NOTE

개질키토산막을 통한 물-에탄올의 투과증발분리 : 3. 술폰화키토산막

이 영 무 · 신 은 미 · 정 창 남*
한양대 공업화학과 · *순천대 고분자공학과
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Pervaporation Separation of Water-Ethanol through Modified Chitosan Membranes : 3. Sulfonated Chitosan Membranes

Young Moo Lee, Eun Mi Shin and Chang Nam Chung*
Department of Industrial Chemistry, College of Engineering, Hanyang University, 133-791, Seoul, Korea
**Department of Polymer Engineering, Sunchon University, Sunchon, Korea*
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INTRODUCTION

In the preceding papers we obtained the results on the pervaporation performance of chitosan-acetic acid complex membrane and modified chitosan membranes.[1,2] For complex membranes, the effect of alkali treatments was examined on the basis of molecular features. For chemically modified chitosan membranes, membranes containing carboxyl group showed high separation efficiencies. Chitosan was chosen as a base material because it is easily obtained in the nature. Chitosan is the deacetylated product of the alkali treatment of chitin.[3]

Pervaporation is a membrane separation process that can be applied to separate organic-water mixtures. A great deal of research efforts has been focused on the separation near the azeotropic composition. For this application, a lot of work has been done to develop more efficient membranes. Good selectivities for water have been obtained by modifying the membrane structure using ionic or hydrophilic groups. Several researchers[4~7] have reported the pervaporation performance of chitosan membranes, but none of them published on the sulfonated chitosan membranes.

Selective separation of solute requires strong adsorptions in the membranes caused by a strong interaction such as hydrogen bonding. It is expected that the sulfonyl group might have a strong interaction with water through hydrogen bonding and water might selectively permeate through a membrane containing a sulfonyl group. The present study investigates the pervaporation performance of sulfonated chitosan membrane.

EXPERIMENTAL

Materials

Chitin was obtained from crab shell by modified Hackman method.[8] Chitin was subsequently deacetylated with NaOH solution to obtain chitosan. A detailed manufacturing method for chitin and chitosan has been described elsewhere.[1,3] Acetic acid, sodium hydroxide, methanol, ethanol, pyridine, and glutaraldehyde were from Duksan

Phamaceutical Co. Chlorosulfonic acid was from Nakarai Chemicals.

Characterization

For structural determination, elemental analyser (Perkin Elmer Model 240) was used.

Preparation of Chitosan Membrane

2g of chitosan was added to 200 ml of 2 wt% aqueous acetic acid solution at room temperature with stirring. Polymer solution (pH=3.5) was filtered with glass filter to remove dirts and undissolved chitosan, and then cast onto a glass plate to manufacture the chitosan membrane. After drying the membranes at room temperature for more than 12 hours, the membranes were treated with 1 N aqueous sodium hydroxide solution for one day, and dried at room temperature.

Preparation of Sulfonated Chitosan Membrane

0.071 mole of chlorosulfonic acid was slowly dropped at 0 ℃ in 0.371 mole of pyridine. After the reaction mixture reaches the room temperature, dry chitosan membrane was put into the solution and reacted for one hour at 110℃.[9] The membrane was washing in 70 wt% methanol aqueous solution. The membrane was crosslinked with 0.025 wt% glutaraldehyde in 70 wt% aqueous methanol solution for 15 minutes to one hour by fifteen minute increment. The membranes were coded with 3, 4, and 5 depending upon the sulfonation time. The crosslinked membrane is washed with methanol and dried at room temperature.

Pervaporation Experiment

Detailed procedure for performing the pervaporation experiment can be found elsewhere.[1,2,10~12]

RESULTS AND DISCUSSION

Chitosan membrane shows a high mechanical strength and water absorption values as described in Table 1. A chitosan membrane, 1, is surface-treated to make sulfonated chitosan membranes, 2-5, (Fig. 1) and the sulfonated chitosan membrane is subsequently crosslinked with glutaraldehyde, the membrane becomes brittle as the Young's modulus is about twice that of chitosan membrane. The water uptake value of the crosslinked membrane becomes less and ethanol swelling is generally higher than those of chitosan. The substitution degree of sulfonyl groups in the membranes[3~5] was calculated from the elemental analysis and

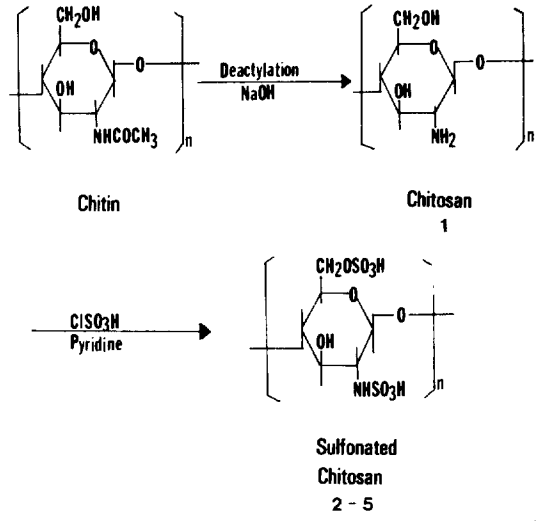

Fig. 1. Synthesis of sulfonated chitosan membrane.

Table 1. Properties of Sulfonated Chitosan Membranes

Sample	Crosslinking Time* [min]	Tensile Strength [N/mm]	Final Elongation [%]	Young's Modulus [N/mm]	Swelling Degree [%]		
					Water	95% Ethanol	90% Ethanol
1	–	103.88	74	127.4	204	9.4	31.1
2	0	67.62	37	274.4	158	37.3	56.2
3	15	28.42	14	264.6	100	16.3	52.7
4	30	23.52	11	245.0	138	12.9	21.4
5	60	33.32	18	254.8	126	12.0	18.0

* Crosslinking with glutaraldehyde (see experimental section).

listed in Table 2. It ranges from 0.5% to 0.86%.

Fig. 2 shows the effect of crosslinking time on the pervaporation performance of sulfonated chitosan membrane tested with 90 wt% ethanol at 25℃. For samples with crosslinking time of less than fifteen minutes, membranes became dissolved in water or swelled to a great extent. When the membrane was treated with glutaraldehyde for more than an hour, it became brittle and could not be tested for its separation efficiency.

The separation factor and the flux decreased as the membrane was crosslinked with glutaraldehyde for more than fifteen minutes. Flux decline is attributed to the chain immobility and the decrease in free volume due to the crosslinking.

Table 2. Elemental Analysis of Sulfonated Chitosan

Sample	C	H	N	O	S	Degree of Substitution (%)
3	40.00	6.14	6.72	47.02	0.12	0.51
4	39.30	5.37	5.83	49.39	0.12	0.55
5	40.80	6.07	6.52	46.44	0.17	0.86

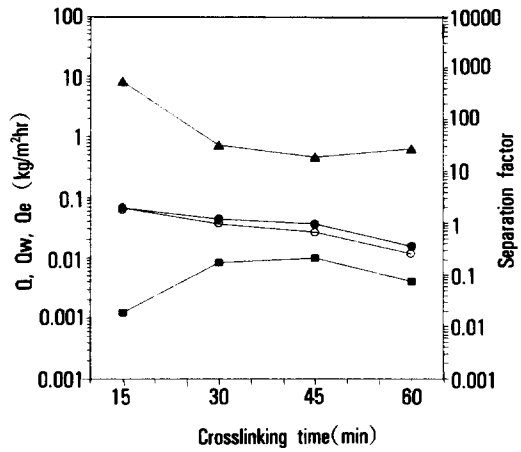

Fig. 2. Effect of crosslinking time with 0,025 wt% glutaraldehyde methanol solution on separation factor (▲), total flux(●), water flux(○), and ethanol flux (■) through sulfonated chitosan membrane. Feed solution=90 wt% ethanol ; membrane thickness=50 μm.

The decrease in selectivity with crosslinking is believed that the number of sites forming hydrogen bond between water and the sulfonyl groups could be reduced due to the crosslinking. This explanation is supported by the results in Table 1 where the membrane swells more in ethanol and less in water as the membrane is sulfonated and subsequently crosslinked.

Using the membrane 3, we investigated the effect of the feed temperature on the membrane performance (Fig. 3). The feed temperature was varied from 28℃ to 75℃. The separation factor toward water was in the range of 1000 to 2000 and we obtained the flux values of 0.05-0.14 kg/m^2 · hr. Membrane 3 shows a remarkable stability to temperature, that is, a temperature-independent separation factor. Generally the most of the membrane including the previously reported chitosan membrane and modifided chitosan membrane[1,2] was rather sensitive to feed temperature so that the flux increased while the separation factor decreased with the feed temperature. Polyion complex membrane, however, shows a temperature-independency in separation factor.[13] Since the sulfonated chitosan membrane is crosslinked, the

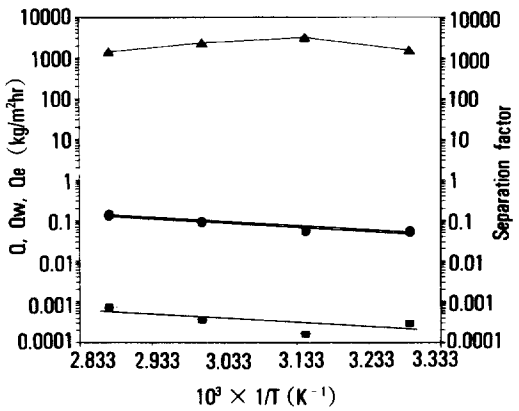

Fig. 3. Effect of feed temperature on separation factor (▲), total flux(●), water flux(○), and ethanol flux (■) through sulfonated chitosan membrane crosslinked with 0.025 wt% gluataraldehyde-70 wt% aqueous methanol solution for 15 minute. Feed=90 wt% ethanol ; membrane thickness=30 μm.

chain immobilization has been increased due to the crosslinking. The activation energies calculated from Fig. 3 were 6.9 kcal/mole and 11.17 kcal/mole for the water and the ethanol permeation, respectively.

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