Elastic Deformation Mechanics of Cellulose Nanocrystals

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Abstract

Cellulose nanocrystals (CNC) have great potential for polymer nanocomposite materials. However, a fundamental understanding of the CNC properties and their role in composite property enhancement is not currently available. To address this issue, we are developing atomic force microscopy (AFM) protocols combined with molecular dynamics (MD) and continuum modeling techniques that enable characterization of individual CNCs. AFM can be used to measure topography, pull-off force, stiffness and bending of CNCs, which are then related using the models to physical, chemical, mechanical and deformation properties, respectively. This paper outlines the development of a fully atomistic model of an individual CNC and its validation by comparison of predicted geometric, energetic, and elastic properties of the material to previous modeling results and experimental measurements.

Introduction

Currently, there is a growing push from consumers, industry, and government for products that are made from renewable and sustainable resources, biodegradable, nonpetroleum based, carbon neutral, and have low environmental, health and safety risks. Cellulose based particles fit this strict criteria and are currently being used in variety of products such as paper based products (paper, packaging, filters,), cellophane, artificial tears, food additives (thickener, emulsion stabilizer, fiber), chronic wound treatment (scaffolding structure for tissue engineering, artificial blood vessels, cartilage, etc), and filler material within drug tablets. Recent research into the properties and applications of crystalline cellulose particles has demonstrated an opportunity for the development of a new platform of high strength cellulose based nanocomposites [1]. One type of crystalline cellulose particles being investigated is the cellulose nanocrystal (CNC).

Cellulose is present in a wide variety of living species (trees, plants, tunicates-a group of abundant saclike filter feeding organism found in the oceans), and provides the base reinforcement structure used by organisms for high mechanical strength, high strength-to-weight ratio, and high toughness. Cellulose is a linear chain of glucose molecules \((\text{C}_6\text{H}_{10}\text{O}_5)_n\); \(n=10,000\) to 15,000) as shown in Figure 1a. During tissue growth multiple cellulose chains self-assemble into microfibrils (via hydrogen bonding), which are composed of crystalline and amorphous regions. By selectively dissolving the amorphous regions with acid hydrolysis, the remaining crystalline regions can be liberated [2]. These nanoscale cellulose crystals are called CNCs, and are 3 to 20 nm in diameter and 100 to 3000 nm long (depending on the cellulose source). The mechanical properties of CNCs are greater than those of other cellulosic materials, and in some cases superior to those of more traditional reinforcement materials. For example,
the axial elastic modulus of CNCs is 110-180 GPa [3, 4], while that of Kevlar is ∼130 GPa [5].

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 that, 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 material properties such as elasticity, adhesion, hardness, topography, and conductivity at scales down to atomic resolution. Figure 2 shows an AFM topography image of CNCs on mica. One technique of applying AFM to assess CNC properties is force-displacement mode, where the force \( (F) \) is recorded as a function of the sample displacement \( (Z) \) [6]. This process results in a force-displacement curve \( (FZ \text{ curve}) \). To describe the indentation of the AFM tip into the CNC surface, the \( FZ \) curve must be converted into a force v.s. tip-surface distance curve \( (Fd \text{ curve}) \). This is accomplished by subtracting the cantilever deflection \( (D) \) from the sample displacement, i.e. \( d = Z - D \). Sample material properties can be extracted from an \( Fd \) curve by fitting an appropriate material-mechanics model to the data. However, because of assumptions that are made (e.g. isotropic, continuous materials) the ability of these models to quantitatively predict material properties can be called into question.

The long term goal of this research is to address this issue via nanoscale experiments and simulation. We have developed a fully atomistic model of a CNC that, by eliminating the typical material and geometric assumptions, we will use to extract material properties from direct AFM measurements [7]. In this paper we present the details of this model and its validation.

**Methodology**

Development of the atomistic model for CNCs consisted of building of the initial structure (cellulose repeat unit, cellulose chain, crystal structure, and particle geometry), defining the force fields necessary to describe atomic interactions, equilibrating the CNC structure, and then validating the model-predicted material properties. These steps are described sequentially below.
CNC Structure and Force Field

The cellulose repeat unit is shown schematically in Figure 1, consisting of two glucose rings bridged by the 1→4 glycosidic bond. The glucose rings are parallel “up”, so that the chain-direction (z) position of the O₅ atom is greater than that of the C₅ atom [8]. The hydroxymethyl conformation was chosen to be t₂g, meaning the hydroxymethyl is pointing in the negative z direction (i.e. the C₆-O₆ bond points in the direction of the O₂ in the adjoining glucose ring as shown in Figure 1b). This is the dominate conformation for the crystalline structure of natural cellulose (Iβ and Iα) [8].

Crystalline cellulose consists of multiple cellulose chains that are arranged parallel up and edge-to-edge [8]. We model the monoclinic crystal structure of Iβ cellulose which has the following unit cell parameters [8]: a = 0.7784nm, b = 0.8201nm, c = 1.0380nm, α = 90°, β = 90°, γ = 96.5°, V = 0.6583nm³. The cellulose Iβ unit cell consists of two parallel cellulose chains (as opposed to antiparallel), one positioned at the corner and the other at the center of the unit cell (Figure 3). The center chain is shifted by c/4 relative to the corner chain in the axial direction. We used a positive shift in the z-direction, however, it cannot be determined by experiment if it is a positive or negative z-direction shift.

The next step is to assemble the unit cell described above into a supercell that is more representative of a CNC particle. The dimensions of the supercell are 4×8×8 of the unit cell, the respective lengths along each axis are: Lₓ = 4a = 3.1136nm, Lᵧ = 8b = 6.5608nm, and Lₗ = 8c = 8.3040nm. With this supercell the cellulose chains consist of n = 8 repeat units. By connecting the ends of the chains through covalent bonds, we can efficiently model an sufficiently long chain or CNC. The shape of the cross section, Lₓ × Lᵧ, is rectangular, an approximation of a CNC particle, in which the cross-sectional area is close to the average value from experiment [9]. Periodic boundary conditions (pbc) are applied in all three directions. Non-periodic boundary conditions can be used to model an isolated cellulose crystal, as will be done for direct comparison of simulation with AFM indentation studies (future work). In this current work we focus on a model using full pbc’s to facilitate analysis of the elastic properties of the cellulose crystal.

All atomic interactions are described by the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field [10]. This model takes into consideration bond, angle, dihedral and out of plane interactions, which makes it one of the best choices to model polymeric materials. The non-bonded interactions include both van der Waals and electrostatic forces which, when used in combination, model the hydrogen bond (H-bond). It was suggested as early as 1985 [11] that the native cellulose crystal formation

Figure 2: AFM topography image of Tunicate CNCs deposited on mica.
Figure 3: Cross section of Iβ unit cell with two cellulose chains each consisting of 16 glucose rings. Unit cell parameters (values given in Table 1) are identified on the figure.

and its high elastic properties are related to the H-bond patterns and strength. The initial configuration of the system is identified using commercial Materials Studio software and all subsequent molecular dynamics simulations are performed using the LAMMPS simulation tool [12] with a time step of 1 femtosecond.

**Equilibration**

Our CNC supercell is equilibrated from its initial structure through a two-step process. First, the cell parameters are fixed while atoms inside the supercell are allowed to change their position. Then, we allow the supercell size to change to allow equilibration of the whole system. Detailed procedures and conditions are described below.

The initial velocities of all atoms were prescribed according to a Maxwell distribution corresponding at 600K. The system was then cooled to 300K during a time period of 1 picosecond. It was equilibrated at that temperature for another 3 picoseconds followed by energy minimization using the conjugate gradient method with an energy error tolerance of $10^{-8}$. The system was equilibrated using molecular dynamics simulation in the nvt ensemble (constant number of particles, volume, and temperature) to allow the atoms to attain their stable positions given the prescribed initial unit cell.

After the internal structure was equilibrated, it was then necessary to allow the supercell itself to relax. The supercell was allowed to change its inner coordinates as well as its cell parameters at a temperature of 300K and an environmental pressure of 1 atm. The supercell is constrained by 1 atm pressure in all three directions but the volume is not fixed, so the overall dimensions of the structure can change according to its inner pressure. This equilibration procedure allows the supercell and its components atoms to naturally approach their stable positions.

**Elasticity Calculation**

The elastic behavior of the CNC was predicted by stretching and compressing the equilibrated supercell in the axial (z) direction in increments of 0.3nm as shown in Figure 4. The resultant
stress-stain curves were then used to predict chain stiffness. Since, the internal stress is a linear function of the z direction changes of the supercell, the slope gives the elastic modulus in z direction. The cross-section area of the supercell is kept constant during the simulation, which means we do not take dilation effects into account. To ensure that this constant area assumption is reasonable, the stretching or compressing length must be within 5% of the total chain length, such that we can ignore the total change of volume.

Results

To validate the CNC model, predicted unit cell parameters, minimum potential energy, and axial elastic modulus are compared to experimentally measured values and previous simulation results.

Unit Cell Parameters

The unit cell parameters \((a, b, c)\) are measured after the model equilibration process during which they are unconstrained and can therefore differ from their initial values. Since the initial values were obtained from experimental diffraction measurements, consistency with the equilibrium model values will indicate that the force field we are using (in this case COMPASS) correctly predicts the experimentally measured structure.

<table>
<thead>
<tr>
<th>Table 1: Cellulose I(\beta) crystalline unit cell parameters.</th>
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<tr>
<td><strong>Unit Cell Parameters</strong></td>
</tr>
<tr>
<td>a (nm)</td>
</tr>
<tr>
<td>b (nm)</td>
</tr>
<tr>
<td>c (nm)</td>
</tr>
<tr>
<td>volume (nm(^3))</td>
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</table>

The calculated unit cell parameters are given in Table 1. Compared with the experimental data, we can see that the relaxed unit cell has nearly the same cell parameters as the experimental ones: the relative differences in unit cell length are less than 1%. Note that at this point, due to software limitations, we assume that the unit cell angles do not change. The negligible difference between the model predicted and experimentally measured cell parameters indicates that the initial crystalline structure is stable using the COMPASS force field. We have also compared our equilibrium model cell parameters to results reported from previous molecular dynamics simulations performed by Eichhorn and Davies [13] and Tanaka and Iwata [14], both of which use Materials Studio software with COMPASS forcefield, Table 3. The \(c\) spacing of our model is smaller than both studies, while \(a\) and \(b\) spacings are slightly larger than those reported by Eichhorn and Davies. These small differences are likely due to the fact that we used different molecular dynamics simulation software. However, our simulation results are in agreement (differences less than 1%) with the experimental data which supports validity of the model.

Energetics

The potential (configurational) energy at 300K is calculated for the I\(\beta\) structure in its minimum energy configuration, averaging over 1 picoseconds. The total potential energy calculated is 15.2 kcal mol\(^{-1}\) glucose\(^{-1}\), which is comparable to the result obtained by Eichhorn and Davies [13] as shown in Table 3. A detailed breakdown of the contributions to the total
potential energy is shown in Table 2. Both the pair energy and molecule energy contribute to the total potential energy. It is important to note that the pair energy is associated with modeling the H-bond, which is a critical structural component. The most significant components of the molecule energy are the bond, angle and dihedral interactions. The improper (out-of-plane) interaction in cellulose appears to have little effect.

<table>
<thead>
<tr>
<th>Energy Contribution</th>
<th>Equilibrium Model Value (kcal mol⁻¹ glucose⁻¹)</th>
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<tbody>
<tr>
<td>Pair Energy</td>
<td>8.1</td>
</tr>
<tr>
<td>—Van der Waals</td>
<td>-2.5</td>
</tr>
<tr>
<td>—Coulomb</td>
<td>10.6</td>
</tr>
<tr>
<td>Molecule Energy</td>
<td>7.1</td>
</tr>
<tr>
<td>—Bond</td>
<td>8.3</td>
</tr>
<tr>
<td>—Angle</td>
<td>16.2</td>
</tr>
<tr>
<td>—Dihedral</td>
<td>-17.4</td>
</tr>
<tr>
<td>—Improper</td>
<td>-0.02</td>
</tr>
<tr>
<td>Total Potential Energy</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Figure 4: (a) The model system in equilibrium at 300K. (b) Compression and (c) tension of the supercell in the axial z direction (bottom surfaces fixed).

Elastic Modulus

Molecular dynamics simulation of the supercell in tension and compression provide information about the material elasticity. The calculated variation of potential energy with axial length is shown in Figure 5a. When there is a strain (i.e. an increase or decrease from the equilibrium length), the energy increases and internal stresses are built up within the supercell. The corresponding stress-strain curves are shown in Figure 5 ((b)–compression; (c)–tension). The slopes of the two linear functions are the elastic moduli of cellulose Iβ: 139 GPa in compression and 155 GPa in tension. These values are bound by experimental data which range from 110-180 GPa [3, 4]. Differences between experimental and modeling results are likely attributable to the model cellulose supercell being a perfect crystalline structure, whereas in experiment, measurement of a perfect crystal is unlikely. Our results
Figure 5: (a) Total potential energy of the 4×8×8 unit cell varies with axial length, z. In compression, z ranges from 82.388 Å (its equilibrium length) to 80.042 Å. In tension, z ranges from 82.388 Å to 86.038 Å. (b) and (c) Linear stress-strain function in compression (slope 139 GPa) and tension (slope 155 GPa), respectively.

Table 3: Comparison of our model-predicted unit cell parameters, potential energy, and elastic moduli with previously reported simulation results [13, 14].

<table>
<thead>
<tr>
<th>Parameters/Properties</th>
<th>Simulation Result</th>
<th>Ref [13]</th>
<th>Ref [14]</th>
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<tbody>
<tr>
<td>a (nm)</td>
<td>0.779</td>
<td>0.756</td>
<td>N/A</td>
</tr>
<tr>
<td>b (nm)</td>
<td>0.820</td>
<td>0.805</td>
<td>N/A</td>
</tr>
<tr>
<td>c (nm)</td>
<td>1.030</td>
<td>1.043</td>
<td>1.046</td>
</tr>
<tr>
<td>Potential energy (kcal/mol/glucose)</td>
<td>15.2</td>
<td>15.3</td>
<td>N/A</td>
</tr>
<tr>
<td>Compressive modulus (GPa)</td>
<td>139</td>
<td>149</td>
<td>130</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>155</td>
<td>149</td>
<td>125</td>
</tr>
</tbody>
</table>

were also compared to previous simulation-predicted elastic moduli (Table 3). It was found that our axial modulus is comparable to that reported by Eichhorn and Davies, but higher than that reported by Tanaka and Iwata. However, it is well known that the chain stiffness calculation is highly dependant on the simulation process and initial structure used to obtain it. Therefore, variations from model to model are expected.

Conclusions

We have developed a fully atomistic model of the cellulose Iβ unit cell based on the latest experimental data using the COMPASS force field to model interactions. The supercell (4×8×8 a single unit cell of Iβ) can be used as part of the infinitely large perfect crystal as described in this paper, as well as an isolated single crystal cellulose which is useful in further work. The calculation of the potential energy and elastic properties of cellulose are comparable to those reported from previous molecular dynamics simulations and experimental studies. Thus, the model can be used with confidence for further predictions of cellulose Iβ crystal properties and behaviors.

Acknowledgments

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References


