

Preparation and Characterization of HY Zeolite-Filled Chitosan Membranes for Pervaporation Separation

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ABSTRACT: A novel zeolite (HY)-filled polymeric chitosan membrane was prepared. The membrane was characterized by wide-angle X-ray diffraction and a swelling test. The pervaporation (PV) experiments were also performed for an ethanol–water system. The results showed that the crystalline structure of chitosan was damaged with increase in the zeolite content, indicating a strong interaction between the HY zeolite and chitosan. The separation factor of the ethanol–water mixture by PV was improved by the filling zeolite. When the HY zeolite content in the membrane was 20 mass %, the separation factor reached the maximum and remained constant during the PV process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1144–1149, 2001

Key words: HY zeolite; chitosan; crystallinity; interaction

INTRODUCTION

Chitosan [poly- β (1 \rightarrow 4)-D-glucosamine] is a derivative of chitin [poly- β (1 \rightarrow 4)-*N*-acetyl-D-glucosamine] obtained through an *N*-deacetylation process.¹ Chitin is the major component of the arthropod shell, such as of shrimp, lobster, and crab. Chitin and chitosan are widely used in many fields, such as in the food industry, the textile industry, papermaking, agriculture, and cosmetics.² In the past decades, chitosan was used in biomedical research as a membrane material due to its non-toxicity, biological compatibility, biodegradability, and easy membrane-forming nature.^{2,3}

As a membrane material, chitosan has been extensively studied in the separation of an ethanol and water system.^{4–9} However, the performance of a pure chitosan membrane is not satisfactory due to the larger free volume between the molecular chains.¹⁰ Its membrane performance

can be improved by blending it with other polymers, such as PVA¹¹ and silk fibroin.¹² Alternatively, incorporation of a high-selectivity zeolite into the membrane can also be effective. For instance, Gao et al.¹³ studied the pervaporation (PV) separation of a hydrophilic zeolite-filled PVA membrane for an organic–water system using a membrane reactor. In our previous research, we reported on a hydrophobic zeolite-filled silicone rubber membrane to separate alcohol–water mixtures.¹⁴

In this study, chitosan was incorporated into a hydrophilic HY zeolite in different ratios. The effect of the crystalline structure on the swelling properties as well as the PV properties of the HY zeolite-filled chitosan membranes was studied.

EXPERIMENTAL

Materials

Chitin was obtained from the Dalian Chitosan Factory (Liaoning Province, China). NaY zeolite

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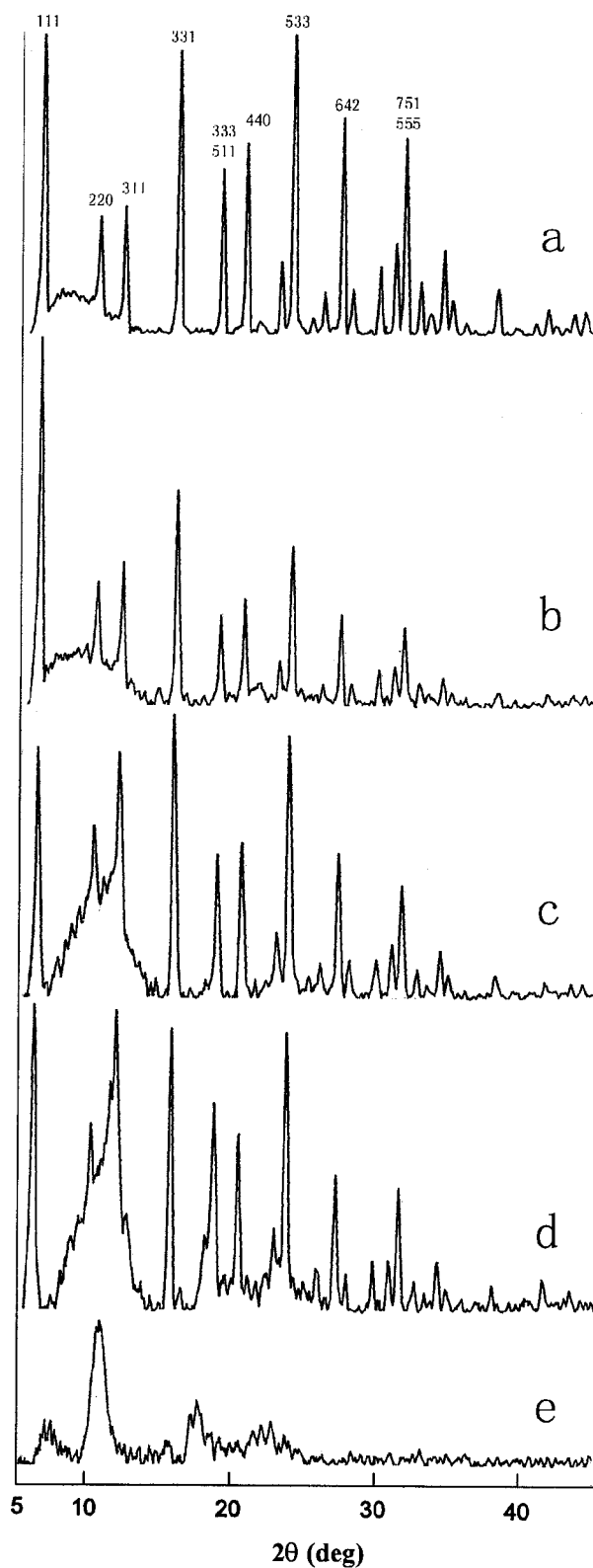


Figure 1 WAXD patterns of HY-filled chitosan membranes without further treatment. Chitosan content in the membrane: (a) 0 mass %; (b) 40 mass %; (c) 60 mass %; (d) 80 mass %; (e) 100 mass %.

Table I Characteristic Peak Positions (2θ) of HY Zeolite in HY Zeolite-filled Chitosan Membranes without Further Treatment

Chitosan Content (%)	$h^2 + k^2 + l^2$						
	3	8	11	19	27	32	34
0	6.12	10.09	11.83	15.61	18.64	20.32	23.62
40	6.08	10.06	11.78	15.56	18.64	20.29	23.60
60	6.05	10.01	11.75	15.52	18.57	20.24	23.56
80	5.94	9.90	11.62	15.46	18.44	20.17	23.45

(Si/Al = 2.47) was provided by the Wenzhou Chemical Industry (Zhejiang Province, China). All other reagents were analytical grade and were used without further purification.

Chitin was deacetylated in a 50 mass % NaOH solution at a ratio of 0.1 kg/dm² in a stainless-steel kettle at 373 K for 5 h under a N₂ atmosphere. The resulting chitosan was washed to neutral and dried for further use. The degree of *N*-deacetylation and the molecular weight were determined by viscometry and titration methods, respectively.^{15,16} The final deacetylation degree was 92% and the molecular weight was about 600,000. The NaY zeolite was added into a 10 mass % NH₄Cl aqueous solution at 350 K for 1 h under stirring for ion exchange. The ion-exchange degree of Na⁺/NH₄⁺ was about 80%. Afterward, the zeolite was dehydrated and decomposed to remove NH₃ at 870 K for 3 h; then, the HY zeolite was obtained.¹⁷

Preparation of HY Zeolite-filled Chitosan Membranes

A chitosan solution (1.5 mass % in 1.0 mass % acetic acid) was mixed with the HY zeolite in appropriate ratios and was intensively stirred at room temperature for 12 h. The mixed solution was filtered and left overnight to release the effervescence to form a homogeneous solution. Then, the solutions were spread onto glass plates in a dust-free atmosphere at room temperature. After being dried for about 48 h, the membranes were obtained.

Wide-angle X-ray Diffraction (WAXD)

The WAXD patterns were recorded at room temperature using a Rigaku D/max-rB X-ray diffractometer. The X-ray source was Ni-filtered CuK α

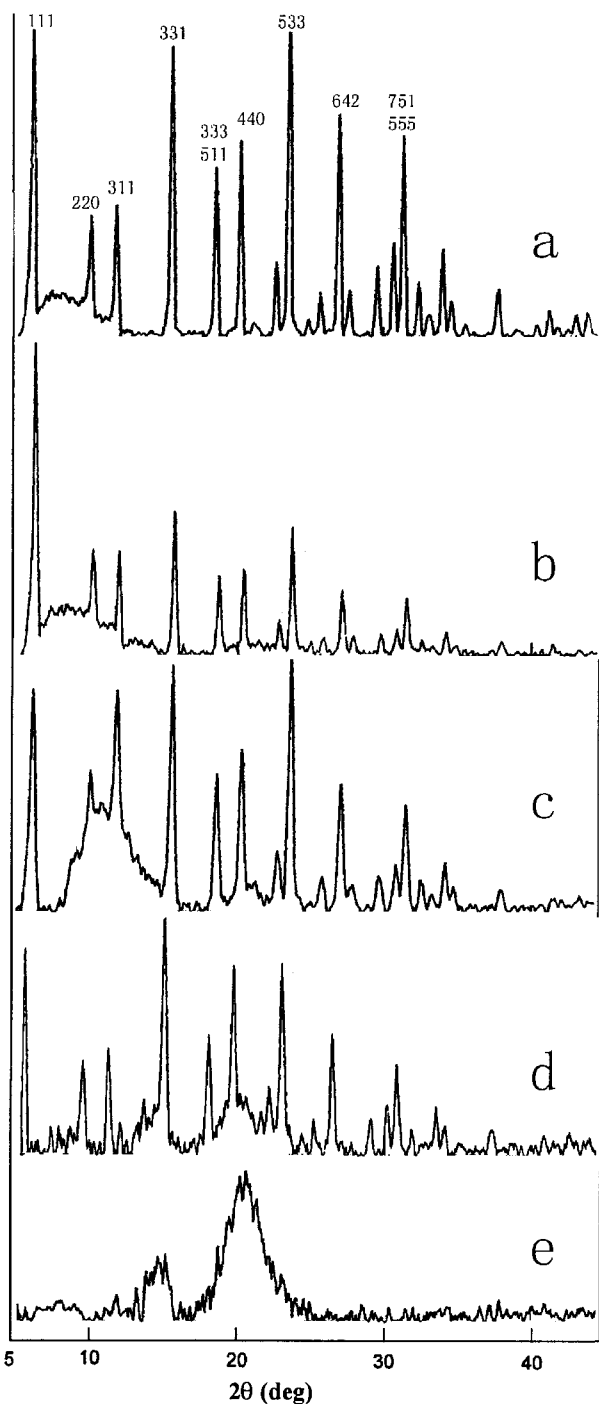


Figure 2 WAXD patterns of HY-filled chitosan membranes treated by ammonia water–ethanol mixture for 24 h. Chitosan content in membrane: (a) 0 mass %; (b) 40 mass %; (c) 60 mass %; (d) 80 mass %; (e) 100 mass %.

radiation (40 kV, 100 mA). The dried membranes of uniform thicknesses were mounted on aluminum frames and scanned from 5° to 45° at a speed of 6° per min.

Swelling Experiments

The dry chitosan membrane as well as HY zeolite-filled chitosan membrane samples were weighed and subsequently immersed in a 90 mass % ethanol–water mixture for 24 h at room temperature. The swollen samples were weighed immediately after careful blotting. The swelling ratio S_w was estimated using the following equation:

$$S_w = (W_s - W_d)/W_d \quad (1)$$

where W_d and W_s are the masses of the dry and swollen membranes, respectively.

PV Experiment

The PV experimental setup was explained in our previous work.¹⁴ Both the PV cell and the porous support plate were made of Teflon. The pressure on the downstream side was maintained below 30 Pa. The permeate was collected in a cold trap cooled by liquid nitrogen. The compositions of the feed and permeate were measured by a gas chromatograph (GC).

The membrane performance was evaluated by calculating the separation factor, α , and the flux, J , which are defined as follows:

$$\alpha = (P_e/P_w)/(F_e/F_w) \quad (2)$$

$$J = W/(A \times \Delta t) \quad (3)$$

where P and F are mass fractions of the permeate and the feed, respectively; subscripts e and w denote ethanol and water, respectively; W is the mass of the permeate (g); A is area of the membrane (m^2); and t is the collection time (h).

RESULTS AND DISCUSSION

WAXD of HY Zeolite-filled Chitosan Membranes

The WAXD patterns of the HY zeolite, pure chitosan membrane, and HY zeolite-filled chitosan membranes are shown in Figure 1. Chitosan exists in two crystal forms: form I has the major crystalline peaks at 11.2° and 18.0°, while form II has major peaks at 15.0°, 20.9°, and 23.8°.^{16,18} However, the pure chitosan membrane cast from the solution shows mainly the form I structure. The HY zeolite shows a crystalline form as published earlier.¹⁷ After incorporating the HY zeo-

Table II Comparison of Characteristic Peak Positions (2θ) of HY Zeolite in HY Zeolite-filled Chitosan Membranes

State of Zeolite	$h^2 + k^2 + l^2$						
	3	8	11	19	27	32	34
Original	6.12	10.09	11.83	15.61	18.64	20.32	23.62
Before treatment	5.94	9.90	11.62	15.46	18.44	20.17	23.45
After treatment	5.53	9.49	11.22	15.05	18.07	19.75	23.03

HY zeolite content in membrane: 20 mass %.

lite into chitosan (the HY zeolite content is not more than 40 mass %), the membranes show the characteristic peaks both of the HY zeolite and chitosan. When the HY zeolite content increases to 60 mass %, no characteristic peak of chitosan was presented in the WAXD spectra and then the crystalline form of the HY zeolite-filled chitosan membranes are almost identical to that of the HY zeolite. Since chitosan cannot be crystallized when the content of the HY zeolite is greater than 60 mass %, and from the molecular structure of the HY zeolite as well as chitosan, it can be seen that the HY zeolite contains many hydroxyl groups, which can form strong interactions with the amino groups of chitosan. The reason for the impediment of crystallization in chitosan may be due to the strong interaction between the HY zeolite and chitosan in the membrane while the HY zeolite content reaches a certain maximum value. Because of the interaction between the HY zeolite and chitosan, the characteristic peaks of the HY zeolite have shown some changes due to the presence of chitosan. As shown in Table I, with an increase in the chitosan content, the characteristic peaks of the HY zeolite in the membranes move to the lower position when compared to the pure HY zeolite. The change in 2θ is about 0.2° between the membranes having a chitosan content is 0 and 80 mass %.

Chitosan can change its crystal form by treatment in a regenerated bath—a mixture of ammonia water and alcohol. After treatment, the crystal form of chitosan will change from form I to form II.^{16,18} Figure 2 shows the X-ray diffraction patterns of HY zeolite-filled chitosan membranes after such treatment. The crystal form of chitosan in the membrane with 20 mass % HY zeolite content changes from form I to form II. However, when the HY content in the membrane is 40 mass %, although chitosan may have some crystalline structure, it does not change much. This may be

due to the strong interaction between the HY zeolite and chitosan, which hinders the crystal formation change of chitosan. This hindrance seems to depend on the extent of interaction between the HY zeolite and chitosan. When the zeolite content in the membrane is only 20 mass %, chitosan dominates and interacts to a lesser content with the zeolite, so that crystal formation occurs. Moreover, the crystalline peak position of the HY zeolite also changes in the membrane after treatment. The results given in Table II indicate that the peaks shift to a much lower angle (about 0.5° lower) compared to those before treatment. This suggests that there is a strong interaction between the HY zeolite and chitosan in the HY zeolite-filled chitosan membranes.

Swelling and PV Results of HY Zeolite-filled Chitosan Membranes

Figure 3 presents the result of the swelling ratio of the HY zeolite-filled chitosan membranes in a

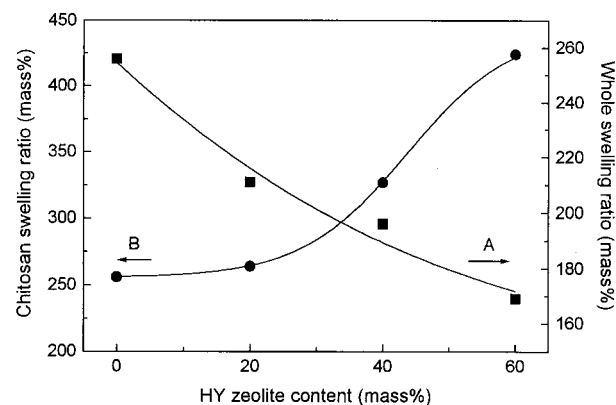


Figure 3 Swelling ratio of HY zeolite-filled chitosan membranes in 90 mass % ethanol aqueous solution at room temperature.

90 mass % ethanol–water mixture. Curve A is the whole swelling ratio [calculated from eq. (1), where W_d and W_s are the total mass of the HY zeolite and chitosan in the membrane before and after the swelling experiment, respectively] of the membrane, which decreases with increase of the zeolite content in the membrane. However, this may not completely reflect the behavior of the membrane because the HY zeolite is always saturated and the mass does not change whenever the zeolite content in the membrane is changed. Therefore, by deducting the zeolite mass in the membrane, the swelling ratio of the chitosan part in the membrane was calculated (see curve B). The data indicate that the swelling ratio of chitosan increases with increase in the zeolite content; this is quite the opposite to curve A. The membrane swells more in the amorphous state than in the crystalline structure and this is in accordance with the results obtained from the WAXD measurement.

Both the HY zeolite and chitosan are hydrophilic so that HY zeolite-filled chitosan membranes can be used in the separation of the ethanol–water mixture by PV. The PV properties of the membranes with different zeolite content are presented in Table III. These results indicate that separation factors are improved by filling the HY zeolite in the chitosan membrane because of the high water selectivity of the zeolite.

The influence of operation time on the PV properties of HY zeolite-filled chitosan membranes was also tested. From Figure 4, it is found that with an increase in time, the separation factor of the pure chitosan membrane and the 20 mass % HY zeolite-filled chitosan membrane remains constant, while the membranes that contain 40 and 60 mass % zeolite decrease significantly. In the

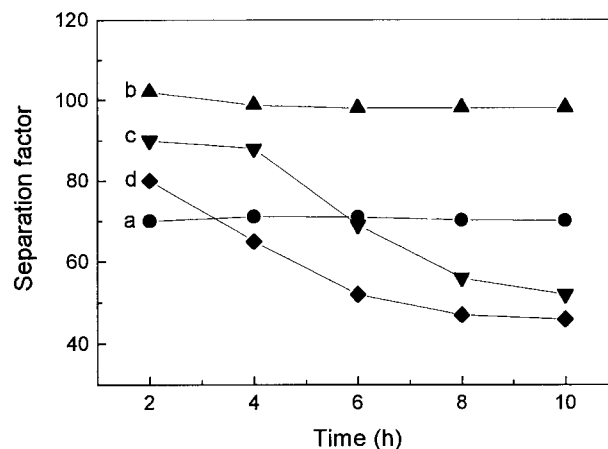


Figure 4 Influence of operation time on separation factor of HY zeolite-filled chitosan membranes. HY zeolite content in membrane: (a) 0 mass %; (b) 20 mass %; (c) 40 mass %; (d) 60 mass %.

latter case, the change of the separation factor reflects the decrease of the stability of the membranes. As discussed before, the zeolite-filled membranes are maintained by the strong interaction between the HY zeolite and chitosan. During the PV processes, when water molecules diffuse into the membranes (in high zeolite content membranes, the crystallinity of chitosan decreases so that the membranes become swollen; see Fig. 3), the swelling decreases the interaction between the HY zeolite and chitosan; this might result in some tiny cracks developing at the interface between the zeolite and chitosan, which allows ethanol molecules to pass through. The reason that the 20 mass % HY zeolite-filled chitosan membrane manifests good stability through the PV process is due to the high crystallinity of chitosan which strongly resists the swelling effect.

CONCLUSIONS

In this study, we prepared a novel hydrophilic zeolite (HY)-filled polymeric chitosan membrane. The unique structure of the membrane was maintained due to the strong interaction between the HY zeolite and chitosan. The membranes were used to separate the ethanol–water mixture. At low HY zeolite content, the chitosan maintains its crystallinity and the membrane shows the best and most stable PV separation characteristics for the ethanol–water mixture.

Table III Separation Properties of Ethanol–Water Mixture through HY Zeolite-filled Chitosan Membrane by PV

Zeolite Content (mass %)	α	J ($\text{g m}^{-2} \text{h}^{-1}$)
0	70	398
20	102	353
40	90	472
60	80	490

The ethanol content in the ethanol–water mixture was 90 mass %. All data shown here were collected in the first 2 h.

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