Application Note # 158

# Predicting Cellulose Nanocrystals Dispersibility using MP-SPR


*Cellulose nanocrystals (CNCs) are rod-shaped nanomaterials utilized in biomedical devices, emulsion stabilizers, rheological modifiers and in various other composite applications. Multi-Parametric Surface Plasmon Resonance (MP-SPR) is a highly sensitive label-free method used to study surface changes. Swelling of CNC films was measured using MP-SPR to probe particle–particle cohesion in the film and thus predict dispersibility of the film. This study focuses on CNC agglomerates which may be present during nanocomposite compounding.*

*Water swollen CNC films showed a 14 ± 2% increase in thickness when compared to dry CNC films. Organic solvents increased the volume of hydrophilic CNC films less than water: acetone by 4% and methanol, acetonitrile, isopropanol and ethanol in the range of 6 to 8%. The hydrogen bonding ability of the solvent correlated well with film swelling. Nevertheless, highly polar aprotic acetonitrile was equally effective as alcohols.*


## Introduction

Surface Plasmon Resonance (SPR) is a well-established method used to determine kinetics and affinity of biomolecular binding reactions. Nowadays, SPR is applicable also in material characterization. Comprehensive Multi-Parametric Surface Plasmon Resonance (MP-SPR) instruments can perform measurements in an exceptionally wide angular range (40-78 degrees) and can utilize more than one wavelength, thus making MP-SPR an outstanding tool especially for materials characterization.

MP-SPR can measure adsorption of molecules and the same measurement provides also information on layer thickness and its optical properties. For mostly transparent materials, the measured layer thickness can range from nanometers up to micrometers. Layer characterization can be seamlessly done in air and in various solvents without any change in the instrument setup. The elastomer-coated prism used with MP-SPR allows oil-free operation, which combined with the handy sensor slide holder (Figure 1) enables further characterization of the coating with other methods, such as AFM or SEM. Additionally, the sensor slide can be easily coated *in situ* and *ex situ*.

**Figure 1.** The convenient sensor slide holder of MP-SPR Navi™ allows easy functionalization of a sensor *in situ* and *ex situ*. There is a multitude of methods for coating, such as spray coating, CVD, MBE, ALD, sol-gel deposition, Langmuir-Blodgett monolayer depositions, spin coating, dip coating, self-assembly, electrochemistry etc. Additionally, the sensor slide can be further characterized using AFM, SEM or microscopy.

## Materials and methods

CNCs were prepared by sulfuric acid hydrolysis. The CNC dimensions were 4 – 15 nm by 50 – 306 nm with an average length of 8 nm and 122 nm respectively, measured from 100 particles by AFM. $SiO_2$ coated SPR sensor slides were cleaned using piranha solution (3:1 concentrated sulfuric acid to hydrogen peroxide). CNCs were spin coated under $N_2$ gas at 4000 rpm for 30 s with a 7 second acceleration/deceleration time. Layer thickness was controlled by varying the CNC suspension concentration between 1 and 3 weight percent. Sensor slides were heat-treated at 80 °C for 8 hours in order to remove water from the film, and then moisturized and reheated (overnight) to achieve reduction of orientation in the film (Reid et al. 2016).

Cellulose films were characterized in air and in liquids using MP-SPR Navi™ 200-L OTSO instrument. Swelling was monitored *in situ* during 30 minutes in water, acetone, methanol, acetonitrile, isopropanol, and ethanol (Figure 2).

Thickness and refractive index of the CNC films were determined using 2 wavelength (670 nm and 785 nm) method. The sensor slide was measured before and after CNC deposition. Cellulose has a Sellmeier-type dispersion and the dispersion value (dn/dλ) was estimated to be -0.0271 $\mu m^{-1}$ at the wavelengths used (Sultanova et al. 2009). Volume averaging theory (VAT) introduced by Braun and Pilon, was utilized to determine volume fraction of solvent in the swollen film.

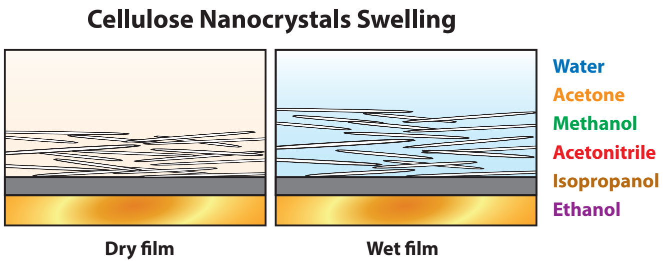


**Figure 2.** Swelling of cellulose nanocrystals (CNC) was studied using MP-SPR. Dry and wet films were studied in various solvents to predict dispersibility of the film for composite applications.

## Results and discussion

In air CNC film thickness was 39.7 ± 0.6 nm and refractive index 1.458 ± 0.008 (Figure 3). A CNC film is rougher than the $SiO_2$ coating which can be seen from the change in peak minimum intensity, when full SPR curves before and after the coating are compared (Figure 3). MP-SPR results were in good agreement with the 40 ± 5 nm thickness measured by AFM.

Composition of the spin coated CNC film in air was calculated to be 20 ± 2% air and 80 ± 2% CNC by volume. The highest volume fraction of swollen film was in water, as expected due to hydrophilic nature of CNC (Figure 4). Less swelling is occurring in the non-aqueous solutions. The amount of swelling

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increased in presence of acetone, methanol, acetonitrile, isopropanol, and ethanol (ordered by degree of swelling).

Additionally, CNC films were measured with increasing flow-rates (100-500 µL/min). Despite large swelling and increased shear stresses (0.3 – 1.4 dyne per $cm^2$) on the surface, CNC film was not removed from the $SiO_2$ surface in the range of flow-rates studied.

Based on the literature, it was assumed that CNC films would swell by increasing inter-particle spacing. CNCs are insoluble in the solvents used. However, solubility parameters as "dispersibility parameters" combined with SPR swelling allow prediction of CNC – CNC cohesive interactions in aqueous and non-aqueous environments. The cohesive interactions of CNCs remain strong in all of the solvents tested, and are caused by attractive van der Waals forces.

See also how MP-SPR can be used to measure binding of solubilizing agent (NMMO) to cellulose nanofibrils (CNFs) in water and methanol to determine the best solvent for the partial dissolution treatment (Orelma et al. 2017).

## Conclusions

MP-SPR was utilized to predict particle–particle cohesion and film dispersibility. MP-SPR offers exciting solutions for characterization of soft thin films. Film deposition can be done *in situ* and *ex situ*, before film characterization in air and in liquids. MP-SPR Navi™ instruments capture full SPR curve within a few seconds and do not require vacuum. Following the real-time label-free measurements using MP-SPR, coatings can be cleaned in order to reuse the sensor or further analyzed *ex situ*. MP-SPR provides both layer properties and interactions from one experiment.

See more about polymer characterization using MP-SPR: mass and thickness of block-co-polymers adsorbed on cellulose nanofibrils (CNF), and adsorption of serum components onto the poly(ethylene glycol) polymer brushes (Application Note #149).

## Original publication

Reid et al., Nanoscale, 2016, 8, 12247

## References


Orelma et al., Cellulose, 2017, DOI 10.1007/s10570-017-1229-6

Sultanova et al. Acta Physica Polonica A 116, 585-587 (2009)


| Recommended instrumentation for reference assay experiments |
| --- |
| MP-SPR Navi™ 200 OTSO or 210A VASA with additional wavelength (-L) |
| Sensor surfaces: $SiO_2$, metal or other inorganic coatings |
| Software: MP-SPR Navi™ Control, DataViewer, and LayerSolver |

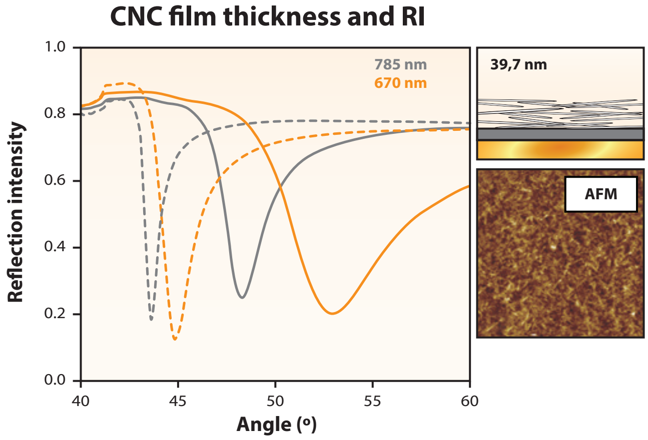


**Figure 3.** Thickness and refractive index of CNC film measured in air. Full SPR curves before coating (dashed line) and with CNC film (solid line). Based on two wavelength analysis (670nm and 785nm), dry CNC film thickness were 39.7 ± 0.6 nm and refractive index was 1.458 ± 0.008. Results were in good agreement with the thickness measured by AFM 40 ± 5 nm.

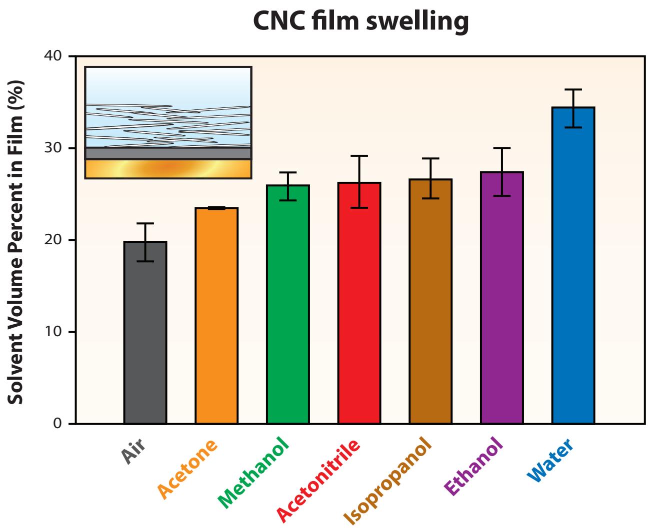


**Figure 4.** Volume percent (vol%) of solvent and air in the CNC film. Highest volume fraction of swollen film was observed in water and less swelling occurred in the non-aqueous solutions.




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