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Electrospinning of native cellulose from nonvolatile solvent system

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ABSTRACT

Improving and understanding the electrospinnability of native cellulose in room temperature ionic liquids (RTIL) have been a hot issue in recent years. In this study, the electrospinning of cellulose in a highly efficient RTIL of 1-allyl-3-methylimidazolium chloride (AMIMCl) was investigated. The introduction of co-solvent dimethyl sulfoxide (DMSO), which significantly decreased the surface tension, viscosity and entanglement density of the network and increased the conductivity of the spinning dope, contributed to a continuous jet. The problems lying in nonvolatility and the high ionic strength of the RTIL, which unavoidably led to the standing up vertically, adhesion and contractions of the wet fibers during the electrospinning process, were successfully resolved using a rotating copper-wire drum as a collector and solidifying the jet under high relative humidity. The water vapor played an important role in leading to "skin formation" which helped to stabilize the fibrous morphology, and finally smooth ultra-thin regenerated cellulose fibers were obtained. The combination of solvent system and collecting apparatus and conditions provided not only an effective method of producing ultra-thin native cellulose fibers on a large scale, but also a fundamental solution to other electrospinning systems with high ionic strength and nonvolatility. Measurements on WAXD and FT-Raman indicated that the electrospun cellulose fibers were almost amorphous with a little crystallization presented the polymorph of Type-II, which was totally different from the native cellulose with the dominated polymorph of Type-I.

1. Introduction

Electrospinning is one of the simplest and most effective methods for producing micro/nanofibers with an extremely high surface area to volume ratio on a sub-cellular scale [1–5]. Until now, many synthetic and natural biopolymers have been electrospun into ultra-thin fibers; however, electrospinning of some natural biopolymers is still a challenge and the fundamental reason for the electrospinnability is not clear, such as cellulose [6–10]. Cellulose, the most abundant natural resource on earth, is categorized as a linear polysaccharide. It has many advantages such as its biocompatibility, biodegradability and regenerative properties, for which reason cellulose is widely used in packaging, textiles industries, and biomedical material fields [11,12]. Fabrication of ultra-thin native cellulose fibers via electrospinning has drawn great attention in recent years.

However, it is difficult to create non-derivative cellulose fibrous membranes via electrospinning because it cannot be dissolved in common solvents or melted due to its high crystallinity, which is enhanced by an extensive hydrogen bonding network. Therefore, selecting proper solvents is important in completing the electrospinning process of cellulose. Currently, there are several known effective solvents for cellulose [13], among which LiCl/DMAC (dimethylacetamide), NMMO (*N*-methylmorpholine-*N*-oxide), and nonvolatile room temperature ionic liquids (RTIL) were attempted to be used in electrospinning of the native cellulose [14–18]. Recently, RTIL, as a newly generated solvent family for native celluloses, with particular advantages such as excellent dissolution ability, high thermal stability, easy to recycle due to its nonvolatility, forming many different species by adjusting the structure of its cations or anions, etc. [19–21], has a great potential application in cellulose industry as green solvent. Although RTIL can dissolve cellulose very well, in most cases electrospinning of this cellulose solution in RTIL is difficult and the process is hard to control for continuous jets and fiber production. The high viscosities, high ionic strength and nonvolatility of the RTIL could unavoidably lead to the standing up vertically [16], adhesion and contractions of the wet fibers during the electrospinning process, which were also problems to other reported solvent systems [15,17]. Therefore, the difficulties in fabrication and productivity of cellulose fiber will limit the practical applications of these electrospun nanofibrous membranes [15].

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In this study, the electrospinning process of cellulose in a mixture of a highly efficient ionic liquid of 1-allyl-3-methylimidazolium chloride (AMIMCl) [22] and DMSO was investigated. The aim of this investigation is to discover the key factors influencing cellulose/ionic liquid electrospinning process and explore possible alternative fiber production methods. It has been found in our studies that the fiber morphology is mainly determined by the method used to collect and solidify the fibers, which was also observed by other groups [14,15]. However, by using a rotating drum composed of parallel copper wires as the collecting apparatus and changing the humidity of the environment, the fiber fabrication can be improved dramatically. The special RTIL solvent system and electrospinning conditions helped us to understand the electrospinning mechanism of cellulose in RTIL. In addition, the polymorphs of electrospun cellulose fibers were characterized by WAXD and FT-Raman measurements. The significance of electrospinning of cellulose on an industrial level lies in making large-scale potential applications of ultra-thin cellulose fibers in hemodialysis membranes, ultrafiltration membranes, grading purification materials, catalyst carriers, insulation clothing and other biomedical possibilities [23,24].

2. Experimental

2.1. Materials

Cotton linters (polymerization degree (DP), 1600) were used as the raw material from which cellulose fibers were obtained. The ionic liquid AMIMCl was synthesized according to the literature [23]. Double distilled water, ethanol, and dimethyl sulfoxide were obtained from Beijing Chem. Co. (Beijing, China). All materials were used without further purification.

2.2. Preparation of spinning solution

The cellulose sample was dried at 70 °C for 3 h in a vacuum oven. Cellulose/AMIMCl solutions with concentrations of 1 wt%, 3 wt%, 5 wt% were prepared by dissolving appropriate amounts of the cellulose samples into 100 mL AMIMCl solutions in a flask, respectively. The mixture was then stirred at 80 °C for approximately 2 h until the cellulose sample was completely dissolved. The cellulose/AMIMCl solutions were mixed with DMSO at specific mass ratios and gently stirred for 1 h at room temperature. Finally, cellulose solutions in AMIMCl/DMSO were obtained as shown in Table 1.

2.3. Electrospinning

The electrospinning setup is shown in Fig. 1. A high voltage power supply (The Beijing Machinery & Electricity Institute, China) was employed to generate the electric field. The applied voltage (over a range of 0–50 kV) was fixed at 15 kV and the tip-to-collector distance was fixed at 12 cm. A rotating drum (with a diameter of 8 cm) composed of parallel copper wires (with a separation of 0.8 cm and diameter of 0.15 cm) was used as the collector. The rotation speed was set at 300 r/min. An aluminum foil and an ethanol bath connected to the ground were also used as collectors for comparison. The electrospinning solutions were placed into a 5 mL syringe with a capillary tip which had an inner diameter of 0.3 mm. A syringe pump was used to feed cellulose solution into the needle tip at a rate of 50 μL/min. The environmental humidity of the electrospinning process was maintained at 60% relative humidity using a humidifier (The Beijing YADU YC-E433CL, China). After electrospinning at room temperature, the cellulose fibers were immersed in ethanol for 12 h and then washed with ethanol until there was no ionic liquid AMIMCl found by elemental analysis (C, H, N, S, Cl). The cellulose casting films were prepared from the 5 wt% cellulose/AMIMCl solutions. After 1-h immersion in water, the films were rinsed by distilled water and ethanol for many times to remove the residual AMIMCl. Both the electropsun cellulose fibrous membranes and casting films were placed into a vacuum oven at 50 °C for 30 min to dry off the resident solvent.

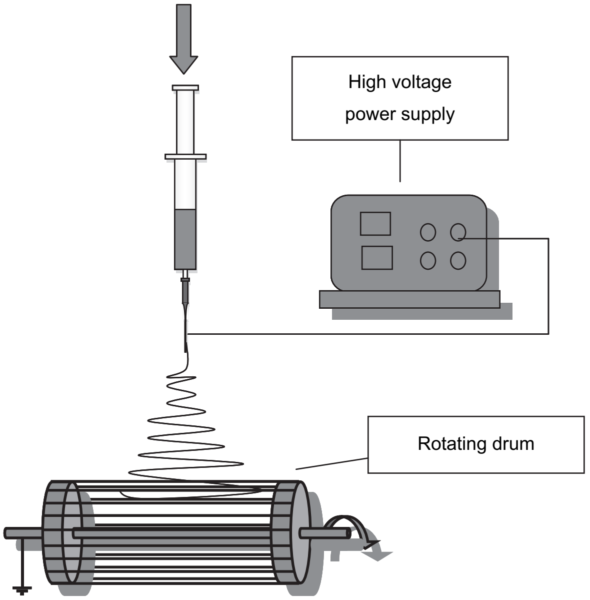

Fig. 1. Schematic representation of the electrospinning setup.

Table 1
Physical properties of the cellulose solutions and its electrospinnability

Type of solution[a]	Surface tension (mN/m)	Conductivity (mS/cm)	Spinnability[b]	Fiber diameter (nm)
0 wt%, 1:0	61.94	0.15	–	–
0 wt%, 1:2	47.05	5.58	–	–
1 wt%, 1:0	–[c]	–	–	–
1 wt%, 1:2	47.50	5.53	+	–
3 wt%, 1:2	47.46	5.60	++	300–600
5 wt%, 1:2	48.25	5.61	+++	500–800
5 wt%, 1:1	48.39	4.03	–	–
5 wt%, 1:4	45.84	6.51	+++	100–300
5 wt%, 1:8	44.81	6.07	+	–

[a] wt%: mass ratio of cellulose in cellulose/AMIMCl, mass ratio of cellulose/AMIMCl mixture to DMSO was defined as 1:n.

[b] +++: very stable jet and continuous process; ++: stable process with some jet disturbances; +: electrospraying; –: too viscous to be electrospun.

[c] –: These results could not be obtained.

2.4. Characterization

The morphologies of the electrospun fibers were observed by scanning electron microscopy (SEM, HITACHI S-4300). All rheological measurements were performed on a strain-controlled rheometer ARES (TA Instruments, USA) at 25 °C. The parallel geometry was used for the measurements of the cellulose/AMIMCl solutions, and the Couette geometry was used for the measurements of the cellulose/AMIMCl/DMSO solutions. Frequency sweeps were carried out for angular frequencies $\omega = 0.01$–100 rad/s at a strain amplitude of 1%. Shear measurements were performed in a range of shear rates from 0.05 s^{-1} to 20 s^{-1}. The surface tension of (cellulose/AMIMCl)/DMSO solutions was measured through a surface tension meter (Dataphysics). The conductivity of the cellulose solution was measured by the conductivity meter (DDS-307A, Rex Shanghai). The mass of the fibrous membranes was measured after being dried in a vacuum oven at 50 °C for 30 min before and after dipping into ethanol. Elemental analysis of electrospun fibers was conducted using an electron microprobe (EDAX, PHOENIX, America). Wide-angle X-ray diffraction (WAXD) analysis was performed on a D8 advance X-ray powder diffractometer (Bruker Co.) with Cu K_α radiation ($\lambda = 0.15406$ nm) at a generator voltage of 40 kV and generator current of 40 mA. The scanned 2θ range was from 1.5° to 40° with a scanning rate of 8° min^{-1}. FT-Raman spectra were recorded on a Raman spectrometer (EQUINOX 55, Accessory) at 2 cm^{-1} resolution with 200 scans. Factor analysis was performed on the materials in the range of 300–1500 cm^{-1}.

3. Results and discussions

3.1. Electrospinning of cellulose using AMIMCl as solvent

The cellulose/AMIMCl solutions were prepared at three different concentrations of 1 wt%, 3 wt%, and 5 wt%. The shear viscosities of the transparent solutions increased noticeably with the increase in concentration as shown in Fig. 2a. Even at a concentration of 1 wt%, the shear viscosity of the solution was above 100 Pa s at a shear rate of 0.1 s^{-1}, and the fluidity of the solution was visibly poor. When the cellulose concentrations were increased to 3 wt% and 5 wt%, the solutions were too viscous to be electrospun, that is, the solutions were hard to be pumped to the tip of the needle and the droplet at the metal capillary tip deformed little even under a strong electric field. Electrospinning of the cellulose/AMIMCl solution with a 1 wt% concentration was attempted. Under the applied voltage, no visible Taylor cone was observed, but the sphere-like droplet became bigger and bigger and finally the droplet was spattered with little extension unlike the usual electrospinning process. As a result, no fibers could be obtained from the rotating wire drum, and only several droplets could be collected using the aluminum foil as a collector, as shown in Fig. 4a.

It can be seen from Fig. 2b that both storage modulus G' and loss modulus G'' increased with the increase in cellulose concentration, which indicates that both the viscosity and elasticity of the system have increased. It has been accepted that the shift of the cross-over point of G' and G'' could reflect the change of physical crosslinking degree of the studied system [25,26]. In other words, the network caused by either chain entanglement or crosslinking is becoming tight and enhanced when the dynamic cross-over point shifts to a low frequency. As Fig. 2b shows, the cross-over point shifted to the low frequency with the increase in cellulose concentration. This reflected that the originally rigid cellulose chains became flexible through the interaction between cellulose chains and AMIMCl, which inevitably led to the result that the network in cellulose/AMIMCl system with relatively high concentration was too tight to be elongated during the electrospinning process. Furthermore, for cellulose/AMIMCl systems, the surface tension and conductivity could not be obtained due to their unusual high viscosity. However, the high surface tension (61.94 mN/m) and poor conductivity (0.15 mS/cm) of the AMIMCl did not benefit the fiber formation either, as shown in Table 1.

3.2. Electrospinning of cellulose using AMIMCl/DMSO mixture as solvent

In order to improve the electrospinnability of cellulose, a co-solvent, DMSO, was added into the cellulose/AMIMCl solution at a specific mass ratio to decrease the viscosity [27] and surface tension of the solutions. As Table 1 shows, the surface tension of AMIMCl/DMSO solvent system was much lower than that of pure AMIMCl solvent system. DMSO, as a co-solvent, could increase the conductivity (Table 1) and decrease the surface tension (Table 1) and viscosity (Fig. 3a) of the electrospinning dopes distinctly without any cellulose precipitate forming, even in solutions with high DMSO/AMIMICl mass ratios (8:1). In addition, the conductivity of the cellulose/AMIMICl/DMSO solutions increased with the increase in DMSO content. It seems that all the changes of the spinning dopes containing DMSO benefit the fiber formation.

The electrospinning process was carried out in an environmental humidity of approximately 60%, and the rotating drum was used as a collector. It was found that with the increase in DMSO content, the electrospinnability of cellulose dopes improved and continuous electrospinning process with continuous jet could be gradually observed. When the mass ratio of AMIMCl to DMSO was constant (1:2), with increases in cellulose concentration, the electrospinning process became more continuous. This indicates that the formation of uniform fibers requires a proper polymer concentration, that is, proper chain entanglements [28]. To further investigate the effect of DMSO, the mass ratio of cellulose to AMIMCl was kept at 5 wt%, and with the increase in DMSO content, the electrospinnability of the cellulose dopes was studied in detail. When the ratio of DMSO/AMIMCl was only 1:1, even with relatively low surface tension (48.39 mN/m) the dope with high viscosity (as shown in Fig. 3a) did not flow well and the droplet could not be extended completely in an electric field. When the ratio of DMSO/

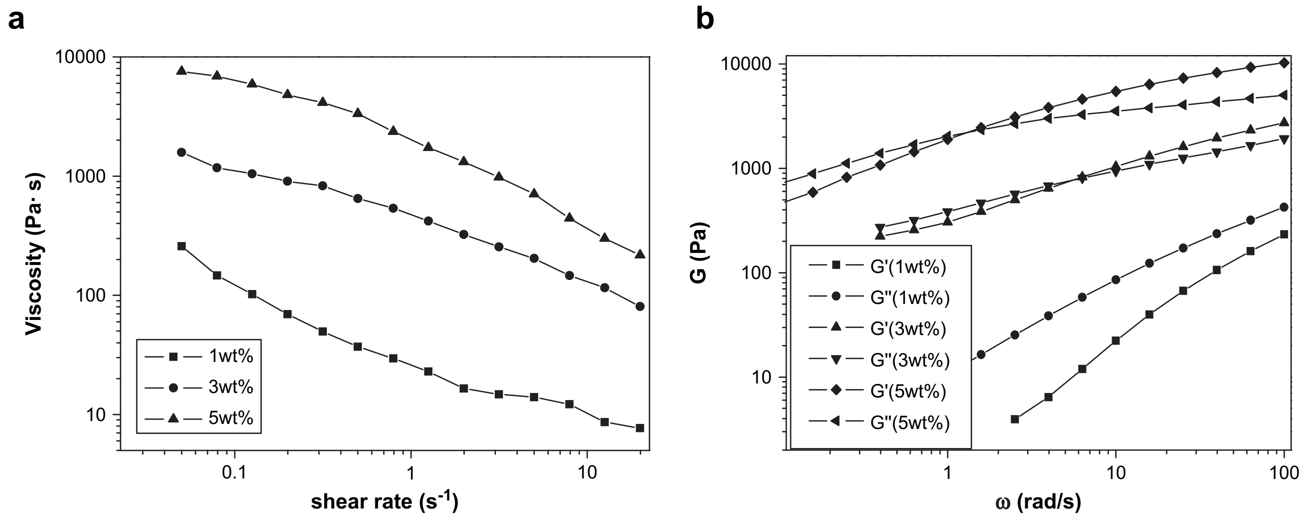

Fig. 2. Rheological measurements on the cellulose/AMIMCl solutions: (a) viscosity as a function of shear rate, (b) storage modulus (G') and loss modulus (G'') as functions of frequency at a strain amplitude of 1%. The concentration of cellulose in cellulose/AMIMCl is 1 wt%, 3 wt%, and 5 wt%.

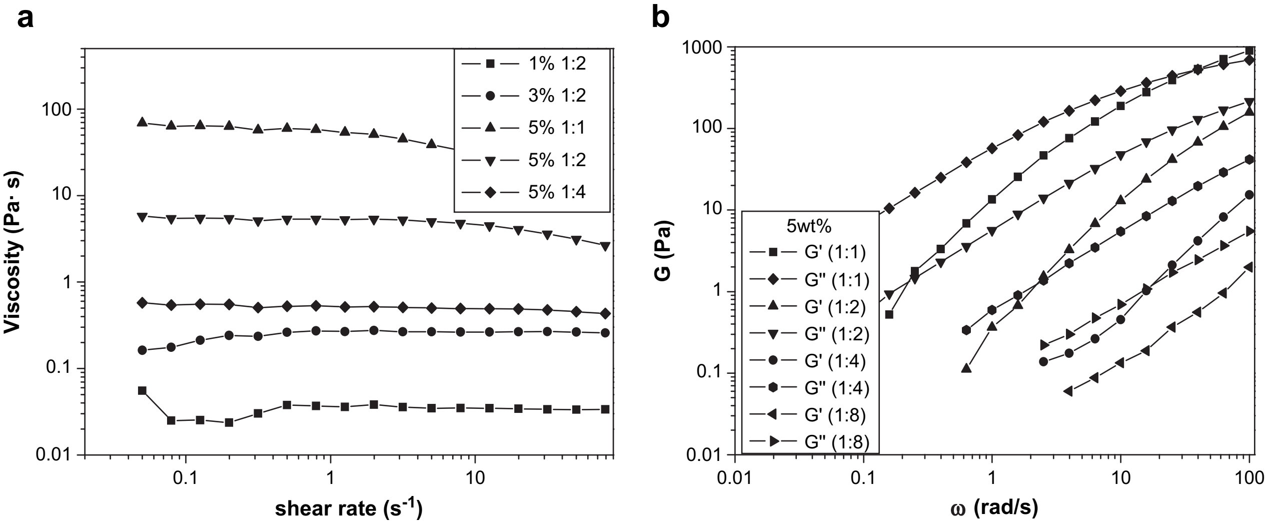

Fig. 3. Rheological measurements on the (cellulose/AMIMCl)/DMSO solutions: (a) viscosity as a function of shear rate, (b) storage modulus (G′) and loss modulus (G″) as functions of frequency at a strain amplitude of 1%. The mass ratio of cellulose in cellulose/AMIMCl is 1 wt%, 3 wt%, and 5 wt%, and mass ratio of cellulose/AMIMCl mixture to DMSO was defined as 1:n.

AMIMCl was 8:1, electrospraying was observed and no fibers could be collected. This could be supported by the fact that the fibers could not be formed as the concentrations of solutions were below the critical electrospinning concentration [28]. As Fig. 4b–d shows, smooth cellulose fibers could be obtained only when the polymer concentration and solvent ratio were in the proper range.

It can be observed from Fig. 3b that the cross-over point shifted to the high frequency with the increase in DMSO content, which indicated that the entanglement density of the network could be weakened by the introduction of the co-solvent DMSO. As a result, a stable jet could be obtained finally. Therefore, it can be concluded that the contribution of chain entanglement (or both viscosity and elasticity), surface tension and conductivity should be adjusted simultaneously in this study in order to suppress the Rayleigh instability and enhance the whipping instability of the jet and finally achieve the satisfied spinnability [29]. Therefore, the addition of DMSO contributed to the formation of a continuous jet.

It is known that fiber diameter was mainly controlled by changing the solution properties and the electrospinning process parameters [9]. Under smooth fiber processing conditions, the

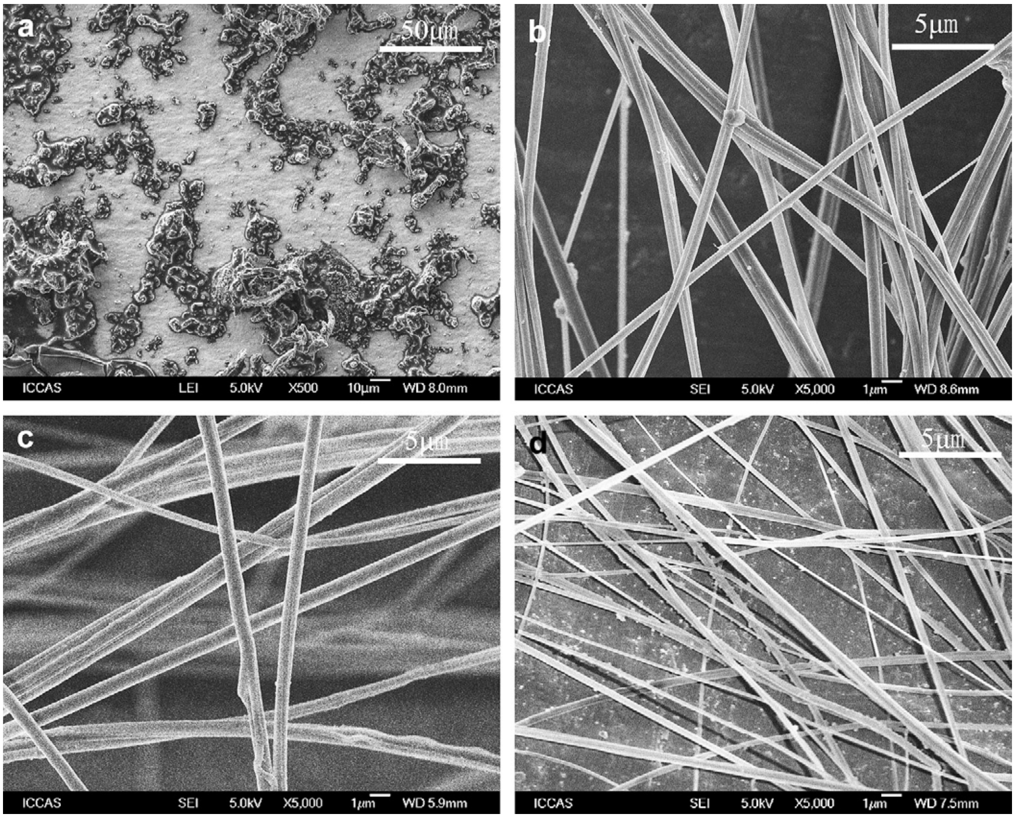

Fig. 4. SEM images of cellulose fibers at different cellulose concentrations and different AMMIMCl/DMSO ratios. (a) 1 wt%, 1:0; (b) 3 wt%, 1:2; (c) 5 wt%, 1:2; (d) 5 wt%, 1:4; (a) aluminum foil was used as a collector; (b–d) rotating wire drum was used as a collector.

processing parameters, such as the voltage and distance form the needle tip to the collector, have little impact on the cellulose fiber diameter. It has been demonstrated that the fiber diameter is mainly determined by the surface tension, viscosity, conductivity of the spinning solution. With a lower surface tension, lower viscosity and higher conductivity, a smaller fiber diameter can be produced as shown in Table 1. The average fiber diameter of cellulose was in the range of 100–800 nm.

3.3. *Optimization of the collecting method*

It was found that under a high electric field, all fibers stood straight up on the collector; however, most wet fibers collapsed into droplets when the electric field was withdrawn. This phenomenon was also reported by another group [16] with the solvent system of DMAC/LiCl. Cellulose/AMIMCl was a special solution system due to the high ionic strength and nonvolatility of AMIMCl. The large number of ions existing in the fiber had a strong response to the electrostatic force, which might surpass the effect of the gravitational force. Therefore all the fibers containing nonvolatile ionic liquid were forced to stand straight in the electric field as opposed to lying on the collector [16]. When the electric field was turned off, the fibers collapsed as there was no force left opposing gravity, and the high surface tension of the nonvolatile AMIMCl caused them to contract into droplets. Generally, the morphologies of cellulose fibers were mainly determined by the processes of collection and solidification. The cellulose/AMIMCl/DMSO solution (5 wt%, 1:2) was electrospun to investigate the effect of different collectors and solidification method on the fiber fabrication.

When the aluminum foil was used as a collector, all wet filaments were standing vertically. Once the applied voltage was turned off, most collected wet filaments or jets contracted into droplets. A few filaments might have kept the fibers' morphology, but with larger diameters, which can be seen from Fig. 5a. In order to solidify the fibers, the ethanol bath was used as a collector to remove the nonvolatile AMIMCl. It was observed that all wet filaments still stood vertically and would not sink in the ethanol bath. Only a few standing wet filaments could be pulled into the ethanol by moving the bath. Furthermore, most of the cellulose fibers collected from the ethanol bath adhered strongly (Fig. 5b) because the newly produced fibers were piling up on the surface of the bath much faster than they were sinking. Another possible reason might be that the removal of AMIMCl was too slow to keep up with the fiber production. As the wet filaments containing a lot of AMIMCl were very malleable and susceptible to shrinking, it seemed that additional traction force provided by a rotating wire drum might be an ideal solution to the above mentioned problem. When the rotating wire drum was used as a collector, it was found that the wet filaments were rolling collected by the copper-wire drum and partially fibers were orientated perpendicular to the wires. Finally, smooth cellulose nanofibers were successfully fabricated, as shown in Fig. 5c. It was accepted that the support and traction provided by the aligned copper wires delayed the contraction of the fibers caused by the surface tension effect and prolonged the time for solidification of the filaments.

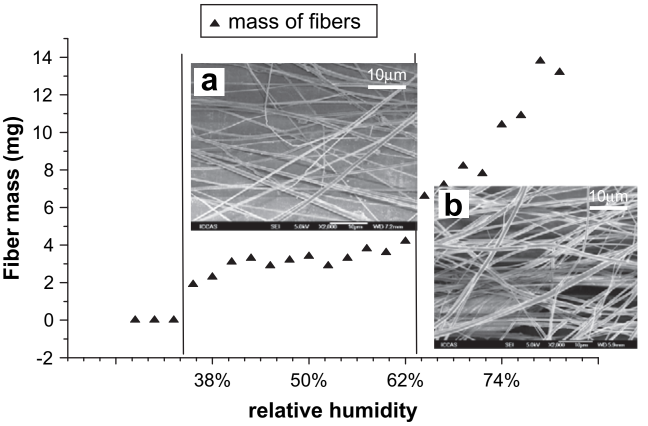

Fig. 6. Effect of humidity on fiber productivity. The solution (5 wt%, 1:2) was electrospun with a rotating wire drum as collector. The fibers were collected after electrospinning for 5 min and the mass of fibers was measured after removing residual solvents under different relative humidity; (a) relative humidity is 45%; (b) relative humidity is 75%.

It was also observed that the success of fibers' fabrication is not only related to the special collection method, but also related to the environmental humidity. With increase in the relative humidity, the production efficiency of cellulose fibers increased dramatically. As shown in Fig. 6, no fibers were obtained within 5 min of electrospinning (concentration of 5 wt%, AMIMCl/DMSO = 1:2) when the relative humidity was less than 30%; when the relative humidity was in the range of 30–64%, around 2–4 mg fibers were obtained within 5 min of electrospinning; when the relative humidity was above 64%, more than 6 mg fibers could be produced and the productivity could reach to 14 mg when the relative humidity was 80%. The phenomenon might be attributed to the "skin formation" during the spinning process and subsequently prevent the newly formed fiber from adhering together. It has been discovered in previous research that AMIMCl is a good solvent for cellulose while water is a coagulated solvent. AMIMCl can completely miscible with water in any ratio; therefore, the regenerated cellulose materials were easily obtained by coagulating cellulose/ionic liquid solution in the water. The inter- and intra-molecular hydrogen bonds of cellulose reformed due to the presence of water, which were disrupted during dissolving in AMIMCl [22]. In the

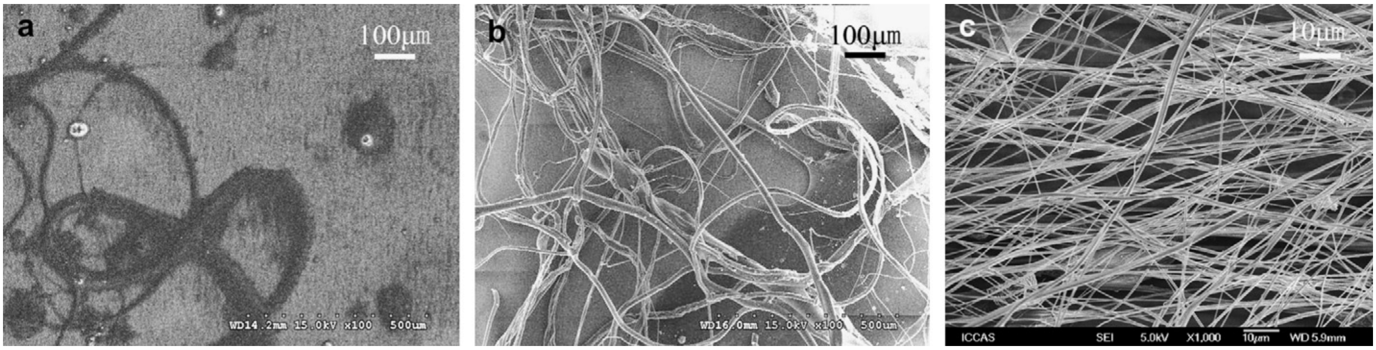

Fig. 5. SEM images of cellulose fibers collected by different collection methods. The solution (5 wt%, 1:2) was electrospun under the humidity around 60% by (a) aluminum foil; (b) aluminum foil in ethanol bath with moving liquid surface; (c) a rotating copper-wire drum. All fibers were washed by ethanol and dried in vacuum oven.

present study, the water vapor could cause the cellulose coagulate from the surface of the wet jets and the shape of the jets could be kept during the collecting process. The “skin” formation could help to keep the shape and mass of the formed fibers, and further hinder the shrinkage of the fiber jet and promote the ultra-thin cellulose fiber fabrication. This special solidification method provides a new way for the electrospinning of polymer in nonvolatile solvent.

When the cellulose at the surface of the fibers was coagulated into a “skin” by the water vapor, almost all of the cellulose/AMIMCl was kept inside the fibers. In order to remove the AMIMCl, electrospun cellulose fibers were kept immersed in ethanol for 12 h. The mass of dried fiber was measured before and after its immersion in ethanol, and it was found that the mass of the fibers after immersion was less than that of the original one. The resultant mass of cellulose was equivalent to the concentration of cellulose in the electrospinning dope. The element analysis results (Fig. 7) showed that N and Cl elements could be observed in the fibrous products without immersion in ethanol. However, no N and Cl elements existed in the electrospun cellulose fibers after immersion in ethanol. These results implied that AMIMCl was kept in the fibers during the electrospinning process and could be removed by immersion in the ethanol bath. Therefore, the ultra-thin cellulose fibers could be finally produced by the above mentioned methods in a large scale and have the potential applications in many fields.

3.4. Crystallization of the electrospun cellulose fibers

The polymorphic changes in the structure of cellulose during the regeneration are essential for understanding the industrial processing of the cellulosic materials. The transformation of cellulose Type-I into Type-II could be caused by mercerization or regeneration of native cellulose [30]. The native cellulose generally presents polymorph of Type-I with the highest degree of intermolecular and intramolecular hydrogen bonding, and the crystalline polymorph of Type-II forms when cellulose is treated with water or methanol during the regeneration [30]. In this study, the polymorphs of native cellulose, cellulose casting film and electrospun cellulose fibers were investigated in detail.

As shown in Fig. 8, X-ray diffraction patterns revealed that the natural cellulose presented the polymorph of Type-I (characteristic peaks at $2\theta = 14.7°$, $16.4°$, $22.5°$) [18], while the electrospun cellulose fibers and the cellulose casting film were mostly amorphous (amorphous peak at $2\theta = 20.8°$). As mentioned before, most of the inter- and intra-molecular hydrogen bonds of cellulose were destroyed when dissolving in AMIMCl [22]. The fast coagulation and regeneration of cellulose from the ionic solution might lead to the difficulty in re-crystallization of cellulose chains.

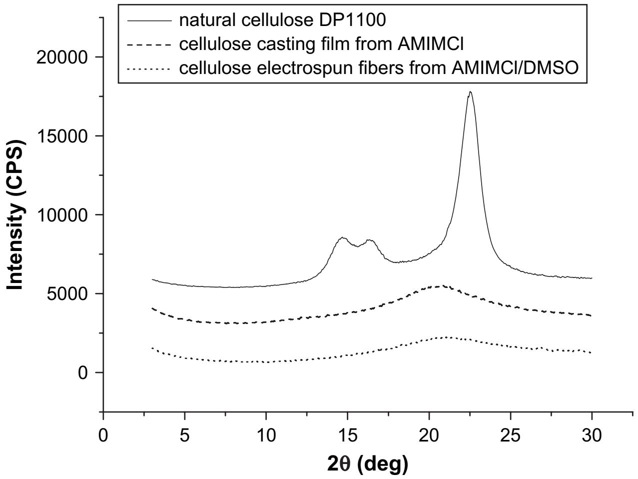

Fig. 8. X-ray diffraction patterns of natural cellulose (cotton), casting film of cellulose and electrospun cellulose fibers.

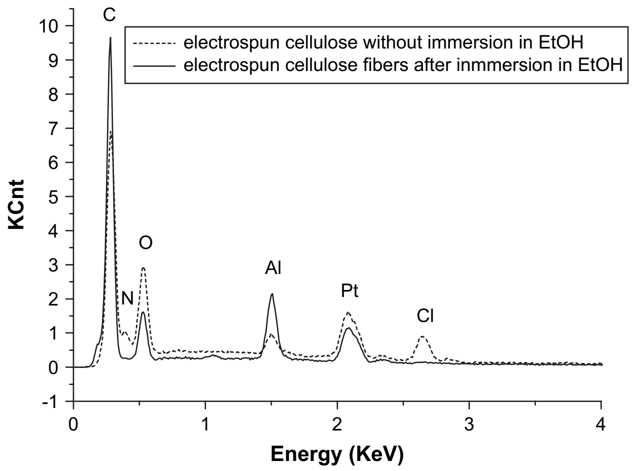

Fig. 7. EDAX analysis of electrospun cellulose fibers before and after immersion in EtOH to remove the AMIMCl.

FT-Raman spectra, as a rapid analytical tool for detecting the polymorphs of polymers, were used to characterize the crystalline polymorphs of cellulose. As shown in Fig. 9, The natural cellulose presented Type-I polymorph, as characterized by five typical Raman peaks: 379 cm^{-1}, 435 cm^{-1}, 894 cm^{-1} and 1457–1479 cm^{-1} [31]. However, the electrospun cellulose fibers and casting cellulose films showed Type-II polymorph, as clearly characterized at peaks of 354 cm^{-1}, 420 cm^{-1}, 896 cm^{-1} and 1461 cm^{-1} [31]. Therefore, it can be concluded that the cellulose in AMIMCl regenerated by water had rather low crystallinity and the typical polymorph was Type-II.

4. Conclusions

In this study, the electrospinning of cellulose in a mixed solvent system of AMIMCl/DMSO was investigated for the first time. It was found that the cellulose/AMIMCl solution could not be electrospun even at a cellulose concentration of only 1 wt%. The introduction of DMSO demonstrated a decrease in the surface tension, entanglement density of the network and viscosity of the spinning solution that stabilized the whipping instability of the jet and improved the

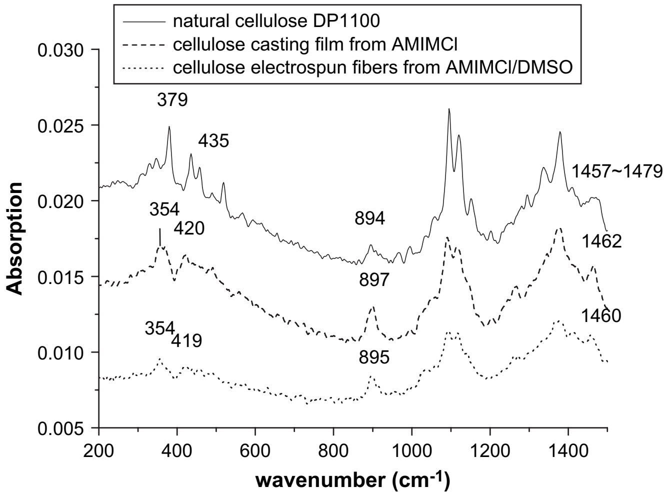

Fig. 9. FT-Raman spectra of natural cellulose (cotton), casting film of cellulose and electrospun cellulose fibers.

electrospinnability of the mixture dramatically. Therefore, the chain entanglement density, viscosity, surface tension and conductivity should be adjusted simultaneously in this study in order to suppress the Rayleigh instability and enhance the whipping instability of the jet and finally achieve the satisfied spinnability.

This present study provides a simple and practical method of fabricating biopolymers fibers through the electrospinning of their viscous solutions. For the special nonvolatile solvent AMIMCl, a rotating drum composed of parallel copper wires was used as a collector in order to avoid the contraction of the wet fibers. As the relative humidity of the environment was increased, a “fiber skin” was formed due to the coagulation of the cellulose on the surface of the fibers with little adhesion between fibers and the production efficiency of cellulose fibers increased significantly. This particular collecting and solidification method was a successful technique which can be used for other spinning solutions with nonvolatile solvents or solvents of low volatility. It was verified that the regenerated electrospun cellulose fibers had rather low crystalline degree and the typical polymorph was Type-II. The improvements made in the electrospinning of native cellulose allow the production of ultra-thin cellulose fibers to be carried out in a large scale.

Acknowledgements

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