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Parameters Affecting the Chiral Nematic Phase of Nanocrystalline Cellulose Films

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ABSTRACT: Nanocrystalline cellulose (NCC) is extracted from woody biomass using acid hydrolysis. It has unique strength and distinctive optical/conductive/magnetic properties. When a suspension of NCC is air-dried, it forms a film with unique characteristics (e.g., iridescence) linked to the formation of chiral nematic structure. In this contribution, the effects of ionic strength, temperature, suspension concentration, and exposure to magnetic field on the morphology of NCC are examined. The influence of these parameters on chiral nematic phase is investigated at a macroscopic level using circular dichroism and polarized microscopy. It is demonstrated that the addition of salt to NCC suspensions, NCC concentration, temperature, and the presence of a magnetic field all have an effect on the pitch of the chiral nematic structure. For example, drying of the NCC film in the presence of a 0.2 T external magnetic field increases the pitch, in a manner dependent on drying time. The implication of these results for the structure and properties of NCC is discussed.

Introduction

Nanocrystalline cellulose (NCC) is extracted as a colloidal suspension by acid hydrolysis of cellulosic materials, such as bacteria, cotton, and wood pulp. NCC has unique properties that make it an interesting starting point for the development of new materials. It is constituted of cellulose, a linear polymer of $\beta(1\rightarrow4)$-linked D-glucose units, the chains of which arrange themselves to form crystalline and amorphous domains. NCC suspensions can be used to form films that have chiral nematic structure and crystallinity, with possible applications as optically variable films and ink pigments for security papers, since the optical properties cannot by reproduced by printing or photocopying.[1]

Cholesteric structure consists of stacked planes of molecules aligned along a director (n), with the orientation of each director rotated about the perpendicular axis from one plane to the next.[2] This structure forms spontaneously in solutions of rigid-rod-like molecules, such as tobacco mosaic virus,[3] poly(tetrafluoroethylene),[4] boehmite,[5] and fd phage.[6] When the particles involved are optically active, chiral nematic structure may be formed. Colloidal suspensions of cellulose crystallites form chiral nematic structure upon reaching a critical concentration.[7] The chiral nematic pitch can be affected by adding electrolyte.[8] Chiral nematic structure whose pitch is of the order of the wavelength of visible light reflects circularly polarized light.[9] The wavelength of this selectively reflected light changes with the viewing angle, leading to an iridescent appearance. By simply casting films from suspensions of NCC, cellulose films with the optical properties of chiral nematic structures can also be prepared.[1]

Crystallinity, defined as the crystalline fraction of the sample, is another important structural characteristic of cellulose. Hydrogen bonding between cellulose chains can stabilize the local structure in cellulose and play a role in the formation of crystalline domains.[10] The physical and chemical behavior of cellulose is strongly influenced by its degree of crystallinity. For example, the crystallinity of cellulose directly influences the accessibility for chemical derivatization, swelling, and water-binding properties.[11]

In this contribution, we investigate how parameters such as ionic strength, temperature, suspension concentration, and exposure to magnetic field affect the morphology of NCC. It has been previously shown that the manner in which NCC suspensions are used to form films has an impact on the properties of the film. Specifically, the influence of these parameters on the chiral nematic phase is investigated at a macroscopic level using circular dichroism and polarized microscopy. The effect of these parameters on the crystallinity of NCC is also investigated at a microscopic level using ^{13}C CPMAS solid-state NMR and X-ray powder diffraction methods.

Materials and Methods

Materials. A fully bleached, commercial softwood was milled to pass through a 0.5 mm screen in a Wiley mill to ensure particle size uniformity and increase surface area. Aliquots of concentrated sulfuric acid (95−98%) (Aldrich) were diluted to 64 wt % solution by adding the concentrated acid under magnetic stirring to various amounts of deionized (DI) water cooled in an ice bath so that the specific gravity of the diluted solution measured by a hydrometer gave the correct values, for example, a value of 1.5421 for 64 wt % solution at 20 °C. The milled pulp (40.0 g o.d.) was hydrolyzed in sulfuric acid (8.75 mL of a sulfuric acid solution/g pulp) at a concentration of 64 wt % and a temperature of 45 °C. The sulfuric acid solution was heated to the desired temperature, added to the pulp in an Erlenmeyer flask in a hot water bath heated to the same temperature, and allowed to hydrolyze the pulp under stirring with an impeller at high speed for 25 min. The cellulose suspension was then diluted with cold, DI H_2O ($\sim$10 times the volume of the acid solution used) to stop the hydrolysis and allowed to settle overnight. The clear top

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layer ($\sim$2.0 L out of the total volume of 3.5 L) was decanted, and the remaining white cloudy layer was centrifuged. The clear, top layer ($\sim$4/5 of the total volume) after centrifugation was decanted off, and DI H_2O (same volume as that which had been decanted off) was added and mixed with the remaining thick white suspension and then centrifuged again. Such a procedure was repeated three times. The initial decanting ($\sim$2.0 L solution) and the subsequent centrifugation/decanting/DI H_2O dilution/washing procedure removed practically all soluble cellulose materials. The thick white suspension after the last centrifugation and decanting of the clear, top layer was placed inside dialysis membrane tubes (12 000−14 000 molecular weight cutoff) and dialyzed against slow running DI water, for 1−4 days, unless otherwise specified. The procedure was continued until, when the membrane tubes containing the extracted cellulose materials were placed periodically in DI H_2O, the pH of the water became constant over a period of 1 h. The suspension from the membrane tubes was dispersed by subjecting it to ultrasound treatment in a Fisher Sonic Dismembrator (Fisher Scientific) for 10 min at 60% power.

Film Preparation. Solid NCC films were made by slow evaporation of the colloidal suspension under ambient conditions on 1.0 cm ×3.5 cm glass slides. Magnetically aligned films were prepared by drying the NCC suspension in a 0.2 T magnetic field. The glass slides were placed adjacent to a 11.7 T magnet, so that the surface of the slide was perpendicular to the direction of the magnetic field. This was confirmed using a Bell 620 Gmeter (model HTB4-0608). Because of the negative diamagnetic susceptibility of cellulose, this alignment should promote the formation of a planar texture, as the NCC crystallites tend to orient with their long axes perpendicular to the magnetic field.[12,13]

CD Spectroscopy. CD spectra were measured using a Jasco J810 Spectropolarimer. Samples were set perpendicular to the incident cross-polarized light and scanned at 100 nm/min with a step resolution of 0.2 and 1 nm bandwidth.

Polarized Microscopy. Photomicrographs were taken by using a Nikon Microphot-FXA optical microscope equipped with a camera and crossed-polarizers. The magnification of the micrographs was 40×.

^{13}C CP/MAS Solid-State NMR Spectroscopy. ^{13}C CP/MAS NMR measurements were carried out with a 4 mm triple-resonance MAS probe on a Bruker 500 MHz spectrometer operating at a ^{13}C frequency of 125.768 MHz. The samples were ground using a mortar and pestle prior to being packed into 4 mm ZrO_2 rotors. 2048 scans were accumulated. The spinning speed was set to 6.5 kHz and a contact time of 1 ms[14−16] for the ramped cross-polarization step.[16] Decoupling was achieved using the SPINAL-64 sequence[17] and a field strength of 90.9 kHz. The spectra were referenced to external adamantane, δ_{CH} = 29.50 ppm and δ_{CH_2} = 38.56 ppm relative to TMS.[18]

X-ray Diffraction. Diffraction data were collected on the films dried in the presence of a 0.2 T magnetic field for 0.5, 2.5, 4.5, 6.5, and 8.0 h (i.e., evaporation rate = 200, 40.0, 22.2, 15.4, and 12.5 μL/h, respectively), using a previously described method.[19] Briefly, a Bruker D8 Advance powder X-ray diffractometer equipped with a Cu Xα X-ray tube, a diffracted beam graphite monochromator, and NaI scintillation detector was used with the generator set to 40 kV and 40 mA. Data were collected from 2θ = 5°−90° using a step size of 0.02° and a counting time of 1 s/step. 1.00 mm divergence and antiscatter slits were used with a 0.2 mm receiving slit, and the sample was rotated during data collection. The films were mounted on zero-background Si plates. The peaks were assigned according to the monoclinic unit cell for cellulose I.[20] The crystallinity was obtained from the X-ray intensity, as described by Hamad and Hu.[19]

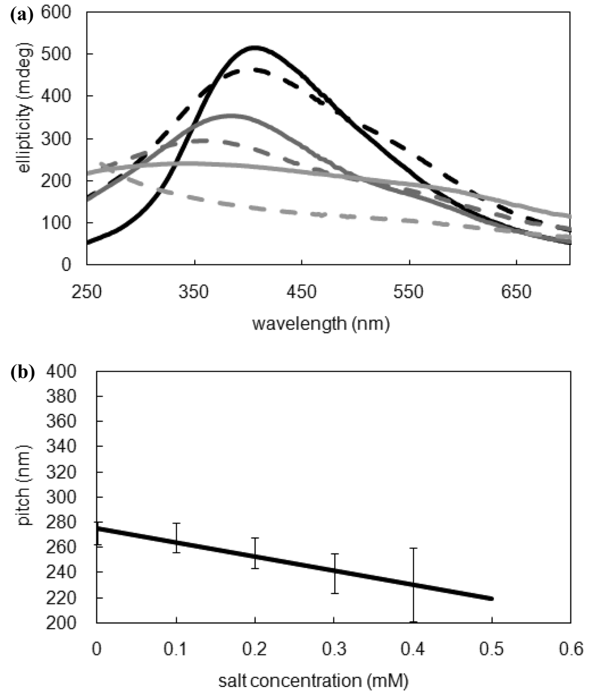

Figure 1. (a) CD spectra of cellulose films produced from 1% w/w NCC suspensions with 0 (black), 0.1 (black dashed), 0.2 (dark gray), 0.3 (dark gray dashed), 0.4 (gray), and 0.5 mM (gray dashed) NaCl at room temperature. (b) Plot of the calculated chiral nematic pitch as a function of the concentration of added NaCl. The error bars represent the error associated with determining the maximum reflection wavelength in the CD spectra. A value of 1.5 was used for the refractive index *n*. The fit yielded the following parameters: $y = (-112 \pm 12)x + (275 \pm 3)$, $R^2 = 0.9672$.

Results

Effect of Ionic Strength. The formation of the chiral nematic structure in NCC films was studied as a function of added NaCl concentrations. The NCC suspension (1% w/w) and an appropriate amount of a 10 mM NaCl stock solution were mixed to achieve the desired electrolyte concentration before evaporation. The mixture was then allowed to evaporate to produce clear films which displayed colors on the surface ranging from red to violet when light was reflected on the sample, as previously reported.[1] CD spectra of the cellulose films were recorded in the wavelength range of 250−675 nm and are shown in Figure 1a. Since the CD signal arises from the difference in the absorption of left-handed and right-handed circularly polarized light,[21] a positive signal indicates that the samples possess left-handed chiral nematic structure,[22] regardless of salt concentration. In other words, the orientations of the pseudolayers (as defined by the director) in the samples are arranged in an anticlockwise fashion along the chiral nematic axis. The CD signal can also be used to extract information on the chiral nematic pitch, *P*, which is the distance required for the pseudolayers to complete one full rotation, since *P* is related to the wavelength of maximum reflection, λ, by

$$\lambda = nP \qquad (1)$$

where *n* is the average refractive index.[9] This relationship is valid when the incident light is normal to the surface of the crystallite, as was the case in the experiments performed here. A plot of pitch as a function of salt concentration (Figure 1b) shows that the chiral nematic pitch of the resulting film decreased as a linear function of increased salt concentration (n = 1.5). Note that a pitch could not be determined for the concentration of 0.5 mM NaCl because there was no longer a peak observed in the CD spectrum (Figure 1a). Indeed, at this and higher salt concentrations, the chiral nematic phase is fully perturbed, in agreement with previous reports.[8] To verify that the pitch does decrease with increasing NaCl concentration, an optical micrograph of a film of NCC in the presence of 0.1 mM NaCl and 0.4 mM NaCl was taken. As can be seen by the characteristic fingerprint and the spacing between the periodic extinction contours (Supporting Information Figure S1), which corresponds to half of the cholesteric pitch (P), salt does indeed have the effect of reducing P.

In order to determine whether a parameter that affects chiral nematic phase will also affect crystallinity, the crystallinity of the samples described above was assessed using ^{13}C CPMAS solid-state NMR. As reported in a number of studies,[18,23−27] the ^{13}C spectrum of cellulose I consists of the peak arising from the C1 carbon in the cellulose backbone in the 100−110 ppm range, the C4 peak in the 80−93 ppm range, the C2/C3/C5 peaks in the 70−80 ppm range, and finally the C6 peak in the 60−68 ppm range (Figure S2 in Supporting Information). The C4 and C6 regions each have a separate peak which corresponds to the C4 and C6 carbons in the amorphous region of the sample. To determine crystallinity, therefore, the fraction of the amorphous component, $X_{\mathrm{amorphous}}$, of the C4 atoms in the sample is calculated as the ratio of the peak area of the C4 atoms located in amorphous domains and the overall area of all the C4 atoms. The peak area was determined by deconvolution of the spectra using the DMFIT program.[28] The crystallinity is then given as

$$X_{\mathrm{c}} = 100\% - X_{\mathrm{amorphous}} \qquad (2)$$

For consistency, a similar ratio was calculated using the peaks corresponding to C6 atoms. It is important to note that the crystallinity measurement by solid-state NMR is hampered by the fact that the crystalline and amorphous regions have different relaxation times and that the peak intensities of the C4 and C6 amorphous resonances are sensitive to any residual water which may be present. In order to address this, X-ray powder diffraction measurements on the set of films dried in a magnetic field for different times were also performed (vida infra). X-ray powder diffraction is insensitive to relaxation effects and residual waters.

It was found that, within the experimental errors associated with determining crystallinity by solid-state NMR and X-ray powder diffraction, crystallinity is not affected by the ionic strength (data not shown).

Effect of Temperature. Previous studies have shown that temperature can influence the chiral nematic structure in suspensions of cellulose derivatives.[29−31] Depending on the different substitutions and the degree of substitution of the cellulose, the effect is varied. A statistical theory for the chiral nematic ordering of polypeptide solutions has been used to predict the temperature dependent pitch (P) of the chiral nematic structure in cellulose derivative solutions:[32,33]

$$\frac{1}{P} = C\left(\frac{T_N}{T} - 1\right) \qquad (3)$$

where T is temperature, C is a constant which is a function of the solution concentration and the molecular weight of the solute polymer, and T_N is the compensation temperature, defined as the temperature at which the pitch is infinite.

To our knowledge, the effect of temperature on the chiral nematic structure in pure NCC samples has not been determined to date. In order to investigate the effect of temperature on the formation of chiral nematic structure in NCC films, a suspension at the concentration of 2.0% w/w was dried at various temperatures. The evaporation temperature of 4 °C was achieved by drying the sample in the fridge (evaporation rate = 2.5 μL/h). One sample was dried at room temperature (evaporation rate = 5.0 μL/h), while the other samples were dried in an incubator with the temperature set at 40 °C (evaporation rate = 25.0 μL/h), 50 °C (evaporation rate = 50.0 μL/h), 60 °C (evaporation rate = 100 μL/h), or 70 °C (evaporation rate = 133.3 μL/h). The CD spectra, shown in Figure 2a, show positive peaks, indicating that the handedness of these films was left-handed and independent of temperature. However, the wavelength of maximum reflection light changed as a function of the drying temperature. A plot of the inverse pitch as a function of reciprocal temperature (Figure 2b) yielded a straight line, as predicted by the equation above.[32] T_N, as evaluated from the extrapolation of the plot to infinite pitch, was −67 °C. The change in pitch was also confirmed using polarized microscopy on the film generated at 4 and 70 °C (Supporting Information Figure S3). The crystallinity of these same samples was determined as outlined in the previous section (data not shown) and found to be independent of temperature, within experimental error.

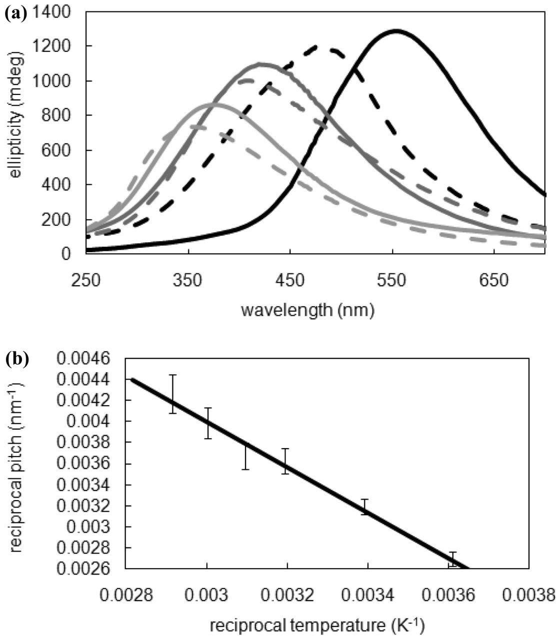

Figure 2. (a) CD spectra of cellulose films produced from 2.0% w/w NCC suspensions at 4 (black), 22 (black dashed), 40 (dark gray), 50 (dark gray dashed), 60 (gray), and 70 °C (gray dashed). (b) Plot of reciprocal pitch of the NCC films as a function of reciprocal drying temperature. The error bars represent the error associated with determining the maximum reflection wavelength in the CD spectra. The fit yielded the following parameters: $y = (-2.2 \pm 0.1)x + (0.0105 \pm 0.0001)$, $R^2 = 0.9884$. The equivalent plot of pitch of the NCC films as a function of drying temperature can be found in the Supporting Information (Figure S6).

Effect of Suspension Concentration. Studies on the chiral nematic structure of solutions of poly(γ-benzyl-L-glutamate, poly(γ-benzyl-D-glutamate), and poly(γ-alkyl-L-glutamate) have shown that the chiral nematic pitch (P) depends on the concentration (c) of the polymer, according to[33]

$$\ln(1/P) = k\ln(c) + A \qquad (4)$$

where A is a constant dependent on the solvent, temperature, and the molecular weight of the solute polymer and k is typically below 2 and is solvent-dependent. This relationship has not been applied to cellulose yet, but the effect of

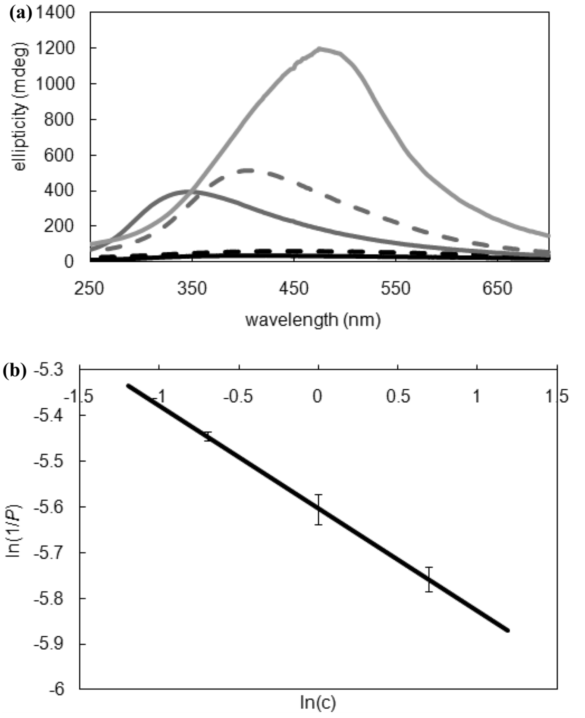

Figure 3. (a) CD spectra of cellulose films produced from NCC suspensions with the concentrations of 0.1% (black), 0.2% (black dashed), 0.5% (dark gray), 1.0% (dark gray dashed), and 2.0% w/w (gray) at room temperature. (b) Plot of ln(1/*P*) of the NCC cellulose films against ln(*c*) of cellulose crystallites. The error bars represent the error associated with determining the maximum reflection wavelength in the CD spectra. The fit yielded the following parameters: $y = (-0.225 \pm 0.002)x - (5.602 \pm 0.001)$, $R^2 = 0.9999$. The equivalent plot of pitch of the NCC films as a function of concentration can be found in the Supporting Information (Figure S7).

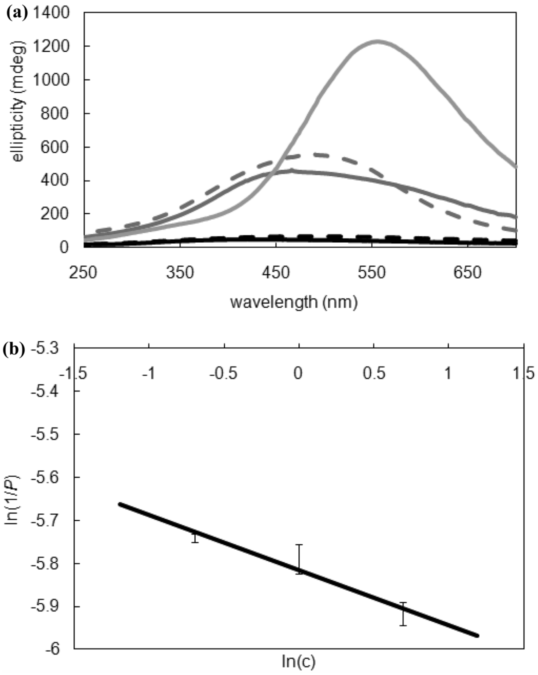

Figure 4. (a) CD spectra of cellulose films produced from NCC suspensions with the concentration of 0.1% (black), 0.2% (black dashed), 0.5% (dark gray), 1.0% (dark gray dashed), and 2.0% w/w (gray) in the 0.2 T magnetic field at room temperature. (b) Plot of ln(1/*P*) of the NCC cellulose films made in the magnetic field against ln(*c*) concentration of cellulose crystallites. The error bars represent the error associated with determining the maximum reflection wavelength in the CD spectra. The fit yielded the following parameters: $y = (-0.13 \pm 0.03)x - (5.82 \pm 0.02)$, $R^2 = 0.9404$. The equivalent plot of pitch of the NCC films as a function of concentration can be found in the Supporting Information (Figure S8).

suspension concentration on chiral nematic order has been observed for cellulose derivatives.[34,35] We have therefore investigated the effect of suspension concentration on the chiral nematic phase using the NCC cellulose sample described throughout. The original 2.0% w/w cellulose suspension was diluted to the following series of concentrations: 0.1, 0.2, 0.5, and 1.0% w/w. The suspensions were dried at room temperature. To ensure that the films consisted of the same amount of material per slide, 400 μL of the 0.5% w/w suspension, 200 μL of the 1.0% w/w suspension, and 100 μL of the 2.0% w/w suspension were used. Deionized water at pH 6.3 was used to dilute the sample, minizing any potential contribution arising from the presence of electrolytes (as outlined above).

The CD spectra (Figure 3a) of the resulting films showed a positive peak for the films produced from 0.5, 1.0, and 2.0% w/w suspensions, but no obvious peak was observed for the films produced starting from 0.1% and 0.2% w/w suspensions. These observations indicated that the chiral nematic structure of the films produced from 0.5%, 1.0%, and 2.0% w/w suspensions was left-handed. In other words, dilution did not change the handedness of the NCC films. The pitch, on the other hand, increased as a function of increasing concentration. Figure 3b shows that eq 4 can be fit to the experimental data very well ($k = -0.225 \pm 0.002$; $A = 5.602 \pm 0.001$). In summary, this suggests that the initial suspension concentration has an effect on the chiral nematic structure formed in the NCC films. Again, polarized microscopy images obtained for films produced from 0.5% and 2% w/w suspensions support the CD findings (Supporting Information Figure S4). The crystallinity of the NCC films was again found to be independent of initial suspension concentration (data not shown).

Effect of Magnetic Field. Previous studies have shown that when a suspension of cellulose crystallites is allowed to dry in a homogeneous magnetic field, the crystallites exhibit an alignment with their long axes perpendicular to the direction of the field, indicating a negative diamagnetic susceptibility anisotropy.[12] In other words, the chiral nematic axis is parallel to the external magnetic field applied.[8,13] This section will focus on the studies of the effect of magnetic field on the chiral nematic structure and crystallinity of the NCC films.

In a first instance, the chiral nematic structure of the NCC films produced in a magnetic field was studied by drying the NCC suspensions using the same range of concentrations as in the previous section, but in an external magnetic field. Since the glass slides were kept perpendicular to the direction of the external magnetic field, the chiral nematic axis is perpendicular to the surface of the glass slides. As shown in Figure 4a, the CD spectra of the NCC films produced from 0.5%, 1.0%, and 2.0% w/w suspensions exposed to a magnetic field consisted of a strong positive peak, indicating that the chiral nematic phase was left-handed, while the CD spectra of the films produced from 0.1% and 0.2% w/w suspension did not yield any apparent peaks in this wavelength range. For the films with chiral nematic structure, the wavelength of the maximum reflection increased as the original suspension concentration increased. These data was fit to eq 4 (Figure 4b). As mentioned above, for the films dried outside the magnetic field, the value of A was 5.602 ± 0.001 and the value of k was -0.225 ± 0.002. For the

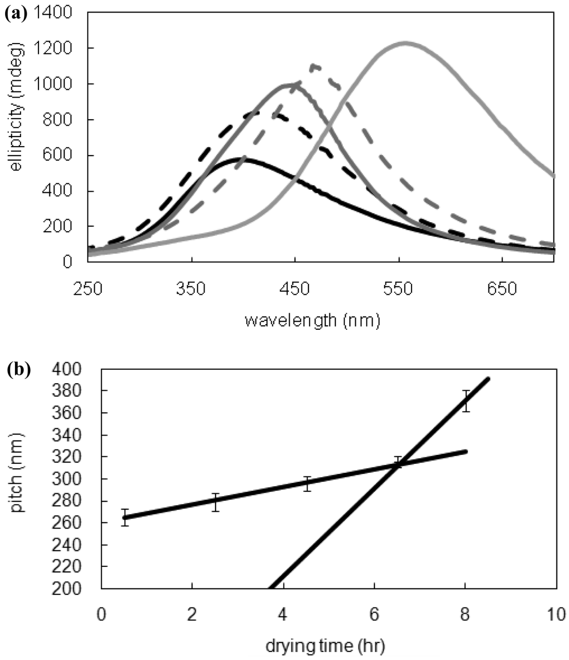

Figure 5. (a) CD spectra of cellulose films produced from 2.0% w/w NCC suspensions exposed to a 0.2 T magnetic field for 0.5 (black), 2.5 (black dashed), 4.5 (dark gray), 6.5 (dark gray dashed), and 8.0 h (gray) at room temperature. Note that all the samples are equally dry (as visible by eye) prior to the spectroscopic measurements. (b) Plot of the calculated chiral nematic pitches of the NCC cellulose films as a function of the drying time in a 0.2 T magnetic field. The fit yielded the following parameters: $y = (8.1 \pm 0.6)x + (260 \pm 3)$, $R^2 = 0.9865$ (first 4 data points).

films dried in the magnetic field, however, the values were 5.82 ± 0.02 and −0.13 ± 0.03 for A and k, respectively. In both cases, the values of A were similar. Because A is a constant dependent on the solvent, temperature, and the molecular weight of the solute polymer, the applied magnetic field did not affect this constant significantly. However, the magnetic alignment significantly changed the k value. A comparison of Figures 4 and 5 indicates that the calculated chiral nematic pitch increased when the samples were dried in the presence of a magnetic field. The magnetic field did not help to reintroduce the chiral nematic phase in suspensions of low concentrations (0.1%−0.2% w/w), as there was still no detectible iridescence in the visible range. Polarized microscopy images obtained for films produced from 0.5% and 2% w/w suspensions in the presence of a magnetic field support the CD findings (Supporting Information Figure S4). Finally, the crystallinity of the NCC films is independent of concentration (data not shown).

In a second instance, the chiral nematic structure of NCC films was also studied as a function of exposure time to the magnetic field. The films were prepared from a 2.0% w/w NCC suspension air-dried in the presence of a 0.2 T magnetic field for 0.5, 2.5, 4.5, 6.5, and 8.0 h (i.e., evaporation rate = 200, 40.0, 22.2, 15.4, and 12.5 μL/h, respectively). The evaporation rate of the samples was controlled. For example, for the sample dried for 8 h, the evaporation process was slowed down by covering the sample with a Petri dish. The CD spectra of the resulting films are shown in Figure 5a. There was an apparent positive peak in all the CD spectra, indicating the handedness of the films remained left-handed as the exposure time in the magnetic field increased. Moreover, the maximum reflection shifted to longer wavelengths as the drying time increased (Figure 5b). Polarized microscopy images obtained for films dried for 0.5 and 8 h in the presence of a magnetic field support the CD findings (Supporting Information Figure S5). We chose to fit the data in Figure 5b using two linear functions, yielding the relation between the chiral nematic pitch and drying temperature in the magnetic field indicated the figure. The fits suggest that there is a change in the slope after around 6.5 h of drying time. Finally, the crystallinity of the NCC films is independent of magnetic field exposure time.

Discussion

When nanocrystalline cellulose is extracted from wood using sulfuric acid hydrolysis, the result is a suspension consisting of rods (also known as whiskers) that are ∼5 nm in width and ∼150 nm long that neither precipitate nor flocculate. The rods have an overall negative charge density, so that if they are present in dilute aqueous solution, they will form a single isotropic phase where the particles experience electrostatic repulsion. If the concentration of the suspension is increased (e.g., by removal of water), however, then phase separation occurs: the sample is divided into an isotropic phase on top and an anisotropic phase at the bottom of the tube.[7,8,13,36,37] In the latter phase, the proximity of the rods causes them to self-orient along a vector director, thereby resulting in the formation of a nematic liquid crystal. When the suspension reaches a critical concentration, the rods form a chiral nematic ordered phase, which displays characteristics typical of a cholesteric liquid crystal (i.e., rods organized in layers, with a director axis which varies from layer to layer in a periodic fashion). Upon full drying of the suspension, the rods remain in this arrangement. As a result of the chiral nature of the material, NCC films display interesting optical properties such as iridescence. It is important to note that the phase-forming ability of cellulose depends on the acid chosen for hydrolysis.[2]

Over the years, a number of studies have demonstrated how it is possible to perturb the chiral nematic phase in pure NCC, using salt,[8] magnetic fields, and shear alignment.[38] The disruption of the cholesteric phase in NCC is believed to occur via the perturbation of the interactions between the rods, resulting in the formation of helically twisted rods.[38,39] In addition to this work, recent studies have proposed refined structures of cellulose I.[40] Putting these findings together, a structural model of NCC can be build at the molecular, rod, and liquid crystal level (Figure 6). The data reported in this work allow us to examine, on the one hand, what happens to NCC at a molecular level (Figure 6a) as a function of ionic strength, temperature, suspension concentration, and exposure to magnetic field and, on the other, what happens to NCC at the chiral nematic phase level (Figure 6c) as a function of these same parameters.

Effect of Ionic Strength. The ionic strength in a cellulose suspension can affect the formation of the anisotropic phase.[8] Since the cellulose rods have an overall negative charge density, the sodium ion in NaCl interacts strongly with the surface of the NCC rods, thereby shielding the surface charges and reducing the effect of Coulombic repulsion.[38] As described by Stroobants et al.,[41] in this case, twisting forces between polyelectrolytes will impede the ordering of the charged NCC rods. This will prevent the parallel alignment of the charged NCC rods, shifting the Onsager isotropic−anisotropic phase transition to higher concentrations. In other words, with increasing electrolyte concentration, the critical concentration required to spontaneously form the anisotropic phase increases, and consequently the pitch and the volume fraction of the anisotropic phase in the biphasic cellulose suspension decrease. The data here indicate that when the suspension is dried to form a film, this lower pitch is preserved (Figure 1a,b); i.e., the drying process does not interfere with the interaction of the rods.

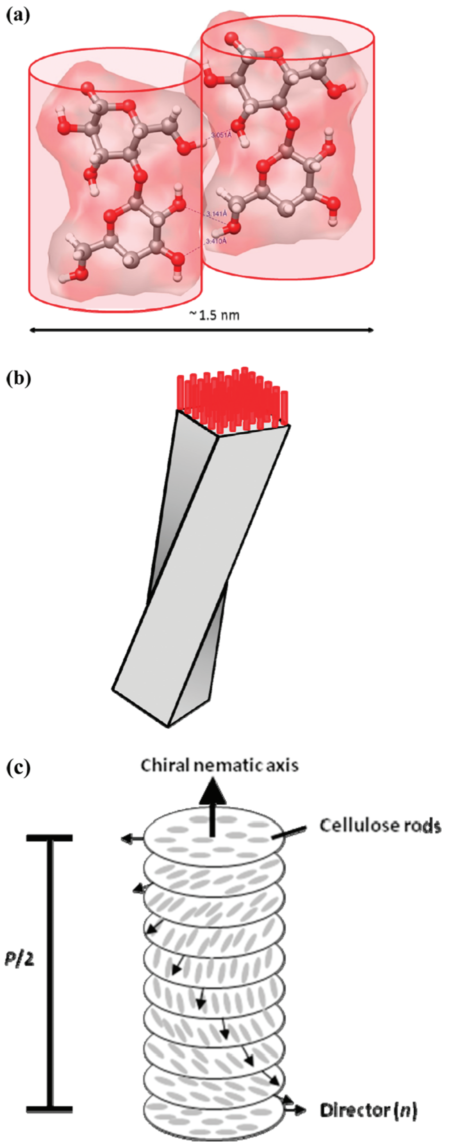

Figure 6. The three levels of structure in NCC films: (a) Model of two cellulose I chains in crystalline domains, based on the findings of Witter et al.[40] The red cylinders represent the cellulose chains. (b) Assuming that the rods which come together to form the chiral nematic phase are 3 × 3 nm, then roughly nine of the cellulose I chains, shown in red, would form a rod (gray). As reported by Orts et al.[38] and by Lima and Borsali,[39] these rods are helically twisted along their length of 20−200 nm, in the presence of high salt, for example. (c) The (straight or helically twisted) rods come together in layers to form the chiral nematic phase of NCC.

The effect of NaCl on the molecular structure in NCC films has never, to our knowledge, been directly investigated. The crystallinity data obtained suggest that the presence of sodium does not significantly impact the propensity of the cellulose chains to become amorphous. Although a very slight trend of decreased crystallinity with increased salt concentration could be gleaned from the data, the errors associated with the methods used here, namely ^{13}C solid-state NMR (estimated error in crystallinity = ±5−10%) and X-ray powder diffraction (estimated error in crystallinity = ±1−10%), preclude any definitive conclusions. In other words, to gain insight into the effect ionic strength (and all other parameters studied here) on the molecular structure of the cellulose chains in NCC films (Figure 6a), other approaches need to be developed.

Effect of Temperature. A number of studies on derivatives of cellulose (e.g., (hydroxypropyl)cellulose,[42] (2-ethoxypropyl)-cellulose,[29] and (acetyl)(ethyl)cellulose[30,43]) have shown that the pitch of the chiral nematic phase is highly dependent on temperature. For (hydroxypropyl)cellulose and (2-ethoxypropyl)cellulose, it was found that P increases with increased temperature, whereas for (acetyl)(ethyl)cellulose samples with low degrees of acetyl substitution, P decreases with increased temperature, as observed here for our NCC samples. It has been shown that the type and degree of substitution on the cellulose chains affect the critical concentration required for the formation of the chiral nematic ordered phase and the temperature at which thermotropic phases exist.[29] So presumably, in the case of (acetyl)(ethyl)cellulose samples with low degrees of acetyl substitution and the NCC samples studied here, the interaction between the rods is weaker, thereby requiring a higher critical concentration to spontaneously form the anisotropic phase. As mentioned above, an increased critical concentration signifies a decrease in the pitch and the volume fraction of the anisotropic phase in the biphasic cellulose suspension. The interaction between the rods could be weakened by either unfavorable interactions between the substituents on the cellulose or the flexibility of the rods. If the former were true, then one would expect rods made from cellulose with the less bulky acetyl and ethyl groups (or in the case of NCC, no substituents) to favor rod−rod interactions and packing. Since this is not the case, then flexibility must play a role and the observation that higher temperatures (i.e., more flexibility) result in lower pitch is validated.

Effect of Suspension Concentration. The phenomenological observations of Uematsu and Uematsu[33] have led to a relationship of pitch in the cholesteric phase as a function of temperature (eq 3) and concentration (eq 4). The data obtained here agree with both equations, as discussed above and shown in Figure 3. It was found that as the suspension concentration increases, so does the pitch. This agrees with other findings[8] which suggest that an increased suspension concentration promotes the formation of proportionately more anisotropic phase. As the volume fraction of the anisotropic phase increases, then so does the pitch of the chiral nematic phase.

Effect of Magnetic Field. A number of studies have shown that drying suspensions of nanocrystalline cellulose in a magnetic field results in a marked alignment with their long axis perpendicular to the direction of the field.[12,13] Here, we have demonstrated that the presence of a magnetic field also has the effect of increasing the pitch of the chiral nematic phase (Figure 4) and that the pitch increases with increasing exposure time (Figure 5). Indeed, for a 0.5% w/w NCC suspension, the pitch goes from 232 nm outside the magnetic field to 311 nm for suspensions exposed to the magnetic field. Likewise, the pitch in a 2.0% w/w NCC suspension varies from 317 nm outside the magnetic to 371 nm for suspension exposed to a magnetic field. The magnetic field, however, did not help to promote chiral nematic phase formation in suspensions of low concentrations (0.1−0.2% w/w), as there was no detectible CD signal for these samples. These observations suggest that the magnetic field does not influence the formation of chiral nematic structure but only has an effect on the pitch of the resulting films. The increase in chiral nematic pitch may be due to the magnetic alignment of cellulose crystallites, given their anisotropic shapes and nonzero magnetic susceptibilities. This might cause the tilt angle between the directions of directors in adjacent pseudolayers to decrease.[45,46] Similar effects have been observed for DNA[47,48] and other liquid crystals.[49]

Conclusions

In this contribution, we have investigated the effects of ionic strength, drying temperature, suspension concentration, and exposure to magnetic field on both the chiral nematic pitch and the crystallinity of NCC films. We have confirmed previous studies that showed that pitch decreases with increasing NaCl concentration. We have shown that the relationships put forth by Uematsu and Uematsu[33] relating the pitch in the chiral nematic phase to temperature and suspension concentration also apply to the NCC films studied here. Finally, we have demonstrated that NCC films dried in a magnetic field have increased pitch. We have examined how each of these parameters affects the crystallinity, as determined primarily by ^{13}C solid-state NMR, but also in some instances by X-ray powder diffraction. We have observed no significant changes in crystallinity as a function of these parameters, within the experimental errors associated with these methods. Finally, we have attempted to explain our findings in terms of a model where the cellulose chains pack together to form rods or whiskers. According to this model, when the whiskers are perturbed, there is a discernible effect on pitch but not on the crystallinity of NCC in the films.

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Supporting Information Available: Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) Note: for cases where the evaporation rate is not explicitly given, it can be assumed to be ca. 5.0 μL/h as well, as the samples were dried at room temperature.