Atomic Force Microscope Characterization of Cellulose Nanocrystal Transverse Properties

Abstract. *A comprehensive understanding of cellulose nanocrystal (CNC) properties will enable material designers, modelers, and manufacturers to make informed decisions in the development of new products and materials based on CNCs. Atomic force microscopy (AFM) is a tool that is uniquely suited for the characterization of the structural, mechanical, and chemical properties of nanometer-sized objects. We have used AFM to study the transverse elastic modulus of isolated tunicate CNCs. Included in this work is a comprehensive uncertainty analysis of our data, which is key for making meaningful comparisons between AFM measurements.*

Keywords. cellulose nanocrystals, atomic force microscope, elastic modulus, material properties.

Ryan Wagner[1,2], Arvind Raman [1,2] and Robert Moon[1,3,4]

[1] Birck Nanotechnology Center, Purdue University
[2] School of Mechanical Engineering, Purdue University
[3] School of Material Engineering, Purdue University
[4] Forest Products Laboratory, U.S. Forest Service

Introduction. Atomic force microscopy (AFM) is a tool which can characterize materials with nanometer-scale position resolution [1]. An AFM can measure structural, elastic, viscoelastic, chemical, and electrical properties of samples. An AFM consists of a sharp tip attached to a cantilever (Fig. 1). The tip is brought near a sample surface by means of piezoelectric actuators, and the motion of the cantilever is monitored by an optical beam deflection system. Based on the motion of the cantilever, information about the sample's structural, mechanical, electrical, and chemical properties can be inferred. An AFM can operate in air, liquid, and vacuum environments and on conducting and nonconducting samples, giving it a distinct advantage over many competing microscopy techniques.

AFM has been used to characterize cellulose nanomaterials (CN) and CN composites. Properties such as topography [2], transverse elasticity [3] and adhesion [3], axial elasticity [5], and chemical reactivity [6] have been measured. Although this is a good start, additional research is needed to develop fully a set of baseline properties which would be useful to material modelers, designers, and manufacturers. One specific shortcoming of much prior research is the lack of a comprehensive analysis of measurement uncertainty, which under certain conditions can be quite large for AFM.

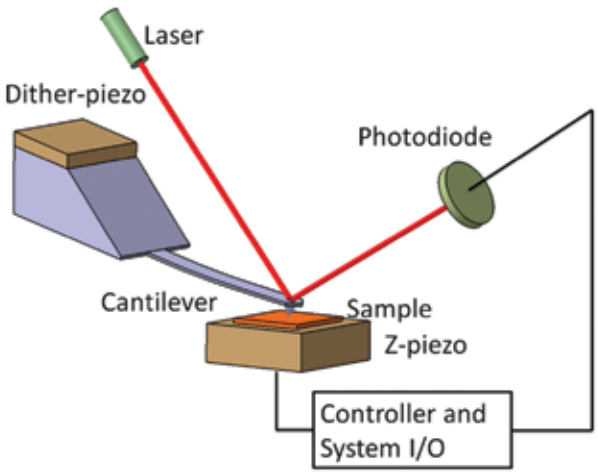

Figure 1. *Schematic of a typical AFM system.*

Methodology. For AFM imaging, a 0.1 mg ml^{-1} aqueous tunicate CNC suspension was deposited on a freshly cleaved mica surface. A Nanotec AFM (Nanotec, Tres Cantos, Spain), the WSxM software [7], and HSC20 cantilevers (Team Nanotec, Villingen-Schwenningen, Germany) with a nominal spring constant of 3 Nm^{-1} were used to measure tip-sample force versus extension of the piezoelectric actuator on the apex of an isolated CNC in a nitrogen environment. The transverse elastic modulus of the tunicate CNC was computed by fitting a model to the tip-sample interaction force [8].

Results. We have carefully measured the transverse elastic modulus of an isolated tunicate CNC using force-displacement AFM (Fig. 2) [8]. We have taken into account all the major uncertainties associated with the AFM system to report a quantitative number that should be comparable to other reported measurements from different research groups using different experimental techniques. Our technique is an improvement over prior work because we have included the systematic uncertainties associated with the AFM system, rather than simply stating the standard deviation of repeated measurements. Repeated measurements do not capture uncertainties that are systematic in nature. For a single isolated tunicate CNC, we found the transverse elastic modulus to be 8.8 GPa. The 95% confidence interval associated with this measurement ranges from 2.8 GPa to 22 GPa. This measurement is done with a maximum force of 10 nN and a maximum indentation into the sample of less than 1 nm. This small force and indentation and the fact that no changes

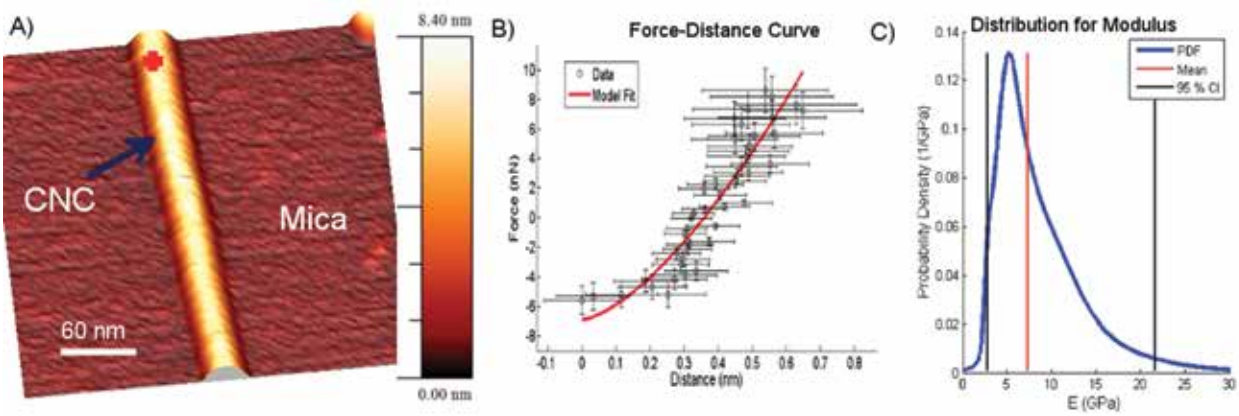

Figure 2. *A) AFM topography image of a tunicate CNC to be measured. B) Single-force distance measurement from the apex of the CNC, including estimates of uncertainty in force and distance. C) Probability density function (PDF) computed from 100 measurements from along the apex of the CNC. The integral of the PDF between two values (i.e., from E_1 and E_2) gives the probability that the measured elastic modulus falls between E_1 and E_2. The mean value of these measurements is 8.8 GPa, and the 95% confidence interval ranges from 2.8 GPa to 22 GPa [8].*

in sample topography were observed after the measurement gives us confidence that we are observing the elastic response of the CNC. The final reported value is a combination of 100 repeated measurements from along the apex of the CNC.

Conclusions. AFM is capable of measuring the material properties of a sample with nanometer-scale resolution. We have used a simple AFM technique to measure the transverse elastic modulus of a single isolated tunicate CNC. This measurement includes a comprehensive uncertainty analysis to ensure that the measurement is truly quantitative in nature and careful control of measurement forces to ensure that the material response is elastic in nature. This caution should help ensure that this measurement can be compared to results from different laboratory groups measured with different techniques.

Although our measurements and those reported in the literature provide an excellent starting point, more work is needed to develop a comprehensive understanding of the properties of CNCs. Our measurements are reported using a single AFM technique, on a single cellulose type, and on a single CNC. This work needs to be expanded in the same rigorous faction to multiple AFM techniques, with multiple cellulose sources, and on many CNC crystals. These data will enable the development of CNC-based products and materials to proceed in an informed and hopefully accelerated fashion.

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Compiled and Edited by:
Michael T. Postek
Robert J. Moon
Alan W. Rudie
and
Michael A. Bilodeau

Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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