Dissolution and utilization of chitosan in a 1-carboxymethyl-3-methylimidazolium hydrochloride ionic salt aqueous solution

Jiaxuan Feng, Hongjun Zang, Qing Yan, Mingguang Li, Xinqiang Jiang, Bowen Cheng
State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Department of Environmental and Chemistry Engineering, Tianjin Polytechnic University, Tianjin 300387, China
Correspondence to: H. Zang (E-mail: chemhong@126.com)

ABSTRACT: 1-Carboxymethyl-3-methylimidazolium hydrochloride ([IMIM–COOH]Cl), a new ionic salt, is proposed as a green, promising solvent for dissolving chitosan. However, because of the optimal dosage of chitosan dissolved in [IMIM–COOH]Cl, a 12 wt % [IMIM–COOH]Cl aqueous solution was selected as an optimum solvent system for dissolving chitosan. The structures of the original and regenerated chitosan were characterized by Fourier transform infrared spectroscopy and X-ray diffraction analysis. Scanning electron microscopy was used to visualize the morphological features of the reconstituted chitosan membranes. Meanwhile, the absorbance, tensile strength, and breaking elongation of the chitosan membranes were measured. The results reveal that 10–11 wt % was an optimal chitosan concentration for preparing membranes. Furthermore, the adsorption capacity for Cu(II) ion of the chitosan membranes was increased with the chitosan concentration decreased from 12 to 8 wt %. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41965.

INTRODUCTION

Chitosan is a natural renewable resource that can be obtained from chitin through an *N*-deacetylation process. It possesses many unique properties, which include biocompatibility, biodegradability, nontoxicity, and excellent film-forming ability.[1,2] Enormous efforts have been made toward its potential applications in wastewater purification, pharmaceuticals, cosmetics, metal chelating agents, textiles, and so forth.[2–4] In application, the chitosan membrane is the main use of chitosan; it has a large surface and short diffusion path and has been widely applied in chemistry, food, fermentation, sewage treatment, and so on. Although chitosan is normally insoluble in water and most conventional organic solvents because of its stable and compact crystalline structure, acetic acid, formic acid, hydrochloric acid, and some strong polar protic solvents, such as trichloroacetic acid and dichloroacetic acid, have been found to dissolve chitosan.[5–7] However, these solvents have many drawbacks, such as a high volatility, strong causticity, and serious pollution. Therefore, the discovery of a new green solvent to dissolve chitosan is its most important issue that needs to be solved.

In the past 2 decades, ionic liquids (ILs) have gained considerable attention because of their unique properties, such as a negligible vapor pressure, nonflammability, lack of a burning point, and excellent thermal stability.[8] Moreover, ILs have a remarkable ability to dissolve cellulose, hemicellulose, and all kinds of carbohydrates.[9,10] In view of the good solubility of ILs, chitin and chitosan, whose structures are similar to that of cellulose, have also been introduced to intersect with ILs. Xie et al.[11] investigated the adsorption of CO_2 with chitosan and chitin as reversible sorbents in 1-butyl-3-methylimidazolium chloride and obtained a 10 wt % chitosan/IL solution at 110°C in 5 h of reaction time. However, the 10 wt % chitosan/IL solution was semiclear and viscous. Wu et al.[12] reported that 1-butyl-3-methylimidazolium acetate was a better solvent than 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride, which dissolved about 6 wt % chitosan at 110°C. Chen et al.[13] found that the solubility of chitosan increased almost linearly with increasing hydrogen-bond-accepting ability of the ILs. Li et al.[14] synthesized a series of amino acid ILs and found that a glycine hydrochloride IL aqueous solution had a better dissolution performance because of the small steric hindrance of glycine for easily entering the inside of chitosan, but the largest solubility only reached 6.32 wt %. Meanwhile, the degradation of chitosan is serious in the process of dissolution.

As reported in the previous literature and other articles, we know that imidazolium-based ILs are still better solvents for chitosan because of their excellent thermal stability and low degradation for chitosan. Moreover, a series of activating groups, such as Cl−[15] and —COOH,[13] in ILs are in favor of dissolving chitosan by breaking the hydrogen bonds between intermolecular and intramolecular chains of chitosan.[12] Therefore, in our study, we selected an IL, 1-carboxymethyl-3-methylimidazolium hydrochloride ([IMIM–COOH]Cl), to dissolve chitosan. In the [IMIM–COOH]Cl aqueous system, chitosan could be dissolved quickly at low temperatures and its molecular weight did not change sharply.

Accordingly, an efficient approach for the preparation of chitosan membranes was obtained with this solution. In this article, we report the preparation of a chitosan dense membrane and its application in Cu(II)-ion adsorption. Chitosan is a natural chelating polymer, and it exhibits an excellent capability for removing Cu(II) ions from aqueous solution due because of the primary amine groups in its structure.[16,17] Copper is an essential nutrient in trace amounts, but at higher levels, it is toxic to plants, algae, and humans. Thus, the importance of removing this element from wastewater is a well-known issue. When chitosan membranes were treated with copper sulfate ($CuSO_4$) solutions, the Cu(II) ion was chelated by chitosan through the amine groups in the membrane. The Cu(II)-ion adsorption capacity was satisfactory, and the properties of the chitosan membranes produced in this system were studied.

EXPERIMENTAL

Materials
Chitosan (white crystalline powder, deacetylation degree = 87.2%) was purchased from Shandong Ak Biotech Co., Ltd. (Jinan China) and was used directly after it was dried without further purification. Its viscosity-average molecular weight (M_v) was about 360,000, as determined on the basis of viscosity measurements.[18] N-Methylimidazole (analytical reagent, 99%) and methyl chloroacetate (analytical, 99.0%) were purchased from Aladdin Reagent Co. (Shanghai, China). Mineral acids (36.5 wt % hydrochloric acid) were supplied by Beijing Chemicals Co., Ltd. (Beijing, China). All of the other chemicals were supplied by local suppliers and were used without further purification.

Synthesis of [IMIM–COOH]Cl
The preparation and purification of [IMIM–COOH]Cl were done according to the known literature[19] with minor modifications. At first, freshly distilled N-methyl imidazole (16.42 g, 0.2 mol) and 20 mL of acetone were mixed in a 250-mL, three-necked flask in an ice–water bath. Then, methyl chloroacetate (21.73 g, 0.2 mol) was added dropwise to the mixture with a magnetic stirrer. During the process, a white solid formed, and the solid was washed with diethyl ether (3 × 30 mL) and dried in vacuo for 24 h. As follows, the crude product and HCl aqueous solution (36–38 wt %) in a molar ratio of 1:1.1 were refluxed at 80°C for 12 h. The solvent was removed under reduced pressure until no steam was generated. The residue was washed with acetone three times and kept in vacuo for 24 h; then, a white crystalline [IMIM–COOH]Cl was obtained.

The melting point was 203°C and recorded on an electrothermal apparatus in accordance with the literature. So, it was an ionic salt (IS) and was not considered as an IL according to the common definition. Meanwhile, the water content was 1.01%, as tested by thermogravimetric analysis (Figure S1). [IMIM–COOH]Cl remained stable under 210°C.

^{1}H-NMR (300 MHz, D_2O, δ): 8.66 (s, 1H), 7.36 (s, 1H), 7.36 (s, 1H), 4.97 (s, 2H), 3.79 ppm (s, 3H). (Figure S2). ^{13}C-NMR (300 MHz, D_2O, δ): $d = 169.9$, 137.4, 123.5, 123.5, 49.9, 36.0 ppm (Figure S3).

Measurements
The IR spectra of the native and regenerated chitosan were recorded on a PerkinElmer 2000 Fourier transform infrared (FTIR) spectrometer with KBr pellets. The X-ray diffraction (XRD) experiments were performed on a Rigaku X-ray diffractometer with a RINT2000 wide-angle goniometer with Cu Kα radiation at 40 kV and 100 mA. The diffraction intensity profiles were recorded in the region of scattering angles 3–50°. The membrane morphology was investigated by scanning electron microscopy (SEM; Hitachi S-4800) with an accelerating voltage of 10 kV. Both the surface and a cross section (prepared by the fracturing of the membrane under liquid nitrogen) were scanned after the sample was coated with a thin layer of gold. The absorbance of the membranes was recorded on a Mapada UV-670 spectrophotometer with a quartz cell (1 cm) at different wavelengths.

Dissolution and Regeneration of Chitosan
In our study, we achieved the optimal conditions were screening the temperature and concentration of the IS aqueous solution. All of the dissolution experiments were performed in a 100-mL, three-necked flask with IS with a mechanical stirrer. The temperature of the dissolving process was controlled by an oil bath.

An IS aqueous solution (2 wt %) was prepared by the dissolution of 0.5 g of IS into 24.5 mL of deionized water. Then, chitosan was gradually loaded into the IS aqueous solution under different temperatures. When chitosan was completely dissolved in the IS aqueous solution, another portion of chitosan was added to the solution until the solution was saturated. Finally, a light yellow and clear chitosan solution was obtained.

A series of aqueous solutions with various [IMIM–COOH]Cl loadings were prepared; the total mass was 25 g. The chitosan powder was added in portions of only 5 wt % of the IL each time, and the solid allowed to dissolve before each new addition.

After filtration for the removal of the undissolved chitosan, 1 mol/L NaOH was slowly added to the filter to precipitate out the chitosan. Then, the NaOH aqueous solution was removed by air-pump filtration. Afterward, the resulting chitosan was washed to neutrality by distilled water and dried for further use.

Determination of the Molecular Weights of Chitosan
The molecular weight (M_v) of the chitosan was determined by the viscometry method with an Ubbelohde capillary viscometer (i.d. = 0.5–0.6 mm). Before the measurement of flow times, the

Table I. Dosage of Chitosan Dissolved in a 2 wt % IL Aqueous Solution at Different Temperatures

Temperature (°C)	25	40	50	60	70	80	90	100
Dosage of dissolved chitosan (g)	Undissolved	Partially dissolved	0.7800	0.8820	0.9291	0.9487	0.9477	0.9055

chitosan samples were dissolved in a 0.1 mol/L CH_3COOH–0.2 mol/L NaCl solution at 25°C. Then, M_v was calculated according to the classic Mark–Houwink equation:[18]

$$[\eta] = 1.81 \times 10^{-3} M_v^{0.93}$$

where η is the intrinsic viscosities.

Preparation of the Chitosan Membrane
When the chitosan was completely dissolved in the IS aqueous solution, it was filtered by a screen cloth (400 mesh) and stored at room temperature for 6 h to remove the bubbles. The obtained chitosan solutions were cast on a flat and level glass plate; the proper membrane thickness was achieved with a film applicator. Then, the glass plate was immersed in a 5 wt % aqueous NaOH solution/ethanol (v/v = 1:1) coagulation bath for 12 h. Finally, the membranes were peeled from the plates and washed with distilled water to remove the remaining NaOH, dried at room temperature for 24 h, and stored in a desiccator for further use. We found that the membranes made by a low concentration of chitosan solution were thin and soft than those made by a higher concentration when the membranes were dry.

Mechanical Properties of the Chitosan Membrane
The mechanical performance was measured with a CMT4503 electromechanical universal testing machine (MTS Systems Co., Ltd., China) at room temperature; the membranes were cut into strips 50 × 10 mm^3, and three strips were measured for each sample. The extension velocity was 100 mm/min, and the return velocity was 200 mm/min. We used the following equations:

$$\alpha = F/bd \qquad (1)$$

$$\beta = (\Delta L/L_0) \times 100\% \qquad (2)$$

$$\Delta L = L - L_0 \qquad (3)$$

where α is the tensile force (MPa), F is the maximum capacity (N), b is the width of the membranes (mm), d is the thickness of the membranes as measured by a vernier caliper, β is the elongation (%), ΔL is the increasing length after stretching (mm), L is the breaking length after deformation (mm), and L_0 is the scale distance of the former membranes (mm).

Copper-Ion Adsorption
Chitosan has stronger ability to adsorb Cu(II) ions from $CuSO_4$ compared to other salts.[20,21] In this experiment, copper solutions with concentrations of 10, 35, 90, 200, 400, 500, 700, 800, and 1000 mg/L were prepared by the dissolution of hydrated copper sulfate ($CuSO_4 \cdot 5H_2O$) in water. From spectrophotometric measurements with the equipment from Mapada, calibration curves for the Cu(II)-ion concentration were obtained at a 740-nm wavelength. The curve was adjusted by linear regression.

We carried out batch adsorption experiments by soaking five samples (polymer concentrations = 8–12 wt %), with each weigh-

ing 0.1 g, in a 40-mL aqueous solution containing 200 mg/L $CuSO_4 \cdot 5H_2O$. The mixtures were left standing for 24 h at room temperature with magnetic stirring before the membranes were separated from the solutions; this was followed by the measurement of the copper concentration in the solution with a spectrophotometer. This adsorption period was sufficient for the sample to reach adsorption equilibrium. The adsorption capacity (Q) of copper was calculated with the following equation:

$$Q = (C_0 - C_{eq}) \times V/m$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of metal ions in the liquid phase (mg/L), respectively; V is the volume of the solution (L); and m is the amount of chitosan membrane (g). An equal amount of ethylene diamine tetraacetic acid (EDTA) solution (0.2 mol/L) as a color development reagent was added to the copper solution before spectrophotometric measurements.

RESULTS AND DISCUSSION

Dissolution of Chitosan in [IMIM–COOH]Cl
To obtain a homogeneous system of chitosan, a suitable solution temperature is necessary. We put 0.5 g of chitosan into 25 mL of an IS aqueous solution. The results are shown in Table I. Chitosan could not be dissolved in a 2 wt % IS aqueous solution at 25°C, but most of the chitosan dissolved at 40°C. When the temperature was raised to 50°C, chitosan was completely dissolved in the IS aqueous solution. Meanwhile, it seemed that a much higher dissolution temperature had small effect on the practical improvement of the concentration of chitosan even when the temperature was 100°C. In terms of green and sustainable chemistry, 50°C was chosen as the optimal temperature.

The amount of chitosan dissolved was affected by the different concentrations of IS aqueous solutions during the reaction course. When the dosage of IS was increased from 2 to 12 wt %, the amount of chitosan dissolved increased obviously, from 3.03 to 12.79 wt % (Figure 1). Then, the amount of chitosan dissolved stayed constant or even started to decrease. With consideration of both the reactive efficiency and economic factors, a 12 wt % IS aqueous solution was chosen in our study.

The FTIR spectrum of the regenerated chitosan was similar to that of original chitosan [Figure 2(a)]. The band at 3420 cm^{-1} was due to —NH_2 bond stretching vibrations.[22] The bands at 1654 and 1324 cm^{-1} were referenced as amides I and III,[22] respectively. The absorption band at 1598 cm^{-1} was assigned to the amino deformation mode.[22] The amide II band disappeared in the FTIR spectra, mainly because it overlapped with the band of amino deformation vibrations. The absorption band at 1156 cm^{-1} was characteristic of the asymmetric stretching of the C—O—C bridge.[23] The band at 1079 cm^{-1} was attributed to the skeletal vibration involving C—O stretching.[23] The band
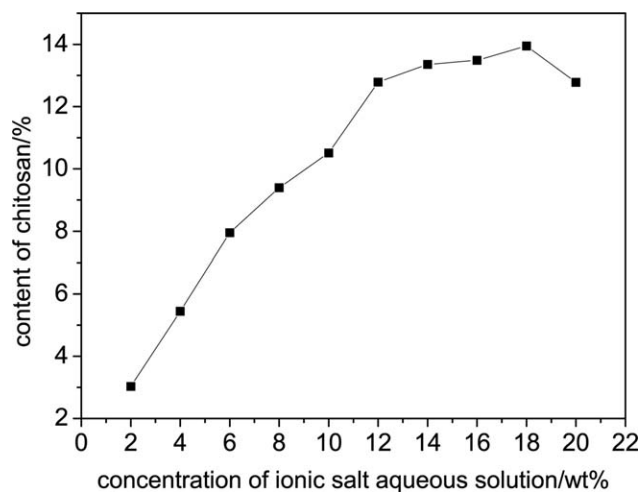
Figure 1. Effect of the concentration of the IS aqueous solution on the dosage of chitosan in the solution system. The experimental conditions included a temperature of 50°C, a dissolution time of 5–120 min, and an oil bath.

at 897 cm^{-1} was assigned to the absorption peaks of β-(1–4)-glycosidic bonds in chitosan.[24] The FTIR spectra suggested that the important functional groups were still present, and the main polysaccharide chain structure remained after regeneration.

As shown in Figure 2(b), the XRD profiles of all of the samples showed obvious diffraction peaks at about $2\theta = 10.5$ and $20.0°$, respectively; this indicated that all of the regenerated chitosan samples prepared from [IMIM–COOH]Cl were in accordance with the raw chitosan. This also proved that there was no crystal structural change for chitosan during the dissolution and regeneration processes. On the other hand, the peak intensity at $2\theta = 10.5°$ was less than that of raw chitosan; this was attributed to the full destruction of the crystal region of the raw chitosan during the dissolution process and the fact that some amorphous areas could not be reconstituted to crystals. Meanwhile, the fact that the peak at $20.0°$ almost did not change suggested that the

decrease in the crystallinity was small. Hence, we confirmed that [IMIM–COOH]Cl is a promising solvent for dissolving chitosan and preparing regenerated chitosan membranes.

In contrast, the same weight of chitosan was added to 12 wt % CH_3COOH aqueous solutions at 50°C for 1 h, 50°C for 5 h, and 70°C for 1 h, respectively. The mass of dissolved chitosan changed little. Meanwhile, the M_v values of the reconstituted chitosan dissolved in the CH_3COOH aqueous solution were as same as those dissolved in the [IMIM–COOH]Cl aqueous solution. Moreover, the XRD profiles and the FTIR spectrum of the regenerated chitosan dissolved in chitosan are shown in Figure 3(a,b). The FTIR spectrum was the same as before; the functional groups were still present. The XRD profiles changed obviously, and this indicated that the crystallinity of chitosan decreased sharply. In addition, CH_3COOH has a high volatility and will pollute the environment. Therefore, the [IMIM–COOH]Cl aqueous solution was a better solvent than the CH_3COOH aqueous solution.

M_v of Regenerated Chitosan Affected by Different Dissolution Temperatures and Dissolution Times

Figure S4 (see the Supporting Information) shows that the dissolution time had a significant effect on the M_v of regenerated chitosan in the 12 wt % IS aqueous solution. The M_v of the regenerated chitosan decreased obviously as the dissolution time was extended from 1 to 7 h, but the trend downward became slow afterward. The dissolution temperature had the same impact on the M_v; this showed that the increasing the reaction temperature reduced the M_v of regenerated chitosan (Figure S5, Supporting Information). However, the trend remained stable when the temperature was greater than 80°C.

Preparation of the Chitosan Membrane with a Desirable Chitosan Concentration

The concentration of chitosan greatly influenced the preparation, crafting, and properties of the membrane. With increasing chitosan concentration, the viscosity of the system increased simultaneously; however, the degree of uniformity and flexibility of the membrane decreased during the process. When the
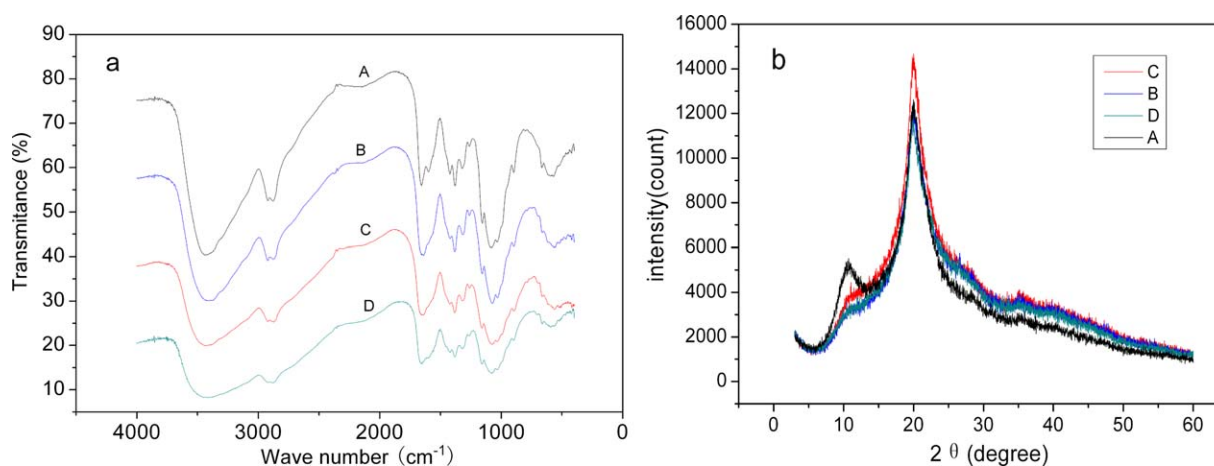

Figure 2. (a) FTIR spectra and (b) XRD patterns of the (A) original chitosan and (B–D) regenerated chitosan dissolved in an [IMIM–COOH]Cl aqueous solution for 5 h at 50°C, dissolved in an IS aqueous solution for 1 h at 50°C, and dissolved in an IS aqueous solution for 1 h at 70°C, respectfully. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
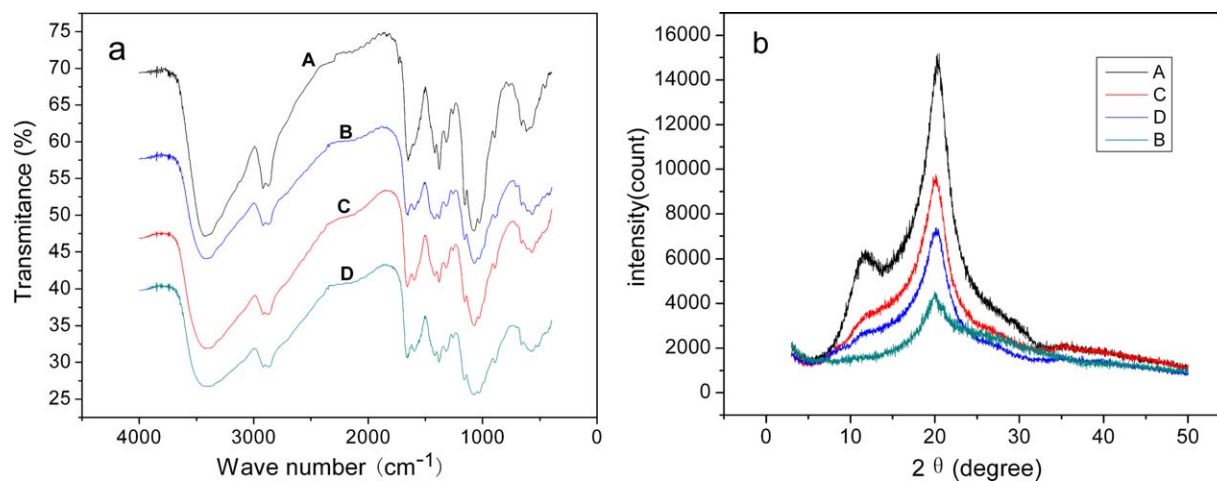
Figure 3. (a) FTIR spectra and (b) XRD patterns of the (A) original chitosan and (B–D) regenerated chitosan dissolved in a CH$_3$COOH aqueous solution for 5 h at 50°C, dissolved in an IS aqueous solution for 1 h at 50°C, and dissolved in an IS aqueous solution for 1 h at 70°C, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration was low, the properties and production efficiency of the membranes decreased. Therefore, it was necessary to prepare excellent membranes with a desirable chitosan concentration. It was easy to prepare a 1–12 wt % chitosan solution, and the resulting chitosan/IS solution was clear and viscous. However, when the concentration of chitosan was above 13 wt %, the viscosity of the system was very high, and the bubbles could not be removed. Under the high-viscosity condition, the chitosan membrane could not be formed. Meanwhile, when the con-

centration of chitosan was below 7 wt %, the viscosity of the system was very low. The chitosan solution could not adhere to the glass, so the chitosan membrane could not be formed. Hence, we dissolved chitosan at final concentrations of 8, 9, 10, 11, and 12 wt % in the [IMIM–COOH]Cl aqueous solution.

Figure S6 (see the Supporting Information) shows that the absorbance of chitosan membrane decreased with increasing wavelength from 330 to 700 nm. At the same wavelength, the
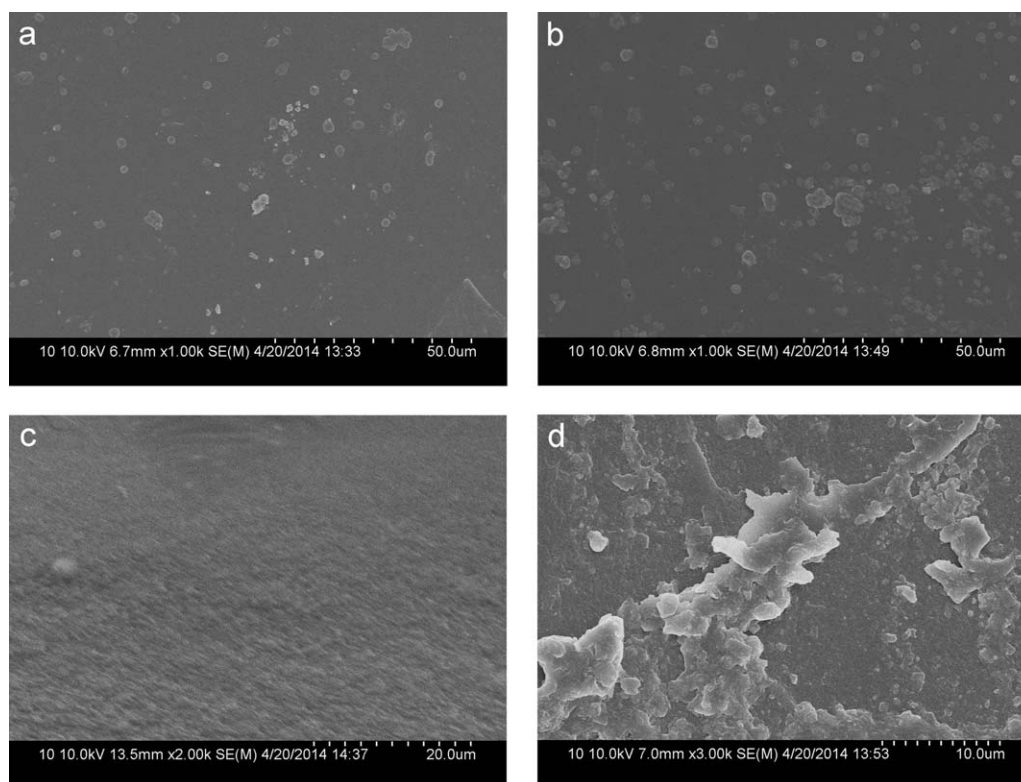

Figure 4. SEM photographs of the dense chitosan membrane: (a) top surface (magnification 1000×), (b) bottom surface (magnification 1000×), (c) cross section (magnification 2000×), and (d) after Cu(II) adsorption (magnification 3000×).
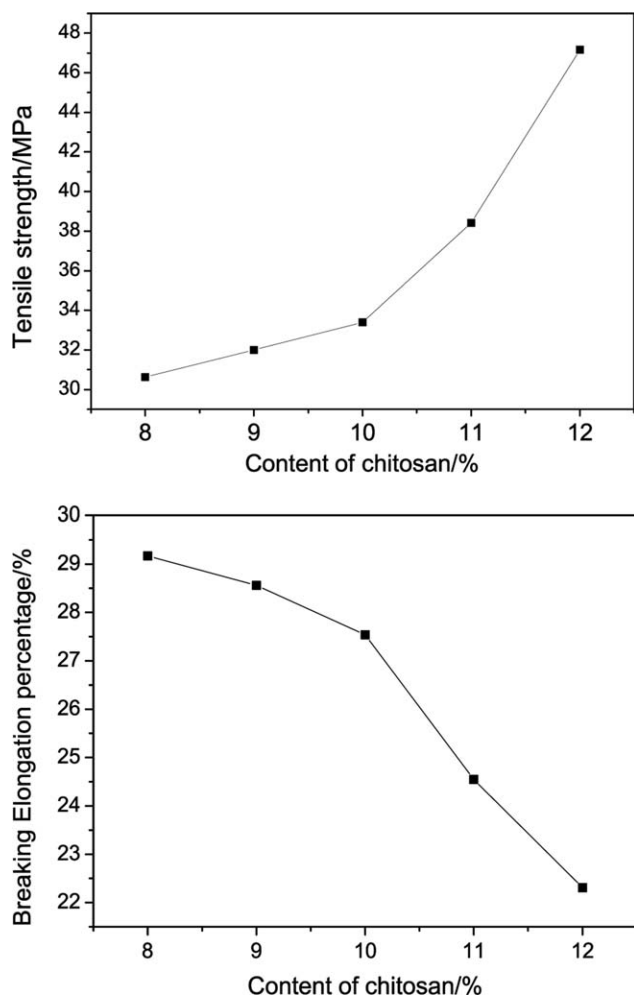
Figure 5. Effect of the content of chitosan on the tensile strength and the breaking elongation of the membranes.

absorbance increased as the chitosan loading increased. This was mainly because of the thickness of the chitosan membrane. What is more, a low content of chitosan formed a more transparent solution, and even small particles of chitosan could be dissolved thoroughly.

The surface and cross-sectional morphologies of the chitosan membrane were observed by SEM. The SEM images, including the surface morphology after Cu(II) adsorption, are given in Figure 4. The chitosan membranes were all made by a 10 wt % chitosan solution. In the chitosan membrane, both the top [Figure 4(a)] and bottom [Figure 4(b)] surfaces were smooth and

Table II. Amount of Copper Adsorbed by the Membranes After 24 h

Content of chitosan (wt %)	Copper-ion adsorption (mg/g)
8	74.4
9	70.0
10	66.2
11	59.2
12	56.7

presented a crack-free appearance. The cross-sectional image [Figure 4(c)] also showed a dense structure. As shown in Figure 4(d), the adsorbent surface became abnormal, and a layer of Cu(II) substance was adhered to the surface.

Tensile Strength and Breaking Elongation Percentage Values of the Chitosan Membranes

As shown in Figure 5, the tensile strength of the membranes increased, and the breaking elongation decreased with increasing chitosan concentration. The structure and content of the polymer greatly affected the tensile strength. When the concentration was high, the amount of chitosan was big in unit volume, the intermolecular force of chitosan membrane was strong, the intermolecular crosslinking was tight, and the tensile strength was larger. On the other hand, the solvent was thick and difficult to deaerate, so the membrane was uneven and showed much bubbling during the process of drying. When the concentration was low, the liquidity was good, and the membrane was very smooth and formed. Meanwhile, the flexibility was good, and this led to a high breaking elongation. On the whole, the optimum content of chitosan for the preparation of the membranes was 10–11 wt %.

Copper Adsorption on Chitosan Membranes

The adsorption capacity of heavy metals usually depends on the molecular groups that perform the chelation. Table II lists the amounts of copper adsorbed on the different membranes at $C_0 = 200$ mg/L. Higher adsorption amounts were associated with lower polymer concentrations in the casting solution. Because the same weight of chitosan membrane was used, the chitosan membranes made by lower chitosan concentrations were thin. This resulted in a bigger surface and made more amino groups available for chelation with copper ions.

CONCLUSIONS

A homogeneous [IMIM–COOH]Cl aqueous solution system was developed, which possessed excellent solubility for chitosan. In this system, the M_v of regenerated chitosan was affected by different dissolution temperatures and times. The M_v values, FTIR spectra, and XRD studies of the regenerated chitosan showed that the chitosan could retain its crystalline structure and crystallinity properties when it was dissolved at 50°C in 1 h. An environmentally friendly approach for the synthesis of dense chitosan membranes was used in this IS system. The tensile strength, breaking elongation, absorbance, and copper-ion adsorption of the membranes made by different chitosan loadings were measured.

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. Rinaudo, M. *Prog. Polym. Sci.* **2006**, *31*, 603.

3. Ravi Kumar, M. N. V. *React. Funct. Polym.* **2000**, *46*, 1.

4. Ravi Kumar, M. N. V.; Muzzarelli, R. A. A.; Muzzarelli, C.; Sashiwa, H.; Domb, A. *J. Chem. Rev.* **2004**, *104*, 6017.

5. Rinaudo, M.; Pavlov, G.; Desbrieres, J. *Polymer* **1999**, *40*, 7029.

6. Rinaudo, M.; Pavlov, G.; Desbrieres, J. *Int. J. Polym. Anal. Charact.* **1999**, *5*, 267.

7. Pillai, C. K. S.; Paul, W.; Sharma, C. P. *Prog. Polym. Sci.* **2009**, *34*, 641.

8. Yue, C. B.; Fang, D.; Liu, L.; Yi, T. F. *J. Mol. Liq.* **2011**, *163*, 99.

9. Fukaya, Y.; Hayashi, K.; Wada, M.; Ohno, H. *Green Chem.* **2008**, *10*, 44.

10. Zhu, S. D.; Wu, Y. X.; Chen, Q. M.; Yu, Z. N.; Wang, C. W.; Jin, S. W.; Ding, Y. G.; Wu, G. *Green Chem.* **2006**, *8*, 325.

11. Xie, H. B.; Zhang, S. B.; Li, S. L. *Green Chem.* **2006**, *8*, 630.

12. Wu, Y. S.; Sasaki, T.; Irie, S.; Sakurai, K. *Polymer* **2008**, *49*, 2321.

13. Chen, Q. T.; Xu, A. R.; Li, Z. Y.; Wang, J. J.; Zhang, S. *J. Green Chem.* **2011**, *13*, 3446.

14. Li, L.; Yuan, B.; Liu, S. W.; Yu, S. T.; Xie, C. X.; Liu, F. S.; Guo, X. Y.; Liang, S. *J. Appl. Polym. Sci.* **2012**, *123*, 3772.

15. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.

16. Wan Ngah, W. S.; Endud, C. S.; Mayanar, R. *React. Funct. Polym.* **2002**, *50*, 181.

17. Schmuhl, R.; Krieg, H. M.; Keizer, K. *Water SA* **2001**, *27*, 1.

18. Fan, J. S.; Chen, G. H.; Sun, M. K.; Hua, Z. *J. Ocean Univ. Qingdao* **2002**, *32*, 296.

19. Fei, Z. F.; Zhao, D. B.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. *J. Chem. Eur. J.* **2004**, *10*, 4886.

20. Guibal, E. *Sep. Purif. Technol.* **2004**, *38*, 43.

21. Wang, X. P.; Shen, Z. Q. *Polym. Int.* **2000**, *49*, 1426.

22. Yue, W.; He, R.; Yao, P.; Wei, Y. *Carbohydr. Polym.* **2009**, *77*, 639.

23. Zhang, C.; Ping, Q.; Zhang, H.; Shen, J. *Eur. Polym. J.* **2003**, *39*, 1629.

24. Wang, W.; Du, Y.; Qiu, Y.; Wang, X.; Hu, Y.; Yang, J.; Cai, J.; Kennedy, J. F. *Carbohydr. Polym.* **2008**, *74*, 127.