau} - m_0)}{m_{\tau}}, \quad (1)$$

where  $m_0$  and  $m_{\tau}$  are the weights of dry and solvent swollen membranes, respectively. The swelling experiments were carried out at constant temperature, and the membranes were weighed at room temperature. The free liquid on the surface of the swollen membrane must be removed carefully by using filter paper before being weighed.

### Pervaporation and evaporation measurements

A schematic diagram of the PV apparatus and a detailed procedure for performing the PV experiment can be found in our previous publication.<sup>21</sup> The membrane was placed in the stainless steel permeation chamber; the membrane area in contact with the feed was 15.9  $\text{cm}^2$ ; the temperature of the feed mixture was kept constant using a thermostatically thermocouple; the vacuum in the downstream side of the apparatus was maintained about 100 Pa. The permeation vapor was condensed by liquid nitrogen ( $\text{N}_2$ ). The composition of the permeation flux was analyzed by gas chromatograph. The experiment was repeated at least twice to reduce the experimental inaccuracies for each membrane in PV. The permeation flux ( $J_p$ ) and the separation factor ( $\alpha_p$ ) for all membranes were calculated according to the following equations:



**Figure 1** The schematic diagram of the vapor permeation apparatus.

$$J_p = \frac{\Delta g}{A \times \Delta t} \quad (2)$$

$$\alpha_{p\ i/j} = \frac{y_i/y_j}{x_i/x_j}, \quad (3)$$

where  $\Delta g$  is the permeation weight during the operation time,  $A$  is the membrane area, and  $\chi$ ,  $y$  are the weight fractions in the feed and permeate, respectively.

The schematic diagram of the vapor permeation apparatus can be seen in Figure 1. The effective membrane area was 25 cm<sup>2</sup>, which was fixed in a membrane cell. The vapor was prepared by bubbling nitrogen gas separately into two single-solvent tanks, and then the vapor mixture was used as the feed. The composition of the mixture could be adjusted by changing the tank temperature and gas flow rate independently. The pressure in the feed stream was maintained at nearly atmospheric pressure and the pressure in the membrane downstream is below 100 Pa. The permeate was weighed, and the concentration of the permeate and retained vapor was measured by using a gas chromatograph. The permeation flux ( $J_E$ ) and the separation factor ( $\alpha_E$ ) for all membranes were calculated according to the following equations:

$$J_E = \frac{\Delta g}{A \times \Delta t} \quad (4)$$

$$\alpha_{E\ i/j} = \frac{y_{ip}/y_{jp}}{x_{if}/x_{jf}}, \quad (5)$$

where  $\Delta g$  is the permeation weight during the operation time;  $A$  is the membrane area;  $\chi_f$ ,  $\chi_p$ ,  $y_f$ ,  $y_p$  are the weight fractions in the feed and permeate, respectively.

## RESULTS AND DISCUSSION

### Membrane characterization

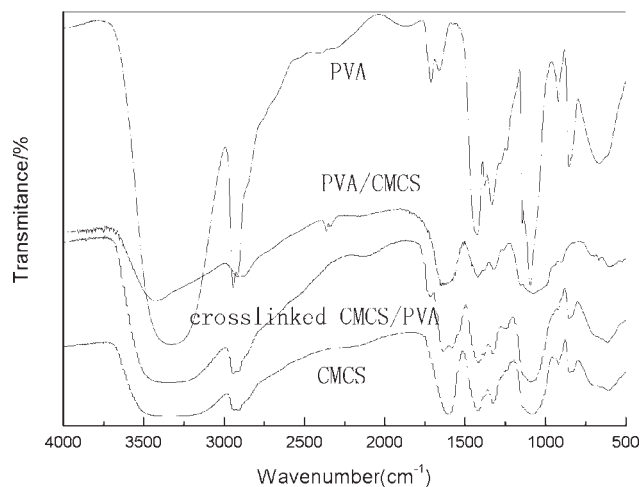
The homopolymer solutions of PVA, CMCS, and their blend solutions were optically clear. No phase separation or precipitation was observed even after keeping the mixture for a longer time at an ambient temperature.

### FTIR analysis

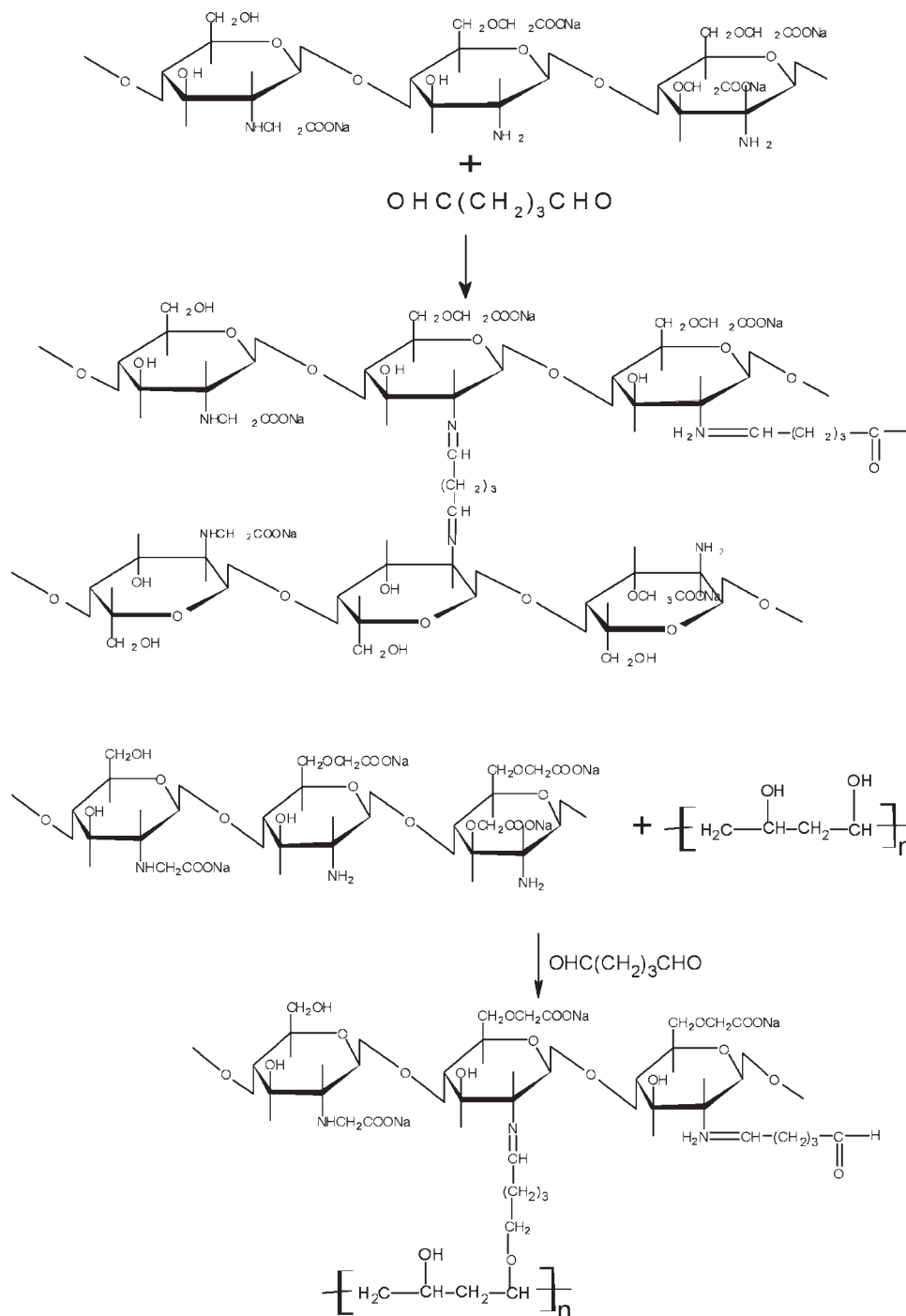
Figure 2 shows the FTIR spectra of the pure PVA, pure CMCS, CMCS/PVA blend membrane, and crosslinked CMCS/PVA blend membrane with GA. For CMCS FTIR spectrum, the peak of  $-\text{COO}$  (1598 cm<sup>-1</sup>), 1070–1136 cm<sup>-1</sup> ( $-\text{C}-\text{O}-$ ), and the  $-\text{NH}_2$  (1592 cm<sup>-1</sup>). The absorption bands of  $\text{O}-\text{H}$  and  $\text{N}-\text{H}$  stretching appeared at 3000–3600 cm<sup>-1</sup> with the adding of PVA, the absorption bands at 3000–3600 cm<sup>-1</sup> in the FTIR spectrum of the CMCS/PVA membranes became sharp and shifted to the lower wave numbers. In crosslinked CMCS/PVA FTIR spectrum, the absorption peak at 1720 cm<sup>-1</sup>, which is attributed  $\text{C}=\text{O}$  group of aldehyde. The peaks at 1090 and 1240 cm<sup>-1</sup>, which are attributed to  $\text{C}-\text{O}$  and  $\text{C}-\text{O}-\text{C}$  groups, due to acetal or ether linkage formation after the crosslinking took place. FTIR analysis confirms the crosslinking of CMCS and PVA by the reaction of hydroxyl group of PVA and amine group of CMCS with the aldehyde group of GA. The crosslinking reaction schematic diagram is shown in Figure 3.

### X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of the pure PVA, pure CMCS, and CMCS/PVA membranes are given in Figure 4. As can be seen from Figure 4, the



**Figure 2** FT-IR spectrum of PVA, CMCS, CMCS/PVA, crosslinked CMCS/PVA blend membranes.



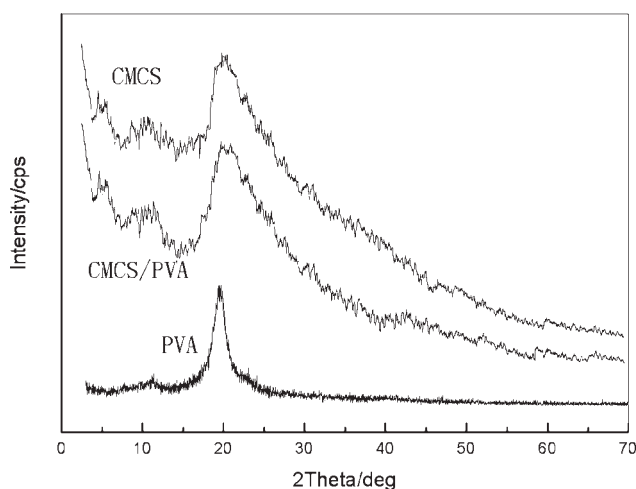
**Figure 3** The schematic diagram of crosslinking reaction of CMCS/PVA by GA.

broad peaks observed in the XRD pattern around  $10^\circ$  of  $2\theta$  indicate the average intermolecular distance of the amorphous part and relatively sharp semicrystalline peaks are centered at around  $20^\circ$  of  $2\theta$ . The spectrum of pure PVA exhibits a strong crystalline peak centered at  $2\theta$  value around  $20^\circ$ . Weaker crystalline peaks are observed at  $2\theta$  value near  $10^\circ$  and  $40^\circ$ . The percent of crystallinity, calculated as the ratio of the area of the crystalline peaks to the total area under the crystalline peaks

and the amorphous halo, is 52%. The crystallinity decreases with adding of the CMCS, which indicated that interaction between CMCS and PVA.

#### DSC analysis

Thermal properties of the blend membranes were examined by DSC. The results are shown in Figure 5. The endothermic peak in the range of  $220\text{--}230^\circ\text{C}$  suggests that some chain scission and loss of water

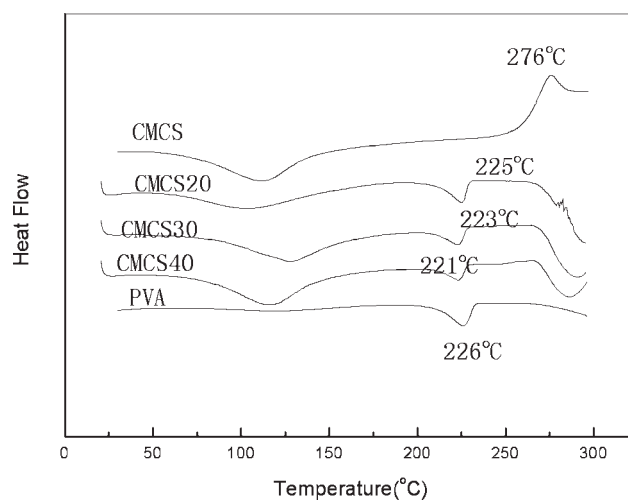


**Figure 4** XRD of pure PVA, pure CMCS, and CMCS/PVA blend (8 : 2).

molecules coming from the  $\text{-OH}$  groups of CMCS and PVA occurred. The endothermic peaks shifted to the lower temperature with increasing content of CMCS, owing to enhancement of intermolecular interaction in the blend membranes. The exothermic peak of the membranes CMCS appears at  $276^\circ\text{C}$ , owing to the decomposition of CMCS, but disappears in the blend membranes. The results is the same as Zhang et al.<sup>10</sup> The results of FTIR, XRD, and DSC analyses confirm the miscibility of the blends.

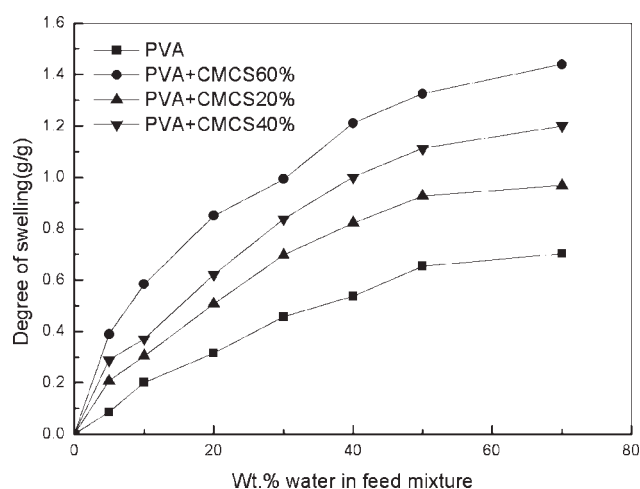
### Swelling performance

Swelling sorption behavior of various feed alcohol mixtures was investigated for predicting the PV performance at various feed alcohol concentrations. The DS of water/ethanol feed in pure PVA and PVA/CMCS blend was measured at a constant temperature of  $25^\circ\text{C}$ , the results are presented in Figure 6. As can be seen from it, the DS increases with the increasing of the water content. This is due to the fact that all membranes are highly hydrophilic and have an increase of strong interaction between molecules and the membrane containing  $\text{-NH}_2$ ,  $\text{-OH}$ , and  $\text{COO}^-$  groups. This is understandable, because most hydrophilic polymer membranes show an enhanced degree of swelling at high water content. It also can be seen that the DS increases with an increase in CMCS content, for membranes, an increase in the degree of swelling with CMCS content of the membrane, which can be explained by the fact that: (1) according to Wan et al.,<sup>22</sup> the crystallinity degree of CS was found to be relatively low, from 5 to 24%. CMCS has a more irregular molecular structure and its crystallization is more difficult. However, PVA is semicrystalline polymers consisting of amorphous and crystalline phases. The crys-



**Figure 5** DSC thermograms of PVA, CMCS, and PVA/CMCS blend of various CMCS content.

tallity degree should be recognized as having an influence on water sorption ability of the polymer.<sup>23</sup> The combination of CMCS and PVA in the CMCS/PVA membrane formed a loose polymer network, and it will results in a change in the chain flexibility and in supermolecular structure which is related to the ability of packing and ordering of its chains. (2) An affinity of the membranes to water molecules can be improved by increasing the content of carboxylic acid groups. It is expected that the carboxyl group might have a strong interaction with water through hydrogen bonding and a membrane containing carbonyl groups might selectively permeate water. CMCS consists of  $\text{-CH}$ ,  $\text{-OH}$ ,  $\text{-CH}_2$ ,  $\text{-NH}$ ,  $\text{-NH}_2$ ,  $\text{-COOR}$ , and  $\text{-O-}$ . The values of molar attraction constant of various groups proposed by Hoy are shown in Table I. The solubility parameter



**Figure 6** Effects of the blend ratio of CMCS/PVA and feed alcohol concentrations on DS at 2% GA concentration.

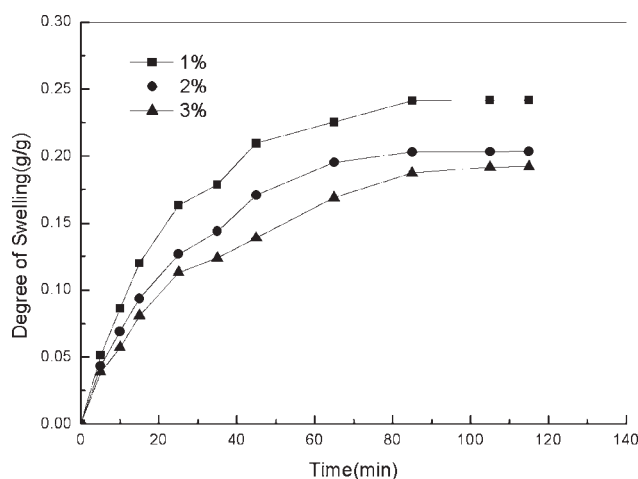
**TABLE I**  
Molar Attraction Constant of Various Groups of CMCS

Group	Molar attraction constant, $F$
—CH	176
—OH	462.0
—CH <sub>2</sub>	269.0
—NH	368
—NH <sub>2</sub>	595
—COOR	688
—O—	235.5

of CMCS is  $46.71 \text{ J}^{1/2} \text{ cm}^{3/2}$ , which is close to that of water ( $47.9 \text{ J}^{1/2} \text{ cm}^{3/2}$ ).<sup>22,24,25</sup>

#### Effect of crosslinking agent on swelling

Figure 7 shows the effect of the crosslinking agent content on swelling kinetics of PVA–CMCS blend membrane at 95% ethanol feed. As can be seen from it, the equilibrium degree of swelling decreases with the concentration of the crosslinking agent in the membrane, which may be because the crosslinking density of the polymer chains grows. Moreover, with increasing crosslinking agent concentration, more hydroxyl groups in PVA and more hydroxyl and amino groups in CMCS were consumed because of the crosslinking reaction. As we all know, hydroxyls form acetals by reacting with aldehyde, and amino groups form Schiff base by reacting with aldehydes.<sup>26</sup> Therefore, as the crosslinking reaction happens, the blend becomes less capable of hydrogen bonding with water molecules because of the intermolecular and intramolecular crosslinking caused both by acetalization and the formation of the Schiff base, resulting in a decreased degree of swelling at equilibrium.<sup>27</sup>

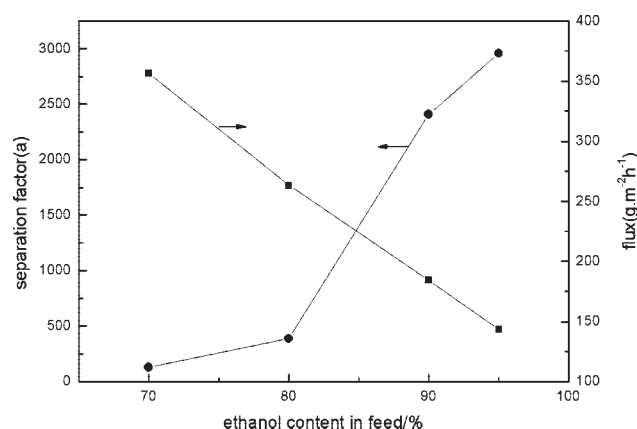


**Figure 7** Swelling kinetics of PVA–CMCS blend membrane at 95% ethanol feed (25 °C) at different GA concentration.

#### Pervaporation performance

##### Effect of feed concentration

The effect of feed concentration on membrane PV performance was studied. The results are showed in Figure 8. The separation performance of the cross-linked CMCS–PVA (8 : 2)/PAN composite membrane by 2% GA was investigated at a constant temperature of 45°C. The permeation flux increases and the selectivity decreases with increasing water content in the feed solution. The tendency for the permeate flux to increase with feed concentrations is similar to the swelling behavior of membranes. The behavior is consistent with the previous studies in the dehydration of aqueous organic mixture through hydrophilic polymeric membranes.<sup>28,29</sup> Results of the studies in the literature on the separation of ethanol–water mixtures are listed in Table II for comparison purposes. As can be seen from the Table II, the resulted membrane is a good PV membrane for the separation of ethanol–water mixtures. It is mainly because of —OH in PVA and the introduction of —COOH groups and further increase of —OH groups by the incorporation of CMCS. Mass transport through hydrophilic CMCS/PVA membrane occurs by solution-diffusion mechanism.<sup>36</sup> According to the solution-diffusion mechanism, with higher water concentration in the feed mixture, the amorphous regions of the membrane are more swollen and the polymer chains become more flexible, thereby, resulting in the diffusion coefficients of ethanol and water to increase. On the other hand, the extent of water sorption in the membrane correspondingly increases with an increase in feed water content resulting in increased flux. The separation factor depends on the partition of two components between the feed solution and the upstream layer of the membrane as well as on the difference of their diffusivities across the membrane. The



**Figure 8** Effect of feed concentration on pervaporation performance of PVA/CMCS blend membrane. (Test conditions: CMCS : PVA 8 : 2, 45 °C, 2% GA concentration).

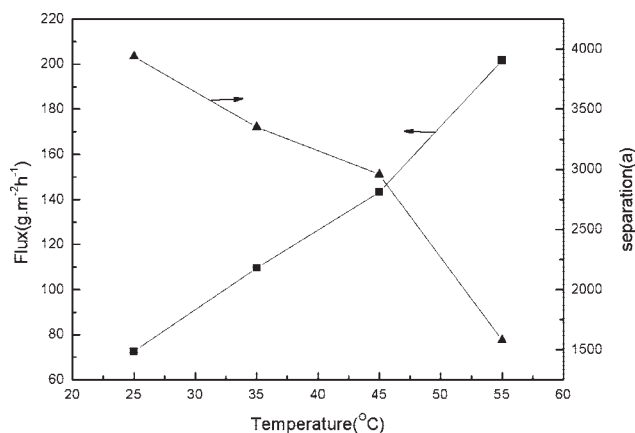
**TABLE II**  
**Comparison of PV Performance of Membrane in Present Study with That of Membranes Reported in the Literature for Water and Ethanol Mixtures**

Types of membrane	Solution mixture	Sep. factor	Flux, $\text{g m}^{-2} \text{h}^{-1}$	Thickness ( $\mu\text{m}$ )	$T$ ( $^{\circ}\text{C}$ )	Ref.
Phosphorylated CS	Ethanol (90 wt %)/water	600	200	$\sim 20$	70	30
$\text{H}_2\text{SO}_4$ crosslinked CS	Ethanol (90 wt %)/water	1791	472		75	31
CS/PAA	Ethanol (95 wt %)/water	$>19,000$	22	45–50	80	32
Carboxymethylated CS/alginate	Ethanol/water	$\infty$	8	–		10
CS/HEC	Ethanol (90 wt %)/water	10,491	112	30–35	25	33
PVA multilayer	Ethanol (80 wt %)/water	600	500	10	80	34
CS/PVA	Ethanol (95 wt %)/water	185	30	–	50	35
CMCS/PVA	Ethanol (95 wt %)/water	2959	140	$\sim 30$		Present work

swelling water caused of the membrane, which is preferential affinity toward water increases with increasing the water content in the feed, the water permeation flux increases. Swollen water molecules at high water concentration act as plasticizing agents in this case.

#### Effect of temperature

The PV process is known to be temperature dependent as both flux and separation factor are influenced by the change in temperature. Temperature dependence of PV performance of CMCS/PVA blend is shown in Figure 9. As can be seen from Figure 9, the total flux increases and the selectivity decreases as feed temperature increases. The increase in a flux may be due to the increased free volume of the polymers and enhanced kinetic energy of the permeate, which assists their diffusivity through the matrix of the membrane. The effect of temperature on the separation factor of membrane was explained by considering two parallel effects of temperature on the membrane. One is increasing polymer chain mobility and facilitating the diffusion of both components.



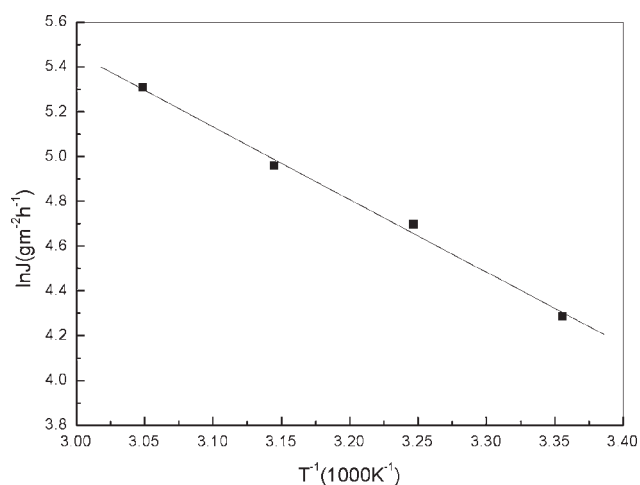
**Figure 9** Effect of operation temperature on pervaporation performance of the PVA/CMCS blend membrane. (Test conditions: CMCS: PVA 8 : 2, 95 wt % ethanol concentration, 2% GA content).

The other is weakening the interaction between ethanol molecule and the membrane, lowering the sorption of ethanol. Moreover, water molecules having relatively smaller molecular sizes than ethanol could diffuse through the pores of the dense membrane more easily at higher temperature.

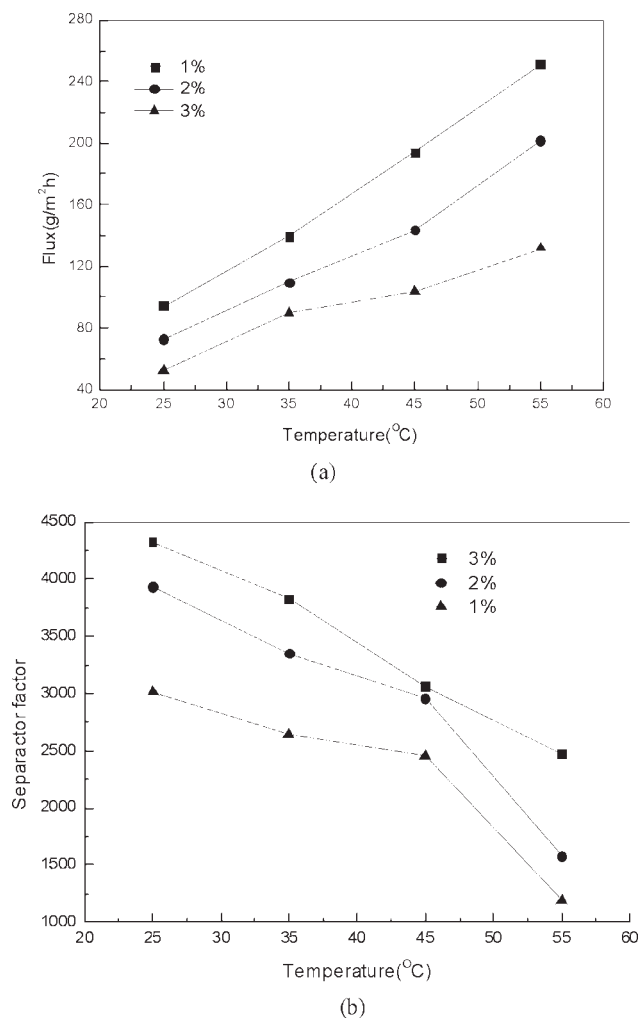
Figure 10 shows that the total flux following the Arrhenius relationship with feed temperature. The Arrhenius-type expression is expressed in eq. (4).

$$J = A \exp(-E/RT), \quad (4)$$

where  $A$  is constant,  $E$  the apparent activation energy for permeation,  $T$  the absolute temperature, and  $R$  the gas constant.  $E$  depends on both the activation energy for diffusion and the heat of solution. These parameters will be changed as a result of changes in solubility and in chain segment mobility. The apparent activation energy for transport could be calculated from the slope of the Arrhenius plot. The apparent activation energy thus calculated for 8 : 2 CMCS/PVA membrane PV process is  $27.03 \text{ KJ mol}^{-1}$  for 95 wt % ethanol solution. A comparatively lower  $E$  obtained in this study implies that the PV of EtOH/ $\text{H}_2\text{O}$  azeotrope



**Figure 10** The total flux following the Arrhenius relationship with feed temperature.



**Figure 11** Effect of GA content on pervaporation performance of the membrane (a) Flux, (b) Separation factor. (Test conditions: CMCS: PM 8 : 2, 95 wt % ethanol concentration).

may be more facilitate in PVA/CMCS when compared with the other membranes. The  $E$  is also dependent on the nature of the membrane material and feed composition, the reported values<sup>37,38</sup> range from 15 to 53 KJ mol, for various other polymers.

#### Effect of crosslinking agent content

Crosslinking is an efficient strategy to control excessive swelling of membranes. In principle, a polymer material with higher crosslinking density has lower membrane mobility and a more compact network structure, resulting in less flux and less liquid solubility. Moreover, with increasing crosslinking degree, free volumes and hydrophilicity of the polar membrane decrease while mechanical increases. Therefore, crosslinking controls the hydrophilic-hydrophobic balance and increases solubility selectivity. There are a number of research groups using GA to crosslink CS composite membranes for PV dehydration and their membranes performed very well.<sup>39,40</sup> In this study, GA was used as the crosslinking agent for the CMCS/PVA 8 : 2 blend membrane, sulfuric acid performed as catalyst, and PV dehydration of the crosslinked CMCS/PVA membrane was carried out for aqueous solutions with 95 wt % ethanol. It is shown in Figure 11. As we can see from it, the permeation flux decreases and separation factor increases with increasing GA content. The result is the same as the previous report.<sup>11</sup> Because of the many reactions between GA and CMCS and PVA, this results in an increase of the crosslinking density of the membrane top layer of the CMCS-PVA/PAN composite membrane. Therefore, the chain mobility and swelling ability of CMCS and PVA decrease. The crosslinked membrane is a good PV membrane for the separation of ethanol-water mixtures, the flux is about 143 g m<sup>-2</sup> h<sup>-1</sup> and the separation factor is 2959 at 2% crosslinking agent concentration and 45°C.

Pervaporation performance of the CMCS/PVA 8 : 2 blend membrane for dehydration of other organics

Table III shows the PV performance of dehydration of three other organics. It can be seen from Table III that the CMCS/PVA 8 : 2 blend membrane gives

**TABLE III**  
Pervaporation Performance of the CMCS/PVA 8 : 2 Blend Membrane for Dehydration of Acetic acid, Isopropanol, Ethanol, and Dioxane

Feed	$J$ (kg m <sup>-2</sup> h <sup>-1</sup> )	$\alpha$	$\sigma_{\text{solv}}$ (10 <sup>-3</sup> J m <sup>-3</sup> ) <sup>1/2</sup>	$\sigma_{\text{water}}$ (10 <sup>-3</sup> J m <sup>-3</sup> ) <sup>1/2</sup>	$\Delta\sigma_{ij}$ (10 <sup>-3</sup> J m <sup>-3</sup> ) <sup>1/2</sup>
10 wt % water-dioxane	0.386	640	20.5	47.9	27.4
10 wt % water-isopropanol	0.232	3654.7	23.9	47.9	24.0
10 wt % water-acetic acid	0.196	540	25.8	47.9	22.1
10 wt % water-ethanol	0.184	2407.5	26.0	47.9	21.9

$J$ , permeation flux of the membrane;  $\alpha$ , separation factor;  $\sigma_{\text{solv}}$ , solvent solubility parameter;  $\sigma_{\text{water}}$ , water solubility parameter;  $\Delta\sigma_{ij} = \sigma_{\text{water}} - \sigma_{\text{solv}}$ .



**TABLE IV**  
**Comparison of Pervaporation and Evapomeation Performance for Dehydration of Ethanol**

Ethanol (wt %) in feed	Pervaporation		Ethanol (wt %) in feed vapor	Evapomeation	
	Flux ( $\text{kg m}^{-2} \text{h}^{-1}$ )	Separation factor		Flux ( $\text{g m}^{-2} \text{h}^{-1}$ )	Separation factor
70	356.5	129.3	69.4	45.9	175.5
80	263.3	387.43	78.6	34.7	243.7
90	184.4	2407.5	90.7	12.1	1329.9
95	143.3	2959.5	95.3	6.48	9931.6

both good flux and separation factor in dehydration of acetic acid, dioxane, isopropanol, and ethanol. Especially, the flux of different organics is in the order of dioxane > isopropanol > acetic acid  $\approx$  ethanol. It is in the agreement with the solubility parameters difference ( $\Delta\sigma_{ij}$ ) of the solvent and water as given in Table III. This is probably due to the interaction between solvent with water was in the order  $\Delta\sigma_{\text{dioxane}} > \Delta\sigma_{\text{isopropanol}} > \Delta\sigma_{\text{acetic acid}} \approx \Delta\sigma_{\text{ethanol}}$  as given in Table III.

#### Comparison of pervaporation and evapomeation performance for dehydration of ethanol

Evapomeation is a new technology of gas-phase dehydration. It is different from PV. In this process, the vapor of feed contacts surface of the membrane directly and the operation is carried out at a temperature above the boiling point of the feed.<sup>41</sup> It is possible to enhance the flux by raising operation pressure and temperature. This process can be integrated with fractional distillation to simplify chemical technological process. Comparison of the PV and evapomeation performance for the separation of water from water and ethanol using a CMCS/PVA blend membrane at 45°C is shown in Table IV. It can be seen from table, compared with PV, the evapomeation process possesses higher separation factor and lower permeation flux. The evapomeation performance of CMCS/PVA blend membranes will be further investigated in our laboratory.

#### CONCLUSION AND FURTHER WORKS

CMCS was obtained by modifying the naturally available CS, and it is used to prepare blend PV membranes for ethanol dehydration by adding different amounts of PVA. Membranes were cross-linked with a GA/sulfuric acid mixture, and CMCS followed by the crosslinking reaction with GA, which imparts the membrane good strength and membrane performance to water in terms of flux and selectivity. The structure and compatibility of the blend membranes were characterized by FTIR, XRD, and DSC. PV dehydration of the blend mem-

brane was tested for different ethanol concentrations. Effect of operation conditions on sorption performance and PV performance of the blend membrane are investigated. The membrane of CMCS/PVA blend ratio of 8 : 2 exhibited a high separation factor of 2959 with a reasonably high water flux value of  $0.14 \text{ kg m}^{-2} \text{ h}^{-1}$  at the azeotropic feed composition (95 wt % of ethanol) at a temperature of 45°C.

Membrane stability and other membrane performances of the flat composite membranes and the hollow fiber composite membranes will be investigated. Moreover, the amplification effect of the hollow fiber membrane will also be studied.

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