



Activation of corn cellulose with alcohols to improve its dissolvability in fabricating ultrafine fibers via electrospinning



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ABSTRACT

Water and four small molecular alcohols are respectively used to activate corn cellulose (CN cellulose) with the aim to improve the dissolvability in DMAc/LiCl. Among all these activated agents, monohydric alcohols are found to produce the optimal effect of activation in the whole process including of activating, dissolving, and electrospinning of CN cellulose. Meanwhile, well distributed fibers with the diameter of 500 nm–2 μm are fabricated in electrospinning. Understanding the activation effect of monohydric alcohols with water and polyhydric alcohols, the most effective activated agent is ascertained with the characteristics of small molecular size, low viscosity, and single functionality. This work is definitely initiated to understand the critical principle of CN cellulose in dissolving. Accordingly, a feasible methodology is also established to prepare ultrafine cellulose fibers with good morphology in electrospinning.

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1. Introduction

As an important biomass, cellulose is recognized as the most promising substitute for the petroleum polymers in the wide range of areas, such as filtration, biomedical applications, and protective clothing, because of its renewability, biodegradability, and abundance in nature (Somerville et al., 2004; John & Thomas, 2008). However, due to the rather strong chain packing produced by inter- and intra- molecular hydrogen bonding between cellulose molecules, cellulose cannot be melted and is almost undissolved in common solvents (Bjorn, Gunnar, & Lars, 2010; Swatloski, Spear, Holbrey, & Rogers, 2002). Consequently, it is inevitable to show a tremendous difficulty in processing. Till today, many researchers are still trying their best to create an easy and practical dissolving technology for the processing of cellulose (Himmel et al., 2007; Knull & Kennedy, 2003; Masa, Alloin, & Dufresne, 2005; Phillips, Beeson, Cate, & Marletta, 2011).

During the past decades, many novel solvents such as DMAc/LiCl (McCormick, Callais, & Hutchinson, 1985), alkaline/urea/water (Cai et al., 2008) and ionic liquids (Biswas, Shogren, Stevenson, Willett,

& Bhowmik, 2006; Swatloski et al., 2002) are gradually invented to dissolve cellulose. DMAc/LiCl exhibits excellent advantages such as low-toxicity, ability to dissolve different cellulose types without significant degradation. Compared with the other solvents, DMAc/LiCl is the most suitable solvent for industrial application in future.

The dissolving of cellulose in DMAc/LiCl is always required a pre-activation. Without activation, the process of cellulose dissolving will last for a very long time and only swelling of cellulose can be taken place. Although many references mentioned the activation of cellulose before dissolving (Dupont, 2003; Ishii, Tatsumi, & Matsumoto, 2008; McCormick et al., 1985; Potthast et al., 2002; Regiani, Frollini, Marson, Arantes, & Seoud, 1999; Zhang et al., 2014), in fact, the mechanism of the activation is not clear. Firstly, the activation usually contains many uncertain complex procedures (Ishii et al., 2008; Regiani et al., 1999; Sjöholm, Gustafsson, Eriksson, Brown, & Colmsjo, 2000;), but design and composition of these procedures are short of theoretical guidance. Secondly, water is mainly used as the activated agent to promote dissolving (Dupont, 2003; Potthast et al., 2002; Zhang et al., 2014), but in fact water is also reported to be mainly used as a common agent of precipitation to regenerate cellulose from its solution (Gupta, Hu, & Jiang, 2013; Ni et al., 2013, 2014). It also provides a paradoxical contradiction in logic to understand the promoting effect of the activation in cellulose dissolving. From these research results, it is

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not hard to know the activation-dissolving methodology has not established.

Along with the thinking, in this paper, we choose water, monohydric (methanol, ethanol) and polyhydric (ethylene glycol, glycerol) as activated solvents, respectively. By examining the changes of molecular structure and solution properties of cellulose in the whole process of activation, dissolving, and electrospinning, the activation effect of each activated solvent will be systematically evaluated. This research will not only provide forceful experimental evidence to further understand the principle of cellulose activation in dissolving, but it also suggests a suitable way to fabricate ultrafine electrospun cellulose fibers with good morphology.

2. Experimental

2.1. Materials

Corn cellulose (CN cellulose, DP ~1440, Cr 56.5%) from corn cob is purchased from Jinan Shengquan Group Co., Ltd. DP is decided by the standard test methods for intrinsic viscosity of cellulose (ASTM D1795-94 (2001)). LiCl is purchased from Aladdin Reagent and dried at 160 °C for 2 h before use. Deionized water, methanol, ethanol, ethylene glycol, glycerol and DMAc are supplied by Aladdin Reagent. All the solvents are analytical grade and used without further purification.

2.2. Activation of the cellulose

CN cellulose is dried under vacuum at 120 °C for 12 h to completely remove the moisture. And then, activation is processed by immersing the CN cellulose in solvents at room temperature for 1 h. After that cellulose is filtered in a vacuum oven to remove the residual solvent.

Fourier transform infrared (FTIR) characterization is performed on a Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer from Thermo-Fisher Scientific. Scanning is carried out from 500 to 4000 cm^{-1} and 32 scans are used to test each sample. The activated cellulose is firstly pressed into a mould with 10^8 Pa pressure in hydraulic machine to squeeze out excess solvent. Then the 2 mg original cellulose or activated cellulose is picked out and pressed with 300 mg KBr to form a small piece for the FT-IR tests.

X-ray diffraction (XRD) is employed to determine the crystal structure and the crystallinity of the activated cellulose by Siemens D5000 X-ray Diffractometer. The diffracted intensity of Cu K α radiation generated at 40 kV and 40 mA was measured in the range of 2θ between 5° and 45°. The degree of crystallinity is obtained from the area ratio of the crystal phase to the total phases (both crystal and amorphous phases) after deconvoluting the peaks in XRD pattern.

2.3. Dissolution of the activated cellulose

DMAc is firstly heated to 105 °C to get rid of the residual water and then cooled to 80 °C. Dry LiCl is added into DMAc under magnetic stirring until completely dissolved to produce 9 wt% DMAc/LiCl solvent. After cooling to room temperature, the activated CN cellulose is added to the DMAc/LiCl solvent under vigorous agitation for 24 h. The weight ratio between CN cellulose and DMAc/LiCl solvent is controlled at 3/97.

Dynamic light scattering (DLS) experiments are performed on a laboratory-built goniometry equipped with a 5 W Argon ion laser ($\lambda_0 = 514.5$ nm, Spectra Physics, USA). The dilute concentration of the activated CN solution at the 0.2 mg/mL is chosen to run the test. The size of the random coil of the cellulose in dilute solution is evaluated in detail. Rheological properties of cellulose solutions are

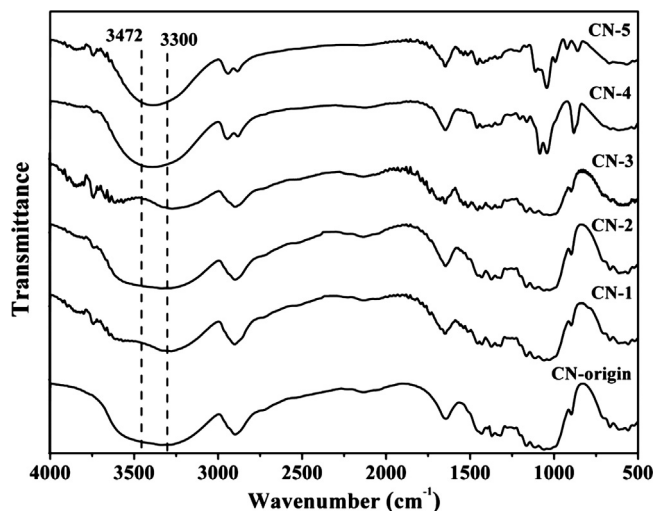


Fig. 1. The FTIR of the CN cellulose before and after activation. The numbers followed with CN are pointed to the type of the activated solvents (1 water, 2 methanol, 3 ethanol, 4 ethylene glycol, and 5 glycerol).

also characterized by Dynamic Analyzer RDA. Rheological experiments are conducted at 25 °C with a stress-controlled rheometer (ANTON PAAR Physical MCR 301) equipped with cone/plate geometry (diameter 60 mm, angle 1°, plate-to-plate gap 0.104 mm). The cellulose solutions are equilibrated for at least 20 min prior to the test. Both steady and dynamic modes are performed. For the steady-shear experiments, an equilibration time of 20 s is given at each data point. The frequency-sweep measurements are conducted in the linear viscoelastic regime of the samples (determined previously by dynamic stress sweep measurements) over a frequency range of 0.01–500 rad/s.

2.4. Electrospinning

The solution of CN cellulose is separated by centrifugation to remove the undissolved impurities. And then, the cellulose solutions are electrospun into ultrafine fibers by using a single 5 mL syringe setup (Zhao et al., 2005) under 18–21 kV. The syringe is fixed with a stainless steel needle with inner diameter of 0.5 mm and 22 mm in length as a capillary. The tip of the needle is cut flat. A grounded custom-made rotating roller collector wrapped around by aluminum foil is utilized to collect the ultrafine fibers. The feed rate of the solution is controlled at 1.8 mL/h, and the needle is positioned 10–15 cm from the collector. During fiber collection, a water spraying device is applied to the collector for the DMAc/LiCl system to promote fast solidification of fibers and remove the solvent of LiCl and DMAc effectively. The obtained fibers are then removed from the aluminum foil and completely dried under vacuum at 60 °C.

The morphology of the collected fibers is observed using scanning electron microscope (SEM, Hitachi TM-1000) after gold coating.

3. Results and discussion

3.1. Microstructure of CN cellulose after activation

In the experiment, CN cellulose is firstly activated by water and alcohols. FT-IR spectrums of the CN cellulose before and after activation are shown in Fig. 1. From the curve of the original CN cellulose, it shows two typical absorption bands at 3472 cm^{-1} and ~3300 cm^{-1} with respect to the stretching vibrations of intramolecular and intermolecular hydrogen bonds. After activation by water, methanol and ethanol, the absorption bands on the

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