Atomistic Simulation of Nanoscale Indentation on Cellulose Nanocrystals

Abstract. *The elastic modulus and hardness of cellulose nanocrystals in the transverse direction were obtained from atomistic simulations of nanoscale indentation, a method that has close connections to experimental measurement techniques. The model described the interaction between a hemispherical indenter and the* (I $\bar{1}$ 0) *surface of a cellulose Iβ rod. The transverse elastic modulus predicted by the model was found to be in good agreement with experimentally measured results for individual cellulose nanocrystals.*

Keywords. cellulose nanocrystals, mechanics, atomistic simulations elastic properties, AFM

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Introduction. Understanding the structure and mechanics of CNCs at a fundamental level can facilitate development of CNC composites as well as broaden our general knowledge of CNC behavior as a nanomaterial. In this research, atomistic simulations are used to predict the elastic properties of cellulose Iβ, a natural form of CNCs, in the transverse direction by modeling nanoscale indentation. A nanoscale indentation model directly links atomistic simulations to atomic force microscopy (AFM) indentation experiments. This approach provides not only new validation methods for model predictions, but also can be used to assess model parameters associated with different types of bonding within and between multiple cellulose Iβ lattice planes.

Methodology. A model of a cellulose Iβ crystal was constructed using the Materials Studio software (Fig. 1). The (I $\bar{1}$ 0) surface of cellulose Iβ was created and placed facing upwards. Periodic boundary conditions were applied in the axial direction and free boundaries in the other two transverse directions, producing effectively a cellulose Iβ rod with a finite thickness and width and an infinite length. The bottommost cellulose molecules were fixed to maintain structural rigidity. The ReaxFF force field was used with the LAMMPS modeling software to describe all atomic interactions.

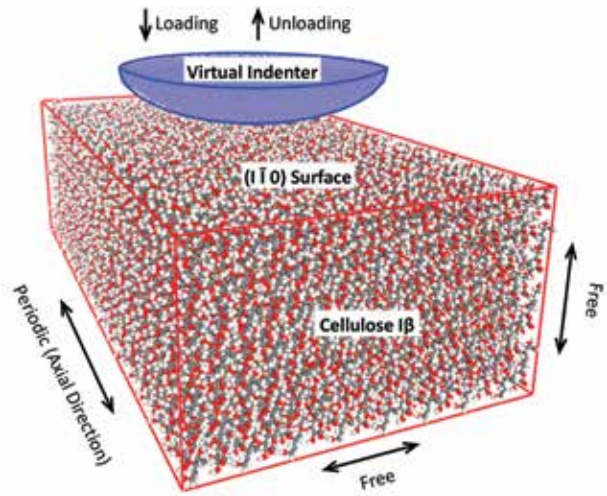

Figure 1. *Schematic of the simulation system for nanoscale indentation composed of a cellulose Iβ rod with a hemispherical nanoscale indenter. The indentation surface is* (I $\bar{1}$ 0)*. The loading and unloading directions and boundary conditions are indicated.*

A virtual hemispherical indenter was used to indent the cellulose Iβ rod. The indenter was placed above the (I $\bar{1}$ 0) surface and brought down towards the surface at a constant speed to simulate the indentation loading process. Once the indenter moved a certain depth into the surface, the unloading process was simulated by bringing the indenter up away from the surface at the same speed until the indenter returned to its original position. The transverse elastic modulus (E_T) and hardness (H) were calculated by analyzing the relationship between the loading force (F) and indentation depth (d), the F-d curve, during the unloading process.

Results. Figure 2a shows a cross section of the simulation system. The loading force F is the total force in the vertical direction on the projected contact area (which is a circle with its diameter shown by the solid black line). The indentation depth d is the distance from the surface of the cellulose rod to the bottom of the indenter. During

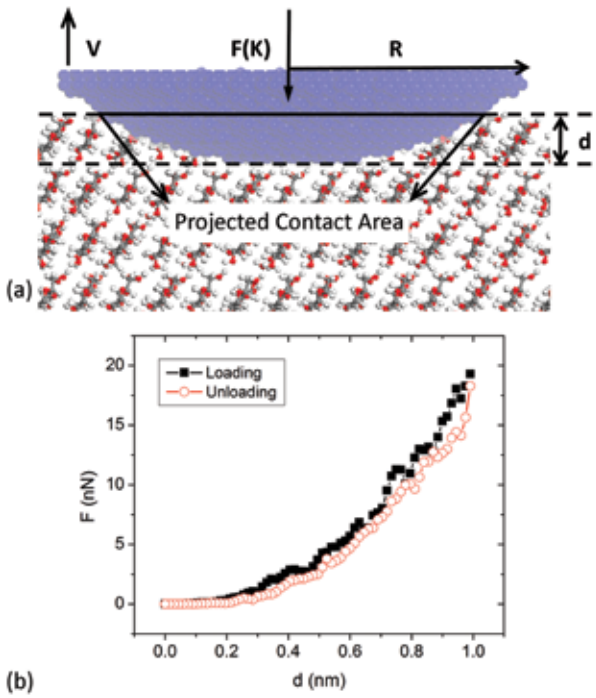

Figure 2. *(a) Cross section of the nanoscale indentation simulation system, with the loading force F labeled, which is a function of the force constant K, the indentation depth d, the indenter radius R, and the indentation speed V. (b) F-d loading and unloading curves with preferred model parameters, with the latter to be used for calculating the transverse elastic modulus and hardness.*

both the loading and unloading processes, model parameters must be chosen before the simulation. Some of these that most significantly affect the results are the indenter radius R, the force constant K, and the indentation speed V. The indenter radius is one of the most important parameters in nanoscale indentation because it will change the projected contact area and the resulting effective strain profile beneath the indenter, which affects the transverse elastic modulus and the hardness. The force constant controls the magnitude of the loading force applied to the surface of the cellulose rod. A larger force constant results in a non-negligible interaction force at shallower indentation depths and a greater maximum loading force. The indentation speed determines how fast the indenter is approaching or moving away from the surface.

Using statistical analysis, we found that the effects of indenter radius, force constant, and indentation speed in a slower simulation range on the predicted elastic modulus in the transverse direction were statistically insignificant. Preferred model parameters were used to generate the unloading F-d curve (Fig. 2b) which predicted the transverse elastic modulus E_T=5.1±0.7GPa and the hardness H=0.7±0.3GPa, both averages and standard deviations obtained from five independent simulations. The E_T value is reasonable in comparison to AFM experimental nanoscale indentation measurements.

Conclusions. Simulations of nanoscale indentation described the interaction between a hemispherical indenter with the (I $\bar{I}$ 0) surface of a cellulose Iβ rod. Three major factors—indenter radius, loading force, and indentation speed—were examined in terms of their effect on the transverse elastic modulus and hardness. It was shown that the indenter's size and the loading force had little effect on the results in the tested range. The indentation speed had little effect as well for speeds in the slower simulation range. The prediction transverse elastic modulus was in good agreement with AFM nanoscale indentation results. This agreement illustrates the possibilities of developing nanoscale indentation models to predict the elastic behavior of individual cellulose crystals.

Reference

Wu, X., Moon, R. J., and Martini, A., Crystalline cellulose elastic modulus predicted by atomistic models of uniform deformation and nanoscale indentation. Cellulose 20:43–55 (2013).

Acknowledgements. The authors are grateful to financial support for this research provided by the Forest Products Laboratory under USDA grant: 11-JV-11111129-087 – Atomic-Scale Modeling of Cellulose Nanocrystals and for CNC material, and to the Air Force Office of Sponsored Research, grant: FA9550-11-1-0162.

Production and Applications of Cellulose Nanomaterials

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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ISBN: 978-1-59510-224-9
TAPPI PRESS Order Number: 0101R332
Printed in the United States of America