Carbohydrate Polymers 97 (2013) 300–305

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

High tenacity regenerated chitosan fibers prepared by using the binary ionic liquid solvent (Gly·HCl)-[Bmim]Cl

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ARTICLE INFO

Article history:
Received 24 January 2013
Received in revised form 17 April 2013
Accepted 22 April 2013
Available online 3 May 2013

Keywords:
Chitosan fibers
High tenacity
Ionic liquid
Solvent

ABSTRACT

A binary ionic liquid system was confirmed to be a promising solvent to dissolve chitosan, and the regenerated chitosan fibers were prepared by wet and dry-wet spinning technique respectively. The SEM results show that the chitosan fibers prepared by wet spinning technique present striated surface and round cross section, and the chitosan fibers prepared by dry-wet spinning technique present smooth surface and irregular cross section. The mechanical testing results show that the regenerated chitosan fibers present relatively high tenacity, especially, these prepared by dry-wet spinning process present excellent strength and initial modulus, i.e. 2.1 cN/dtex and 83.5 cN/dtex, which is stronger than that of most reported chitosan fibers. The FT-IR results show that the dissolution of chitosan in the binary ionic liquid system is due to the protonation of $-NH_2$ groups in the chitosan chains. Furthermore, a possible reaction during the dissolution and regeneration process is proposed.

1. Introduction

Chitosan has attracted great attention and has been broadly applied in medicine and other areas due to its excellent biological characteristics, biocompatibility, biodegradation and absorptivity (Pillai, Paul, & Sharma, 2009). As known, chitosan can be used in tissue engineering (Costa-Pinto, Reis, & Neves, 2011), crop protection, food preservation (Muzzarelli et al., 2012), waste water purification (Wan Ngah, Teong, & Hanafiah, 2011) and etc. Chitosan fibers, an important product form of chitosan, have been investigated for many years, and present potential application in many fields (Hirano, 2001). Tuzlakoglu, Alves, Mano, and Reis (2004) produced chitosan fibers by wet spinning technique to process tissue engineering scaffolds, and the developed scaffolds present proper strength and degradation properties. Desai, Kit, Li, and Zivanovic (2008) prepared chitosan nanofiber by electrospinning of chitosan/poly(ethyleneoxide) (PEO) (95:5) blend solution, and the prepared nonwoven fiber mattress with potential application in air and water filtration. Albanna, Bou-Akl, Walters, and Matthew (2012) used chitosan fibers as reinforcement to improve the mechanical properties of chitosan-based heart valve scaffolds. Notin, Viton, David, et al. (2006) and Notin, Viton, Lucas, and Domard (2006) prepared chitosan fibers by pseudo dry spinning process with a smooth, regular and uniform striated surface. Besides, Geng, Kwon, and Jang (2005) prepared chitosan nanofiber by electrospinning in concentrated acetic acid solution, and Pati, Adhikari, and Dhara (2011) prepared ultrafine chitosan fibers by modified wet-spinning technique as well. However, the low strength limits for further development of chitosan fibers, and a lot of efforts have been tried to overcome the shortage. Yang, Dou, Liang, and Shen (2005) and Knaul, Hudson, and Creber (1999a) studied the cross-linking of chitosan fiber by dialdehydes respectively, and found that the crosslinked chitosan fibers hold good tenacity. Notin, Viton, David, et al. (2006) and Notin, Viton, Lucas, et al. (2006) prepared chitosan fibers by gel-spinning technique, and the obtained fibers exhibit good mechanical properties as well. Knaul, Hudson, and Creber, (1999b) studied the effect of coagulation bath on strength of chitosan fibers, and optimized the technical conditions. Besides, some chitosan-based composite fibers are also developed, i.e. alginate/chitosan (Wang et al., 2009), chitosan/multi walled carbon nanotube (Mahdieh, Mottaghitalab, Piri, & Haghi, 2011), chitosan/silver particles and etc. (Qin, Zhu, Chen, & Zhong, 2007). However, until now, all the chitosan processing is based on acetic acid, dichloroacetic acid, trifluoroacetic acid (Sangsanoh & Supaphol, 2006) or sodium thiocyanate (Kawasaki, 1999), and some of them are corrosive and harmful to human health. Therefore, it is urgent to offer a method for manufacturing chitosan fibers with high tenacity using a solvent, which is nontoxic and environmentally friendly.

In recent years, ionic liquids (ILs) are proposed as green solvents due to their thermal stability, negligible vapor pressure, potential for recycling and etc. ILs exhibit strong dissolving power for protein and polysaccharide (Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2010), i.e. silk fibroin (Silva et al., 2012), cellulose

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0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.04.080

(Swatloski, Spear, Holbrey, & Rogers, 2002), chitin and chitosan. Qin, Lu, Sun, and Rogers (2010) extracted the high molecular weight chitin from crustacean shells using 1-ethyl-3-methylimidazolium acetate ([C_2mim]OAc) as solvent, at the same time, chitin films and fibers were prepared as well. Zhu, Han, Cheng, and Wu (2011) studied the dissolubility of chitosan in four kinds of imidazole-based ILs, i.e. [Bmim]Cl, 1-butyl-3-methylimidazolium acetate ([Bmim]Ac), 1-allyl-3-methylimidazolium chloride ([Amim]Cl) and 1-ethyl-3-methylimidazolium acetate ([Emim]Ac), and found that the four kinds of ILs can dissolve chitosan and 15.5 wt.% of chitosan/[Emim]Ac solution can be prepared at 110 °C. Xie, Zhang, and Li (2006) claimed that chitosan could be dissolved in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) to form a semi-clear and viscous solution, which can be used as reversible CO_2 solvent. Li et al. (2012a) claimed that aqueous solution of Gly·HCl was a good solvent for chitosan with different deacetylation degrees and molecular weights, and the prepared chitosan solution presents relative low viscosity, furthermore, the chitosan fibers was prepared (Li et al., 2012b). Nonetheless, there are still few reports on the preparation of chitosan fibers using ILs as solvent.

The aim of this work is to show a method to prepare chitosan fibers with high tenacity using binary ionic liquid system as solvent, which is composed of glycine hydrochloride (Gly·HCl) and [Bmim]Cl. A homogeneous chitosan solution was prepared, and the chitosan fibers were manufactured by wet and dry-wet spinning processes respectively. The prepared chitosan fibers were characterized by FT-IR and WAXD, which provide the information on the dissolution and regeneration process of the materials. SEM was used to visualize the morphology of the prepared fibers, and strength testing was used to evaluate its mechanical performance. Furthermore, the possible reaction during the dissolution and regeneration was investigated as well.

2. Experimental

2.1. Materials and reagents

Chitosan powder (800 cP, 1 wt.% in 1% acetic acid at 25 °C; deacetylation degree 90%; source: snow crab) was purchased from Introduction of Jinhu Crust Product Co. Ltd. (Qingdao, China), and dried at 105 °C until constant weight before use. Its viscosity average molecular weight (M_v) is about 9.76×10^5 g/mol, which is calculated by the Mark–Houwink equation according to reference (Wang, Bo, Li, & Qin, 1991). Glycine and hydrochloric acid (HCl, 36–38 wt.%) were purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received. Industrial-grade N-methylimidazole, 1-chlorobutane and ethanol (content >99.5%) were purchased from Shanghai Jiachen Chemical Co. Ltd. (Shanghai, China). N-methylimidazole and 1-chlorobutane were purified by distillation before use, ethanol was used as received.

2.2. Synthesis of ILs

Gly·HCl and [Bmim]Cl were synthesized as follows. 37.5 g glycine and 60.9 g HCl aqueous solution (36–38 wt.%) were added to a round-bottomed flask fitted with magnetic stirring, until glycine was fully dissolved. The mixture was kept at 60 °C for 6 h, and cooled to room temperature. Water was removed through vacuum distillation, the residue was washed with ethanol three times, and kept in vacuum for 24 h, and a white crystalline of Gly·HCl was obtained. [Bmim]Cl was prepared as follows. The mixture of purified N-methylimidazole 41.05 g and 1-chlorobutane 55.54 g were added to a round-bottomed flask fitted with reflux condenser and magnetic stirring, kept in 80 °C for 24 h, ethyl acetate was used to remove the residual N-methylimidazole and 1-chlorobutane using extraction method, then in vacuum for 48 h. A purified [Bmim]Cl was obtained.

Their 1H NMR spectra are shown as follows:

Gly·HCl: 1H NMR (400 MHz, D_2O, TMS), δ4.65 (2H, s).
[Bmim]Cl: 1H NMR (400 MHz, D_2O, TMS), δ0.88–0.92 (3H, t), 1.23–1.28 (2H, m), 1.75–1.79 (2H, t), 3.87 (3H, s), 4.17–4.20 (2H, t), 7.75 (1H, d), 7.83 (1H, d), 9.35 (1H, s).

2.3. Preparation of spinning solution and chitosan fibers

The preparation of spinning solution was described as followed, a certain amount of chitosan powder was added into 10 wt.% Gly·HCl/[Bmim]Cl solvent system to form 5 wt.% chitosan dispersion, and heated at 80 °C under mechanical stirring for 1 h to obtain a homogeneous, viscous (the viscosity is about 5 Pa s at 80 °C) and amber solution. The obtained solution is stable, can be stored at room temperature for at least a number of months without any phase separation, and there have not obvious viscosity decrease as well. In general, it is necessary to filtrate the solution with the 400 mesh filter and remove the bubble under vacuum in order to satisfy the spinning requirement.

The preparation of chitosan fibers was described as followed, the filtered solution was extruded through a spinneret with 30 holes (60 μm diameter) under the 0.4 MPa compressed air, then immersed in an ethanol coagulation and 5 wt.% sodium hydroxide solution successively. The schematic representation of spinning process is shown in Fig. 1a, diameter of all the rollers is 17.5 cm. The fibers, which are collected between coagulation bath and neutralization bath were named as primary chitosan fibers. The fibers which are collected after washing bath and air dried were named as regenerated chitosan fibers, as shown in Fig. 1b. The fibers A and B are prepared by wet and dry-wet spinning technique respectively, its density and moisture content under equilibrium conditions at 25 °C and 65% relative humidity are 1.45 g/cm^3, 12.5% and 1.46 g/cm^3, 11.4% respectively.

2.4. Characterization

2.4.1. Microscopy

The surface morphology of the prepared chitosan fibers was studied in a Jeol Jsm-5600lv (Jeol Ltd., Tokyo) scanning electron microscope (SEM). The fibers were washed with ethyl ether for several times and sputter-coated with gold. For the observation of cross section, the fibers were fractured under liquid nitrogen.

2.4.2. Thermo gravimetric analyzer (TGA)

Thermal analysis of the chitosan samples was performed on a TG 209 F1 Iris (Netzsch Gertebau GmbH, Germany) under nitrogen atmosphere. In each experiment, about 5–10 mg sample was filled in an aluminum pan and the TG was recorded by raising the temperature from 50 °C to 1000 °C at a heating rate of 10 °C/min.

2.4.3. Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) was performed on Nicolet 8700 (Thermo Electron Corp, USA) at room temperature. The fiber samples were cut into powder and mixed with KBr to prepare pellets. All spectra were recorded with an accumulation of 32 scans with a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}.

2.4.4. Wide angle x-ray diffraction

Wide angle X-ray diffraction (WAXD) analysis was performed for raw chitosan, primary chitosan fiber and regenerated chitosan fiber, using a Rigaku D/Max-2550 (Rigaku Corp, Tokyo) with Cu radiation operated at 40 kv and 200 mA, from 5° to 60° in steps of 0.02°.

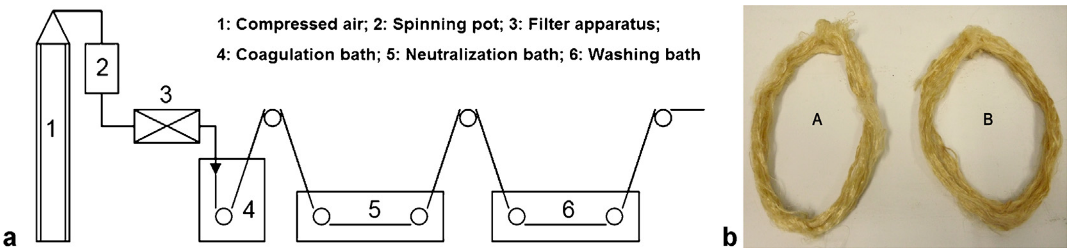

Fig. 1. (a) Schematic representation of spinning process; (b) the obtained chitosan fibers A and B which were prepared by wet and dry-wet spinning technique respectively.

2.4.5. Mechanical testing

Tensile strength of the prepared fibers was performed on XQ-1fiber tensile tester (Shanghai New Fiber Instrument Co. Ltd., Shanghai) with an extension speed of 5 mm/min under equilibrium conditions at 25 °C and 65% relative humidity. The fineness of the fibers was measured through weight method. For the wet tensile test, the fiber was immersed in distilled water at room temperature for 5 min, gently blotted with tissue paper to remove excess water on the surface, and tested. The statistical results came from 20 measurements for each sample.

Table 1
mechanical property of the prepared chitosan fibers.

Sample ID	Fiber A (wet spinning)		Fiber B (dry-wet spinning)	
	Dry	Wet	Dry	Wet
Strength (cN/dtex)	1.5	1.1	2.1	0.9
Initial modulus (cN/dtex)	71.0	52.9	83.5	29.3
Elongation (%)	8.1	6.1	11.9	15.3

3. Results and discussion

3.1. Morphology and mechanical characterization

As shown in Fig. 2, fiber A prepared by wet spinning technique shows a striated surface and rounded cross section, while fiber B prepared by dry-wet spinning technique shows a smooth, uniform surface and irregular cross section. That is because the air gap in dry-wet spinning technique makes the extruded spinning drops more homogeneous, and there is no time to uniform the spinning drops in wet spinning technique. Furthermore, when the filaments are immersed in the coagulation bath, the shrinkage difference between the cortex and core makes the fiber B presents irregular shape, however, the difference in fiber A is unconspicuous, which contributes to its rounded cross section. On the other hand, the diameter of fiber A and B is about 16 μm and 37 μm respectively, which is mainly due to the draw ratio difference of roller. As compared with the scaly chitosan fibers (Hirano, 2001), the chitosan fibers in this study present relatively homogeneous structure, and there are fewer flaws. Therefore, it can be inferred that this chitosan fibers will present excellent mechanical properties.

The typical stress–strain curves of fiber A and B under dry and wet conditions are displayed in Fig. 3, and its number data in Table 1 indicates that the chitosan fibers prepared by dry technique present superior strength and initial modulus at dry state, i.e. 2.1 cN/dtex and 83.5 cN/dtex respectively, which is stronger than that of most chitosan fibers reported in literatures. Even the chitosan fibers prepared by wet technique also present relatively high strength and initial modulus at dry state, i.e. 1.5 cN/dtex and 71.0 cN/dtex respec-

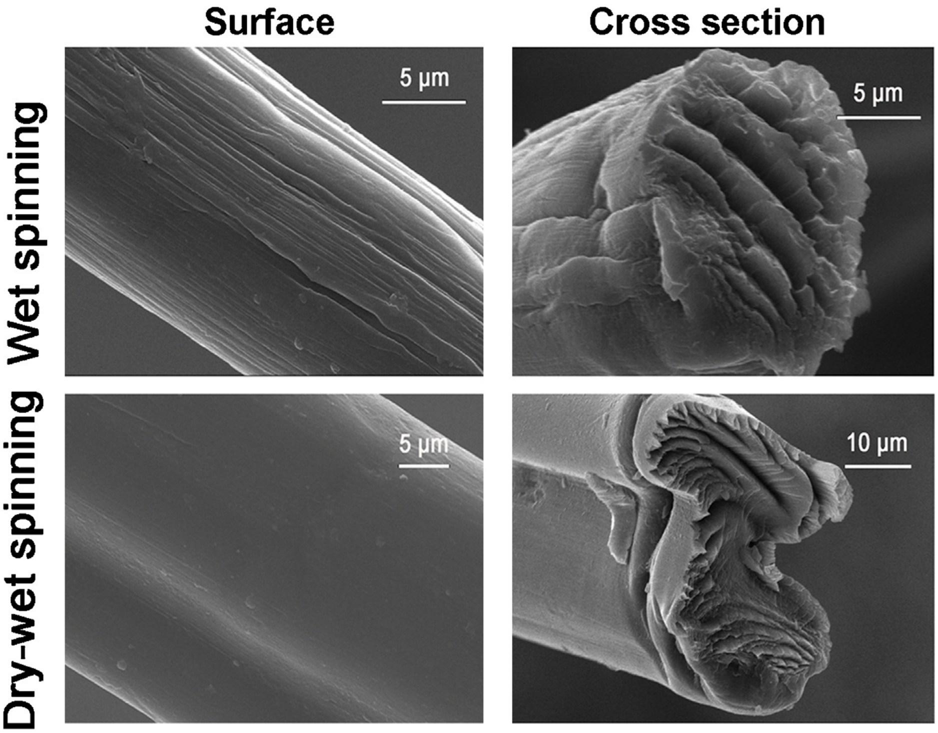

Fig. 2. Morphology of the prepared chitosan fibers A and B.

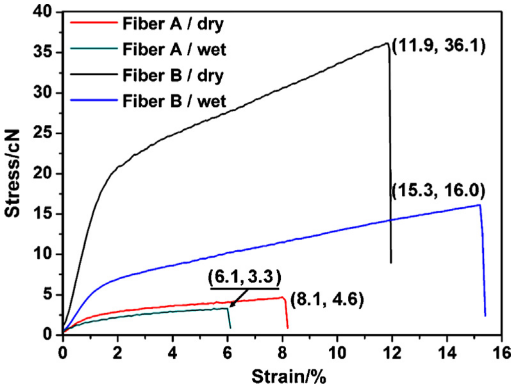

Fig. 3. Typical stress–strain behavior of the prepared chitosan fibers.

Table 2
Thermal analysis results of the raw chitosan powder and prepared chitosan fibers.

Sample ID	Raw chitosan powder	Fiber A	Fiber B
T_{onset} (°C)	283	268	272
T_{end} (°C)	333	328	325
Residual ratio wt.%	31	35	38

tively. Therefore, the binary ionic liquid system is a promising solvent to prepare the regenerated chitosan fiber with high tenacity, which holds potential application in many fields, especially in biomedicine. However, their strength and initial modulus at wet state is inferior, especially, the strength of fiber B at wet state is decreased 57% from 2.1 cN/dtex to 0.9 cN/dtex. That is because the presence of water has a pronounced swelling effect on the chitosan fibers, which makes the macromolecules chains become somewhat uncoiled and separated, hence the sliding friction between chains is very low (Spinks et al., 2006).

3.2. Thermal analysis

The TG and corresponding DTG curves of raw chitosan and regenerated chitosan fibers are shown in Fig. 4a and b respectively. The thermal analysis results are summarized in Table 2. According to the TG results, all samples suffer a weight loss (about 8 wt.%) at about 100 °C, which is associated with the volatilization of absorbed moisture, and a sharp weight loss (about 50 wt.%) at about 300 °C, which is associated with the pyrolysis of chitosan macromolecule chains. The regenerated chitosan fibers reveal a little lower onset (T_{onset}) and end (T_{end}) decomposition temperature than that of raw chitosan, which may be related to the relatively weak inter- and intra-molecular hydrogen-bond interactions and poor crystallinity of the regenerated chitosan fibers (Liu et al., 2011). Besides, the regenerated chitosan fibers A and B show similar thermal behavior, which indicate that they share the similar structure. Furthermore, it should be emphasized that the weight residual of regenerated chitosan fibers at 1000 °C is higher than that of raw chitosan. That is due to the removal of some relatively unstable impurities and low molecular weight components during the dissolution and regeneration process (Wu, Sasaki, Irie, & Sakurai, 2008).

3.3. Structure analysis

FT-IR and WAXD were used to assist our understanding toward the dry-wet spinning process. Fig. 5a shows the FT-IR spectrogram of raw chitosan, regenerated chitosan fibers and primary chitosan fibers, which are collected between the coagulation bath and neutralization bath. It can be seen that the absorption peaks of raw chitosan and regenerated chitosan fibers are observed at 1657 cm^{-1}, 1583 cm^{-1} and 1658 cm^{-1}, 1585 cm^{-1} respectively, which is assigned to the stretching of amides I and II. However, The absorption peaks of primary chitosan fibers are observed at 1630 and 1525 cm^{-1} respectively, which is corresponding to the stretching of the protonated amino ($-NH_3^+$) groups. Therefore, the dissolution of chitosan in the binary ionic liquid system is due to the protonation of $-NH_2$ groups in the chitosan chains, which is different from the dissolution of cellulose in [Bmim]Cl (Feng & Chen, 2008). And the deprotonation of the $-NH_3^+$ occurs in the neutralization bath, where makes the primary chitosan fibers fully regenerated. There are little difference between the spectrograms of regenerated chitosan fiber and raw chitosan, this indicates that the prepared chitosan fiber has no derivatization after regeneration.

Fig. 5b shows the WAXD profiles of raw chitosan, primary chitoan fibers and regenerated chitosan fibers. The obvious diffraction peaks at about 10° and 20° are observed for the raw chitosan and regenerated chitosan fibers, which is in accordance with the characteristic peaks of α-chitosan. This indicates that there is no change about the crystal structure during the dissolution and regeneration process. However, the diffraction peaks at about 10° and 20° are almost disappeared for the primary chitosan fibers. This is due to the fully destroy of crystal region of raw chitosan during the dissolution process, which has not been reconstituted in the coagulation bath. The present crystal structure of regenerated chitosan fibers is formed during the drafting process in neutralization bath. Nonetheless, there are still many amorphous areas that cannot be reconstituted, which contributes to the decrease of crystallinity, as confirmed by the fact that the peak intensity of regenerated chitosan fibers is a little lower than that of raw chitosan. Besides, there are some sharp peaks for the primary chitosan fibers, which is maybe ascribed to the presence of Gly·HCl. When the spinning drops are extruded from spinneret and immersed in coagulation bath, the diffusion between solvent and coagulator occurs. [Bmim]Cl is miscible with ethanol and Gly·HCl is slightly

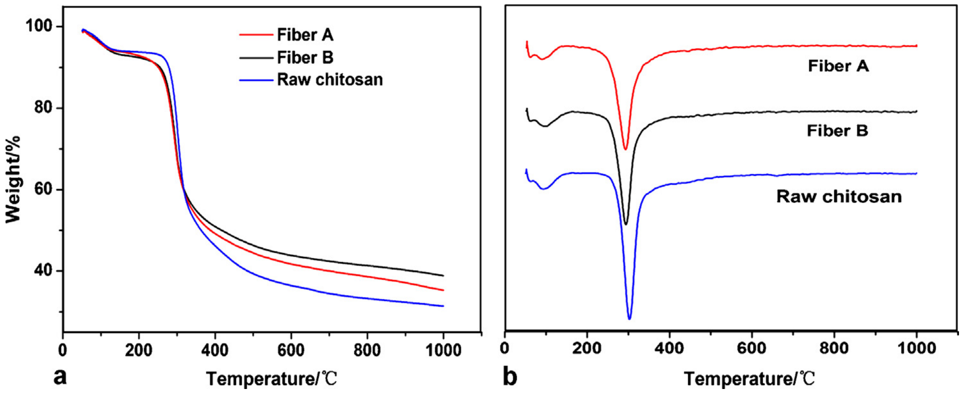

Fig. 4. TG and DTG curves of the raw chitosan powder and prepared chitosan fibers.

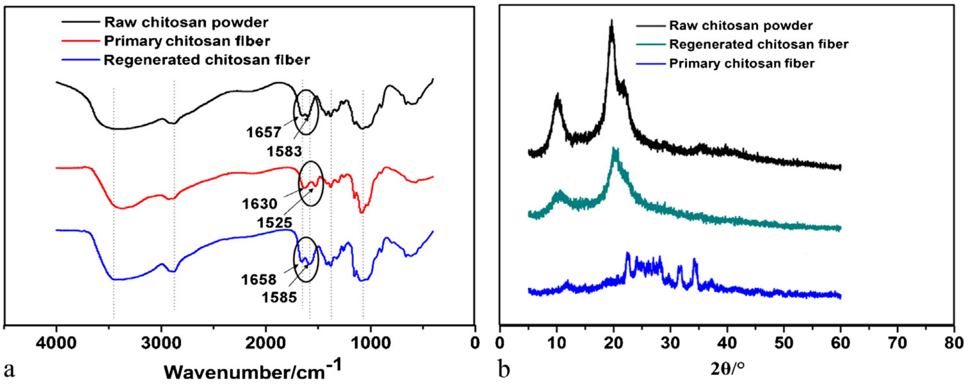

Fig. 5. FT-IR and WAXD profiles of the raw chitosan powder, primary chitosan fiber and regenerated chitosan fiber.

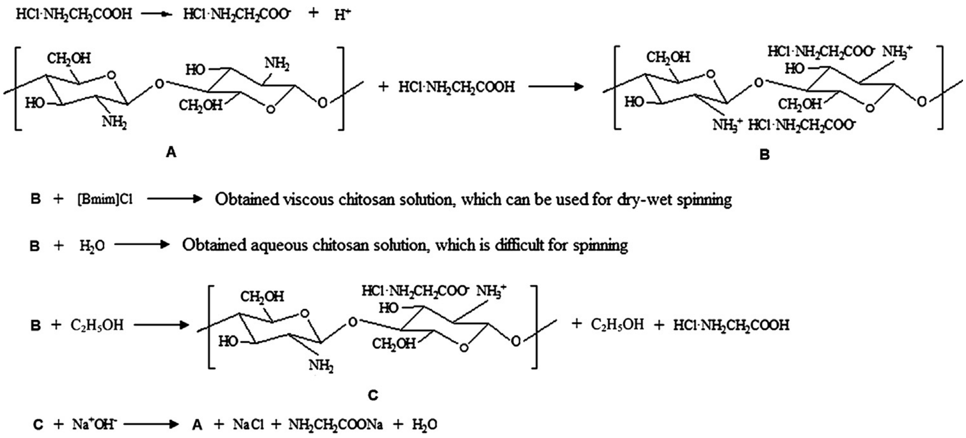

Fig. 6. Possible reaction during the dissolution and regeneration process.

soluble in ethanol, therefore, most [Bmim]Cl and a few Gly·HCl are displaced by ethanol, furthermore, some Gly·HCl residual is attached to the surface of primary chitosan fibers, which contribute to the small sharp peaks in the WAXD profile.

3.4. *Possible reaction*

From the above analysis, a possible reaction during the dissolution and regeneration process is proposed, as shown in Fig. 6. When Gly·HCl is dissolved in [Bmim]Cl, H^+ will be detached. Furthermore, the detached H^+ combines with the amino ($-NH_2$) group in the chitosan chains to make it protonated (Caroni, De-Lima, Pereira, & Fonseca, 2012), and the protonated chitosan can be dissolved in [Bmim]Cl. Certainly, the protonated chitosan can be dissolved in water as well, however, the spinnability of the aqueous solvent is bad. Therefore, [Bmim]Cl is chosen as solvent matrix to prepare spinning solution. In the regenerated process, when the extruded solution pass through the coagulation bath, ethanol replaces the [Bmim]Cl in solution, and makes the $-NH_3^+$ deprotonation partly, which is confirmed by the fact that the collected primary chitosan fibers can be dissolved in water. When the primary chitosan fibers pass through the neutralization bath, the residual $-NH_3^+$ is deprotonated thoroughly at the presence of NaOH, and make the primary chitosan fibers fully regenerated.

4. Conclusions

The regenerated chitosan fibers prepared by dry-wet spinning technique present excellent strength and initial modulus, i.e. 2.1 cN/dtex and 83.5 cN/dtex, which is stronger than that of most chitosan fibers reported in literatures. The SEM results show that the chitosan fibers prepared by dry-wet spinning technique present smooth surface and irregular cross section, and the chitosan fibers prepared by wet spinning technique present striated surface and round cross section. The FT-IR results show that the dissolution of chitosan in the binary ionic liquid system is due to the protonation of $-NH_2$ groups on the chitosan chains. Besides, this paper achieves the dry-wet spinning of chitosan solution due to the application of binary solvent system (Gly·HCl)-[Bmim]Cl as compared with the existing reports where the chitosan fiber was prepared by wet spinning process.

Acknowledgements

This work is supported by grants from the National High-tech Research and Development Projects (863, 2012AA03A605), the National Science Foundation of China (No. 51103019 and No. 21174027), Program for New Century Excellent Talents in University (No. NCET-12-0827). Program of Introducing Talents of Discipline to Universities (No. 111-2-04) and Innovation Funds for PhD Students of Donghua University.

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