Anisotropic Elasticity of Crystalline Cellulose: Atomistic Modeling & Experiments

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ABSTRACT

The significant potential for cellulose nanocrystals (CNCs) to be used in a wide variety of products is currently limited by a lack of complete characterization of their material properties. The objective of this research is to address this issue via complementary nanoscale experiments and simulation. In this paper we present findings from the first phase of the research. From the experimental perspective we report atomic force microscope measurements of the transverse elastic modulus of tunicate CNCs, and, using molecular dynamics simulation, we investigate the effects of model structure on predictions of axial elasticity. Careful consideration is given to understanding the uncertainty inherent in such measurements with the eventual goal of allowing for true sample-to-sample and modeling-to-experiment comparison.

INTRODUCTION

In spite of the great potential of CNCs as a functional nanoparticle for nanocomposite materials, a fundamental understanding of CNC properties and their role in composite property enhancement is not available. One reason is, at this scale, we are at the limit of the sensitivity needed for quantitative property measurement. Atomic force microscopy (AFM) is a metrology technique that can characterize surface topography (Figure 1a) and material properties such as elasticity, adhesion, and conductivity down to sub-nanometer resolution. There are several ways in which AFM can be used to characterize CNC properties. The most commonly used technique of applying AFM to measure CNC properties is force-displacement mode, where the force (F) is recorded as a function of the sample displacement (Z) [1]. This results in a force-displacement curve (F-Z curve). To describe the indentation of the AFM tip into the CNC surface, the F-Z curve must be converted into a force v.s. tip-surface distance curve (F-D curve).

INTRODUCTION

In spite of the great potential of CNCs as a functional nanoparticle for nanocomposite materials, a fundamental understanding of CNC properties and their role in composite property enhancement is not available. One reason is, at this size scale, we are at the limit of the sensitivity needed for quantitative property measurement. Atomic force microscopy (AFM) is a metrology technique that can characterize surface topography (Figure 1a) and material properties such as elasticity, adhesion, and conductivity down to sub-nanometer resolution. There are several ways in which AFM can be used to characterize CNC properties. The most commonly used technique of applying AFM to measure CNC properties is force-displacement mode, where the force (F) is recorded as a function of the sample displacement (Z) [1]. This results in a force-displacement curve (F-Z curve). To describe the indentation of the AFM tip into the CNC surface, the F-Z curve must be converted into a force v.s. tip-surface distance curve (F-D curve).

This is accomplished by subtracting the cantilever deflection (δ) from the sample displacement (D = Z −δ). This is also referred to as the force vs. tip indentation curve. Sample material properties can be extracted from an F-D curve (Figure 1b) by fitting an appropriate material-mechanics model to the data. However, because of assumptions that are made (e.g. elastic response, isotropic properties, and continuum mechanics descriptions) the use of these models to invert the F-D curve into a quantitative measure of local material property is an open question.

METHODS

AFM elastic property measurements were performed with a Nanotec atomic force microscope and Dulcinea controller (Tres Cantos, Spain). WSxM software version 4.0 Develop 13.0 was used for data collection and analysis. F-Z curves were collected under dry conditions (0.1 % relative humidity) on isolated Tunicate-derived CNCs [2] deposited on freshly cleaved mica (Figure 1a). Details of the tunicate CNC preparation method are given in van den Berg et al. [2]. The F-Z curves where first converted into F-D curves, then the DMT model [3] was used extract an elastic modulus (Figure 1b) [4]. Team Nanotec (www.team-nanotec.de) HSC20 cantilevers with a nominal spring constant of 3 N/m were used for imaging. The individual stiffness of each cantilever was calibrated with a scanning electron microscope. Force curves where mapped over a 400 nm by 400 nm region with a Z-peizo displacement of 20 nm with a maximum force of 10 nN. Data points were selectively analyzed from the “apex” of the CNC crystal (Figure 1a).

Cellulose was modeled using a fully atomistic molecular dynamics (MD) simulation in which inter-atomic interactions are described by the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field [8]. Materials Studio commercial software was used to generate the initial configuration and the MD simulations were run using LAMMPS freeware [9]. We modeled single cellulose chains 8, 16, and 32 glucose units long, and a cellulose crystal (Figure 1c) consisting of chains 16 glucose units long and
4x8 unit cells (cellulose Iβ having the following parameters: \( a = 0.7784\)nm, \( b = 0.8201\)nm, \( c = 1.0380\)nm, \( \alpha = 90^\circ\), \( \beta = 90^\circ\), \( \gamma = 96.5^\circ\) \[10\]). All boundaries were periodic, and the single chain models were placed in the middle of a simulation domain large enough to ensure the chain would not interact with itself across the periodic boundary. Equilibration of a single chain consisted of allowing the atoms in the simulation cell to approach positions dictated by the interaction model at 300K using MD simulation in the NVT ensemble (constant number of particle, volume, and temperature). The crystal model required a two-step equilibrium process. First, the atoms inside the crystal were allowed freedom of movement during an MD run in the NVT ensemble at 300K while the dimensions of the simulation domain were fixed. Then, the crystal structure itself was allowed to change during an MD run in the NPT ensemble (constant number of particles, pressure, and temperature) at 300K and 1 atm.

RESULTS

Based on the DMT model the mean value for the transverse modulus of a Tunicate CNC is around 5-10 GPa \[11\]. There are several issues that need to be kept in mind while considering this mean modulus value. These modulus values were extracted by applying an isotropic model to an anisotropic material. This implies that this number is not a true transverse modulus but rather a “model equivalent” elastic constant that can be used for sample to sample comparison. Models that are more sophisticated need to be applied to extract true elastic constants. There is a large systematic uncertainty associated with the AFM calibration parameters and the propagation of this uncertainty through the experimental setup is complicated. This uncertainty is not addressed when reporting only a mean value. Improvements can be made on the methods for collected and analyzing elastic data on nanoscale structures, this is ongoing work that will be presented in a subsequent paper \[7\].

The axial elasticity of the single chains and cellulose crystal are calculated by extending the simulation domain in the axial direction incrementally. The minimum potential energy of the system in its extended configuration is then calculated. This process is repeated to generate a plot of energy as a function of axial length, and the data is fit to a third order polynomial equation (Figure 1d). The derivative of this function yields force which can be divided by area to obtain stress \[12\]. Elasticity is then the slope of the linear relationship between stress and strain. We find that the size of the model cellulose significantly affects predicted elasticity. Specifically, initial testing indicates that elasticity will increase with both chain length and crystal size (Figure 1e). We anticipate that model predictions will approach a constant value at some crystal size, and research in this direction is in progress \[13\].

<table>
<thead>
<tr>
<th>Model</th>
<th>Axial Elasticity</th>
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<tbody>
<tr>
<td>Single 8 Glucose Chain</td>
<td>77 GPa</td>
</tr>
<tr>
<td>Single 16 Glucose Chain</td>
<td>86 GPa</td>
</tr>
<tr>
<td>Single 32 Glucose Chain</td>
<td>94 GPa</td>
</tr>
<tr>
<td>4x8 Crystal of 16 Glucose Chains</td>
<td>182 GPa</td>
</tr>
</tbody>
</table>

Figure 1

CONCLUSIONS

The objective of this research is to characterize the elasticity of cellulose nanocrystals via complementary AFM measurement and MD modeling. We have shown that both experimental measurements and model predictions are extremely sensitive, and that quantitatively understanding the uncertainty inherent in such techniques, with the eventual goal of allowing for true sample-to-sample and modeling-to-experiment comparison, will be critical to being able to fully characterize the elasticity of crystalline cellulose.
References