Cellulose Transparent and Flexible Films Prepared from DMAc/LiCl Solutions

Hasan Sadeghifar,^a Richard Venditti,^a* Joel J. Pawlak,^a and Jesse Jur^b

Cellulose transparent and flexible film was prepared by dissolving microcrystalline cellulose powder in Dimethylacetamide/Lithium Chloride (DMAc/LiCl) followed by regeneration in acetone and subsequent washing with water. The solution was cast on a glass plate. The interactions of water molecules and the swollen cellulose in the gel were examined by differential scanning calorimetry, DSC. An increased melting point of water in the gel indicated the presence of stronger bonding between water and cellulose than in the non-modified cellulose. The prepared dried films had 63 g/m² weight and 0.06 mm thickness with 1.14 g/cm³ density.The prepared dry film exhibited high transparency, around 95% with visible light. The transparency and mechanical properties of the films were stable at high temperature (120°C) and exposure to UV irradiation. Thermal analysis of the prepared sample indicated film stability up to 275 °C. The tensile strength of the cellulose film was around 120 MPa with about 10% strain to break. The mechanical properties of the films were stable in alkali and acidic solutions.

Keywords: Cellulose film; DMAc/LiCl; Transparent film; Flexible film

Contact information: a: Departments of Chemistry and Forest Biomaterials, Organic Chemistry of Wood Components Laboratory, North Carolina State University, Raleigh, North Carolina 27695, United States; b: Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina 27695, United States; *Corresponding author: Richardv@ncsu.edu

INTRODUCTION

Cellulose, the most abundant polymer in nature, is renewable, biodegradable, and biocompatible. Production of cellulose and cellulose derivatives-based flexible and transparent films were investigated (Ass et al. 2006; Qi et al. 2009; Zhang et al. 2012). The traditional solvent systems that have been used for cellulose contain heavy metal complexes, and serious environmental issues have been reported (Wang et al. 2016). Using non-metal complexes with lower environmental concern as processes for natural products has attracted much attention in the last decade (Zhu et al. 2006; Qi et al. 2009; Wang et al. 2016). Dissolution of native cellulose has been studied extensively, and a variety of solvent systems have been reported (Morgenstern and Kammer 1999). Generally, solubilizing cellulose without changing its chemical structure is difficult (Hattori et al. 2002; Ass et al. 2006). Among a wide range of cellulose solvents, DMAc/LiCl is one of the most studied solvents for native cellulose, first described in 1979 (McCormick and Lichatowich 1979). Generally, the solubility of cellulose in DMAc/LiCl depends strongly on the cellulose source, its molecular weight, and degree of its crystallinity. In general, the solubility of each cellulose source should be evaluated separately in order to maximize its solubility (Isogai and Atalla 1998; Ass et al. 2006).

Native cellulose offers great opportunities for different types of products, including packaging, electronics, medical devices, and substrate films (Kim *et al.* 2006; Mahadeva

et al. 2011). Cellulose is low cost and biodegradable, promising an environmental solution to the plastic waste issue. Further, novel regenerated cellulose products such as unique cellulose fibers, functional fibers for separation applications, and aerogels have been fabricated successfully from native cellulose film (Ass *et al.* 2006; Cai *et al.* 2007; Qi *et al.* 2009; Zhu *et al.* 2013).

Cellulose films have a much better thermal stability compared to plastic substrates, with lower coefficients of thermal expansion, *e.g.* as low as around 5×10^{-5} C⁻¹ (Huang *et al.* 2013), whereas for polyethylene and polypropylene this number is much higher, around 18 to 20 x 10^{-5} C⁻¹. Cellulosic films can also tolerate much higher processing temperatures than common plastics (Moon *et al.* 2011). However, cellulose is not a thermoplastic and cannot be molded into certain shapes in the way that plastic can. The high transparency and flexibility of cellulosic films may allow them to replace plastic substrates in a wide range of applications, especially as a substrate for electronic applications (Mannsfeld *et al.* 2010; Huang *et al.* 2013; Petritz *et al.* 2013; Petritz A. *et al.* 2013; Muhl *et al.* 2014; Mühl and Beyer 2014). Various devices have been successfully demonstrated on plastic substrates including transistor backplanes, thin film transistors, organic light emitting diodes, and other applications.

Precipitation and coagulation of native cellulose solutions into transparent, uniform, and soft flexible films is a challenge. A few studies have investigated the effect of coagulation conditions on the properties of the regenerated native cellulose film. The main coagulation solvents reported for cellulose film are H_2SO_4 and Na_2SO_4 (Yang *et al.* 2011), acetone, ethanol, water, and mixtures of different solvents (Zhang *et al.* 2012; Geng *et al.* 2014).

In this study, DMAc/LiCl solvent was used to dissolve cellulose, and such solutions were evaluated for the first time in a single research project with different combinations of acetone, methanol, and water to determine the best cellulose film formation condition. Structures, morphology, mechanical properties, transparency, and thermal properties of the prepared cellulose film were studied.

EXPERIMENTAL

Materials

Microcrystalline cellulose (Avicel HP-105), Sigma-Aldrich, was used in air-dry state. DMAc, LiCl, acetone, and methanol were used with purity more than 99.5%.

Preparation of Cellulose Solution

Depending on the desired concentration of the cellulose solution, dry cellulose and DMAc were mixed together as reported by the authors previously (Sadeghifar *et al.* 2017) with modification. The mixture was heated up to 130 to 160 °C and kept at this temperature for 10 to 30 min to find the optimum pretreatment condition. LiCl equal to 8% of DMAc was then added to the mixture, and the mixture was kept at the elevated temperature for an additional of 10 min. The mixture was allowed to cool down slowly to ambient temperature and then stirred for 12 h at room temperature using a closed container with a magnet bar. The final transparent cellulose solution was kept in a refrigerator at about 4 °C. Solutions with up to 8% of cellulose concentration were prepared.

Cellulose Film Preparation

A 3 to 8% concentration of prepared cellulose solution (in DMAc/LiCl) was cast on a smooth and flat glass plate. The thickness of the solution on the plate was from 2 to 5 mm. The cast cellulose solution was washed (immersed in a bath) with different solvents including acetone, methanol, and water, to find the best coagulation solvent. The final wet regenerated native cellulose film was washed with a stream of water for 5 hours to remove all solvents and LiCl. The washed wet film was dried at room temperature on the same glass plate.

UV-Visible Analysis

The optical properties and transparency of cellulose films were investigated using a Varian 300 UV-Visible spectrometer in the 200 to 600 nm wavelength range. A wavelength of 550 nm was used for the determination of film transparency (Zhu *et al.* 2013).

Thermo-gravimetric Analyses

Thermo-gravimetric analyses were performed using 10 to 15 mg sample in a TA TGA-Q500 instrument to determine the mass loss during heating. The samples were dried at 105 °C for 20 min before being heated to 600 °C at a heating rate of 10 °C/min under 50 mL/min nitrogen gas flow. The TA DSC-Q500 instrument was used for evaluation of bound water properties in cellulose and prepared cellulose wet gel. The sample was cooled to -20 °C first, and the temperature was increased around 3 °C/min using a modulated DSC to monitor free and bond water in the cellulose and the prepared wet gel.

XRD

The crystallinity of the original cellulose (MCC), wet and dried cellulose films were determined using a Rigaku Smartlab X-ray diffractometer. The diffractometer was equipped with Be-filtered Cu-K α radiation with a wavelength of 1.54 Å generated at 35 kV and 25 mA. The samples were scanned from a 2θ from 5 to 45° at an increment of 0.05°. Relative crystallinity was calculated from the intensity measurements using the Segal equation (Segal *et al.* 1959),

$$XC\% = ((I_{002} - I_{AM})/I_{002})100$$
(1)

where I_{002} represents the maximum intensity of (002) lattice diffraction peak at a diffraction angle around $2\theta=22.5^{\circ}$, and I_{AM} represents the intensity scattered by the amorphous component in the sample, evaluated as the lowest intensity at 2θ of 18°

Scanning Electron Microscopy (SEM)

Analysis of film surfaces was performed by scanning electron microscopy (SEM) after coating sample with gold using a Phenom, G2 Pro system at different magnifications with 10 kv acceleration voltage.

Mechanical Properties

The tensile strength of the prepared film was measured using an Instron 4465 machine at room temperature using deformation rates of 2.5 mm/min. Stress-strain property was measured using ASTM 638 standard. Folding of the film was carried out using a TAPPI folding endurance of paper tester (MIT tester) (Revision of T511 om-02).

The test specimen was held under 0.9 kg tension and subjected to repeated folding; the number of fold necessary to cause failure is taken as a measure of folding endurance.

Surface Tension and Contact Angle

A surface electro-optic, PHX-300 device was used to measure contact angle. A droplet of water, around 0.1 mL, was placed on the surface of the specimen with a syringe. Ten photographs were taken over a 1 min period. The results were the average of at least three measurements of each sample.

RESULTS AND DISCUSSION

The cellulose dissolution in DMAc/LiCl was carried out in three steps. Briefly, the dried microcrystalline cellulose mixed with DMAc and heated at different temperatures from 130 to 160 °C for 10 to 30 min. Then 8% of LiCl to DMAc was added and heated for more 10 min. Finally, the mixture was cooled to room temperature and stirred for 12 h. It was determined that preheating of the cellulose sample in DMAc for 30 min at 140 °C and then the addition of 8% LiCl produced the best results. Visually the sample was dissolved after 3 h; however, the conditions employed were 12 h stirring at room temperature. Cellulose easily dissolved up to a 10% concentration (w/w) (Fig. 1A).



Fig. 1. cellulose solution (A), its regenerated films in acetone (B) and water (C) and acetone regenerated film microscopic surface image (D)

A glass plate was prepared in the lab for cellulose film casting. The cellulose solution was degassed by centrifugation at 5000 rpm for 5 min before casting. To optimize the best condition of film preparation, different concentrations of cellulose solution from 3 to 8% with various thickness of cellulose solution on the plates were examined. The thickness of the cellulose solution was controlled at 2 to 5 mm using a coating applicator. After casting cellulose solution on the plate was gently immersed into a

regeneration solvent bath, and a transparent cellulose wet gel was formed. The cellulose gel was kept in precipitation solution for 1 h, and then washed with a stream of deionized water for 5 h to remove the salt completely (Nayak *et al.* 2008). For the preparation of cellulose films, various solvents were investigated as precipitation solvents, including water, methanol, ethanol, and acetone. The wet regenerated cellulose films were fixed on the same plate with adhesive tape to prevent shrinkage and were then dried at room temperature for 24 h.

Films prepared by water, methanol, and ethanol did show a uniform structure after drying and indicated gas bubbles with dark condensed spots in the film structure (Fig. 1C). Only the acetone-coagulated film followed by washing with water indicated a uniform and smooth structure (Fig. 1B) visually and under the microscope (Fig. 1D). The solubility of LiCl in water, methanol, ethanol, and acetone was different. The solubility of LiCl in water (63.7) and methanol (42.4 g/100 mL) was high compared to acetone (4.11 g/100 mL) (Zhang *et al.* 2015). It seems that the rapid removal of LiCl from the wet gel during precipitation with water, methanol, and ethanol is a source of the non-uniform structure in the dried films of these materials. It has been reported that long washing times of prepared wet cellulose films with water improved film quality (Nayak *et al.* 2009). The prepared and dried films in the present work were flexible, non-tacky, smooth, and transparent. The average film weight was 63 g/m² with 0.06 mm thickness and 1.14 g/cm³ density.

The wet prepared transparent cellulose film contained a 6 to 1 water to cellulose ratio. To have an understanding of bonding between water and the cellulose wet gel, DSC analysis at a heating rate of 3 °C/min was used to determine the bonded water melting point in prepared cellulose wet gel and non-modified cellulose powder. Distilled water was used as a control (Fig. 2)



Fig. 2. Melting point of free and bond water in non-modified cellulose (MCC) and cellulose wet gel

The melting point of distilled water was determined to be around 0.25 °C. The free water melting point was visible in both cellulose and the wet film at about the same temperature. However in both samples, the melting point of the bound water was shifted, to 2.25 °C in cellulose and 3.78 °C in the regenerated cellulose wet gel. This indicates the presence of stronger bonding between water and cellulose gel than the non-modified cellulose.

Transparencies of cellulose films were characterized with a UV-vis spectrometer. The results of UV-vis characterization of samples around 55 μ m thickness is illustrated in

Fig. 3. Transmittance of the cellulose film sample was around 95% at 550 nm, which is excellent for transparent substrate use. The sample had a high transparency, not only in the visible region, 550 nm, but also in the near ultraviolet region (transmittance was around 80% at 250 nm), which was greater than other cellulose films reported in the literature (Ifuku *et al.* 2007; Qi *et al.* 2009; Huang *et al.* 2013; Zhao *et al.* 2014; Zhang *et al.* 2015).

To understand the stability of the film transparency at high temperature and under UV irradiation, dried cellulose films were heated at 120 °C for 1 h and also irradiated by UV light (using a Xenon lamp) for 2 h. Figure 3A indicates the stability of prepared film under high temperature and irradiation, which is important for film applications in outdoor and extreme irradiation conditions. To our knowledge, the effect of heat and UV irradiation on cellulose film transparency has not been reported before in a published article.



Fig. 3. Cellulose film transparency at different condition

Cellulose fibers are known to display X-ray diffraction (XRD) patterns with the main diffraction signals at 2θ values of 15° , 22.5° , and 34° attributed to the diffraction planes 101, 002, and 040, respectively. Figure 4 illustrate the XRD patterns obtained for the MCC and its prepared cellulose films. Crystallinity of the original MCC cellulose sample was around 85% (Segal *et al.* 1959). After dissolution of cellulose in the DMAc/LiCl system and regeneration in acetone, the wet gel indicated an amorphous structure almost without any crystal structure. However, the wet gel of regenerated cellulose showed a peak around $2\theta = 14^{\circ}$, which indicated a re-arrangement in the wet state of the cellulose film after drying. However, after comparing this result to other crystalline cellulose reference structures, it was not possible to detect what type of cellulose crystallinity was present.



Fig. 4. XRD spectra of cellulose, wet and dried cellulose film

After drying the wet film, three diffraction peaks at 13.4°, 14.5°, and 21° appeared. In comparison to the original microcrystalline cellulose (MCC), in the regenerated dried cellulose film, all three dimensional plane peaks shifted to lower degrees, indicating that the d-spacing of the planes increased. For example, the d-spacing of the 002 plane (2Θ =22.5°) of MCC based on Bragg's Law is 0.395 nm, but after cellulose regeneration and drying, this spacing increased to 0.404 nm. However, the crystallinity of the dried film (38%) was much lower than original cellulose sample (85%).

The wettability of the cellulose film was investigated. Also to understand the surface behavior of the prepared films in acidic and alkali solutions, cellulose films were immersed in a solution of sulfuric acid with pH 2.4 and NaOH with pH 12 for 24 h, rinsed, washed with water, and dried at room temperature. All contact angles were measured after the water drop contacted the surface. Figure 5 shows water droplets on the surface of the films. The contact angle for native cellulose film is about $73^{\circ} \pm 1.6$. Treatment of the films with acidic and alkali water reduced the contact angle from 73° in cellulose film to around $65^{\circ} \pm 1.8$. These observations indicate that the materials can be exposed to acidic and alkali conditions without significant surface property changes.



Fig. 5. Contact angles of dried cellulose film using water, acidic, and alkaline solution

The mechanical properties of the substrates are important for roll-to-roll processing of lightweight and flexible electronic devices and other applications as well as for the enduse functionality (Petritz A. *et al.* 2013). To study the mechanical properties, stress–strain tests were done with an Instron 4465 instrument to evaluate the mechanical properties of the cellulose films. A folding test with a MIT folding tester was used to measure flexibility and bending enhancement of samples. Figure 6A shows the stress–strain curves for the dried cellulose film. The cellulose film has a tensile strength of 118 MPa, with yield strength of 81 MPa and a Young's modulus of 3200 MPa at 6% water content. The maximum strain for the cellulose film at this level of water content was 10%. The tensile index of the prepared film was 1.75 MPa/g, a material value independent of the film thickness. In comparison with other cellulose film prepared with different methods and reported in the literature (Qi *et al.* 2009; Moon *et al.* 2011; Geng *et al.* 2014; Zhang *et al.* 2015; Yuan *et al.* 2015; Wang *et al.* 2016) (with the tensile strength of around 60 to 90 MPa), the prepared cellulose film possessed similar strength properties. In comparison with synthetic polymers such as PET (around 50 to 100 MPa) (Chen *et al.* 2011) this product indicated much better results. It should be noted that, due to nature of cellulose sources, coagulation process, and thickness of the film, it is hard to compare data.

To understand the strength properties of the prepared cellulose film in acidic and alkali solution, cellulose film was immersed in solutions of sulfuric acid with pH of 2.4 or NaOH with pH 12 for 24 h. Then the film was washed with water and dried at air temperature for 24 h, and its tensile strength was measured (Fig. 6). All results are tabulated in Table 1. The results indicated that the cellulose film was stable in both acidic and basic solutions. Only the cellulose film immersed in the alkali solution showed a slightly reduction in stress at break and modulus of elasticity, but no differences were observed after treatment in the acidic solution. The high pH alkali solution can cause cellulose swelling and is a reasonable explanation for the small reduction in tensile strength.



Fig. 6. Stress-strain curves of cellulose film and treated film in acidic and alkaline solution

Another important parameter for cellulose flexible films as a substrate for different applications is its folding ability. A folding-endurance test is used to measure the ability of a film to maintain its strength after repeated folding. The cellulose film was broken after around 3000 times folding under 0.45 kg stretch loading and 1400 times with a 0.9 kg load (Table 1). This demonstrates a very high flexibility and stability of the film against folding forces. Results of cellulose films folding strength were compared with regular office printing paper. Office printing paper under a 0.9 kg stretch loading showed only around 90 folds to break. The effect of pH on the prepared cellulose film mechanical properties and investigation of its folding strength were reported for the first time in this article.

Sample	Breaking strength (MPa)	Tensile index (MPa/a)	Breaking strain (%)	Modulus (MPa)	Film Density (g/cm ³)	Folding under load (lb)
Cellulose film	(111 0)	1.75	(70)	2000	(9,011)	(10)
(CF)	110		10	3200	1.14	1438
CF treated in pH 2.4	112	1.77	9	3200	1.15	1380
CF treated in pH 12	93	1.47	9	2500	1.05	1265

Table 1. Tensile Properties of the Cellulose Film and its Treated Samples in

 Acidic and Alkaline Solutions

The thermal degradation behavior of the cellulose source (MCC) and cellulose dried film are indicated in Fig. 7. All samples were heated at 105 °C for 20 min before heating to 700 °C under oxidative conditions. The main thermal degradation for the original cellulose, MCC, occurred between temperatures of 300 to 350 °C, and the maximum degradation temperature was 335 °C. More than 90% of MCC weight was lost at 350 °C. The initial weight loss for the cellulose film started at around 275°C, and the maximum degradation happened around 305 °C. However, at 350 °C, only 50% of its weight was lost. The lower initial degradation temperature of the cellulose films can be attributed to a lower crystallinity of the regenerated film compared to the original cellulose. However, the thermal stability of the prepared films is high enough for various applications.



Fig. 7. Thermal degradation of microcrystalline cellulose and prepared film

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CONCLUSIONS

- 1. Non-derivatized cellulose films with high transparency, flexibility, and mechanical properties were prepared using DMAc/LiCl as a solvent with optimized conditions to produce transparent and smooth films.
- 2. Precipitation of the cellulose solution in several coagulating liquids indicated that acetone followed by washing with water was the best system to produce well-formed films.
- 3. The prepared film was stable against high temperature, UV irradiation, high and low pH solution and demonstrated high tensile and folding strength.

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