Isolation of Cellulose from Poplar Wood by Nitric Acid-Ethanol Treatment and Its Effect on the Quality of Films Cast from Ionic Liquid

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Cellulose was successfully isolated from poplar wood chips using a two-step treatment for controlled times. The treatment included nitric acid-ethanol pretreatment and mechanical dispersion. The cellulose specimens were then dissolved in an ionic liquid and cast to prepare cellulose films. The prepared samples and films were examined using scanning electron microscopy (SEM), High Performance Liquid Chromatography (HPLC), Fourier-transform spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and ultraviolet-visible spectroscopy (UV-Vis). The results showed that lignin and hemicellulose reacted and dissolved in the nitric acid-ethanol mixture solution, which broke the biomass recalcitrance and promoted cellulose dispersion in the solvent for preparing uniform films. However, a large amount of cellulose was hydrolyzed within the fourth treatment, resulting in a remarkable decrease in the tensile strength of the films. After three repetitions of treatments, the cellulose had a better average degree of polymerization, crystallinity, and thermal stability. The films had the highest tensile strength of 32.8 MPa, elongation at break of 47.5%, and transmittance that exceeded 80% at the wavelength range of 600 nm to 800 nm, which indicated that the samples were more suitable for film fabrication.

INTRODUCTION

As a major component of biomass, cellulose is a polysaccharide of ß-D-glucopyranose moieties linked through ß-(1,4) glycosidic bonds with well documented polymorphs; it is found in wood, cotton, flax, hemp, jute, and other plants (Sun *et al.* 2004). Cellulose is versatile and useful in a variety of applications such as photoelectric materials (Jung *et al.* 2015), energy storage (Zhao *et al.* 2017), supercapacitors (Yang *et al.* 2012), hemostatic dressings (Lewis *et al.* 2013), and packaging materials (Dong *et al.* 2014). The cellulose chains are arranged in a regular orientation and aggregated into bundles to form microfibril structure. Hemicellulose, cellulose and lignin together with a small amount of pectin, protein, extract, and ash make up lignocellulose (Agbor *et al.* 2011; Chen *et al.* 2018). The complex cross-linked structure and compositions make it difficult to isolate cellulose by a simple method (Crews *et al.* 2014; Ji *et al.* 2015).

Chemical pulping processes including kraft, sulfite, and soda pulping are commonly used in industry remove other components and thereby isolate high-purity cellulose (López *et al.* 2000; Fatriasari *et al.* 2017; Shao *et al.* 2017). These processes use reagents to cook the raw materials at high temperature; then the remaining solids are

bleached to obtain cellulose with superior whiteness and purity (Nicholson *et al.* 2017). The procedures are complex, and waste liquors from the cooking and bleaching processes may cause environmental concerns (Yang *et al.* 2016). To avoid that, many new, simple, and green methods for extracting cellulose have been developed, and nitric acid treatment was one of them. In this paper, the nitric acid-ethanol mixture was used for cellulose isolation. The NO_2^+ of nitric acid act as an electrophile of electrophilic substitution reaction nitrifies the ortho and para positions of the phenolic hydroxyl groups and replaces methoxy groups to nitro groups, which nitrifies and oxidizes lignin (Brendel *et al.* 2000). Furthermore, the hemicellulose is hydrolyzed and oxidized by nitric acid (Liu *et al.* 2014). Thus, two major components of fibers are simultaneously removed to purify cellulose. The ethanol added in the reaction enhances the solubility of the nitrified and oxidized lignin and reduces the hydrolysis and oxidation of cellulose (Fan *et al.* 2013; Zhou *et al.* 2016). The LiCl/DMAc ionic liquid solution used for film fabrication is recyclable and can be reused for the economic consideration and environmental concerned.

This study focused on the isolation of cellulose by nitric acid-ethanol treatment and its effect on the quality of prepared films. The cellulose extraction efficacy was evaluated by the morphology, chemical composition, chemical structure, crystal structure, crystallinity, and thermal stability of cellulose samples. The mechanical properties and transmission performance of the fabricated films were investigated, providing further research with theoretical supports.

EXPERIMENTAL

Materials

Ten years of fast-growing poplar (*Populus cathayana* Rehd.) sapwood harvesting residues were obtained from the Baihe Forestry Bureau of Jilin (Baihe, China). The wood was cut into small chips of approximately 3 cm to 3.5 cm × 0.5 cm to 0.7 cm × 0.2 cm to 0.3 cm pieces as lignocellulosic feedstock. Ethanol (aq, 95 vol%), nitric acid (aq, 65 wt%), anhydrous lithium chloride (LiCl), dimethylacetamide (DMAc, with a moisture content of less than 0.1%), and other analytical reagents used in the experiment were all analytical grades. All reagents were purchased from Tianjin Fuyu Fine Chemicals Co., Ltd. (Tianjin, China). LiCl and DMAc were stored in a desiccator. LiCl was heated at 105 °C for 10 min to drive off the residual moisture before used.

Isolation of Cellulose

Initially, nitric acid was added to ethanol at a volume ratio of 1:4 (v/v) and stirred to prepare a uniform solution. In a ground-glass fitted Erlenmeyer flask, wood chips were soaked in the solution with a solid and liquid ratio of 1:25 (w/v), and then refluxed in boiling water bath for 1 h. The mixture was poured into a fiber disintegrator (ZT16-00, Xingping Zhongtong Test Equipment Co. Ltd., Xingping, China) to be dissociated at 5000 r/min for 2 min and then stored until the residues precipitated. The insoluble residues were filtered and washed using hot water until they reached neutral pH. The sample was dried at 105 °C to a constant mass. After the first treatment, the obtained residue was named once treated nitric acid-ethanol cellulose (NEC1) for convenience.

The above experimental procedure was repeated using NEC1 instead of the wood chips, namely the sample was treated twice, and then repeat the experimental procedure. The cellulose obtained after twice, three times, and four times of treatments were labeled

as NEC2, NEC3, and NEC4, respectively.

Preparation of Cellulose Films

LiCl was added to a DMAc reagent at a weight ratio of 4:45 (w/w) to prepare the ionic liquid LiCl/DMAc. NEC1 toNEC4 were dissolved in the LiCl/DMAc with a weight ratio of 1:49 (w/w), and then heated and stirred in an oil bath at 105 °C for 2 h. The solution was cooled to room temperature and remained for 12 h to eliminate bubbles.

The transparent cellulose solution was uniformly cast onto glass plates to pre-solidify in air. The solidified gels were immersed in the distilled water bath at 20 °C for 0.5 h to remove the residual solvent. The wet cellulose hydrogel samples were dried at room temperature to obtain uniform films. The average thickness of the films was 85 to 115 μm. The films were immersed in a 10% glycerin aqueous solution, dried at room temperature, and stored for further use.

Characterization

Cellulose morphology

The micromorphology of cellulose was observed by scanning electron microscopy (SEM; Quanta200, FEI, Golden, CO, USA) at low acceleration voltages of 12.5 kV. The cellulose was coated with gold by a vacuum sputter coater before observation.

Cellulose chemical composition

The degree of polymerization (ISO 5351 2010), extracts (TAPPI T 204 cm-17 2017), acid-insoluble lignin and acid-soluble lignin (TAPPI T 222 om-15 2015), holocellulose (GB/T 2677.10 1995), α-cellulose (TAPPI T 203 cm-09 2009), and pentosans (TAPPI T 223 cm-10 2010) of wood chips and cellulose samples were determined. The yield of cellulose was estimated as

$$y(\%) = \frac{w_1}{w} \times 100 \qquad (1)$$

where w_1 is the dry weight of the obtained cellulose and w is the dry weight of the wood material.

The lignin, hemicellulose and cellulose content were determined by the method (NREL LAP-002 1996) as a comparison. The content of glucan, xylan, and arabinan was determined by a HPLC system (1260 Infinity II, Agilent, Santa Clara, CA, USA) with an Evaporative Light-scattering Detector (ELSD) employing an Agilent ZORBAX NH2 column for the calculation of cellulose and hemicellulose content. Acetonitrile-water mixture of 75:25 (V/V) was used as an eluent. The column was maintained at 40 °C. Samples were processed at an eluent flow rate of 0.6 mL/min.

Cellulose chemical structure

Fourier transform infrared (FT-IR) spectra were collected on a Frontier instrument (Perkin Elmer, Foster, CA, USA) in the range of 700 cm^{-1} to 4,000 cm^{-1} with a resolution of 4 cm^{-1}.

Cellulose crystal structure and crystallinity

An X-ray diffractometer (XRD; D/max 2200, Rigaku, Tokyo, Japan) with Ni-filtered Cu Kα radiation was utilized at an operating voltage of 40 kV and current of 35 mA to analyze the crystal structure of samples. The diffraction intensities were collected

between $2\theta = 5°$ to $40°$ at a scanning rate of $4°/min$. The relative crystallinity index (CrI) was estimated using the Segal's method as shown in Eq. 2,

$$CrI(\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \qquad (2)$$

where I_{200} is the maximum peak intensity of (002) lattice diffraction at approximately $2\theta = 22.6°$, which represents the region of both crystalline and amorphous of cellulose, while I_{am} at approximately $2\theta = 18°$ represented only the amorphous region.

Cellulose thermal stability

The thermal stability of the samples was measured by thermogravimetric analysis (TGA) using a TG analyzer (Pyris 1, Perkin Elmer, Shelton, CT, USA) at a heating rate of 10 °C /min from 50 °C to 750 °C under nitrogen atmosphere.

Film mechanical properties

According to the ISO 1924-2 (2008) standard, mechanical property tests were conducted at room temperature using a universal testing machine (IMT-202F, International Material Tester Co. Ltd, Dongguan, China). The cross-head speed was 5 mm/min. The dimensions of the test films were 50 mm × 10 mm × 0.1 mm to 0.2 mm.

Film light transmittance

The light transmittance spectra of cellulose films were observed through an ultraviolet spectrophotometer (Cary 100, Agilent Technologies Inc., Walnut Creek, CA, USA) with a scanning wavelength range of 200 nm to 800 nm.

RESULTS AND DISCUSSION

Analysis of Cellulose Morphology and Chemical Composition

The color of poplar sapwood chips was light, as shown in Fig. 1a. When treated with nitric acid, a series of color reactions occurred in the conifer aldehyde structure of lignin, turning the color of the samples to yellow (Liu *et al.* 2015).
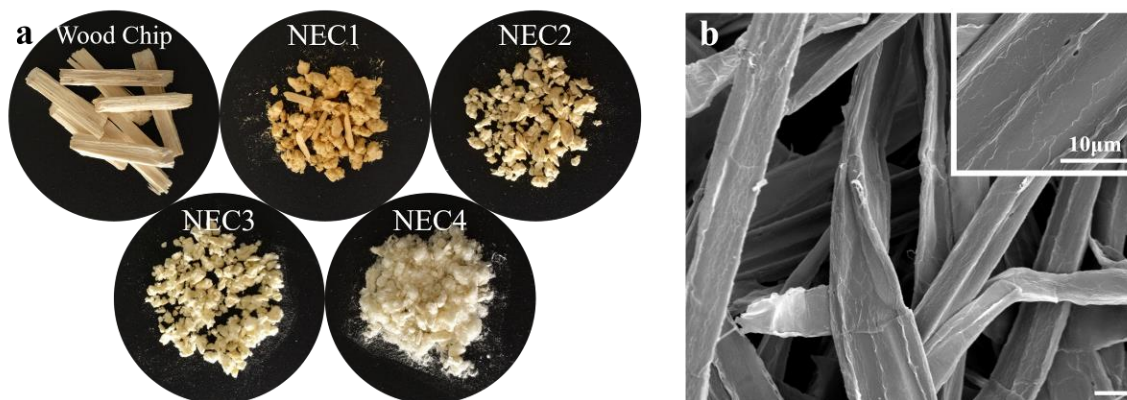

Fig. 1. Macroscopic and microcosmic morphology of wood chips and cellulose samples:
(a) Macroscopic morphology of wood chips and cellulose samples; (b) SEM micrographs of NEC3

During the first treatment, the contact area between the surface of the wood chips and the solution was small. Only the outer fiber reacted with the nitric acid. Thus, some inner wood chips did not dissociate. However, among the second treatment of samples, all the pieces in NEC2 completely dissociated. The color of NEC1 to NEC4 gradually became lighter and eventually turned to white, the color of cellulose, which suggested that a large amount of lignin was oxidized and nitrated by nitric acid.

The SEM image of NEC3 (Fig. 1b) shows that, after the treatment, the dispersion effect of cellulose was better, the fiber shape became flat due to the acid erosion, and the mechanical dispersion treatment also lead to some bent fibers (Zhang *et al.* 2007; Chandra C. S. *et al.* 2016).

Dilute acid hydrolysis and polyphase hydrolysis results in the degradation of cellulose in the nitric acid-ethanol mixture (Rodríguez-Chong *et al.* 2004). During the first treatment, the nitrate ion initially hydrolyzes the glycosidic bond in the amorphous region, and most amorphous regions are involved in reaction. Thus, the degree of polymerization (DP) of cellulose was reduced to approximately 870, as shown in Fig. 2. The experiment was repeated five times to ensure less uncertainty regarding the mean values. Additionally, a large number of lignin and hemicellulose molecules were dissolved, resulting in a dramatic weight loss of the sample, and the yield of cellulose dropped to 63.38%. Notably, the DP of the cellulose from treated wood chips was higher than that from treated wood flour (approximately 500) under the same conditions.

During the subsequent treatments, the acid hydrolysis reaction mainly occurred on the surface of the microcrystalline region. The reaction gradually slowed down, the rate of decline in the yield of cellulose also slowed down, and the DP of the cellulose was maintained in a small range to reach a level-off degree of polymerization (LODP) (Kontturi *et al.* 2016). The DP of NEC4 was greatly reduced, revealing that a large amount of cellulose was hydrolyzed.
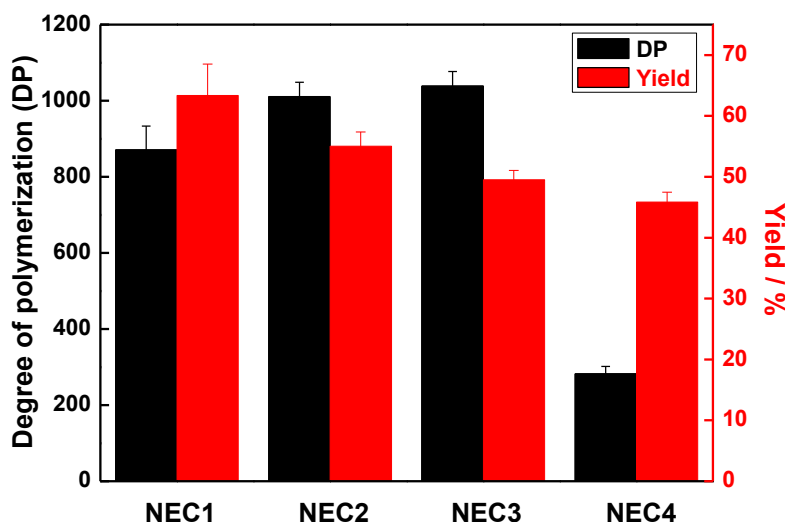

Fig. 2. Yield of cellulose and average degree of polymerization of wood chips and cellulose samples

The content of components determined by standards and NREL procedure is summarized in Table 1. The content of extracts was reduced after treatments because the ethanol and water dissolved a certain amount of the organics and carbohydrates.

The first treatment of the samples removed approximately 60% of the acid-

insoluble lignin, while lignin removal reached 80% in the second treatment, and the acid-soluble lignin was the same situation as before. A possible reason for this phenomenon was that the surface fibers of the wood chips were infiltrated by the solution and the surface layer of lignin was dissolved. Nevertheless, the surface fibers were softened but not dispersed. The inner fibers and lignin were covered and hard to participate in the reaction. The surface fibers were removed with subsequent mechanical dispersion, exposing the inner layer fibers. The inner layer of lignin was dissolved in the second treatment. However, it was difficult to completely remove the lignin. A small amount of lignin was entrapped within the cellulose microcrystalline region that was hard to dissolve (Araki *et al.* 1998). When the content of the acid-insoluble lignin was reduced to 0.44%, the acid-soluble lignin content was 0.55% after three treatments, indicating that the nitrification and oxidation of lignin was significant.

Hemicellulose content is calculated by the difference between holocellulose and α-cellulose content, which contains hemicellulose and the degradation products of cellulose (Brice and Morrison 1982; Chen *et al.* 2011). The content from woodchips to NEC4 was 33.47%, 15.68%, 13.34%, 12.10%, and 26.60%, respectively. The content decreased at first and then increased, while the hemicellulose content (represented by pentosan content) of the samples decreased, indicating that the degradation product increased.

The increase of glucan suggested an increase in cellulose content, while the α-cellulose content decreased at the fourth treatment, and the DP of cellulose dropped sharply. It was indicated that many parts of the cellulose microcrystalline regions were dispersed, leading to more hemicellulose and cellulose that became hydrolyzed and converted to degradation products. This corresponded to the observations of the degraded α-cellulose. The loss of xylan and arabinan were attributed, in part, to the hydrolysis of polysaccharides, especially hemicelluloses. The solid residue after sulfuric acid hydrolysis was composed primarily of Klason lignin, the results obtained in two methods are similar.

Table 1. Composition of Wood Chips and Cellulose Samples

Sample	Wood Chips	NEC1	NEC2	NEC3	NEC4
Extracts (%)	2.66	2.04	1.64	1.30	0.95
Acid-insoluble Lignin (%)	20.03	7.86	1.32	0.44	0.24
Acid-soluble Lignin (%)	2.38	2.11	0.91	0.55	0.40
Holocellulose (%)	81.38	92.12	95.01	98.32	98.76
α-Cellulose (%)	47.91	76.44	82.67	86.22	72.16
Pentosan (%)	12.95	6.91	5.48	4.99	2.87
Acid-insoluble Lignin (%) [a]	20.68	7.02	1.29	0.56	0.33
Glucan (%) [a]	43.54	73.42	82.37	84.60	85.29
Xylan (%) [a]	14.57	9.88	7.67	6.02	4.28
Arabinan (%) [a]	0.73	0.64	0.51	0.35	0.32

[a], Calculated from NREL procedure

Analysis of Cellulose Chemical Structure and Crystallinity

Changes in the chemical composition and chemical structure of samples can be illustrated by FT-IR, as shown in Fig. 3. The absorbance peaks at 2901, 1430, 1372, 1163, and 898 cm^{-1} were the peaks of cellulose that appeared in the spectra of each sample. The peaks at 1595, 1508, and 1461 cm^{-1} represented phenyl ring structure of lignin (Li *et al.* 2016). The peaks at 1595 and 1508 cm^{-1} belonged to aromatic skeletal vibrations and C=O stretching, and the peak at 1461 cm^{-1} were assigned to the stretching of methoxyl-O-CH$_3$ (Yang *et al.* 2007). The intensity of these bonds decreased when the treatment times increased, which indicated the better efficiency in the nitrified and oxidized of lignin. The peaks at 1732 and 1243 cm^{-1} were the stretching and bending vibration peaks of the carbonyl group. The carbonyl group may be attributed to the LCC complex, and the decrease of intensity suggested the removal of hemicellulose. The signal at 1639 cm^{-1} was enhanced, which corresponded to an increase in hemiacetal and carboxyl groups, and represented an increase in oxidized groups, revealing that the proportion of oxidized cellulose increased.
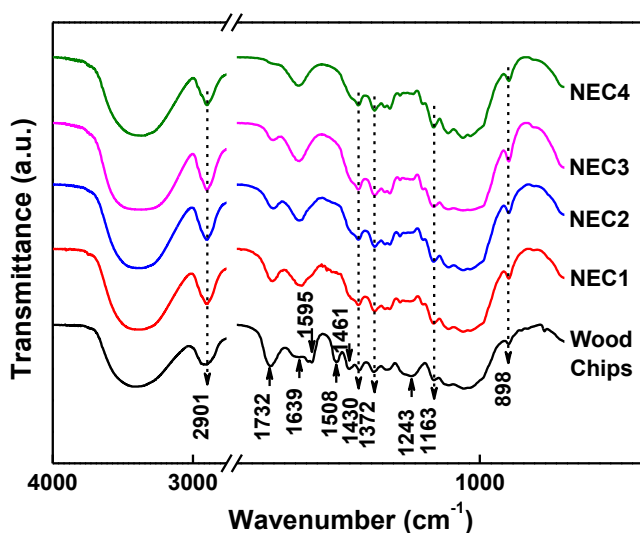

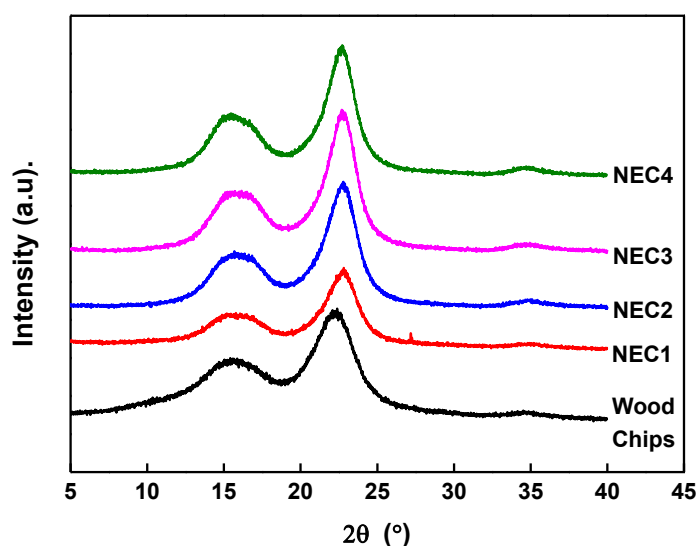**Fig. 3.** FTIR Spectra of wood chips and cellulose samples

Fig. 4. XRD patterns of wood chips and cellulose samples

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XRD patterns were used to analyze the crystallinity of the samples, as shown in Fig. 4. Typical diffraction peaks of all the samples exhibited at 2θ at approximately 15.6 and 22.7°. The crystal lattice of the obtained samples was type I, which demonstrated that the nitric acid treatments did not change the native crystal lattice of cellulose. The crystallinity index of cellulose affects the mechanical properties and thermal stability of the material (Poletto *et al.* 2013). It can be quickly calculated by the Segal method, but the result may be not accurate (Park *et al.* 2010). The crystallinity of wood chips to NEC4 were 59.31%, 68.69%, 71.57%, 73.31%, and 73.44%, respectively. The increase in crystallinity of the samples was mainly due to the removal of lignin and hemicellulose, and the hydrolysis of cellulose in the amorphous region as well (Chandra C. S. *et al.* 2016).

Analysis of Cellulose Thermal Stability

The thermogravimetric curve (TG) and a derivative of thermogravimetric curve (DTG) of samples are shown in Fig. 5. The DTG curve showed slight descending peaks at 50 °C to 105 °C, which was caused by the evaporation of adsorbed water of the samples. The TG curve showed weight loss of the wood chips at 200 °C, indicating the degradation of lignin and hemicellulose. The curve drops sharply at 260 °C, revealing that a large amount of lignin and hemicelluloses were degraded (Alemdar and Sain 2008). Meanwhile, the components of cellulose samples underwent degradation. All curves dropped quickly at 310 °C, reaching the maximum loss rate at 355 °C to 360 °C, and the rate was slower until 380 °C, demonstrating the loss of cellulose (Oun and Rhim 2015). The range of the thermal degradation curve gradually narrowed between the TG and DTG curves, suggesting that the thermal stability of cellulose was enhanced and the proportion also increased. When the temperature exceeded 400 °C, the residual parts of lignin and hemicellulose were subject to aromatic cyclization, and the weight no longer decreased.
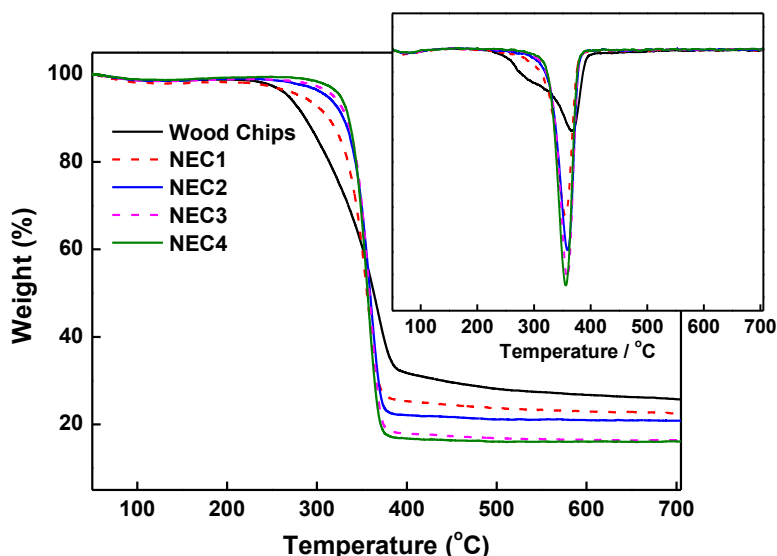

Fig. 5. TG curves of wood chips and cellulose samples. The insets show the DTG curves

Analysis of Cellulose Film Properties

The films prepared by the regenerated cellulose displayed superior elasticity and bending performance, while the lignin content had an emphasis effect on the mechanical properties of the film. During the dissolving process, the LCC structure formed by lignin, hemicellulose, and cellulose was difficult to disperse in solvent, resulting in non-uniform

fabricated films. The lignin content from NEC1 to NEC3 decreased from 7.86% to 0.44%, leading to the decreased LCC structure content, which made the film structure more uniform. Thus, the tensile strength of the films increased from 7.72 MPa to 32.76 MPa and elongation at break increased as shown in Fig. 6. In the fourth treatment, the cellulose that conferred structural support was hydrolyzed, and the DP was greatly reduced, which decreased strength of the intermolecular bonding of cellulose fibers, resulting in a sharp decrease in the tensile strength and an increase in elongation at break of the film (El-Sakhawy and Hassan 2007).
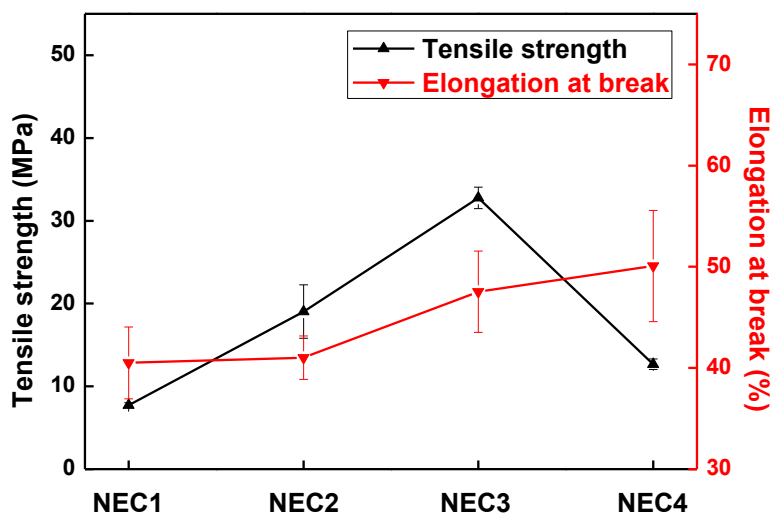
Fig. 6. Mechanical properties of cellulose films

The pre-solidified process facilitated solvent evaporation and increased the cellulose concentration of the film. Thus, the water was hindered from entering the liquid film to form a porous structure during the solvent-non-solvent bidirectional diffusion of the gel process. Due to the dense packing of the cellulose, the films exhibited higher transparency as shown in Fig. 7.
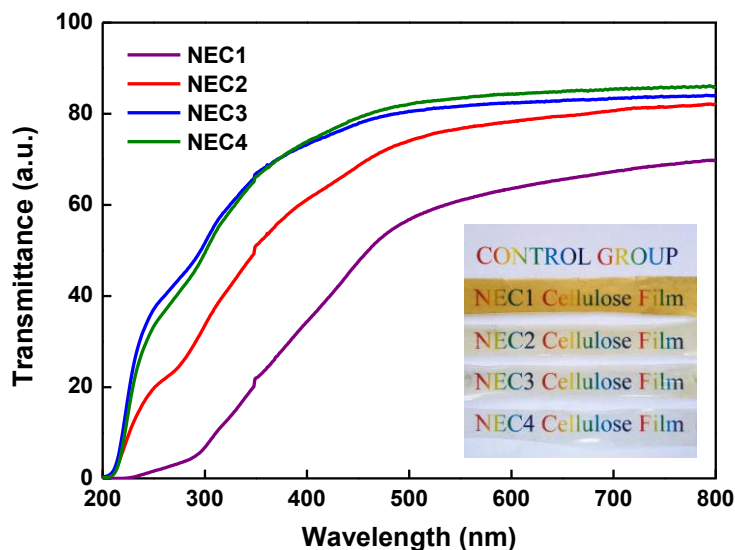
Fig. 7. UV-vis transmittance spectra of cellulose films

The transmittance of films with a thickness of 0.15 mm exceeded 80% at the wavelength range of 600 nm to 800 nm, corresponding to the reported high transparency cellulose-based composite films (Yano *et al.* 2014). The lignin content that absorbed light was reduced, which was a key factor for raising the transmittance of films.

CONCLUSIONS

1. After three treatments, approximately 95.6% of lignin and 63.8% of hemicellulose were successfully removed from samples of poplar wood. As a result, the yield of cellulose was 49.5%, the average degree of polymerization was 1038, the crystal lattice was type I, and the crystallinity was 73.3% and exhibited superior thermal stability. The films showed the highest tensile strength of 32.8 MPa, elongation at break of 47.5%, and transmittance of over 80% at the wavelength range of 600 nm to 800 nm, indicating that the samples were more suitable for film preparation.

2. During the reaction, a large amount of lignin was oxidized and nitrated, and the hemicellulose was hydrolyzed by nitric acid. The ethanol added in the reaction enhances the solubility of the nitrified and oxidized lignin and reduces the hydrolysis and oxidation of cellulose. The dispersion effect of cellulose was enhanced. The fiber shape became flat due to the acid erosion, and the mechanical dispersion treatment also bent some fibers.

3. The cellulose was partially oxidized by nitric acid during the treatment process, and the degradation reactions occurred in the acid environment, resulting in an overall reduction in the yield of cellulose.

4. Lignin and hemicellulose reacted and dissolved in the nitric acid-ethanol mixture solution, which broke the biomass recalcitrance and allowed cellulose to be more easily dispersed in ionic liquid for preparing the uniform films. However, a large amount of cellulose was hydrolyzed within the fourth treatment, resulting in a remarkable decrease in the tensile strength of the resulting films.

ACKNOWLEDGEMENTS

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