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New binary ionic liquid system for the preparation of chitosan/cellulose composite fibers

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ABSTRACT

A binary system consisting of acidic ionic liquid glycine hydrochloride (Gly·HCl) and neutral ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) is proposed to be cosolvent for chitosan and cellulose, the spinning solution of chitosan/cellulose can be prepared in one step. The regenerated chitosan/cellulose composite fiber with 9.4 wt.% chitosan was prepared through dry–wet spinning process. SEM shows that the chitosan is scattered on the surface and interior of the composite fiber. WAXD shows that the degree crystallization of the composite fibers is far less than that of raw materials. The result of elemental analysis (EA) indicates that there is little weight loss of chitosan during the spinning process. Moreover, the prepared composite fiber presents good thermal stability, i.e. its T_{onset} is 305.1 °C, and excellent mechanical property, i.e. its tensile strength is 4.63 cN/dtex. All the results show that Gly·HCl/[Bmim]Cl binary system is a promising solvent for the preparation of chitosan/cellulose composite fiber.

1. Introduction

Cellulose is the most abundant natural polymer in the world, which has been widely used in paper, paint, textile, food, pharmaceutical industries, etc. Chitosan is the partially deacetylated polysaccharide of naturally chitin, well known to be biocompatible, biodegradable, nontoxic and antibacterial. The products made from chitin and its derivatives can be used in biomedical, crop protection and food preservation (Muzzarelli, 2011; Muzzarelli et al., 2012). However, its poor mechanical and processing properties and its insolubility in common organic solvents have delayed its basic research and applications. At present, the composite of chitosan and cellulose has been explored as a convenient method to develop composite membranes and fibers, which hold many beneficial properties, i.e. anti-inflammation, deodorization, and antibiosis, and can be used for dermal wounds and tissue engineering (Fernandes, Freire, Silvestre, Neto, & Gandini, 2011; Ko, Sfeir, & Kumta, 2010). Furthermore, the chitosan/cellulose composite fibers present excellent mechanical properties, which is beneficial for the application.

In the literatures, N-acylchitosan fiber and N-acylchitosan/cellulose composite fiber was prepared by traditional viscose-type method at 10–15 °C, where the coagulating bath contains aqueous 10.0 wt.% H_2SO_4, 25.0 wt.% Na_2SO_4 and 1.3 wt.% $ZnSO_4$ (Hirano & Midorikawa, 1998). Chitin/cellulose blend filaments were prepared through high wet modulus procedure, and the blend filaments have an effective biostatic effect on *Staphylococcus aureus*, *Escherchia coli*, and *Corinebaterium michiganence* (He, Ma, & Sun, 2009). Chitosan derivate/cellulose composite fiber was also prepared from its blend solution in NMMO/H_2O as solvent (Zhuang, 2005). Among all the investigated solvent systems, the traditional viscose method is a highly polluted way which uses carbon disulfide, hazardous to the environment and human health, and NMMO is unstable and tends to release atom oxygen upon heating, which attacks the macromolecular chain and leads to strong degradation, the mechanical properties of the fiber decrease. Therefore, the choice of an environment friendly and stable solvent for fiber spinning is very important.

Recently, ionic liquids are regarded as green solvents to replace the volatile organic compounds in various processing and synthesis industries. Ionic liquids hold many particular characters, i.e. thermal stability, negligible vapor pressure, potential for recycling, etc., and take the honor of green solvent in 21 century (Rogers & Seddon, 2003). Many researchers committed to the field since American scientist Rogers reported that 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) can dissolve cellulose directly. From then on, a series of ionic liquids were synthesized, and its dissolving power for cellulose, chitosan and chitin were studied (Pinkert, Marsh, Pang, & Staiger, 2009; Seoud, Koschella, Fidela, Dorn, & Heinze, 2007). In the literatures, 1,3-dimethylimidazolium chloride ([Dmim]Cl) and [Dmim]Cl/[Hmim]Cl (1-H-3-methylimidazolium chloride) was reported to dissolve cellulose and chitosan respectively, the

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chitosan/cellulose blended membrane and fibers were prepared from the blended solution, which not only presented compact structure but also possessed good mechanical properties (Xiao, Chen, Wu, Wu, & Dai, 2011). However, the temperature for the synthesis of [Dmim]Cl is high, up to 170 °C, which is unfeasible for the large-scale production. Therefore, it is of great importance to develop a simple and efficient solvent system.

The scope of this work is to develop a fully new solvent system for the preparation of chitosan/cellulose composite fibers. The cosolvent system, consisting of the acidic liquid glycine hydrochloride and the neutral ionic liquid 1-butyl-3-methylimidazolium chloride, is a good solvent for both cellulose and chitosan. A homogeneous chitosan/cellulose spinning solutions can be prepared in one step. The composite fibers were prepared through wet and dry–wet spinning processes respectively, its characterization and mechanical properties were also described. We have not found any other reports on the use of such a bisolvent system to prepare chitosan/cellulose composite fiber in one step.

2. Experimental

2.1. Materials

Cellulose pulp with degree of polymerization 500 obtained through cupriethylene diamine method was purchased from Fujian Nanping Paper Co. Ltd. (Nanping, China). Chitosan (food grade, $\eta = 50$ cp, deacetylation degree > 90%) was purchased from Introduction of Jinhu Crust Product Co. Ltd. (Qingdao, China). Cellulose pulp and chitosan were dried at 105 °C until constant weight before use. Industrial-grade N-methylimidazole and 1-chlorobutane were purchased from Shanghai Jiachen Chemical Co. Ltd. (Shanghai, China), and purified through distillation before use. Glycine, hydrochloric acid (HCl, 36–38 wt.%) and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and used as received.

2.2. Synthesis of ILs

Glycine hydrochloride (Gly·HCl) was synthesized as followed (Liang et al., 2010), 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 ethyl acetate three times, and kept in vacuum for 24 h, a white crystalline of Gly·HCl was obtained. [Bmim]Cl was prepared according to the reference (Huddleston, Willauer, Swatloski, Visser, & Rogers, 1998). 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, then in vacuum for 48 h. A purified [Bmim]Cl was obtained.

Their ^{1}H NMR spectra are shown as follows:

Gly·HCl: ^{1}H NMR (400 MHz, D_2O, TMS), δ 4.65 (2H, s).

[Bmim]Cl: ^{1}H NMR (400 MHz, D_2O, TMS), δ 0.88–0.92 (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

0.95 g Gly·HCl, 94.05 g [Bmim]Cl, 0.5 g chitosan and 4.5 g cellulose were added to a round-bottomed flask together, and the mixture was stirred at 80°C for 12 h to obtain a homogeneous, transparent and amber solution. The solution is stable, which can be stored for one month at room temperature without any phase separation, and its viscosity is about 50 Pa s at 80°C. In order to satisfy the spinning requirements, the solution was degassed under vacuum for 48 h.

2.4. Spinning

The chitosan/cellulose composite fiber was prepared by wet and dry–wet spinning procedure respectively. The degassed solution was filtered through nylon net with pore size 600 meshes to remove the undissolved substance and other impurities. And then, the filtered solution was extruded under the pressure of 0.4 MPa through a spinneret with 80 μm hole diameter. The coagulation and washing bath was distilled water. The spinning speed for the wet and dry–wet procedure is 1.8 m/min and 1.5 m/min respectively, the extruded speed for both solutions is 2 ml/min, and the process can be continued until the solution exhausted. Besides, all the apparatus of the spinning, including spinneret, filter, coagulation and washing bath, rollers, etc., are made of stainless steel. The obtained fibers were treated with boiling water to remove the remaining solvents, and air dried to afford the regenerated chitosan/cellulose composite fibers.

2.5. Measurement

A Jeol Jsm-5600lv (Jeol Ltd., Tokyo) scanning electron microscope was used to study the surface morphology of the fiber. The fibers were extracted with ether for several times, and then, the fiber surface was coated with gold for SEM observation. Wide-angle x-ray diffraction measurements were conducted by a Rigaku D/Max-2550 (Rigaku Corp, Tokyo) with Cu radiation operated at 40 kV and 200 mA, the fiber samples were cut into powder for test. Elemental analyses were performed on Elmentar Vario El III (Elmentar Crop, Germany). Thermal gravimetric analysis (TGA) measurements were performed on TG 209 F1 Iris (Netzsch Gertebau GmbH, Germany) at a heating rate of 10 °C/min in nitrogen atmosphere. The tensile strength was measured on XQ-1 fiber tensile tester (Shanghai New Fiber Instrument Co. Ltd., Shanghai) with an extension rate of 5 mm/min. The statistical results came from 10 measurements for each specimen.

3. Results and discussion

3.1. Dissolution of chitosan and cellulose in ILs

It is well known that [Bmim]Cl can dissolve cellulose directly. For the Gly·HCl/[Bmim]Cl binary system, the content of Gly·HCl is only 1 wt.%, there is not any influence on its power for dissolving cellulose, but endow it with the power for dissolving chitosan. 10 wt.% cellulose solution and 5 wt.% chitosan solution can be readily prepared in the binary system respectively.

Gly·HCl/[Bmim]Cl binary system were employed to dissolve chitosan and cellulose together at 80°C. The obtained solution is transparent, homogeneous and stable, which can be used for further spinning and preparation of chitosan/cellulose composite fiber. The spinning schematic diagram is shown in Fig. 1. Besides, the binary system can be recovered through distillation under

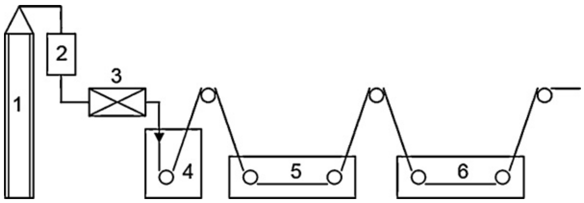

Fig. 1. The flow diagram of spinning process. 1: compressed air; 2: spinning pot; 3: filter apparatus; 4: coagulation bath; 5 and 6: washing bath.

Fig. 2. Photograph of the chitosan/cellulose composite fiber prepared by dry–wet spinning.

vacuum, the yield comes up to 99 wt.%. Furthermore, the ^{1}H NMR spectra of the recycled Gly·HCl/[Bmim]Cl has no difference as compared with the fresh one, which still maintains strong dissolving power for chitosan and cellulose.

3.2. Morphologies observation

The photograph and SEM images are shown in Figs. 2 and 3 respectively. A smooth surface and round cross section are observed for the prepared composite fibers, as shown in Fig. 3a and b. This is different from the surface and cross section of general viscose fiber, which has fluted surface and zigzag cross section. Besides, there are conspicuous spots on the surface, as shown in Fig. 3c and d, which is attributed to the existence of regenerated chitosan. The results indicate that the preparation of chitosan/cellulose composite fiber by the binary solvent system is feasible.

The elemental analysis was conducted to study the content of chitosan in the composite fiber to evaluate whether the content of chitosan included in composite fiber was in accordance with the original quantity. The N element content in the composite fiber is 0.74%. Since there is no N element in cellulose, the N content must be attributed to the existence of chitosan. On the other hand, the EA results show that C/H ratio of the composite fiber is about 5.9:1, while the C/H ratio in chitosan and cellulose are 7.2:1 and 6.5:1 respectively. Therefore, there must be the third component that lows the C/H ratio. It is very easy for the regenerated chitosan or cellulose to absorb the moisture in the air since both materials have numerous hydrophilic hydroxyl groups, the existence of moisture in the sample play an important role for the EA results. Through a series of calculation, the contents of chitosan, cellulose and water in the regenerated composite fiber are about 8.5 wt.%, 81 wt.% and 10.5 wt.% respectively. If the absorbed water is excluded, the contents of chitosan and cellulose turn to be 9.4% and 90.6% respectively, which is approximately in accordance with the ratio of the added chitosan as raw materials. The results show that chitosan are fully dissolved in the binary system and fully regenerated, there is no mass loss of chitosan during the spinning and regenerated process.

3.3. WAXD profile analysis

The WAXD profiles of raw materials and regenerated materials are shown in Fig. 4. As shown in Fig. 4a, the WAXD intensity of regenerated composite fiber is far less than that of the raw cellulose pulp, which implies a lower crystallinity of the composite fibers. On the other hand, a pair of diffraction peaks of raw cellulose pulp is observed at 2θ angle of 22.4° and 15.7° respectively, which are known as the crystal structure of cellulose-I. A pair of diffraction peaks of regenerated composite fibers is observed at 2θ angle of 20.6° and 12.7° respectively, which are known as the crystal structure of and cellulose-II. The results indicate that the dissolving process not only decreases the crystallinity but also changes the crystal pattern. The dissolving process can be narrated as followed: ionic liquid solvent system destroys the crystal regions in cellulose and chitosan during the dissolution process, and amorphous regions are formed at the same time. However, the macromolecular chains and new crystal structure are reconstituted under the stretching action during the spinning process. Nonetheless, there are still many areas that cannot be reconstituted, which lead to

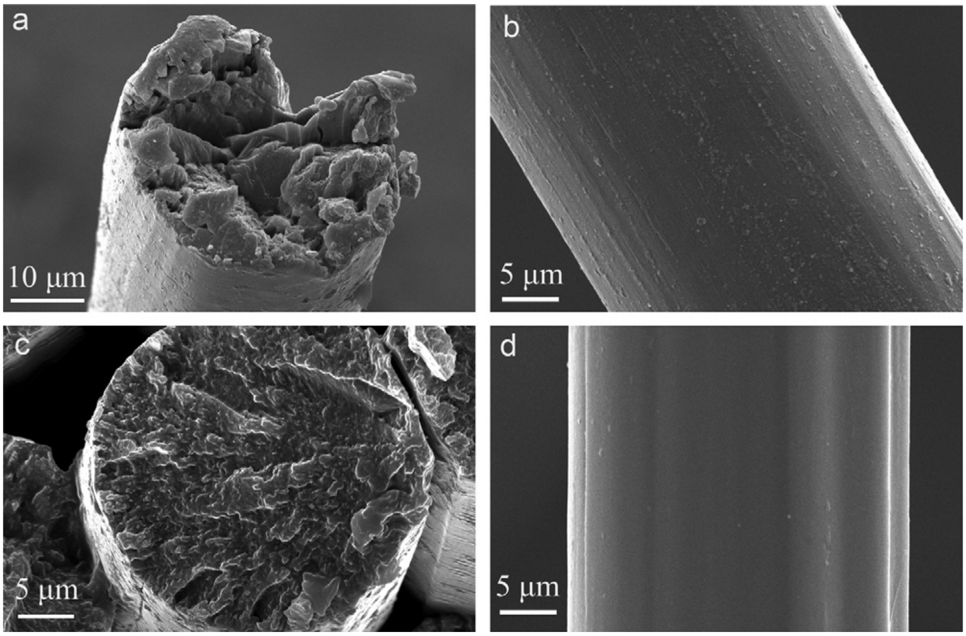

Fig. 3. SEM images of the composite fiber (a, b) and cellulose fiber (c, d).

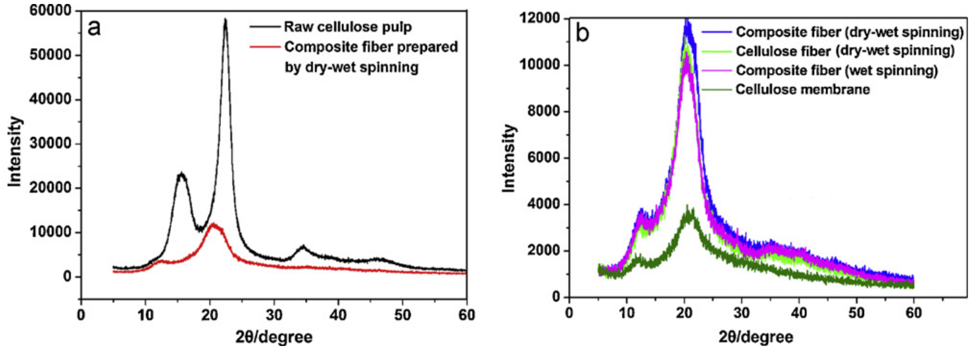

Fig. 4. WAXD profiles of the raw material and regenerated materials.

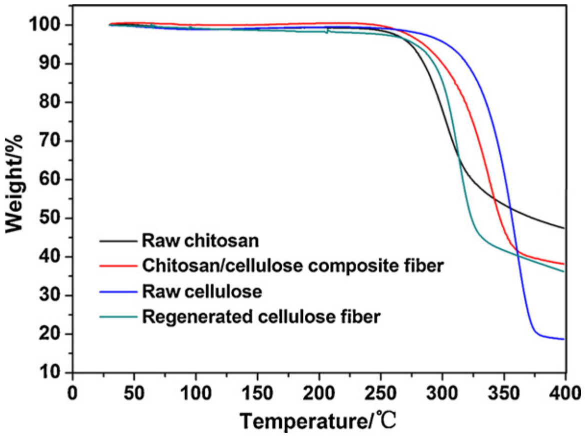

Fig. 5. TGA curves of the raw materials and regenerated materials.

the lower crystallinity of regenerated fibers than that of the raw materials.

The WAXD of the regenerated composite fiber, regenerated cellulose fiber and regenerated cellulose membrane are shown in Fig. 4b. The spectra of the four samples are similar, the diffraction peak intensity of regenerated composite fiber prepared by dry–wet spinning is a little stronger than that of the other samples, and the diffraction peak intensity of regenerated cellulose membrane is the weakest. The extent of stretch plays an important role on the degree of crystallinity, the stretch ratio in dry–wet spinning process is super due to the existence of air gap, and there is little stretch during the preparation of membrane. Therefore, the crystallinity of regenerated composite fiber prepared by dry–wet spinning is the highest, and that of regenerated cellulose membrane is the lowest. It can be concluded that the introduction of chitosan has a little effect on the crystallinity of composite fiber, which is mainly caused by stretch.

3.4. Thermal analysis

As shown in Fig. 5 and Table 1, the thermal stability of regenerated cellulose fiber is lower than that of raw cellulose. Raw cellulose begins to degrade at 331.5 °C and reaches a peak at 360.2 °C, the onset and maximum degradation temperature for the regenerated cellulose fiber is 295.5 °C and 313.1 °C respectively, which is a little lower than that of the regenerated chitosan/cellulose composite fiber, i.e. 305.1 °C and 337.5 °C respectively. Among the four samples, the thermal stability of raw chitosan is the lowest, whose onset degradation occurs at 278.1 °C and reaches a peak at 302.2 °C. The result of TGA shows that the thermal stability of raw chitosan and regenerated cellulose fiber is inferior, but the regenerated chitosan/cellulose composite fiber is superior. Therefore, the incorporation of chitosan improves the thermal properties of composite fiber.

Table 1
The data analysis of TGA curves, T_{onset} refers to the temperature that material begins to degrade, T_{max} refers to the temperature that material degrades the fastest.

Sample ID	T_{onset} (°C)	T_{max} (°C)
Raw chitosan	278.1	302.2
Regenerated composite fiber	305.1	337.9
Raw cellulose	331.5	360.2
Regenerated cellulose fiber	295.5	313.1

On the other hand, the char yield of regenerated cellulose fiber is about 35 wt.% at 400 °C, which is higher than that of raw cellulose, i.e. 20%. Since the char yield of raw chitosan is the highest, i.e. 47.5%, as compared to the other samples, this makes the char yield of chitosan/cellulose composite fiber higher than that of pure regenerated cellulose fiber. As reported in the literature (Zhang et al., 2007), regenerated cellulose fiber is characterized by its relatively high char yield, which makes it a good precursor for carbon fiber. In this case, the regenerated chitosan/cellulose composite fiber will be a promising precursor for the preparation of carbon fiber.

3.5. Mechanical properties analysis

The typical stress–strain curves of fibers are shown in Fig. 6 and Table 2 respectively. The addition of chitosan significantly improves the tensile strength of the regenerated cellulose matrix. As compared to the regenerated cellulose fiber, the tensile strength of the chitosan/cellulose composite fiber has increased by 88% from 2.46 to 4.63 cN/dtex, and the tensile modulus increased by 115%

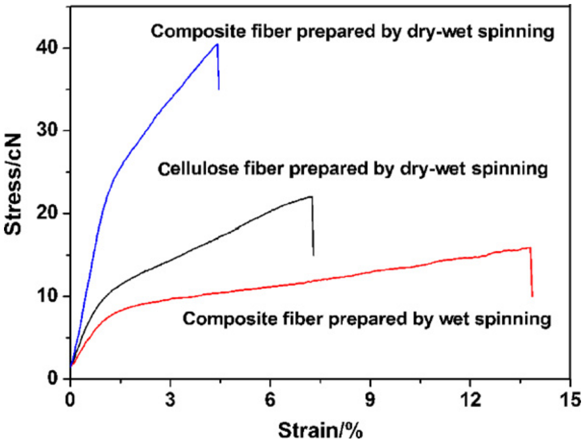

Fig. 6. Typical stress–strain behavior for the three kinds of fiber.

Table 2
Mechanical properties of the regenerated composite fiber and cellulose fiber.

Sample ID	Fineness (dtex)	Ratio of dry stretch (%)	Dry intensity (cN/dtex)	Initial Young modulus (cN/dtex)
Composite fiber prepared by dry–wet spinning process	8.15	4.58 ± 0.38	4.63 ± 0.31	233.12 ± 16.31
Composite fiber prepared by wet spinning process	8.48	13.79 ± 1.52	1.74 ± 0.13	70.75 ± 7.34
Cellulose fiber prepared by dry–wet spinning process	8.30	7.23 ± 0.84	2.46 ± 0.18	108.43 ± 10.63

from 108.43 to 233.12 cN/dtex, however, the elongation at break decreased by 36% from 7.23% to 4.58%. The enhanced mechanical properties are due to the uniform dispersion of chitosan and the hydrogen bond between chitosan and cellulose. It is well known that chitosan have amino group and hydroxyl groups and cellulose have hydroxyl groups, it is easy for them to form some interaction, i.e. hydrogen bond. The structure of chitosan is similar to that of cellulose, which ensures the excellent compatibility between them. The excellent compatibility and strong interaction between chitosan and cellulose macromolecules greatly enhance the interfacial adhesion and thus significantly improve the mechanical properties of the composite fiber.

On the other hand, the tensile strength of the composite fibers prepared by wet spinning is only 1.74 cN/dtex, which is far less than that of the composite fibers prepared by dry–wet spinning. It is due to the low stretch during wet spinning process, which leads to the chitosan macromolecules chains exist in curling state. In this case, the introduction of chitosan will be as a defect. Therefore, the introduced chitosan reinforce the regenerated cellulose matrix, but the strong stretch is necessary in order to obtain fibers with excellent mechanical properties.

4. Conclusions

In this study, a novel binary solvent system consisting of glycine hydrochloride and 1-butyl-3-methylimidazolium chloride is reported to fully dissolve chitosan and cellulose together. The regenerated chitosan/cellulose composite fiber is prepared by dry–wet spinning and wet spinning process respectively, where water is used as coagulation bath. SEM shows that chitosan exists on the surface and interior of the composite fiber. EA result shows that there is no mass loss of chitosan during the dissolving and regenerating process. WAXD results indicate that crystallinity of the regenerated composite fiber is far less than that of raw cellulose pulp. The introduction of chitosan has little effect on the crystallinity of composite fiber which is mainly caused by stretch. TGA results indicate that the regenerated composite fiber has better thermal stability and higher char yield than that of regenerated cellulose fiber, which make it a promising precursor for the preparation of carbon fiber. The dry intensity of composite fiber prepared by dry–wet spinning process and wet spinning process is 4.63 cN/dtex and 1.74 cN/dtex respectively, which indicates that the existence of air gap plays an important role on the fiber strength. Since the dry intensity of cellulose fiber prepared by dry–wet spinning process is 2.46 cN/dtex. The results indicate that the introduction of chitosan can reinforce the intensity of fiber, while a sufficiently strong stretch is also necessary in order to obtain fibers with excellent mechanical properties. As compared to the reported solvents in most references, there is no doubt that the Gly·HCl/[Bmim]Cl binary system is simple, convenient and effective for the preparation of chitosan/cellulose composite fiber.

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