

Impact of Colloidal Stability on Cellulose Nanocrystals Self-Ordering in Thin Films

Charles Bruel*, Jason R. Tavares, Pierre J. Carreau, Marie-Claude Heuzey**

Research Center for High Performance Polymer and Composite Systems (CREPEC),
Chemical Engineering Department, Polytechnique Montreal,
PO Box 6079, St. Centre-Ville, Montreal, QC H3C 3A7, Canada.

*charles.bruel@polymtl.ca

**marie-claude.heuzey@polymtl.ca

ABSTRACT

Sulfuric acid hydrolyzed cellulose nanocrystals (CNC) display interesting self-ordering properties in water. Applications include water casting of optically active CNC-based materials and composites. N,N-dimethylformamide (DMF)-cast materials do not display as good properties. Variations in CNC colloidal stability between water and DMF were proposed as an explanation for these behaviors. Here, we monitored the variations in optical properties of thin films cast from water, DMF, and their binary mixtures. Results are interpreted in light of the colloidal stability of CNC in these media.

Keywords: cellulose nanocrystals, thin films, self-assembly, solvent casting, colloidal stability.

1 INTRODUCTION

Cellulose nanocrystals (CNC) are biosourced and biodegradable rod-like nanomaterials with high expectations regarding their potential as fillers for nanocomposite applications [1, 2]. Despite CNC's mechanical and chiral properties [2, 3], CNC-based composites have been somewhat disappointing due to the difficulty encountered when dispersing these predominantly polar particles in non-polar matrices [1, 2]. This illustrates the need for protocols to improve dispersion and allow the transfer of CNC's useful properties to less polar media. Understanding of the mechanisms underlying the formation of CNC chiral self-assemblies is a key factor for developing novel applications in composite reinforcement, optical sensors, optical encryption, and chiral templating [3].

Scaled up to 1 ton/day [4], the most common process for CNC extraction involves a sulfuric acid hydrolysis that results in the introduction of sulfate half-ester groups on their surface [5]. Negatively charged, the particles may then form chiral nematic self-assemblies in water suspensions above certain concentration thresholds [3]. While the addition of up to 30-40 wt% of a water-soluble polymer such as poly(ethylene glycol) (PEG) interferes only slightly with the structure formation [6], 2-D percolation networks form down to a CNC weight fraction of 0.25 wt% upon water-casting of the nanocomposites [7].

Water-based processes are, however, unfit for non-polar polymers such as poly(lactic acid) (PLA). In recent years, PLA/CNC nanocomposites – a fully biosourced material – have been a hot topic in the literature [8] and N,N-dimethyl-formamide (DMF) one of the most common solvent for their casting due to its polarity [8, 9]. DMF, with its high dielectric constant ($\epsilon = 38.3$ at 20 °C) [10], is expected to be a good media to trigger CNC self-organization. A comparative rheological study of solvent-cast PEG and PLA/CNC nanocomposites, however, showed that CNC disperse better and form stronger percolation networks in PEG than in PLA [11]. The state of the CNC dispersion in water and DMF during the casting process was proposed as a potential explanation for this difference [11]. Indeed, while CNC form stable colloidal suspensions in water, they sediment within 40 h in DMF [12].

Here, we performed a comparative study of solvent-cast CNC thin films in binary mixtures of water and DMF in order to support this hypothesis. The level of CNC self-organization within the thin films, assessed through the quality of their iridescence, was monitored as a function of the colloidal stability of the suspensions.

2 MATERIALS AND METHODS

Sulfuric acid-hydrolyzed CNC, neutralized with Na⁺ counter-ions, were provided by Celluforce (Montreal, QC, Canada) as a spray-dried powder. Characterized as rod-like nanoparticles (~165 nm long times ~13 nm in diameter) with 3.4 –OSO₃Na groups per 100 anhydroglucose units (S/C atomic ratio of 0.0057), they have a zeta-potential of -48 mV in water at a pH of ~6.8 [13]. N,N-dimethylformamide was purchased from Sigma-Aldrich (purity of 99.90%). Distilled water was employed.

10 mL of the solvents or of their binary mixtures were added to 0.30 g of CNC in glass vials (2.1 cm radius). Dispersion was achieved through an ultrasonication treatment (Cole-Parmer ultrasonic probe with a CV334 converter and a tapered microtip). It operated at a frequency of 20 kHz, a power of ~29 W, and a total energy of 10,000 J/g_{CNC} with a pulse cycle ON-OFF of 5–2 s. Within 5 min of their sonication, the suspensions (10 mL) were poured in aluminium dishes. The solvent was evaporated for 72 h in an oven operating at 60 °C and atmospheric pressure with a slight air circulation.

Optical analysis was performed with a hyperspectral microscope (Olympus BX51, CytoViva[®]) operating with a 150 W quartz halogen light source (Fiber-Lite DC-950, Dolan Jenner Industries). Light intensity was kept constant at 40% from sample to sample and imaging was performed in reflective mode employing a 10X lens and an optical camera (Retiga-2000R Fast 1394, QImaging) without any filters.

3 RESULTS AND DISCUSSION

Our previous works on CNC colloidal stability [12, 14] demonstrated that our CNC form suspensions that are stable in water but fully sediment in DMF over time. Based on the Hansen solubility parameters theory, these results predicted that the addition of a small quantity of water percentage to DMF can provide a partial stability to the CNC particles, through an improvement of both the chemical affinity of the particles for their surrounding media and of the electrostabilizing effect [12]. The CNC state of dispersion significantly worsened as the volume fraction of DMF increased, going from transparent to opaque (Figure 1.a). The suspensions were stable (no sediment) up to 50 vol% of DMF, semi-stable (a sediment formed, but the supernatant remained cloudy over time) up to 90 vol% of DMF, and unstable (full sedimentation) beyond.

Upon casting, these suspensions yielded thin films whose optical properties, assessed visually, matched the various states of CNC colloidal stability (Figure 1). Stable suspensions yielded overall transparent films with a textured iridescence. Partially stable suspensions gave opaque films, but whose top layer was iridescent. DMF-cast films were discontinuous and fully opaque on both sides. They were made of CNC islands held together by thinner portions.

Optical microscopy micrographs (Figure 2), captured with a same light intensity, highlight the quality of the iridescence and of CNC self-ordering. Iridescence is indeed caused by the self-assembly of CNC in helicoidal structures whose pitch is in the range of visible wavelength [3]. The lighter the micrograph, the better is the quality of CNC helicoidal self-organization. The top side of the film (the one that was exposed to air during drying) was found to be systematically lighter than the bottom side (exposed to the aluminium dish) and to contain fewer defects. In water-cast films, defects, unobservable on the top side of the film, take the form of what seems to be CNC bundles 10-30 μm long and 2-3 μm wide at the film bottom. At 50 vol% of DMF in the initial binary mixtures, these small bundles cohabit with larger defects up to 200 μm in length and 15 μm in width on both sides of the film. From 80 vol% of DMF, the loss of the film optical transparency reflects sharply on the iridescence patterns and the larger defects, still slightly noticeable at 80 vol% of DMF are no longer distinct from the background at 90 vol% of DMF. On the bottom side, the surface gets more textured and iridescence is progressively lost. DMF-cast films present low to no

iridescence. While the bottom side is covered by millimeter long cracks that separate the different CNC islands, the top side present greater continuity, thus highlighting that the cohesion of the thin film is maintained by a thin crust located at the top layer of the film.

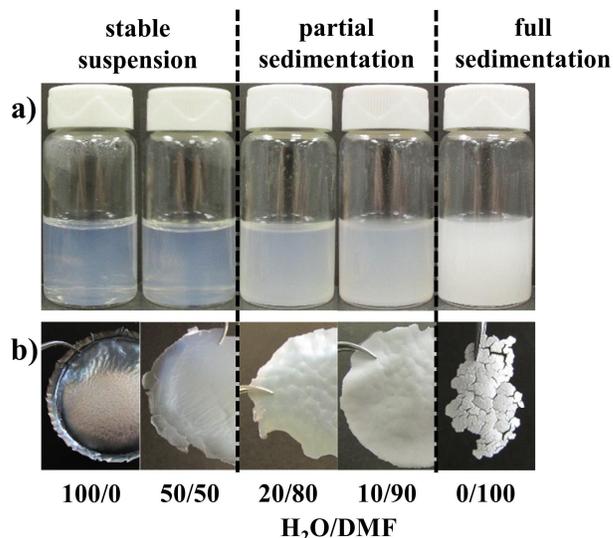


Figure 1: CNC colloidal behavior over time.

(a) Pictures of CNC suspensions (30 mg/mL) taken 5 min after sonication and just before pouring in the aluminium dishes for the solvent casting of the thin films (viewed from their top side) (b).

Our CNC, having 3.4 $-\text{OSO}_3\text{Na}$ groups per 100 anhydroglucose rings [13], are negatively charged upon redispersion provided that the solvent has a dielectric constant, ϵ , sufficiently high to trigger the dissociation of the $\text{O}^\delta-\text{Na}^{\delta+}$ bond. Dispersion is expected to induce significant dissociation and electrostatic stabilization for solvents with $\epsilon > \sim 11$ at room temperature [15]. Phase transition of sulfuric acid hydrolyzed CNC can be triggered by an increase in CNC concentration [3]: starting from a colloidal suspension, and if given sufficient time, CNC may form chiral nematic structures that keep evolving into gel-like glassy states. At this point, any further reorganization of the particles is made sterically impossible [3].

In water ($\epsilon = 80.1$ at 20 $^\circ\text{C}$ [10]), our CNC have a zeta-potential of ~ -48 mV at a pH of ~ 6.8 [13] and can form chiral nematic self-assemblies from given concentration thresholds [3]. These structures are preserved upon drying, thus yielding iridescent thin films [3]. DMF, itself a high dielectric constant solvent ($\epsilon = 38.3$ at 20 $^\circ\text{C}$), is expected to be a good media to trigger dispersion and self-organization of the CNC.

Sedimentation and evaporation are similar in that they both create gradients in CNC concentration that may locally trigger CNC phase transitions. Self-ordering is indeed expected to occur first in high concentration regions and then to propagate to lower concentration areas [16]. Upon drying of a stable media, CNC concentration increases

close to the air-liquid interface due to mass transfer limitations and CNC are expected to self-organize from the air-liquid interface in a top-down process [16]. Sedimentation tends, on the contrary, to create a bottom-up gradient in CNC concentration. Upon drying of an unstable suspension, a competition between a top-down and a bottom-up self-organization of the CNC is thus expected.

process, the increase in concentration appears to be slow enough to enable CNC to form chiral nematic structures that preserve their optical properties upon gelation. The sedimentation-driven bottom-up self-organization, however, seems to occur too fast to enable for the formation of chiral nematic structures. CNC likely form disordered percolated networks, labelled as glassy by Lagerwall et al. [3]. Up to 50 vol% of CNC, self-ordering appeared to be mostly a homogeneous top-down process. The presence of small defects and the fact that the bottom side was always darker than the top side, even in pure water, is an indication that sedimentation cannot be fully avoided upon casting. It is worth pointing out that water, having a lower boiling point than DMF [10], evaporates faster and that the volume fraction of DMF is thus expected to increase upon drying, thus reducing the colloidal stability of the CNC over time. In pure DMF, the process seems to be mostly bottom-up although the greater continuity observed at the top-layer of the film can be interpreted as a sign of the likely coexistence of the two processes.

4 CONCLUSION

Using water, DMF, and binary mixtures of water/DMF as solvents, we monitored the loss in iridescent properties of the thin films as the volume fraction of DMF in the initial media increases. The optical micrographs highlight the competition occurring between sedimentation and evaporation driven self-ordering in the thin films. Only the latter is found to result in interesting optical properties. The corresponding networks are found to be more continuous, and to provide greater cohesion to the films. These results support our previous observations regarding the comparative state of CNC dispersion in water and DMF-cast nanocomposites [11]. Ongoing work will focus on finding additives susceptible to preserve CNC self-ordering potential in DMF in order to promote the formation of CNC networks upon casting of nanocomposites.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Cellulose (Montreal, QC, Canada) for providing the CNC, as well as the financial support from FPIInnovations (Pointe-Claire, Québec, Canada), PRIMA Québec, the National Science and Engineering Research Council (NSERC), and the Fond de Recherche du Québec – Nature et Technologies (FRQNT). Dr. W. Y. Hamad (FPIInnovations) is thanked for his personal contribution in this project.

REFERENCES

- [1] Y. Habibi, L.A. Lucia and O.J. Rojas, “Cellulose nanocrystals: chemistry, self-assembly, and applications,” *Chemical Reviews*, 110(6), 3479-3500, 2010.
- [2] R.J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, “Cellulose nanomaterials review:

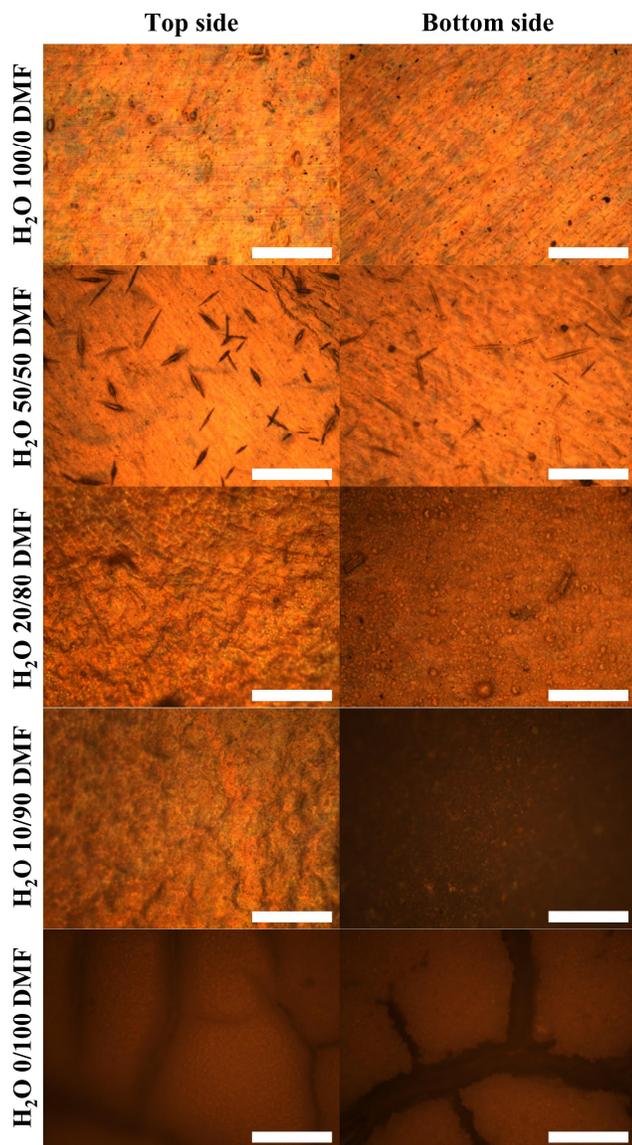


Figure 2: Optical microscopy micrographs of CNC thin films cast from binary mixtures of H₂O and DMF observed in reflective mode with a same luminosity of white unpolarised light. Scale bar is 250 μ m.

Our results suggest this competition to be significant at 10 and 20 vol% of water in DMF. These tests yielded films whose top and bottom optical properties differed strongly: the top side was highly iridescent while the bottom side appeared more textured and lacked optical properties. During the top-down evaporation-induced self-organization

- structure, properties and nanocomposites,” *Chemical Society Reviews*, 40(7), 3941-3994, 2011.
- [3] J.P.F. Lagerwall, C. Schütz, M. Salajkova, J.H. Noh, J.H. Park, G. Scalia and L. Bergström, “Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films,” *NPG Asia Materials*, 6, e80, 2014.
- [4] J. Miller, “Nanocellulose. State of the industry. December, 2015,” TAPPI International Conference on Nanotechnology for Renewable Materials, 2015. <http://www.tappinano.org/media/1114/cellulose-nanomaterials-production-state-of-the-industry-dec-2015.pdf>, accessed on 2019/04/16.
- [5] W.Y. Hamad, “Cellulose Nanocrystals Properties, Production and Applications,” Wiley, Chichester, UK, 2017.
- [6] M. Gu, C. Jiang, D. Liu, N. Prempeh and I.I. Smalyukh, “Cellulose Nanocrystal/Poly(ethylene glycol) Composite as an Iridescent Coating on Polymer Substrates: Structure-Color and Interface Adhesion,” *ACS Applied Materials & Interfaces*, 8(47), 32565, 2016.
- [7] Q. Beuguel, J.R. Tavares, P.J. Carreau and M.-C. Heuzey, “Rheological behavior of cellulose nanocrystal suspensions in polyethylene glycol,” *Journal of Rheology*, 62, 607-618, 2018.
- [8] J.-M. Raquez, Y. Habibi, M. Murariu, P. Dubois, “Polylactide (PLA)-based nanocomposites,” *Progress in Polymer Science*, 38(10-11), 1504-1542, 2013.
- [9] D. Bagheriasl, P.J. Carreau, B. Riedl, C. Dubois and W.Y. Hamad, “Shear rheology of polylactide (PLA) -cellulose nanocrystal (CNC) nanocomposites,” *Cellulose*, 23(3), 1885-1897, 2016.
- [10] D. Lide, “CRC Handbook of Chemistry and Physics,” CRC, Boca Raton. Florida., 85th edn, 2004.
- [11] Q. Beuguel, D. Bagheriasl, C. Bruel, J.R. Tavares, P.J. Carreau and M.-C. Heuzey, “Comportement rhéologique à l'état fondu de nanocomposites à base de nanocristaux de cellulose (CNCs),” *Rhéologie*, 34, 10-16, 2018.
- [12] C. Bruel, J.R. Tavares, P.J. Carreau and M.-C. Heuzey, “The structural amphiphilicity of cellulose nanocrystals characterized from their cohesion parameters,” *Carbohydrate Polymers*, 205, 184-191, 2019.
- [13] Q. Beuguel, J.R. Tavares, P.J. Carreau and M.-C. Heuzey, “Ultrasonication of spray- and freeze-dried cellulose nanocrystals in water,” *Journal of Colloid and Interface Science*, 516, 23-33, 2018.
- [14] C. Bruel, Q. Beuguel, J.R. Tavares, P.J. Carreau and M.-C. Heuzey, “Apparent Structural Hydrophobicity of Cellulose Nanocrystals,” *The Journal of Science and Technology for Forest Products and Processes*, 7, 13-23, 2018.
- [15] Ph.C. Van Der Hoeven and J. Lyklema, “Electrostatic stabilization in non-aqueous media,” *Advances in Colloid and Interface Science*, 42, 205-277, 1992.
- [16] O.F. Aguilar Gutierrez and A.D. Rey, “Biological plywood film formation from para-nematic liquid crystalline organization,” *Soft Matter*, 13, 8076-8088, 2017.