

FORMATION OF CORNCOB CELLULOSE FIBER
WITH UNIFORM MORPHOLOGY IN ELECTROSPINNING BY USING
Cu(OAc)₂ AND METHYL HEXADECANOATE

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Ultrafine corncob cellulose fibers with uniform morphology were electrospun, in the presence of Cu(OAc)₂ and methyl hexadecanoate in the spinning solution. After adding Cu(OAc)₂, both the conductivity of the solution and the chain entanglement of cellulose were controlled to impact the morphology of electrospun cellulose fibers. Uniform diameter distribution can be only obtained under proper conditions (namely, the concentration of Cu(OAc)₂ of 0.1%). Then, methyl hexadecanoate was further used to reduce the chain entanglement of cellulose in the solution. Electrospun cellulose fibers with the diameters around ~500 nm and uniform diameter distribution were finally obtained. The use of organic salts and single functional group contained additive provides a feasible and important method to control fiber methodology of cellulose via electrospinning.

Keywords: cellulose, electrospinning, fiber, morphology, chain entanglement

INTRODUCTION

As the most abundant biomass resource, with many advantages, such as biocompatibility, chemical stability and biodegradability, cellulose is a promising alternative to fossil resources in producing novel polymer materials and environmentally neutral products.¹⁻³ If cellulose can be prepared into superfine fibers, it will exhibit good application potential in the areas of biomedical materials, filtration membranes and protective clothing.^{4,5} For this, the structure and morphology of cellulose fibers are of key importance to obtaining high-quality materials and products.

In comparison with traditional wet spinning, electrospinning is a spinning technology that involves applying an external electric field to a polymer solution to produce fibers with the diameter at the micro- and nano-level.⁶⁻⁸ Ultrafine fibers produced by electrospinning show great value in adsorption, filtration and other fields. In

contrast to synthetic polymers, such as polyester, polyurethane, nylon and polyvinyl alcohol, cellulose is very difficult to electrospin because of the high rigidity and strong interaction of its molecular chains, which is induced by the large number of hydroxyls on its glucan chains.⁹

Although, in recent years, many solvent systems, such as DMAc/LiCl,^{10,11} ionic liquids^{12,13} and the alkali/urea aqueous solvent,¹⁴ have been utilized to promote the electrospinning of cellulose, it is still difficult to control the morphology of electrospun cellulose fibers. As reported in the study of Kim and coworkers,¹⁰ only cellulose fiber with rather poor morphology could be obtained during electrospinning by using DMAc/LiCl and NMMO (4-Methylmorpholine N-oxide)/water as solvents. Though the fiber morphology can be improved by pre-activation of cellulose with alcohol and water, with the aim to increase the solubility, uniform

spinning of cellulose fibers can only be realized in a relatively large diameter range – around 1-2 μm .^{15,16} Trifluoroacetic acid (TAF) and NMMO were each used for electrospinning of cellulose to provide better dissolution and stronger molecular entanglement in solution.¹⁷ However, because of the strong solvent volatility of TAF and unexpected reduction in the molecular chain of cellulose induced by NMMO, the electrospinnability and fiber formation became unstable, which led to uneven morphology of electrospun cellulose fibers.¹⁷ Also, ionic liquids, for instance 1-butyl-3-methylimidazolium chloride (BminCl)¹⁸ and 1-allyl-3-methylimidazolium chloride (AmimCl),¹⁹ were utilized to prepare electrospun cellulose fibers. The super dissolving ability of ionic liquids gives enough chain entanglement to the cellulose molecular chains in solution. Accordingly, the electrospinning of cellulose can be carried out at a lower solution concentration.¹⁸ The only problem of the ionic liquid used as solvent concerns its volatility, which results in massive blocks or beads in the morphology of electrospun fibers. DMSO or DMF¹⁹ needs to be added to the ionic liquid for adjustment.

Research has shown that the morphology of electrospun fibers is mainly decided by the ability and level of chain entanglement of the polymer in the spinning solution.²⁰ However, as to cellulose, the high rigidity of molecular chains firstly determines the difficulty to form the traditional physical entanglement between molecular chains; on the other hand, the interaction produced by the large number of hydroxyls on the molecular chain leads to high apparent viscosity at low solution concentration. This contradictory characteristic of cellulose leads to a decline in spinnability and in the uniformity of fiber morphology. Considering the control on the process of electrospinning, on basis of the analysis of the stability and continuity of the solution jet at the end of the Taylor cone, the charge density and conductivity of the spinning solution are undoubtedly recognized as very important to the regulation of fiber morphology, which is deeply affected by the ion state and concentration in solution. Although controlling several parameters of the spinning process, such as accelerating voltage, injecting flow rate, and receiving distance, can improve the morphology of electrospun cellulose fiber to a certain extent, this method cannot replace the control of the thermodynamic nature of the cellulose solution (including solution

concentration, solution composition, conductivity, shear viscosity *etc.*), so as to effectively promote the formation of high-quality electrospun fiber, which is related to the chain entanglement of cellulose.

In our previous research,^{15,16} we had utilized alcohol activation to control the balance between dissolving and precipitation of cellulose. A suitable amount of ethanol was noticed to change the strength of chain entanglement in cellulose to reduce the viscosity of the cellulose solution and to improve the migrating ability of the ions in the solution with DMAc/LiCl used as solvent. As a result, ultrafine fiber, with relatively uniform morphology, was obtained by electrospinning. However, the compatibility between ethanol and cellulose is poor. The control of fiber morphology is only limited to a certain range.

In this work, following the idea to adjust the thermodynamic nature of the cellulose solution, we investigated the use of organic salts and single functional group contained additive in the cellulose solution with DMAc/LiCl. By examining the change of ionic conductivity and the level of chain entanglement of cellulose in the process of dissolving and electrospinning, the effect of $\text{Cu}(\text{OAc})_2$ and methyl hexadecanoate will be systematically analyzed. Based on the control of the composition of the cellulose solution, the formation of ultrafine fiber with uniform morphology in electrospinning is exhibited. This work does not only contribute to the principle of promoting the status of cellulose chains in the spinning solution, but it also further elucidates a feasible way to control the fiber morphology of cellulose via electrospinning.

EXPERIMENTAL

Materials

Cellulose (DP ~1440) from corn cob was purchased from Jinan Shengquan Group Co., Ltd. The DP (degree of polymerization) of the cellulose was examined by the standard test method (ASTM D1795-94 (2001)). Cellulose was dried under vacuum at 120 °C for 12 h to completely remove the moisture before use. Anhydrous cupric acetate ($\text{Cu}(\text{OAc})_2$), methyl hexadecanoate, LiCl, DMAc and ethanol were all of analytical grade, were supplied by Aladdin Reagent and used without further purification.

Preparation of cellulose solution with $\text{Cu}(\text{OAc})_2$ and methyl hexadecanoate

$\text{Cu}(\text{OAc})_2$ was put into 100 mL DMAc with the concentration of 0-0.45% (wt/v) and stirred for 1 h at room temperature. 8% (wt/v) LiCl was added into the

mixture and then stirred for 3 h to prepare mixed DMAc/LiCl/Cu(OAc)₂ solvent. The dissolution of cellulose in the DMAc/LiCl/Cu(OAc)₂ solvent was carried out with two steps. Firstly, 3 g cellulose was soaked and activated in ethanol for 1 h by following the method shown in the reference.¹⁷ After filtration, the cellulose was put in an oven to dry at 80 °C until the residual ethanol reached 40% (weight ratio to cellulose). After that, the activated cellulose was respectively added into the solvents of DMAc/LiCl/Cu(OAc)₂ under vigorous agitation for 48 h. The weight ratio of cellulose to solvent was controlled at 3 wt%. In the other group, methyl hexadecanoate was continuously added into the cellulose solution with the concentration of 0.5-1.2% (wt/v) and stirred for 1 h. The specific components of the cellulose solutions were summarized in Table 1.

Electrospinning

A small amount of undissolved impurities was separated from the cellulose solution by a Buchner funnel. Then, the cellulose solutions were poured into a 5 mL syringe with a fixed hypodermic stainless steel needle (inner diameter of 0.7 mm and 22 mm in length), the tip of which had been cut flat. After setting up the syringe on a microinjection pump (single type, Fisher Scientific), the cellulose solution was electrospun into ultrafine fibers. The metal capillary was connected to high-voltage power supply (Model DW-P503-4AC, Tianjin, China). A grounded custom-made rotating collector wrapped around by a non-woven mat was utilized to collect the ultrafine fibers (as shown in Fig. 1). The feed rate of the solution was controlled at 0.6 mL/h, and the needle was positioned 10-15 cm from the collector. The obtained fibers were then removed from the non-woven mat and dried for 4 h at room temperature.

Table 1
Composition of cellulose solutions for electrospinning

Cellulose, g	DMAc, g	LiCl, g	Cu(OAc) ₂ , g	Methyl hexadecanoate, g
3.051	93.7	8	0	0
3.051	93.7	8	0.0937 (0.1%)	0
3.051	93.7	8	0.1874 (0.2%)	0
3.051	93.7	8	0.3280 (0.35%)	0
3.051	93.7	8	0.4216 (0.45%)	0
3.051	93.7	8	0.0937 (0.1%)	0.4685 (0.5%)
3.051	93.7	8	0.0937 (0.1%)	0.7496 (0.8%)
3.051	93.7	8	0.0937 (0.1%)	1.1244 (1.2%)

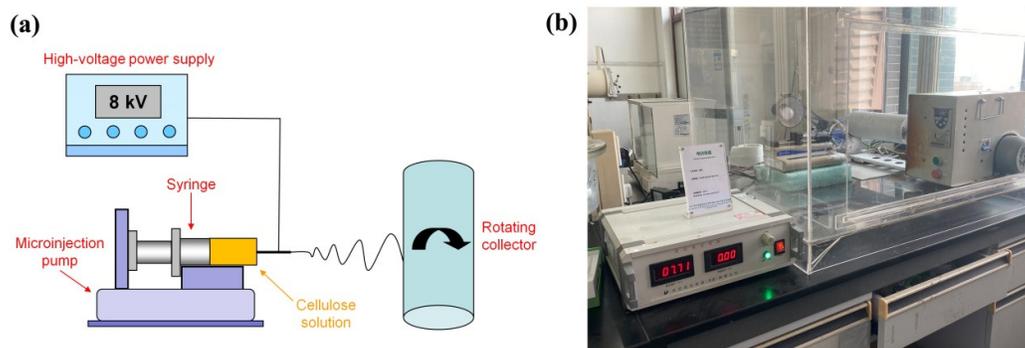


Figure 1: Schematic diagram (a) and photograph (b) of the electrospinning experimental set-up

Characterization

The electric conductivity of the cellulose solutions was determined by a conductivity meter (INESA DOS-307A) at 20 °C. The conductivity electrode was washed with deionized water and completely dried before each test. All the measurements were taken at least three times to calculate the average.

Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrometer from Thermo-Fisher Scientific. A KBr sheet was first pressed in a hydraulic machine, and then, the cellulose solution was used to coat the KBr

sheet for the FT-IR test.

The shear viscosities of the fluids were measured at different shear rates using a dynamic analyzer. A stress-controlled rheometer (Anton Paar Physical MCR 301) was equipped with cone/plate geometry (diameter 60 mm, angle 1°, plate-to-plate gap 0.104 mm). Steady shear measurements were assessed in an equilibration time of 20 s at each data point. For the dynamic stress sweep measurements, the frequency sweep was measured in the linear viscoelastic regime of the samples over a frequency range of 0.01 to 500 rad/s.

The surface tension of the cellulose solutions in

DMAc/LiCl, with the addition of 0.1% Cu(OAc)₂, or with the addition of 0.1% Cu(OAc)₂ and 0.5% methyl hexadecanoate, was determined by the pendant drop method on a contact angle measuring instrument (Dataphysics OCA25, Germany).

A scanning electron microscope (SEM, Hitachi TM-1000) was utilized for the observation of the morphologies of the collected fibers. The dried fiber samples were all gold coated before the test. The diameter of 100 fibers was measured in Photoshop software for the calculation of diameter distribution.

RESULTS AND DISCUSSION

Dissolution of cellulose in DMAc/LiCl/Cu(OAc)₂

Cellulose was firstly dissolved in DMAc/LiCl/Cu(OAc)₂. The mixed DMAc/LiCl/Cu(OAc)₂ solvent and the cellulose solution were each observed and shown in Figure 2. The mixture of DMAc/Cu(OAc)₂ exhibits a pale blue colour (Fig. 2(a)), which reflects the color of Cu²⁺. After being mixed with LiCl, the

color of the mixed solvent changed to yellow (Fig. 2(b)). This is because Cu²⁺ has the ability to form complexes with a large absorption coefficient. The yellow color reflects the formation of the tetrachlorocuprate (II) complex (namely (CuCl₄)²⁻).²¹ In this situation, cellulose with a high DP (~1440) can dissolve in this mixed DMAc/LiCl/Cu(OAc)₂ solvent. After the dissolution of cellulose, the solution appears with a pale brown color (Fig. 2(c)). This result indicates the complexation of (CuCl₄)²⁻ produced by Cu²⁺ does not disappear.

Figure 3 shows optical microscopy images of the 3% cellulose solution in the DMAc/LiCl/Cu(OAc)₂ solvent with Cu(OAc)₂ concentrations of 0.1-0.55%. With the increase in the concentration of Cu(OAc)₂, the solubility of cellulose slightly decreases. For 0.3% Cu(OAc)₂, some undissolved celluloses begin to appear in the image.

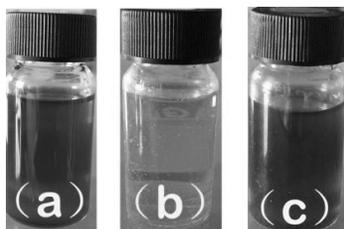


Figure 2: Mixed solvents of (a) DMAc/Cu(OAc)₂ (pale blue in practice), (b) DMAc/LiCl/Cu(OAc)₂ (yellow) and (c) cellulose solution in DMAc/LiCl/Cu(OAc)₂ (pale brown)

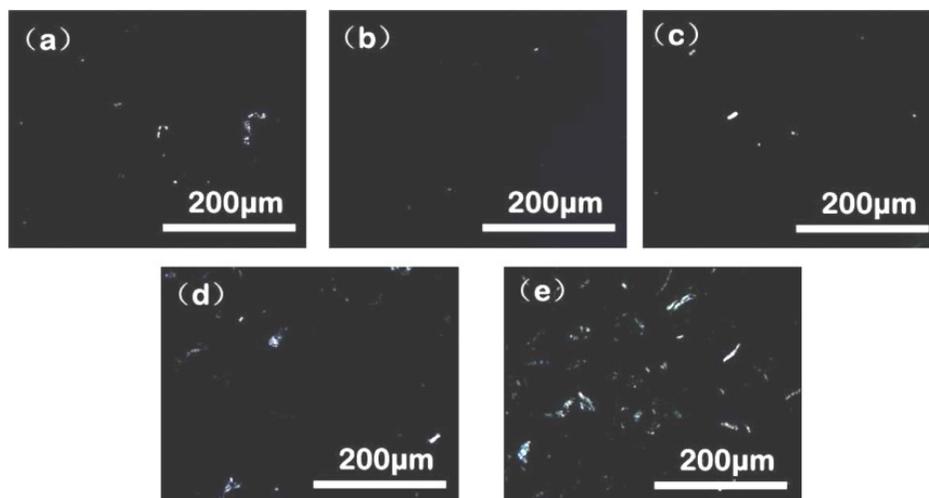


Figure 3: Optical microscopy images of 3% cellulose solution in DMAc/LiCl/Cu(OAc)₂ solution with Cu(OAc)₂ concentrations of (a) 0.1%; (b) 0.2%; (c) 0.35%; (d) 0.45%; and (e) 0.55% (wt/v)

causes a decrease of free ions and a reduction of conductivity. Not only that, a large amount of $(\text{CuCl}_4)^{2-}$ also induces a stronger interaction between the molecular chains of cellulose. It confines the dissolving rate and even capability of cellulose. Figure 6 shows the FT-IR spectra of the cellulose solutions in DMAc/LiCl/Cu(OAc)₂. The absorption bands around 3600 cm⁻¹ and 3306 cm⁻¹ refer to the stretching vibrations of intra- and inter- molecular hydrogen bonds of cellulose.¹⁶ With the increase in the concentration of Cu(OAc)₂, the shape of the absorption band begins to widen. It reflects the formation of a strong and new association of hydrogen bonds, which concerns the interaction between $(\text{CuCl}_4)^{2-}$ and the molecular chains of cellulose. After increasing the concentration of Cu(OAc)₂ to 0.35-0.45%, there appears a small absorption band at 890 cm⁻¹ on the FT-IR curves. It is related to the stretching vibration of the glycosidic bond

of undissolved type I cellulose in the solution.^{24,25} This phenomenon presents a decrease in the solubility of cellulose in the mixed DMAc/LiCl/Cu(OAc)₂ solvent.

Electrospinning of cellulose solution to produce ultrafine fibers

The steady shear viscosities of cellulose solutions were further evaluated (see Fig. 7(a)). In comparison with the cellulose solution without Cu(OAc)₂, the steady shear viscosity of the solution with 0.1% and 0.2% Cu(OAc)₂ shows a lower Newtonian plateau. This result indicates decreased interaction and low molecular entanglement between the molecular chains of cellulose. However, after increasing the concentration of Cu(OAc)₂ to 0.35-0.45%, the steady shear viscosity of the cellulose solution obviously increases. The viscosity value even overcomes that of the solution without Cu(OAc)₂.

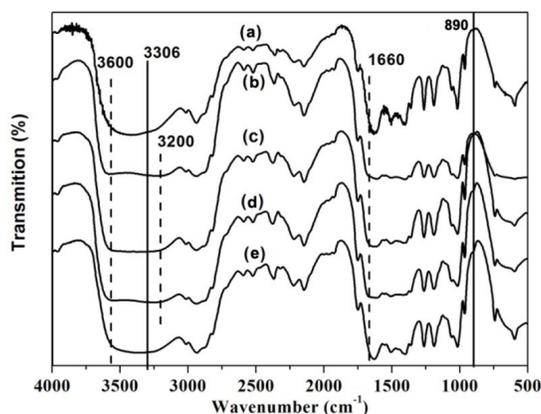


Figure 6: FT-IR spectra of cellulose solutions with different concentrations of Cu(OAc)₂ at (a) 0%; (b) 0.1%; (c) 0.2%; (d) 0.35%, (e) 0.45%

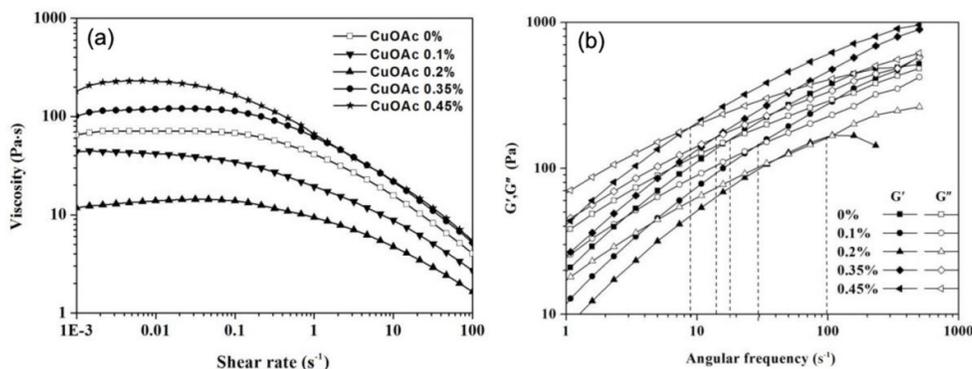


Figure 7: Plots of shear viscosity (a) and dynamic modulus (b) of cellulose solutions in DMAc/LiCl/Cu(OAc)₂ with different concentrations of Cu(OAc)₂

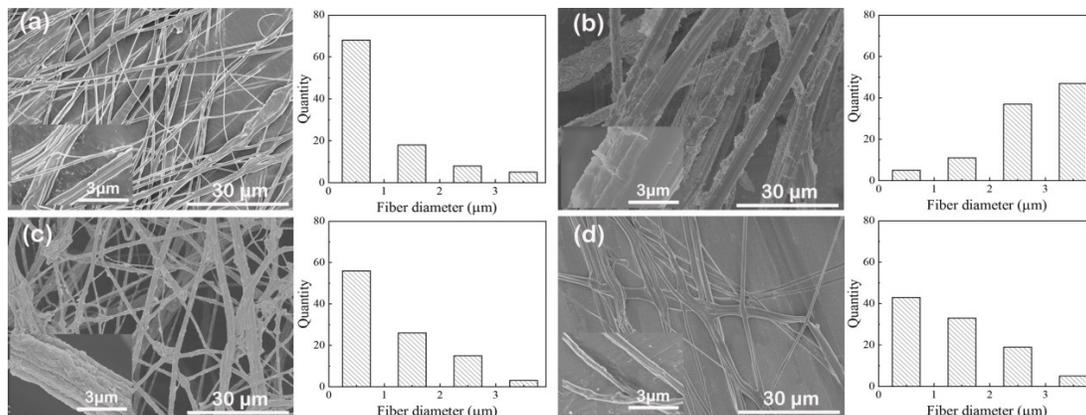


Figure 8: Morphology and diameter distribution of electrospun fiber from the cellulose solution in DMAc/LiCl/Cu(OAc)₂ with different concentrations of Cu(OAc)₂ at (a) 0%, (b) 0.1%, (c) 0.2%, (d) 0.35%

That is because of the quite strong interaction between the molecular chains of cellulose induced by the formed $(\text{CuCl}_4)^{2-}$. The curves of G'' and G' plots against angular frequency of the cellulose solution with Cu(OAc)₂ are shown in Figure 7(b). The change of the gel points clearly shows the status of the entanglement of cellulose chains in solutions. After adding 0.1-0.2% Cu(OAc)₂, the gel points only begin to appear at higher angular frequency, which refers to the low entanglement of molecular chains. After using 0.35-0.45% Cu(OAc)₂, the gel points appear at the area of low angular frequency. It reflects strong entanglement of the molecular chains of cellulose in the mixed DMAc/LiCl/Cu(OAc)₂ solvent.

All the cellulose solutions were used in electrospinning to prepare ultrafine fibers. Figure 8 exhibits the morphologies and diameter distribution of the electrospun fibers obtained from the cellulose solutions with different concentration of Cu(OAc)₂. Without Cu(OAc)₂, only fibers with uneven diameter distribution can be obtained (Fig. 8(a)). This is explained by the low spinnability of corncob cellulose in electrospinning. After adding 0.1% Cu(OAc)₂ to the cellulose solution, due to an enhancement of conductivity, the spinnability is improved. It produces electrospun fibers with relatively uniform diameter distribution. The diameters of the electrospun cellulose fibers are mainly concentrated in the range of 3-6 μm (Fig. 8(b)). Further increasing the Cu(OAc)₂ in the cellulose solution to 0.2%, the diameter of the electrospun fibers begins to decrease (Fig. 8(c)). The diameter distribution of the obtained fibers basically remains uniform to some extent. However, because the chain entanglement of cellulose decreases a lot, there appears some fiber breakage

and a non-fibrous area. Figure 8(d) presents the morphology of the electrospun fibers formed in the solution with 0.35% Cu(OAc)₂. Although the chain entanglement of cellulose is reformed due to the effect of $(\text{CuCl}_4)^{2-}$ in order to satisfy the requirement for the formation of ultrafine fiber in electrospinning, the conductivity of the cellulose solution decreases too much. As a result, fibers with a small diameter and some non-fibrous areas are still produced in electrospinning.

The introduction of Cu(OAc)₂ in the cellulose solution induces a dual effect to impact the formation of fiber in electrospinning. The change of fiber morphologies in electrospinning reflects the comprehensive effects of conductivity and ion complexation in the cellulose solution. Only under proper conditions, electrospun fibers with uniform morphology can be obtained.

Morphology control of electrospun fiber by methyl hexadecanoate

In order to further improve the morphology of electrospun cellulose fiber, methyl hexadecanoate was used to control the chain entanglement in the cellulose solution. Figure 9(a) shows the steady shear viscosities of the 3% cellulose solutions in DMAc/LiCl/Cu(OAc)₂/methyl hexadecanoate with 0.1% Cu(OAc)₂ and 0.5-1.2% methyl hexadecanoate. With the increase in the concentration of methyl hexadecanoate, the steady shear viscosities of the cellulose solutions gradually decrease. These results indicate the interaction between cellulose chains is getting weaker. Because there is only one ester bond in the molecular structure of methyl hexadecanoate, it can interact with a single hydroxyl on the molecular chain of cellulose, which affects the interaction between cellulose chains. This method

of using single functional group contained additive to reduce the interaction between the molecular chains of cellulose was also demonstrated and discussed in detail in our previous researches.^{16,17} That is to say, the chain entanglement of cellulose is decreased with the introduction of methyl hexadecanoate.

The curves of G'' and G' plots against the angular frequency of the cellulose solution in DMAc/LiCl/Cu(OAc)₂/methyl hexadecanoate with 0.1% Cu(OAc)₂ and 0.5-1.2% methyl hexadecanoate are shown in Figure 9(b). With the increase in the concentration of methyl hexadecanoate, the gel point of the cellulose solution gradually moves to the area of high angular frequency. This result provides other evidence to show a decrease in the chain entanglement of cellulose in solution. Figure 10

illustrates the surface tension of the cellulose solution in DMAc/LiCl, with 0.1% Cu(OAc)₂, and with both 0.1% Cu(OAc)₂ and 0.5% methyl hexadecanoate. The cellulose solution in DMAc/LiCl shows a surface tension of 41.06 ± 0.57 mN/m. After adding Cu(OAc)₂, the surface tension is 40.86 ± 0.95 mN/m. No large difference can be found. With the addition of Cu(OAc)₂ and methyl hexadecanoate, the surface tension of the cellulose solution is 38.6 ± 0.17 mN/m. It leads to a slight decrease in surface tension. Comparing the cellulose solutions before and after storage, as exhibited in Figure 11, it can be observed that all the cellulose solutions in DMAc/LiCl, DMAc/LiCl/Cu(OAc)₂ and DMAc/LiCl/Cu(OAc)₂/methylhexadecanoate keep stable after 24 h.

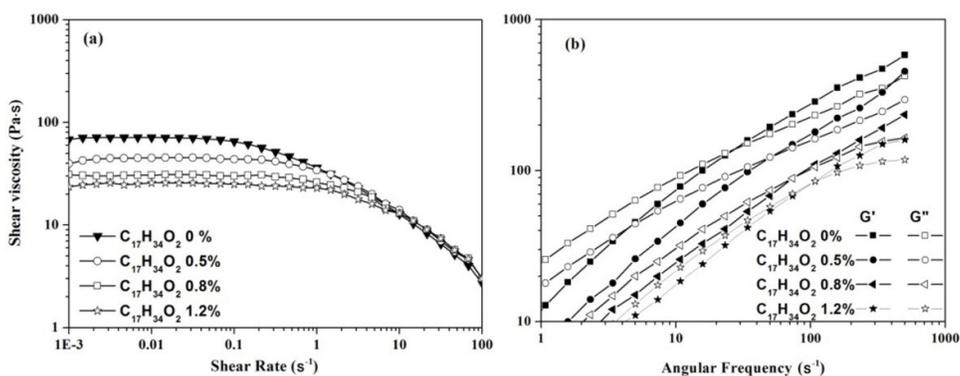


Figure 9: Plots of shear viscosity (a) and dynamic modulus (b) of 3% cellulose solutions in DMAc/LiCl/Cu(OAc)₂/methyl hexadecanoate with 0.1% Cu(OAc)₂ and different methyl hexadecanoate concentration

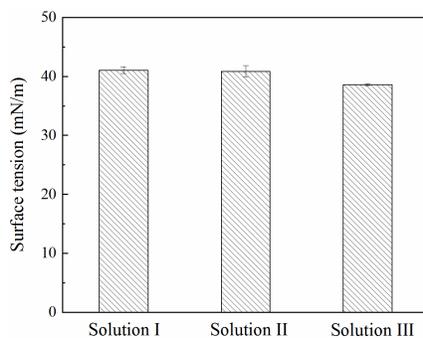


Figure 10: Surface tension of 3% cellulose solution in DMAc/LiCl (Solution I), with addition of 0.1% Cu(OAc)₂ (Solution II), and with addition of both 0.1% Cu(OAc)₂ and 0.5% methyl hexadecanoate (Solution III)

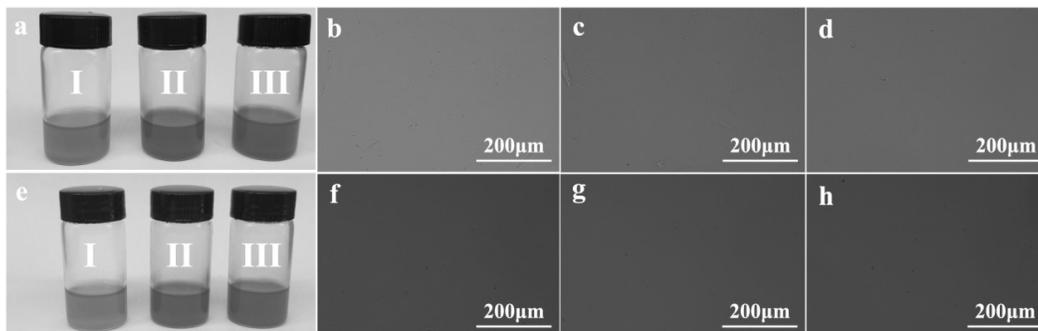


Figure 11: Status of 3% cellulose solution in DMAc/LiCl (Solution I, b, f), with addition of 0.1% $\text{Cu}(\text{OAc})_2$ (Solution II, c, g), and with addition of both 0.1% $\text{Cu}(\text{OAc})_2$ and 0.5% methyl hexadecanoate (Solution III, d, h) just at the beginning of preparation (a-d) and after storage for 24 hours (e-h)

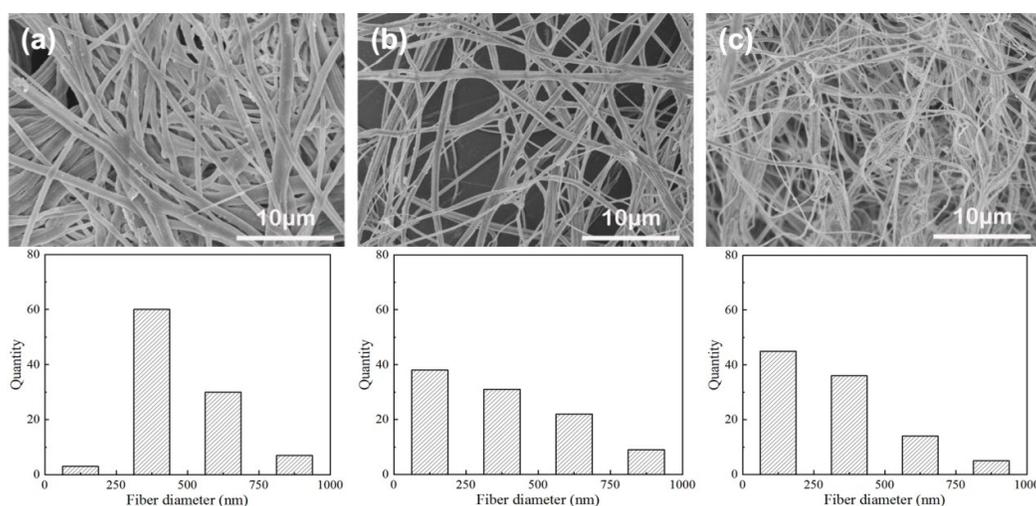


Figure 12: Morphology and fiber distribution of electrospun fiber from the cellulose solution in DMAc/LiCl/ $\text{Cu}(\text{OAc})_2$ /methyl hexadecanoate with 0.1% $\text{Cu}(\text{OAc})_2$ and different concentrations of methyl hexadecanoate of (a) 0.5%, (b) 0.8%, (c) 1.2%

The morphologies and diameter distribution of the electrospun ultrafine fibers obtained by these cellulose solutions are exhibited in Figure 12. With 0.5% methyl hexadecanoate, well distributed electrospun cellulose fibers are obtained, with a surface area lower than $5 \text{ m}^2/\text{g}$ (tested by BET measurement). The diameters of these fibers can be controlled at $\sim 500 \text{ nm}$, with quite good diameter distribution. After increasing the concentration of methyl hexadecanoate to 0.8-1.2%, the diameter distribution becomes uneven. Too low entanglement of the molecular chains of cellulose will break the stability of electrospinning to produce fibers with uniform morphology.

CONCLUSION

$\text{Cu}(\text{OAc})_2$ was used in the cellulose solution with DMAc and LiCl to control the conductivity,

chain entanglement and the electrospinnability of corn cob cellulose. Because of complexation of Cu^{2+} and Cl^- , $(\text{CuCl}_4)^{2-}$ formed in the cellulose solution, impacting the chain entanglement and electrospinning of cellulose. Electrospun cellulose fiber with uniform morphology could be only obtained under proper conditions. On the basis of that, methyl hexadecanoate was further used to reduce the chain entanglement in the cellulose solution. Accordingly, the morphology of electrospun ultrafine fibers could be successfully adjusted. Electrospun cellulose fibers with the diameters around $\sim 500 \text{ nm}$ and quite good distribution were finally prepared.

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