

Pervaporation Properties of a Three-Layer Structure Composite Membrane

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ABSTRACT: A novel composite membrane with a three-layer structure has been prepared. The top layer is a thin dense film of chitosan crosslinked with glutaraldehyde, and the support layer is made of microporous polyacrylonitrile (PAN). Between the dense and the microporous layer, there is an intermolecular crosslinking layer. The performance data show that this is an excellent pervaporation membrane for alcohol dehydration and one-stage separation is attainable for some alcohol/water mixtures such as ethanol/water and isopropanol/water systems, which has a good separation factor of 1410 and a good flux of $0.33 \text{ kg m}^{-2} \text{ h}^{-1}$ for the EtOH/H₂O mixture, and 5000 and $0.43 \text{ kg m}^{-2} \text{ h}^{-1}$ for the i-PrOH/H₂O mixture using 90 wt % alcohol concentration at 70°C. Using 90 wt % methanol aqueous solution at 60°C, a flux of $0.17 \text{ kg m}^{-2} \text{ h}^{-1}$ and selectivity of 123 are also obtained. The structure and performance of the novel composite membrane varies with conditions of membrane preparation, such as hydrolysis degree of PAN membrane, content of crosslinking agent, and heat-curing temperature. The results indicate that the separation factor and the permeation rate of this novel composite membrane increase with the increase of operating temperature. At the same time, the pervaporation properties can be adjusted by changing the structure of the top layer and the middle layer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 740–745, 2000

Key words: pervaporation; water–alcohol mixture; dehydration; novel composite membrane; chitosan

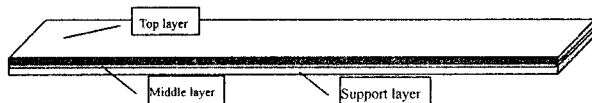
INTRODUCTION

Membrane technology represents one of the most effective and energy-saving means to a wide range of separation processes,¹ so there has been increased interest in the use of pervaporation membrane process for the separation of organic liquid mixtures in recent years. This process has an important advantage for energy saving, which is the ability to separate azeotropic, close-boiling,

or aqueous organic mixtures. The exploitation of a novel polymer membrane for a membrane application has been a continuous research challenge,^{2–4} although technological innovation may result in widening the scope of application of the technology. In response to this research challenge, we have designed and prepared a novel composite membrane with a three-layer structure as shown in Scheme 1. The top layer is a thin dense film of chitosan crosslinked with glutaraldehyde, and the support layer is microporous polyacrylonitrile (PAN) membrane. Between the dense and the microporous layers, there is a middle layer of intermolecular crosslinking. The middle layer was made as follows: part hydrolysis of

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Scheme 1 Schematic drawing cross-section of a three-layer structure composite membrane.

PAN microporous membrane using aqueous sodium hydroxide made some $-\text{CN}$ groups into $-\text{COOH}$ on its surface; when chitosan solution was coated on top of this hydrolyzed PAN membrane, the crosslinking reaction occurred between the $-\text{NH}_2$ groups in chitosan and $-\text{COOH}$ groups. In this paper, a three-layer structure composite membrane has been prepared and the pervaporation properties of water/alcohol mixtures through this membrane have been investigated.

EXPERIMENTAL

Membrane Materials

Chitosan (CS) has a degree of deacetylation of 72.6% and a viscosity average molecular weight of 1.0×10^6 . The support layer was a PAN ultrafiltration membrane provided by the Development Center of Water Treatment, Hangzhou, China. Glutaraldehyde was a solution with 26% content in water, extra pure grade.

Membrane Preparation

PAN microporous membranes were hydrolyzed by immersing in 5% NaOH aqueous solution at 50°C for a given time and then washed thoroughly with deionized water until neutral. The novel composite membrane was prepared by casting the solution, which was made from a mixture of chitosan in 1% acetic acid and 0.54% glutaraldehyde, onto the hydrolyzed PAN microporous membrane, and dried at 55°C , treated in 3% NaOH aqueous solution, and washed thoroughly with deionized water. Then some composite membranes were subjected to heat-curing at a certain temperature for 1 h to effect the crosslinking structure.

Prevaporation

A detailed procedure for performing the pervaporation experiment can be found in our previous article.² The pervaporation experiment were carried out by maintaining the permeate side at re-

duced pressure at 1 mm Hg (133Pa). The permeate vapor was collected in a dry ice/acetone mixture (-77°C) trap. The composition of the permeate was determined by a Shimadzu GC-7A gas chromatograph equipped with 1-m long columns packed with Porapak Q.

The separation factor ($\alpha_{w/alc}$) is defined as follows:

$$\alpha_{w/alc} = \frac{Y_w/Y_{alc}}{X_w/X_{alc}}$$

where X_w and X_{alc} are water and alcohol contents (%) in the feed, respectively, and Y_w and Y_{alc} are water and alcohol contents (%) in the permeate, respectively.

RESULTS AND DISCUSSION

Separation of Water–Ethanol Mixture by Pervaporation Through the Novel Membrane

Effect of Membrane Preparation Conditions

The effect of the hydrolysis degree of the PAN microporous membrane on the pervaporation performance for 90% ethanol aqueous solution at 70°C is shown in Figure 1. The result shows that the separation properties of the composite membrane depends strongly on the hydrolysis time of PAN support layers. The separation factor increases with increasing hydrolyzing time of support membrane, and has a maximum value of 1410 up to 2 h, but the flux decreases. This behavior is attributed mainly to the structure of the

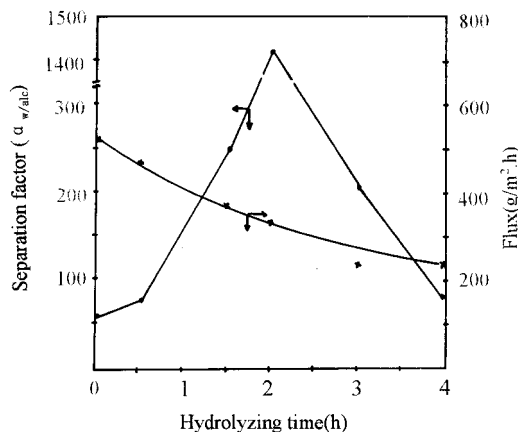


Figure 1 Effects of hydrolyzing time on pervaporation performance for 90 wt % ethanol aqueous solution at 70°C . The crosslinking agent content: 1.0 mg/gCS.

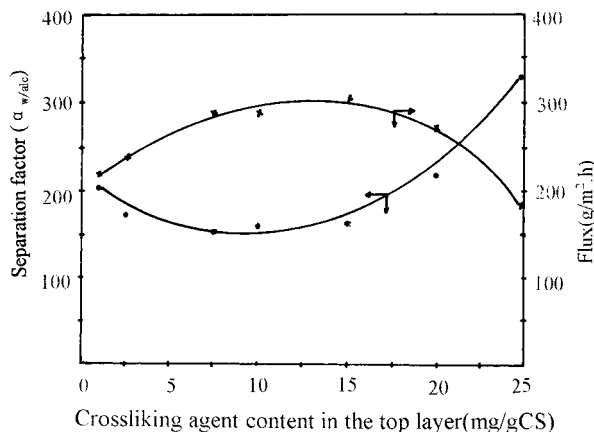


Figure 2 Effects of crosslinking agent content on pervaporation properties of the composite membrane for 90 wt % ethanol aqueous solution at 70°C. Hydrolysis time of support membrane: 3 h.

crosslinking layer and the surface porosity of the sublayer. As the number of $-\text{COOH}$ converted from $-\text{CN}$ on the surface of the PNA support membrane increase with hydrolysis time, the thickness and the crosslinking density of the middle layer in the novel composite membrane rise. At the same time, the surface porosity of the microporous support layer can be changed due to hydrolysis, which also influences separation performance of the composite membrane as reported by G. H. Koops.⁵ Both factors result in this relation between the pervaporation performance and hydrolysis time of the sublayer. So it is very important to hydrolyze the support membrane to a moderate extent.

Figure 2 shows the effects of glutaraldehyde content in the top layer on pervaporation properties of the novel composite membrane. The separation factor decreases and the permeation rate increases with an increase of crosslinking agent. This result is identical to the homogeneous crosslinking chitosan membrane⁶ and can be explained by the structure of the crosslinking membrane. That is, as the membrane separation process is mainly conducted in the amorphous region of the membrane according to the conventional solution-diffusion mechanism, the presence of crosslinking causes a more amorphous region to occur. Meanwhile, as the rate of the crosslinking reaction increases with increasing crosslinking agent, the structure of the crosslinking active layer becomes looser. However, while the content of glutaraldehyde is more than 7.5 mg/gCS, the dependence of pervaporation performance on the

crosslinking agent shows the opposite trend. The reason for causing this difference is not clear and will be under investigation.

The effect of heat-curing temperature on both separation factor and flux for 90 wt % ethanol aqueous solution at 70°C is shown in Figure 3. The results indicate that the heat-curing temperature has strong influence on pervaporation performance. With increasing temperature, the flux decreased and the separation factor increased greatly, due to the increase of the crosslinks between the top layer (chitosan layer) and the hydrolyzed support layer (PAN microporous membrane) by the reaction of the $-\text{NH}_2$ group on chitosan with the carboxylic groups on the surface of the support layer, as well as between chitosan and glutaraldehyde in the top layer.

Influence of Pervaporation Operating Conditions

The results shown in Figure 4 indicate that both the separation factor and flux increase with operating temperature. When the temperature is 70°C, the membrane has a high separation factor of 1410 and a good permeation rate of $0.33 \text{ kg m}^{-2} \text{ h}^{-1}$ for 90 wt % ethanol aqueous solution. This kind of separation behavior with operating temperature is very useful for the industrial separation of ethanol/water mixture and also different from that of the homogeneous chitosan membrane⁶ crosslinked with glutaraldehyde where the separation factor decreases with operating temperature as in most membranes. According to the

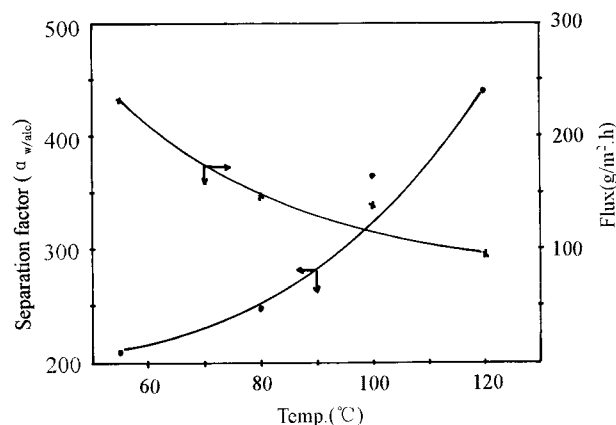


Figure 3 Effects of heat-curing temperature on pervaporation behaviors for 90wt% ethanol aqueous solution at 70°C. The composite membrane is heat-cured for 1 h after being dried at 55°C. Hydrolysis time of the support membrane: 3 h; the crosslinking agent content: 1.0 mg/g CS.

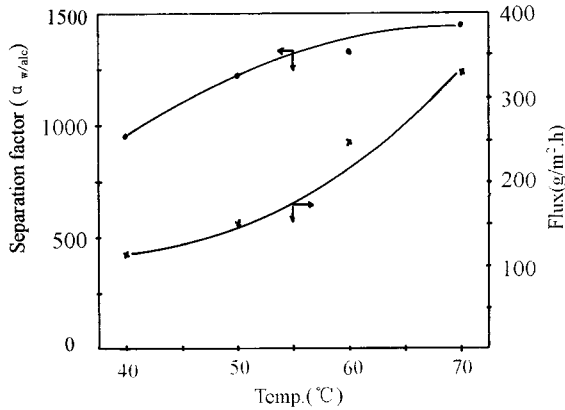


Figure 4 Dependence of pervaporation performance on operating temperature for 90 wt % ethanol solution. Hydrolysis time of support membrane: 2 h; crosslinking agent: 1.0 mg/gCS.

free volume theory, the thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature rises, the frequency and amplitude of chain jumping increase and the resulting free volume become larger, and the diffusion rate of individual permeating molecules and associated permeating molecules are high, so that the total flux increase and the separation factors decrease. As to the novel composite membrane, the mobility of the chitosan molecules is strongly controlled by the structure of intermolecular crosslinking. Therefore, only a small increase of the motion of the polymer molecules will be allowed with increasing the temperature; the result is that the larger molecule alcohol is still limited to easy permeation and smaller

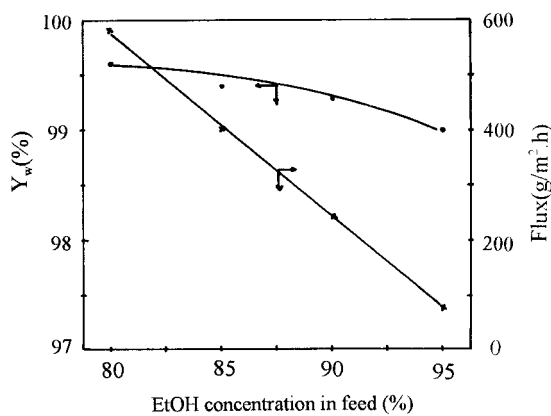


Figure 5 Dependence of pervaporation performance on ethanol concentration at 60°C. Hydrolysis time of support membrane: 2 h; crosslinking agent: 1.0 mg/gCS.

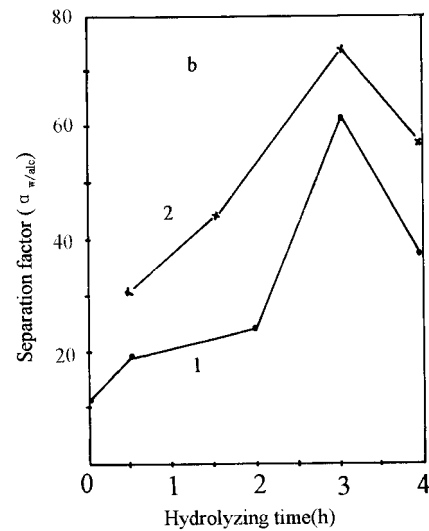
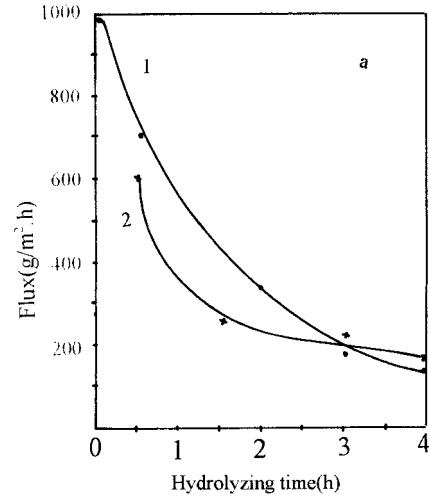


Figure 6 Effects of hydrolyzing time of PAN microporous support layer on flux (a) and separation factor (b) of the novel composite membrane for 90% methanol aqueous solution at 60°C. 1: Crosslinking agent, 1.0 mg/gCS; 2: crosslinking agent, 7.5 mg/gCS.

molecules water easy diffusion. Thus the separation factor increase as shown in Figure 4.

Figure 5 shows the dependence of water content in permeate and permeation rate on the concentration of ethanol in the feed at 60°C. The results show that both the flux and the water content in the permeate decrease with the increase of ethanol concentration in the feed. But water content in the permeate are all higher than 99% within experiment.

Pervaporation Performance of Methanol/Water Mixtures

The effects of the hydrolyzing time of the PAN support membrane on the pervaporation perfor-

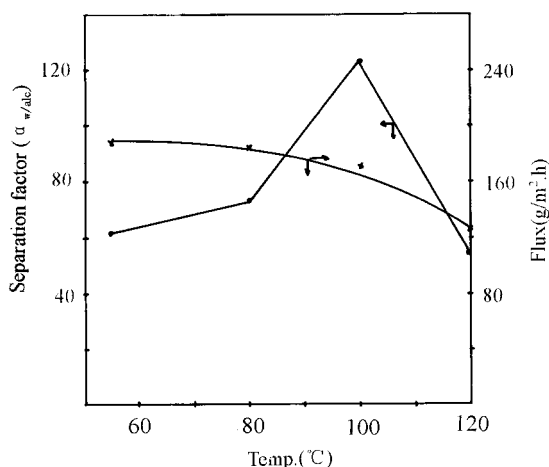


Figure 7 Effects of heat-curing temperature on pervaporation performance for 90% methanol aqueous solution at 60°C. The composite membrane is heat-cured for 1 h after being dried at 55°C. Hydrolysis time of PAN membrane: 3h; crosslinking agent: 1.0 mg/gCS.

mance for 90% methanol aqueous solution at 60°C are shown in Figure 6. The flux decreases with an increase in the hydrolyzing time of the PAN support membrane, but the separation factor increases and reaches a maximum value up to 3 h of hydrolysis time. At the same time, the results shown in Figure 6 indicate that the novel membrane with 7.5 mg/gCS of the crosslinking agent in the active layer give higher separation selectivity than one with 1.0 mg/gCS.

Figure 7 shows the effect of heat-curing temperature on pervaporation performance for 90 wt % methanol aqueous solution at 60°C. The results indicate that with increasing heat-curing temperature the flux decreases, but the separation factor increases markedly and reaches a maximum value at 100°C, which is twice greater than the

selectivity of membrane heat-cured at 55°C. This membrane gave a separation factor of 123 and a flux of 170 g m⁻² h⁻¹

A Comparison of Pervaporation Performance of Several Alcohol/Water Mixtures

A comparison of the pervaporation performances of 90% methanol/water, ethanol/water, and isopropanol/water solutions through the three-layer composite membrane is shown in Table I.

The water selectivity for the higher molecular weight alcohol/water mixtures was much higher than that for the methanol/water system, with nearly complete separation. Nevertheless, the permeation rate was the lowest for the ethanol/water system. This pervaporation behavior of the novel composite membrane is similar to that of a crosslinked chitosan membrane with glutaraldehyde.⁶ The results also show that the separation factors for different mixtures all increase with the increase of operating temperature.

The pervaporation properties of composite membranes with different structures for separating alcohol/water systems are shown in Table II. The novel composite membrane prepared with the hydrolyzed PAN microporous membrane gives a higher separation factor and lower flux for methanol/water and ethanol/water systems, but for the isopropanol/water system higher flux and separation factor—similar in comparison with the normal composite membrane prepared with only PAN ultrafiltration membrane. The data still show that the permeation rate decreases and separation factor increases with increasing the volume of alcohol as to the normal composite membrane. This separation behavior is similar to that of an homogeneous chitosan membrane and can be explained by the volume of alcohol molecules

Table I Effect of Pervaporation Performance on Operating Temperature (Feed Concentration: 90% Alcohol)^a

Operating Temperature (°C)	Methanol/Water		Ethanol/Water		Isopropanol/Water	
	Separation Factor	Flux (g m ⁻² h ⁻¹)	Separation Factor	Flux (g m ⁻² h ⁻¹)	Separation Factor	Flux (g m ⁻² h ⁻¹)
40	16	210	930	110	1110	178
50	18	280	1277	154	1549	219
60	24	340	1325	243	1791	320
70	—	—	1440	330	5000	435

^a Hydrolysis time of PAN membrane: 2 h; crosslinking agent: 1.0 mg/gCS.

Table II Pervaporation Properties of the Composite Membrane Prepared with Different Support Film for Alcohol/Water Mixture (Alcohol Content: 90%, Operating Temperature: 60°C)^a

Composite Membrane	PAN Support Membrane Hydrolyzed for 2 h		PAN Support Membrane Without Hydrolysis	
	Separation Factor	Flux (g m ⁻² h ⁻¹)	Separation Factor	Flux (g m ⁻² h ⁻¹)
Methanol	24	340	11	997
Ethanol	1325	243	54	456
Isopropanol	1791	320	189	209

^a Crosslinking agent: 1.0 mg/gCS.

as A. Mochizuki did.⁷ The difference in pervaporation performance of the composite membrane prepared with different support layers may be attributed to the intermolecular crosslinks between the active and the support layer.

CONCLUSIONS

Novel composite membranes with a three-layer structure have been exploited and studied for the pervaporation separation of alcohol/water mixtures. The membrane has a better pervaporation performance of a separation factor more than 1410 and 0.33 kg m⁻² h⁻¹ flux for the 90 wt % ethanol aqueous solution and separation factor of 5000 and flux of 0.43 kg m⁻² h⁻¹ for the 90 wt % i-PrOH aqueous solution. This kind of membrane also has good separation properties for the 90 wt % methanol aqueous mixture; the separation factor reaches 123. At the same time, the novel composite membrane has very attractive advantages: its separation factor and permeation rate increase

with the increase of operating temperature. This kind of separation behavior is very useful for industrial applications.

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