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# Nanomechanical properties of cellulose nanofibrils (CNF)

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## ABSTRACT

Cellulose is an abundant green polymer, which can be obtained in a variety of nanoscale structures broadly grouped as nano/microfibrils (CNF/MFC), bacterial celluloses (BC) or nano/microcrystals (CNC/CMC). There is increasing interest of nanocelluloses by the research and industrial communities due to increasing available materials (facilities than can produce ton per day), impressive strength properties, low density, renewability and biodegradability. However, one problem is the lack of knowledge on the nanomechanical properties of cellulose nanofibrils, which creates barriers for the scientists and producers to optimize and predict behavior of the final product.

In this research, the behavior of thin filmed (t≤100 µm) cellulose nanofibrils', located on aluminum pin stubs, under nano compression loads were investigated using an Asylum Research MFP-3D Atomic Force Microscope equipped with a nanoindenter. Unloading curves were analyzed using Oliver-Pharr. As a result of 58 successful nanoindents, the average modulus value was estimated as 16.6 GPa with the reduced modulus value of 18.2 GPa. The CNF Modulus values varied between 12.4 GPa – 22.8 GPa with 16.9% coefficient of variation (COV) while the reduced modulus ranged from 13.7 GPa to 24.9 GPa with a 16.2 % COV.

This research provides practical knowledge for producers of nanocellulose, researchers and applications developers who focus on nanocellulose reinforced composite materials.

## INTRODUCTION

Cellulose is a biopolymer, which can be isolated from nature (woods, plants, bacteria and even animals) [1,2]. CNFs have received much attention because of their low density, nonabrasive, combustible, nontoxic and biodegradable properties [3], which makes them suitable for the reinforcement material in composite structures [4].

Previous studies have evaluated the nanomechanical properties of nanocellulose to understand its role in the composite structures. The elastic modulus of regenerated cellulose fibers (Lyocell) was determined as between 12 GPa and 17 GPa while that of viscose cellulose fibers to vary between 7 GPa and 13 GPa [5].

These impressive mechanical properties and the increased availability of large volumes of material (multiple facilities are in place in North America and Europe with production capacities up to 2000 lb per day) have made these organic polymers more attractive for the industry and the researchers. However, the limited knowledge on the nanomechanical properties [6] of cellulose nanofibrils creates an opportunity for research to provide information, which will be of value to the research community and industry.

In this study, the nanomechanical properties of the cellulose nanofibrils (CNFs) were determined using a nanoindentation technique and an MFP-3D Atomic Force Microscope (AFM) equipped with a Nanoindenter (Asylum Research).

## MATERIALS & METHODS

### Sample Preparation

Softwood cellulose nanofibril suspensions were produced at the University of Maine Process Development Center. The solids content (3.4% by wt.) of the CNF suspension were determined (Denver IR 35 Moisture Analyzer). The suspension was poured into 1.5 mL. polypropylene graduated microcentrifuge tubes and ultrasonicated for 1 hour (VWR 550 HT Ultrasonic Cleaner). The ultrasonicated suspension was centrifuged (Eppendorf Minispin Plus) at 14,500 rpm for 10 minutes. The transparent (liquid) portion, diluted portion was placed on aluminum pin stubs, dried at 30 °C for 1 hour, and than located in the heat controlled AFM chamber (24±1 °C) for 24 hours.

### Analysis Tool & Nanoindentation Technique

The atomic force microscope is a tool invented in 1986 by Bining, Quate and Gerber [7], which allows high-resolution 3D imaging of the material surfaces [8]. It also enables the determination of nanomechanical properties of the materials providing force-distance curves. In this research, an Asylum Research MFP-3D Atomic force microscope equipped with a Nanoindenter was used for 3D imaging and nanomechanical measurements. All samples were imaged using tapping mode (non-contact or AC mode) with an Asylum Research AC240TS-10 cantilever tip with a 9±2 nm radius. The spring constant (k) was =2 N/m (0.5-4.4). The first scanning area was chosen 40 micron X 40 micron to understand and evaluate the fibril distribution, than zoomed to the 5 micron X 5 micron area.

Nanoindentation is a technique, which allows determination of the nanomechanical properties of materials. As with any experimental method – it is vital that the procedure used is repeatable and that the instrument is calibrated [9].

In this study, the indenter tip was imaged, particles and dusts on the tip surface cleaned and the area was calculated according to the tips' geometrical shape. The tip was then installed in the Asylum Research MFP-3D Nanoindenter Head located in a temperature-controlled chamber for 24 hours. After the thermal equilibration period, the device was calibrated. Additional detail on the experimental procedures and analytical assumptions are below.

### Indented Area Calculation & Assumptions

The tip used in the integrated nanoindenter was of the Berkovich type. The area of the Berkovich tip was calculated according to its geometrical shape (Equation 1.).

$$A=24*h_c^2 \qquad \text{Eq. 1}$$

where; A: Area ($\mu m^2$) and $h_c$: Contact depth (nm)

The contact area calculation (Eq. 1) assumes that: 1) The Berkokovich tip is geometrically perfect, and 2) The area created on the sample surface is identical to the Berkovich tip area. Due to the significant impact of these assumptions, precautions were taken to ensure a clean tip.

**Berkovich Tip Cleaning Procedure**

A cotton swab was made fluffy by gently pulling the cotton part prior to soaking in ethyl alcohol. Tip cleaning was performed by wiping in one direction, from the threaded end to the tip of the Berkovich probe. The images of the Berkovich tip before cleaning (a) and after cleaning (b) is given in figure 1.

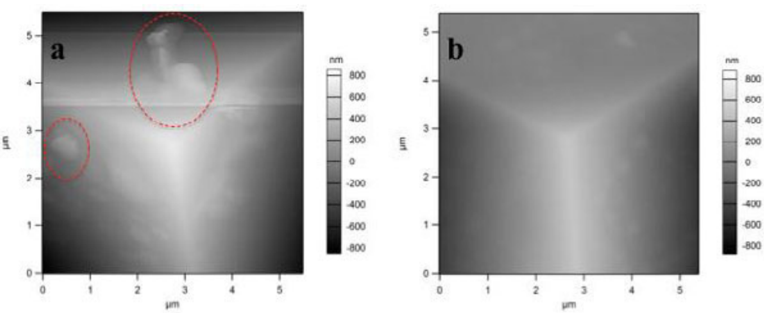


**Fig. 1.** Berkovich tip; a) before cleaning the dust particles (red circled), b) after cleaning

**Calibration & Evaluation of nanoindents**

The nanoindenter was calibrated using sapphire ball and sapphire samples. A three (3)-segment procedure includes loading, hold time and unloading were applied to create the nanoindents on the sample surface. Load-displacement (force-indentation) curves were evaluated by means of the Oliver-Pharr method [10].

The Oliver-Pharr method uses the recorded load-displacement curves by relating the geometrical measurements. For a given tip indentation (displacement) – the contact area is calculated (Eq. 1). Then, stiffness (S) was calculated from the unloading portion of the curve, which is needed to then calculate the reduced modulus. The reduced elastic modulus was determined (equation 2), which provides direct information about the materials' nanomechanical properties by recording the instantaneous response of the material to the applied force.

$$E_r = \frac{1}{2}\sqrt{\pi}\frac{S}{\sqrt{A}} \quad \text{Eq. 2}$$

where; $E_r$: Reduced elastic modulus (GPa) and S: Stiffness (nN/nm)

Finally, the elastic modulus (E) of the material were calculated using the material and tip properties as given in equation 3.

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad \text{Eq. 3}$$

where; E: Elastic modulus of the sample (GPa), ν: Poisson's ratio for the sample, 0.3 [11], $E_i$: Elastic modulus of the tip (GPa), 865 (provided by the manufacturer) and $\nu_i$: Poisson's ratio for the tip, 0.2 (provided by the manufacturer)

## RESULTS AND DISCUSSIONS

### Morphological Properties

Representative CNF samples were imaged as thin films (t≤100 µm) using AFM in different scan areas from $500^2$ micron to 1 $micron^2$ to investigate the fibril distribution. The representative AFM images are given in figure 2.

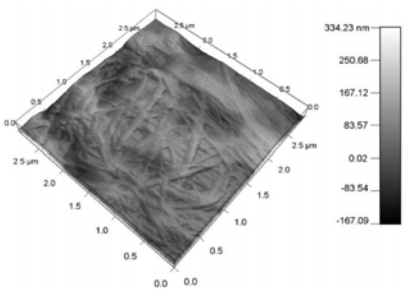


**Fig. 2.** Representative 3D image of CNFs on aluminum pin stub.

As it is shown in figure 2., Cellulose fibrils were obtained in micro scale and these microfibrils branched to the nanofibrils horizontally on the aluminum pin stubs. The significant characteristic of mechanically produced cellulose nanofibrils is the variety in the fibril diameters. The separated fibrils in this study vary between 20 nm to several hundred nanometers.

### Nanomechanical Properties

More than 100 nanoindents were randomly created on CNF samples perpendicular to fiber direction. Each load displacement curve was evaluated and categorized as valid or not. Specifically, curves that exhibited a stiffening effect (Figure 3a) were discarded. Such behavior is speculated to occur due to complex geometric assembly of nanofibrils on the stub tip. Specifically, it is postulated that 1) the tip made slide laterally off the rounded surface, and/or 2) the contacted nanofibril may have deformed and interacted with adjacent nanofibrils. Only indents with a classical response (Figure 3b) were used for analysis. A total of 58 of the 100 curves were judged valid.

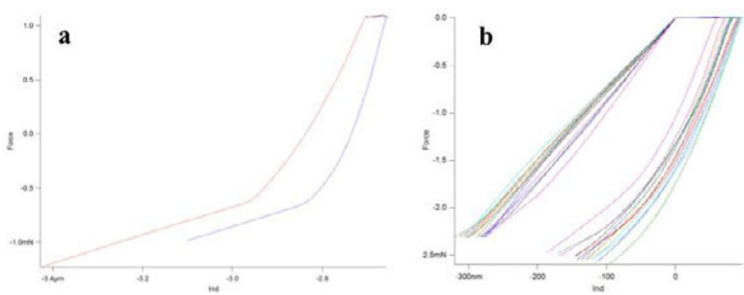

**Fig. 3.** Representative nanoindentation curves; a) rejected nanoindents and b) successful nanoindents.

Calculated CNF modulus, CNF reduced modulus, and the average contact depth values are summarized in Table 1. Also, a detailed comparison of the CNF modulus values from recently performed similar studies is given in Table 2.

Table 1. The nanomechanical properties of CNF

| Method | N, # of indents | CNF Modulus, GPa | CNF Reduced Modulus, GPa | Hc, contact depth, nm |
|---|---|---|---|---|
| Oliver-Pharr | 58 | 16.58 (16.9) | 18.22 (16.2) | 87.4 (16.3) |

Parentheses indicate the coefficient of variation (COV, %).

The average contact depth created on the CNF surfaces through nanoindentations was 87.4 nm with a 16.3 % coefficient of variation. The reduced modulus (Er) was found 18.22 GPa with 16.2 % coefficient of variation. The estimated modulus (E) 16.58 GPa with a 16.9% coefficient of variation.

Table 2. Modulus value comparison with other studies

| Material | Test instrument | Test Method | E (GPa) | Researcher | Date |
|---|---|---|---|---|---|
| CNC | AFM | Compression | 12.8 | Simonsen et al. [12] | 2012 |
| MCC | AFM - NI | Compression | 3.5 | Krishnamachari et al. [13] | 2012 |
| CNC | Prediction | - | 5.1 | Wu et al. [14] | 2013 |
| CNC | Theoretical | - | 6.5-24.5 | Moon et al. [15] | 2014 |
| CNF | AFM - NI | Compression | 15.8 | Yildirim et al. | 2015 |

The CNF modulus values obtained in this work have similar or higher modulus values than the previous studies. This is to be expected given the differing test methods, different raw materials, and nanomaterial production process. In this study, it is shown that CNF modulus vary between 12.4 GPa – 22.8 GPa which is comparable with previous studies.

## CONCLUSIONS

In this work, the nanomechanical properties of celluloce nanofibrils (CNFs), under compression forces perpendicular to its fibre direction, were investigated and reported. The mechanical production process produced significant heterogeneity in fibril diameters, which ended up with problems respectively unstable fibrils, tip sliding, and indentation failures through nanoindentation. These significant application problems were overcome by applying more than 100 nanoindents and using only the flawless, successful nanoindents for the evaluation. This research showed that Oliver-Pharr method is applicable for cellulose nanofibrils however; the berkovich tip should be cleaned carefully before the nanoindentations to prevent incorrect area calculations due to particles on the tip, which directly affects the results.

The nanomechanical properties of the CNFs were discovered in this research. Future work will include investigating the nanomechanical properties of the CNFs through different nanoindentation methods and approaches.

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