2011

A comparative study of cellulose I and II and fibers and nanocrystals

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A COMPARATIVE STUDY OF CELLULOSE I AND II FIBERS
AND NANOCRYSTALS

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in Partial Fulfillment of the
Requirements for the degree of
Master of Science
in
The School of Renewable Natural Resources

by
Yiying Yue
B.S., Heilongjiang Institute of Science and Technology, 2007
August 2011
ACKNOWLEDGEMENTS

I would like to take this precious opportunity to thank my major adviser, Dr. Qinglin Wu and my committee members, Dr. Ioan Negulescu, Dr Alfred D. French, and Dr. Cornelis de Hoop, for their guidance throughout this work.

I am indebted to many of my colleagues in the Engineering Composites Laboratory, School of Renewable Natural Resources, LSU. Dr Haiyun Liu is gratefully acknowledged for introducing me the method of cellulose hydrolysis. Dr. Chengjun Zhou is gratefully acknowledged for helping me resolve technical problems during my experiments. Dr. Qingfeng Shi is thanked for many valuable and enlightening discussions. Dr. Xiaozhou Song is thanked for his skilful experimental assistance.

My deepest thanks go to my family and friends for their support throughout my life. And finally, I would like to thank my boyfriend, Jingquan Han, for spending many weekends and nights in the laboratory with me, and most importantly of all, for his endless love and belief in me.
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ABSTRACT

The influence of sodium hydroxide treatment on the structure of cotton fibers was studied. Compared to raw cotton fibers, the entire bundles of mercerized fibers were converted into a swollen and roughened state. Fourier transform infrared spectrometry (FTIR) indicated that intermolecular hydrogen bonding was enhanced by mercerization treatment. Wide-angle X ray diffraction (WXRD) results showed decreased fiber crystallinity after mercerization. The structure of cellulose II fibers was more thermally stable than cellulose I fibers. Mechanical properties of cotton fiber-reinforced polyethylene oxide (PEO) composites demonstrated that both raw and mercerized cotton fibers enhanced their tensile strength of the PEO matrix, but both made the composites more brittle due to poor fiber dispersion in the PEO matrix.

Cotton nano crystals (CNCs) were fabricated from both raw and mercerized cotton fibers by sulfuric acid hydrolysis combined with a high-pressure homogenization technique. Stable aqueous suspensions from both raw and mercerized CNCs were formed. Transmission electron microscopy (TEM) suggested that there was no obvious change in crystal morphology from raw and mercerized cellulose. Dry mercerized crystals had a much larger bulk density than the dry raw crystals. FTIR and WXRD data showed a clear transition from cellulose I (raw) to II (mercerized) cellulose crystal structure. TGA curves showed that cellulose II CNCs had better thermal stability properties. The storage modulus of cellulose II CNC suspensions at all temperatures were obviously larger than those of cellulose I crystal suspensions at the same concentration level. Cellulose II CNC
suspensions/gels were shown to be more thermally stable in response to temperature changes. Dilute cellulose II crystal suspensions formed an ordered liquid phase displaying chiral nematic orientation in the direction of the vector director at a much lower concentration level compared with cellulose I crystal suspension. Both cellulose I CNC/PEO and cellulose II CNC/PEO composites showed increased tensile strength and elongation at break compared with these of the pure PEO. However, composites with cellulose II crystals exhibited larger tensile strength, and elongation at break than those from composites with raw crystals due to the enhanced hydrogen bonding. Thus, cellulose II nano crystals provide better reinforcement materials for manufacturing advanced nano-composites.
CHAPTER 1. INTRODUCTION

1.1. Background

Cellulose, the most abundant biopolymer resource in the world, is widely considered as a nearly inexhaustible raw material with fascinating structures and properties. Cellulose consists of β-1, 4-D-linked glucose chains, in which the glucose units are in 6-membered rings (i.e., pyranoses), joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring (Siro and Plackett, 2010).

Four different polymorphs of cellulose are known, including cellulose I, II, III, and IV. (KroonBatenburg and Kroon, 1997). Cellulose I and II are the most studied forms of cellulose. In living plants, cellulose I is the most widespread crystalline form, which consists of an assembly succession of crystallites and disordered amorphous regions (Sauperl et al., 2009). The natural crystal is made up of metastable cellulose I with all cellulose strands in a highly ordered parallel arrangement (Revol and Goring, 1981). Two coexisting crystal phases, cellulose Iα and cellulose Iβ are contained in cellulose I. Phase Iα has a triclinic unit cell containing one chain, whereas cellulose Iβ is represented by a monoclinic unit cell containing two parallel chains (Nishiyama et al., 2002). Chemically, cellulose II has higher chemical reactivity than cellulose I and can be made into excellent cellophane, so it is regarded as one of the most useful fibers and has broad applications in chemical industry (Liu and Hu, 2008).

The crystal structure of cellulose I in native cellulose can be converted to that of cellulose II by mercerization (Ciacco et al., 2010; Dinand et al., 2002). During the process of mercerization, entire fibers are converted into a swollen state and the assembly and orientation of microfibrils are completely disrupted. The original parallel-chain crystal
structure of cellulose I changes to anti-parallel chains of cellulose II (Dinand et al., 2002). The dominant hydrogen bond is O2-H---O6 in cellulose I, whereas it is O2-H---O6, O6-H---O6 and O2-H---O2 in cellulose II. Since cellulose II involves chain folding (Langan et al., 1999), its structure is more difficult to unravel and the reverse transformation from cellulose II to cellulose I does not occur (Revol and Goring, 1981). Mercerization depends on type and concentration of the alkaline solution, its temperature, treatment time, the tension of the materials, as well as the additives (Paszner, 1968). Equally important, mercerization treatment has a function of removing hemi-cellulose and impurities, and causes inter-fibrillar regions in ligno-cellulosic fibers to become less dense and rigid, thereby allowing the cellulose microfibrils to rearrange themselves for better chain orientation and packing, leading to an increase in fiber strength (Borysiak and Doczekalska, 2008).

Cellulose nano-crystals are produced by breaking down the cellulose fiber and isolating the crystalline regions (Habibi et al., 2010). Cellulose nano-crystals have been produced from different cellulose sources and observed by a variety of techniques with dimensions ranging from several nanometers to several micrometers (Satyamurthy et al., 2011). Cellulose nano-crystals exhibit an exceptional product characteristics, such as nanoscale dimension, high aspect ratio, high specific strength and modulus, low density, and biodegradability (Siro and Plackett, 2010). Due to their unique physical and chemical properties, cellulose nano-crystals can be potentially applied to various fields, such as material science, electronics, catalysis, biomedical, and energy. For instance, various cellulose nanofibrils, nanocrystals and whiskers have been incorporated into polymer matrices to produce reinforced composites significantly improved mechanical strength (Lu and Hsieh, 2010). Also, aqueous suspensions
of cellulose nanofibrils have been shown to exhibit interesting thickening and suspending properties (Heux et al., 2000).

So far, few investigations have dealt with comparative properties of cellulose I and II nanocrystals. The overall goal of this work was to study transitional properties of cellulose I and cellulose II fibers and nano-crystals. Cotton fibers were chosen as raw material because cotton contains the highest percentage of cellulose (>95%) among natural fibers (Abidi et al., 2010).

1.2. Objectives

The objectives of the research described in this work were:

1) To understand the effect of mercerization treatment on morphology, crystallinity, surface bonding and thermal properties of cotton fibers; and

2) To investigate the effect of mercerization on morphology, crystallinity, surface bonding, thermal, and rheological properties of cotton nanocrystals and crystal suspensions.

1.3. Organization of Thesis

Chapter 1 presents an overall introduction to this thesis.

Chapter 2 presents an investigation of comparative properties of raw cotton and mercerized cotton fibers and their reinforced composites

Chapter 3 presents studies on nano crystals from raw cotton (cellulose I) and mercerized cotton (cellulose II) fibers

Chapter 4 provides an overall conclusion to this thesis.
1.4. References


Paszner L. Effect of Inter- and Intra-Crystalline Swelling on Cellulose Degradation by Gamma-Rays. Sven Papperstidn (1968) 71:822-&.


CHAPTER 2. COMPARATIVE PROPERTIES OF RAW COTTON AND MERCERIZED COTTON FIBERS AND THEIR REINFORCED COMPOSITES

2.1. Introduction

Cellulose contains four molecular chains made of β-1, 4-D- linked glucose chains, and these chains can be placed in several different arrangements (Nishimura et al., 1991; Simon et al., 1988). It was reported that cellulose I structure is made of parallel chains characterized by an intermolecular hydrogen bond network extending from the O2-H hydroxyl to the O6 ring oxygen of the next unit (Nishiyama et al., 2008). The crystal structure of cellulose II is described as anti-parallel mode stabilized by intermolecular hydrogen bond network of O2-H---O6, O6-H---O6 and O2-H---O2 (Langan et al., 1999).

Mercerization treatment in natural cellulose fibers results in the structural transformation from cellulose I (native cellulose) to cellulose II. During the process, the form of the crystalline lattice is changed because of the transformation of hydroxymethyl and polarity of the chains (Oh et al., 2005). However, its fibrous structure is largely maintained. The mercerization process affects the twisting and swelling of cellulose fibers. This is because Na⁺ ions play a crucial role in widening the accessible regions between the lattice planes to allow the ions diffusing into those planes (Gwon et al., 2010). During mercerization, cellulose I proceeds through a crystal-to-crystal phase transformation. The intermediate structure from the parallel-chain structure of cellulose I to the antiparallel-chain structure characteristic of cellulose II is Na-cellulose I (Gwon et al., 2010; Mansikkamaki et al., 2005). Na-cellulose I develops in the amorphous region of cellulose and it has a relatively large distance between the cellulose molecules because OH groups in the cellulose fiber are changed into O-Na groups. After a rinsing process, Na⁺ ions are removed by water and a new
crystalline structure -cellulose II, is achieved.

Although the mechanism for mercerization on fiber properties has been studied by many researchers, the transitional fiber properties need to be further understood. The main goal of the research was to study the transitional properties of cellulose fibers as affected by the mercerization process. Cotton fibers were used as cellulose sources.

2.2. Material and Methods

2.2.1. Raw Material and Processing

Cotton fabrics were provided by the USDA ARS Southern Regional Research Center in New Orleans, LA. The fabric sample was first cut into 5x25-mm pieces using a fabric cutter, which were then processed with a Wiley mill (Arthur H. Thomas Co.) to pass a 100-mesh screen. The obtained cotton particles were randomly divided into two parts and were stored in two separate bags for further processing. Sodium hydroxide (pellets) was purchased from Mallinckrodt (St. Louis, MO). Poly Ethylene Oxide (PEO) with an average molecular weight 900,000 (189456-250G) was purchased from Sigma–Aldrich (St. Louis, MO). These chemicals were used without further processing. All water used was DI water.

2.2.2. Mercerization Treatment

Mercerization of the material was done with one of the two bags of pre-prepared cotton fibers. About 30-g cotton fiber samples were subjected to excessive NaOH solution treatment for 4 h at room temperature. Five NaOH concentrations were chosen, i.e., 0, 5, 10, 15, and 20 wt %. The obtained slurry was filtered and thoroughly washed with DI water until the wash water reached a neutral pH. The prepared fiber samples were then dried at 40 °C in a vacuum oven for 48 hours prior to the analysis of the effects of mercerization. The cotton samples
obtained were coded as Cx with x= 0, 5, 10, 15 and 20 according to the concentration of alkali solution. For instance, the sample with no alkali treatment is designated as C0 and the sample treated with 5% alkali solution is marked as C5.

2.2.3. Preparation of Fiber/Poly Ethylene Oxide (PEO) Composite Films

To prepare fiber/PEO composite films, each of the raw (C0) and mercerized (C20) cotton fiber samples (0.04g each) was dispersed in 20ml distilled water and each mixture was placed in a vial equipped with a magnetic stirrer. The mixture formed a homogeneous suspension after being stirred for 48 hours. Then, 0.4g PEO sample was dissolved in each suspension. After being stirred for 24 hours, two transparent viscous suspensions were formed. They were poured into two aluminum dishes, which were placed in a vacuum oven at 40°C to fabricate PEO/ cotton fiber composite films.

2.2.4. Characterization

2.2.4.1. Morphology Analysis

Morphology of the cotton fibers and PEO/cotton fiber composites was characterized using Field Emission Scanning Electron Microscopy (FESEM, NovaTM Nano SEM 450, Hillsboro Oregon USA). Prior to the analysis, raw and mercerized cotton fibers, and tensile-fractured PEO/cotton fiber composite surfaces were coated with Au and then stuck on metal stubs using double-side adhesive tape. The samples were scanned at a 5k voltage.

2.2.4.2. Fourier Transform Infrared Spectrometry (FTIR)

FTIR spectra of dry fiber samples were taken with a Bruker FTIR analyzer (Tensor-27, Bruker Optics Inc., Billerica, MA) using an attenuated total reflectance (ATR) mode. The data were recorded in the range of 4000-600 cm⁻¹ wave numbers. Each of the samples from
various treatment conditions was pressed into the sample chamber for FTIR measurements. For each condition, three replicated measurements were made.

2.2.4.3. Wide-angle X-ray Diffraction (WXRD)

The super-molecular structure of the raw and mercerized cotton fibers was analyzed with a Bruker/ Siemens D5000 automated wide-angle powder X-ray diffractometer. The X-ray diffraction pattern was recorded in an angle range of 0 to 40°. The wavelength of the Cu/Kα radiation source was 0.154 nm, and the spectra were obtained at 30 mA with an accelerating voltage of 40 kV. X-ray diffraction data were analyzed using the MDI Jade 5.0 software. Curve-fitting was performed to find individual peak regions. The main diffraction peaks were integrated and used to calculate the crystalline index (CI, %) of the samples:

\[
CI(\%) = \frac{I_c}{I_c + I_a} \times 100\%
\]  

[2.1]

where \( I_c \) and \( I_a \) represent the integrated intensities of crystalline and amorphous regions, respectively.

The Scherrer equation was used to calculate the crystal size, \( t \) (nm), which was determined perpendicular to the (200) planes for both cellulose I and cellulose II samples:

\[
t = \frac{K \lambda}{\beta \cos \theta}
\]  

[2.2]

where \( k \) is the correction factor and usually taken to be 0.9, \( \lambda \) is the radiation wavelength, \( \theta \) is the diffraction angle, and \( \beta \) is the corrected angular width at half maximum intensity in radians.

The spacing between the (200) planes, \( d \) (nm), was calculated using the Bragg’s equation:
\[ n \lambda = 2d \sin \theta \]  

where \( n \) is an integer, \( \lambda \) is the wavelength of incident wave, and \( \theta \) is the angle between the incident ray and the scattering plane.

2.2.4.4. Thermal Analysis

The dehydration and degradation behaviors of cotton fiber samples were characterized by a thermo-gravimetric analyzer TGA (Q50, TA Instruments, New Castle, DE) in a nitrogen atmosphere. Specimens of 5 – 10 mg each were tested in a temperature range from 30 to 500 °C. The heating rate was 5°C/min and the nitrogen flow rate was 65ml/min. The weight-loss rate was obtained from derivative thermogravimetric (DTG) data. The onset degradation temperature was defined as the intersection temperature of tangents drawn from a thermo-gravimetric curve, one before inflection caused by the degradation and another from the cellulose degradation step.

2.2.4.5. Film Mechanical Property Analysis

Tensile strength and elongation at break of the cotton fiber-PEO film samples were measured with a TA rheometer (AR2000Ex, TA Instruments, New Castle, DE) using a solid fixture. Small samples with a dimension of 20 (length)×5 (width)×thickness (mm) were carefully cut from manufactured film composites. Each sample was mounted to the tensile fixture with both sample ends securely tied down using fixing screws. The distance between two tensile grips was 5mm (gauge length). The speed of tensile testing was 500 µm/s and five specimens were used for each condition.
2.3. Properties of Raw and Mercerized Cotton Fibers

2.3.1. Morphological Properties

Fig. 2.1a and Fig. 2.1b show the FESEM images of native cotton fibers (C0) and mercerized cotton fibers (C20) at the 2000X magnification level, respectively. The insert in each figure shows an enlarged area at the 10000X magnification level. As shown in Fig. 2.1a, native cotton fibers showed a twisted ribbon like shape and they had a relatively smooth surface, primarily due to wax coating on the fiber surface. After mercerization (Fig. 2.1b), the entire fibers were converted into a swollen and straightened state, indicating that the assembly and orientation of micro-fibrils were completely disrupted. The roughened surface of mercerized cotton fibers was a direct result of removed surface wax layer from the alkali treatment. The roughened fiber surface allows fibers to take dyes easier and may also provide a better bonding surface for fiber-polymer composite systems.

Fig 2.1 FESEM images of raw cotton (a) and mercerized cotton (b) fibers.

2.3.2. FTIR Data

The measured FTIR characteristic bands of raw and mercerized cotton fibers over the
entire range are shown in Figure 2.2. In the spectra, bands at 4000-2995 cm$^{-1}$, 2900 cm$^{-1}$, 1430 cm$^{-1}$, 1375 cm$^{-1}$, and 900 cm$^{-1}$ were found to be sensitive to variations in crystalline and amorphous regions (Oh et al., 2005). Figure 2.3 shows the replots of the FTIR spectra over selected wave numbers to contrast differences among various fibers.

![FTIR spectra](image)

Fig 2.2 The overall FTIR spectra of cotton fibers from C0, C5, C10, C15, and C20 samples.

Fig 2.3a showed a strong hydrogen bonded OH stretching vibration within the region 2995 to 3600 cm$^{-1}$ wavenumbers. The intermolecular hydrogen bonding of O2-H---O6 for raw fiber and O2-H---O6, O6-H---O6 and O2-H---O2 for mercerized fibers (Langan et al., 1999) are shown at 3438 cm$^{-1}$, 3334cm$^{-1}$, and 3293 cm$^{-1}$ positions, respectively (Oh et al., 2005; Schwanninger et al., 2004). The crystal system of cellulose was changed from cellulose I to cellulose II at the 15% and 20% alkali levels, as shown. The IR index (i.e., a ratio of IR intensity at a given wavenumber to that at the reference wavenumber) based on the absorbance peaks at 1054 (>CO/C-C stretching vibration) was chosen to analyze the conformation and hydrogen-bond intensity changes during the treatment (Das and Chakraborty, 2006). The OH stretching vibration within the region 3100–3800 cm$^{-1}$
increased considerably with increase in alkali concentration level. The hydrogen-bond intensities for C0, C5, C10, C15 and C20 samples at the 3334 cm\(^{-1}\) position was 0.286, 0.237, 0.233, 0.302, and 0.324, respectively. The results indicated that sodium hydroxide treatment intensified the intra or inter molecular hydrogen bonding.

Fig 2.3 FTIR spectra of the C0, C5, C10, C15 and C20 cotton fibers with the wavenumber ranges of 3600-2750 (a), 1480-1320 (b), 950-640 (c) and 1225-900 (d).

The maximum absorbance of CH stretching was also shifted from about 2901 cm\(^{-1}\) to a lower wavenumber at 2890 cm\(^{-1}\) after mercerization treatment (Figure 2.3a). The wavenumber at this position was reduced by 5-12 cm\(^{-1}\), which suggested that the different
arrangements caused by changes of angles around β-glycosidic linkages rearrangement (Liu et al., 2010).

The absorbance intensities at 1427 cm$^{-1}$ are assigned as CH$_2$ bending (El-Wakil and Hassan, 2008). The intensities of the peaks at the 1427 cm$^{-1}$ position for C0, C5, C10, C15 and C20 fibers were 0.144, 0.128, 0.133, 0.108, and 0.119, respectively (Fig. 2.3b). The decreased CH$_2$ intensity bending reflects a higher number of disordered cotton structures formed with increased concentration of sodium hydroxide (Krebs, 2008). The little change at 1370 cm$^{-1}$ is attributed to the different CO stretching vibration in cellulose I and cellulose II fibers (Oh et al., 2005).

An important feature of the spectra shown in Fig. 2.3c is that the wavenumber changes from 1160 cm$^{-1}$ to 1156 cm$^{-1}$, indicating Cellulose I crystal structure switched to Cellulose II crystal structure. Also, a decrease of relative intensities of the band at 1161 and 1157 cm$^{-1}$ position suggested that with increased treatment concentrations of alkali, C-O-C stretching vibration bonding was gradually changed beyond the 10% alkali concentration level.

Figure 2.3d shows that the band at 897 cm$^{-1}$ was shifted to the 894 cm$^{-1}$ position. It was reported that the 897 cm$^{-1}$ wavenumber is assigned as β-glucosidic linkage for the cellulose I structure and the 894 cm$^{-1}$ wavenumber for the Cellulose II structure (Gwon et al., 2010). The change occurred was because of the rotation of glucose residue around the glucosidic bond (Ray and Sarkar, 2001). Also, it can be seen that band at 998 cm$^{-1}$ was shifted to 993 cm$^{-1}$. This was also because of the transformation from cellulose I crystal structure to cellulose II crystal structure (Gwon et al., 2010).
2.3.3. WXRD Properties

The diffraction patterns of raw and mercerized cotton fibers (C0 to C20) are shown in Figure 2.4. Three peaks at 2θ = 14.62° (1̅10), 16.29° (110) and 22.48° (200) confirmed that only cellulose I was present for the C0 and C10 samples (Liu and Hu, 2008). As the concentration of alkali increased, a significant variation in diffraction pattern was observed. The crystalline peak was split into two weaker peaks located at 2θ = 20.1 (110) and 2θ = 21.53 (200), indicating formation of cellulose II structure.

![Figure 2.4 X-ray diffraction analysis of raw cotton and mercerized cotton fibers](image)

Crystallinity parameters before and after mercerization are listed in Table 2.1 for various fiber samples. The crystallinity index (CI) values of cotton fibers treated with 0%, 10%, 15%, and 20% NaOH solutions were 81.2%, 83.0%, 64.7%, and 66.5%, respectively. There was a slight increase of CI from C0 to C10 samples, and then CI decreased for C15 and C20. This phenomenon can be explained as follows. The three distinct processes are known during
Table 2.1 Crystallinity parameters for cotton fibers before and after mercerization treatment

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Crystallinity index</th>
<th>d-spacing (200) of the planes (nm)</th>
<th>Crystal size perpendicular to the (200) planes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>81.2 %</td>
<td>0.394</td>
<td>9.12</td>
</tr>
<tr>
<td>C10</td>
<td>83.0 %</td>
<td>0.394</td>
<td>9.27</td>
</tr>
<tr>
<td>C15</td>
<td>64.7 %</td>
<td>0.412</td>
<td>11.75</td>
</tr>
<tr>
<td>C20</td>
<td>66.5 %</td>
<td>0.415</td>
<td>11.05</td>
</tr>
</tbody>
</table>

mercerization: micro-fibril swelling, crystalline areas disruption, and new crystalline lattice formation. At lower NaOH concentrations, the number and size of NaOH hydrates were too small to disrupt the cellulose lattice with high lateral order mode (Lee et al., 2004).

Consequently, the inter-fibrillar regions were likely to be less and less rigid, which made rearrangement of fibers possible (Keusch and Haessler, 1999; Liu and Hu, 2008). As a result, the CI of fibers at lower NaOH concentration levels (i.e., C10) increased in comparison with raw cotton fibers (C0). The crystalline structure of the cotton fiber converted into a swollen state as the NaOH concentration further increased. When the cellulose structure achieved the most swollen state, it became easier for the hydrated hydroxide ions to penetrate the internal crystals, and thoroughly reacted with the fiber, leading to a reduced CI value. However, the rate of penetration of the hydroxide ions became slower due to the increased viscosity of the NaOH solution at the higher concentration levels (e.g., 20%) (Okano and Sarko, 1984; Okano and Sarko, 1985). Thus, the experiment result shows that NaOH concentrations around 15% was probably the most suitable concentration levels for crystal lattice transformation and degradation of cotton fibers at the given temperature level (Dinand et al., 2002). It needs to be pointed out the conversion process from cellulose I to cellulose II also depends on the temperature of NaOH and fiber mixture.

From Table 2.1, it can be seen that inter-planar spacing between adjacent lattices for
native cellulose fibers was equal to 0.394 nm. However, the spacing became larger for the cellulose II fibers. Changes of crystal size in the (200) planes showed a similar tendency. The crystal sizes for cotton fibers varied from 9.12 nm to 11.75 nm. The present results indicated clearly that mercerized cellulose increased crystal size and d space. The results showed that mercerization resulted in agglomeration of the chain or arrangement of strong intermolecular hydrogen bond through the conversion of cellulose I to cellulose II.

2.3.4. Thermal Degradation Properties

Fig 2.5 shows the measured TG (a) and DTG (b) curves of raw and mercerized cotton fibers (C0 to C20). All samples had a small weight loss in low temperature (<110 °C), corresponding to the evaporation of absorbed bond water in the samples. In the high temperature range, all samples showed one similar pyrolysis process. Table 2.2 lists extrapolated onset temperature (T_o, °C), degradation temperature (T_max, °C), the maximum weight loss rate (WLR_max), and char yields (CY, %) for various samples.

It can be seen that the onset and degradation temperatures varied significantly among the fibers with and without treatments (Table 2.2). For raw cotton fibers, T_o occurred around 316.8 °C with thermal degradation temperature, T_max, occurred at 332.7 °C. The degradation behavior of mercerized fibers was significantly different. Onset temperatures for C-5, C-10, C-15 and C20 were 324.39, 310.71, 323.07 and 329.89 °C, respectively. It was reported that the characteristics of the TG changes are closely correlated with the changes in crystallinity as a function of alkalinization time (Liu and Hu, 2008). The CI values of the fibers treated with 0%, 10%, 15% and 20% NaOH solutions were 81.2%, 83.0%, 64.7% and 66.5%, respectively. Thus, an increase of the onset temperature of the C5 sample was because of the fibril
Fig 2.5 TGA and DTG curves of raw cotton and mercerized cotton fibers
Table 2.2 TGA parameters of raw and treated cotton fibers (C0, C5, C10, C15 and C20).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp. T₀ (°C)</th>
<th>Degradation temp. T_max (°C)</th>
<th>Maximum weight loss rate WLR_max (%.min⁻¹)</th>
<th>Char yield CY (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0</td>
<td>316.82</td>
<td>332.70</td>
<td>13.10</td>
<td>6.48</td>
</tr>
<tr>
<td>C-5</td>
<td>324.39</td>
<td>344.35</td>
<td>14.31</td>
<td>8.02</td>
</tr>
<tr>
<td>C-10</td>
<td>310.71</td>
<td>342.50</td>
<td>7.59</td>
<td>10.34</td>
</tr>
<tr>
<td>C-15</td>
<td>323.07</td>
<td>345.71</td>
<td>9.82</td>
<td>12.28</td>
</tr>
<tr>
<td>C-20</td>
<td>320.89</td>
<td>345.32</td>
<td>8.95</td>
<td>15.49</td>
</tr>
</tbody>
</table>

swelling. A sharp fall of onset temperature from C5 to C10 samples was due to partial destruction of the amorphous region. As the concentration of alkali increased, the CI value increased for C15 and C20 samples because fibers also went through a rearranging process to form a new crystalline lattice. It can be seen from Table 2.2 that the degradation temperature T_max and the maximum weight loss rate WLR_max followed the same trend.

Table 2.2 shows that a char yield of 6.48% was recorded for raw cotton fibers, whereas char yields for C-5, C-10, C-15 and C20 samples were 8.02, 10.34, 12.28, and 15.39 %, respectively. This dramatic increase in char yield reflects the level of the β-glycosidic linkages. Thus mercerized cellulose with a stable structure exhibited an increase in char formation (Abbott and Bismarck, 2010).

2.3.5. Tensile Properties of PEO/cotton Fiber Composites

Typical stress-stain curves for pure PEO, PEO/cellulose I cotton fiber (C0) and PEO/cellulose II cotton fiber (C20) composite films are presented in Fig 2.6. The thickness of all films averaged at 60μm. It can be observed that, both raw and mercerized cotton fibers with the proportion to PEO of 1 to 10 enhanced mechanical properties of PEO matrix. Furthermore, compared to the composites of PEO/cellulose II cotton fiber (C20), tensile strength and elongation at break for PEO/cellulose I cotton fiber (C0) composites were
Fig 2.6 Typical stress-stain relationship of PEO, PEO/cellulose I cotton fiber and PEO/cellulose II cotton fiber composites

Fig 2.7 A comparison of measured tensile strength and elongation at break for pure PEO, raw and mercerized fiber/PEO composite films
slightly better. This was thought to be related to the fact that the mercerized fibers had a stronger among-fiber interaction. Thus, it was more difficult to well disperse the mercerized fibers in the PEO matrix, compared with the raw cotton fibers. The non-uniform distribution of long cotton fibers in the PEO matrix also led to increased brittleness of the composites.

2.4. Conclusions

Mercerization of cotton fibers led to the crystal structural transformation from cellulose I to cellulose II. A complete transition occurred at the concentration levels of sodium hydroxide of 15 and 20%. FESEM morphological analysis showed that cotton fibers converted into a swollen and roughened state by mercerization treatment. FTIR and WXRD data indicated that the degree of disorder of the O-H stretching vibration increased, crystallinity and the degree of polymerization decreased sharply during the process of mercerization. TGA curves exhibited that the structure of cellulose II fibers was more stable than cellulose I fibers. Mechanical properties of fiber-reinforced PEO composites suggested that raw and mercerized cotton fibers enhanced the tensile strength of the PEO matrix, but made the composite more brittle. Enhanced fiber dispersion in the PEO matrix could further improve composite properties.

2.5. References


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CHAPTER 3. COMPARATIVE PROPERTIES OF NANOCRYSTALS FROM RAW AND MERCERIZED COTTON FIBERS

3.1. Introduction

In recent years, rod-shape cellulose nanofibers have attracted increasing attention attributed to their biodegradable and biocompatible performance. The material has high stiffness, large specific surface area, high aspect ratio, low density, and reactive surfaces that can facilitate chemical grafting and modification. At the same time, they are inert to many organic and inorganic substances (Chang et al., 2009; Wu et al., 2010; Zivanovic et al., 2007).

Sulfuric acid hydrolysis treatment of raw cellulose is one of the most common processes to remove hemi-cellulose and impurities and to obtain purified cellulose nanocrystals. The properties of the nanocrystals (e.g., shape, length, and diameter) are determined by cellulose sources and the degradation process (e.g., controlled time and temperature for acid hydrolysis, high-pressure homogenization conditions, etc.) (Dong et al., 1996; Lu and Hsieh, 2010). Proper sulfuric acid treatment can provide the crystals with a negatively charged surface from sulfate attachment to hydroxyl groups on the crystal surface. The resultant cellulose nanocrystals form a stable aqueous suspension (Mansikkamaki et al., 2005).

Mercerization treatment is a versatile process for chemical modification of cellulose. It was reported that the process of mercerization results in changes in crystalline structure and many other properties. So far, most investigations dealing with mercerization of cellulose have focused on whole cellulose fibers, i.e., assemblies of large numbers of organized microfibrils (Dinand et al., 2002). Very few investigations have dealt with transitional properties of cellulose I and II nanocrystals. The main goal of this research was to study the
effect of mercerization on the properties of cellulose nanocrystals, including crystallinity, properties of surface and crystal suspension, and crystal-polymer matrix adhesion in polymer composites. Cotton fibers were chosen as the cellulose source.

3.2. Materials and method

3.2.1. Raw Material and Processing

Both un-mercerized and mercerized cotton fibers pre-prepared from experiments described in Chapter 2 were used for this study. Sulfuric acid (95-98%, purity) was obtained from VMR (West Chester, PA). The acid was diluted to make 64% solution for experiments described below.

3.2.2. Preparation of Cotton Nano-Crystals (CNCs)

CNCs were made using 64% sulfuric acid aqueous solution with cotton-to-acid weight ratio of 1 to 10 at 45 ºC temperature. The prepared cotton fibers were pre-mixed with the acid and the mixture was stirred vigorously for 1 hour. Immediately following hydrolysis, the suspension was diluted five-fold to stop the reaction. The suspension was then transferred into centrifuge bottles and was centrifuged at 12,000 rpm for 10 min (Sorvall RC-5B Refrigerated Superspeed Centrifuge, Du Pont Instrument) to separate the crystals in the suspension. The crystals were then washed with distilled water and the mixture was centrifuged again. The process was repeated four to five times for each sample to reduce the acid content. Afterward, regenerated cellulose dialysis tubes (Fisher Scientific, Pittsburgh, PA, USA) with a molecular weight cutoff of 12,000–14,000 were used to dialyze the suspension against distilled water until the water pH reached a value of 7.0.

To further disperse and reduce the size of the cellulose crystals, mechanical treatment
was applied to the chemically treated samples. The suspension of cellulose crystals was processed through a high-pressure homogenizer (Microfluidizer M-110P, Microfluidics Corp., Newton, MA, USA) equipped with a pair of Z-shaped interaction chambers (one 200 µm ceramic, and one 87 µm diamond) under an operating pressure of 207 MPa. Samples after each pass (1-10) through the high-pressure homogenizer were collected for analysis. Then the remaining suspension was collected and part of the material was dried using a freeze-dryer (FreeZone, 2.5 plus, Labconco Corp., Kansas City, MO, USA) to obtain dry CNCs. The remaining suspension was kept in a refrigerator at 10°C. The obtained samples were designated as Nx with x= 0, 5, 10, 15 and 20 to correspond to alkali concentration levels during fiber mercerization treatment. To test re-dispersion property, freeze-dried raw (N0) and mercerized crystals (N20) (0.2g each) were re-dispersed in distilled water to form 1 wt % suspension.

3.2.3. Preparation of Liquid CNC Films and PEO/Liquid CNC Composite Films

The suspensions of 1.0 wt % raw (N0) and mercerized cotton crystals (N20) after being stored in a refrigerator at 10°C for 30 days were poured into polystyrene Petri dishes, which were then placed back in the refrigerator (at 10°C) for slow water evaporation. Two solid films were obtained after 14 days. All films were kept in desiccators for further characterization.

PEO samples (0.4g each) were dispersed in 4ml 1wt % raw (N0) and mercerized (N20) CNC suspensions. Each resultant mixture was placed in a separate vial equipped with one magnetic stirrer. After being stirred for 48 hours, the formed homogeneous suspensions were poured into two separate aluminum dishes, which were then placed in a vacuum oven at 40°C
to fabricate PEO/liquid crystal composite films. Pure PEO films were also made as control following the same procedure.

3.2.4. Characterization

3.2.4.1. Morphology

The morphology of chemically and mechanically treated CNCs was characterized using Transmission Electron Microscopy (TEM) (JEOL 100CX, JEOL USA, Inc) with an accelerating voltage of 80 kV. The 0.1 wt% nanocrystal suspensions were dropped onto copper grids coated with a carbon support film for observation. The specimens were stained with one small drop of 2% uranyl acetate to improve the contrast. Excess liquid on the grid surface was removed with a small piece of filter paper by lightly touching the edge of the grid to absorb the liquid.

Field Emission Scanning Electron Microscopy (FESEM, Nova™ Nano SEM 450, Hillsboro Oregon USA) was used to contrast the ultrastructural changes between raw and mercerized dry crystals, nanocrystal films and crystal/PEO composites. Prior to the analysis, the films of crystal/PEO composites with a dimension of $20 \times 5 \times$ thickness (mm) were cooled for 15 minutes. Then each film sample was stretched using two tweezers to grasp two sides of the sample to fracture it. Surfaces of the fractured crystal/PEO composite, pure nanocrystal films, and the crystals were sputtered with Au. The prepared samples were placed on metal stubs using double-side adhesive tape and scanned at a 5k voltage level.

An Olympus (Tokyo, Japan) BHA-P polarized microscope was used for observation of the orientation of crystals in both raw and mercerized crystal films.
3.2.4.2. Fourier Transform Infrared Spectrometry (FTIR)

FTIR spectra of dry crystal samples were taken on a Bruker FTIR analyzer (Tensor-27, Bruker Optics Inc., Billerica, MA) with an attenuated total reflectance (ATR) mode. The wavenumbers were recorded in the range of 4000-600 cm\(^{-1}\). Each of the freeze-dried samples from various treatment conditions were pressed into the sample chamber for the FTIR measurements. The scan frequency was 64 s\(^{-1}\) and resolution was 4 cm\(^{-1}\). For each condition, three replicated measurements were made.

3.2.4.3. Wide-angle X-ray Diffraction (WXRD)

The super-molecular structure of raw and mercerized CNCs was analyzed with a Wide-angle X-ray diffraction (WXRD). WXRD patterns of the cotton CNCs were recorded by a Bruker/Siemens D5000 automated powder X-ray diffractometer. The diffraction pattern was recorded in an angle range of 0 to 40°. The wavelength of the Cu/Ka radiation source was 0.154 nm, and the spectra were obtained at 30 mA with an accelerating voltage of 40 kV. X-ray diffraction data were analyzed using the MDI Jade 5.0 software. Curve-fitting was performed to find individual peak regions. The main diffraction peaks were integrated and used to calculate the crystalline index (CI, %) of the samples:

\[
CI(\%) = \frac{I_c}{I_c + I_a} \times 100\%
\]  

where Ic (A.u.) and Ia (A.u.) represent the integrated intensities of crystalline and amorphous regions, respectively.

The Scherrer equation was used to calculate the crystal size, \(t\) (nm), perpendicular to the (200) plane for both cellulose I and cellulose II crystals:
\[ t = \frac{K \lambda}{\beta \cos \theta} \]  

where \( K \) is the correction factor and usually taken to be 0.9, \( \lambda \) is the radiation wavelength, \( \theta \) is the diffraction angle in radians, and \( \beta \) is the corrected angular width at the half maximum intensity in radians.

The spacing between the (200) planes, \( d \) (nm), was calculate using the Bragg’s equation:

\[ n \lambda = 2d \sin \theta \]  

where \( n \) is an integer, \( \lambda \) is the wavelength of the incident wave, and \( \theta \) is the angle between the incident ray and the scattering planes.

3.2.4.4. Thermal Degradation Measurements

The dehydration and degradation behavior of CNCs was characterized through thermo-gravimetric analysis (TGA) with a TA Q50 Analyzer (TA Instruments, New Castle, DE) in a nitrogen atmosphere. Specimens of 5 – 10 mg were tested in a temperature range from 30 to 500 °C. The heating rate was 5 °C/min and the nitrogen flow rate was 35ml/min. The weight-loss rate was obtained from derivative thermogravimetric (DTG) data. The onset degradation temperature was defined as the intersection of tangents drawn from thermo-gravimetric curve, one before inflection caused by the degradation and another from the cellulose degradation step.

3.2.4.5. Rheological Properties of CNC Suspensions

The rheological behavior of the CNC suspensions was investigated with a TA AR2000EX rheometer (TA Instruments, New Castle, DE). Instrument configuration included a 40-mm cone-plate geometry (cone angle 1°59’42” and truncation 56 μm) and a
Peltier plate device for maintaining target sample temperature during the measurements. To avoid the evaporation of water in the sample, the 56 μm gap between the cone and Peltier plate was sealed with a solvent trap cover, and the moat on the top of the cover was filled with low viscosity silicon oil.

The raw and mercerized CNC suspensions were adjusted to achieve CNC concentrations of 1.0%, 1.5% and 2.0 wt% prior to measurements. Oscillatory tests were performed in a frequency range of 0.1 to 100Hz and a temperature range of 5 to 60°C to determine rheological response of the crystal samples.

3.2.4.6. Film Tensile Properties

Tensile strength and elongation at the break of the CNC/PEO film samples were measured using the TA AR2000EX rheometer (AR2000, TA Instruments, New Castle, DE) with a solid fixture. The tensile samples with a dimension of 15 (length)×3(width)×thickness mm were carefully cut from larger film samples. During testing, both sample ends were securely mounted on to the testing fixture using mounting screws. The maximum capacity of the load cell was 50 N and tensile gap (gauge length) between two grips was set as 5 mm. The speed of the tensile testing was 500 μm/s and five specimens were tested for each condition.

3.3. Results and Discussion

3.3.1. Property of CNCs and Their Aqueous Suspensions

3.3.1.1. Morphological and Dispersion Property

Fig. 3.1 shows photographs of aqueous suspensions of acid-hydrolyzed cotton crystals (labeled as “0”) and acid-hydrolyzed high-pressure homogenized crystals passed through the
homogenizer for 1 to 10 cycles (labeled as “1, 3, 5, 8, and 10”). For both cellulose I and II crystals, purely acid-hydrolyzed cotton crystals precipitated at the bottom of the test tubes. After one pass through the homogenizer under high pressure (i.e., 207 MPa), it formed a stable opalescent suspension in water. After additional homogenizing treatments, the obtained CNCs were well dispersed in water without visible aggregation. Light blue transparent suspensions were formed as shown by the samples “3” through “10”, which reflected the nano-sized particles in the suspensions. The result indicated that the homogenizing treatment is an effective method for reducing CNC size and for further dispersing them in an aqueous liquid (i.e., water). At the same solid content level, mercerized crystal suspensions became increasingly more viscous as the number of treatment passes increased.

Typical TEM images of raw (a: N0) and mercerized cotton (b: N20) CNCs after ten homogenization passes are shown in Figure 3.2. Both types of crystals had a regular rod-like shape with a high aspect ratio. It was observed raw and mercerized CNCs of typical dimensions ranging mostly from 10 to 167 nm in length and less than 12 nm in width. High-pressure homogenized crystals from samples N0 and N20 after 10 homogenization passes had an average length of 70±34 nm and 66±27 nm; and average diameters of 8.7±1.7 nm and 9.2±2.1 nm, respectively. And the corresponding aspect ratios were 7.7 and 6.9, respectively. Thus, there was no obvious change in crystal sizes from raw and mercerized materials of cotton fibers, considering the fact that only a limited number of crystals were measured with the TEM technique. This indicates that mercerization process did not significantly affect obtained crystal dimensions.
Fig 3.1 Photograph of aqueous suspensions from raw (0-top) and Mercerized CNCs (20-bottom) passed through the homogenizer for 1, 3, 5, 8, and 10 cycles
Fig 3.2 Typical TEM images of CNCs before (a: N0) and after mercerization (b: N20).

To contrast the difference between raw and mercerized crystals, the suspension samples shown in Figure 3.1 were placed in a refrigerator at 10°C for 30 days, and the bottles were then turned up-side down to test the suspension flowability (Figure 3.3). Both homogenized cellulose raw and mercerized CNCs exhibited a time-dependent thickening in viscosity. As shown in Figure 3.3, mercerized crystals (bottom) lost their flowability and exhibited a gel-like behavior, while raw crystals (top) were still flowable. It was thought that mercerized crystals were arranged by an ordered gelation network. This network was constructed by stronger hydrogen or ionic bonding interactions among inter- or intra-molecular chains than these in the native raw crystals. Thus, a more compacted gel network was formed for mercerized crystals. We noticed that when raw and mercerized thickened suspensions were shaken, the phenomenon of thixotropy occurred (Benchabane and Békkour, 2008; Uskokovic, 2008). This was because the hydrogen bond and network built up in the suspensions were not strong enough to resist the destructive shaking force.

Figure 3.4 shows a photomicrograph comparison of freeze-dried raw CNCs (N0) and
Fig 3.3 The photographs of raw (N0-top) and mercerized CNCs (N20-bottom) suspensions passed through the homogenizer for 1, 3, 5, 8, and 10 cycles and stored in a refrigerator at 10°C for 30 days.
mercerized CNCs (N20) with the same weight of material. It can be seen that raw CNCs (N0) apparently had much larger dry volume and lower bulk density compared with mercerized CNCs (N20). This difference in bulk volume was closely related to the dry crystal morphology.

![Comparison of dry raw (N0) and mercerized (N20) CNCs with the same weight.](image)

**Fig 3.4** Comparison of dry raw (N0) and mercerized (N20) CNCs with the same weight.

Figure 3.5 shows the FESEM micrographs at 500 and 20000-time magnification levels of dry raw and mercerized CNCs. At the 500 magnification level, both types of CNCs were seen as particle-like pieces (Fig. 3.5a and Fig 3.5c). The higher magnification photos showed that raw CNCs formed long ribbons with a large inter ribbon voids, while mercerized CNCs were densely packed short particles. The embedded voids for raw dry crystals significantly increased their bulk volume in comparison with densely-packed mercerized crystals.

Figure 3.6 shows four vials containing 1% w/w CNC aqueous suspension. The vials marked with VN0 and VN20 were fresh raw and mercerized crystal suspensions after being
Fig 3.5 FSEM photomicrographs of raw CNCs (N0) (a,b) and mercerized CNCs (N20)(c,d) observed by FSEM with 500 (a,c) and 20000 (b,d) time magnification levels.

passed through the homogenizer for 10 times. The vials marked with RN0 and RN20 were freeze-dried and re-dispersed suspensions of the same materials shown in vials VN0 and VN20, respectively. In case of raw crystals (Fig. 3.6RN0), a translucent dispersion was observed in the re-dispersed suspension. However, re-dispersed mercerized crystals presented the white sedimentation at the bottom of the vial (Fig. 3.6RN20). A thick layer of large particle aggregation indicates that mercerized CNCs were more stable than raw crystals during the re-dispersion treatment. Since ultrasonic wave could not effectively break down the strong hydrogen bonding interactions among inter- or intra-molecular chains, dispersion agents are needed to fully re-disperse the cellulose II crystals.
3.3.1.2. FTIR Results

Figure 3.7 shows the overall FTIR spectra of raw and mercerized cotton crystals. Bands at 4000-2995 cm\(^{-1}\), 2900 cm\(^{-1}\), 1430 cm\(^{-1}\), 1375 cm\(^{-1}\), and 900 cm\(^{-1}\) were found to be sensitive to variations in crystalline and amorphous regions (Oh et al., 2005). The partitioned FTIR characteristic bands of both CNCs are shown in Figure 3.8.

The strong hydrogen bonded OH stretching vibration within the region 2995-3600 cm\(^{-1}\) is shown in Fig 3.8a. The intermolecular hydrogen bonding of O2-H-O6 for raw fibers and O2-H-O6, O6-H-O6 and O2-H-O2 for mercerized fibers (Langan et al., 1999) are shown at 3441 cm\(^{-1}\), 3338cm\(^{-1}\), and 3299 cm\(^{-1}\) positions, respectively (Oh et al., 2005; Schwanninger et al., 2004). The crystal system of cellulose was changed from cellulose I (raw) to cellulose II (mercerized) by mercerization at the 15% and 20% alkali levels, as shown. The IR index (i.e., a ratio of IR intensity at a given wavenumber to that at the reference wavenumber) values based on the absorbance peaks at 1057cm\(^{-1}\) (\(\text{>CO/C-C}\) stretching vibration)
was chosen to analyze the conformation and hydrogen-bond intensity changes for various materials (Das and Chakraborty, 2006). It was calculated that the OH stretching vibration within the region 3100–3800 cm\(^{-1}\) increased considerably with increase in alkali concentration. For instance, the hydrogen-bond intensities for CNCs from samples, N0, N5, N10, N15 and N20 at 3338 cm\(^{-1}\) are 0.304, 0.290, 0.254, 0.313 and 0.330, respectively. The result indicated that sodium hydroxide intensified the intra or inter molecular hydrogen bonding.

![FTIR spectra of N0, N5, N10, N15 and N20 crystal samples.](image)

**Fig 3.7** FTIR spectra of N0, N5, N10, N15 and N20 crystal samples.

For CNCs prepared with different NaOH concentrations, the maximum absorbance of CH stretching was also shifted from about 2901 cm\(^{-1}\) for N0, N5, and N10 to a lower wavenumber at 2890 cm\(^{-1}\) for N15 and N20 after mercerization treatment (Figure 3.8a). The wavenumber decrease at this position averaged 11 cm\(^{-1}\), which suggested that the different arrangements caused by changes of angles around \(\beta-1\), 4-D-glycosidic linkages rearrangement (Liu et al., 2010).
Fig 3.8 FTIR spectra of the N0, N5, N10, N15 and N20 CNCs with wavenumber ranges of 3600-2750 (a), 1480-1320 (b), 950-640 (c), and 1225-900 (d).

The absorbance intensities at the 1427 cm\(^{-1}\) position are assigned as CH\(_2\) bending (El-Wakil and Hassan, 2008). The peak IR index values at 1427 cm\(^{-1}\) for N0 N5, N10, N15 and N20 were 0.099, 0.0934, 0.0936, 0.0876 and 0.0702, respectively (Fig. 3.8b). The decreased CH\(_2\) intensity bending reflects a higher number of disordered crystals formed with increased concentration of sodium hydroxide (Krebs, 2008). The small change at 1370 cm\(^{-1}\) was attributed to the =CH stretching in N0, which was not linearly proportional to that of other samples (Oh et al., 2005).

An important feature of the spectra shown in Fig. 3.8c is that the wavenumber changed
from 1161 cm$^{-1}$ to 1157 cm$^{-1}$, indicating transitional change from cellulose I to cellulose II CNCs. Also, a decrease of relative intensity of the band at 1161 and 1157 cm$^{-1}$ suggested that with increased treatment concentrations of alkali, C-O-C stretching vibration bonding was gradually changed beyond the 10% alkali concentration level.

Figure 3.8d shows that the bands for N0, N5, and N10 at 897 cm$^{-1}$ were shifted to 894 cm$^{-1}$ for N15 and N20. It was reported that 897 cm$^{-1}$ is assigned as β-glucosidic linkage for the Cellulose I structure and 894 cm$^{-1}$ for the Cellulose II structure (Gwon et al., 2010). The change occurred because of the rotation of glucose residue around the glucosidic bond (Ray and Sarkar, 2001). Also, it can be seen that band at 999 cm$^{-1}$ was shifted to 996 cm$^{-1}$, which was also because of the transformation from cellulose I crystal structure to cellulose II crystal structure (Gwon et al., 2010).

Figure 3.9a shows a comparison of FTIR spectra for raw and mercerized cotton fibers and crystals. The spectra indicate the -C-O stretching vibration in 1033, 1057 and 1083 cm$^{-1}$. As shown in Fig. 3.9a, the vibration of crystals was intensified due to the fact that the change occurred in molecular orientation after mercerization. The destroyed amorphous region after acid treatment also contributed to the enhancing of the vibration of crystals (Chen et al., 2010). Also, the =CH symmetrical deformation vibration at 1370 cm$^{-1}$ and the -CH$_2$ bending vibration at 1427 cm$^{-1}$ increased in Fig. 3.9b (Oh et al., 2005). The variety of =CH and –CH$_2$ was probably due to the partial removal hemicelluloses in carbohydrate polymer chain.
Fig 3.9 A comparison of FTIR spectra of raw and mercerized fibers and CNCs with two different wavenumber ranges.

3.3.1.3. WXRD Data

The diffraction patterns of raw and mercerized CNCs (N0 to N20) are shown in Figure 3.10. Three peaks at 2θ=14.76° (110), 16.44° (110) and 22.56° (200) confirmed that only cellulose I was present in the N0 and N10 samples (Liu and Hu, 2008). As the concentration of alkali increased, the crystalline peak was split into two weaker peaks located at 2θ=19.89° (110) and 2θ=21.96° (200) (Figure 3.10), showing typical cellulose II structure. The result further indicates that cellulose II structure from mercerized cotton fiber remained in the crystals.

The calculated crystallinity index (CI) values of raw and mercerized fibers were 81%, 83%, 65% and 67%, respectively, for C0, C10, C15 and C20 (Chapter 2). After acid hydrolysis treatment, CNCs exhibited a reduced CI values of 79%, 76%, 63% and 62% for N0, N10, N15 and N20, respectively (Table 3.1). The changes in the degree of crystallinity during acid hydrolysis treatment were due to degradation of cellulose. Also, the CIs of CNCs decreased with increased the concentration level of alkali, indicating that NaOH had a strong
effect for destroying the crystalline region.

![X-ray diffraction chart](image)

Fig 3.10 X-ray diffraction chart of CNCs without (N0) and with (N10, N15, and N20) mercerization treatment

From Table 3.1, it can be seen that the crystal size and d-space increased from cellulose I to cellulose II CNCs. The possible reason is that that mercerization led to rearrangement in intermolecular hydrogen bond and agglomeration between the chains. Compared to the d-space values from cotton fibers (i.e., 0.394 to 0.415) (Chapter 2), less increase of the d-spacing values for CNCs was seen, from 0.394 to 0.405 (Inagaki et al., 2010). Also, contrast with the variation of crystal sizes from 9.12 to 11.75 for cotton fibers (chapter 2), the crystal size was for the CNCs changed from 8.94 nm to 9.61 nm. This phenomenon indicates that the function of agglomeration of the chain or arrangement in crystal structure caused by mercerization was limited after acid hydrolysis treatment.
Table 3.1 WXRD parameters of CNCs before and after mercerization treatment.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Crystallinity Index (%)</th>
<th>d-spacing (200) of the planes (nm)</th>
<th>Crystal size perpendicular to the (200) planes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0</td>
<td>79.2</td>
<td>0.394</td>
<td>8.94</td>
</tr>
<tr>
<td>N10</td>
<td>75.9</td>
<td>0.394</td>
<td>9.08</td>
</tr>
<tr>
<td>N15</td>
<td>63.0</td>
<td>0.401</td>
<td>9.61</td>
</tr>
<tr>
<td>N20</td>
<td>61.5</td>
<td>0.405</td>
<td>9.54</td>
</tr>
</tbody>
</table>

3.3.1.4. TGA Data

The thermo-gravimetric (TG) and derivative thermo-gravimetric (DTG) curves of CNCs with and without mercerization treatment are shown in Fig. 3.11. The decomposition process is further characterized by extrapolated onset temperatures, degradation temperatures, maximum weight loss rates, and char yields (Table 3.2). All CNC samples had a small weight loss in low temperature (<150°C) range, corresponding to the evaporation of absorbed water. In the high temperature range (>150°C), the degradation behaviors of CNC samples showed difference among them.

It can be shown that the degradation for N0 and N5 had one pyrolysis process. The degradation of N10, N15 and N20 had two well-separated pyrolysis processes in the DTG curves. One process occurred between 150°C and 250°C and the other between 250°C and 500°C. The second process dominated the overall pyrolysis. The two-step pyrolysis for acid-treated nanocellulose crystals has been reported (e.g., Wang et al., 2007). This was attributed to acid sulfate groups on the crystal surface. The extent of the first pyrolysis process depends on the actual number of the sulfate groups on the crystal surface. Neutralization treatment of acid-treated crystals with NaOH reduced the first pyrolysis process.
Fig 3.11 TGA and DTG curves of CNCs with and without mercerization treatment.
From about 250 to 500 °C, a second step of thermal degradation occurred, attributed to the degradation of the cellulose network. It can be seen that raw CNCs showed a typical cellulose decomposition with an onset temperature of 287.28°C (Table 3.2), whereas the degradation of mercerized CNCs was initiated at higher temperatures above 300°C, illustrating that mercerized cotton crystals had better thermal stability properties. This is because the strong interaction of –OH groups in cellulose II required more energy to start the thermal degradation process.

Also, mercerized crystals samples exhibited a decrease in char formation with increased the concentration level of alkali. At 500°C the char yields of were 39.05wt% for N0, and 39.93, 30.85, 26.41 and 17.62 wt % for N5, N10, N15 and N20, respectively. For cotton fibers, the char yields were significantly smaller (Chapter 2). Wang et al (2007) reported a similar result in comparing char yields for cellulose nanocrystals and microcrystalline cellulose. It was attributed to the increased number of free end chains in the nanocrystals with a much smaller particle size. The end chains started decomposition at lower temperatures, and facilitated the char yield increases. The char yield decreased as the extent of mercerization treatment increased.

It can be seen that the CNCs exhibited significantly different thermal behaviors than un-hydrolyzed cellulose fibers (Fig. 2.5, Fig. 3.11). The onset temperature \( T_o \) and maximum decomposition temperature \( T_{\text{max}} \) was considerably decreased, whereas the char yield increased sharply (Table 2.2, and Table 3.2). The reason may be that cellulose degradation was started by cellulose depolymerisation to low molecular weight oligosaccharides and followed by scission of D-glucopyranose (Lin et al., 2009). Strong acid
Table 3.2 Onset degradation temperature, degradation temperature, maximum weight loss rate and char yield of the thermal degradation process in nitrogen of CNCs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp. T_o (°C)</th>
<th>Stage I</th>
<th>Stage II</th>
<th>Char yield CY (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Degradation Temp. T_max (°C)</td>
<td>Maximum weight loss rate WLR_max (%.min^-1)</td>
<td>Degradation Temp. T_max (°C)</td>
<td>Maximum weight loss rate WLR_max (%.min^-1)</td>
</tr>
<tr>
<td>N-0</td>
<td>287.28</td>
<td>-</td>
<td>-</td>
<td>308.79</td>
</tr>
<tr>
<td>N-5</td>
<td>314.63</td>
<td>-</td>
<td>-</td>
<td>337.15</td>
</tr>
<tr>
<td>N-10</td>
<td>307.61</td>
<td>224.28</td>
<td>1.94</td>
<td>335.45</td>
</tr>
<tr>
<td>N-15</td>
<td>304.73</td>
<td>221.45</td>
<td>2.07</td>
<td>333.61</td>
</tr>
<tr>
<td>N-20</td>
<td>303.36</td>
<td>224.85</td>
<td>2.05</td>
<td>336.32</td>
</tr>
</tbody>
</table>

solution can effectively break down the amorphous cellulose (Beck-Candanedo et al., 2005), hence acid treated cellulose showed lower initial temperature and higher char yield because of the destroyed amorphous region.

3.3.1.5. Rheological Properties

The viscosity-time relationship of both raw and mercerized CNC suspensions showed a two-stage process (Fig 3.12a for N0). There was an initial, concentration-dependent plateau. The region showed a true Newtonian behavior, where an increase of shear rate with increased shearing time did not change the mean rod orientation and thus did not change the apparent viscosity. There was a clear transition toward reduced viscosity at the end of the Newtonian plateau and the actual transition time corresponds to the critical shear rate for each concentration level. The viscosity vs shear rate curves of raw and mercerized CNC suspensions at 1.0, 1.5 and 2.0 wt % concentration levels are shown in Fig 3.12b. The data were collected at 20 °C at various shear rates (0.01-100s^-1). The viscosity of both type of CNCs decreased as shear rate increased, indicating a shear thinning behavior. Compared to raw crystals, mercerized crystals had a significantly higher viscosity at the same
concentration level. It was reported that viscosity of the cellulose II sample in sodium hydroxide solutions was approximately twice that of cellulose I sample in the same solvent at the same concentration and temperature (Yasuda et al. 1993). Thus, current results with nanocrystals are in agreement with published data in this field. For both types of crystal suspensions, their viscosity increased with concentration, indicating a gel-like behavior due to the high aspect ratio of the nano-fibril gelation network (Brownsey and Ridout, 1985).

Fig 3.13 illustrates measured storage modulus of CNC suspensions as a function of angular frequency at various temperature levels. (Cael et al., 1975). The storage modulus increased with increased frequency and temperature for both types of CNCs. Storage modulus and angular frequency data were mathematically modeled using the Boltzmann equation:

\[
G' = A_2 + \frac{(A_1 - A_2)}{(AF - X_o)} \left(1 + e^{-\frac{X_1}{AF}}\right)
\]

[3.4]

Where \(G'\) is the storage modulus (Pa), \(AF\) is the angular frequency (rad/s), \(A1, A2, X0\) and \(X1\) are material constants. The obtained model parameters are listed in Table 3.3 and fitted data are shown in Fig 3.13 in comparison with experimental data. The Boltzmann mode provided a good fit of the experiment data.

The \(G'\) values of mercerized CNC suspensions were several times higher than those of raw CNCs at the same temperature and concentration levels. This is related to the difference in the hydrogen bonding between the two systems as shown in the FTIR data. The temperature effort on \(G'\) for raw crystals increased considerably with increase of
Fig 3.12 Relationships between viscosity and time for N0 (a) and between viscosity and shear rate (b) for both N0 and N20.
Fig 3.13 Storage modulus ($G'$) as a function of angular frequency at different temperatures of CNCs before (a) and after mercerization (b) treatment. Symbols are experimental data and lines are fitted values.
Table 3.3 Parameters of the Boltzmann model showing the relationship between storage modulus ($G'$) and angular frequency (rad/s)

<table>
<thead>
<tr>
<th>Temp($^\circ$C)</th>
<th>Model Parameter (N0)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
<td>A2</td>
<td>$x_0$</td>
<td>$x_1$</td>
</tr>
<tr>
<td>10</td>
<td>-450.79</td>
<td>28.97584</td>
<td>-15.3077</td>
<td>3.82743</td>
</tr>
<tr>
<td>20</td>
<td>-680.42</td>
<td>38.80274</td>
<td>-19.1054</td>
<td>4.34283</td>
</tr>
<tr>
<td>30</td>
<td>-877.57</td>
<td>47.36051</td>
<td>-18.2160</td>
<td>3.96996</td>
</tr>
<tr>
<td>40</td>
<td>-1465.52</td>
<td>58.14122</td>
<td>-17.1731</td>
<td>3.47098</td>
</tr>
<tr>
<td>50</td>
<td>-219.50</td>
<td>74.78847</td>
<td>-6.2293</td>
<td>2.12692</td>
</tr>
<tr>
<td>60</td>
<td>-2255.07</td>
<td>128.33520</td>
<td>-6.0001</td>
<td>1.45945</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp($^\circ$C)</th>
<th>Model Parameter (N20)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
<td>A2</td>
<td>$x_0$</td>
<td>$x_1$</td>
</tr>
<tr>
<td>10</td>
<td>-1289.3</td>
<td>100.70</td>
<td>-6.4628</td>
<td>1.7622</td>
</tr>
<tr>
<td>20</td>
<td>-2018.8</td>
<td>177.62</td>
<td>-7.0864</td>
<td>1.8625</td>
</tr>
<tr>
<td>30</td>
<td>-1998.8</td>
<td>253.85</td>
<td>-7.0952</td>
<td>1.9522</td>
</tr>
<tr>
<td>40</td>
<td>-2407.5</td>
<td>336.71</td>
<td>-7.0614</td>
<td>1.9410</td>
</tr>
<tr>
<td>50</td>
<td>-3010.6</td>
<td>431.57</td>
<td>-6.4666</td>
<td>1.7592</td>
</tr>
<tr>
<td>60</td>
<td>-21183.0</td>
<td>539.54</td>
<td>-10.2490</td>
<td>1.9095</td>
</tr>
</tbody>
</table>

Temperature beyond 50°C level, indicating a properly transition. $G'$ at different temperature levels for mercerized crystals was roughly constant over the entire temperature range.

Fig. 3.14 shows storage modulus as a function of temperature at different shear rates. For raw CNC suspensions, there was an initial linear $G'$-temperature relationship up to the 45°C temperature level. The $G'$ increased in a significantly larger rate after that temperature level. For mercerized CNC suspensions, there was an approximately linear $G'$-temperature relationship up to the 60°C temperature level at all shear rate levels.

The measured storage modulus data were re-plotted in a Logarithm scale against $1/Temp (K^-1)$ in Fig 3.15. The data was modeled with the Arrhenius equation:

$$G' = Ae^{-E_{G'}/RT} \quad [3.5]$$
Fig 3.14 Storage modulus (G’) as a function of temperature at different angular frequencies of the CNCs before (a) and after (b) mercerization treatment
Fig 3.15 The relationship between LnG’ and 1/T (K⁻¹) at different angular frequencies of the CNCs before a) and after b) mercerization treatment. Lines showing fit with the Arrhenius Equation.
Table 3.4 Parameters of the Arrhenius equation showing the relationship between Ln-scale storage modulus ($G'$) and 1/Temperature ($K^{-1}$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency (rad/s)</th>
<th>$E_G$ (J·K$^{-1}$)</th>
<th>A (Pa)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose I</td>
<td>0.1</td>
<td>346.04</td>
<td>12.99</td>
<td>0.9762</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>316.05</td>
<td>12.41</td>
<td>0.9761</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>303.27</td>
<td>12.16</td>
<td>0.9696</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>284.11</td>
<td>11.76</td>
<td>0.9516</td>
</tr>
<tr>
<td>Cellulose II</td>
<td>0.1</td>
<td>479.31</td>
<td>18.17</td>
<td>0.9525</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>416.94</td>
<td>16.74</td>
<td>0.9673</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>400.88</td>
<td>16.40</td>
<td>0.9710</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>389.62</td>
<td>16.17</td>
<td>0.9707</td>
</tr>
</tbody>
</table>

After taking the natural logarithm, Eq. 3.5 became:

$$\ln G' = \ln A - \frac{E_G}{RT}$$

[3.6]

where, $E_G$ (J·K$^{-1}$) is the activation energy of viscous flow, $G'$ (Pa) is the storage modulus of cotton nanocrystals, A (Pa) is the pre-exponential constant, T is the absolute temperature (K), and R is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$). A linear regression fit was done using Equation 3.6 to obtain parameters $E_G$ and A. The modeled relationship between $\ln G'$ and $1/T$ is shown in Fig.3.15 and the model parameters are summarized in Table 3.4. The calculated values $E_G$ for raw CNC I were 346.04, 316.05, 303.27, and 284.11 kJ/mol at angular frequencies of 0.1, 1, 10, 100 rad/s, respectively. The $E_G$ values for mercerized CNCs were 479.31, 416.94, 400.88 and 389.62kJ/mol at angular frequencies of 0.1, 1, 10, 100 rad/s. It can be seen that the $E_G$ values for all mercerized CNC samples are higher than those for raw cellulose I nanocrystals, indicating that the suspension of mercerized nano-crystals was less sensitive to temperature change. Moreover, with the increase of angular frequency rate in both raw and mercerized CNCs, $E_G$ decreased. It indicates that the degree of intra or inter molecular association decreased with increased of angular frequency. Thus, CNC II could be used to produce more stable gels in response to the temperature.
3.3.2. Property of CNC-based Composite Films

3.3.2.1. Pure CNC Morphology

Figure 3.16 presents FSEM (a,b) and POM (c,d) micrographs of the surfaces of the films made of raw and mercerized CNCs. It was reported that cellulose concentration in the suspension determines film thickness and that the temperature of the suspension largely affects the surface roughness (Falt et al., 2004). In this study, all films were made of 1.56% w/w suspensions and these suspensions were placed in a refrigerator at 10°C for slow water evaporation. The average thickness of manufactured films was about 50µm. It can be seen that the raw CNCs (cellulose I) were randomly oriented, belonging to the dilute regime (isotropic phase) (Fig 3.16a and c). Stable colloidal suspensions of rod-shape cellulose II CNCs (Fig 3.16b and d) formed an ordered phase displaying chiral nematic orientation. It was thought that the liquid crystals showed a spiral packing along a vector director in each nematic plane and several nematic planes also packed in a helicoidal way (Lima and Borsali, 2004). At the same suspension concentration level, it was much easier for mercerized CNCs to form an ordered liquid crystal phase in the angle of the vector director. This could be related to the anti-parallel molecular structure of cellulose II crystals with a stronger hydrogen bonding.

It should be mentioned that the appearance of the raw CNC films differed depending on the suspension concentration. Dilute suspensions of raw CNCs at 1.56% w/w showed non-directional properties (Fig 3.16a and c). However, the suspension of rod-shape cellulose
crystallites can form an anisotropic phase and show the fingerprint texture when its concentration reaches a certain critical value (Dong and Gray, 1997; Dong et al., 1996; Lima and Borsali, 2004; Yi et al., 2008). This phase was characterized by a self-assembled liquid alignment along a vector director resulting in a chiral nematic ordered crystalline alignment. Lima reported that the chiral nematic orders can be preserved after evaporation of the aqueous solvent, leaving iridescent films of cellulose I (Lima and Borsali, 2004). Godinho reported that this film can be used as electro-optical devices (Godinho et al., 1998). The result of the work shows that aligned crystal films can be formed with much lower concentration for cellulose II crystals. Further work is needed to study the effect of concentration level on the formation of ordered liquid crystal phases to determine the critical concentration level.
3.3.2.2. Tensile Properties of CNC/PEO Composites

Typical stress-strain curves for PEO, cellulose I CNC/PEO, and cellulose II CNC/PEO composite films are shown in Figure 3.17. The tensile strength for mercerized crystal/PEO (N20/PEO) composites was as high as 19.96 GPa, whereas the tensile strength for raw crystal/PEO (N0/PEO) was 16.86 GPa. Also, it can be seen that both of the composites showed increased tensile strength and elongation at break compared to those of the pure PEO, indicating the strong enhancing efforts of CNCs (Figure 3.18). The elongation at break for pure PEO, N0/PEO and N20/PEO were 420%, 690%, and 930%, respectively.

Fig 3.17 Typical stress-strain curve for PEO, raw CNC/PEO, and mercerized CNC/PEO composite films.
Fig 3.18 Comparision of tensile properties of PEO, raw CNC/PEO, and mercerized CNC/PEO composites.

The tensile fractographs of the PEO/crystal composites containing 10 wt % of CNCs observed by FSEM are presented in Fig 3.19. It can be seen that mercerization led to major changes in fracture behavior of the composites. The raw CNC/PEO composites showed a high number of crystal bundle pullout during tensile testing (Fig 3.19a). The mercerized crystal/PEO composites showed a brittle fracture behavior, leading to a relatively smooth fracture surface (Fig 3.19b). The morphology of brittle fracture surface was a very important characteristic and it ultimately determined the tensile behavior of the composites.

The smaller number of crystal bundle pullout on the brittle fracture surface of mercerized crystal/PEO composites indicated a better interaction between the crystals and the matrix. It is well known that physical bonding in PEO/crystal composites was determined by the hydrogen bonds. Consequently, the dispersity for mercerized CNCs were better than raw CNCs. Thus, mercerized CNCs rendered better enhancement efforts in a PEO matrix.
Fig 3.19 Fracture surfaces of CNC/PEO composites for raw (a) and mercerized (b) CNCs

This conclusion can be also seen from the results shown in Fig 3.18. Mercerized CNCs are predominately synthesised in their crystal allomorph type II, which exhibits stronger mechanical performance than cellulose I crystals.

3.4. Conclusions

Transitional properties of cotton nanocrystals with the mercerization treatment were studied in this work. Stable aqueous CNC suspensions from both cellulose I and cellulose II were formed after combined acid-hydrolysis and high-pressure homogenization treatment. TEM measurement showed a similar size between the two types of crystals. Dry cellulose II crystals had a much larger bulk density than the dry cellulose I crystals. The re-dispersibility of cellulose II was largely reduced. FTIR and WXRD data showed a clear transition from cellulose I to II crystals manufactured. TGA curves showed that mercerized cotton crystals had better thermal stability properties. Rheological study indicated cotton nano cellulose suspension exhibited a shear thinning behavior. With increased angular frequency and temperature, the storage modulus of the suspension became larger due to hydrogen bonding interaction. At the same concentration level, cellulose II crystal suspension showed larger storage modulus and they were more stable in response to temperature change. FESEM
showed the cellulose II CNCs were easier to form chiral nematic orientation than cellulose I CNCs at the same concentration level. Both CNC I/PEO and CNC II/PEO composites showed increased tensile strength and elongation at break compared to the pure PEO. The enhancing efforts for cellulose II CNCs were better than cellulose I CNCs due to the enhanced hydrogen bonding and dispersibility.

3.5. References


Mansikkanaki P, Lahtinen M, Rissanen K. Structural changes of cellulose crystallites induced by mercerisation in different solvent systems; determined by powder X-ray


CHAPTER 4. OVERALL CONCLUSIONS

The transformation of crystalline cellulose structure in cotton fibers and nano-crystals from cellulose I to cellulose II through NaOH treatment was investigated using FESEM, WXRD, FTIR, TGA and rheology techniques. The results showed that the process of mercerization enhanced intermolecular hydrogen bonding, reduced crystallinity, and increased fiber and crystal strengths. FESEM morphological analysis showed that cotton fibers were converted into a swollen and roughened state by mercerization treatment. Mercerization treatment increased intra or inter hydrogen bonding. The crystallinity decreased sharply during the process of mercerization. The structure of cellulose II fibers was more stable than cellulose I fibers and thermal properties for cellulose fibers were highly affected by degree of crystallinity. Measured mechanical properties of cotton fiber-PEO composites demonstrated that both raw and mercerized cotton fibers enhanced the tensile strength of PEO matrix, but both made the composite more brittle.

Stable aqueous suspensions from both raw and mercerized CNCs were formed after combined acid-hydrolysis and high-pressure homogenization treatment. Acid treatment led to decreased crystallinity and reduced degradation temperature of the crystals due to the destruction of the amorphous region. TEM measurements showed a similar size and size distribution between the two types of crystals. Dry mercerized crystals had a much larger bulk density than the dry raw crystals. The re-dispersibility of dry mercerized crystals was largely reduced. FTIR and WXRD data showed a clear transition from cellulose I (raw) to cellulose II (mercerized) of the manufactured crystals. The mercerized cellulose II crystals had better thermal stability properties. Rheological study indicated that the storage modulus
of the crystal suspensions increased with the increasing angular frequency and temperature. At the same concentration levels, cellulose II crystal suspension showed much larger storage modulus and the suspensions were more stable in response to temperature change. Dilute cellulose II crystal suspensions formed an ordered liquid phase displaying chiral nematic orientation in the direction of the vector director at a much lower concentration level compared with cellulose I crystal suspension. Both cellulose I CNC/PEO and cellulose II CNC/PEO composites showed increased tensile strength and elongation at break compared with these of the pure PEO. However, composites with mercerized cellulose II crystals exhibited larger tensile strength, and elongation at break than raw crystals due to the enhanced hydrogen bonding. Thus, cellulose II crystals could be better reinforcement materials for advanced nano-composites.
VITA

Yiying Yue was born in Harbin, China, on May 12, 1985. She received a Bachelor of Science degree in environmental engineering from Heilongjiang Institute of Science and Technology, Harbin, China, in July 2007. She systematically studied many chemistry courses, which laid a solid foundation for her post-graduate study. Yiying Yue gained valuable work experience as a Research Assistant in the field of bio-based composites at the Key Laboratory of Bio-based Material Science and Technology, Northeast Forestry University, Harbin, China. She also completed main courses in wood science and technology with excellent grade standing at Northeast Forestry University.

She began her Master of Science degree study in the Fall of 2009 in the School of Renewable Natural Resources at Louisiana State University under the direction of Dr. Qinglin Wu. During this period, she studied properties of nano-cellulose crystals. The exploration in the direction of nano cellulose materials made her feel novel and excited. Yiying Yue will graduate with a Master of Science degree in forestry in May 2011 and will continue her graduate career at LSU.