

Moisture Uptake Characterization in Nanocellulose Using Microwave Cavity

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ABSTRACT

Cellulose nanocrystal films with different helical modulation lengths are characterized. Films are obtained by tuning the rate of evaporation and surface functionalization. Non-contact dielectric measurements are performed using microwave cavity and the water confinement is estimated by employing the classical mixing model with randomly oriented ellipsoidal inclusions. The dielectric constant of absorbed water was found to be significantly smaller than that for free liquid, indicating a limited mobility due to binding with CNC matrix.

Keywords: cellulose nanocrystals, water confinement, dielectric properties.

1 INTRODUCTION

Nanocellulose has been a continuously emerging area of interest over the recent years due to the inexpensive, abundant, and renewable nature of the material source. Cellulose nanocrystals (CNCs) are regarded to be highly useful candidates for a sustainable way of polymer reinforcement. In this regard, investigating the interaction of absorbed water with CNCs is essential to understand its effects on dispersion, wetting, interfacial adhesion, matrix crystallization, and water uptake, all which have critical importance in the utilization and high-scale production of nanocomposites.

Here we consider CNC films cast from water dispersions under controlled drying rate as model structures. For dielectric characterization, a non-contact microwave cavity perturbation method is used [1,2]. The method enables permittivity measurements with adequate accuracy to investigate water confinement in the CNC films. Films are studied via reflectance spectroscopy for measurement of their structural periodicity. In addition, scanning electron microscopy (SEM) is used for imaging, and numerical evaluation of the pitch distributions.

2 EXPERIMENTAL

CNC films were cast from 1.5 % by mass aqueous suspensions inside a sealed Plexiglas chamber. The chamber was supplied with purified air with a relative

humidity of 20 % and temperature of 20 °C. Humidity inside the chamber was varied using an evaporation pad with controlled de-ionized water supply. The mass of the CNC suspension, temperature and the relative humidity (RH) inside the chamber were continuously recorded and RH was adjusted according to a computer algorithm that executes the desired drying rate profile. Two drying rates of -7 mg/min and -13 mg/min were employed.

Sulfated CNCs neutralized to a sodium form (Na-CNC) were obtained from the University of Maine Process Development Center. In addition, Na-CNCs functionalized with methyl(triphenyl)phosphonium cations (MePh3P-CNC) were also cast. [3]

The complex relative permittivity, $\epsilon_r = \epsilon_r' - j\epsilon_r''$, of the CNC films was measured at 7.435 GHz utilizing a non-contact cavity perturbation method [1,2], which allows precise measurement of the dielectric permittivity in quantitative correlation with the moisture content. Specimens of CNC films, size of 8 mm × 15 mm and thickness between 30 μm and 60 μm, were cut from the freshly cast films that typically contain 5 % of water by mass. Water concentration was determined gravimetrically by weighing the specimens on a balance with a readability of 100 nanograms. The initial water content was determined by drying films to constant mass at 120 °C for several hours inside of a glove box. By re-exposing CNC to humid air, the water concentration in CNC was varied from about 0 % to about 9 % by mass. At different time intervals during the adsorption, moisture content in the samples was determined gravimetrically, and cavity measurements were performed at room temperature (20 °C).

The total reflectance and transmittance spectra were recorded from 200 nm to 2000 nm with 1 nm step resolution and at slit widths between 4 nm and 10 nm using a Perkin Elmer Lambda 950 Spectrophotometer equipped with an integrating sphere kit. The combined relative uncertainty in determining the helical pitch from the reflection maximum is ± 5 nm.

The optical microscopy images were obtained in a polarized optical microscope (POM) using a 5× objective with numerical aperture NA = 0.13. The images are obtained in cross polarization configuration.

The cross-sections of the dried CNC films were imaged using an SEM at 2 kV accelerating voltage, a current of 50

pA, and pixel sizes varying between 15 nm to 30 nm. A working distance of 4 mm was used.

3 RESULTS AND DISCUSSION

Measured dielectric constant for slow and fast-dried Na-CNC and MePh3P-CNC films are shown in Table 1.

Material	Drying rate	Dielectric constant by mass of water			
		0%	2%	4%	6%
Na-CNC	Slow (-7 mg/min)	3.31	3.69	3.94	4.40
Na-CNC	Fast (-13 mg/min)	3.10	3.30	3.53	3.70
MePh3P-CNC	Slow (-7 mg/min)	2.98	3.05	3.17	3.36
MePh3P-CNC	Fast (-13 mg/min)	2.99	3.05	3.19	3.39

Table 1: Dielectric constant values of CNC films measured using non-contact resonant cavity perturbation method.

The dielectric constant of the slow dried Na-CNC film is considerably larger compared to films dried at faster rates. In comparison, at the corresponding water concentration, the dielectric constant of phosphonium modified MePh3P-CNC films is smaller, and evidently much less dependent on the drying rate. The measured dielectric constant difference between the specimens dried at different rates can be attributed to the degree of chiral ordering in the films, which we discuss in the following sections.

Figure 1 shows the reflectance spectra of Na-CNC and MePh3P-CNC films obtained at different evaporation rates. The reflectance spectrum is found to get consistently narrower and shift to lower wavelengths when the films are cast at slower evaporation rates. It can be observed that continuous monitoring and control of the drying rate, together with the relative humidity and temperature of the ambient, yields films that are self-organized into well-defined and distinguishably different chiral structures with a characteristic pitch (P). Due to the constructive interference between the propagating and back-reflected waves from this periodic structure the CNC films exhibit a selective Bragg reflection [4,5] at $\lambda_{\max} = (P/2)\sqrt{\epsilon_r}$. Since the dielectric constant of CNC films is about 4 and thus the average refractive index, $n \approx 2$, the helical pitch distribution corresponds directly to the distribution of Bragg reflectance wavelengths.

The films when imaged using polarized optical microscopy displayed multicolored structures in reflectance mode with dominant colors varying based on evaporation conditions and functionalization as shown in Figure 2 together with the corresponding reflectance peak values. The POM images are in agreement with the spectral distributions of the helical pitch P . We also note that the

fast dried Na-CNC film was observed to be colorless as it reflects in the near-infrared wavelengths, beyond the visible range.

In order to further investigate the variations in the optical properties arising from differences in evaporation rates as well as from surface functionalization, we studied the structure of the CNC films using SEM.

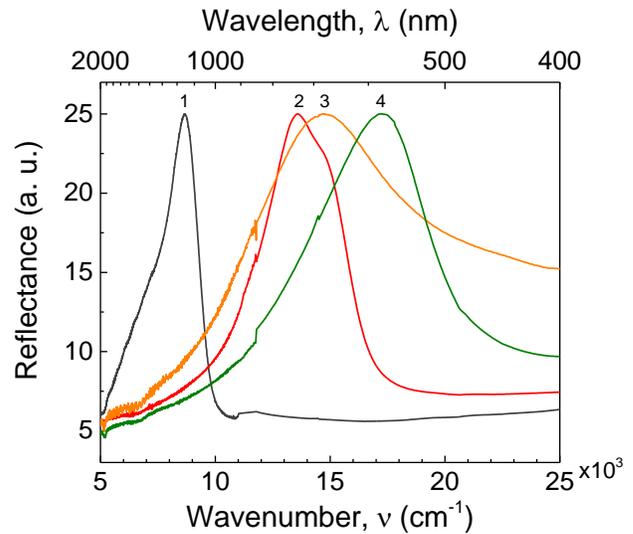


Figure 1: The reflectance spectra of the CNC films by drying rates and functionalization. Na-CNC films: 1 – fast, 2 – slow. MePh3P-CNC films: 3 – fast, 4 – slow. The peak corresponds to the helical pitch, $P \approx \lambda_{\max} = 1/\nu_{\max}$.

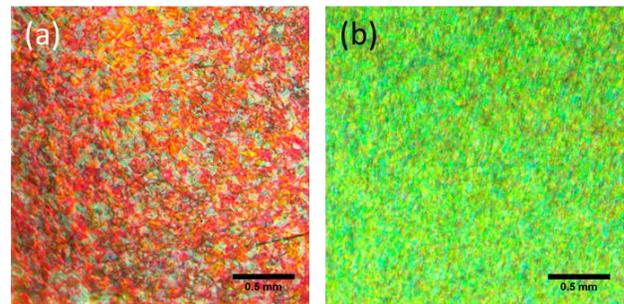


Figure 2: Polarized optical microscope images of (a) Slow dried Na-CNC ($P = 736$ nm). (b) Slow dried MePh3P-CNC ($P = 590$ nm). Scale bars represent 0.5 mm.

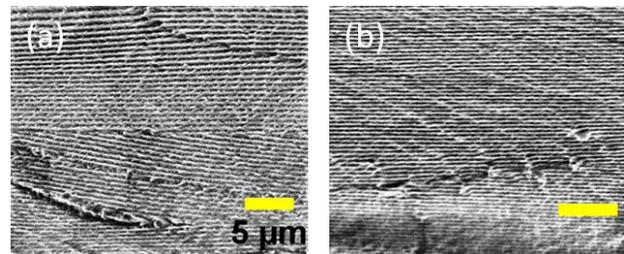


Figure 3: SEM images for (a) Fast dried Na-CNC ($P_1 = 1000$ nm). (b) Slow dried Na-CNC ($P_1 = 606$ nm).

Figure 3 shows the sample SEM images of the cross-section of films. In order to quantitatively evaluate the SEM imaging results, pitch distributions were calculated via image processing. Subsequently, the pitch distributions were fit with Gaussians to obtain peak positions and peak widths (defined at one standard deviation) as shown in Table 2.

Material	Drying rate	P ₁ (nm)	ΔP ₁ (nm)	P ₂ (nm)	ΔP ₂ (nm)
Na-CNC	Slow (-7 mg/min)	606	151	-	-
Na-CNC	Fast (-13 mg/min)	1000	350	1500	250
MePh3P-CNC	Slow (-7 mg/min)	504	186	-	-
MePh3P-CNC	Fast (-13 mg/min)	619	190	1045	149

Table 2: The nominal pitch distributions measured from the SEM images of films.

Comparing the reflectance spectra and the SEM results in terms of the peak wavelengths and peak widths, we find that the calculated pitch distributions are in good agreement with the reflectance data. We note that the SEM helical pitch values are somewhat lower than the pitch from the peak reflectance wavelengths. This is attributed to the fact that the reflectance was measured in air as opposed to SEM images, which were obtained in vacuum. In air, we expect swelling from a small amount of absorbed moisture.

Within the assumption that the water uptake into CNC films occurs in between the crystals rather than the swelling individual nanocrystals, the films can be modeled as a two-phase CNC-water mixture. Here we follow the Maxwell Garnett classical mixing approach with randomly oriented ellipsoidal inclusions of water with semi-axial dimensions $a_x, a_y = a_x, a_z$, along x, y, z directions, respectively. [6,7]

The axial parameters of the water inclusions are obtained by fitting the measured dielectric constant of the films against the mixing model with the axial ratio a_x/a_z and the dielectric constant of water being the fitting parameters. The susceptibility ratio is defined by [7]

$$SR = (\epsilon_{eff} - \epsilon_{CNC}) / (\epsilon_{water} - \epsilon_{CNC}) \quad (1)$$

where ϵ_{water} , ϵ_{CNC} , and ϵ_{eff} are the dielectric constants of the water, the CNC film at 0 % water by mass, and the mixture, respectively.

At our measurement frequency of 7.4 GHz, assuming that the $\epsilon_{water} = 65$ for free water in the mix [8], the calculated ϵ_{eff} results in significantly higher values than the experimental data. Consequently, assuming the water inclusions remain spherical for MePh3P-CNC films, where the drying rate has a negligible effect on the dielectric constant (see Table 1), ϵ_{water} is calculated to be 33. This

indicates a strong interaction between water and CNCs. Setting $\epsilon_{water} = 33$, the axial ratios obtained by fitting the data points to Equation 1 are equal to 30 and 6, for slow-dried and fast-dried Na-CNC films, respectively.

Given that our CNCs differ not only in their mesostructures but also in their affinity to water, we can attribute the water confinement shape in Na-CNCs primarily to intermolecular interaction modulated packing. Na-CNC films from the slow dry process have smaller pitch and therefore tighter packing, which we believe leads to a greater deviation from a spherical shape compared to the fast dried films of lower density and larger pitch. The compression in shape is magnified by the attractive interactions between the hydrophilic Na-CNCs and water. In comparison, in the case of less hydrophilic MePh3P-CNCs, interactions with water are apparently weaker allowing water inclusions to assume spherical shape even in tighter pitch.

4 CONCLUSION

Both the functionalization and the drying rate of aqueous suspensions of CNCs are of critical importance in determining the final film structure, with fast dried films displaying looser packing and larger disorder in long range periodicity as evidenced by SEM images and wider, higher wavelength reflectance peaks.

The microwave cavity perturbation method allowed non-contact dielectric constant measurement of the CNC films. Through an approach using classical mixing models with randomly oriented ellipsoidal water inclusions, it is found that in the case of hydrophilic Na-CNCs, a decreasing pitch led to greater anisotropy in the shape of moisture inclusions (ellipsoidal or platelet-like). In contrast, the structure of hydrophobic phosphonium-cation modified CNC films are found to have little influence on absorbed water inclusions, which remain free and predominantly spherical. These results provide a useful perspective on the current state of understanding of CNCs materials and are beneficial for the realization of CNC functional materials and composites.

REFERENCES

- [1] Obrzut, J.; Emiroglu, C.; Kirillov, O.; Yang, Y.; Elmquist, R. E. Surface Conductance of Graphene from Non-Contact Resonant Cavity. *Measurement*, 87, 146–151, 2016.
- [2] Orloff, N. D.; Obrzut, J.; Long, C. J.; Lam, T.; Kabos, P.; Novotny, D. R.; Booth, J. C.; Liddle, J. A. Dielectric Characterization by Microwave Cavity Perturbation Corrected for Nonuniform Fields. *IEEE Trans. Microw. Theory Tech.*, 62, 2149–2159, 2014.
- [3] Fox, D. M.; Rodriguez, R. S.; Devilbiss, M. N.; Woodcock, J.; Davis, C. S.; Sinko, R.; Keten, S.; Gilman, J. W. Simultaneously Tailoring Surface Energies and Thermal Stabilities of Cellulose Nanocrystals Using Ion Exchange:

Effects on Polymer Composite Properties for Transportation, Infrastructure, and Renewable Energy Applications. *ACS Appl. Mater. Interfaces*, 8, 27270–27281, 2016.

[4] Lagerwall, J. P. F.; Schütz, C.; Salajkova, M.; Noh, J.; Hyun Park, J.; Scalia, G.; Bergström, L. Cellulose Nanocrystal-Based Materials: From Liquid Crystal Self-Assembly and Glass Formation to Multifunctional Thin Films. *NPG Asia Mater.*, 6, e80, 2014.

[5] de Vries, H. Rotatory Power and Other Optical Properties of Certain Liquid Crystals. *Acta Crystallogr.*, 4, 219–226, 1951.

[6] Landau, L. D.; Lifšic, E. M.; Pitaevskij, L. P.; Landau, L. D. *Electrodynamics of Continuous Media; Course of theoretical physics; 2. ed., and enl.; Elsevier, Butterworth-Heinemann: Amsterdam [u.a], 2008.*

[7] Sihvola, A. H. *Electromagnetic Mixing Formulas and Applications; IEE electromagnetic waves series; 1st ed. /Reprint with new cover.; Institution of Engineering and Technology: London, 1999.*

[8] Hasted, J. B. *Aqueous Dielectrics; Studies in chemical physics; Chapman and Hall, New York: London, 1973.*