

# Novel Method of Preparing Microporous Membrane by Selective Dissolution of Chitosan/Polyethylene Glycol Blend Membrane

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**ABSTRACT:** Chitosan membranes with high porosity and good mechanical properties were prepared by selective dissolution of the blend membranes of chitosan (CS) and polyethylene glycol (PEG). The morphology of the obtained porous membranes was characterized by scanning electron microscopy. The pore size changed from 500 nm to several micrometers, depending on the molecular weight of the PEG used. The water permeability of the porous membrane depends on both the pore size and the porosity, except in the case of PEG2000, in which a higher molecular weight of PEG

was used, producing greater water permeability. The tensile strength of the porous membranes obtained by this method was higher in both the wet and the dry state than that of the porous chitosan membranes prepared by using silica particles as porogen. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2840–2847, 2004

**Key words:** chitosan; polyethylene glycol; porous membrane; blend; compatibility

## INTRODUCTION

Chitosan (CS) is an N-deacetylated product of chitosan that is one of the most abundant polysaccharides in nature and has good physical, biological, and biodegradable properties. It is readily processable into films and membranes from most aqueous acid solutions. The membranes obtained by chitosan and its blend have been reported to be suitable for biomedical applications such as controlled release of drugs,<sup>1,2</sup> wound dressings,<sup>3,4</sup> and chromatographic media.<sup>5,6</sup> Among such applications, in many cases, it is necessary to have a porous structure. For example,<sup>5</sup> the membrane chromatography based on porous chitosan membranes has provided some advantages over column chromatography, such as lower pressure drops, higher flow rates, faster binding, and higher productivity.

Many studies have been reported to obtain the microporous structure of chitosan matrix. The phase-inversion technique (i.e., polymer solution is cast and immersed in a coagulation bath) is the traditional method of preparing a porous membrane. The membrane prepared by this method<sup>7</sup> has an asymmetric structure. Porous chitosan membranes also can be prepared<sup>2,8</sup> by cryogenic induced phase separation (CIPS)

of the aqueous chitosan solution. The pore size of the membranes prepared by this method ranges from 10 to 30  $\mu\text{m}$ . Another method<sup>9</sup> consists of casting a suspension of silica particles of selected size into an acidic chitosan solution, removing the solvent by evaporation and dissolving the silica particles in an alkaline solution (chitosan is soluble in acidic, but insoluble in alkaline solutions) afterward. The macroporous chitosan membranes obtained by this method showed efficient purification for proteins and enzymes.<sup>10–12</sup>

Enlightened by the last method cited above, we recognized that porous chitosan membrane could also be prepared by selective dissolution of one component of the binary polymer blend membrane. In fact, the result reported by Amiji<sup>13</sup> showed that chitosan–polyethylene oxide blend membranes had a porous structure throughout the surface. The author suggested that such a porous structure is probably formed from leaching out low molecular weight polyethylene oxide oligomers during the initial hydration of the membranes. In this study, the chitosan/polyethylene glycol blend membranes were purposely dissolved with hot water to produce CS membrane with microporous structure. Factors influencing the structure and properties of the membranes were discussed.

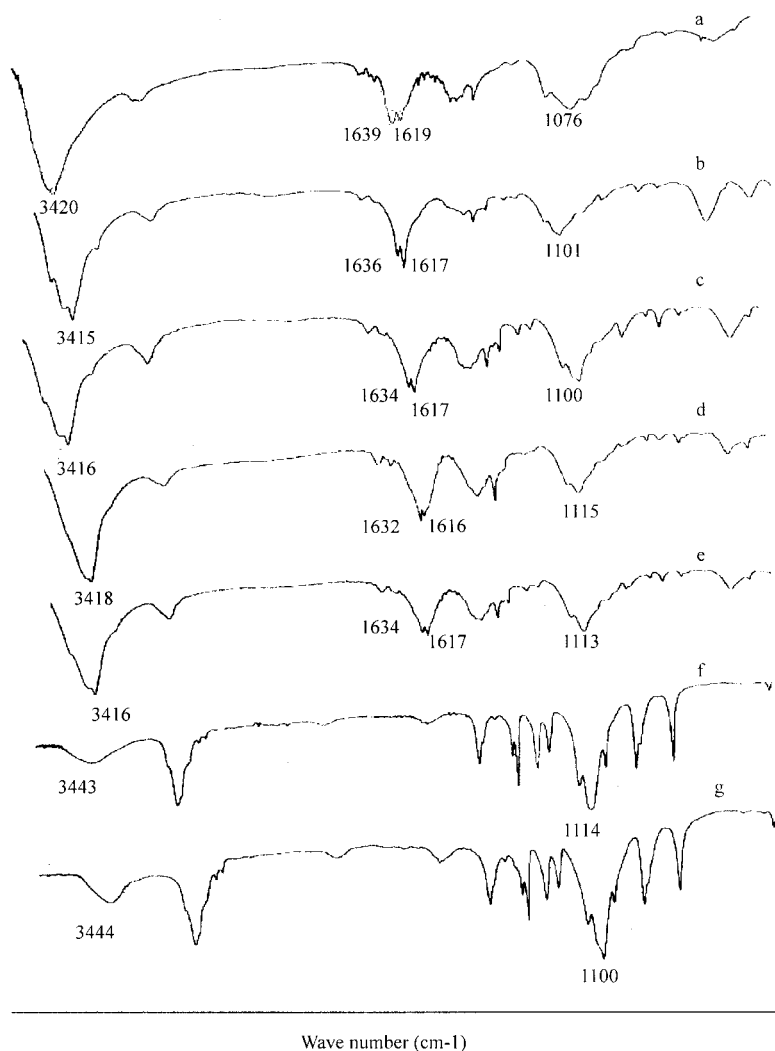
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## EXPERIMENTAL

### Materials

Chitosan (CS, 91% deacetylated, the molecular weight evaluated from its intrinsic viscosity was  $5.6 \times 10^5$ )



**Figure 1** FTIR spectra of various blends: (a) CS; (b) CS/PEG20000 (2/1); (c) CS/PEG20000 (1/1); (d) CS/PEG4000 (2/1); (e) CS/PEG4000 (1/1); (f) PEG4000; (g) PEG20000.

was supplied by Qingdao Haihui Biological Engineering Co. (Qingdao, China). Five kinds of polyethylene glycol (PEG) samples with different molecular weights (PEG20000, PEG10000, PEG6000, PEG4000, and PEG2000) were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Their molecular weights were 20,000, 10,000, 6000, 4000, and 2000, respectively. The water used in the following experiments was obtained by double distillation of deionized water. Sodium hydroxide and acetic acid were all analytical reagents.

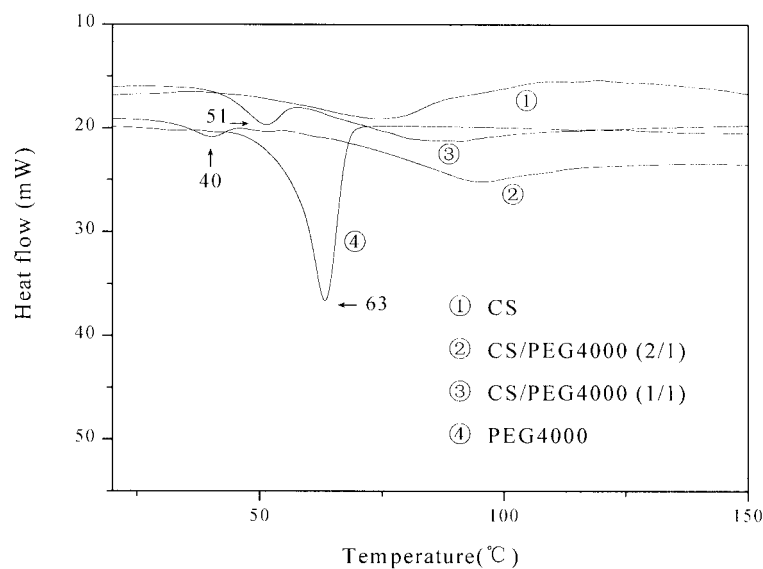
### Membrane preparation

A certain amount of CS and PEG with different mass ratios was dissolved in a 2% acetic acid at room temperature to form a 2–3% solution. The solution was then poured into a clean glass-frame model and dried at 50°C for 7–8 h. The blend membranes were im-

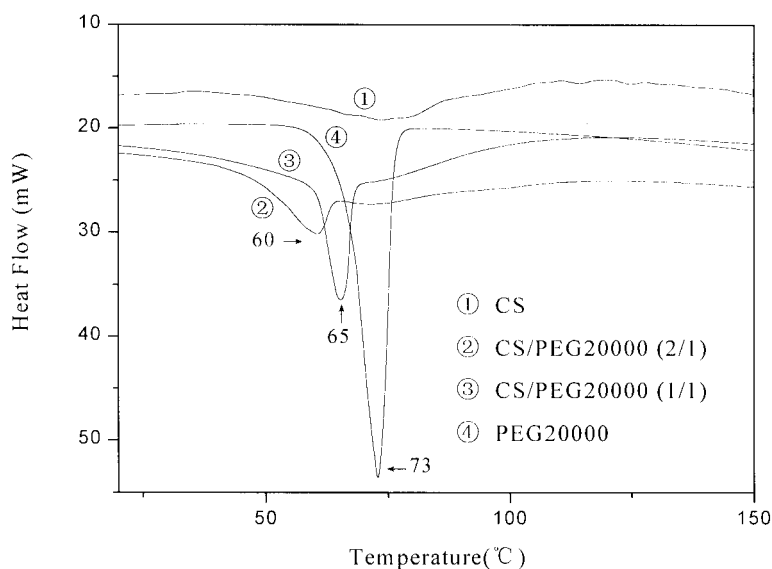
mersed in a 2% aqueous NaOH solution for 30 min after drying. Afterward, the membrane was washed with water to remove the remaining NaOH. Finally, the membrane was kept in water with the bath temperature 80°C for 8 h to dissolve the PEG component and to generate a porous membrane. The heat treatment accelerated the dissolution of PEG and also improved the mechanical properties of the membrane. The wet membrane was wiped with a filter paper to remove the excess water present on the surface of the membrane, then framed onto glass to prevent shrinkage along the surface, and allowed to dry.

### Measurement of the weight ratio of the dissolvable part

Samples of the blend membranes were weighed before and after dissolution. The weight ratio of the extractable part was calculated by



(A)



(B)

**Figure 2** DSC curves of CS/PEG blend membranes: (A) CS/PEG4000 blend system; (B) CS/PEG20000 blend system.

$$\text{Extraction ratio (\%)} = (w_1 - w_2)/w_1 \times 100$$

where  $w_1$  and  $w_2$  indicate the weight of the samples before and after dissolution, respectively.

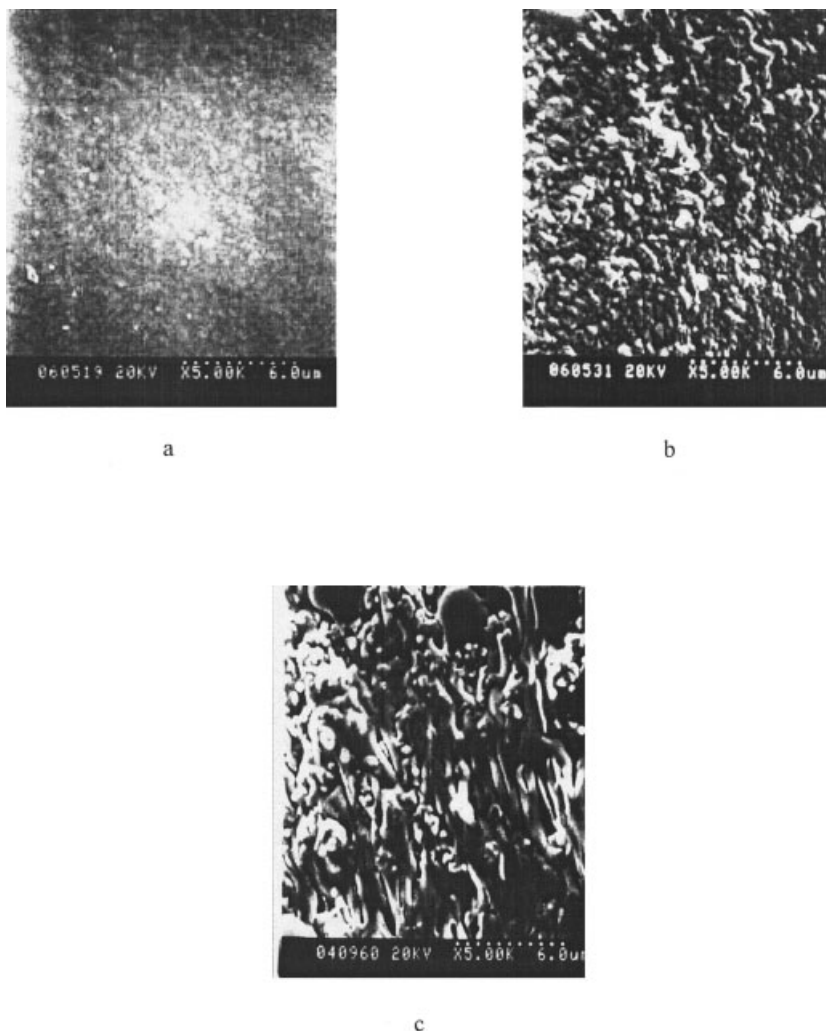
### Tensile testing

The mechanical properties of the membranes were investigated at 25°C using a universal testing instrument with a crosshead speed of 10 mm/min. The results presented were the mean values of five independent measurements.

**TABLE I**  
Results of Differential Scanning  
Calorimeter Measurement

Blend	Mass ratio	$\Delta H_f^a$ (J/g)	$X_{c,PEG}$ (%)
PEG20000		200.4	75.5
CS/PEG20000	2/1	32.4	36.6
CS/PEG20000	1/1	85.2	64.2
PEG4000		160.2	87.8
CS/PEG4000	2/1	11.4	18.7
CS/PEG4000	1/1	26.4	28.9

<sup>a</sup>  $\Delta H_{f,PEG20000}^a = 265.6$  (J/g)<sup>15</sup>;  $\Delta H_{f,PEG4000}^a = 182.5$  (J/g).<sup>16</sup>



**Figure 3** Cryogenically fractured surface of CS/PEG blend membranes: (a) pure CS; (b) CS/PEG20000 (1/1); (c) CS/PEG4000 (1/1).

**Water permeability measurement**

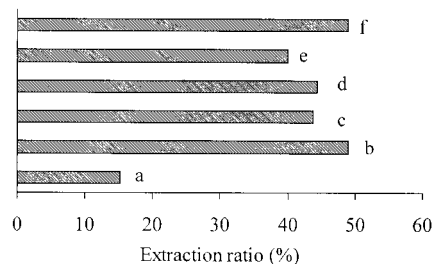
Water permeability of the porous membranes was investigated with a water permeability testing instrument (YSB-II, supplied by Institute of Water Treatment, Hangzhou, China). The porous membrane was placed into a water permeation cell with a porous stainless-steel support plate. The effective membrane area was 3.8 cm<sup>2</sup>. A constant flow rate was applied on the membrane and the value of pressure drop was measured. The smaller the pressure drop, the higher the water permeability.

**Porosity measurement**

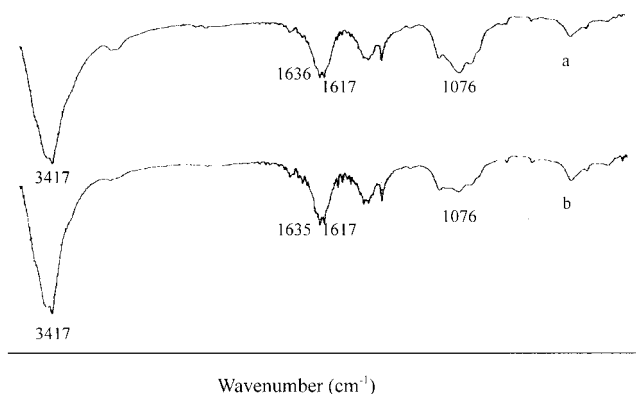
To measure the porosity of the membranes, the dense CS/PEG blend membrane was prepared first, and its density ( $\rho_1$ ) was determined through the measurement of membrane volume and weight. In the same way, the density of porous membrane ( $\rho_2$ ) can be

obtained. The porosity of the sample was estimated by the following formula:

$$\text{Porosity} = (1 - \rho_1/\rho_2) \times 100\%$$



**Figure 4** Influences of PEG variety to the weight ratio of extracted part of the blend [mass ratio: CS/PEG (1/1)] membranes: (a) CS; (b) CS/PEG2000; (c) CS/PEG4000; (d) CS/PEG6000; (e) CS/PEG10000; (f) CS/PEG20000.



**Figure 5** FTIR spectra of the extracted blend membrane: (a) CS/PEG20000 (1/1); (b) CS/PEG4000 (1/1).

### FTIR characterization

The FTIR spectra of the samples were measured with a Perkin–Elmer 6000 FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) in the wavenumber range of 500–4000  $\text{cm}^{-1}$ . Samples for FTIR spectroscopic characterization were prepared by grinding the dry blends with KBr and compressing the mixtures to form disks.

### Differential scanning calorimeter (DSC) analysis

A Perkin–Elmer Pyris 1 DSC was used to measure the thermodynamic properties of the materials. Heating and cooling rates were 10°C/min. The temperature was increased from 0 to 200°C. All experiments were done with dry  $\text{N}_2$  flowing through the calorimeter.

### Scanning electron microscope (SEM) observation

Surface morphology was observed through a scanning electron microscope (S-570, Hitachi, Ibaraki, Japan) after gold coating. The fractured cross-surfaces of the membranes were achieved by breaking the samples deeply cooled in liquid nitrogen.

## RESULTS AND DISCUSSION

### Compatibility of CS and PEG

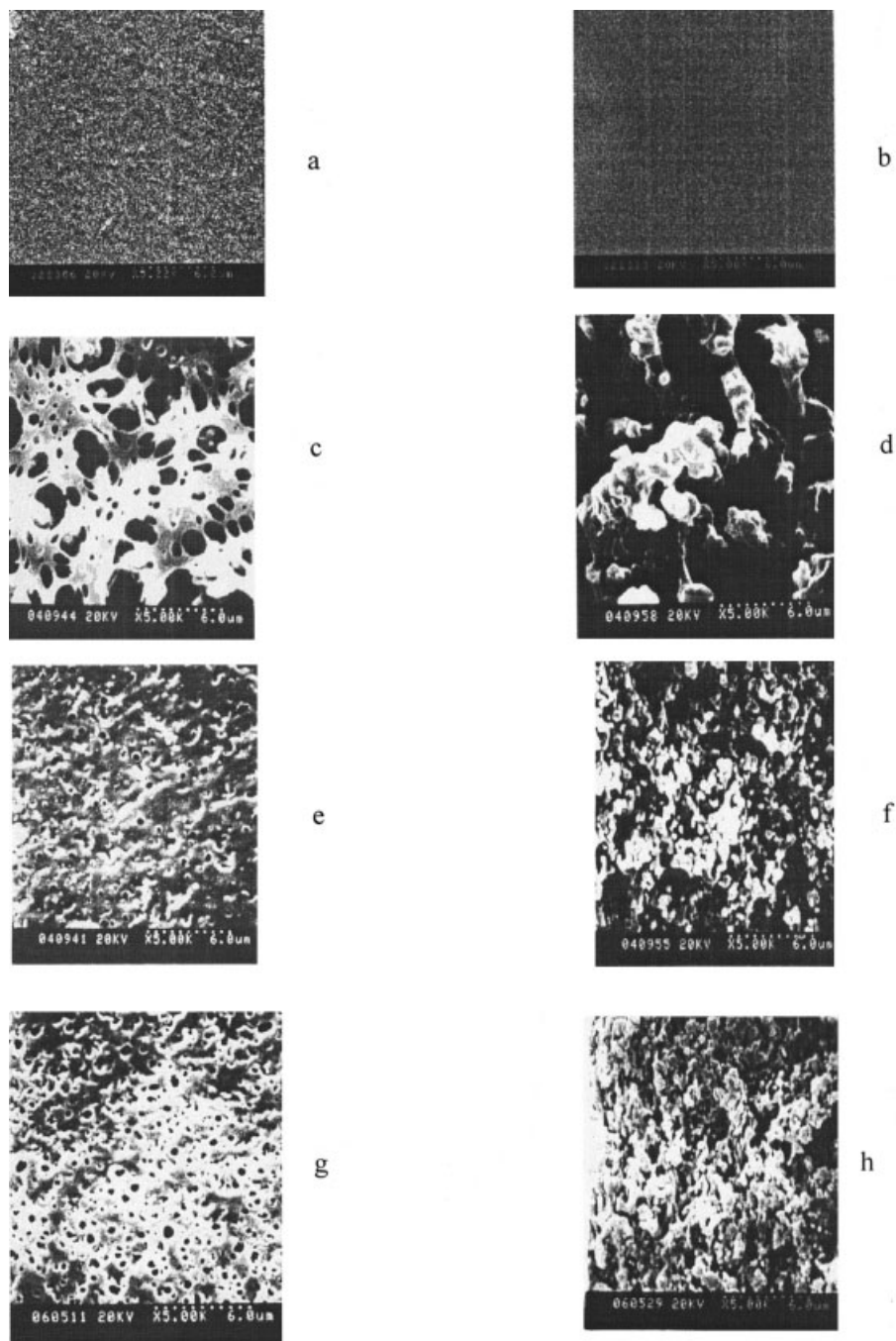
PEG is often used as a porogen to prepare porous membranes by the phase-inversion method.<sup>14</sup> In this article, a dried CS/PEG blend membrane, rather than a gel membrane, was first obtained, and then the PEG component was extracted by hot water to induce a porous structure. The structure of the porous membrane is directly correlated with the phase separation structure of the blend membrane. Hence, the compatibility between CS and PEG is of key importance to the structure of the porous membranes.

The type of hydrogen bonding within CS/PEG blend may be complicated because there are several groups that can form a hydrogen bond in chitosan. Furthermore, PEG may form a new type of hydrogen bonding with these groups competitively. Figure 1 shows the FTIR spectra for CS, PEG, and their blends. The pure chitosan showed absorption bands at 1639, 1619, 1076, and 3420  $\text{cm}^{-1}$ , attributed to the amide I, amide II, C—O, and O—H stretching, respectively. As the PEG was blended, the characteristic peak for amide and O—H stretching shifted to lower wavenumbers (as shown in Fig. 1), confirming that the PEG and the hydroxyl or amino groups of chitosan formed a hydrogen-bonding interaction. Peaks at 1114  $\text{cm}^{-1}$  in PEG4000 and 1100  $\text{cm}^{-1}$  in PEG20000 were assigned to the C—O stretching of polyether, respectively. The related peak can be seen at 1115, 1113, 1101, and 1100  $\text{cm}^{-1}$  in the FTIR spectra of Figure 1(d), (e), (b), and (c), respectively, which assigned to the superposition of C—O stretching vibrations in the ether bond of PEG and chitosan.

The thermal transitions of CS, PEG, and their blends were determined by DSC analyses (Fig. 2). The main feature in the chitosan curve is that there is a large endothermic peak at around 80–90°C, which corresponds to the dehydration of the membranes, and the peak appeared in all the DSC curves of the blend samples. Although chitosan has crystalline regions, the crystalline melting temperature ( $T_m$ ) was not found because of its rigid-rod polymer backbone having strong inter- and intra-molecular bonding. This behavior is frequently detected in many polysaccharides such as cellulose and chitin derivatives. PEG20000 and PEG4000 showed sharp melting peaks at 73 and 63°C, respectively, whereas lower  $T_m$  and broader and weaker melting peaks of PEG within the blends were observed in both cases. As shown in Table I, the heat of fusion of CS/PEG blends did not have a linear relation against the blend ratio. The crystal degree of the PEG component decreased distinctly as the CS content increased, indicating that CS molecules do suppress the growth of PEG crystals in the blend. The formation of the interaction between CS and PEG molecules weakened the crystallization capacities of PEG. Decreases in the heat of fusion and the melting temperature in the PEG4000 blend were more obvious than those in PEG20000, implying a stronger interaction in the low molecular weight case. This could be attributed to its higher content of terminal hydroxyl groups, which could form stronger hydrogen bonding with CS than with the ether group in mid-chain.

The cryogenically fractured cross-sectional surface of the blend membranes is shown in Figure 3. The pure chitosan film exhibited a dense and uniform microstructure. A distinct phase separation was observed in the case of CS/PEG (1/1) blend membranes.

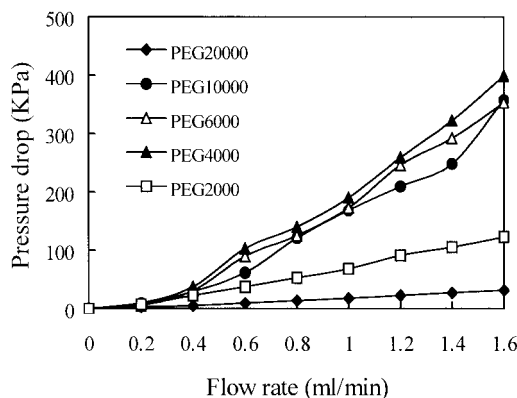




**Figure 6** SEM micrographs of the surface and cross section of the extracted membranes: (a) CS (surface); (b) CS (cross section); (c) CS/PEG20000 (1/1) (surface); (d) CS/PEG20000 (1/1) (cross section); (e) CS/PEG4000 (1/1) (surface); (f) CS/PEG4000 (1/1) (cross section); (g) CS/PEG2000 (1/1) (surface); (h) CS/PEG2000 (1/1) (cross section).

**TABLE II**  
Mechanical Properties and Porosity of the Porous Membranes

Extracted blend membranes (CS/PEG, 1/1)	Porosity (%)	Tensile strength (MPa)		Elongation at break (%)	
		Dry	Wet	Dry	Wet
PEG20000	61.3	9.8 ± 1.6	4.9 ± 2.1	9 ± 2	25 ± 6
PEG10000	52.2	10.5 ± 1.8	3.1 ± 1.1	10 ± 1	22 ± 10
PEG6000	54.3	12.9 ± 2.7	3.7 ± 1.1	13 ± 6	28 ± 5
PEG4000	58.6	9.5 ± 1.5	5 ± 0.3	9 ± 2	46 ± 11
PEG2000	65.5	11.6 ± 2.3	2.5 ± 0.6	12 ± 3	27 ± 7



**Figure 7** Water permeability of the extracted CS/PEG (1/1) blend membranes.

The result indicates that CS and PEG are not very compatible, although they can form hydrogen-bonding interaction.

#### Preparation and characteristics of the porous membranes

Five kinds of PEG with different molecular weight were employed. Figure 4 shows the influences of the kind of PEG to the weight ratio of the extracted part of the blend (mass ratio: CS/PEG 1/1) membranes. For pure chitosan membrane, the weight ratio of the extracted part is 15%. This portion could be attributed to a part of chitosan with lower molecule weight. For the blend membranes, the weight ratio of the extracted part is 40–50%, and the ratio in the cases of PEG20000 and PEG2000 is relatively higher. Considering the 15% in the pure chitosan case, the interesting result is that PEG cannot be extracted completely. Figure 5 shows the FTIR results of the blend membrane after the hot-water treatment. Contrasting with the blend membrane before the hot-water treatment (as shown in Fig. 1), the C—O stretching vibrations shifted to a lower wavenumber ( $1076\text{ cm}^{-1}$ , almost the same wavenumber with its vibration in CS); the amide vibration shifted to a higher wavenumber, but still lower than its peak in CS, which means that in dissolution by hot water the major portion of PEG content within the blend was extracted. However, the hydrogen bonding between CS and PEG was not destroyed completely.

The SEM micrographs of the surface and cross section for porous membranes prepared by selective dissolution of PEG from the CS/PEG blend membranes are presented in Figure 6. The extracted pure chitosan membrane still exhibits uniform and dense microstructure without pores. The extracted blend membranes exhibit a highly porous structure. The photos of cross sections indicate that the membrane has a three-dimensional porous structure, stacked by porous lamella. The pore size depends on the molecular

weight of PEG. The greater the molecular weight of PEG that was used, the larger the pore size that was induced, revealing the poorer compatibility with CS.

The porosity of the membranes is shown in Table II. All the membranes have high porosity (>50%). Among them, the extracted CS/PEG2000 blend membrane has the highest porosity.

#### Properties of the porous membranes

Figure 7 presents the relationship between pressure drop and the flow rate through the extracted blend membranes. The flow rates of water through the membrane were almost equal in the cases of PEG4000, PEG6000, and PEG10000. However, the flow rates of PEG2000 and PEG20000 are much larger than those of the other three formulations under the same pressure. It is well known that the permeability of a porous material is determined by its pore size and porosity. Thus, the highest water permeability of the extracted CS/PEG20000 can be attributed to its largest pore size and high porosity; the high water permeability of the extracted CS/PEG2000 blend membranes can be mainly attributed to their highest porosity. The low water permeability of the other three blend membranes indicated that they have relatively small pore size and low porosity.

The mechanical properties of the porous membranes are also presented in Table II. The tensile strength of the porous membranes obtained by this method are higher in both the wet and the dry state than that of the porous chitosan membranes prepared by using silica particles as porogen (dry/wet: 7.37/0.90 MPa).<sup>9</sup> The main reason is that the smaller pore size structure induced by this method leads to a higher strength. The other may be attributed to the intermolecular hydrogen bonds formed by CS and the unextractable part of PEG during the dissolution process, which can act as physical crosslinking points.

#### CONCLUSIONS

Chitosan membranes with high porosity and good mechanical properties were prepared from selective dissolution of CS/PEG blend membranes. SEM results indicated the presence of a distinct phase separation in the CS/PEG blend. Their compatibility is not very good, although they can form hydrogen-bonding interactions to some degree. With respect to the CS/PEG (1/1) blend membrane, the greatest portion of the PEG content can be selectively dissolved by hot water. Meanwhile, microporous CS membranes with high porosity were obtained. The pore structure and hence the properties of the membrane can be controlled by altering the molecular weight of PEG.

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