Separation of Alcohol–Water Mixture by Pervaporation Through a Novel Natural Polymer Blend Membrane–Chitosan/Silk Fibroin Blend Membrane

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ABSTRACT: A novel natural polymer blend membrane, namely chitosan/silk fibroin blend membrane, was prepared. The selective solubility and the pervaporation properties of alcohol–water mixture were studied. The results showed that the membrane was water selective and the separation factor of ethanol–water mixture could be improved compared to pure chitosan membrane, when silk fibroin content in blend membrane was no more than 40 wt %. The blend membrane exhibited a best performance, (i.e., the water in permeate was large than 99 wt % when silk content was 20 wt % and the crosslinking agent–glutaraldehyde content was 0.5 mol %). The mechanism of improvement on pervaporation properties was explained by reducing the free volume and freeing hydrophilic groups of chitosan because of the strong intermolecular hydrogen bond forming between chitosan and silk fibroin in blend membrane. In addition, the influence of operation temperature and feed concentration as well as the pervaporation properties of isopropanol–water mixture were also studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 975–980, 1999

Key words: natural polymer; chitosan; silk fibroin; pervaporation; alcohol–water mixture

INTRODUCTION

Separation of the alcohol-water mixture by pervaporation through membranes has received increasing attention in industry. The method may provide an economical alternative to distillation for alcohol–water separations and avoids the limitation of osmotic pressure imposed on reverse osmosis process by maintaining the permeate below its saturated vapor pressure.[1,2] Membranes used for pervaporation of the alcohol–water mixture are classified into two categories, water-selective membranes and alcohol-selective membranes. Chitosan (CS) membrane is one of the widely studied water-selective membranes. For pure CS membrane, the separation factor is rather low and the flux is relatively high when it separates ethanol–water mixture.[3,4]

To improve the pervaporation properties of CS membrane, modified CS membranes have been prepared. For instance, Mochizuki et al. have reported the pervaporation properties of a series of CS membranes treated by various salts and acids.[5–7] Our laboratory also has reported the pervaporation properties of CS composite membranes,[8] polyacrylic acid (PAA)-crosslinked CS membrane,[9] and others. Making blend membrane is another effective method used to improve the pervaporation properties of CS membrane. In our previous studies, the pervaporation properties of CS/PVA blend mem-

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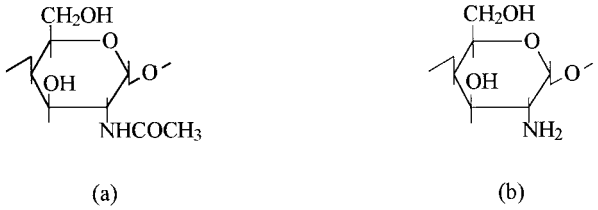

Figure 1 Structure of chitin (a) and chitosan (b).

brane[10] and CS/PAA blend membrane (unpublished work) have been tested.

Recently, another natural polymer, silk fibroin (SF), which was main the part of natural silk and the major amino acid composition of which consists of glycine, alanine, and serine residues (over 85 mol %), was chosen as a component of blend, and a novel natural polymer blend membrane, namely CS/SF blend membrane, was prepared in our laboratory because of the abundant sources and unique properties of natural polymer, such as nontoxicity, degradability, good biological compatibility, and others. The structure,[11] the intelligent behavior,[12] and the chemical valve function[13] of CS/SF blend membrane have been widely studied. In this article, the pervaporation properties of CS/SF blend membrane have been reported.

EXPERIMENTAL

Materials

CS was prepared from chitin (Fig. 1) according to the method described in our previous article.[3] Its viscosity-average mole weight was 3.0×10^6, and the deacetylation degree was 86 mol %, respectively. The CS solution was prepared by dissolving CS in 2 wt % acetic acid.

Raw silk was degummed twice with 0.5 wt % $NaHCO_3$ solution at 100°C for 30 min and then washed with distilled water. Degummed silk was dissolved in 9.5 mol/L LiBr solution. After dialysis against distilled water for 3 days, the solution was filtered and then the SF solution was obtained.

Preparation of Chitosan/Silk Fibroin Blend Membrane

The CS/SF blend membrane was prepared by casting a mixture of 2 wt % CS and 2 wt % SF solution (for crosslinked membrane, adding an appropriate amount of glutaraldehyde) onto a polyether plate and allowing the solvent to evaporate in the air. The thickness of membrane is about 30 μm.

Pervaporation of Chitosan/Silk Fibroin Blend Membrane

A schematic diagram of pervaporation apparatus is shown in Figure 2. A stainless steel cell (A) with an effective area of a flat membrane of 36.5 cm^2 was used. At the downstream side, a pressure of <30 Pa was maintained by means of a vacuum pump (I). The permeate flux was calculated by weighting the permeate condensed in cold trap (C). The water contents in the feed and the permeate were analyzed by means of a chromatography-equipped column of Porapak Q. The performance of membranes in pervaporation was evaluated by the separation factor (α) and the flux (J), calculated as follows:

$$\alpha = \frac{c'_E}{c^0_E} \cdot \frac{c^0_W}{c'_W}$$

$$J = \frac{W}{A\Delta t} (\mathrm{g\ m^{-2}\ h^{-1}})$$

where W was weight of permeate (g), Δt was permeation time (h), A was membrane area (m^2), and c'_E, c^0_E, c'_W, c^0_W were ethanol or water content in permeate or feed, respectively.

Selective Solubility of Chitosan/Silk Fibroin Blend Membrane

Dry CS/SF blend membrane samples were immersed into the ethanol–water mixture for 24 h at

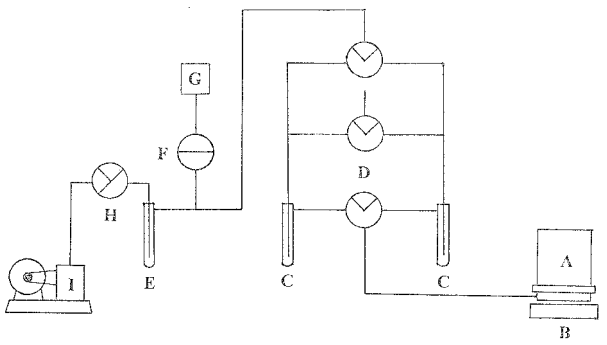

Figure 2 The diagrammatic sketch of the pervaporation apparatus (A: permeation cell; B: magnetic stir; C: cold trap for collection; D: two-way valve I; E: cold trap for protection; F: two-way valve II; G: vacuum meter; H: three-way valve; I: vacuum pump).

room temperature. The swollen samples were put into a glass tube immediately after careful blotting. The glass tube was connected to the pervaporation system described previously instead of the permeation cell A. When the vacuum was obtained, the liquid swollen in the sample was vaporized (desorbed), and then was condensed in the cold trap C. The water contents of the ethanol–water mixture in which the membranes swelled and the desorbed liquid condensed in the cold trap were also analyzed by means of chromatography just the same as the pervaporation process. The water percentage in the total amount the membrane swelled can denote the selective solubility of the membrane in the ethanol–water mixture. The ascertained data of the pervaporation and the selective solubility of the CS/SF blend membranes are the averages of three independent measurements.

RESULTS AND DISCUSSION

Selective Solubility of Chitosan/Silk Fibroin Blend Membrane in Ethanol–Water Mixture

From the structure of CS and SF, it can be seen that both CS and SF have polar (hydrophilic) groups, such as amino group in CS, amide and hydroxyl groups in SF, and others. These polar groups can have some interactions with both water and ethanol. Therefore, when the CS/SF blend membranes were put into pure water or pure ethanol, the membranes were both swollen, although the swelling ratios were different. If the tendency of adsorbing water and ethanol was the same, the membranes would adsorb the same percentage of water and ethanol in the ethanol–water mixture as in the pure water and pure ethanol. With this assumption, the water content in the total adsorption substance when the membrane was swollen in ethanol–water mixture could be calculated from the experimental data, which were obtained while the membranes were swollen in pure water and pure ethanol, as shown in Figure 3 as the calculated line. However, the actual phenomenon was that the CS/SF blend membranes adsorbed a larger percentage water than ethanol in the ethanol–water mixture (i.e., the membranes had a better water selectivity). The results were shown in Figure 3 as the experimental line; as the CS in membrane was larger than 50 wt %, the water accounted for about 98 wt % in the total amount of which the membrane swelled and seemed not dependent on the composition of the membrane. It was clearly found that the water percentage the CS/SF blend membrane actually adsorbed in the ethanol–water mixture was larger than that calculated in every composition. Thus, it could be concluded that the CS/SF blend membrane was a water permselective membrane when it was swollen in ethanol–water mixture.

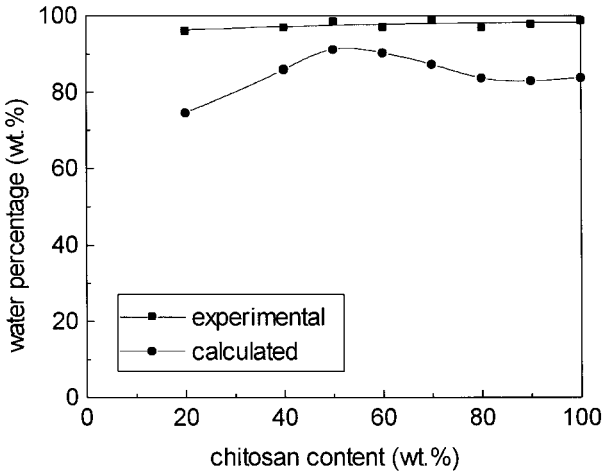

Figure 3 The water percentage in the total amount adsorbed in the ethanol–water mixture of CS/SF blend membranes with different composition (ethanol in mixture: 92.5 wt %, 25°C).

Table I Pervaporation Properties of Ethanol–Water Mixture Through Chitosan–Silk Fibroin Blend Membranes

Fibroin Content (wt %)	α	J_{total} (g m^{-2} h^{-1})	J_{water} (g m^{-2} h^{-1})	$J_{ethanol}$ (g m^{-2} h^{-1})
0	65.8	65.8	54.9	10.9
10	160.4	26.9	24.9	2.0
20	476.5	20.0	19.5	0.5
30	172.1	22.7	21.2	1.5
40	100.0	34.5	30.5	4.0
60	12.0	99.1	48.9	50.2
85	10.3	405.2	183.4	221.8

Ethanol in feed: 92.5 wt %; operation temperature: 50°C.

Pervaporation Properties of Ethanol–Water Mixture Through Chitosan/Silk Fibroin Blend Membranes

As the CS/SF blend membrane could act as a water permselective membrane, it could be used

Table II Pervaporation Properties of Ethanol–Water Mixture Through Crosslinked Chitosan–Silk Fibroin Blend Membranes

Fibroin Content (wt %)	α	J_{total} (g m^{-2} h^{-1})	J_{water} (g m^{-2} h^{-1})	$J_{ethanol}$ (g m^{-2} h^{-1})
0	51.9	81.6	69.8	11.8
10	104.7	35.3	31.5	3.8
20	452.2	22.8	22.2	0.6
30	176.3	31.0	28.9	2.1
40	43.6	75.1	57.9	17.2
60	44.7	97.1	76.3	20.8

Ethanol in feed: 92.5 wt %; glutaraldehyde in membrane: 1.5 mol %; operation temperature: 50°C.

to separate ethanol–water mixture by pervaporation. The pervaporation properties of CS/SF blend membranes were shown in Table I. When SF content in blend membrane was no more than 40 wt %, the separation factors of blend membranes were larger than that of pure CS membrane. In addition, the separation factor reached a maximum when SF content in blend membrane was 20 wt %. In the meantime, the fluxes of blend membranes were rather low, whereas their separation factors were improved. Moreover, when SF content in blend membrane was larger than 40 wt %, the flux increased significantly, whereas the separation factor dropped to the extent which was less than that of pure CS membrane.

Because of the rigid structure of CS chain, the free volume in CS was quite large, so that the water and the ethanol molecule could both pass through the CS membrane easily when separating the ethanol–water mixture by pervaporation, which resulted in a small separation factor and a relatively high flux.[4] However, in CS/SF blend membrane, there was a strong hydrogen bond between CS and SF,[14] so that the flexible SF chain could fill into the free volume of CS, and thus the free volume could be reduced. As a result, the water and ethanol fluxes were both hindered. Because the molecular size of ethanol was quite larger than water, so that the ethanol flux was decreased more than water flux, therefore, the separation factor was improved. Furthermore, with the increase of SF content in blend membrane, the SF became the dominant part. As it was known that the SF membrane showed poor performance in the separation of ethanol–water mixture,[15] so the performance of the CS/SF blend membrane lowered.

Pervaporation Properties of Ethanol–Water Mixture Through Crosslinked Chitosan/Silk Fibroin Blend Membranes

To increase the flux of CS membrane, crosslinking was a common method. Uragami et al.[16] have found that the CS membrane had many intermolecular hydrogen bonds between the hydrophilic groups (—NH_2 and —OH), and the free hydrophilic groups were quite few. Crosslinking CS by glutaraldehyde, some of these hydrogen bonds were broken and free hydrophilic groups could be formed. On the other hand, the free volume of CS would be enlarged by crosslinking. Table II showed the pervaporation properties of crosslinked CS/SF blend membranes, of which the glutaraldehyde content was 1.5 mol %. The results showed the pervaporation properties of the crosslinked membrane had the same tendency as the uncrosslinked membrane. Compared to the uncrosslinked membrane, the flux (both water and ethanol flux) of the crosslinked membrane was increased, whereas the separation factor decreased. This phenomenon indicated that at such glutaraldehyde content, the dominant effect of crosslinking was the enlargement of the free volume of membrane. Though the SF chains could fill into free volume, the free volume was so large that both the

Table III Influence of Crosslinking Agent Content on Pervaporation Properties of Ethanol–Water Mixture Through Chitosan–Silk Fibroin Blend Membranes

Glutaraldehyde Content (mol %)	α	J_{total} (g m^{-2} h^{-1})	J_{water} (g m^{-2} h^{-1})	$J_{ethanol}$ (g m^{-2} h^{-1})
0	476.5	20.0	19.5	0.5
0.5	1235.2	42.1	41.7	0.4
1.5	452.2	22.8	22.2	0.6
2.0	47.7	67.7	54.0	23.7

Ethanol in feed: 92.5 wt %; silk fibroin in membrane: 20 wt %; operation temperature: 50°C.

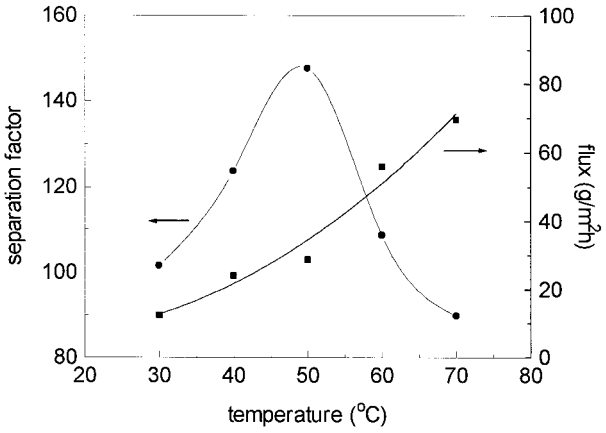

Figure 4 Influence of operation temperature on separation properties of ethanol–water mixture through chitosan–silk fibroin blend membrane by pervaporation (fibroin in membrane: 10 wt %; ethanol in feed: 92.5 wt %).

water and ethanol molecule could pass through the membrane more freely than in the uncrosslinked membrane; therefore, both the water and the ethanol flux increased, and the separation factor decreased.

The ideal condition to improve separation properties is to increase water flux and reduce or not increase ethanol flux. In CS/SF blend membrane system, how to increase the amount of free hydrophilic groups and not to make the free volume too large to hinder ethanol molecule passing through the membrane were key points. Thus, to select a suitable glutaraldehyde content was important. Table III showed that the best glutaraldehyde content was 0.5 mol %, of which the separation factor was 1235 (water in permeate was larger than 99 wt %) with a flux of 42 g m^{-2} h^{-1}.

Table IV Influence of Feed Concentration on the Pervaporation Properties of Ethanol–Water Mixture Through Crosslinked Chitosan–Silk Fibroin Blend Membranes

c^0_W (wt %)	c'_W (wt %)	J_{total} (g m^{-2} h^{-1})	J_{water} (g m^{-2} h^{-1})	$J_{ethanol}$ (g m^{-2} h^{-1})
5.3	89.9	6.1	5.5	0.6
6.5	92.6	26.9	24.9	2.0
15.9	95.1	80.4	76.5	3.9
50.8	91.9	1218.9	1120.2	98.7
78.3	95.7	2349.1	2247.9	101.2

Silk fibroin in membrane: 10 wt %; glutaraldehyde in membrane: 1.5 mol %; operation temperature: 50°C.

Table V Pervaporation Properties of Isopropanol–Water Mixture Through Chitosan–Silk Fibroin Blend Membranes

Fibroin Content (wt %)	Uncrosslinked		Crosslinked	
	c'_W (wt %)	J (g m^{-2} h^{-1})	c'_W (wt %)	J (g m^{-2} h^{-1})
0	98.6	53.4	98.1	62.6
10	98.8	66.0	98.9	75.8
20	98.8	87.9	98.8	102.5
30	98.7	77.8	98.8	78.5
40	98.6	81.4	98.8	82.2
60	<95.0	56.6	96.0	43.2

Isopropanol in feed: 88.0 wt %; glutaraldehyde in membrane: 1.5 mol %; operation temperature: 50°C.

Influence Factors of the Pervaporation Properties

To study the pervaporation properties of CS/SF blend membrane systematically, several influential factors of the pervaporation properties have been investigated. First, the influence of operation temperature was studied and the result of uncrosslinked membrane was shown in Figure 4. With the increase in operation temperature, the flux increased and the separation factor exhibited a maximum at 50°C. The apparent activation energy of transport for ethanol–water mixture could be calculated according to Arrhenius plot; its value was about 37.1 kJ/mol. The flux and separation factor of crosslinked membrane expressed the same tendency when changing operation temperature; its apparent activation energy was about 40.9 kJ/mol.

Table IV showed the pervaporation properties of crosslinked membrane when the water content in feed was altered. The results indicated that the flux and the water content in permeate were both increased with the increase of water content in feed when it was low (<15 wt %). When water content in feed was larger than 50 wt %, the flux increased dramatically, but the water content in permeate remained high. However, for uncrosslinked membrane, the water content in permeate dropped significantly because of the considerable swelling of the membrane when the water content in feed was quite large.

The separation properties of isopropanol–water mixture through the CS/SF blend membranes were also tested. In Table V, it could be seen that the pervaporation properties were improved compared to pure CS membrane both in un-

crosslinked and crosslinked membrane when SF in membrane was no more than 40 wt %.

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