# Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 8585

www.rsc.org/materials

PAPER

# Preparation of high strength chitosan fibers by using ionic liquid as spinning solution

Lu Li,<sup>*a*</sup> Bing Yuan,<sup>*b*</sup> Shiwei Liu,<sup>*a*</sup> Shitao Yu,<sup>*a*</sup> Congxia Xie,<sup>*b*</sup> Fusheng Liu,<sup>*a*</sup> Xianying Guo,<sup>*c*</sup> Lijun Pei<sup>*a*</sup> and Baoquan Zhang<sup>*d*</sup>

*Received 29th January 2012, Accepted 1st March 2012* DOI: 10.1039/c2jm30555k

The morphology and mechanical properties of chitosan fibers obtained by wet-spinning using chitosan– [Gly]Cl (glycine chloride) ionic liquid as spinning dope solution are reported for the first time. The objectives were to understand both how the microstructure of the fibers could be modified and how the mechanical properties were improved by means of using [Gly]Cl ionic liquid as the spinning solution. In the new system, the main component chitosan (the degree of deacetylation was 86%, the molecular weight was about  $1.5 \times 10^6$ ) was dissolved in an aqueous [Gly]Cl ionic liquid solution; the fibers were then spun using a sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>)/ethanol (C<sub>2</sub>H<sub>5</sub>OH) aqueous solution as the coagulant, and then directly dried under freeze-drying. The fibers spun from the above mentioned system have the chitosan I crystal form, and the breaking tenacity ( $3.77 \text{ cN dtex}^{-1}$ ) is 4 times more than that ( $0.86 \text{ cN dtex}^{-1}$ ) from an acetic acid system. The orientation and crystallinity of fibers spun in [Gly]Cl solution was enhanced with an increase of spin stretch ratio, and thereby the mechanical properties of the fibers were improved. Moreover, the fibers had a smooth surface as well as a round and compact structure. More to the point, the used [Gly]Cl could be recovered by simple post processing and the chitosan fibers spun in the recycled [Gly]Cl solution also had a strong breaking tenacity. Therefore, this study verified that [Gly]Cl is a new spinning dope solution for preparing chitosan fibers with strong mechanical properties.

# 1. Introduction

Chitosan is widely used in the pharmaceutical and biomedical fields for its bioresorbability,<sup>1</sup> biocompatibility,<sup>2</sup> degradability<sup>3</sup> and non-toxicity.<sup>4</sup> Moreover, it plays an important role in cell regulation and tissue regeneration.<sup>5,6</sup> In this context, the technology of preparing chitosan fibers is a hot topic in the field of ecological materials.

Chitosan is readily soluble in most aqueous acid solutions, such as acetic acid, because of the basicity of the primary amine groups, and several research groups have prepared wet-spun chitosan fibers using aqueous acidic solutions with aqueous alkaline coagulating baths.<sup>7</sup> However, the poor tensile strength of chitosan fibers, especially in the wet state, is a key deficiency.

Numerous methods are available for improving the mechanical properties of chitosan fibers. Chemical modifications of wet-spun chitosan fibers, which are widely studied, involve the use of crosslinking agents such as epichlorohydrin<sup>8,9</sup> during the coagulation step, post-treatments with glyoxal,<sup>10-12</sup> or glutaraldehyde,<sup>11</sup> or the immersion of fibers in solutions containing phosphate and phthalate ions, polyhedral oligomeric silsesquioxane (POSS) and single-walled carbon nanotubes (SWNT).13,14 In the meantime, some literature provides significant information regarding physical treatments to improve the mechanical properties of wetspun chitosan fibers. The studies of Qin15 and Knaul16 demonstrated that the Young's modulus and tenacity could be improved by increasing the draw ratio in the washing and drawing baths, and possibly via the drying step, and the influence of the jet-stretching ratio was discussed.<sup>17</sup> Although the mechanical properties of chitosan fibers could be improved by physical or chemical methods, the two methods still have drawbacks. For a chemical method, some chemical assistants will be added to the chitosan fibers, and these assistants may affect the antibiotic property of the chitosan fibers. A physical method, which could not change the composition of the chitosan fibers, would need specific equipment and treatments in the process. For jet-stretching,17 compared with the traditional method, an ammonia tank would need to be added, which brings great safety concerns to the process. At the same time, both physical methods

<sup>&</sup>lt;sup>a</sup>College of Chemical Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao 266042, P. R. China. E-mail: yushitaoqust@126.com; Fax: +86 0532 84022719; Tel: +86 0532 84022864

<sup>&</sup>lt;sup>b</sup>Key Laboratory of Eco-Chemical Engineering, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao 266042, P. R. China

<sup>&</sup>lt;sup>c</sup>College of Chemistry, Chemical Engineering & Environment, Qingdao University, 308 Ningxia Road, Qingdao 266071, P. R. China

<sup>&</sup>lt;sup>d</sup>College of Materials Science and Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao 266042, P. R. China

and chemical methods use chitosan-acetic acid as the spinning dope solution. The usage of acetic acid has many drawbacks such as toxicity, strong volatility and pollution; in addition, it is difficult to recover the used acetic acid. Therefore, based on previous work on the preparation of wet-spun chitosan fibers, our work aims to develop a new strategy to improve the mechanical properties of wet-spun chitosan fibers through optimizing the spinning dope solution, not through post-treatments. As is well known, the mechanical properties of chitosan fibers are due to the structure of the chitosan molecular chain in the fiber. Natural chitosan has a complex inter- and intra-molecular hydrogen-bond network, which makes it insoluble in water and leads to the chitosan molecule being curled.<sup>18</sup> In the normal process of preparing the chitosan spinning dope solution, the solvent could cut the inter- and intra-molecular hydrogen bonds, and with the fracture of the hydrogen bonds, the curled chitosan molecule becomes more linear. At the same time, the chain becomes even more regular after drawing during the process of spinning, so the tensile strength of the chitosan fibers is increased.<sup>19</sup> In other words, the more regular the linear array of chitosan molecules, the better the mechanical properties of the wet-spun fibers. From the above mechanism, the interaction between the solvent and chitosan in the spinning dope solution is the major factor which affects the structure of the wet-spun chitosan. Therefore, to design a new green solvent that could make the chitosan molecules tend towards a linear arrangement in the spinning dope solution will be a strategy to improve the mechanical properties of wet-spun chitosan fibers.

Ionic liquids (ILs) are promising alternatives of "green solvents" for their properties such as negligible vapor pressure, broad liquid regions, high thermal stabilities, and no burning or explosive point.<sup>20</sup> ILs widely possess excellent solubility for inorganic compounds, organic compounds and polymer materials, so they have been used in the fields of electrochemistry, organic synthesis, separation and materials preparation.<sup>21</sup> It has been reported that ionic liquids show good solubility for cellulose,<sup>22</sup> whose structure is similar to that of chitosan. Therefore, it was possible to discover optimal ILs for dissolving chitosan via designing the anion and cation of ionic liquids. However, chitin may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group.23,24 Both are polymers of monosaccharides made up of β-(1-4)-2-acetamido-2-deoxy-β-dglucose and  $\beta$ -(1-4)-2-deoxy- $\beta$ -d- glucopyranose units, respectively (Fig. 1). Chitosan is the N-deacetylated derivative of chitin with a typical DA (degree of acetylation) of less than 0.35 (Fig. 1). It is, thus, a copolymer composed of glucosamine and Nacetylglucosamine. Natural chitosan forms a more complex inter- and intra-molecular hydrogen-bond network than cellulose, due to the existence of an additional acetoamide or amino group in its structural repeating unit. In addition, making up the skeletons of many animals such as crustaceans, chitosan is generally found to have larger molecular weights than cellulose which is mainly derived from plants. As a result, it is generally more difficult to dissolve chitosan than cellulose materials. Previous studies on dissolving 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-.25 However, our preliminary experiments showed that those imidazolyl

chlorinated ILs reported to be good solvents of cellulose could not dissolve chitosan at room temperature.<sup>26</sup> It is well known that 2% acetic acid solvent can dissolve chitosan well at room temperature. Therefore, we suggest that ILs that is composed of -COOH and -Cl can be potential solvents of chitosan. For this reason, [Gly]Cl was designed and synthesized to test its solubility towards chitosan. Fortunately, our study verified that [Gly]Cl was an excellent solvent for chitosan. Moreover, to reduce the viscosity, the above IL was diluted to give a series of aqueous solutions with different concentrations. Among these, an IL aqueous solvent system with stronger dissolving ability, lower viscosity and slight degradation of chitosan was selected. Therefore, an environmentally friendly and efficient solvent system for wet-spun chitosan fibers was obtained. In this study, the chitosan fibers were prepared via [Gly]Cl-aqueous solvent as the dope in a wet spinning process and the morphology and mechanical properties of the spun fibers were examined. A preliminary report of this work has been presented elsewhere.<sup>26</sup>

# 2. Experimental

## 2.1 Materials

Chitosan (the degree of deacetylation was 86% and molecular weight was about  $1.5 \times 10^6$ ) was received from Yuhuan Chem. Co. Ltd and the material was directly used after drying without further purification. All the other reagents were purchased from Aldrich.



Fig. 1 Chemical structures of chitosan, chitin and cellulose.



Fig. 3 Curves of apparent viscosity vs. shear rate about chitosan/4% [Gly]Cl spinning dope solution.

**Table 1** Effect of composition and temperature of coagulation on the<br/>properties of chitosan fibers (dope: 6.5% chitosan in 4% [Gly]Cl, extru-<br/>sion rate: 13.6 m min<sup>-1</sup>, stretching ratio: 1.2, yarn dried with freeze<br/>drying;  $T = 20 \pm 2$  °C, water content =  $(35 \pm 5)\%$  (w/w); "—" Na<sub>2</sub>SO<sub>4</sub><br/>precipitation, a: volume ratio v(2% Na<sub>2</sub>SO<sub>4</sub> aqueous<br/>solution):  $v(C_2H_5OH)$ )

	Breaking tenacity/cN dtex <sup>-1</sup>										
Volume ratio	10 °C	15 °C	20 °C	25 °C	30 °C						
10:1	0.21	0.30	0.42	0.45	0.23						
10:2	0.39	0.42	0.58	0.65	0.35						
10:3	0.56	0.88	1.28	1.30	0.43						
10:4	0.63	0.90	1.03	1.15	0.44						
10:5	0.62	0.92	0.95	1.01	0.46						
10:6	_	—	_	—	0.47						



Fig. 4 The XRD of native chitosan and chitosan in solution.



Fig. 5 The XRD of native chitosan and chitosan fibers.

#### 2.2 Preparation and characterization of IL

[Gly]Cl was synthesized according to the method reported in the literature.<sup>27</sup> H<sub>2</sub>O (0.55 mol) and HCl (0.08 mol, 36%) were added into a flask (100 mL) with a stirrer, thermometer, Allihn-type condenser and constant pressure spherical drop funnel. The mixture was stirred while Gly (0.05 mol) was slowly added to the

**Table 2** Influence of different spinning dope solutions on the mechanical properties of chitosan fibers (dope: A: 6.5% chitosan in 4% [Gly]Cl, B: 6.5% chitosan in 4% acetic acid; extrusion rate: 13.6 m min<sup>-1</sup>, stretching ratio: 1.4, yarn dried with freeze drying;  $T = 20 \pm 2$  °C, water content = (35 ± 5)% (w/w))

	Breaking strength/cN			Breaking tenacity/ cN dtex <sup>-1</sup>			Elongation at break (%)			Initial modulus/cN dtex <sup>-1</sup>		
Dope		Max	Min		Max	Min		Max	Min		Max	Min
Acetic acid [Gly]Cl	3.72 11.13	4.47 13.9	2.89 9.63	0.86 3.77	1.04 4.83	0.67 3.21	1.58 1.91	2.28 3.47	1.06 0.47	0.19 2.30	0.32 2.87	0.04 1.53



**Fig. 6** Schematic illustration of transformations of curly chitosan to linear chitosan during the process of fiber preparation by dissolving chitosan in [Gly]Cl.



**Fig. 7** Curves of shear stress *vs.* shear rate of the different systems. A: 6.5% chitosan/4% acetic acid and B: 6.5% chitosan/4% [Gly]Cl.



Fig. 8 The morphology of cross-sections of chitosan fibers from the different spinning dopes.

flask. After Gly was dissolved in the mixture, the flask was heated to 60 °C and the reaction was carried out at 60 °C for 8 h. When the reaction was completed, the flask was allowed to cool to room temperature and then water was removed by vacuum to obtain a white solid. The white product was washed by ethyl acetate. The resulting white precipitate [Gly]Cl was isolated by filtration then dried in vacuo at 60 °C for 24 h. Yield: 5.08 g (91%). The structure of the IL was verified by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and FT-IR. [Glv]Cl: <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O): δ 3.78 (s, 2H), 4.70 (s, 1H); <sup>13</sup>C-NMR  $(125 \text{ MHz}, D_2 \text{O})$ :  $\delta 40.13$ , 170.08. The structure was as follows: Cl [\*NH<sub>3</sub>-CH<sub>2</sub>-COOH] IR (KBr): v 3434 (v, -NH<sub>3</sub>\*\* -CH<sub>2</sub>-COOH\*),  $3009 (\upsilon_{as}, -CH_2*-COOH), 1714 (\upsilon_{as}, -C=O*), 1596 (\delta,$ -NH3\*+), 1495 (δ, -CH2\*-CO-), 1423 (δ, -COOH\*), 1255 (υ, -C-O\*), 1117 (υ, -N-C\*), 903 (ω, -O-H\*), 861 (δ, -N-H\*), 638, 496. The NMR spectra of the ionic liquid were recorded with a 500 MHz Bruker spectrometer in DMSO or CDCl<sub>3</sub> and calibrated with tetramethylsilane (TMS) as the internal reference. FT-IR was recorded with a Nicolet-510P. The spectra were collected over the range of 4000-400 cm<sup>-1</sup>.

#### 2.3 Preparation of spinning dope solution

A typical spinning dope solution was prepared by dissolving chitosan in 400 mL of 4% acetic acid (w/w) or 4% [Gly]Cl (w/w) aqueous solution at 30 °C. The chitosan powder was slowly added to the solution to make sure the chitosan could be completely dissolved. The dissolving process was observed by a polarizing microscope. When the chitosan was completely dissolved in the acetic acid or IL, a black field could be observed through a polarizing microscope. Different concentrations (w/w %) of chitosan/4% acetic acid or chitosan/4% [Gly]Cl were prepared: 5% (21 g), 6% (25.5 g), 6.5% (27.8 g) and 7% (30.1 g). The concentrationa of the spinning dope solutions of chitosan/4% [Gly]Cl were determined by rheological experiment (Section 2.7). When the effect of urea on the properties of the fibers was studied, urea was added to the chitosan/4% [Gly]Cl solution, and the amount of urea was w(urea) : w(chitosan) = 1 : 100.

#### 2.4 Wet spinning of chitosan fibers

The spinning dope solution was filtered through a candle filter system before adding it to the reservoir of the spinning system, where it was degassed under vacuum. A laboratory scale extrusion unit was used (Fig. 2), comprised of a reservoir, a metering pump (1 mL rev<sup>-1</sup>), and a spinneret (20 holes, 80 pm diameter). The filaments were coagulated in a dilute Na<sub>2</sub>SO<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH bath, with an immersion length of *ca.* 100 cm. The take-up rollers, drawing system, drying rollers, and the winding up procedure were described previously. The filaments were washed and dried by freeze-drying.

#### 2.5 Regeneration and recycling of [Gly]Cl

After spinning, the solution in the coagulation bath and washing bath was gathered into a flask, and then was distilled. During the distillation, the solution became thicker and  $Na_2SO_4$  salt was precipitated. At this time, the distillation was terminated and the flask was allowed to cool to room temperature. The  $Na_2SO_4$  was isolated by filtration and then dried *in vacuo* at 60 °C for 24 h; the recovery rate of  $Na_2SO_4$  was above 95%. The filtrate was

**Table 3** Influence of different stretching ratios on the mechanical properties of chitosan fibers (dope: 6.5% chitosan in 4% [Gly]Cl, extrusion rate: 13.6 m min<sup>-1</sup>, yarn dried with freeze drying;  $T = 20 \pm 2$  °C, water content =  $(35 \pm 5)\%$  (w/w))

~	Breaking strength/cN			Breaking tenacity/ cN dtex <sup>-1</sup>			Elongation at break (%)			Initial modulus/cN dtex <sup>-1</sup>		
ratio		Max	Min		Max	Min		Max	Min		Max	Min
1.1	5.35	6.62	3.40	0.85	1.10	0.54	0.83	1.38	0.22	0.23	0.38	0.10
1.2	5.45	6.69	3.78	1.27	1.53	0.95	0.94	1.45	0.37	0.24	0.42	0.15
1.3	13.32	14.25	12.45	2.90	3.25	2.67	1.68	1.89	0.96	1.82	1.99	1.58
1.4	11.13	13.9	9.63	3.77	4.83	3.21	1.91	3.47	0.47	2.30	2.87	1.53



**Fig. 9** SEM of chitosan fibers of different stretching ratios formed by wet spinning.

a mixture of [Gly]Cl and water, and here it was assumed that the [Gly]Cl was not lost during the process of recuperation. Some water was then added to the mixture to give 400 mL solution (reservoir volume is 500 mL), and chitosan was added to the solution to prepare a spinning dope solution according to the method in section 2.3. The amount of chitosan was  $\leq 27.8$  g, because the spinning dope solution of 6.5% chitosan/4% [Gly]Cl has 27.8 g chitosan.

### 2.6 Characterization of chitosan or chitosan fibers

The mechanical properties of the chitosan yarn samples, such as the breaking strength, breaking tenacity, elongation at break, and initial modulus, were measured on an Instron tensile tester,



Fig. 10 SEM showing the effect of urea on the morphology of chitosan fibers.

model 1122, with load cell-type 1105. The gauge length was 20 mm and the extension rate was 20 mm min<sup>-1</sup>. The test was performed at 20 °C, 65% R.H. The figures quoted are the averages of 10 tests; the standard deviation was generally less than 5%. When required, tests were also performed on yarns previously immersed in water at room temperature, to obtain wet strength values.

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

X-ray powder diffraction patterns of the samples were obtained on a XB-3A instrument using monochromatic Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm). It was operated at 40 kV and 100 mA. The experimental conditions correspond to a step width of 0.02° and scan speed of  $2\theta$  min<sup>-1</sup> and diffraction region  $2\theta = 10-60^\circ$ .

The average diameter of fibers was evaluated using a transmission optical microscope (Leitz), from 10 values measured on different points of the monofilament.

The denier (D = weight (g) per 9000 m of monofilament) of each chitosan fiber sample was determined by weighing at least 20 m of chitosan monofilament. The length (L) of the monofilament was determined by two methods. The first method measured the length of several fibers to achieve a sufficient total

**Table 4** Influence of textile assistant (urea) on the mechanical properties of chitosan fibers (dope: w(urea) : w(chitosan) = 1 : 100, 6.5% chitosan in 4% [Gly]Cl, extrusion rate: 13.6 m min<sup>-1</sup>, stretching ratio: 1.3, yarn dried with freeze drying;  $T = 20 \pm 2$  °C, water content =  $(35 \pm 5)\%$  (w/w))

Textile assistant	Breaking strength/cN			Breaking tenacity/ cN dtex <sup>-1</sup>			Elongation at break (%)			Initial modulus/cN dtex <sup>-1</sup>		
		Max	Min		Max	Min		Max	Min		Max	Min
Urea No	15.63 13.32	18.35 14.25	13.16 12.45	1.82 2.90	2.19 3.25	1.50 2.67	1.06 1.68	2.12 1.89	0.28 0.96	0.91 1.82	1.00 1.99	0.82 1.58



Fig. 11 The effect of urea on the structure of chitosan in [Gly]Cl solvent.

length over 20 m. The results of the pilot method controlled the second one. Thus, the length was the result of the multiplication of the time of spinning (min) by the roller 2 speed ( $v_2$  in m min<sup>-1</sup>). In both cases, the precision was  $10^{-3}$  g. An average denier was calculated from the two methods.

After measuring the diameter and the denier of each sample of fiber, we could deduce their density by the following equation:<sup>28</sup>

$$d = 20\sqrt{\frac{W}{\pi\rho}}$$
 or  $d = 20\sqrt{\frac{10D/9}{\pi\rho}}$ 

where d is the diameter ( $\mu$ m), W the weight of 10000 m of monofilament (dtex),  $\rho$  the density (g cm<sup>-3</sup>) and D the denier.

#### 2.7 Rheological experiment on chitosan solvent

A solution (100 mL) containing a certain amount of chitosan was prepared by dissolving the chitosan powder in distilled water containing 4% acetic acid or 4% [Gly]Cl at room temperature. The chitosan solution was then filtered and subsequently sonicated to remove trapped air bubbles. The final product (chitosan/ 4% acetic acid solution or chitosan/4% [Gly]Cl solution) had a light yellow color and a pH of 5-6. The rheological characterization of the hydrogel samples was performed in a C-VOR rheometer from Bohlin Instruments, Inc., USA, fitted with a cone-and-plate geometry (cone angle of  $4^{\circ}$  and diameter of 20 mm or 40 mm) and a circulating environmental system for temperature control. The rheometer used is a shear stress controlled instrument that consists of applying a torque (force) and measuring the resultant displacement (movement). Torque and displacement are converted to "rheological format" by means of the measuring system constants. To prevent drying of the samples during experiments, a steel ring of 60 mm was placed around the measuring geometry, the annulus was filled with water, and the sample holding region was sealed with an insulated cover. As soon as the sample was introduced onto the plate, the data were collected. The test methods employed were oscillatory temperature, time, stress, and frequency sweeps at a constant temperature of 25 °C and a pH of 5-6.

#### 3. Results and discussion

#### 3.1 Concentration of spinning dope solution

The parameter of viscosity was regarded as the primary criterion for the selection of a suitable concentration of chitosan/4% [Gly] Cl spinning solution. Fig. 3 shows the flow curves of the chitosan/ 4% [Gly]Cl solutions of various concentrations. It can be seen from Fig. 3 that the chitosan/4% [Gly]Cl solution is a shearthinning fluid that belongs to the class of non-Newtonian fluids. As the concentration increases, the shape of the curve changes gradually from near Newtonian behavior, at a solution concentration of 5%, to non-Newtonian shear thinning at higher concentrations. The solution viscosity was low when the chitosan content was below 6%. Dramatic increases in solution viscosity occurred at higher chitosan concentrations, with the 7% solution showing a viscosity of more than 340 poises. The 6% solution showed a solution viscosity of about 87.6 poises, but 100 poises is typical of a wet spinning solution. A 6.5% chitosan solution was, therefore, used as the spinning dope.15

#### 3.2 Composition and temperature of coagulation bath

The spinning dope solution of chitosan was spurted out from the spinning jet into the coagulation bath one and two, and in the coagulation bath the thread of chitosan and the coagulator were interdiffused to form the chitosan fiber.

**Table 5** The mechanical properties of chitosan fibers from regeneration of [Gly]Cl as the solution (dope: 6.5 or 5.9% chitosan in 4% [Gly]Cl, extrusion rate: 13.6 m min<sup>-1</sup>, stretching ratio: 1.3, yarn dried with freeze drying;  $T = 20 \pm 2$  °C, water content = (35 ± 5)% (w/w))

		Breaking strength/cN			Breaking tenacity/ cN dtex <sup>-1</sup>			Elongation at break (%)			Initial modulus/ cN dtex <sup>-1</sup>		
No.	Amount of chitosan/g		Max	Min		Max	Min		Max	Min		Max	Min
1	26.0	13.32	14.25	12.45	2.90	3.25	2.67	1.68	1.89	0.96	1.82	1.99	1.58
2	26.0	12.85	13.45	11.32	2.44	3.05	2.57	0.58	0.83	0.24	1.52	1.78	1.02
3	23.6	11.37	13.21	10.22	1.80	2.89	1.43	0.63	0.87	0.27	0.93	1.23	0.75

In the traditional wet-spinning method, acetic acid is often used as the solution, and the coagulator is a mixture of NaOH and  $C_2H_5OH$  aqueous solution.<sup>14,29,30</sup> NaOH can neutralize acetic acid interdiffused from the spinning dope solution and  $C_2H_5OH$  can accelerate interdiffusion between the spinning dope solution and coagulator and improve the form of the chitosan fibers. When [Gly]Cl was used as the solution, a mixture of NaOH and  $C_2H_5OH$  aqueous solution was also used as the coagulator to prepare chitosan fibers with excellent properties. However, NaOH can react with the carboxylic group of [Gly]Cl to form the sodium salt so the [Gly]Cl is difficult to recover. Therefore, it is important to find a new coagulator that can promote the form of the chitosan fibers and be beneficial for the regeneration of [Gly]Cl.

Na<sub>2</sub>SO<sub>4</sub> aqueous solution can promote dehydration of mucilage glue to form fibers,<sup>15,31</sup> which is a good inspiration for the present work.  $SO_4^{2-}$  can improve the thread of chitosan to keep their micelle and form the fibers by the effect of static electricity between macromolecule chains. Here a mixture of 2% Na<sub>2</sub>SO<sub>4</sub> aqueous solution and C<sub>2</sub>H<sub>5</sub>OH at different ratios was investigated to determine a suitable ratio mixture as coagulator, and the results can be seen in Table 1. At 20-25 °C, when the ratio of 2%  $Na_2SO_4/C_2H_5OH$  in the aqueous solution was too high, the surface of the chitosan fiber was quickly solidified, leaving the gel-like middle part of the fiber, and thus the fiber was badly prepared with poor morphological and mechanical properties. When the ratio of 2% Na<sub>2</sub>SO<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH in the aqueous solution was too low, the fiber was formed slowly, also causing unsatisfactory mechanical properties. For a balanced ratio, a mixture of  $v(2\% \text{ Na}_2\text{SO}_4)$ :  $v(C_2H_5\text{OH}) = 10:3$  was a suitable coagulator. At the same time, the effect of the coagulation temperature was investigated. From Table 1 it can be seen that the chitosan fibers had the best mechanical properties at 20-25 °C. When the temperature was 30 °C, the fiber was rapidly formed but sometimes broken due to the intensive molecular movement. When the temperature was below 20 °C, the fiber was slowly formed and the solubility of Na<sub>2</sub>SO<sub>4</sub> in the water and ethanol decreased. In conclusion, the mixture of  $v(2\% \text{ Na}_2\text{SO}_4) : v(\text{C}_2\text{H}_5\text{OH}) =$ 10: 3 was selected as coagulator and the process of coagulation was carried out at 20-25 °C.

# 3.3 Preparation of chitosan fibers using chitosan-[Gly]Cl as spinning dope solution

The traditional wet spinning for preparing the chitosan fibers is as follows: a solution of 6.5% chitosan/4% acetic acid as dope, 2% NaOH as coagulating bath.<sup>6</sup> According to the above test, we first carried out wet spinning for preparing chitosan fibers using a 6.5% chitosan/4% [Gly]Cl solution as dope and a mixture of  $v(2\% \text{ Na}_2\text{SO}_4) : v(\text{C}_2\text{H}_5\text{OH}) = 10 : 3$  as coagulating bath. At the same time, the mechanical properties of the fibers prepared by the new path were investigated, and the results can be found in Tables 2 and 3.

The mechanical properties of fibers using chitosan/[Gly]Cl as the dope are better than those fibers using chitosan/acetic acid as the dope, as the breaking tenacity increased from 0.86 to 3.77 (Table 2). This result commendably confirms our opinion. The XRD profiles of chitosan in different solutions, chitosan fibers from different dopes and native chitosan are shown in Fig. 4 and

Fig. 5. From Fig. 4, it can be seen that chitosan/IL and chitosan/acetic acid show a slight, broad diffraction peak centered near  $2\theta = 28^\circ$ , which can not be eliminated by decreasing the chitosan concentration or prolonging the time of dissolution, and no diffraction peak centered near  $2\theta = 12^{\circ}$  compared with crystalline chitosan. This result implies that the crystalline domains in the chitosan particles are incompletely disrupted by [Glv]Cl or acetic acid during the dissolving process. Anyway, we can conceive that such a treatment should make chitosan more flexible than crystalline chitosan.<sup>32</sup> For Fig. 5, the chitosan fibers from [Gly]Cl are still type I configuration, but the chitosan fibers from acetic acid are changed to amorphous because the diffraction peak centered near  $2\theta = 12^{\circ}$  disappears and the diffraction peak near  $2\theta = 20^{\circ}$  is weak and broad. It is well known that chitosan type I has stronger molecular forces than amorphous chitosan,33,34 so the chitosan fibers from [Gly]Cl has stronger mechanical properties than those from acetic acid. Therefore, we design the schematic illustration of the transformation of curly chitosan to linear chitosan during the process of fiber preparation by dissolving chitosan in [Gly]Cl. In a solution of chitosan/ [Gly]Cl, [Gly]Cl is a strong electrolyte, and [Gly]<sup>+</sup> and Cl<sup>-</sup> uniformly distribute in water in ionic form. Even more importantly, [Gly]<sup>+</sup> can easily enter the network structure of chitosan to disrupt the inter- and intra-molecular hydrogen bonds (Fig. 6). In addition, chitosan is a cationic polyelectrolyte in dilute acid solution, and [Gly]<sup>+</sup> increases the repulsion between cations in the chitosan molecules, which further stretches the chitosan molecular chain in solution and prompts curly chitosan molecules to become linear; at the same time, the chitosan molecules are rearranged to increase the strength of the fibers in the drawing force.35

Furthermore, in acetic acid solvent, the extensibility of chitosan molecules is poor and the breaking tenacity of the fibers is also poor. From Fig. 7, it can be seen that at low shearing rates regions of the flow curve, the initial slope of 6.5% chitosan/4% acetic acid is steeper than that of 6.5% chitosan/4% [Gly]Cl. It is suggested that the degree of tangling of chitosan molecular chains is high in acetic acid and the high aggregative state strengthens the force of hydrogen bonding between the chitosan molecules.<sup>36</sup> Besides the force of the hydrogen bonds, van der Waals' forces between the chitosan molecules form a physical cross-linking point, and the active power decreases at room temperature, so that the extensibility of the fibers from acetic acid is weaker than that of those from [Gly]Cl, in agreement with the results of the mechanical properties.<sup>36</sup> On the other side, SEM was be used to observe cross-sections of fibers from acetic acid and [Gly]Cl (Fig. 8). From the images, it can be seen that the cross-sectional area of the fibers is approximately circular and hence the fibers could be cylindrical. The fracture surface of the fiber from acetic acid is rough, uneven and inadequate (Fig. 8); the fracture surface of the fiber from [Gly]Cl is uniform, smooth and adequate, and the results prove the above deduction. It is well known that the intensity of the fiber is due to the orientation of chitosan molecule and the modulus is due to the crystallinity. With the increasing degree of orientation, the degree of order and crystallinity was enhanced, and furthermore, the strength and modulus of the fibers was amplified and the breaking elongation lessened. The results are in agreement with the XRD.

When the dope was ejected from the spinneret orifice, the fiber received the force of extrusion and friction from the ambient spinneret orifice, and the force caused orderly macromolecular association of the fibers to arrange along the axis of the orifice.13 However, the orientation of the fibers is unstable, and a swelling effect can be produced during the process of fiber extrusion, and meanwhile the effect leads to a macromolecule of newly disordered astatic state after being ejected. Therefore, the only way to enhance the strength of the fibers is by drawing. In this part, the mechanical properties and morphology of the chitosan fibers are investigated after drawing to stretching ratios of 1.1, 1.2, 1.3 and 1.4 (Table 3). From the data of Table 3, with the increase of drawing times, the fibers are obviously strengthened and tenacity strength hugely enhanced. In addition, the toughness and strength of the fibers are improved; it is agreed to use chitosan/ acetic acid as the dope. It can also be seen from the SEM (Fig. 9); the fiber is smoother and denser with the increasing of drawing time. It is suggested that with the increasing of drawing times, macromolecular fibers are more uniformly arranged along the direction of the force.37

# 3.4 Effect of addition agent on the mechanical properties of chitosan fibers

So far, the effect of an addition agent on the structure of the chitosan molecule in acid solvent has been widely studied by researchers.35 Chen38,39 studied the effect of urea on the conformational change of chitosan. The results showed that urea made the conformation of the chitosan molecules extend, and the molecular conformation even changed when the amount of urea added was enough. In this part, urea was added to the dope of chitosan/[Gly]Cl to improve the strength of the chitosan fibers. However, from the mechanical properties of the chitosan fibers, the properties of the fibers without urea are better than of those with urea (Table 4). It was also observed that the surface of the fibers was rough from SEM (Fig. 10). The reason may be that [Gly]<sup>+</sup> can easily enter the network structure of chitosan to disrupt the inter- and intra-molecular hydrogen bonds (Fig. 11). In addition, chitosan is a cationic polyelectrolyte in dilute acid solution, and [Gly]<sup>+</sup> increases the repulsion between cations in the chitosan molecules, which causes further stretching of the chitosan molecular chain in solution and prompts curly chitosan molecules to become linear. When urea was added, -NH2 could competitively form new hydrogen bonds with chitosan, which shields the positive charge of the chitosan molecule. As a result, the intermolecular repulsion decreased, the linear structure recovered to the curly structure, and finally the viscosity of the dope was low and the properties of the fibers dropped.<sup>40</sup>

#### 3.5 Regeneration of [Gly]Cl as the solution

The regenerated [Gly]Cl was used as a solution to dissolve chitosan to prepare a spinning dope solution. The properties of chitosan fibers prepared using the recycled [Gly]Cl are shown in Table 5. From Table 5 it can be seen that the solubility of [Gly]Cl was not obviously decreased and the chitosan fibers also had good properties when [Gly]Cl was used twice. It is suggested that [Gly]Cl is of excellent stability and can be recycled. However, during the regeneration process, the loss of [Gly]Cl can not be avoided, so the solubility of [Gly]Cl for chitosan decreased resulting in the properties of the chitosan fibers decreased.

## 4. Conclusions

In this paper, we reported a new solvent, that is [Gly]Cl, for chitosan materials. The results from XRD experiments suggested that the chitosan fibers from [Gly]Cl have a crystal structure close to type I, the same as the native chitosan, and the chitosan fibers from acetic acid have a crystal structure close to type II, implying that a transition of crystal form may occur during the dissolving and the recovery processes. On the basis of these results, it is possible to establish a new biomass-ionic liquid platform (BILP) for processing and homogeneous chemical modifications of chitosan. Such a BILP can be also used as a pretreatment technique for many heterogeneous chemical reactions and enzyme degradations in chitosan-based polysaccharides. We then demonstrated that chitosan fibers exhibited good mechanical properties by using 6.5% chitosan (Mw =  $1.5 \times$ 10<sup>6</sup>)/4% [Gly]Cl as a spinning dope solution, without any agents or post-treatments commonly used in the literature. The increase of breaking tenacity (from 0.86 to 3.77 cN dex<sup>-1</sup>) and initial modulus (from 0.19 to 2.3) of the stretched fibers could be explained considering the evolution of the morphological properties. Moreover, [Gly]Cl has excellent stability as the chitosan fibers have good properties using recycled [Glv]Cl as a solution. It is important to underline that the results, in term of the mechanical properties, of the chitosan fibers obtained by using chitosan/[Gly]Cl as a dope from our gel-spinning process, are better than in previous studies. Thus, the improved mechanical properties of the wet-spun chitosan fibers prepared in this study should contribute to their use in biomedical applications as hernioplasty, suturation or wrinkle filling. They are also particularly useful for making materials such as yarns and woven, nonwoven or knitted fabrics.

## Acknowledgements

The authors thank Program of 863 (2009AA03Z426), National Natural Science Foundation of China (No.20876080 and 21106074), High-Tech Innovation Project Specialized Plan of Shandong Province (2007ZCB01369) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (20093719110002), Application foundation projects of Qingdao (10-3-4-4-11-jch), Shandong outstanding young and middle-aged scientist research award funded projects (BS2009 CL033) for financial support.

# References

- H. Tang, P. Zhang, T. L. Kieft, S. J. Ryan and S. M. Baker, Antibacterial action of a novel functionalized chitosan-arginine against Gram-negative bacteria, *Acta Biomater.*, 2010, 6, 2562–2571.
- 2 R. H. Fu, S. P. Liu, C. W. Ou, C. M. Huang and Y. C. Wang, Spatial control of cells, peptide delivery and dynamic monitoring of cellular physiology with chitosan-assisted dual color quantum dot FRET peptides, *Acta Biomater.*, 2010, 6, 3621–3629.
- 3 R. D. Souza, P. Zahedi, C. J. Allen and P. M. Micheline, Biocompatibility of injectable chitosan-phospholipid implant systems, *Biomaterials*, 2009, 30, 3818–3824.

- 4 L. Wang and J. P. Stegemann, Glyoxal crosslinking of cell-seeded chitosan/collagen hydrogels for bone regeneration, *Acta Biomater.*, 2011, **7**, 2410–2417.
- 5 M. Dash, F. Chiellini, R. M. Ottenbrite and E. Chiellini, Chitosana versatile semisynthetic polymer in biomedical applications, *Prog. Polym. Sci.*, 2011, **36**, 981–1014.
- 6 W. S. Xia, P. Liu, J. L. Zhang and J. Chen, Bioogical activities of chitosan and chitooligosaccharides, *Food Hydrocolloids*, 2011, 25, 170–179.
- 7 Fuji Spinning Co. Ltd., Method for manufacturing chitosan fiber, Japanese Patent 6059123, 1985.
- 8 Y. C. Wei, S. M. Hudson, J. M. Mayer and D. L. Kaplan, The crosslinking of chitosan fibers, J. Polym. Sci, 1992, 30, 2187–2193.
- 9 S. H. Lee, S. Y. Park and J. H. Choi, Fiber formation and physical properties of chitosan fiber crosslinked by epichlorohydrin in a wet spinning system: The effect of the concentration of the crosslinking agent epichlorohydrin, J. Appl. Polym. Sci., 2004, 92, 2054–2062.
- 10 Q. Yang, F. Dou, B. Liang and Q. Shen, Studies of cross-linking reaction on chitosan fiber with glyoxal, *Carbohydr. Polym.*, 2005, 59, 205–210.
- 11 J. Z. Knaul, S. M. Hudson and K. A. M. Creber, Crosslinking of chitosan fibers with dialdehydes: Proposal of a new reaction mechanism, J. Polym. Sci., 1999, 37, 1079–1094.
- 12 S. Hirano, K. Nagamura and M. Zhang, Chitosan staple fibers and their chemical modification with some aldehydes, *Carbohydr. Polym.*, 1999, **38**, 293–298.
- 13 J. Z. Knaul, S. M. Hudson and K. A. M. Creber, Improved mechanical properties of chitosan fibers, *J. Appl. Polym. Sci.*, 1999, 72, 1721–1732.
- 14 J. Chen, L. S. Loo and K. Wang, Enhanced mechanical properties of novel chitosan nanocomposite fibers, *Carbohydr. Polym.*, 2011, 86, 1151–1156.
- 15 C. E. George and Y. Qin, Wet spinning of chitosan and the acetylation of chitosan fibers, *J. Appl. Polym. Sci.*, 1993, **50**, 1773–1779.
- 16 J. Z. Knaul, PhD thesis, *Improved mechanical properties of chitosan fibers*, Royal Military College of Canada, Kingston, Ont., Canada, 1998.
- 17 N. Laure, V. Christophe, A. Pierre, R. Cyrille and D. Alain, Morphology and mechanical properties of chitosan fibers obtained by gel-spinning: Influence of the dry-jet-stretching step and ageing, *Acta Biomater.*, 2006, 2, 387–402.
- 18 C. E. Bracker, J. R. Herrera and S. B. Garcia, *Chitin*, Pergamon Press, Oxford, 1977.
- 19 W. P. Ban, J. G. Song, D. S. Argyropoulos and L. A. Lucia, *Ind. Eng. Chem. Res.*, 2006, 45, 627–633.
- 20 C. B. Yue, D. Fang, L. Liu and T. F. Yi, Synthesis and application of task-specific ionic liquids used as catalysts and/or solvents in organic unit reactions, *J. Mol. Liq.*, 2011, 163, 99–121.
- 21 C. Wang, W. J. Zhao, H. R. Li and L. P. Guo, Solvent-free synthesis of unsaturated ketones by the Saucy–Marbet reaction using simple ammonium ionic liquid as a catalyst, *Green Chem.*, 2009, 11, 843–847.

- 22 G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahelnberg, H. Kopacka, T. Roder and H. Sixta, Ionic liquids: current developments, potential and drawbacks for industrial applications, *Lenzinger Berichte*, 2005, 84, 71–85.
- 23 M. Rinaudo, Chitin and chitosan: Properties and applications, Prog. Polym. Sci., 2006, 31, 603–632.
- 24 M. N. V. Ravikumar, A review of chitin and chitosan applications, *React. Funct. Polym.*, 2000, 46, 1–27.
- 25 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, Dissolution of cellose with ionic liquids, J. Am. Chem. Soc., 2002, 124, 4974–4975.
- 26 S. Liang, H. H. Ji, L. Li and S. T. Yu, Dissolution performance of amino acid ionic liquid for chitosan, *High. Poly. Mater. Sci. & Eng.* (*Chinese*), 2010, 26, 703–705.
- 27 Y. Kou, G. H. Tao, L. He, The method on preparation of amino acid ionic liquids, CN200410009958.3, 2005.
- 28 R. Hagege, Fibres à usage techniques—Fibres, fils et tissus textiles, *Techni. de l'Ingenieur*, 1993, A 3980.
- 29 S. Salmon and S. M. Hudson, Shear-precipitated chitosan powders, fibrids, and fibrid papers – observations on their formation and characterization, J. Polym. Sci., Part B: Polym. Phys., 1995, 33, 1007–1014.
- 30 K. D. Nelson, A. A. Romero-Sanchez, G. M. Smith, Drug releasing biodegradable fiber implant, US 6596296, 2003.
- 31 L. P. Du, C. Q. Xu and Z. M. Guo, Studies on the solubility of chitosan, *Chemical Engineer (Chinese)*, 1990, 6, 10–12.
- 32 H. Xie, S. Zhang and S. Li, Chitin and chitosan dissolved in ionic liquids as reversible sorbents of CO<sub>2</sub>, *Green Chem.*, 2006, 8, 630– 633.
- 33 T. D. Jiang, Chitin, Chemical Industry Press, 2006.
- 34 R. Minke and J. Blackwell, The structure of a-chitin, J. Mol. Biol., 1978, **120**, 167–181.
- 35 J. Cho, M. C. heuzey, A. Begin and P. J. Carreau, Viscoelastic properties of chitosan solutions: Effect of concentration and ionic strength, *J. Food Eng.*, 2006, 74, 500–515.
- 36 J. D. Ferry, Viscoelastic Properties of Polymers, 3rd edn, John Wiley & Sons, 1980.
- 37 H. Struszczyk, Preparation of Chitosan Fibres, *Italy: Atec Edizioni*, 1997.
- 38 M. L. Tsaih and R. H. Chen, Effect of molecular weight and urea on the conformation of chitosan molecules in dilute solutions, *Int. J. Biol. Macromol.*, 1997, 20, 233–240.
- 39 R. H. Chen and M. L. Tsaih, Urea-induced conformational changes of chitosan molecules and the shift of break point of Mark– Houwink equation by increasing urea concentration, J. Appl. Polym. Sci., 2000, 75, 452–457.
- 40 R. K. Mohammad, Calculation of Mark-Houwink-Sakurada(MHS) equation viscometric constants for chitosan in any solvent-temperature system using experimental reported viscometric constants data, *Carbohydr. Polym.*, 2007, 68, 477– 488.