# Glycine Hydrochloride Ionic Liquid/Aqueous Solution System as a Platform for the Utilization of Chitosan

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**ABSTRACT:** Glycine hydrochloride ([Gly]Cl), a room-temperature ionic liquid (IL), is proposed as a new, good solvent for chitosan with different deacetylation degrees and molecular weights. However, considered from the viscosity of a solution of chitosan and [Gly]Cl, a 2% [Gly]Cl IL aqueous solution was selected as an optimum solvent system for dissolving chitosan. X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy were used to visualize the modifications of the native structures of chitosan during the dissolution and the regeneration processes, morphological features, and properties of the reconstituted chitosan membranes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3772–3780, 2012

**Key words:** biopolymers; membranes; X-ray

## INTRODUCTION

Chitosan, a linear (1,4)-linked biopolysaccharide, is an *N*-deacetylated derivative polyelectrolyte of chitin and the second-most abundant natural polysaccharide after cellulose; it has an excellent biodegradability, biocompatibility, and nontoxicity.[1] To this end, enormous efforts have been made toward its potential applications in biofabrication,[2] pharmaceuticals,[3] biomedicine,[1–4] food,[5] textiles,[6] and so forth. In application, the chitosan membrane is the main use of chitosan, which has been widely applied in chemistry, pharmaceuticals, food, fermentation, sewage treatment, and so on.[7] However, there are many hydroxyl and amido groups in chitosan, and these groups can form hydrogen bonds between intermolecular and intramolecular chains of chitosan. The complex aggregation and high crystallinity of chitosan remain unsolved in many solvents, so the application of chitosan membranes is limited because of its poor solubility. Acetic acid and sometimes formamide/methanol, formamide/ethanol, methanol, ethanol, and pyridine as solvents can dissolve chitosan.[8] However, these solvents have many drawbacks, such as high toxicity, strong volatility, and serious pollution. Therefore, the discovery of a new green solvent to dissolve chitosan is the most important issue that needs to be solved.

Ionic liquids (ILs) are a promising alternative for green solvents because of their properties, such as a negligible vapor pressure, broad liquid regions, high thermal stabilities, and no burning point or explosive characteristics.[9] ILs possess so excellent solubility for inorganic compounds, organic compounds, and high polymer materials that they have been widely used in the fields of electrochemistry, organic synthesis, separation, and material preparation.[10] It was reported that ILs had a good solubility of cellulose,[11] whose structure is similar to chitosan. Therefore, it has been possible to discover optimal ILs for

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dissolving chitosan via a the design of the anion and cation of ILs. For example, 1-butyl-3-methylimidazolium hydrochloride( [Bmim]Cl), good solvent for cellulose, was the first IL used as a solvent for chitosan.[12] Xie and Zhang[13] found that the solubility of chitosan [deacetylation = 88%, viscosity-average molecular weight ($M_w$) = $3 \times 10^5$ to $4 \times 10^5$] could reach 2% in [Bmim]Cl at 110°C. Moreover, the regeneration of chitosan could be achieved by the addition of methanol or water to this homogeneous system. Wu et al.[14] synthesized 1-butyl-3-methylimidazolium acetate ([Bmim]Ac) and found that it could dissolve 3–6% chitosan. In the chitosan/[Bmim]Ac system, the anion of ILs could form hydrogen bonds with the amidos or hydroxyls of chitosan and break the intermolecular and intramolecular hydrogen bonds of chitosan synchronously. The synergy made the chitosan dissolve. These results imply that the binding affinity of hydrogen between carboxyl groups and chitosan was superior to that between $Cl^-$ and chitosan. However, as reported in the literature so far, there have been some problems, such as high viscosity, narrow soluble range (one only can dissolve the chitosan with $M_w = 3 \times 10^5$ to $6 \times 10^5$), and requirements of high temperatures and long dissolution times in the ILs–chitosan system. Therefore, it was very important to discover a new solvent with a low viscosity and strong dissolving ability for the preparation of chitosan membranes.

As a part of our systematic research on dealing with chitosan in IL systems, here, we report a benign approach to the synthesis of chitosan membranes in a glycine hydrochloride ([Gly]Cl) IL aqueous system. First, to achieve good dissolving ability for chitosan with a wide range of molecular weights at room temperature, a series of ILs with different activating groups, such as —Cl, —OH, —COOH, and —CN, were designed and prepared. Moreover, to reduce the viscosity, these ILs were made into aqueous solutions with certain concentrations. This was a meaningful work. Furthermore, an IL aqueous solvent system with a stronger dissolving ability, lower viscosity, and slight degradation of chitosan was selected. Accordingly, an environmentally friendly and efficient approach for the preparation of chitosan membranes was obtained in this optimal system, and the properties of the chitosan membranes produced in this system were studied.

## EXPERIMENTAL

### Materials and Instructions

#### Materials

Chitosan was obtained from Qingdao Haisheng Co., Ltd. (Qingdao, China). The deacetylation degree (DD) was estimated with the $^1$H-NMR method, and $M_w$ was estimated by viscosity determination. All of the other reagents were analytical grade.

#### Instructions

The NMR spectra of the ILs were recorded with 500-MHz Bruker spectrometer (Germany) in dimethyl sulfoxide or $CDCl_3$ and calibrated with tetramethylsilane as the internal reference.

IR spectra were recorded on a Nicolet 510P Fourier transform infrared (America, FTIR) spectrometer in the range 4000–400 $cm^{-1}$ with KBr powder containing about 1 wt % of sample.

X-ray powder diffraction patterns of the samples were obtained on an XB-3A X-ray diffractometer (Japan) with monochromatic Cu Kα radiation (λ = 0.15418 nm). It was operated at 40 kV and 100 mA. The experimental conditions corresponded to a step width of 0.02°, a scan speed of 2°/min, and a diffraction region of 2θ = 10–60°.

The morphological structures of the fiber were observed by a Hitachi S-2600HS scanning electron microscope (Japan) with a 15-kV accelerated voltage. Samples were gold-coated by ion sputtering with a JEOL JFC-1100-E and a current of 10 mA for 90 s before observation.

### Methods

#### Preparation and characterization of [Gly]Cl

[Gly]Cl was synthesized according to a method reported in the literature.[15] The structure of the ILs was verified by $^1$H-NMR, $^{13}$C-NMR, and FTIR spectroscopy.

[Gly]Cl: $^1$H-NMR (500 MHz, $D_2O$, δ): 3.78 (s, 2H), 4.70 (s, 1H). $^{13}$C-NMR (125 MHz, $D_2O$, δ): 40.13, 170.08.

The structure was as follows: Cl—[$^+NH_3$—$CH_2$—COOH].

IR (KBr): 3434 (υ, —$NH_3$*$^+$—$CH_2$—COOH*), 3009 ($\upsilon_{as}$, —$CH_2$*—COOH), 1714 ($\upsilon_{as}$, —C=O*), 1596 (δ, —$NH_3$*$^+$), 1495 (δ, —$CH_2$*—CO—), 1423 (δ, —COOH*), 1255 (υ, —C—O*), 1117 (υ, —N—C*), 903 (ω, —O—H*), 861 (δ, —N—H*), 638, 496.

#### Dissolution of chitosan

An IL aqueous solution (2%) was prepared by the dissolution of 1 g of IL into 49 mL of deionized water and chitosan with different DD and $M_w$ values, which were gradually dissolved in it under continuous stirring for 3 h at 30°C. The dissolution process was observed with a BS-5080 polarizing microscope (China). When chitosan was completely dissolved in the IL aqueous solution, a black field could be observed through the polarizing microscope. Acetone was used to separate chitosan, and

**TABLE I**
**Results of the Dissolution of Chitosan with Different $M_w$ and DD Values in [Gly]Cl[a]**

| No. | DD (%) | $M_w$ ($\times 10^6$)[a] | Concentration (wt %) | $M_w$ ($\times 10^6$)[b] |
|---|---|---|---|---|
| 1 | 86.9 | 1.06 | 5.0 | 0.87 |
| 2 | 75.3 | 1.06 | 4.2 | 0.90 |
| 3 | 60.2 | 1.06 | 3.3 | 0.93 |
| 4 | 87.3 | 1.23 | 4.1 | 0.99 |
| 5 | 76.4 | 1.23 | 3.5 | 1.02 |
| 6 | 59.8 | 1.23 | 3.0 | 1.07 |
| 7 | 88.1 | 1.48 | 3.9 | 1.15 |
| 8 | 73.5 | 1.48 | 3.4 | 1.19 |
| 9 | 60.4 | 1.48 | 2.9 | 1.23 |

[a] Native chitosan materials.
[b] Regeneration of chitosan.

then, the acetone was removed by air-pump filtration. After the chitosan was dried for 24 h, its $M_w$ was evaluated by the measurement of its viscosity on the basis of an Ubbelohde method.

### Determination of the molecular weights of chitosan

$M_w$ of chitosan was measured by viscosity determination. The viscosity values of the chitosan samples were measured in 0.20 mol/L NaCl + 0.1 mol/L $CH_3COOH$ at 25°C with an Ubbelohde capillary viscometer (inner diameter (Ø) = 0.5–0.6 mm). The molecular weight was determined according to the classic Mark–Houwink equation: The intrinsic viscosity $[\eta] = 1.81 \times 10^{-3} M \times 0.93$.[16,17]

### Preparation of the chitosan membrane

Chitosan was gradually dissolved in an IL aqueous solution (2%) or acetic acid under continuous stirring and heating for 6 h. When chitosan was completely dissolved in the IL aqueous solution or acetic acid, it was filtered by a strainer (400 mesh) and deaerated by a centrifuge. The solvent was naturally spread by tape casting, and the chitosan membrane was prepared after ethanol was added. The ethanol used was collected for reduced-pressure distillation to recover ILs. The reusability of ILs for preparing chitosan membranes was studied.

### Characterization of the chitosan membrane

The extension strength and elongation of the chitosan membranes were measured by a CT-AI-7000M electronic tensile force machine (China). The extension velocity was 500 mm/min, and the return velocity was 800 mm/min. The formulas were as follows:

$$\text{Tensile force: } \delta = \frac{F}{bd} \quad (1)$$

$$\text{Elongation: } \varepsilon = \frac{L - L_0}{L_0} \times 100\% \quad (2)$$

where δ is the tensile force (MPa), $F$ is the tensile force (N), $b$ is the width of the sample (mm), $d$ is the width (mm), ε is the elongation (%), $L$ is the scale distance of the broken sample (mm), and $L_0$ is the scale distance of the former sample (mm).

## RESULTS

### Dissolution of chitosan in [Gly]Cl

The aim of building a homogeneous system of chitosan was the preparation of chitosan membranes and chitosan fibers; therefore, in this study, chitosan ($M_w = 1 \times 10^6$) is the object of examination. Also, ethanol or acetone was used to regenerate chitosan from a [Gly]Cl aqueous solution and acetic acid. Obviously, both ethanol and acetone could form a hydrogen bond with IL or acetic acid and then extract chitosan immediately. Furthermore, they all had low boiling points, so they were easy to separate and recycle.

Table I shows that chitosan with $M_w$ = 1.0–1.5 × $10^6$ and DD = 60–90% could be dissolved in a 2% [Gly]Cl aqueous system, and the $M_w$ of regenerated chitosan all inordinately decreased. Next, to deeply understand the dissolving behavior of chitosan in [Gly]Cl, chitosan with $M_w = 1.0 \times 10^6$ and DD = 87.6% was used as an example. At the same time, as shown in Table II, the solubility of chitosan was greater in [Gly]Cl than in acetic acid. Moreover, the degradation of chitosan was lower in [Gly]Cl than in acetic acid; this played an important role in the formation of the chitosan membrane.

The X-ray diffraction (XRD) profiles of regenerated chitosan precipitated from [Gly]Cl and acetic acid solutions and the native chitosan materials are shown in Figure 1. The XRD pattern of the regenerated chitosan from acetic acid [Fig. 1(C)] showed a series of strong diffraction peaks that were remarkably different from those of the corresponding native chitosan [Fig. 1(A)]. It can be seen from Figure 1(C) that the regenerated chitosan sample engendered a series of strong diffraction peaks, which corresponded to the 2θ = 15–40° diffraction peaks appearing in the profile of the native chitosan, and

**TABLE II**
**Effect of the Different Solvent Systems on Chitosan[a]**

| No. | Solvent | Concentration (wt %) | $M_w$ ($\times 10^6$)[b] | Viscosity (MPa) |
|---|---|---|---|---|
| 1 | $CH_3COOH$ | 3.8 | 0.76 | 1520 |
| 2 | [Gly]Cl | 5.0 | 0.87 | 45600 |

[a] Chitosan DD = 86.9% and $M_w = 1.06 \times 10^6$.
[b] Regeneration of chitosan.

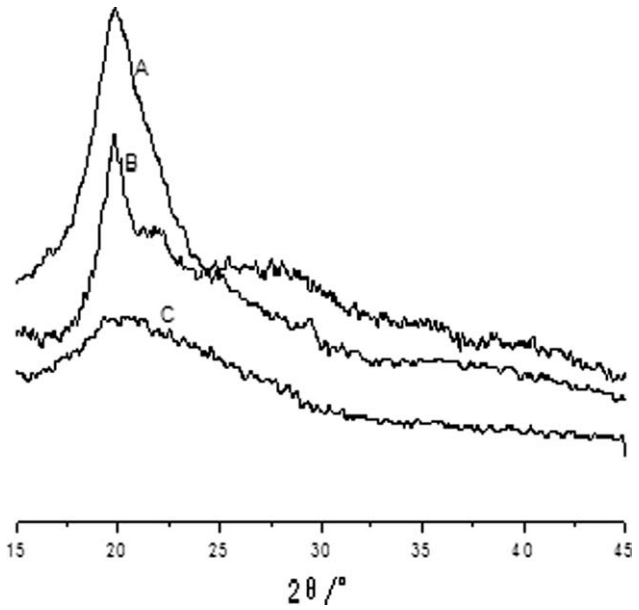


**Figure 1** XRD of (A) native chitosan, (B) regenerated chitosan from [Gly]Cl, and (C) regenerated chitosan from $CH_3COOH$.

the intensities were evidently lost compared with those of the native chitosan. In contrast, with [Gly]Cl as a solvent, the regenerated chitosan samples gave rise to XRD profiles [Fig. 1(B)] that were also more remarkably lower on intensities than those of the corresponding native ones. In fact, two relatively weak diffraction peaks could be distinguished in the large-angle region (at 22.5 and 27.5°) for the former [Fig. 1(A)].

Figure 2 shows the FTIR spectra of the native and regenerated chitosans from [Gly]Cl. In the spectrum of the native chitosan [Fig. 2(B)], two absorption peaks were observed at 3263 and 3109 $cm^{-1}$;

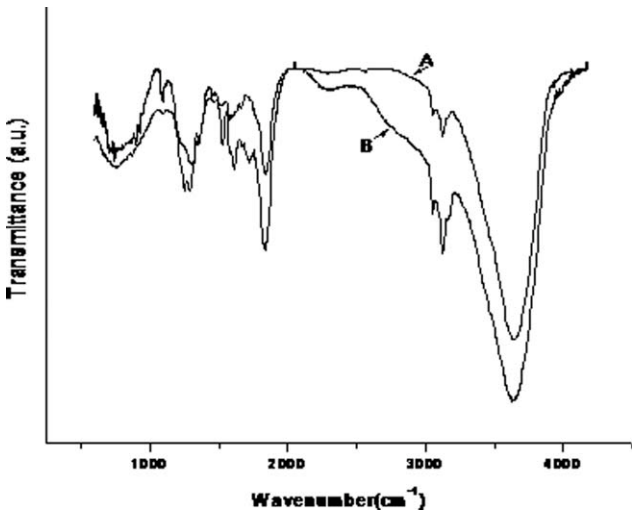


**Figure 2** FTIR spectroscopy of (A) regenerated chitosan from [Gly]Cl and (B) native chitosan.

**TABLE III**
**Dissolution Performance of Recycled [Gly]Cl[a]**

| Cycle | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Concentration (%) | 5.00 | 4.89 | 4.75 | 4.73 | 4.74 |

[a] Dissolution conditions: ILs in mixed solvents were recovered by a rotary evaporator to remove water and acetone. The dissolution performance of the recycled ILs was investigated with the same method used for the fresh ILs and described in Table I.

the peak at 3263 $cm^{-1}$ is generally assigned to the N—H stretching restricted by the intermolecular C(2)$NH\cdots O$=C(7) H bonds, and the peak at 3109 $cm^{-1}$ is generally assigned to the O—H stretching restricted by the intermolecular C(6)$OH\cdots H$—O—C(6′) H bonds.[18,19] In addition, the spectrum of the native a-chitin was characterized by a splitting of the amide I vibration at 1660 and 1629 $cm^{-1}$; these peaks were assigned to the stretching of C=O groups hydrogen-bonded to N—H groups of the adjacent chain and the stretching of the C=O groups bifurcated by the formation of an additional hydrogen bond to the primary OH groups of the same chain, respectively.[20,21] In contrast, evident differences were observed when we compared the IR spectra of the regenerated chitosan from [Gly]Cl solvent [Fig. 2(A)] with that of the native one [Fig. 2(B)]. In the spectra of the regenerated chitosan, there were considerable decreases in the aforementioned peaks.

Table III shows that the dissolving ability of IL did not change a lot, and repeated use was successfully realized. From the results of detection, it was easy to draw the conclusion that the 2% [Gly]Cl aqueous system was an excellent solvent system of chitosan.

### Synthesis of chitosan membranes

In this part, the apparent and mechanical properties of the chitosan membranes were mainly examined in the form of the concentration of chitosan, dissolving system, and drying temperature, and chitosan with $M_w = 1.0 \times 10^6$ and DD = 87.6% was an example.

Table IV and Figure 3 describe the effect of the concentration of chitosan in the [Gly]Cl aqueous system on the apparent and mechanical properties of

**TABLE IV**
**Effect of the Content of Chitosan on the Membranes**

| No. | Chitosan (%) | Viscosity (MPa) | Membrane situation | Softness |
|---|---|---|---|---|
| 1 | 1.0 | 72.5 | Uniform | Soft |
| 2 | 2.0 | 525 | Uniform | Soft |
| 3 | 3.0 | 1,600 | Uniform | Less soft |
| 4 | 4.0 | 10,000 | Asymmetric | Less crisp |
| 5 | 5.0 | 45,600 | — | — |

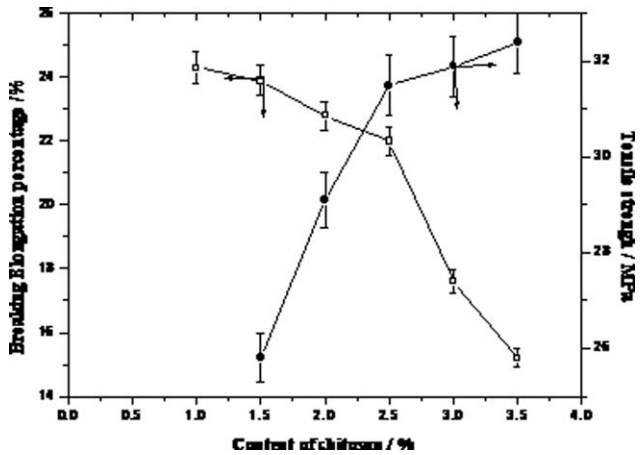


**Figure 3** Effect of the content of chitosan on the tensile strength and breaking elongation percentage.

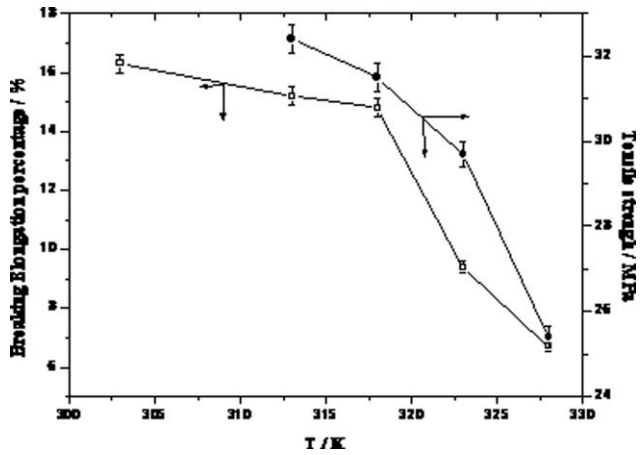


**Figure 4** Effect of the temperature ($T$) on the tensile strength and breaking elongation percentage.

the chitosan membranes. As shown in Table IV, the viscosity of the system increased with the increase in concentration, yet the degree of uniformity and flexibility of the membrane decreased during the process. Finally, when the concentration of chitosan was 5%, the viscosity of system reached 45,600 MPa; under the high-viscosity condition, the chitosan membrane could not be formed. It can be seen in Figure 3 that the tensile strength of the membranes increased and the breaking elongation decreased with the increase of concentration. On the whole, the optimum concentration of chitosan for the preparation of the membranes was 2–2.5%. Next, with 2% chitosan solvent as an example, the effects of the dissolving system on the apparent and mechanical properties of chitosan membrane are discussed.

Table V summarizes the properties of the chitosan membrane in the [Gly]Cl and acetic acid systems. The viscosity in the [Gly]Cl system showed no obvious difference from that in acetic acid, and a uniform membrane was formed in both systems; on the contrary, there were remarkably different on mechanical properties in the two systems. Evidently, the membrane from [Gly]Cl was of better tensile strength and breaking elongation than that from acetic acid. Next, with the 2% chitosan/[Gly]Cl solvent as an example, the effects of the drying temperature on the apparent and mechanical properties of chitosan membrane are discussed.

Figures 4 and 5 sketch the relationships between the drying temperature and the apparent and mechanical properties of the chitosan membranes. The chitosan membranes had good mechanical properties and high density when they were dried at about 40°C (Fig. 4). However, its mechanical properties and density decreased when the membrane was dried at about 55°C. Naturally, the scanning electron microscopy (SEM) pictures showed that chitosan membrane had a smooth and uniform surface at a drying temperature of 40°C. In contrast, the chitosan membrane had many bubbles and a nonuniform surface at a drying temperature of 55°C (Fig. 5).

Table VI shows that the membrane situation of these recycled ILs did not change a lot after two cycles. In the third recycling process, part of the ILs was lost so that the membrane had a rough surface and opacities. All of these results show that the 2% [Gly]Cl aqueous solution system had a good stability for membrane preparation.

## DISCUSSION

Chitin may be regarded as cellulose with the hydroxyl at position C-2 replaced by an acetamido group.[22,23] Both are polymers of monosaccharides made up of β-(1-4)-2-acetamido-2-deoxy-β-D-glucose and β-(1-4)-2-deoxy-β-D-glucopyranose units, respectively (Fig. 6). Chitosan is the *N*-deacetylated derivative of chitin with a typical degree of acetylation of less than 0.35 (Fig. 6). It is, thus, a copolymer composed of glucosamine and *N*-acetylglucosamine. Natural chitosan forms more complex intermolecular

**TABLE V**
**Effect of the Membrane on Different Systems**

| System | Viscosity (MPa) | Breaking elongation (%) | Tensile strength (MPa) | Membrane situation | Softness |
|---|---|---|---|---|---|
| Acetic acid | 1500 | 20 | 13.3 | Uniform | Soft |
| [Gly]Cl | 1600 | 31 | 15.2 | Uniform | Soft |

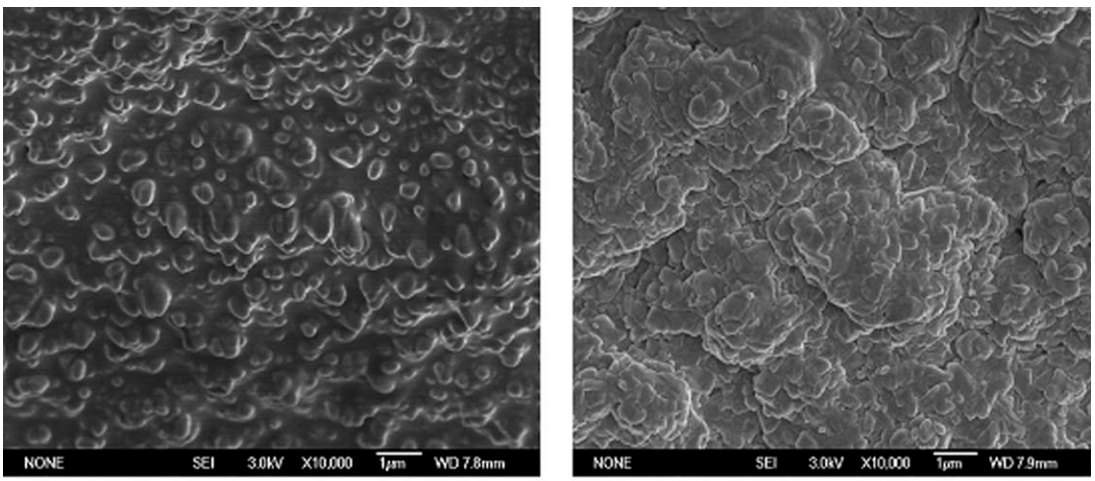


**Figure 5** SEM of the cross section of the membrane at different drying temperatures.

and intramolecular hydrogen-bond networks than cellulose because of the existence of an additional acetoamide or amino group in its structural repeating unit. In addition, composing the skeletons of many animals, such as crustaceans, chitosan is generally found to have a larger molecular weight than cellulose, which is mainly derived from plants. As a result, it is generally more difficult to dissolve chitosan than to dissolve cellulose materials. Previous studies on the dissolution of cellulose by ILs have suggested that the solvation mainly involves the interaction of the hydroxyl protons of the carbohydrate with the strong hydrogen-bonding and coordinating anions, in particular, $Cl^-$.[24] However, our preliminary experiments showed that those imidazolyl chlorinated ILs, reported to be good solvents of cellulose, could not dissolve chitosan with satisfactory results.[25] It is well known that a 2% acetic acid solvent can dissolve chitosan well. Therefore, we suggested that an IL that was composed of —COOH and —Cl could become an excellent solvent of chitosan. For this reason, [Gly]Cl was designed and synthesized. Fortunately, it was verified that [Gly]Cl really was an excellent solvent of chitosan from all the research results.

A study on intrinsic viscosity, FTIR spectroscopy, and powder XRD showed that the molecular weight and DD were collectively responsible for the solubility in the conditions of random deacetylation of acetyl groups, which resulted from the intermolecular forces.[26] The solution properties of chitosan , thus, depended not only on its average degree of acetylation but also on the distribution of the acetyl groups along the main chain, in addition to the molecular weight.[27,28] Apart from DD, the molecular weight was also an important parameter that significantly controlled the solubility and other properties.[29–31] Hence, the solubility of [Gly]Cl for chitosan with different molecular weights and DDs was studied (Table I). We confirmed that [Gly]Cl really was an excellent solvent of chitosan. As can be easily understood, on the one hand, [Gly]Cl was composed of —COOH and —Cl, which could form hydrogen with $—NH_2$ or —OH of chitosan; on the other hand, Gly was of small steric hindrance, which made it easy to enter the inside of chitosan. The synergistic action of the two aspects made the structure of chitosan loose and accelerated dissolution and the dispersion of chitosan in the [Gly]Cl system. The concept is illustrated in Figure 2, in which the H-bond networks formed in the native chitosan were greatly destroyed in the dissolution process by the [Gly]Cl solvent and the H-bond network could not be completely reconstituted during the regeneration process by the coagulants.[14] However, with not only [Gly]Cl but acetic acid as solvents, chitosan could all be inordinately

**TABLE VI**
**Results of Repeated Use of ILs**

| No. | 1 | 2 | 3 |
|---|---|---|---|
| Amount of chitosan (g) | 1 | 1 | 0.95 |
| Membrane situation | Uniform, transparent | Uniform, transparent | Rough surface, opacities |

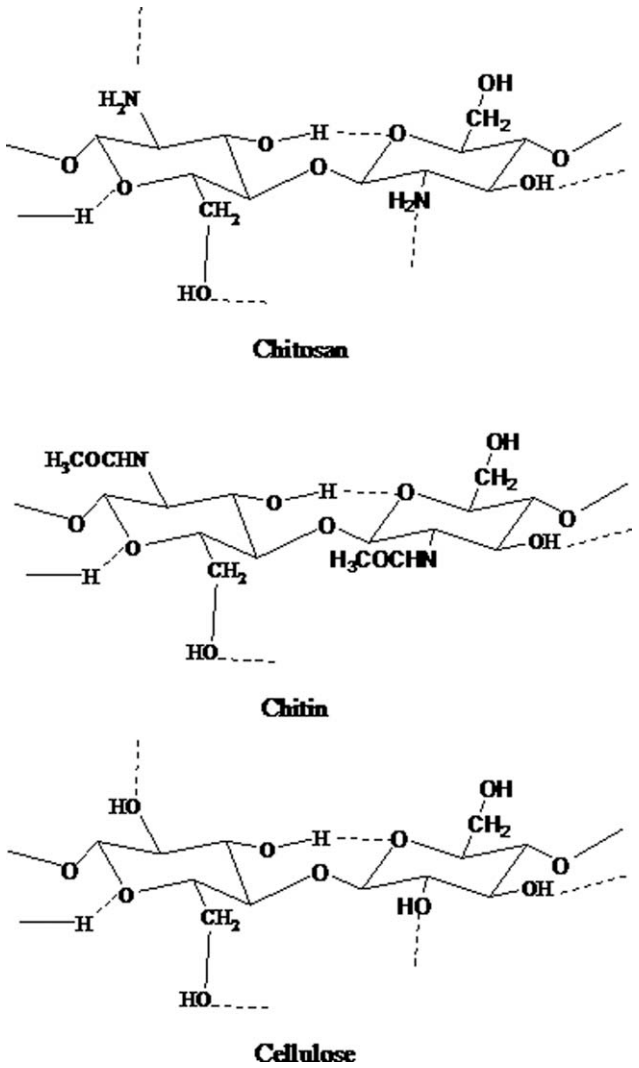


**Figure 6** Chemical structures of chitosan, chitin, and cellulose.

degraded during the process of dissolution and regeneration, as shown in Tables I and II. At the same time, Figure 1 sketches these phenomenon, in which the crystal structure of native chitosan was suffered a remarkable decrease after being dissolved by the acetic acid and [Gly]Cl.[14] Moreover, the results suggest that the regenerated chitosan from [Gly]Cl had a relatively higher crystallinity than that from acetic acid. We cam claim that the zwitterion of [Gly]Cl could form hydrogen with $-NH_2$ or —OH of chitosan; and the new hydrogen increased the steric hindrance, which guarded the glycosidic bond.[32,33]

The concentration of chitosan greatly influenced the preparation craft and property of the membrane. With increasing concentration, the intermolecular force and twining node concentration all increased. These factors all hindered the orientation of macromolecules and jumping diffusion. When the concentration was low, the properties and production efficiency of the membranes decreased. Therefore, it was necessary to prepare excellent membranes to select desirable chitosan concentration.

From Table IV, it can be seen that when the concentration of chitosan was 2–3%, the viscosity was low. The reason was that macromolecular chain of chitosan dissociated in the solvent in the form of curliness in low concentration, so the intermolecular force was relatively small, and the intramolecular force from the structure cell was large. The intramolecular force mainly depended on the molecular amount of chitosan and the flexibility of chains in the solvent. When the concentration was more than 4%, the viscosity of the solvent quickly increased, and the mobility was very weak. The reason was that the intermolecular force was the main factor controlling the viscosity in high concentration. The curliness of different chains was close to each other, and twining formed between different chains. With the increasing of twining nodes, the movement of the chains decreased, so the viscosity of solvent of chitosan quickly increased. In addition, when a chitosan of high concentration was used to prepare the membrane, the surface of the membrane was very uneven.[34,35]

From Figure 3, it can be seen that the tensile strength of the chitosan membrane increased with increasing concentration. The structure, molecular weight, and molecular arrangement of polymer greatly affected the tensile strength. When the molecular weight was unchanged, the concentration was higher, the amount of chitosan was bigger in unit volume, the intermolecular force of chitosan membrane was stronger, the intermolecular crosslinking was tighter, and the tensile strength was larger. When the concentration was low, the liquidity was good, and the membrane was very smooth and formed. On the other hand, when the concentration was high, the solvent was thick and was difficult to be deaerated, so the membrane was uneven and had much bubbling during the process of drying. Otherwise, the elongation of the membrane decreased with increasing concentration (Fig. 3).[34,35]

The chitosan membrane was had good mechanical properties and a high density when it was dried at about 40°C (Figs. 4 and 5). Under 40°C, the water was moderately evaporated from the surface of membrane, and the molecules of chitosan were ranked in an orderly manner in the membrane. The breaking elongation was low because the molecules moved slowly and could not rank in an orderly manner in the membrane below 40°C. However, the mechanical properties and density decreased when the membrane was dried at about 55°C. The reason was that at this temperature, the water quickly evaporated, and the molecules could

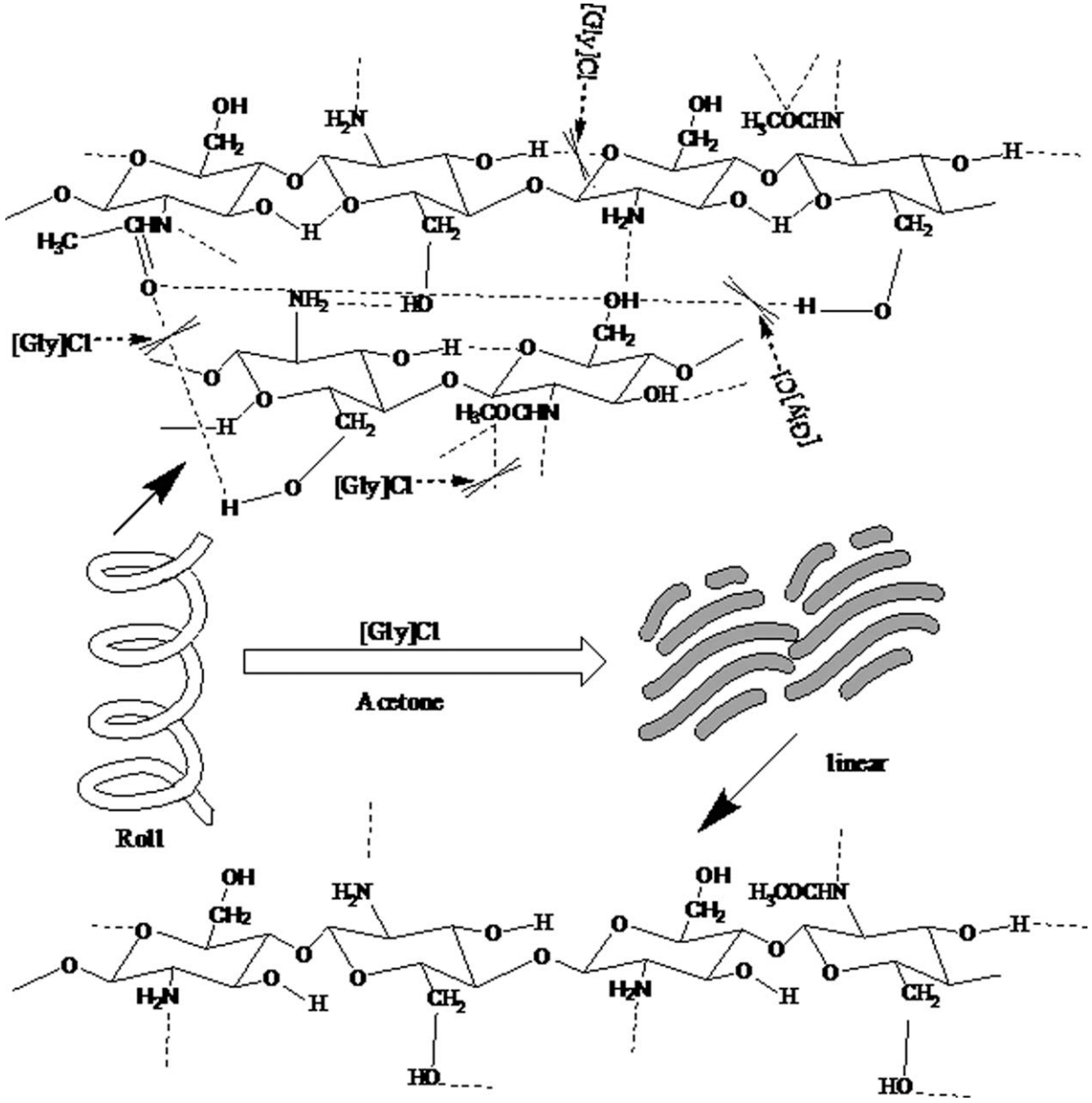


**Figure 7** Schematic illustration of the transformations of curly chitosan to linear chitosan in during the process of the membrane prepared by the dissolution of chitosan in [Gly]Cl.

not rank in orderly manner before forming the membrane. SEM verified the explanation (Figs. 4 and 5).[36,37]

From Table V, it can be seen that different solvent systems greatly affected the mechanical properties of membrane of chitosan. This was because the small steric hindrance of the Gly cation, which easily entered the intermolecular area of chitosan, broke the intermolecular and intramolecular hydrogen-bond network of chitosan to stretch the chitosan molecular chain. For example, as in Figure 7, the structure of chitosan was loose and the active volume enlarged, and then, the membrane had high mechanical properties. As for acetic acid, it made chitosan degrade, so the membrane was of poor mechanical properties. The results agreed with the mechanism of solvation.[38]

## CONCLUSIONS

Chitosan membranes were synthesized in a homogeneous [Gly]Cl aqueous solution system, which possessed excellent solubility for chitosan. Chitosan membranes prepared in this IL system showed better properties, including a soft, uniform, large breaking elongation and tensile strength, compared to those prepared in the acetic acid system. The separation and recycling of ILs were easy with only a slight loss of activity. Therefore, an environmentally friendly approach for the synthesis of chitosan membranes was provided.

## References


1. Lu, G. Y.; Kong, L. J.; Sheng, B. Y.; Wang, G.; Gong, Y. D.; Zhang, X. F. Eur Polym J 2007, 43, 3807.
2. Yi, H. M.; Wu, L. Q.; Bentley, W. E. Biomacromolecules 2005, 6, 2881.
3. Ravi Kumar, M. N. V.; Muzzarelli, R. A. A.; Muzzarelli, C.; Sashiwa, H.; Domb, A. J. Chem Rev 2004, 104, 6017.
4. Berger, J.; Reist, M.; Mayer, J. M.; Felt, O.; Peppas, N. A.; Gurny, R. Eur J Pharm Biopharm 2004, 57, 19.
5. Shahidi, F.; Arachchi, J. K. V.; Jeon, Y. J. Trends Food Sci Technol 1999, 10, 37.
6. Lim, S. H.; Hudson, S. M. Carbohydr Polym 2004, 56, 227.
7. Muzzarelli, R. A. A. Carbohydr Polym 1983, 3, 53.
8. Pillai, C. K. S.; Paul, W.; Sharma, C. P. P. Polym Sci 2009, 34, 641.
9. Brennecke, J. F.; Maginn, E. J AIChE 2001, 47, 2384.
10. Wang, C.; Zhao, W. Green Chem 2009, 11, 843.
11. Laus, G.; Bentivoglio, G. Lenzinger Berichte 2005, 84, 71.
12. Lu, X.; Zhang, Q.; Zhang, L. Electrochem Commun 2006, 8, 874.
13. Xie, H.; Zhang, S. Green Chem 2006, 8, 630.
14. Wu, Y. S.; Sasaki, T.; Satoshi, I.; Sakurai, K. Polymer 2008, 49, 2321.
15. Xie, Y.; Zhou, N.; Cao, J. J Clin Rehab Tissue Eng Res 2008, 12, 4579.
16. Imoto, T.; Yagishita, K. Agric Biol Chem 1971, 35, 1154.
17. Fan, J. S.; Chen, G. H.; Sun, M. K.; Hua, Z. J Ocean Univ Qingdao 2002, 32, 296.
18. Minke, R.; Blackwell, J. J Mol Biol 1978, 120, 167.
19. Cho, Y.; Jang, J.; Park, C.; Ko, S. Biomacromolecules 2000, 1, 609.
20. Damon, S. E.; Rudall, K. M. Discuss Faraday Soc 1950, 9, 251.
21. Focher, B.; Naggi, A.; Torri, G.; Cosani, A.; Terbojevich, M. Carbohydr Polym 1992, 17, 97.
22. Rinaudo, M. Prog Polym Sci 2006, 31, 603.
23. Ravi Kumar, M. N. V. React Funct Polym 2000, 46, 1.
24. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. J Am Chem Soc 2002, 124, 4974.
25. Liang, S.; Ji, H. H.; Li, L.; Yu, S. T.; Liu, F. S.; Xie, C. X. High Polym Mater Sci Eng 2010, 26, 70.
26. Rao, M. S.; Nyein, K. A.; Trung, T. S.; Stevens, W. F. J Appl Polym Sci 2007, 103, 3694.
27. Kim, K. M.; Son, J. H.; Kim, S. K.; Weller, C. L.; Hanna, M. A. J Food Sci 2006, 71, E119.
28. Peniche, C.; Argüelles-Monal, W. Macromol Symp 2001, 168, 1.
29. Schiffman, J. D.; Schauer, C. L. Biomacromolecules 2007, 8, 594.
30. Zhou, H. Y.; Chen, X. G.; Kong, M.; Liu, C. S.; Cha, D. S.; Kennedy, J. F. Carbohydr Polym 2008, 73, 265.
31. Zhou, X.; Zhang, X.; Yu, X.; Zhang, X.; Fu, Q.; Liu, B. Biomaterials 2008, 29, 111.
32. Domard, A. Int J Biol Macromol 1987, 9, 98.
33. Rinaudo, M. Prog Polym Sci 2006, 31, 603.
34. Guo, Z.; Xing, R.; Liu, S.; Zhong, Z.; Ji, X.; Wang, L. Carbohydr Polym 2008, 71, 694.
35. Li, X.; Feng, Q.; Jiao, Y.; Cui, F. Polym Int 2005, 54, 1034.
36. Notin, L.; Viton, C.; Lucas, J.-M.; Domard, A. Acta Biomater 2006, 2, 297.
37. East, G. C.; Qin, Y. J Appl Polym Sci 1993, 50, 1773.
38. Urbanczyk, G. W. Fibers Text East Eur 1996, 4, 34.