



Characterisation of cellulose films regenerated from acetone/water coagulants



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ABSTRACT

A precooled aqueous solution of 7 wt% NaOH/12 wt% urea was used to dissolve cellulose up to a concentration of 2 wt%, which was then coagulated in an acetone/water mixture to regenerate cellulose film. The volume ratio of acetone to water (φ) had a dominant influence on film dimensional stability, film-forming ability, micromorphology, and mechanical strength. The film regenerated at $\varphi = 2.0$ showed excellent performance in both dimensional stability and film-forming ability. Compared to that from pure acetone, the cellulose film from the acetone/water mixture with $\varphi = 2.0$ was more densely interwoven, since the cellulosic fibrils formed during regeneration had pores with smaller average diameter. The alkali capsulated in the film during film formation could be released at quite a slow rate into the surrounding aqueous solution. The regenerated cellulose film with adjustable structure and properties may have potential applications in drug release and ultra filtration.

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1. Introduction

Cellulose is well known as one of the world's most abundant and renewable natural resources (Armaroli & Balzani, 2006; Kim, Yun, & Ounaies, 2006; Klemm, Heublein, Fink, & Bohn, 2005; Mohanty, Misra, & Drzal, 2002; Turner, Spear, Holbrey, Daly, & Rogers, 2005). Due to its fascinating structure and excellent properties, such as fast biodegradability, environmental friendliness and good thermal stability, cellulose is increasingly regarded as one of the most promising raw materials for solving various problems, especially the oil crisis and environmental pollution (Goh, Tan, Lee, & Bhatia, 2010; Saxena, Adhikari, & Goyal, 2009; Scott, 1999). Cellulose use can be roughly classified into three aspects: direct use, degradation into small molecules and chemical modification based on its superstructure. In the biofuel field, a very promising treatment is to achieve the direct conversion of cellulose into long-chain polyols that imitate the components of petroleum (Fukuoka & Dhepe,

2006; Huber, Iborra, & Corma, 2006; Yan et al., 2006). A so-called 'green' chemical method known as acid hydrolysis in near-critical water combined with hydrogenation under a catalyst is attracting significant attention (Deng, Tan, Fang, Zhang, & Wang, 2009; Ji et al., 2008; Luo, Wang, & Liu, 2007; Zheng et al., 2009). Chemical modification, which provides a means of tuning the physical and chemical properties of cellulose to increase its functionality and broaden its application scope, plays a central role in cellulose application (John & Anandjiwala, 2007).

Direct use without any chemical derivation has also received considerable attention recently. The key challenge here is to disrupt the numerous inter- and intra-molecular H-bond networks among the chains of cellulose to make it soluble in desired solvents. Thus far, a few solvent systems for cellulose dissolution have been developed, including *N,N*-dimethylacetamide (DMAc)/LiCl, *N*-methylmorpholine *N*-oxide (NMMO) and some ionic liquids (Kulpinski, 2005; Liebert, Heinz, & Edgar, 2010; McCormick, Callais, & Hutchinson, 1985; Nishio & Manley, 1988; Rosenau et al., 2002). The textile fibres prepared from NMMO are called lyocell and exhibit outstanding performance such as regular circular cross sections, high crystallinity and excellent mechanical strength (Fink, Weigel, Purz, & Ganster, 2001). However, NMMO is expensive, unstable and difficult to recover. Ionic liquid is another attractive medium due to its non-volatility and easy recovery (Remsing, Swatoski, Rogers, & Moyna, 2006; Wu, Wang, Wang, Bian, & Li,

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2009; Zhu et al., 2006), but research in this direction is still in its infancy with a long way to go before industrial applications can be developed.

A new cellulose solvent known as the NaOH/urea/H₂O system has attracted increasing interest (Cai & Zhang, 2005, 2006; Cai et al., 2007, 2008; Chen et al., 2007; Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2008; Guo, Zhou, & Zhang, 2011; Qi, Cai, Zhang, & Kuga, 2009; Weng, Zhang, Ruan, Shi, & Xu, 2004). In this system, only very cheap chemicals, such as NaOH and urea are adopted. The NaOH, urea and H₂O system needs to be precooled below −10 °C. Most importantly, no toxic substances are used or produced throughout the dissolving process, so it is considered a truly 'green' cellulose-dissolving method.

Cellulosic materials, including films, fibres and aerogels, can be regenerated from the cellulose aqueous solution by a variety of coagulants. A few studies have investigated the effects of coagulating conditions on the properties of the regenerated cellulose (RC) materials. Specifically, 5 wt% H₂SO₄/5 wt% Na₂SO₄ aqueous solutions are reported to be a good coagulant to achieve excellent mechanical properties (Zhang, Mao, Zhou, & Cai, 2005). Briefly, the RC materials are formed in coagulants mainly through the processes of ionic diffusion, primary-particle generation, secondary-particle growth and particle amalgamation (Inamoto, Iwata, Matsui, & Okajima, 1999; Inamoto, Miyamoto, Hongo, Iwata, & Okajima, 1996; Manabe, Kamata, Iijima, & Kamide, 1987).

In this study, we used a NaOH/urea/H₂O system to dissolve cellulose and an acetone/water mixture was selected as the coagulant to obtain RC films. The migration of NaOH from the cellulose solutions to the coagulants was investigated, and the capsulation and releasing behaviour of NaOH from the RC films were examined. The dimensional stability, structures, morphology and mechanical strength of the RC films were also studied. Our results are expected to provide valuable information on fabricating cellulosic materials, further expanding cellulose applications.

2. Experimental

2.1. Materials

The cellulose (cotton linter pulp) was supplied by China Silver Hawk Chemical Fibre Co., Ltd. (Gaomi, China). The average degree of polymerisation (DP) is 525. NaOH, urea and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. Double distilled water was used throughout the experiment.

2.2. Film preparation

As reported elsewhere (Cai & Zhang, 2005, 2006; Cai et al., 2007), an aqueous solution of 7 wt% NaOH/12 wt% urea was precooled to −12 °C in a refrigerator for 20 min, to which a known weight of native cellulose (NC) was dispersed with vigorous agitation for 5 min. The transparent cellulose solution was centrifuged at 4000 rpm for 10 min to remove the insoluble residuals and air bubbles. RC film was then prepared using a template method. Briefly, a mould was made using a tape frame stuck to a sheet of glass plate. The cellulose solution was then cast in the mould and immediately dipped into the coagulant for 5 min to obtain wet RC films. The chemicals remaining in the film were removed by thorough rinsing with deionised water. Finally, the film was dried at a constant temperature (30 °C) and humidity (65%) for 24 h.

2.3. Instrumental analysis

2.3.1. Acid–base titration and conductivity measurement

The amount of NaOH that migrated into the coagulant or stayed in the film was determined by acid–base titration against

0.1257 mol L^{−1} HCl with phenolphthalein as an indicator. A PHS-3C exact digital pH meter was used. The weight of the cellulose solution (2 wt%) was fixed at 1 g and the total volume of the coagulant was 20 mL. Conductivity measurements were performed on a conductivity meter, DDSJ-308A (China). First, the conductivity (κ) of 120 mmol L^{−1} NaCl was measured. Then, the κ of the same NaCl solution was measured with a wet or wetted RC film placed between the two platinum electrodes to inspect the barrier effect of the films on small ions.

2.3.2. Fourier transformation infrared (FT-IR) and wide-angle X-ray diffraction (WAXD) measurements

The FT-IR spectra of the dried RC films (ground into powders) were recorded on a Nexus 670 infrared spectrometer (Thermo Nicolet Electron Corporation, USA) using the KBr-disc method. WAXD analysis on the RC films was carried out by a conventional reflection method using a Cu K α target at 40 kV and 30 mA. X-ray diffraction patterns were recorded in a 2 θ range of 5–40°. The degree of crystallinity (χ_c) was calculated according to the peak separation method from the peak areas of the (1 $\bar{1}$ 0), (1 1 0) and (2 0 0) planes. The apparent crystal size (ACS) was estimated using Scherrer's equation (1):

$$ACS = \frac{0.9\lambda}{\beta(\cos \theta)}, \quad (1)$$

with $\beta = (B^2 - b^2)^{1/2}$, where λ is the wavelength of the incident X-rays (1.5406 Å); θ is the diffraction angle corresponding to the (1 $\bar{1}$ 0), (1 1 0) and (2 0 0) planes; b is the instrumental constant (0.1°); and B is the half width in radians of the diffraction angle of the (1 $\bar{1}$ 0), (1 1 0) and (2 0 0) planes.

2.3.3. Transmission electron microscopy (TEM) and scanning electric microscopy (SEM) observation

A drop of 2 wt% cellulose solution was placed on a TEM grid (carbon grid, 3.02 mm, 200 meshes) with most of the liquid removed quickly using a piece of blotting paper, leaving a very thin film stretched over the grid. Thus, an ultra-thin RC film was formed by dipping it into a coagulant. The grid was then soaked in plenty of deionised water to remove the residual NaOH and urea. After staining by a 2% uranyl acetate aqueous solution, the grid was dried in ambient air for 60 min, followed by observation on a JEOL 100cx II TEM (Japan) at an accelerating voltage of 100 kV. For SEM observations, the RC film was fractured in liquid nitrogen and the fractured surface was then sputtered with gold and checked using a JEOL JMS-6700 SEM (Japan).

2.3.4. Surface tension measurements

Surface tensions (γ) at different cellulose concentrations were determined on a Processor Tensiometer K12 (Swiss) using a traditional Wilhelmy method.

2.3.5. Mechanical strength tests

The mechanical strength of the RC films (dimensions 0.4 cm × 5 cm with a thickness of 38–40 μ m) was measured using a universal testing machine (Tianchen Testing Machine Manufacturing Co., Ltd., China) at a crosshead speed of 1 mm min^{−1}. A gauge length of 2 cm was used. To ensure data accuracy and reproducibility, at least five specimens were measured for each type of film.

All of the experiments were carried out at 20.0 ± 0.5 °C, unless otherwise stated.

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