HARDWOOD CELLULOSE NANOCRYSTALS: MULTI-LAYERED SELF-ASSEMBLY WITH EVIDENCE OF CIRCULAR AND DISTINCT NEMATIC PITCH

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It is our honor to dedicate this paper to Prof. Bogdan C. Simionescu, in recognition of his excellent life-long contribution to science.

In this study, the formation of a self-assembly pattern and the nematic pitch of cellulose nanocrystals (CNCs) have been investigated first in a liquid state *via* Optical Microscopy (OM) and then in a dry state using Field Emission Scanning Electron Microscopy (FE-SEM). Furthermore, the surface characteristics of self-assembly patterns of hardwood bleached kraft pulp cellulose nanocrystals (HW-CNCs) were investigated under FE-SEM. HW-CNCs had a rod-like structure with a length of 202 $\pm$ 52 nm and width of 14.9 $\pm$ 3.9 nm. The circular patterns of self-assembled layers, with a differential area ranging from 3.0 μm to 30 μm, were evident. Furthermore, the HW-CNC thin film showed a left-hand twist and a self-ordering structure. Such characteristics of CNCs open substantial possibilities for building bio-based three-dimensional (3D) nanostructures or 3D nanoengineering materials. In this work, we have demonstrated the self-assembly of CNCs in multi-layers with circular patterns and distinct nematic pitch.

Keywords: cellulose nanocrystal, circular self-assembly, multi-layered, chiral nematic pitch, FE-SEM

INTRODUCTION

Bio-based nanomaterials that exhibit self-assembly characteristics and nematic pitch have attracted much research interest in recent years. Their unique self-assembling ability has been investigated in order to assess their suitability for building three-dimensional (3D) nanostructured materials and functional materials.[1] Furthermore, the self-assembly of nanomaterials is influenced by factors such as force balance, hydrogen bonding, hydrophobic and hydrophilic forces.[1-5] It has been reported that, after self-assembly, CNCs exhibited a form of chiral nematic or smectic phase (parallel chains), which were confirmed by various models.[4] The self-assembly characteristics of CNCs have been studied using polarized microscopy and SEM techniques.[2-6] As reported earlier, the self-organization/assembly of CNCs was observed in liquid phase and in thin films.[2-8] Hai *et al.*[8] investigated the surface characteristics and self-assembly of CNCs prepared from different cellulose sources.

To our knowledge, circular multi-layered self-assembly of CNCs and their chiral nematic pitch have not been investigated in any earlier reports.[2-6] In a recent paper,[9] Hai *et al.* examined the circular self-assembly of CNCs produced from electron-beam treated cellulose. However, the formation of circular multi-layered CNCs was not remarked in that study. The present work assessed circular multi-layered self-assemblies of HW-CNCs, as well as their chiral nematic pitch, by using Optical Microscopy (OM) and Field

Emission Scanning Electron Microscopy (FE-SEM), and the findings were confirmed both for the surface and cross-section of thin films.

EXPERIMENTAL

Materials and methods

Bleached hardwood kraft pulp was received from a supplier from Canada. The pulp consisted of a mixture of aspen and poplar, and was used in the preparation of HW-CNCs. The pulp had a CED intrinsic viscosity of 15.4 centipoise and an α-cellulose content of 87%. Sulfuric acid (98% purity) was supplied by Daejung Chemicals (South Korea) and was used for the isolation of CNCs. The extraction of CNCs from hardwood bleached kraft pulp was performed as per the procedure described by Hai *et al*.[8]

Equipment

The surface characteristics of the isolated CNCs were analyzed using FE-SEM, TEM and Optical Microscopy (OM). For TEM, the isolated HW-CNCs (0.5%w/v) were further diluted to 0.005% for surface characterization. A micro-drop of the 0.005% solution was deposited on a copper grid and air dried at room temperature before the TEM observations. For OM, 1 µL of the CNC (0.5%) suspension was deposited on a glass slide for observation in a liquid state. For FE-SEM, 1 µL of the 0.5% CNC solution was deposited on a mica disk with a diameter of 10 mm and air dried at room temperature. Two different HW-CNC samples, of 0.005% and 0.5% concentrations, were used for the morphological study of the multi-layer assemblies. Furthermore, the dried CNC samples were coated with platinum (Pt) for 60 s before the FE-SEM studies were performed.

RESULTS AND DISCUSSION

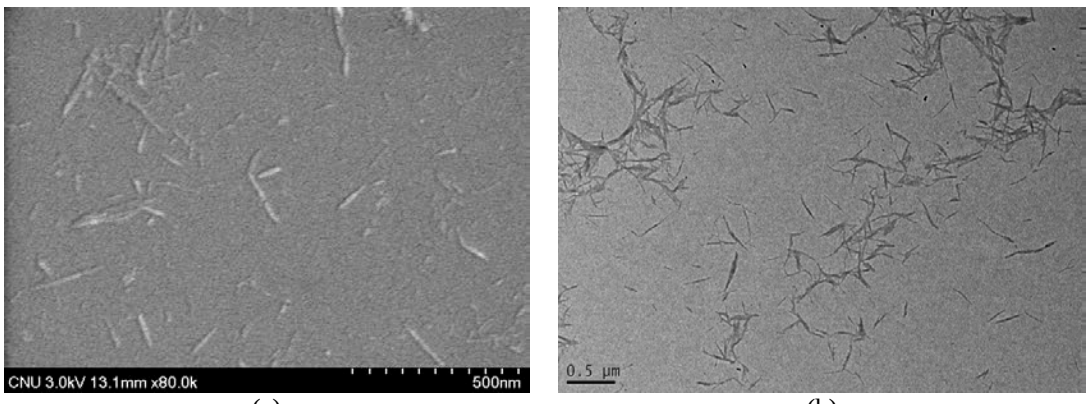
Surface morphology of HW-CNCs

The CNC self-assembly characteristics were analyzed using high magnification FE-SEM, while TEM was used to measure the length and width of HW-CNCs. The aspect ratio of the prepared CNCs was around 15 (with a length of 202 ± 52 nm and a width of 14.9 ± 3.9 nm), as shown in Figure 1a and b.

The layer-by-layer self-assembly of CNCs in a thin film has been reported in various studies.[4,6-8,10-11] During the investigation by FE-SEM in the present study, the phenomenon of multi-layer self-assembly of CNCs in a thin film was observed. The results indicated that CNCs assembled into several layers, having distinct size and shape. FE-SEM images revealed that the multi-layered self-assembly of HW-CNCs could be produced without limitations.

After drying the self-ordered CNC suspension, it was subjected to cross-polarizer microscopy and a fingerprint pattern or a chiral nematic pitch could be remarked. A clear image of the circular self-assembly of HW-CNCs (0.5%) in the suspension was observed under OM, as shown in Figure 2. Interestingly, the CNC suspension exhibited the phenomenon of circular self-assembly in both liquid and dried form. The circular self-assembly of CNCs in the dried state was confirmed by FE-SEM, as illustrated in Figure 3. Based on a survey of the published literature, no other evidence on circular multi-layered self-assembly of a CNC suspension in wet and dry state has been reported so far.

Revol *et al*. reported the self-assembly of CNCs in the wet state occurs due to the critical concentration of CNCs, force balance and other conditions.[12] Lee *et al*. and Jee *et al*. stated that the self-assembly of the CNC colloid in a wet system is due to force balance, colloidal interfacial interaction, and heating or cooling.[1,13]



(a) (b)

Figure 1: FE-SEM (a) and TEM (b) images showing the morphology of HW-CNCs (0.005% conc.)

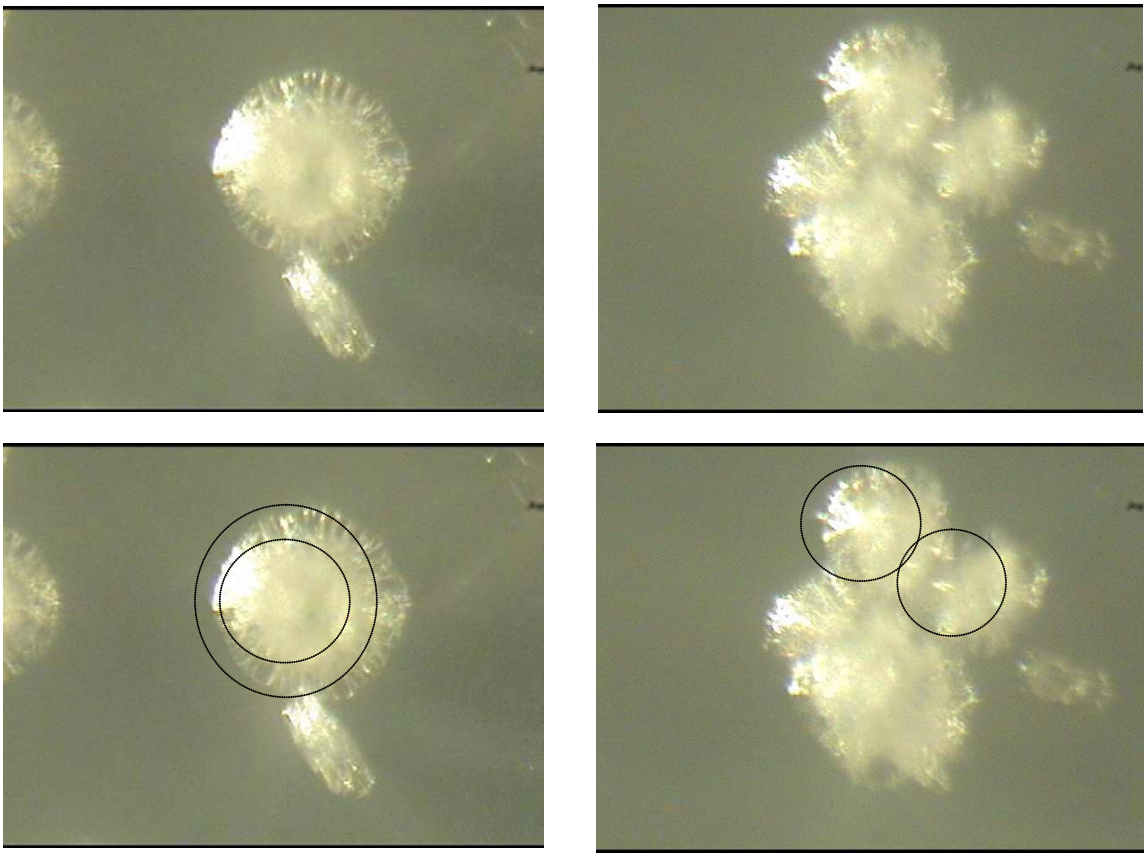
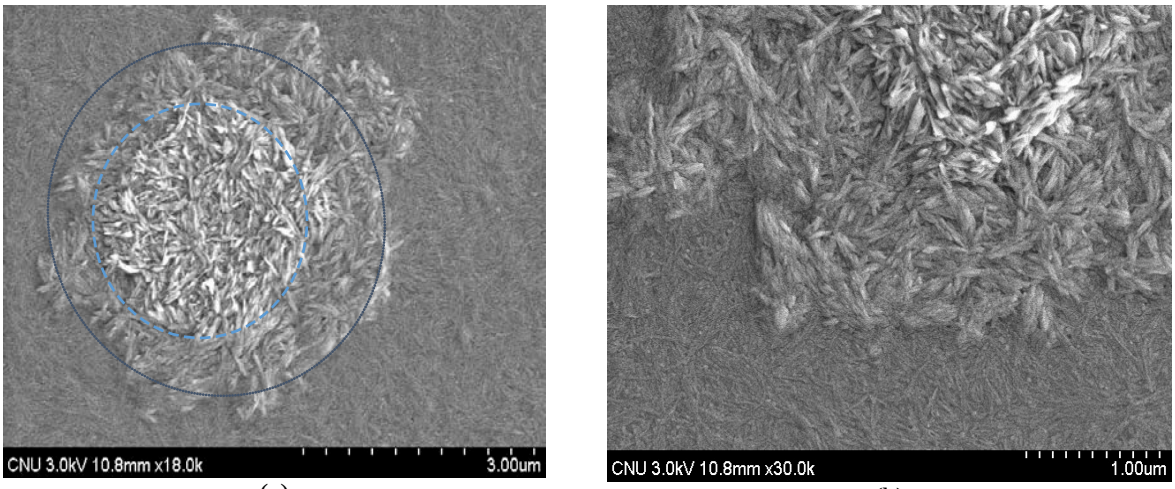


Figure 2: Self-assembly of HW-CNC (0.5%) suspension observed using Optical Microscopy (OM)



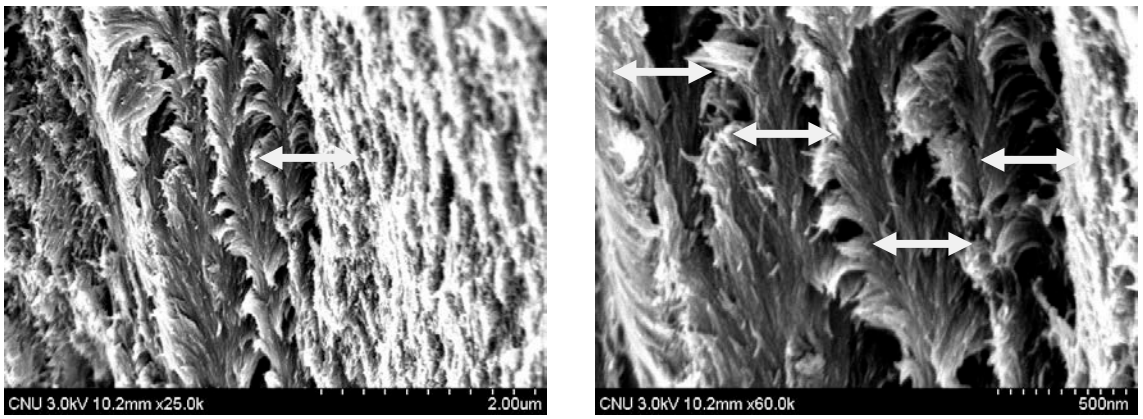
(a) (b)

Figure 3: FE-SEM morphology of multi-layered HW-CNCs at 0.5% conc.; (a) Evidence of circular self-assembly and (b) Twist

Jee *et al*. mentioned that the presence of the temperature gradient and of surface charge makeup makes possible the self-ordered and layer-by-layer formation of three-dimensional assemblies.[13] Therefore, it can be concluded that the circular self-assembly of CNCs in the wet state observed in this study is due to the low-temperature condition (4 °C). Picard *et al.* mentioned that the evaporation during drying led to self-ordering of CNCs into smectic liquid crystals, which is a liquid multilamellar structure.[6] The findings of our study indicate that these

multilamellar structures solidify into a multilamellar film within a thin film, as shown in Figure 4. The self-assembly of HW-CNCs exhibited two to three different circular patterns that can be distinguished as seen in Figure 2.

Moreover, the circular layered formation of CNCs was evident under FE-SEM. As previously discussed, the circular self-assembly of nanocrystals is due to hydrogen bonding, electrostatic force and other conditions.



(a) (b)

Figure 4: Cross-section of multi-layered CNC thin film (fractured) observed under FE-SEM (a) 2.0 μm and (b) 500 nm, as per image scale bar

The results support a novel approach to developing circular self-assembled CNC materials, 3D nanostructures, 3D engineering structures or other hybrid materials. As seen in Figure 3a and b, the multi-layered circular self-assembly of HW-CNCs, at a concentration of 0.5%, presents evidence of chiral nematic state and twist, which is in accordance with the findings reported by Gray *et al*.[4]

The surface characteristics of the HW-CNC thin film cross-section were observed by FE-SEM and presented in Figure 4a and b. The film exhibits the self-assembly of CNC multi-layers with a left-hand twist and distinct nematic pitch. The studies by Lee and Habibi *et al*. reported self-ordered or self-assembled (liquid phase) CNCs.[2-3] In this research, we have provided evidence of self-ordered or self-assembled HW-CNCs, which, as revealed by the FE-SEM images, are not limited to a few layers.

CONCLUSION

The CNCs obtained in this study had a rod-like structure, a length of 202 $\pm$ 52 nm and width of 14.9 $\pm$ 3.9 nm. OM and FE-SEM investigations confirmed the circular self-assembly of the HW-CNC suspension in the liquid and dried states. Furthermore, we demonstrated the formation of multi-layered self-ordering CNC films (at a concentration of 0.5% w/v) on the surface of the mica disk. Under FE-SEM, the multi-layered circular self-assembly of the HW-CNC thin film exhibited chiral nematic pitch and a self-ordered pattern of CNCs. The development of multi-layered circular self-assemblies of CNCs could open up new perspectives for preparing three-dimensional bio-based engineering materials.

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