Photonic crystals with nanocellulose

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ABSTRACT

It is demonstrated that upon evaporation, an aqueous well-dispersed Nano Crystalline Cellulose (NCC) solution self organizes into solid multilayer iridescent films. Each multilayer is made of sub microfibers, themselves made of arrays of flocs. The control of initial salt concentration leads to specific colours. This is due to the NCC liquid crystallization that is smectic-like. This new understanding provides a simple explanation for NCC crystallization and photonic properties. Adding the fact that smectic liquid crystals are known for their interesting rheological properties, this combination of scientific expertise should lead us to a new brand of industrial inks.

Keywords: Ink, smectic, liquid crystal, nanocrystalline, cellulose, floculation, iridescence, fibrillation, multilayer.

1 INTRODUCTION

The printing industry is seeking a new ink formula involving environmental friendly materials. It has been demonstrated for decades that after evaporation, a NCC suspension turns into a colourful solid film (1-4). It was also found that the NCC spectral characteristics depend on various parameters, like the sonication energy, ionic concentration, the initial NCC concentration.

Globally, this appears to be a complex multi parameter problem. In order to create an easy-to-use NCC based ink, a fundamental research study was carried out to better understand the basic reactions leading to colours, and therefore to simplify the ink formulation.

This report is showing that with evaporation, arrays of flocs are produced in the aqueous dispersion, and self-arrange in smectic-like crystals. Once dried up, the smectic crystal becomes a multilayer solid film. Interference is therefore the basic principle that creates the beautiful colours.

This also can be an important factor for inks as smectic crystals are associated with viscosity, and the control of viscosity is a key factor for ink formulation. Therefore, colours and viscosity are linked together by a small set of parameters.

2 MATERIAL AND METHOD

NCC raw dispersions were provided to us by a major industry (5). In this case, the NCC preparation followed a typical protocol involving sulphuric acid. To uniformize the starting dispersion, the raw NCC dispersion was first filtered through a 1.2-micron pore size membrane (GFC, glass microfiber, Whatman) to remove micro contaminants and aggregates. Then, the filtrate was passed through a resin (Mixed bed, MTO Dowex, Marathon MR-3, Supelco Analytical) to remove ions and leave only pure water. The resulting dispersion was passed again though another 1.2-micron filter to remove any possible resin particles. To study the effects of sonication, the 4% w/v NCC dispersions were powerfully treated with a Vibra Cell, CV 18 sonic rod, for various periods of times before each experiment. To study the effect of ionic concentrations, pure NaCl were mixed with NCC dispersions and sonicated all together. The set-ups used are presented in the next sections.

2.1 Light Diffraction

The set-up was made of a 1 mW He-Ne laser, passing through a NCC dispersion in a Petri dish. The emerging laser beam was reflected onto a white screen. Images of the screen were taken with a Canon EOS 5D Mark II camera. High resolution raw 5616 x 3744 pixel array pictures were shot at every 15 seconds for a few minutes, then automatically at every 15 minutes for 10 hours. The room was in complete darkness all the time. In the field of the camera was a digital balance with a luminous display, all doors opened. On its plateau was an identical NCC preparation. Therefore, from each picture, the NCC concentration can be calculated.

2.2 Optial Microscopy

The NCC dispersions were deposited onto a microscope slide, and then covered with a microscope cover slip. The evolution of the suspension was closely observed under a microscope objective, in phase contrast with cross polarizers (Nikon, Optiphot-2, Japan).

A 4% NCC dispersion was also inserted into a capillary tube. The planes also were formed and observed with the same microscopic set-up.

2.3 AFM

Individuals NCC nanofibers were examined with a Nanosurf Easy Scan 2 AFM, equipped with Image Metrology A/S SPIP 5.0.1 software. In order to achieve this image, the NCC dispersion was diluted, sonicated, put onto mica and dried.

Solid films made with various NCC dispersions were prepared and analysed with the same AFM. The procedure was quite simple. The film surface was first scanned. Then, the NCC film was broken and the edges scanned. Clear staircase-like structures can be seen on the fractures area of a blue solid film. Thanks to the AFM high precision, the step height can be easily determined. It will be demonstrated that the height of the solid NCC films steps is directly related to the reflection peak. The results are compiled in the Table 1.

2.4 SEM

A Hitachi S-4300SE/N (VP-SEM) was used. The NCC solid film surface was first examined. Basically, the surface did not show any interesting features. Then, the NCC solid films were broken, and observed edge upward. A clear stratification was observed. In the stratification, the typical arced-like structures were observed. This is very consistent with our AFM observations (see results), as well as previous reports (1-4).

2.5 Absorption Spectroscopy

The solid film was examined with a standard absorption spectrophotometer. In this case, it was used to measure the degree of attenuation due to reflection. The peak attenuation wavelength depends basically on two parameters: sonication energy and salt concentration. The more sonicated the dispersion, the redder the peak absorption is. On the contrary, the higher the salt concentration, the bluer the final film is. This will be discussed in the corresponding section.

2.6 Reflection Spectroscopy

A spectrofluorometer (USB 4000, Ocean Optics Inc.) specially equipped for reflection spectroscopy was also used. This is essentially a flash xenon lamp PS-2 emitting from UV to IR at a rate of 10 pulses per second. The flashes were funnelled into UV fibre and conducted to the sample. A special holder kept perpendicular the fibre few millimetres above the targeted surface. Around the emitting light fibre, a cluster of fibres conducted the reflected light to a detector array monochromator. The whole spectrum was taken in few seconds. The results are the mirror image of the attenuation spectra.

3 THE BASIC MODEL

The evaporation of the dispersion in the Petri dish tends to produce the following sequence of diffraction patterns: a uniform halo (see Figure1), a segmented halo, a hexagon, only a two spot pattern and finally, the pattern fades away. One rational sequence of events is that tiny smectic-like liquid crystals - acting like small gratings - are produced at the very beginning. Then the small smectic-like liquid crystals grow larger till reaching the size of the laser beam. Then a two spot diffraction pattern is observed. Knowing the parameters making the images, it is easy to calculate the pitch. The gradual disappearance of the diffraction pattern means the smectic-like planes is essentially a phase grating. When the distance between planes is getting smaller, the light left for interference decreases, and the diffraction pattern fades away. The moment of its disappearance can tell us the width of the planes.

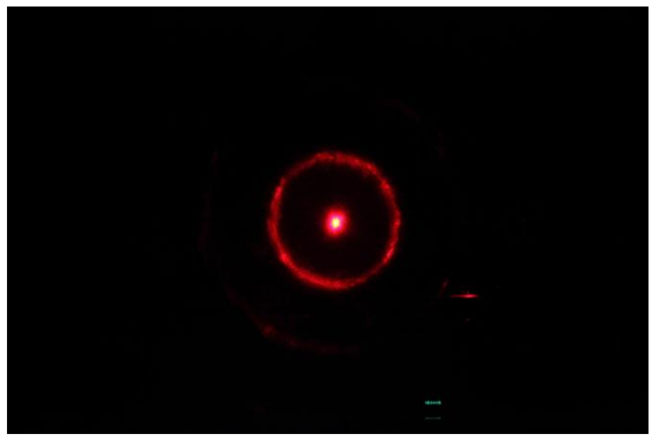

Figure 1: Circular halo made by the laser beam passing through a NCC dispersion. This indicates the presence of a diffracting structures randomly oriented.

Based on the physics of gratings, a plot of the water content against the pitch was made. A quasi-linear decrease was observed. Evaporation and pitch are therefore connected. One possibility is new smectic planes are simply added as evaporation keeps going. Once the plane-to-plane distance is too small to insert new planes, the grating pitch remains the same in water.

It is noteworthy that all decreases of the grating pitch seem to converge at about 2 microns. At that point, the halos or spots fade away. This is probably due to the fact that the grating period is related to center-to-center line distance. The width of the open space between two planes is the total grating period minus the width of the plane, according to AFM observations few microns long. Therefore, when the planes are about to contact, very small quantities of light are passing. In order to test this hypothesis, a higher NCC concentration was used. As expected, a sharp change in the smectic-like shrinking kinetics was observed at about 2 microns.

After evaporation, the solid film was observed with a phase contrast microscope. It shows that the solid liquid is polycrystalline. When the solid film is broken to pieces, the fragments are observed. It is obvious that the fragment edge follows a line with frequently observed 90° angles. This is incompatible with the helical model, since in thickness, the nanorod angular rotation is supposed to be in small angle increments from one layer to the other. On the contrary, this is very consistent with the present smectic-like liquid crystal model, as the fractures are along the 1D axis or perpendicular to it.

When edges are observed, it is possible to see the multilamellar structure indicating a clear stratification process, in a surprisingly regular manner, much better than expected from a rough dispersion. This regularity is responsible for the iridescence appearance.

The observation by AFM of the multilayer is probably one of the most sticking discoveries of this paper. When fractured, the solid edges are scanned. It appeared that individuals NCC gather into flocs, then 1D arrays (see Figure 2), then multilayers (see Figure 3).

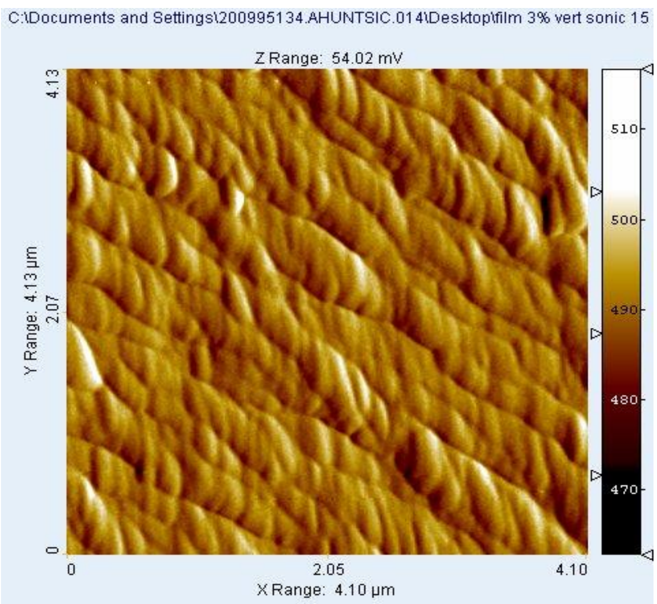

Figure 2: Arrays of NCC flocs. The arrays are several micron long, and about 400 nm wide. Each floc is about 200 nm thick.

This sequence of aggregation is an interesting aspect of this report. According to a recent publication (6), flocculation depends on the fiber length and shape. The AFM pictures indicates that the NCC fibers have an heterogeneous shape. With evaporation, the distance between the fibers decreases, which increases flocculation. As the number of flocs increases, a process of aggregation between flocs themselves happens. The process of aggregation in the bulk phase has been studied (7), and it is the first one to occur, before agregation at the surface.

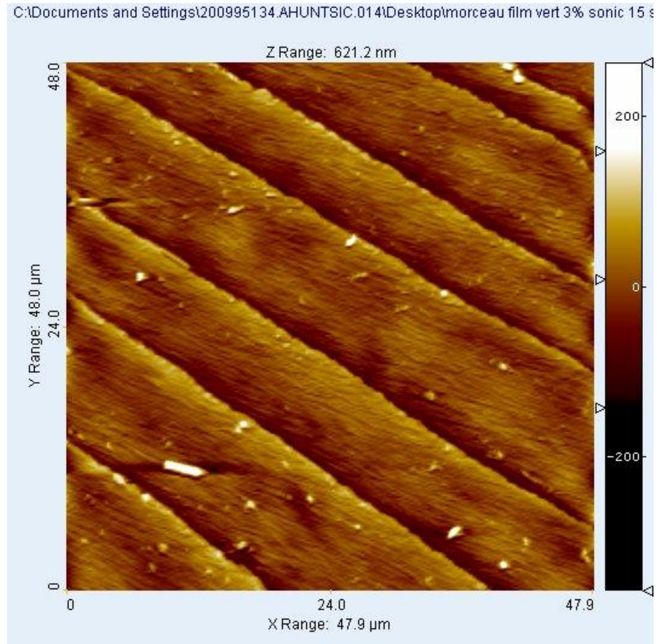

Figure 3: staircases observed in the NCC final solid film This is a multilayer, each layer being made of the fibers seen in figure 2.

The distances from one step to the other are reported in the Table 1 (see Discussion). In this table, it can be seen that the distances are related to the sonication energy as well as the salt concentration. We will further document this trend with absorption and reflection spectroscopy.

4 EFFECT OF SALT

A series of solid films were analyzed by absorption spectroscopy from UV to IR. The peak absorption is shifted toward IR when sonication is stronger. At the opposite, when salt is added, the shift is toward the blue.

Using the Ocean Optics spectrofluorometer, configured for reflection spectroscopy, several reflection spectra were taken. Contrary to the absorption spectra, the general spectrum shape is surprisingly very pure. We observe a sharp increase of reflectivity near the peak on the blue side, and a slow decrease of reflectivity on the red side. This shape is common to all solid samples. The peak is moving accordingly to sonication and salt concentrations. The results are gathered in the Table 1.

5 DISCUSSION

In this report, we have clearly demonstrated that the NCC forms multilayers. This is due to the natural tendency of fibrous matter to flocculate in the liquid phase. Then, the flocs seem to make micrometer long arrays. Self-organisation continuing, the arrays self arrange in smectic-like liquid crystals. The arrays are now parallel one to the other, forming loose liquid planes. The planes are vertical in the Petri dish, therefore the arrays are parallel to the Petri dish surface.

While evaporating, the liquid planes are slowly drifting one toward the others, until entering into contact before evaporation. After evaporation, the 1D arrays are stacked one above the other, in a parallel manner.

At the Table 1, the resulting optical effects are compiled. The salt concentration, the sonication energy together with the direct AFM measurement of the distance between layers, the absorption and the reflection peaks are shown.

Table 1: absorption and reflection peaks of NCC solid films

Film	**Salt**	**Son.**	**AFM**	**Δz**	**Abs.**	**Ref.**
Color	Y/N	secs	nm	nm	nm	nm
Violet	**More**	**No**	**113**	**19**	**358**	**350**
Blue	**Less**	**No**	**150**	**20**	**371**	*******
B-G	**No**	**No**	**136**	**16**	**454**	**450**
Green	**No**	**15**	**204**	**48**	**539**	**520**
Red	**No**	**600**	**344**	**53**	**795**	**700**
Trans.	**No**	**1200**	**460**	**95**	**1100**	*******

Table 1: Peak reflection for NCC multilayer system. The color are B-G for Blue-Green, and Trans. for transparent. Ref. is for reflection. Δz is for the standard deviation.

Interestingly, there is a simple relationship connecting the interlayer distance and the peak absorption. Plotting the peak wavelength against AFM observation, a slope of about 2.2 is obtained. Since light makes twice the distance between two layers before to interfere, the average refractive index is then half of the slope value, that is around n = 1.1. Assuming that a 1D array is a cylinder with a refractive index of 1.5, and the packing is orthogonal, it is easy to calculate that the effective refractive index is very close to 1.1.

The AFM pictures are strongly suggesting that the optical model is a simple multilayer. A computer simulation for multilayer coating in optics was performed. Basically, by adjusting the parameters, it is possible to reproduce the general reflection curve observed with the NCC solid films. The results for the simulations are converging toward the concept that the multilayer structure is fundamentally responsible for the observed iridescence. Interestingly, it seems that only the top two or three layers contributes to the general reflection.

6 CONCLUSION

In this report, it was demonstrated that NCC nanofibrils in aqueous dispersions self aggregates into flocs, then to arrays, then to smectic-like liquid crystals. During the evaporation process, the smectic planes get closer until contact. After complete evaporation, the 1D arrays are piled up in a lamellar structure, capable of producing iridescence.

The NCC self-organization is smectic-like, not cholesteric. Coincidentally, the chiral smectic liquid crystal is capable of showing the same effects than cholesteric in liquids and solids. Because of its smectic nature, it becomes naturally a multilamellar photonic crystal after evaporation. Our interpretations of the absorption spectrum, the diffraction patterns as well as the optical, SEM and AFM images are all consistent with the smectic-like liquid crystal model. This is an important breakthrough in the comprehension of NCC color properties, which should allow a much easier industrial development for NCC optical properties applications, particularly in the ink industry.

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