Nano Crystalline Cellulosic Nematic monocrystals optical properties

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ABSTRACT

Optically active solid films were produced by leaving to evaporate Nano Crystalline Cellulose (NCC) liquid dispersions. A NCC is a nanorod around 5 x 10 x 150 nm^3. It is real nanocrystals, as each cellulose making molecules are distributed inside a square lattice. If the aqueous dispersion is left to evaporate, microscopic liquid crystals appear very quickly and grow. The final result is a solid film showing vivid colors ranging from blue to red. In some conditions, it also becomes transparent, its optical activity being in the IR spectral region. It is also demonstrated that the solid film is in fact a mosaic made of several mono crystals. In good conditions, each crystal reaches the millimeter to centimeter scale. It is believed that twists in their crystalline nanostructure combined with their surface electric charges are responsible for their auto organization in bulk volume into liquid crystals. This generally accepted statement is however questioned in this report.

Keywords: nano crystalline cellulose, cellulose nanocrystal, self-organization, optical and structural properties

1 INTRODUCTION

The interest on NCC's optical properties is growing quickly. Since it is possible to generate colors with only natural and recyclable materials, like wood fibers, the application potential is highly interesting for the printing industry.

In order to follow the generation of color from the aqueous dispersion, new equipment was introduced in this study by our team. This is the laser light diffraction optical set-up. Thus, the liquid crystallization kinetics and the lattice dimensions in water were measured from just after shaking the dispersion for a better homogeneity to equilibrium. To better understand the role of electric charges in this process, the ionic concentration was measured and controlled. Although a powerful sonicator was initially used to better disperse the dilution, it also became a key player in the understanding of the crystallization process.

The optical activities of the polycrystalline solid film were observed with various optical set-ups and microscopes. The observations are converging toward the conclusion that the NCC nanorods in the aqueous suspension self organize into loosely organized thin layers. The layers are roughly parallel one to the other, with water in between. Upon drying, these liquid formations are shrinking gradually by the removal of water to multiple solid plates, stacked one on top of the other.

This research is very promising. This material coming from the forest, is easy to produce and abundant. Mass applications in several optical components may be possible, very respectful of the environment.

An interesting potential commercial application of NCC is to make colored films or active displays without using pigments. Since the material used in this work comes from the Canadian forest, it can be said NCC are environmental friendly. However, to better exploit any chromatic effect from NCC, it is obvious that the self organization mechanism present in the aqueous phase has to be better understood and controlled.

Indeed, several theories already exist (1,2). They all rest on the ability of the NCC to self orient, due to a combination of electric charges on the NCC surface, and twists in the NCC nanocrystals structure, a dislocation that should be present on all NCC, in an equal manner. These defects would provide the nanorods an asymmetric electric cloud around its main body, resulting with a helical structure.

Although quite satisfactory from the point of view of a conceptual model that explains most chromatic observations, this model is revisited. Nonobstantly, the most important point remains the color control and the industrial application.

2 MATERIAL AND METHOD

In order to better understand the organization structure, and the influence of various parameters, several instruments of various types were used. Also, our manipulations were either on the aqueous dispersion, or after evaporation, on the solid thin film.

The liquid dispersion was received from the local pulp and paper industries (FP Innovation, Paprican Division, Pointe-Claire, P. Québec, Canada). The NCC nanorods were prepared by exposing the cellulosic dispersion to sulfuric acid. The chemical reaction digests the amorphous component faster than the crystalline nanostructure. At some point, mostly nanostructures are remaining and the reaction is stopped. Therefore, the nanocrystals are

separated from the rest and dispersed in water. The chemical process has charged the nanorods with electric negative charges.
The preparation was delivered to our laboratories free from any other components for instance salts or fungicides. The initial concentration is around 4% w/v. Then, the dispersion is first hand shaken, and then sonicated for 5 minutes with a Sonics Vibra cell ultrasonic (130 W, 20 kHz). It is centrifuged to remove remaining large aggregates, and forced through a 400 nm filter to further reduce the undesired formations. The dispersion is therefore passed through a resin bed (MTO-Dowex Marathon MR-3, SUPELCO Analytical). From this point, this is the NCC working preparation. It can be modified by adding sodium chloride to study the impact of ionic screening on the colloidal suspension.

The dispersion is then analyzed with a spectrophotometer. Assuming that the NCC dimensions are small compared to the wavelength, the Rayleigh diffusion is used to monitor the NCC size. Although the size distribution of nanorods is only estimated, and directly measured by AFM, it quickly reveals any changes in the average size for instance after an energetic sonication.

2.1 Preparation of thin solid disks

The NCC dispersion was deposited in Petri dish. The dish was placed in heavy Pyrex desiccators, itself placed onto foam. The assembly was installed on the shelf. If left to evaporate at 20 °C, fan like crystals are seen. If placed in a cold chamber kept at 4 °C, cubic crystals are seen. The final results are therefore a matter of crystallization conditions.

2.2 Laser diffraction

A new and simple optical set up was introduced. This is a He-Ne laser and a 5 mm glass cylinder containing NCC dispersed in water. The laser beam was focused at the center of the cylinder with a 250 mm focal converging lens. The resulting pattern was projected onto a screen 3 meters away. Typically, when only water was present, the result is a simple bright spot at the center of the screen with no other feature. With either latex, glass or other one hundred nanometer scale colloidal dispersions, a large quantity of speckles was seen moving at random around the central spot, without apparent slowing down after 10 minutes. With NCC dispersions, the initial rapid motion is followed by an apparent full stop within one or two minutes, depending of the initial concentration. The next motion is very slow, several orders of magnitude below the initial speed.

As the motion slows down, a ring of diffraction appears around the central spot. It reveals the formation of liquid crystals in the aqueous dispersion. Then later, a second ring appears wider than the first one, revealing a second diffraction order, thus a larger organization. As the time passes by, more rings appear, and they become brighter. This indicates a higher degree of organization with time. The time required for the first ring formation is within one minute.

2.3 Atomic force microscopy

The NanoSurf easyScan 2 model of Atomic Force Microscope (AFM) was used. It is equipped with image software for a better contrast. The resolution limit allows the visualization of the molecular network. We can therefore easily see an individual nanorod, and the resulting organization after evaporation.

2.4 Scanning electron microscopy

In order to have a view of the stacking of plates one on top of the other, the solid thin films were broken and seen on the thickness side by a Scanning Electron Microscope (SEM). The images were then contrasted for a better analysis.

2.5 Optical microscopy

The resulting thin solid films, after evaporation, were observed with an optical microscope. Pictures were taken with a commercial 10 Mega pixel digital camera. Polarizers were also introduced in the optics, to better observe individual single crystals embedded in the films. Also, the films were broken into pieces. Then, single crystals were isolated and observed individually.

2.6 Sonication

A powerful sonication was used to disperse the NCC in the aqueous volume. However, it became apparent that the effect of sonication was more subtle. Usually, the sonicator was used at full power, for a given number of seconds. The instrument is able to give us the quantity of energy invested.

3 OBSERVATIONS

At the figure 1, an AFM image of a diluted aqueous NCC dispersion sonicated for 10 minutes and left to evaporate on a glass plate is showed. The glass plate was previously cleaned with acid and rinsed with Millipore deionized water. Observations showed nanorods chains connected by thin bridges apparently left over by the chemical reaction. From several pictures, the length distribution of each individual nanorod was established, and an average value was found. This wide size distribution is very common.

An interesting fact is that energetic sonication does not influence NCC morphology. This conclusion is confirmed by the light scattering measurement.

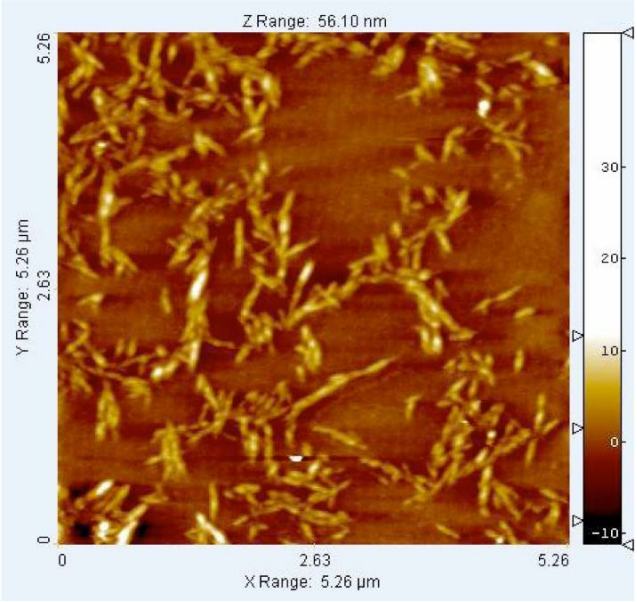

Figure 1: AFM picture of NCC after an energetic sonication. The nanorod chains are apparently intact.

A laser beam, after passing through a NCC aqueous dispersion, shows diffraction pattern. Right after shaking, only the central spot appears with moving speckles around it. After one minute, a steady circular ring appears. This shows that great quantities of small liquid crystals are formed, beginning almost immediately after shaking. Three minutes later, the circle becomes a hexagon (see above). This shows that the nanorod liquid crystals are growing into larger organization, proven by the appearance of new concentric rings. If this dispersion is shaken again, all patterns disappear, leaving again the central spot with speckles. Therefore, the process is reversible.

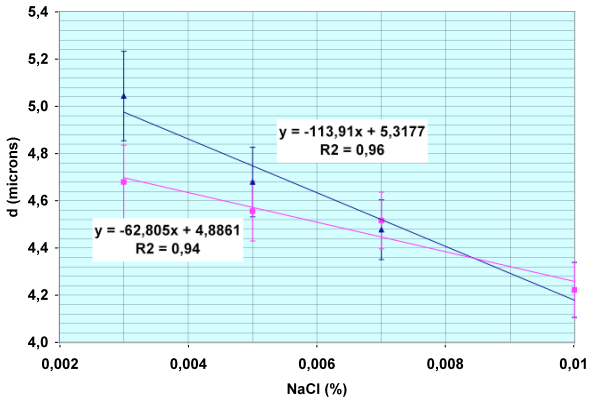

Figure 2: The liquid crystal lattice distance related with the salt concentration in neutral (square) and acidic (round) dispersions. A He-Ne laser beam passing through a NCC dispersion (5.53 % w/v) produces diffraction rings.

The crystal lattice distance d can be estimated by the following equation (for the cylindrical container):

$$d = \frac{m\lambda L}{nR} \qquad (1)$$

m is the diffraction order, L distance between the NCC dispersion and the screen, n the refraction index, R the ring horizontal radius, and λ the laser wavelength.

Once left to dry in a Petri dish, the preparations are showing bright colors, from blue to red. Pictures of Figure 3 are illustrating this effect. The films were also observed by optical microscopy as shown in Figure 4. Using crossed polarizers, square crystals formation were clearly observed. As well, the fingerprint pattern was also seen. Interestingly, this square pattern is one centimeter long. This was due to a very slow thinning of the NCC films.

Figure 3: Petri dishes after the evaporation of NCC dispersions. The thin solid films final colors are due to the rotation of the light electric field. The reflection spectrum is complementary to the absorption spectrum.

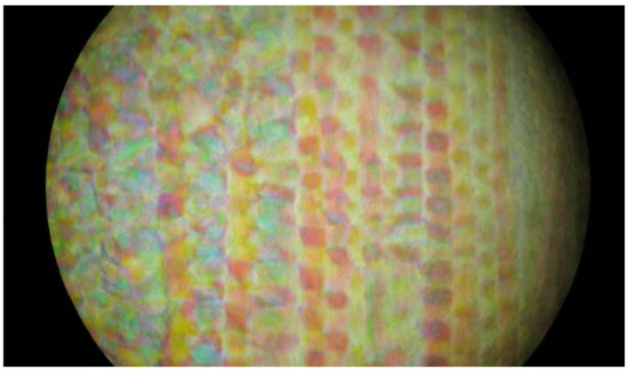

Figure 4: optical microscopic image of NCC solid thin films. Note the square formations.

These thin films were analyzed by spectroscopy. The peak wavelength is clearly dependent on the salt concentration. Increasing the salt concentration, the peak

went from red to blue. Interestingly, the rate of chromatic shift is very similar to the one calculated on figure 2. This means that once formed, the liquid crystal keeps its structure while drying up to solid film. The lattice distance in the aqueous dispersion compared to the solid state is about 12 to 1.

AFM images of the solid film show a multilamellar system (Figure 5).

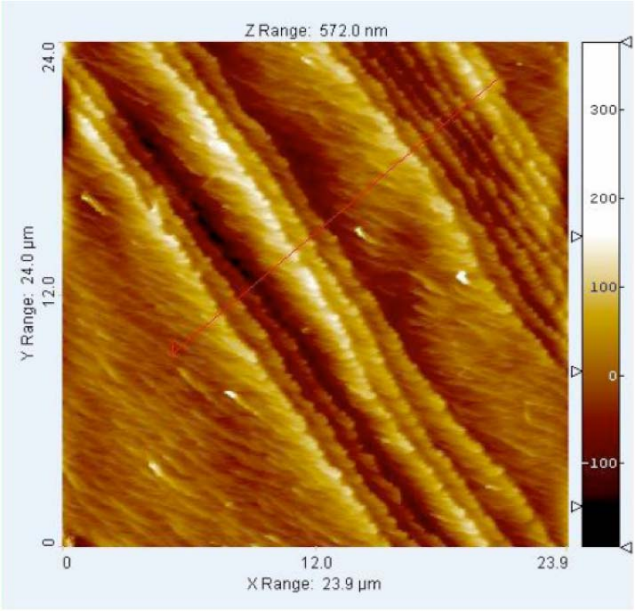

Figure 5: AFM picture of a NCC solid thin film. The lamellar structure can be easily seen. The general orientation of NCC fibers is also clearly visible. Each lamella is in the order of 100 nm thick.

The same system could be seen by SEM, and optical microscopy. The distance center-to-center is well below the micrometer. The orientation of the fibers is the same from plane to plane. The solid films spectra will have to be considered from the logic of the Bragg reflexion of a multilayer system.

4 CONCLUSION

Our experiments demonstrated that NCC self-organize in multilayers. Through AFM, SEM and optical observations, the research team established that the orientation of nanorod remained the same from one layer to the subsequent one. A possible interpretation is that our diffraction pattern of the aqueous dispersion comes from NCC liquid lamella stacked up after drying.

Our built model (3) verifies well this behavior. This behavior is mainly due to the fact that the real nanorods are not so identical, rather different in size, shape, and charge.

Instead of a long helical structure, a stratification of nanorods is observed. We keep studying these organizations, and a publication with a more detailed analysis will follow.

Nevertheless, the main point is that NCCs are capable to produce bright colors using wood and water. The following steps are to improve the contrast and better control the color opacity and wavelength.

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