

# Controlling Alignment in Cellulose Nanocrystal Coatings

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## ABSTRACT

We report how the interplay between dispersion microstructure and shear affect the morphology and optical properties of cellulose nanocrystals (CNC) coatings. CNC produced by the sulfuric acid hydrolysis of natural cellulosic materials are increasingly being recognized for their potential in advanced materials applications. CNC are known to follow lyotropic liquid crystalline phase behavior; they self-assemble into a cholesteric phase when dispersed in water above the critical concentration. The cholesteric polydomain structure of the CNC dispersion can be preserved during drying. When shear forces are imposed, coatings can be prepared with different alignment allowing for control over birefringence and optical interference. Investigations on the phase behavior and shear response of aqueous CNC dispersions have been used to develop a process for making CNC coatings with controlled properties. These results provide a foundation for functional coatings for a range of optical and sensing applications.

**Keywords:** cellulose nanocrystal, liquid crystal, coatings

## 1 INTRODUCTION

Cellulose, the world's most abundant macromolecule,<sup>1</sup> has long been an important material for a variety of industries, most notably, the pulp and paper industry and the textiles industry. The recent interest in renewable raw materials and environmentally sustainable products has sparked a renewed interest in cellulose research. Due to their excellent strength and stiffness, cellulose nanocrystals (CNC) have been widely studied as a reinforcing agent in polymer nanocomposites. However, recently CNC have been considered as renewable building blocks for advanced materials.<sup>2</sup> Some potential applications include iridescent films for security papers, polarizing rotators for lasers, optical storage devices, stimuli-responsive fluids, optical filters, and applications in nanomedicine and nanosensing.<sup>3</sup>

Cellulose nanocrystals are predominantly isolated through acid hydrolysis of native cellulose fibers, where the

amorphous regions of the fiber are preferentially hydrolyzed.<sup>4</sup> If sulfuric acid is used, negatively charged sulfate groups are introduced onto the surface of the CNC. These CNC are easily dispersible in water due to ionic stabilization from the sulfate groups.<sup>5</sup> When dispersed in water CNC are known to follow lyotropic liquid crystalline phase behavior, and assemble into a cholesteric phase at high enough concentration.<sup>6</sup> Cholesteric liquid crystals possess local nematic order, where all the rods are aligned parallel to a director, however, the layers are rotated periodically around a helical axis perpendicular to the director.<sup>7</sup> In this structure, the distance for a full rotation around the helical axis is known as the pitch.

It has been shown that upon drying a CNC dispersion, the cholesteric structure can be preserved in a dried film.<sup>7</sup> Pan et. al. discovered that pitch in these films can be tuned by controlling the properties of the initial dispersion, such as concentration, temperature and ionic strength, as well as by drying the film in the presence of a magnetic field.<sup>8</sup> Using small angle light scattering, Orts et. al. confirmed that at high enough shear rate the alignment of the CNC changes from cholesteric to nematic, with the order further increasing with shear rate.<sup>9</sup>

In this study, we investigated preserving dispersions' liquid crystalline and shear alignment in dried films. By changing the order of the nanocrystals with shear, the birefringence of the material can be tuned, resulting in tunable optical interference when placed between crossed polarizers. However, this behavior is highly dependent on the initial state of the dispersion and on the rotational relaxation of the rods during drying. The results of this research could lead to inexpensive and easy to fabricate bandpass filters and reflective polarizers for a variety of optical application.<sup>10</sup>

## 2 EXPERIMENTAL

**Isolation of Cellulose Nanocrystals.** Whatman ashless filter aid (cotton cellulose) was used as the raw material for CNC isolation. The CNC were isolated through acid hydrolysis using 64 wt % sulfuric acid at 45°C for 50

minutes, after which the reaction mixture was quenched with cold deionized water (DIW). The reaction mixture was then centrifuged and washed with DIW three times. The resultant CNC slurry was dialyzed against DIW until the pH remained constant. Ultrasonication was then used to disperse the CNC. The dispersion was then allowed to evaporate at ambient conditions, with samples taken over a range of concentration. The concentrations were measured by thermogravimetric analysis (TGA) and converted to volume percent using the densities of crystalline cellulose and water.

**Polarized Optical Microscopy.** Pictures were taken using a Nikon Eclipse 80i optical microscope with a LU Plan Fluor 20x/0.45NA Nikon objective lens. For sheared CNC dispersions the microscope was equipped with a Linkam CSS450 Optical Rheology Stage. These images were taken at room temperature with an L Plan SLWD 20x/0.35NA Nikon objective lens. Crossed polarizers were used for all images with the shearing direction oriented at 45° with respect to the polarization axis.

### 3 RESULTS

Previous work has shown that for our CNC the isotropic to biphasic, biphasic to liquid crystalline, and liquid crystalline to gel transitions occur at approximately 3.0, 10.4, and 13.5 vol % respectively.<sup>11</sup> Each of these regions has a significantly different microstructure which was shown to effect the shear response of the dispersion. Therefore, in this study we investigated one concentration from each of the phase regions, namely 3.0, 7.0, and 12 vol % for the isotropic, biphasic, and liquid crystalline regimes, respectively.

First, the dispersion properties were investigated at shear rates from 0.1 to 100 s<sup>-1</sup> using polarized optical microscopy equipped with a shear stage. When an isotropic sample is viewed between crossed polarizers no light can pass through the analyzer and the image appears completely dark. However, anisotropic samples are birefringent, meaning that they have two indices of refraction. In a birefringent sample, incident polarized light is split into two rays, which travel at different speeds and are rotated at 90° with respect to one another. These are known as the ordinary and the extraordinary rays. When these rays exit the birefringent specimen they recombine into an elliptically polarized beam of which some portion can pass through the analyzer resulting in an image. Additionally, since the rays travel at different speeds, a phase difference is introduced, allowing for constructive and destructive interference at different wavelengths, and resulting in brightly colored images. This phenomenon was first studied

by Michel-Levy and Lacroix in 1888.<sup>12</sup> They noted that the interference color seen is a function of the sample thickness and birefringence. As birefringence is a function of order in the liquid crystal,<sup>13</sup> we can use the Michel-Levy interference color chart to estimate changes in CNC alignment.

For the isotropic 3.0 vol % dispersion, at low shear rates the dispersion remains isotropic, and the polarized microscope image is completely black. However, at a shear rate of 25.1 s<sup>-1</sup> light is able to pass the analyzer, indicating that the CNC are being oriented by shear. The intensity of the light increases with increasing shear rate, however up to a shear rate of 100 s<sup>-1</sup> the interference color remains in the first order grey region of the Michel-Levy chart. This indicates that when starting from an isotropic dispersion, highly ordered dispersions will be difficult to obtain through shear alone.

Unlike the isotropic dispersion, the 7.0 vol % biphasic dispersion and the 12 vol % liquid crystalline dispersion exhibit birefringence even at rest. This is due to the ordered liquid crystalline regions present in the dispersion. However, these dispersions have a polydomain structure, where the director of each liquid crystalline domain is oriented in a different direction. This results in non-uniform optical interference throughout the sample as shown in Figure 1. By shearing the dispersions the directors can be aligned resulting in a macroscopically aligned system. This is seen by a uniform interference color throughout the sample.

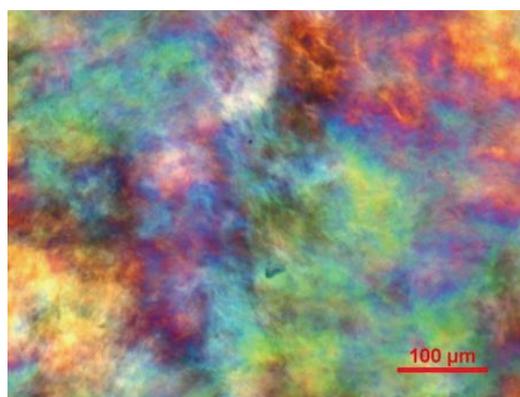


Figure 1. Polarized optical microscope image of a 12 vol % CNC dispersion at rest.

The 7.0 vol % biphasic dispersion exhibits a uniform interference color at shear rates as low as 0.1 s<sup>-1</sup>. As the shear rate is increased the color is seen to change. By utilizing the Michel-Levy interference color chart you can see the colors stepping up the chart from a first order blue at 0.1 s<sup>-1</sup> to a third order green at 100 s<sup>-1</sup>. As the sample

thickness was held constant, this indicates an increase in the birefringence and therefore an increase in order with increasing shear rate. Images at selected shear rates are shown in Figure 2.

Surprisingly, at low shear rates the 12.0 vol % liquid crystalline dispersion does not order as well as the biphasic dispersion. A polydomain structure can still be seen at shear rates as high as  $2.51 \text{ s}^{-1}$ . However, as the shear rate is increased to  $100 \text{ s}^{-1}$  more uniform colors are seen. We believe that higher shear rates are required to macroscopically align the liquid crystalline dispersion due to the significantly higher viscosity. Images at selected shear rates are shown in Figure 3.

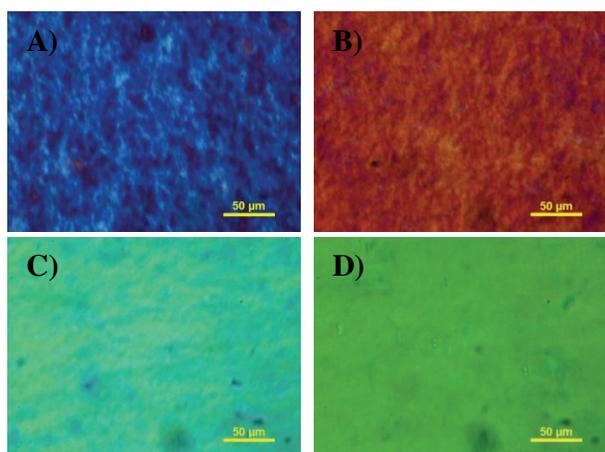


Figure 2: Polarized optical microscope images of a 7.0 vol % CNC dispersion at A)  $0.158 \text{ s}^{-1}$ , B)  $0.631 \text{ s}^{-1}$ , C)  $6.31 \text{ s}^{-1}$ , and D)  $100 \text{ s}^{-1}$ .

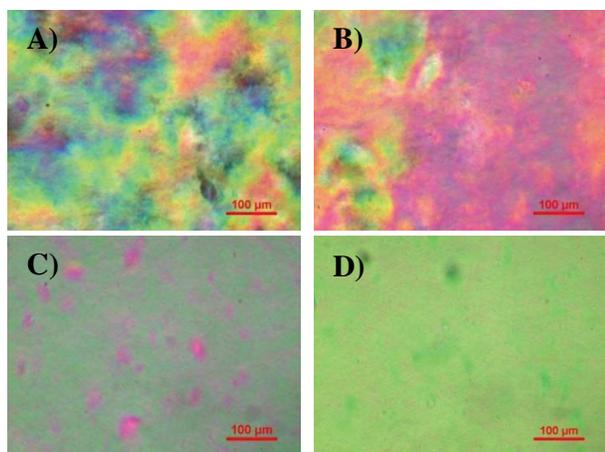


Figure 3: Polarized optical microscope images of a 12 vol % CNC dispersion at A)  $0.398 \text{ s}^{-1}$ , B)  $1.00 \text{ s}^{-1}$ , C)  $2.51 \text{ s}^{-1}$ , and D)  $25.1 \text{ s}^{-1}$ .

In order to retain the shear aligned structure in a film, it is important for the rotational relaxation time of the rods to

be significantly longer than the drying time of the film. The relaxation time of the dispersions was investigated by shearing at a high shear rate and capturing a time lapse of polarized microscope images after the cessation of shear. The 3.0 vol % isotropic dispersion fully relaxed almost immediately after shearing was stopped. The 7.0 vol % biphasic dispersion slowly relaxed over 90 minutes, with the interference colors changing as birefringence, and therefore order, was reduced. In the much more viscous 12 vol % liquid crystalline dispersion, the shear induced structure was maintained over a 90 minute time span. This 90 minute time span is sufficient for a thin CNC film ( $\sim 100\text{-}200 \text{ }\mu\text{m}$  wet thickness) to dry. Selected images from the relaxation time lapse are shown in Figures 4 and 5.

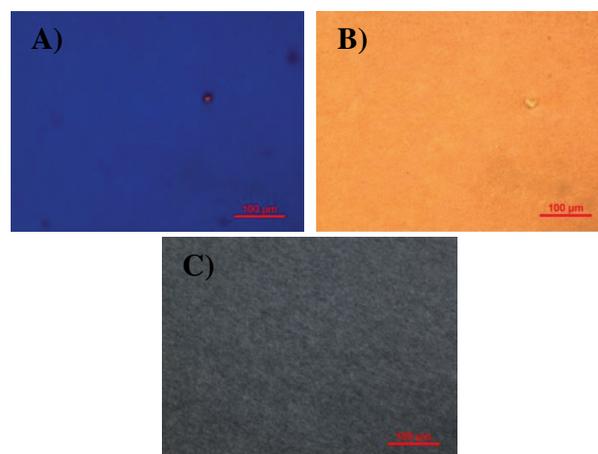


Figure 4: Polarized optical microscope images of a 7.0 vol % CNC dispersion A) 0 minutes after shearing, B) 40 minutes after shearing, and C) 90 minutes after shearing.

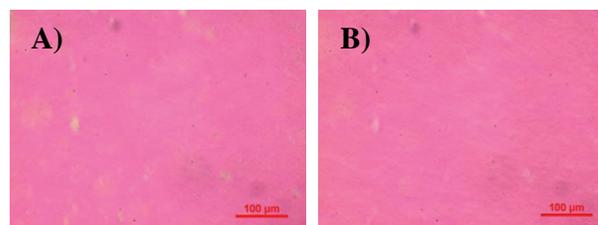


Figure 5: Polarized optical microscope images of a 12 vol % CNC dispersion A) 0 minutes after shearing, and B) 90 minutes after shearing.

A Guardco Microm II film applicator was used to prepare sheared CNC films on UV/Ozone treated glass slides by doctor blade coating. The film wet thickness was set at  $250 \text{ }\mu\text{m}$ , and a syringe pump was used to push the film applicator and vary the applied shear rate. For the 7.0 vol % dispersion films were prepared at shear rates from  $0.158 \text{ s}^{-1}$  to  $6.31 \text{ s}^{-1}$ . At low shear rates image color was not uniform, indicating a biphasic polydomain structure with

little macroscopic alignment. This is likely due to CNC relaxation during the film drying. However, at higher shear rates the image color was much more uniform, indicating a macroscopically aligned film. Images of these films can be seen in Figure 5. As seen in the shear stage microscopy study, shear rates greater than  $25 \text{ s}^{-1}$  were required to fully align the CNC in the 12 vol % dispersion. With our current syringe pump setup, it is not possible to apply films with controlled shear rates over  $\sim 10 \text{ s}^{-1}$ . Therefore, a new film application device will be necessary to explore 12 vol % films as we continue this study.

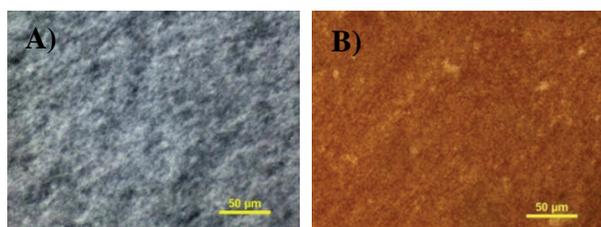


Figure 5: Polarized optical microscope images of CNC films prepared with shear rates of  
A)  $0.158 \text{ s}^{-1}$  and B)  $6.31 \text{ s}^{-1}$

#### 4 CONCLUSIONS

Aqueous dispersions of sulfuric acid hydrolyzed CNC follow lyotropic liquid crystalline phase behavior and form a cholesteric polydomain phase above the critical concentration. Macroscopic order can be introduced into these dispersions by the application of shear forces. At low concentration in the isotropic regime high shear rates are required to align the nanocrystals. Additionally, at low concentration, the rotational relaxation time of the rods is too fast for aligned film formation. As the concentration is increased, shear induced alignment is assisted by liquid crystalline self-assembly. This allows for macroscopic alignment at significantly lower shear rates. Eventually, we believe that the increasing viscosity begins to hinder alignment at low shear rates, and again increased shear rates are necessary. However, the increased viscosity also produces longer rotational relaxation time, allowing for the shear induced microstructure to be preserved in dried films.

#### REFERENCES

[1] R.M. Brown, "Cellulose Structure and Biosynthesis: What is in Store for the 21<sup>st</sup> Century?" *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (3), 487-495, 2004.  
[2] T.H. Wegner and P.E. Jones, "Advancing Cellulose-Based Nanotechnology," *Cellulose*, 13 (2), 115-118 2006.  
[3] M. Roman and W. Winter, "Cellulose Nanocrystals: From Discovery to Application," *Proceedings of*

International Conference on Nanotechnology, Atlanta, Georgia, April 26, 2006.

[4] G. Davidson, "The Rate of Change in the Properties of Cotton Cellulose Under the Prolonged Action of Acids," *Journal of the Textile Institute Transactions*, 34 (10), T87-T96, 1943.  
[5] R. Marchessault, F. Morehead, and M.J. Koch, "Some Hydrodynamic Properties of Neutral Suspensions of Cellulose Crystallites as Related To Size and Shape," *Journal of Colloid Science*, 16 (4), 327-344, 1961.  
[6] J.F. Revol, H. Bradford, J Giasson, R. Marchessault and D. Gray, "Helicoidal self-ordering of cellulose microfibrils in aqueous susoension," *International Journal of Biological Macromolecules*, 14 (3), 170-172, 1997.  
[7] A.M. Donald, A.H. Windle and S. Hanna, *Liquid Crystalline Polymers*, Cambridge University Press, 2006.  
[8] J. Pan, W. Hamad and S.K. Straus, "Parameters Affecting the Chiral Nematic Phase of Nanocrystalline Cellulose Films," *Macromolecules*, 43, 3851-3858, 2010.  
[9] W.J. Orts, L. Godbout, R.H. Marchessault, and J.F. Revol, "Enhanced Ordering of Liquid Crystalline Suspensions of Cellulose Microfibrils: A Small Angle Neutron Scattering Study," *Macromolecules*, 31, 5717-5725, 1998.  
[10] J. Adams, W. Haas and J Dailey, "Cholesteric Films as Optical Filters," *Journal of Applied Physics*, 42 (10) 4096-4098, 1971.  
[11] E.E. Urena-Benavides, G. Ao, V.A. Davis and C.L. Kitchens, "Rheology and Phase Behavior of Lyotropic Cellulose Nanocrystal Suspensions," *Macromolecules*, 44, 8990-8998, 2011.  
[12] A. Michel-Levy and A. Lacroix, "Les Mineraux des Roches," *Librairie Polytechnique*, Paris, 1988  
[13] P.G. de Gennes, *The Physics of Liquid Crystals*, Oxford University Press, 1974.