Ionic Conductivity and Related Properties of Crosslinked Chitosan Membranes

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ABSTRACT: Crosslinked chitosan membranes were prepared with a relatively low degree of crosslinking with epichlorohydrin and glutaraldehyde as crosslinking agents under heterogeneous and homogeneous conditions, respectively. The tensile properties, crystallinity, swelling index, and ionic conductivity of the crosslinked membranes were investigated. A significant decrease in the crystallinity and a large change in the swelling ratio of the crosslinked membrane were observed. In comparison with the uncrosslinked chitosan membrane, when the chitosan membrane was crosslinked with an appropriate degree of crosslinking under homogeneous conditions, its ionic conductivity after hydration for 1 h at room temperature increased by about one order of magnitude. In addition, with a lower concentration of the crosslinking agent, the tensile strength and breaking elongation of the crosslinked membrane were almost unchanged. Moreover, up to a critical value, the tensile strength of the membrane increased gradually, and the breaking elongation decreased slowly. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 306–317, 2003

Key words: crosslinking; membranes; polyelectrolytes

INTRODUCTION

Chitosan, the *N*-deacetylated polysaccharide derived from chitin [poly(*N*-acetyl-D-glucosamine)], has attracted significant interest in view of its varied proposed novel applications, including such areas as pharmaceutical and biomedical engineering, paper production, textile finishes, photographic products, cements, heavy metal chelation, wastewater treatment, and fiber and film formation.[1,2] As a copolymer, chitosan is readily converted into fibers, films, coatings, and beads as well as powders and solutions, and this further enhances its usefulness. Because chitosan has free amino groups and hydroxyl groups on its backbone, which are easily modified by many organic reactions,[3] it also has a high potential for development into sophisticated functional polymers with properties quite different from those of synthetic polymers.

Chitosan can also act as a cationic polyelectrolyte.[4] With respect to its ionic properties, the chitosan membrane has been used for the active transport of chloride ions in aqueous solutions.[5] In a similar way, when a chitosan membrane is swollen in water, the amino groups may be protonated and leave the hydroxyl groups free, and this may contribute to ionic conduction in the membrane. Because of the crystalline nature of chitosan, highly crystalline portions in the chitosan membranes obviously render resistance to water uptake and, in turn, hinder hydroxide ion transport in the membranes. To reduce the crystallinity of the membrane, we considered a chemical crosslinking of the chitosan membrane. It may be expected that when the crystallinity of the chitosan membrane is significantly decreased, a higher amount of water uptake in the membrane will be reached, and so an optimized membrane structure for ionic transport will be obtained. To this end, in this work, glutaraldehyde (GA) and epichlorohydrin (ECH) were selected as crosslinking agents. GA is frequently used for crosslinking chitosan membranes, whereas ECH has the advantage of not eliminating the cationic amine function of chitosan, which plays an important role in facilitating ionic transport in the membranes.[6,7]

Although some physical properties of crosslinked chitosan membranes, such as the crystallinity, swelling ratio, tensile strength, and elongation, have previously been investigated, we needed to do a comprehensive report as a baseline for our study of ionic conductivity in chitosan membranes. The objective of this study was to optimize some of the processing conditions for preparing crosslinked chitosan membranes that would yield good membrane properties and an ionic conductivity as high as possible in the membranes.

EXPERIMENTAL

Materials

Chitosan (a shrimp-based product) was received in the form of flakes from Sigma–Aldrich Canada, Ltd. (Oakville, Canada), with a claimed viscosity of 800–2000 cps for a 1 wt % chitosan solution in 1% (v/v) aqueous acetic acid. Its molecular weight was reported by the supplier to be high. The following chemicals were all obtained and used as reagent grades from either Sigma–Aldrich Canada or Caledon Laboratories, Ltd. (Georgetown, Canada): acetic acid, sodium acetate, *N*-acetyl-D-glucosamine (NAG; 99%, formula weight (FW) 221.21), sodium hydroxide pellets, ECH (99%), GA (25% by weight in water), ammonium hydroxide (38%), and methanol. Deionized water (resistivity $> 1.8 \times 10^7 \ \Omega$ cm) was used for all samples.

Degree of deacetylation (DDA) and molecular weight of chitosan

The chitosan sample was treated further in a 50% NaOH aqueous solution under air with constant stirring, for 1 h, at 100°C so that its DDA would be increased. The reaction product was washed subsequently in deionized water until it showed a neutral pH and was dried in a convection oven at 50°C for 2 days. The process was repeated one more time with a sample from the reaction production of the first deacetylation step under the same conditions for 2 h under air. This product was also washed repeatedly in deionized water until a neutral pH was obtained and was dried first in a convection oven at 50°C for 2 days and then in a vacuum oven at 50°C for 24 h.

The DDA of chitosan was estimated with first-derivative ultraviolet spectroscopy recording on a CARY 5E ultraviolet–visible/near-infrared spectrometer (Mississauga, Canada) according to reported methods.[8] A calibration curve from NAG was generated according to our previously reported method.[9] The average linear regression value of the calibration curve used in the various sample analyses was 0.9913. The water content of the chitosan sample was determined with a Texas Instruments 2050 TGA thermogravimetric analyzer (New Castle, DE). The sample was heated from 25 to 300°C at 10°C/min under nitrogen. The loss in weight of the chitosan sample up 180°C was taken to be the result of water evaporation. Repeated thermogravimetric analysis runs on the same chitosan sample showed a difference of as much as a 1.4% loss in weight due to water. This relatively large error in the water content value of chitosan was considered the largest factor contributing to the error in the DDA calculation.

The viscosities of the chitosan samples were measured in a solvent system of 0.25*M* CH$_3$COOH and 0.25*M* CH$_3$COONa with an Ubbelohde capillary viscometer (Cannon model 75 F107) (Roselle, NJ), which yielded an average flow time of 110.47 ± 0.5 s in a viscometer bath at 25 ±0.05°C. Five dilutions were used for each chitosan solution, and at least five flow time measurements were made for each dilution. The overall error in the intrinsic viscosity, resulting mainly from the flow time and concentration uncertainties, was estimated to be ±0.6 dL/g, which led to a maximum error of ±4.1% in the value of the viscosity-average molecular weight. The correlation coefficients were better than 0.946 for all chitosan samples.

Preparation of the chitosan membrane

The membrane preparation consisted of dissolving chitosan in a 1 wt % aqueous acetic acid solution with a 0.5–1.0 wt % chitosan concentration. The solution was filtered through a 40-μm filter for the removal of undissolved chitosan and debris and was cast onto a polystyrene plate. After drying at room temperature for 2 days, the membranes were mounted on a stainless steel holding device and immersed in a 2% NaOH aqueous solution for 1 h for neutralization. They were then washed intensively with deionized water, air-dried for 1 day, and then dried at 50°C in a vacuum oven until a constant weight was reached.

Crosslinked chitosan membrane

The chitosan membranes were crosslinked with GA or ECH as a crosslinking agent under heterogeneous and homogeneous conditions, respectively. For heterogeneous crosslinking, the water-swollen membranes were placed in an aqueous solution of either GA or ECH and were allowed to react for a given time at the required temperature. For the former (GA), the concentration varied from 50 to 150 ppm, and the reaction was conducted at ambient temperature for 24 h. For the latter (ECH), a 0.067*M* NaOH solution (pH 10) was employed as the catalyst, and the concentration of ECH varied from 0.001 to 0.05*M*. The reaction was maintained at 40°C for 2 h. All of the crosslinked membranes were subsequently washed repeatedly in deionized water until they exhibited a neutral pH; they were air-dried for 1 day and then dried at 50°C in a vacuum oven until a constant weight was reached.

For homogeneous crosslinking, 1 g of chitosan was dissolved in 100 mL of a 1% (v/v) aqueous acetic acid solution at ambient temperature, and this was followed by the addition of the given amount of GA (the concentration of GA varied from 50 to 150 ppm) with stirring for 30 min. Before the crosslinking reaction occurred, the blend solution was filtered through a 40-μm filter and then cast onto a polystyrene plate. Solvent removal and simultaneous crosslinking were done at room temperature for 24 h. The dry

TABLE I
Deacetylated Chitosan Sample Information

Sample code	% DDA (±3.1%)	% Water + impurities (±5.1%)	M_v (±1.7%)	Deacetylation conditions
Ch-H	75.4	4.1	2.4×10^6	As received from Aldrich
Ch-H-1	89.3	4.2	1.5×10^6	Ch-H, 1 h, 50% NaOH, 100°C, air
Ch-H-2	97.6	3.8	9.3×10^5	Ch-H-1, 2 h, 50% NaOH, 100°C, air

crosslinked membrane was neutralized in an ammonia/methanol solution (1:8 v/v) for 2 h, washed with deionized water until neutrality was achieved, air-dried for 1 day, and then dried at 50°C in a vacuum oven to a constant weight.

Infrared spectra

A Nicolet 510P Fourier transform infrared (FTIR) spectrometer (Madison, WI) was used to record the infrared spectra of crosslinked chitosan membranes with a resolution of 2 cm^{-1} (64 scans) in the transmission mode. The membranes were dried until a constant weight was obtained before the spectra were made, and the sample chamber was purged with dry nitrogen gas. The average thickness of the membranes was around 40 μm.

Wide-angle X-ray diffractometry

The wide-angle X-ray diffractograms were recorded at room temperature with a Scintag X1 X-ray diffractometer (Cupertino, CA). The X-ray source was Ni-filtered Cu Kα radiation (45 kV and 40 mA). The dried membranes were mounted on aluminum frames and scanned from 5 to 45° (2θ) at a speed of 2°/min. To measure the relative crystallinity percentage (X_c) of the membranes, we measured the amorphous areas and the areas of the crystalline peaks. X_c was calculated with the following relationship:[10]

$$X_c = [A_c/(A_c + A_a)] \times 100\% \qquad (1)$$

where A_c and A_a are the areas of the crystalline and amorphous peaks, respectively. Three specimens were measured for each sample.

Swelling index (SI)

The crosslinked membrane (mass = W_d) was immersed in an excess amount of deionized water at ambient temperature until the swelling equilibrium was attained. The mass of the wet membrane (W_w) was obtained after the gentle removal of surface water with blotting paper. Five specimens were measured for each sample. SI was then calculated on the basis of the masses of the wet membrane and dry membrane with the following formula:

$$SI = [(W_w - W_d)/W_d] \times 100\% \qquad (2)$$

Tensile testing

The ultimate tensile strength and percentage of the breaking elongation of the membranes were evaluated on an Instron model 4206 tensile testing machine (Canton, MA) according to the standard method (ASTM D 882). The test specimens were cut into strips 70 mm long and 25 mm wide with an accuracy of ±1 μm. The relative humidity, gauge length, and crosshead speed were 50%, 30 mm, and 5 mm/min, respectively. All specimens were drawn at ambient temperature, and all data were instantaneously recorded with a computer. At least five specimens were measured for each sample, and the quoted results are the average values.

Ionic conductivity

The conductance measurements were made according to a reported method.[11] A Hewlett–Packard model 4194A impedance/gain-phase analyzer (Tokyo, Japan) was used for an impedance spectroscopy analysis of the membranes. Complex impedance measurements were carried out in the AC mode, in the frequency range of 0.1–10^4 kHz, with a 1-V amplitude of the applied AC signal. The dry membranes were sandwiched between two brass blocking electrodes in the measurement cell. For impedance analysis in the swollen state, the membranes were immersed in deionized water at room temperature for the required time. Before measurements were started, the surface water was removed, and then the swollen membrane was placed quickly between electrodes in the measurement cell. The water content of the membrane was assumed to remain constant during the short period of time required for the measurements. Five specimens were measured for each sample

RESULTS AND DISCUSSION

DDA and viscosity-average molecular weight

Because the amino groups in chitosan may impart increased conductivity to the chitosan membrane, the chitosan samples were deacetylated before they were used to prepare the membranes. The original chitosan
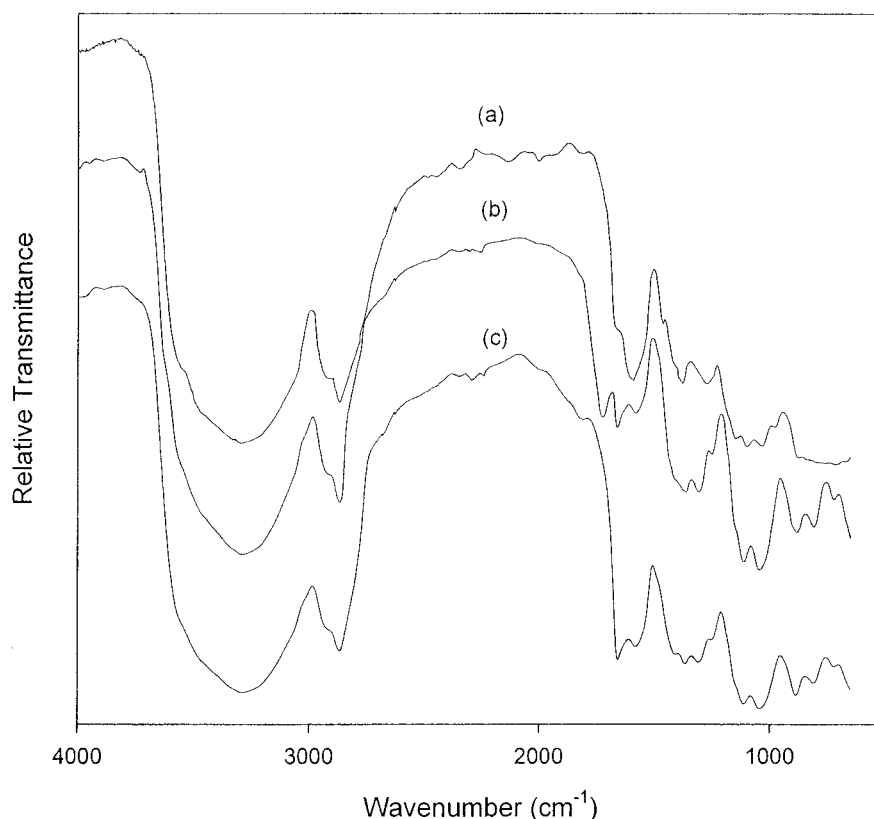
Figure 1 FTIR spectra of chitosan membranes: (a) uncrosslinked, (b) crosslinked with 100 ppm GA (homogeneous crosslinking), and (c) crosslinked with 80 ppm GA (heterogeneous crosslinking).

sample and two deacetylated chitosan samples are designated Ch-H, Ch-H-1, and Ch-H-2, respectively. The relevant information concerning these three samples is summarized in Table I. Although it is somewhat difficult to completely deacetylate chitosan, as shown in Table I, after successive treatments,[12] the DDA of Ch-H-2 reached a value as high as 97.6%, and it was not degraded very much with respect to the original chitosan sample. Viscometry is the most common method for determining the molecular weight of polymers with the Mark–Houwink–Sakurada equation. The use of viscometry for chitosan, however, is not always straightforward because of its complex hydrodynamic behavior, which greatly depends on its DDA and the solvent system used, as well as the temperature. The 0.25M CH$_3$COOH/0.25M CH$_3$COONa solvent system was used here because it yields a viscosity-average molecular weight of chitosan that is nearly independent of DDA in the range above 70%. With this solvent system, the viscosity-average molecular weight of chitosan was determined with the following equation:[13]

$$[\eta] = 1.40 \times 10^{-4} \, M_v^{0.83} \qquad (3)$$

where η and M_v are the intrinsic viscosity and viscosity-average molecular weight, respectively.

Characterization of the crosslinked membranes

Pure chitosan membranes are colorless, whereas membranes crosslinked by GA or ECH are light yellow; this may indicate the presence of conjugated double bonds in the structures. More clear evidence can be drawn from FTIR spectra. Figure 1 displays a comparison of the FTIR spectra of chitosan membranes, chitosan membranes crosslinked by 100 ppm GA under homogeneous conditions at room temperature for 20 h, and chitosan membranes crosslinked by 80 ppm GA under heterogeneous conditions at room temperature for 20 h. Two main mechanisms have been proposed to explain the crosslinking of chitosan by GA: Shiff base formation leading to the formation of imine-type crosslinking and Michael-type adducts with amine groups leading to the formation of carbonyl groups on the polymer structure.[14,15] In our case, the reaction between CHO and NH$_2$ functions (Shiff base formation) is indicated [Fig. 1(c)] by a peak centered around 1665 cm^{-1}, which can be attributed to imine groups,[16,17] when the membrane is crosslinked under heterogeneous conditions. In Figure 1(b), the peak located around 1725 cm^{-1} can be assigned to carbonyl groups,[18] and the characteristic absorption of the amine groups at 1665 cm^{-1} may still be observed; this suggests that there are both Michael-type adducts and
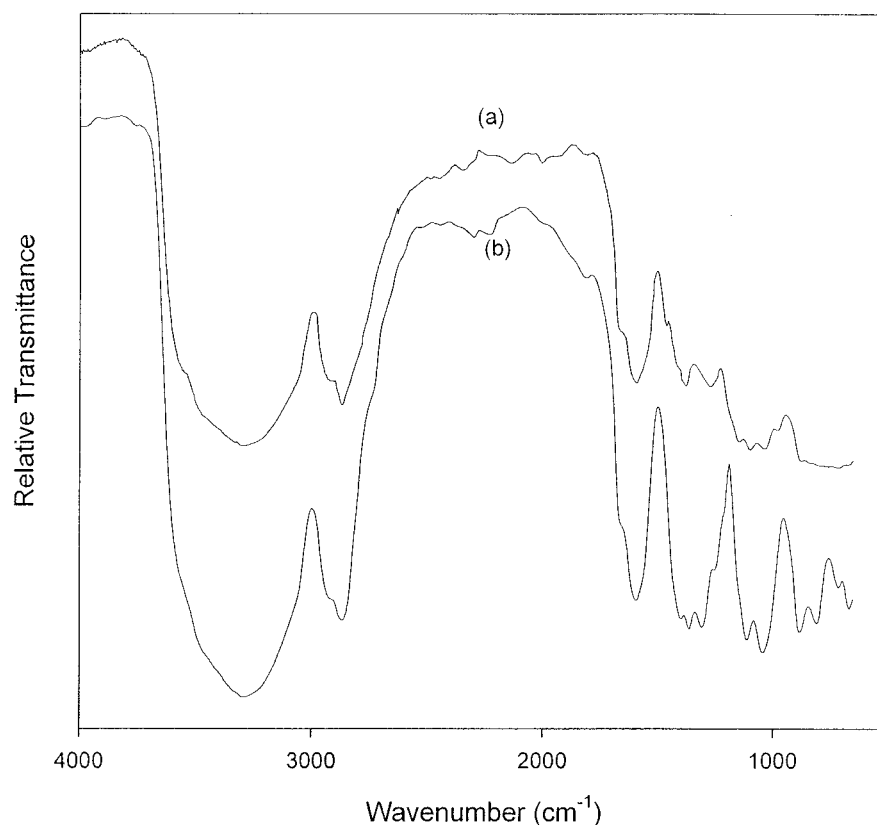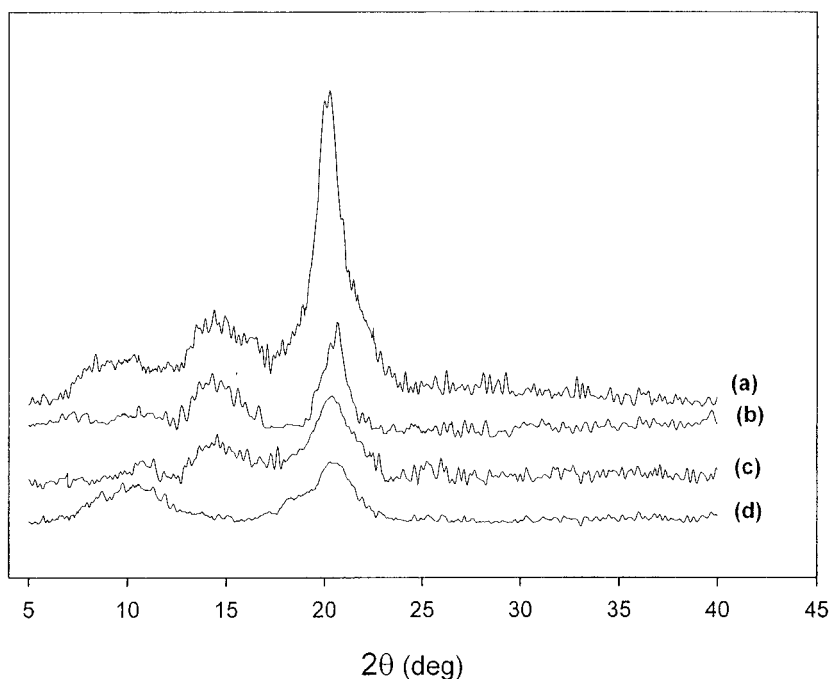
Figure 2 FTIR spectra of chitosan membranes: (a) uncrosslinked and (b) crosslinked with 0.02M ECH (2 h, 40°C, heterogeneous crosslinking).

Shiff base formation in the membrane when the membrane is crosslinked under homogeneous conditions. Meanwhile, ECH is a base-catalyzed crosslinking agent and, therefore, can be used only under heterogeneous conditions for crosslinking the chitosan membrane. The corresponding FTIR spectrum is shown in Figure 2. It exhibits an absorption at 1650 cm^{-1}, which represents the amide I carbonyl stretch as a shoulder on the amide deformation peak at 1600 cm^{-1} and is in agreement with reported results.[19]

The chemical crosslinking of chitosan membranes largely depends on the crosslinking agents used and the crosslinking conditions. The X-ray patterns are illustrated in Figure 3, whereas the corresponding crystallinity and SI values of crosslinked chitosan membranes are listed in Tables II and III. The X-ray patterns shown in Figure 3 indicate that, with respect to the uncrosslinked membrane, the crystalline structure of the crosslinked membranes is not significantly modified under heterogeneous crosslinking conditions, although the peak intensity in Figure 3(b,c) decreases markedly. Contrary to this observation, in Figure 3(d), the crystalline domains in the crosslinked membrane are partially destroyed under homogeneous crosslinking conditions, so that the peak around $2\theta = 15°$ disappears totally, the peak around $2\theta = 10°$ is shifted slightly to a higher diffraction angle, and the

peak at $2\theta = 20°$ is deformed by the addition of a small shoulder. Similar observations also have been described in the literature for chitosan crosslinking under homogeneous conditions.[20,21] As expected, in Tables II and III, the crystallinity of the membranes decreases gradually with an increasing concentration of the crosslinking agent, and the membranes crosslinked by GA under homogeneous conditions show a much lower crystallinity. This may arise from different crosslinking conditions. For heterogeneous crosslinking, the membranes are crosslinked as swollen solids, and these membranes already have their own crystalline structures before the crosslinking reaction. The crosslinking reactions, therefore, mainly occur on the surface or epidermal areas, and the crystallinity of the membrane is decreased, but the basic crystalline structures are still maintained because the molecules of the crosslinking agent can hardly diffuse through the membrane. However, for homogeneous crosslinking, the crosslinking reaction occurs throughout the whole membrane. It is thought that intermolecular crosslinking occurs, but not intramolecular crosslinking;[22] as a result, with the same concentration of the crosslinking agent, different crystalline structures and much lower crystallinities in homogeneous membranes are obtained.

Figure 3 X-ray diffraction patterns of chitosan (Ch-H-2) membranes: (a) uncrosslinked, (b) crosslinked with 80 ppm GA (heterogeneous crosslinking), (c) crosslinked with 0.02M ECH (2 h, 40°C, heterogeneous crosslinking), and (d) crosslinked with 100 ppm GA (homogeneous crosslinking).

As can be seen in Tables II and III, SI of the crosslinked membrane increases slightly at first and then decreases gradually with an increasing concentration of the crosslinking agent. As we know, for chitosan membranes, the swelling properties are simultaneously controlled by both the crystallinity and crosslinking degree. Normally, the growing crystalline portion in the membrane prevents water from entering the membrane, and the larger the crystallinity is of a chitosan membrane, the smaller SI is of the membrane.[23] However, as the crosslinking degree in the membranes increases with an increase in the concentration of the crosslinking agent, the crystalline structure of the membrane will be destroyed to some extent, and a lower crystallinity results and the crosslinked membrane becomes looser;[24] this may enhance the interaction between the hydrophilic groups (i.e., amine groups and hydroxyl groups) and water molecules and eventually increase SI of the membrane. This may be the reason that SI of crosslinked membranes increases slightly at first. However, when the membrane is crosslinked to a higher extent and

TABLE II
Crystallinity and SI of Chitosan Membranes Crosslinked by GA

Concentration of crosslinking agent (ppm)	Ch-H crystallinity (%, ±1.1%)	SI (%, ±3.1%)	Ch-H-1 crystallinity (%, ±1.9%)	SI (%, ±3.2%)	Ch-H-2 crystallinity (%, ±1.7%)	SI (%, ±3.6%)
Heterogeneous crosslinking						
0	11.4	45	14.2	41	19.5	30
40	10.6	50	13.3	44	18.3	35
60	10.1	48	11.7	46	17.8	39
80	9.3	44	10.2	42	15.1	33
100	8.1	40	9.6	38	13.4	27
120	7.3	35	8.5	33	11.6	21
150	6.5	29	7.6	27	9.3	16
Homogeneous crosslinking						
40	7.1	56	10.1	50	12.4	42
60	6.2	61	8.7	55	10.5	46
80	5.4	68	7.1	52	8.2	41
100	4.3	62	6.3	47	6.6	36
120	3.7	53	4.9	41	5.2	30
150	2.1	42	3.8	33	4.4	23

TABLE III
Crystallinity and SI of Chitosan Membranes Crosslinked by CEH

Concentration of crosslinking agent (mole)	Ch-H crystallinity (%, ±1.4%)	SI (%, ±2.5%)	Ch-H-1 crystallinity (%, ±1.5%)	SI (%, ±3.1%)	Ch-H-2 crystallinity (%, ±1.2%)	SI (%, ±2.9%)
0	10.7	46	13.4	41	18.9	31
0.001	10.1	52	12.9	45	17.8	36
0.005	10.2	55	11.6	48	16.2	40
0.01	9.1	49	10.2	43	14.7	36
0.02	8.3	44	9.7	38	12.1	32
0.03	7.5	38	8.3	32	10.4	27
0.05	4.5	28	5.6	21	6.8	16

may attain an uncertain threshold, more hydroxyl groups or amine groups in chitosan are consumed because of the crosslinking reaction, and the chitosan molecules in the crosslinked membranes are held together more tightly. Therefore, the crosslinked membrane becomes less capable of hydrogen bonding with water molecules because of the intermolecular and intramolecular crosslinking caused by both acetalization and the formation of the Shiff base, and this results in a decreased SI at equilibrium. This SI behavior of crosslinked membranes has also been observed in the literature.[25,26]

Tensile properties

The variance of the tensile strength and breaking elongation with an increasing concentration of the crosslinking agent is illustrated in Tables IV and V. As shown in Tables IV and V, when the concentration of the crosslinking agent is lower, corresponding to a lower crosslinking degree in the membrane, the tensile strength and breaking elongation of membrane are almost unchanged within experimental error. Only

after the concentration of the crosslinking agent is increased to a critical value does the tensile strength of the membrane increase gradually, and inversely the breaking elongation of the membrane decreases. Normally, larger crystalline regions and higher crystallinity in a membrane can enhance the mechanical strength of the membrane if only one factor, the crystallinity of the membrane, has been considered.[27] Once the membrane is crosslinked, its crystalline structure will be deformed to some extent, and the crystallinity of the membrane may be decreased; this decreases the tensile strength of the membrane. However, the membrane is also enhanced by crosslinking between chitosan molecules, although the crosslinking degree is low. This may explain why the tensile strength and breaking elongation of a membrane are almost unchanged when the concentration of the crosslinking agent is low. When the concentration of the crosslinking agent is increased to a certain point, after which a higher crosslinking degree is achieved, enough bridges and even a crosslinked network may be set up between the chitosan molecules so that the tensile strength of the membrane is enhanced further.

TABLE IV
Tensile Properties of Chitosan Membranes Crosslinked by GA

Concentration of crosslinking agent (ppm)	Ch-H tensile strength (MPa, ± 3.4%)	Breaking elongation (%, ±1.8%)	Ch-H-1 tensile strength (MPa, ±2.7%)	Breaking elongation (%, ±1.6%)	Ch-H-2 tensile strength (MPa, ± 3.1%)	Breaking elongation (%, ± 1.2%)
Heterogeneous crosslinking						
0	37	25	41	22	44	20
40	38	24	40	21	45	20
60	38	25	42	22	45	19
80	41	22	44	20	47	18
100	45	20	47	18	50	16
120	48	19	51	17	54	14
150	51	18	55	16	59	12
Homogeneous crosslinking						
40	29	30	32	28	38	26
60	30	30	33	27	40	25
80	31	31	35	28	41	27
100	35	29	39	25	44	23
120	40	26	43	23	47	21
150	42	24	45	21	49	20

TABLE V
Tensile Properties of Chitosan Membranes Crosslinked by ECH

| Concentration of crosslinking agent (mol)	Ch-H tensile strength (MPa, ±2.9%)	Breaking elongation (%, ±1.7%)	Ch-H-1 tensile strength (MPa, ±2.6%)	Breaking elongation (%, ±2.1%)	Ch-H-2 tensile strength (MPa, ±3.2%)	Breaking elongation (%, ±1.4%)
0	37	26	40	21	45	17
0.001	36	25	41	22	45	18
0.005	37	26	42	22	46	16
0.01	40	24	44	19	48	15
0.02	45	22	48	18	51	13
0.03	51	21	53	17	55	12
0.05	52	20	54	16	56	11

The dependence of the breaking elongation of the membrane on the concentration of the crosslinking agent can be attributed to the fact that the plasticity of the membrane is decreased and the fragility of the membrane is increased after the membrane is crosslinked to some extent. In fact, the disappearance of the plastic regions with am increasing degree of crosslinking has been reported for membranes crosslinked with glyoxal and GA.[28,29]
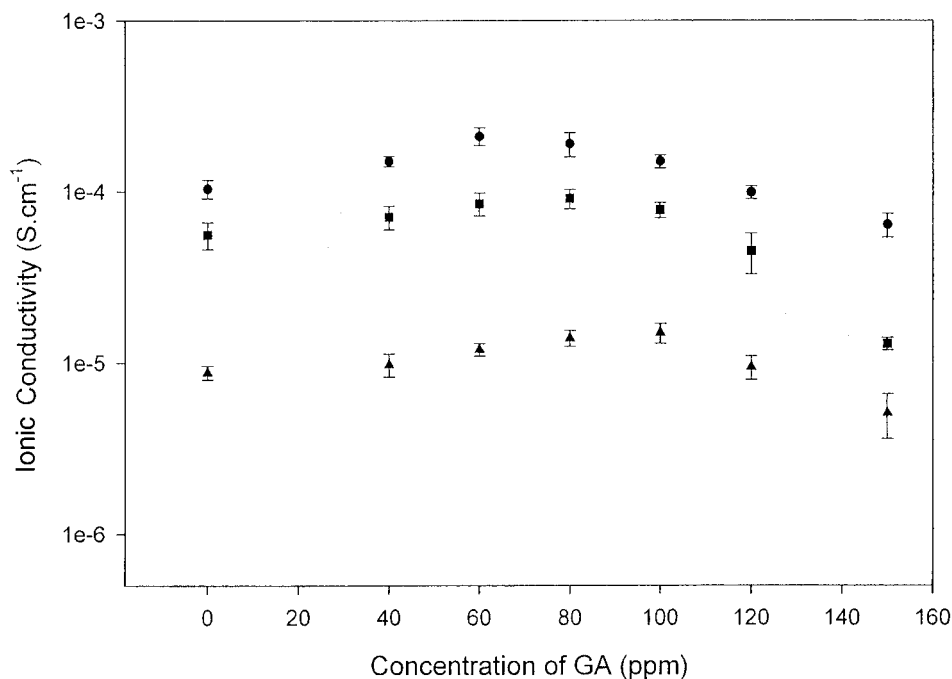
Ionic conductivity of the membranes

The ionic conductivity of the crosslinked chitosan membranes was determined with the complex impedance method. All impedance measurements were performed before and after hydration of the membranes.

Membranes in the dry state exhibit ionic conductivities between 10^{-9} and 10^{-10} S cm^{-1}, and the entire conduction process occurs after the water is incorporated into the membranes. Typical complex-plane plots of imaginary impedance ($-Z''$) versus real impedance (Z') for the membranes after hydration for 1 h at room temperature are illustrated in Figure 4. These spectra consist of two well-defined regions in the complex plane: a typical partial semicircle arc in the high-frequency zone that is related to the conduction process in the bulk of the membrane and a linear region in the low-frequency zone that is attributed to the solid electrolyte–electrode interface.[30] The starting point of the arc at a low frequency for most of the samples, which is normally frequency-dependent, is obtained around 100 kHz; at this point, the phase angle is also
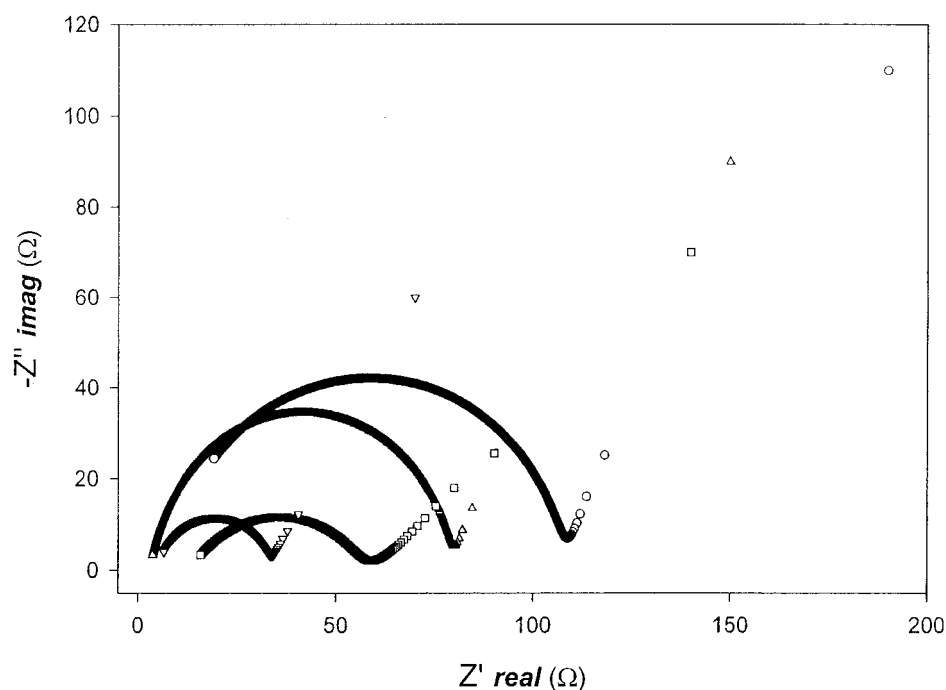
Figure 4 Impedance spectra of chitosan (Ch-H) membranes after hydration for 1 h at room temperature (AC mode; amplitude of the applied signal = 1 V; frequency range = 0.1–10^4 kHz): (○) uncrosslinked, (△) crosslinked with 80 ppm GA (heterogeneous crosslinking), (□) crosslinked with 0.02M ECH (2 h, 40°C, heterogeneous crosslinking), and (▽) crosslinked with 100 ppm GA (homogeneous crosslinking).
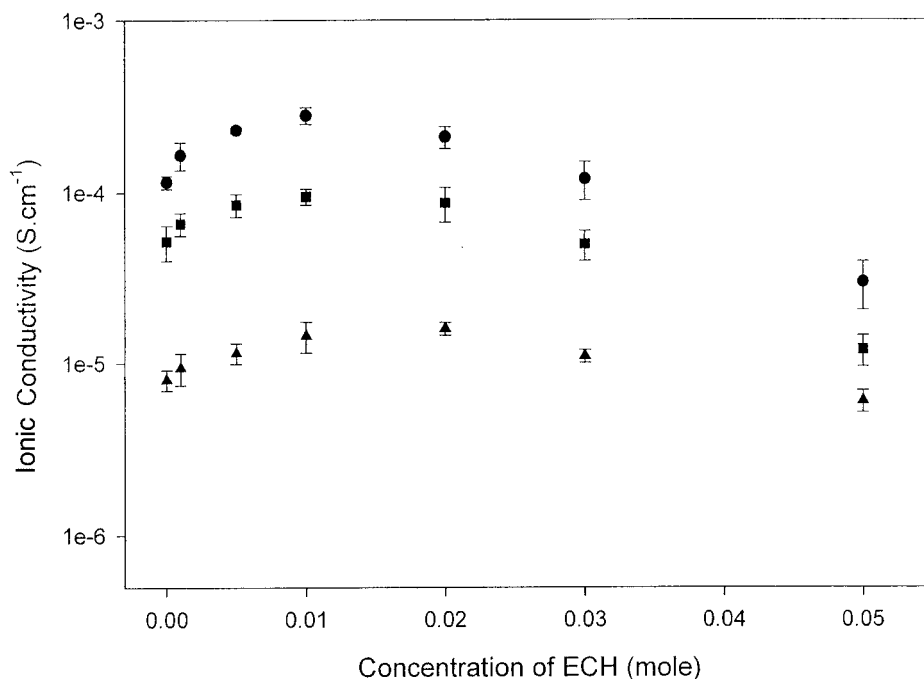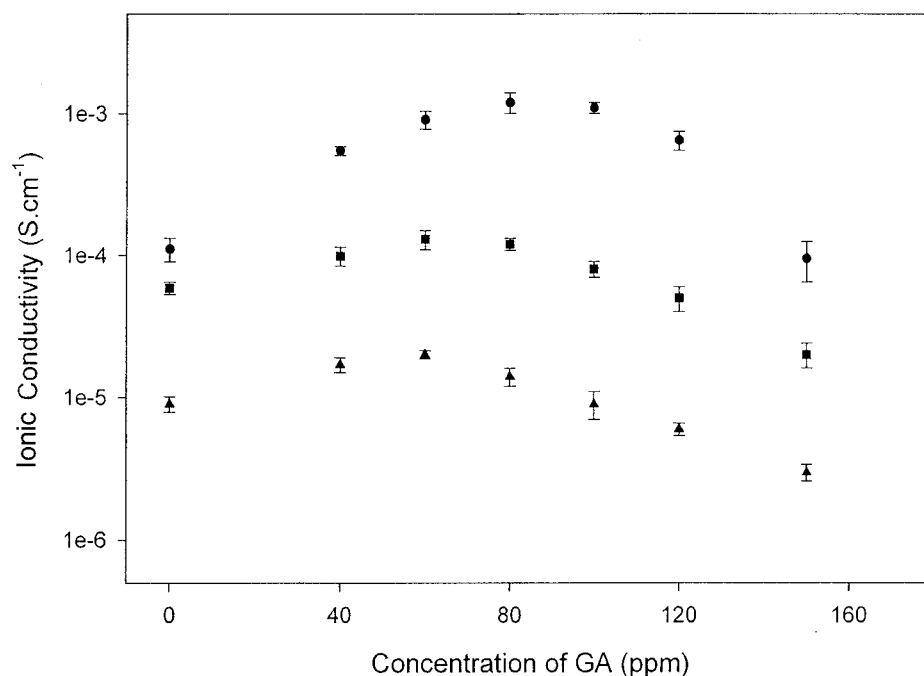
Figure 5 Variation in the ionic conductivities of membranes crosslinked with GA (heterogeneous crosslinking) with the concentration of the crosslinking agent after hydration for 1 h at room temperature (AC mode; amplitude of the applied signal = 1 V; frequency = 10^2 kHz): (●) Ch-H, (■) Ch-H-1, and (▲) Ch-H-2.

quite small and near zero. Because the complex impedance will be dominated by the ionic conductance when the phase angle is close to zero, all the conductivities reported in this article were obtained with the

Z' values, for which the frequency is near 100 kHz. The variations in the conductivities of membranes crosslinked by GA or ECH under heterogeneous or homogeneous conditions with the concentration of the

Figure 6 Variation in the ionic conductivities of membranes crosslinked with ECH (heterogeneous crosslinking, 2 h, 40°C) with the concentration of the crosslinking agent after hydration for 1 h at room temperature (AC mode; amplitude of the applied signal = 1 V; frequency = 10^2 kHz): (●) Ch-H, (■) Ch-H-1, and (▲) Ch-H-2.

Figure 7 Variation in the ionic conductivities of membranes crosslinked with GA (homogeneous crosslinking) with the concentration of the crosslinking agent after hydration for 1 h at room temperature (AC mode; amplitude of the applied signal = 1 V; frequency = 10^2 kHz): ($\bullet$) Ch-H, ($\blacksquare$) Ch-H-1, and ($\blacktriangle$) Ch-H-2.

crosslinking agent are illustrated in Figures 5–7. In Figures 5–7, with respect to the uncrosslinked membranes (corresponding to a zero concentration of the crosslinking agent), the ionic conductivities of the crosslinked membranes first increase slightly to a certain point when the concentration of the crosslinking agent is lower and then decrease with an increasing concentration of the crosslinking agent. Furthermore, the Ch-H membrane, which has a lower DDA and higher molecular weight than other two (Ch-H-1, Ch-H-2), also gives a higher conductivity than the others under both types of crosslinking conditions and regardless of whether GA or ECH is employed. In addition, in Figure 7, the Ch-H membrane shows a higher conductivity when it is crosslinked with GA under homogeneous conditions and with an optimized concentration of the crosslinking agent, which is between 80 and 100 ppm. These results indicate that when chitosan membranes are crosslinked to an appropriate degree, their ionic conductive properties may be improved and their conductivities may be increased further.

As pointed out previously, the ionic conductance will occur only after the membrane is hydrated. This may be explained by the following tentative mechanism. When water is incorporated into chitosan membranes, the free amino groups in the chitosan backbone, which are weak alkaline groups, are partly protonated ($NH_2 + H_2O \leftrightarrow NH_3^+ + OH^-$), and this leads to the formation of hydroxide ions. Because the NH_3^+ groups are bonded on the backbone, only OH^- ions

are free to move and give an ionic current under the action of an AC signal. According to this tentative mechanism, the crosslinked membrane with a higher DDA, which contains more NH_2 groups than to a lower DDA chitosan membrane, should give a higher ionic conductivity. However, with high-DDA chitosan, some more substantial crystalline regions will be formed because of intramolecular hydrogen bonding; water will be prevented from entering the crystalline portion, and a large resistance to water incorporation will result. This finally decreases the concentration of OH^- groups in the swollen membrane and, in turn, the ionic conductivity of the membrane.

The ionic conductivity of the chitosan membrane may be useful for an alkaline polymer electrolyte fuel cell for which a membrane for hydroxide ion transport is needed. As long as the water and hydroxide ions are supplied continuously, the chitosan membrane can act as a hydroxide ion carrier, and the fuel cell can work in an uninterrupted way. For comparison, the Nafion N117 membrane, the most effective and available membrane used in practical fuel-cell systems,[31] has an ionic conductivity of approximately 2.6×10^{-2} S cm^{-1},[32] whereas the ionic conductivity of chitosan membranes with a relatively lower degree of crosslinking and a proper DDA (Ch-H) show an ionic conductivity of about 10^{-3} S cm^{-1}. Although the conductivity of the crosslinked Ch-H membrane is still about one order of magnitude lower than that of the Nafion N117 membrane, it can be improved significantly by the modification of the hydroxyl groups or amino

groups with suitable chemical or physical methods. In addition, the tensile strength of crosslinked chitosan membranes is also high enough for fuel-cell applications. For example, the Nafion N117 membrane has a tensile strength in the dry state of about 43 MPa,[33] whereas some crosslinked chitosan membranes obtained in this work have a tensile strength of the same order (see Tables IV and V).

The ionic conductivity of the ionomeric membrane is strongly dependent on the membrane structure and membrane water content. The water uptake characteristics for Nafion membranes under various conditions have intensively been investigated. It is now clear that, with the aid of gaps between strings of spherical ion aggregates in the membrane, the water in the membrane can provide percolation pathways for ionic transport,[34,35] and an ionomeric membrane containing more water may give a higher conductivity[36,37] In our case, as pointed out previously, the crystallinity of crosslinked membranes generally decreases with an increasing concentration of the crosslinking agent, and with an appropriate degree of crosslinking, the SI values increase to a maximum. As expected, comparing Table II and Figure 7, we find that the Ch-H membrane, which is crosslinked with GA (with a concentration of around 80 ppm) by homogeneous crosslinking, has the largest SI and also shows the highest conductivity (near 10^{-3} S cm^{-1}).

However, a fundamental difference in the ionic functionality between the Nafion membrane and chitosan membrane has to be pointed out: the Nafion membrane is a proton conductor and can only be used for an acidic polymer electrolyte fuel cell,[38] whereas the chitosan membrane is a hydroxide ion conductor and may be used for an alkaline polymer electrolyte fuel cell. Further studies on the ionic conductivity of modified chitosan membranes and their possible applications in alkaline polymer electrolyte fuel cells are currently in progress, and relevant results will be reported in the near future.

CONCLUSIONS

Crosslinked chitosan membranes were prepared with ECH and GA as crosslinking agents under heterogeneous and homogeneous conditions, respectively. The crystalline structure of the membranes was not significantly modified by heterogeneous crosslinking, but the crystalline domains in the crosslinked membranes were partly destroyed by homogeneous crosslinking. The crystallinity of the crosslinked membranes decreased gradually with an increasing concentration of the crosslinking agent. There was a certain point for each crosslinked membrane, before which the SI of the membrane increased slightly and after which it decreased gradually with an increasing concentration of the crosslinking agent. With a lower concentration of

the crosslinking agent, the tensile strength and breaking elongation of the membranes were almost unchanged, and after the concentration of the crosslinking agent was increased to a critical value, the tensile strength of the membranes increased gradually and the breaking elongation of the membranes decreased slowly. Compared with the uncrosslinked chitosan membrane, the crosslinked chitosan membranes with lower DDA values and higher molecular weights gave a relatively high conductivity, and when this kind of chitosan membrane was crosslinked with an appropriate degree of crosslinking with GA under homogeneous conditions, its ionic conductivity after hydration for 1 h at room temperature could be increased around one order of magnitude. The ionic conductivity of the chitosan membranes was not improved significantly when they were crosslinked with ECH, even though ECH does not eliminate the cationic amine function of chitosan.

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