PRELIMINARY MODULUS CALCULATIONS FOR CELLULOSE Michael Santiago Cintrón Alfred D. French Glenn P. Johnson SRRC, USDA-ARS New Orleans, LA

<u>Abstract</u>

The Young's modulus is a measure of the inherent stiffness of an elastic material. In the case of cellulose, it quantifies the ability of the material to undergo changes in length as tension or compression forces are applied. The modulus can be calculated by performing tensile tests on cotton fibers or, as in this study, by stretching molecular models in a computer program. However, considerable disparities between values from different experimental tensile tests and among molecular modeling calculations are observed. With this study we attempt to ascertain the roles of intermolecular hydrogen bonding and other intra- and intermolecular details from molecular models in modulus determinations. To achieve this, modulus calculations with empirical force fields and quantum mechanics were performed with cellobiose models capable of intramolecular hydrogen bonds as well as some analog models that cannot make hydrogen bonds.

Introduction

Cellulose, a primary component of plant cell walls in green plants, is the most abundant biopolymer in the world. Because the cotton fiber is a complete cell, cellulose is also found in the fibers that envelop seeds of the cotton plant. That fiber, when ginned and spun, is used in the textile industry to produce clothes, household effects and a multitude of industrial products. While much is known regarding the industrial processing of cotton and other cellulosic products, further understanding of the cotton fiber structure and how it relates to properties of the bulk material could result in improved cotton products via genetic engineering.

Cellulose chains are believed to aggregate into highly ordered arrays that contain periodic amorphous regions. Both components, the crystalline and amorphous regions, contribute to the mechanical properties of the bulk material, with the ordered regions greatly influencing stiffness and tenacity. The crystalline component of cellulose can be examined using theoretical methods because a high quality crystal structure is available. A large range of experimental and theoretical modulus values have been reported for the main forms of cellulose, with some theoretical studies showing almost no difference between the cellulose I and II forms (167 GPa for cellulose I, and 162 – 163 GPa for cellulose II; Tashiro et al., 1991; Kroon-Batenburg et al., 1986). Yet, more recent experimental and theoretical results show a significant gap in the value (about 130 GPa for cellulose I and 90 GPa for cellulose II: Marhöfer et al., 1996; Eichhorn et al., 2005; Sakurada et al., 1962), which suggests that the increased intramolecular hydrogen interactions in cellulose I contribute to its higher molecular stiffness. With this study we are attempting to increase understanding of the molecular basis for stiffness and how the cellulose structural components of intra- and intermolecular hydrogen bonding contribute to cellulose stiffness. To achieve this, cellobiose models were constructed from previously reported cellulose I structural coordinates (Nishiyama et al, 2002), and empirical force fields (i.e.; MM3 and MM4) used to compute stored energy potentials of deformed states (stretched and compressed) of the models. This work also addresses a need for second generation molecular mechanics calculations of cellulose that take into account the anomeric effect (Tanaka, et al., 2006). Simplified cellobiose analogs with no intramolecular hydrogen bonding capacity were also examined. Our preliminary results are comparable to recent cellulose I modulus values, and suggest that intramolecular hydrogen bonding is an important component of molecular stiffness.

Methods

Three cellulose analogs were constructed using crystallographic data reported for cellulose I. For the first model, 1,4'-O-dimethylcellobioside (**DMCB**), model cellulose molecules were truncated to two β -glucose units capped at the O1 and O4 atoms of adjacent glucose residues with methyl groups. A 1,4-O-dimethyl- β -glucoside (**DMG**) model was similarly created. Also, a cellobiose analogue in which hydroxyl groups at the C-2, C-3 and C-6 carbons were replaced with hydrogen atoms was produced, 2,3,6,2',3',6'-hexadeoxy-1,4'-O-dimethylcellobioside (**DODMCB**). Molecular mechanics calculations were carried out using the 1996 version of MM3 and the 2003

dielectric constant ($\varepsilon = 1.5$). Additional Density Functional Theory, B3LYP/6-311G**+, quantum mechanics (QM) calculations were carried out for **DMG** using Jaguar. For all the molecular models the positions of the O1 and O4' (O4 for **DMG**) atoms were restricted using constraints in the molecular modeling program, with one end fixed at the origin and the other atom moved to various terminal oxygen distances. The restricted structures were energy minimized, and their resulting internal energy plotted as a function of the length of the models. The force required to elicit molecule deformation is obtained from the first derivative of a quadratic fit of the energy plot. Stress values are determined by dividing force values by the cross sectional area of the cellulose molecule, a value that equals half of the unit cell volume divided by the c-axis distance. Stress values are then plotted against strain, and the slope of the resulting straight line is the value for the Young's modulus.

Results and Discussion

Examples of the relative energies of **DMG** as calculated with the empirical force field methods MM3 and MM4 are shown in Figure 1. These molecular mechanics (MM) energies are simplified considerations that take account of energies from bond deformation (stretching or compression), bond angle bending and bond torsion. MM calculations also consider energies arising from van der Waals forces, electrostatic interactions and hydrogen bonding. It should be noted that while the functional forms for these contributions are not simple harmonic oscillators, their estimation in a region of little stress can provide a successful model that avoids quantum mechanical (QM) calculations. Electronic structure theory calculations, also called QM calculations, are in principle more accurate, but, even in their lowest level of theory, the time to perform them is significantly longer than the time for empirical methods. Still, QM calculations from molecular mechanic methods and a QM method are shown in Figure 1. MM3 and MM4 calculations provided equilibrium O1 – O4 distance of 5.43 Å, while the QM method resulted in a slightly longer, 5.47 Å, distance. The similarity in equilibrium distances and in the rate of increase for the relative energies suggests that the MM3 and MM4 programs provide reliable models for energy minimization calculations and equilibrium structure determination for simple carbohydrate analogues.



Figure 1. Energy O1 – O4 distance for 1,4-*O*-dimethyl- β -glucoside (**DMG**) as calculated with MM3 (\circ), MM4 (\blacktriangle) and Jaguar (\Box). **DMG** is shown to the right. MM3 and MM4 calculations were performed using 1992 hydrogen bonding parameters and dielectric constant of 1.5. Density Functional Theory calculations performed with Jaguar used B3LYP/6-311G**+. Each data set is shown fitted with a second order polynomial.

The relative energies as a function of terminal oxygen atom distance of **DMCB** were calculated with MM3 and MM4, and are shown in Figure 2a. The stress-strain plots for both sets of data are shown in Figure 2b. The moduli for **DMCB** as determined by MM3 and MM4 are 122 GPa and 110 GPa, respectively. These results are comparable to values previously reported for the cellulose I modulus.



Figure 2. a) Energy O1 – O4' distance for 1,4'-*O*-dimethylcellobioside (**DMCB**) as calculated with MM3 (\circ) and MM4 (\blacktriangle) using 1992 hydrogen bonding parameters. Both sets of calculations were performed with a standard dielectric constant, $\varepsilon = 1.5$. Molecule elongation points were fitted with a second order polynomial (darker fit) and the first derivative of the resulting equation used to obtain stress values. Note that a quadratic fit that includes all MM3 deformation points (faint line) was not ideally quadratic. b) Stress-strain plot for the same model. The slopes of the resulting lines provide the values of the Young's moduli. The **DMCB** moduli were calculated as 122 GPa for MM3 and 110 GPa for MM4.

To better understand the contribution of intramolecular hydrogen bonding interactions to molecular stiffness, modulus calculations were performed with a cellobiose analog model incapable of hydrogen bonding, **DODMCB**. For this analogue, terminal oxygen atoms were methylated, and the hydroxyl groups at the C-2, C-3 and C-6 carbons were each replaced with a hydrogen atom. Figure 3 shows the stress-strain plot for the analogue. The modulus value was calculated to be 54.9 GPa with MM3, a significantly lower value than those obtained for **DMCB**. While this value will be compared to future results from MM4 and QM methods, preliminary results suggest that intramolecular hydrogen bonding plays an important part in molecular stiffness.



Figure 3. Stress strain plot for 2,3,6,2',3',6'-deoxy-1,4'-*O*-dimethylcellobioside (**DODMCB**) as calculated with MM3 (•) ($\epsilon = 1.5$). **DODMCB** is shown to the right. The analogue modulus was calculated as 54.9 GPa for MM3. Note the significant loss in molecular stiffness with the loss of the hydroxyl groups.

Elongation of **DMCB** affected the molecular geometry of the models. Figure 4 shows a progression of energyminimized **DMCB** structures that includes the most compressed, lowest energy intermediate, and most extended points as calculated with MM3. Stretching of the molecule results in small changes to all bond lengths and angles. Significantly, bonds in the backbone of the molecule also show a small increase in length as the molecule is stretched.



Figure 4. Most compressed and most extended 1,4'-O-dimethylcellobioside (**DMCB**) molecules, along with the lowest energy intermediate. Coordinates of the O4' atoms are all fixed (left-hand end), while the O1 atoms are located with 0, 0, and c coordinates, depending on the amount of compression or stretch.

The variation in molecular length of **DMCB** is shown in Figure 5. While the distance between O4' and O1 only changes by 0.18 Å, the distance between O4 and an O1 – O4' virtual bond is decreased in the longest model by 0.53 Å compared to the shortest model. Also, the values of the angle between the O4' – O4 and O4 – O1 virtual bonds change by 12.9° between the shortest and longest model. Thus, the stretching of the molecule straightens it out.



Figure 5. Variation in molecular length of 1,4'-*o*-dimethylcellobioside (**DMCB**) The angle between the O4' – O4 and O4 – O1 virtual bonds changes by 12.9° between the shortest and longest model. The distance between O4 and the O1 – O4' virtual bond is decreased in the longest model by 0.53 Å relative to the shortest model.

Conclusions

Preliminary results from this work show a significant gap between modulus values of the cellulose models, **DMCB** and **DODMCB**. The significant difference in the modulus values, suggests that intramolecular hydrogen bonding contributes considerably to molecular stiffness. Changes in the molecular geometry of the **DMCB** during stretching showed a straightening of the model and gradual changes in bond angles and lengths. Because hydrogen bonds have only 10% of the strength of C – O covalent bonds, it is surprising that the addition of two hydrogen bonds can essentially double the stiffness of a covalently bonded cellulose backbone. Future studies will include cellobiose models that contain crystal neighbors that might restrict some of the geometry changes and could reveal the role of intermolecular hydrogen bonding in molecular stiffness.

References

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