Effect of Cellulose Nanocrystal Alignment on Thermo-Mechanical Response

Abstract. *The alignment of cellulose nanocrystals (CNCs) can be used to create property anisotropy within bulk CNC films. This quality was evaluated on the thermo-mechanical properties of various tape-cast aligned CNC films. Mechanical properties were measured by dynamic mechanical analysis (DMA) and the in-plane coefficient of thermal expansion (CTE) by contact-free digital image correlation (DIC). Results showed a high-level anisotropy that corresponded to the degree of CNC alignment within the films.*

Keywords. cellulose nanocrystals, Herman's order parameter, tape casting, digital image correlation.

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Introduction. Cellulose nanocrystals (CNC) can exhibit a high degree of orientation under the influence of electric, magnetic, and shear forces. Such forces can be used independently or in combination to align CNCs successfully. Tape casting of CNC aqueous suspensions offers significant advantages over other nanoparticle alignment techniques (industrial scaleup) and has been demonstrated to be very effective in aligning cellulose nanocrystals. Multiple variables such as pH, drying conditions, type of substrate, and nanoparticle concentration must be tuned to achieve different orientations in CNC films. Amid several techniques used to determine nanoparticle alignment (e.g., atomic force microscopy, stereology, etc.), two-dimensional X-ray diffraction (2D-XRD) combined with Herman's order parameter calculations are attractive because a quantitative description of CNC alignment through the thickness of the films can be obtained. [1] Thus, understanding the interconnection between CNC alignment and thermo-mechanical response in CNC films will provide insight into property-wise material designs.

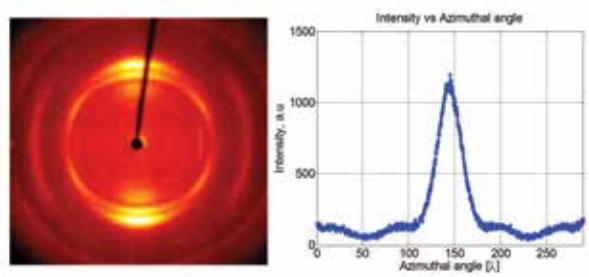

Figure 1. *(left) 2D-XRD pattern of an aligned CNC film with S=0.45. (right) Intensity vs. azimuthal angle around (200) plane.*

Methodology. Aqueous CNC suspensions provided by the U.S. Forest Product Laboratory were adjusted in pH and concentration to achieve both stability and appropriate rheological response. The resulting suspensions were cast at different shear rates over glass substrates and left to evaporate at ambient conditions. The CNC films were characterized by thermal gravimetric analysis (TGA), 2D-XRD, dynamic mechanical analysis (DMA), and contact-free digital image correlation (DIC) [2]. The 2D-XRD measurements (Bruker GADDS X-Ray Diffractometer, Cu_{α} source) used the (200) plane reflections along the azimuthal angle to characterize CNC alignment. DMA tests, using a special tabbing setup to align and hold CNC films properly using the tension clamps, measured the mechanical properties under ambient conditions. The DIC measurements used an inverted Zeiss optical microscope coupled with a heating stage to capture images at different temperatures from room temperature to 100°C. The images were processed for contrast enhancement and then correlated using a MATLAB open-source routine [3] together with the Image toolbox.

Results. Cast CNC films were pretreated at 100°C to remove any physisorbed water. After obtaining 2D-XRD scanned signals of the CNC films (Fig. 1), an integration of the intensity of the (200) plane for cellulose Iβ vs. azimuthal angle from 0°C to 180°C is necessary to calculate the Herman's order parameter (S). A random film is represented by S=0.0, whereas a perfectly aligned one will yield a narrow and sharp distribution represented by S=1.0. CNC films prepared by tape casting will usually exhibit a Herman's order parameter in the range from 0 to 0.8.

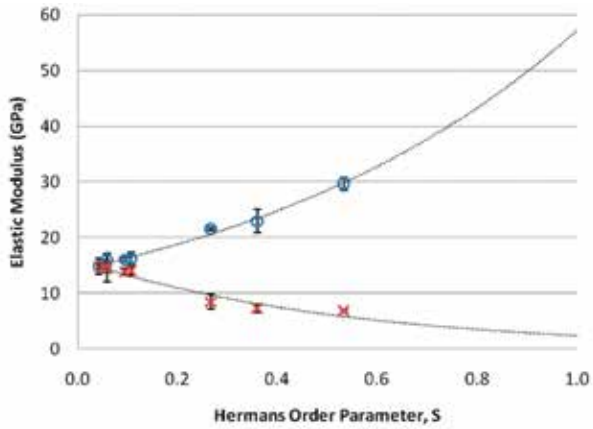

Figure 2. *CNC axial (o), and transverse (x) elastic moduli as a function of orientation in aligned CNC films [4].*

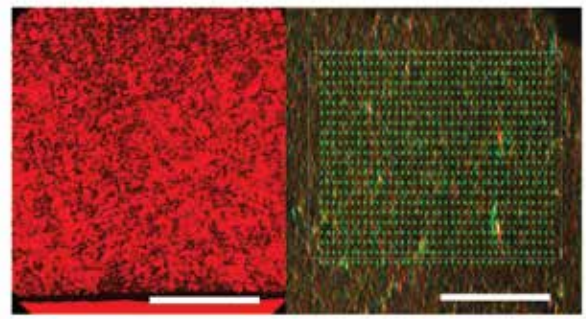

Figure 3. *a) Random CNC film b) Correlation grid for thermal expansion measurement of an aligned CNC film using DIC. Scale bar 500 μm.*

An evident anisotropic response is found for cast CNC films as we compare the elastic modulus (Fig. 2) in the casting direction (axial) with that in the perpendicular direction (transverse). The CTE in the axial direction of a S=0.45 CNC film made using DIC with a high-contrast speckle pattern (Fig. 3) is 14 ppm/K, whereas a random film shows a CTE of 25 ppm/K. Therefore, as the order parameter increases in the axial direction, so does the elastic modulus, whereas the CTE decreases. As expected, CNC films tested in the transverse direction yielded the opposite response. The CTE of the same S=0.45 CNC film in the transverse direction is 85 ppm/K, which is similar to the value obtained for reinforced polymers.

Conclusions: The preparation of high-quality CNC films involves the interaction of multiple parameters that must be finely tuned to design property-wise films and materials. The Herman's Order Parameter, combined with two-dimensional X-ray diffraction, provides reliable information about CNC alignment throughout the sample thickness, as compared to superficial alignment determination techniques. The in-plane CTE can be determined using DIC in a non-contact fashion, a characteristic that becomes vital in sensitive CNC film testing. As CNC alignment increases within the films, the thermal and mechanical properties are reinforced in the aligned direction, while they are relaxed in the perpendicular direction. Conceptually, CNC films can exhibit both ceramics-like and polymer-like properties depending on film orientation.

References

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Production and Applications of Cellulose Nanomaterials

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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