## CALCULATIONS OF YOUNG'S MODULI FOR CELLULOSE I<sub>β</sub> Michael Santiago Cintrón Glenn P. Johnson Alfred D. French SRRC, USDA-ARS

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## <u>Abstract</u>

Young's modulus provides a measure of a material's resistance to deformation. Modulus values can be calculated by performing tension tests on cotton fibers or, as in this study, by stretching molecular models in a computer program. Herein we present a series of Young's modulus estimations that relied on molecular mechanics (MM) and quantum mechanics (QM) calculations with models of cellulose  $I_{\beta}$ . MM computations used the second generation empirical force field MM3; a force field that considers the anomeric effect. MM3 and QM computations (B3LYP/6-311G\*\*+) with a disaccharide cellulose model and an analogue incapable of making hydrogen bonds revealed a considerable contribution of intramolecular forces to the molecular stiffness of cellulose  $I_{\beta}$ . MM3 calculations with longer cellulose chains models (10 glucose units) resulted in a modulus value, 126.0 GPa, comparable to reported modulus values for cellulose  $I_{\beta}$  crystallites.

### **Introduction**

Young's modulus, which is sometimes called an elastic modulus, is a measure of material's resistance to deformation. Cellulose-containing materials exhibit a moderate resistance to deformation; a property that places these materials as attractive fillers in industrial composites (Azizi Samir et al., 2005). Cotton fibers represent one such material. Cotton fibers envelop the seeds of the cotton plant and are mostly composed of cellulose (>90%). They are abundant and relatively inexpensive. Yet, the structural aspects that grant cotton fibers with a moderate resistance to deformation are not well understood.

In cotton fibers, cellulose chains are believed to grow into ordered arrays with periodic amorphous regions. While both components contribute to the mechanical properties of the bulk material, the ordered regions are believed to greatly influence the stiffness (resistance to deformation) of the fibers. Theoretical modulus calculations that modeled the deformation of cellulose molecular models have been reported, progressing with new insights on cellulose structure. Yet, a large range of modulus values have been reported for cellulose  $I_{\beta}$ , with some theoretical studies showing a significant contribution from hydrogen bonding to the molecular stiffness of cellulose  $I_{\beta}$  (ca. 40% contribution; Tashiro et al., 1991). More recent reports discount this contribution (ca. 15%; Eichhorn et al., 2006). Given the large range of theoretical values of cellulose chain stiffness, 57-180 GPa (Eichhorn et al., 2005 and references therein), it is fair to say that considerable disparities exist among molecular modeling determinations. In addition, the structural basis for the molecular stiffness of cellulose is not well understood.

With this study we are attempting to increase understanding of the molecular basis for stiffness, and how cellulose structural components, intra- and intermolecular hydrogen bonding contribute to cellulose stiffness. To achieve this, cellulose  $I_{\beta}$  models were constructed from previously reported structural coordinates (Nishiyama et al, 2002), and empirical force fields (i.e.; MM3) and QM methods were used to compute stored energy potentials of deformed states (stretched and compressed) of cellulose models. Also, simplified cellulose analogs limited in their ability to form intramolecular hydrogen bonds were examined. Our preliminary results suggest that intramolecular hydrogen bonding is an important component of molecular stiffness.

### **Methods**

Cellulose models were constructed using crystallographic data reported for cellulose I (Nishiyama et al, 2002). Model disaccharide and decasaccharide molecules were truncated to two or ten  $\beta$ -glucose units and the terminal oxygen atoms capped with methyl groups (Figure 1). Also, disaccharide and decasaccharide analogues in which hydroxyl groups at the C-2, C-3 and C-6 carbons were replaced with hydrogen were produced. Molecular mechanics calculations were carried out using the 1996 build of the MM3, and minimizations were performed using 1992 hydrogen parameters with a standard or elevated dielectric constant ( $\epsilon = 1.5$  or 7.5, respectively). Additional Density Functional Theory, B3LYP/6-311G\*\*+, quantum mechanics (QM) calculations were carried out for the disaccharide

models. For all the molecular models the positions of the terminal oxygen atoms were restricted using a 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 chain, a value which is obtained from the volume of the crystalline unit cell. Stress values are then plotted against strain, and the slope of the resulting straight line is the value for the Young's modulus.



Figure 1. A 1,4'-*O*-dimethyl-β-cellobioside (**DMCB**) molecule with only the hydrogens attached to O2' and O3 shown.

#### **Results and Discussion**

Elongation of disaccharide cellulose  $I_{\beta}$  model, **DMCB**, as simulated with the modeling programs MM3 and with QM results in modulus estimations with values significantly lower than previously reported. Figure 2a shows a curve of relative energy vs. O1-O4' distance for the elongation and compression of **DMCB** as minimized with MM3 and QM. A quadratic fit that included all deformation points did not properly fit compression points (dashed fit of MM3 curve), likely from minimization limitations imposed by the spatial restraints. As such, fits containing elongation points were used for the force/modulus determinations. The corresponding stress-strain plots (Figure 2b) revealed a Young's modulus value of 85.2 GPa for DMCB. In contrast, QM determinations resulted in a higher modulus value of 99.7 GPa. We note that these modulus estimations are significantly lower than recent experimental determinations for cellulose  $I_{\beta}$ , 115–145 GPa (Eichhorn et al., 2005 and references therein).



Figure 2. a) Relative energy vs. O1-O4' distance for **DMCB** as calculated with MM3 and QM (B3LYP/6-311G\*\*+.) Elongation points were fitted with a second order polynomial (darker fit in MM3) and the first derivative of the resulting equation was used to obtain force values. b) Stress-strain plots for the same models. The slopes of the resulting lines provide the Young's moduli; 85.2 GPa for MM3 and 99.7 GPa B3LYP/6-311G\*\*+.

Intermolecular hydrogen bonding provides a considerable contribution to the molecular stiffness of the disaccharide cellulose analogue 2,3,6,2',3',6'-hexadeoxy-1,4'-*O*-dimethyl-β-cellobioside (**DODMCB**). Modulus calculations were performed with an analogue of the **DMCB** model incapable of forming hydrogen bonds (**DODMCB**). For this analogue, hydroxyl groups at the C-2, C-3 and C-6 carbons were replaced with hydrogen atoms. Disruption of intermolecular hydrogen bonds results in a model with a significantly lower modulus than that of **DMCD**, 37.6 GPa with MM3 and 33.0 GPa with QM (obtained from the slopes of fits shown if Figure 3).



Figure 3. Stress-strain plot for **DODMCB** as calculated with MM3 and B3LYP/6-311G\*\*+. The **DODMCB** moduli were calculated as 37.6 GPa for MM3 and 33.0 with B3LYP/6-311G\*\*+.

Molecular mechanics calculations with an elevated dielectric constant confirm the significant contribution of intramolecular hydrogen bonding to the molecular stiffness of the disaccharide cellulose model. Calculations with a dielectric constant of 7.5 effectively reduce the contribution of hydrogen bonds by about 80% in the energy minimization calculations. As a result, MM3 calculations demonstrated a **DMCB** modulus value of 42.9 GPa (Figure 4). This value is slightly higher than that of the cellulose analogue, **DODMCB** (vide supra).



Figure 4. Comparison of stress-strain plots of **DMCB** and **DODMCB** as determined by MM3. **DMCB** modulus calculations were performed with a standard and elevated dielectric constant,  $\varepsilon = 1.5$  and 7.5.

MM3 calculations with models of longer cellulose chains demonstrate a higher resistance to deformation. Given the importance of intramolecular hydrogen bonding to the modulus determinations for the disaccharide cellulose model, we explored whether the low number of hydrogen bonds in the short models could limit their stiffness, and partially explain why our initial modulus values fall below the range of previous theoretical and determinations. Calculations with a decasaccharide cellulose model, 1,4'-O-dimethyl-β-cellodecaoside (**DMCD**), resulted in a modulus of 126.0 GPa, a value almost 50% larger than that of the two-unit **DMCB** model. Interestingly, the 9 distinguishable disaccharide repeating units in **DMCD** display an average O1-O4' distance of 10.37 Å. This distance is close to the value observed in crystal structures of cellulose I (10.38 Å). In comparison, the **DMCB** models showed a MM3 equilibrium distance of 10.40 Å. Intramolecular hydrogen bonding deficient analogue of **DMCD**, 2,3,6,2',3',6'-hexadeoxy-1,4'-*O*-dimethyl-β-cellodecaoside (**DODMCD**), displays a modulus 63.3 GPa, a contribution of ca. 50% to the molecular stiffness of the model. The increase in modulus for the analogue decamer compared to the analogue dimer shows there may be an additional overall chain-length effect from long-range forces. We note that while QM and MM determinations with the disaccharide cellulose models underestimate modulus values, they correctly predict the significant contribution of intramolecular hydrogen bonding to cellulose molecular stiffness.



Figure 5. Comparison of stress-strain plots for the decasaccharide cellulose model **DMCD** and its analogue **DODMCD** as determined by MM3.

### **Conclusions**

Results presented herein show a significant gap between modulus values of disaccharide cellulose models (DMCB) and analogues incapable of hydrogen bonding interactions (DODMCD). Calculations with longer cellulose chains, DMCD and DODMCD, confirm this gap, and results in modulus values comparable to reported modulus determinations. The significant decrease suggests that intramolecular hydrogen bonding contributes considerably to molecular stiffness of our disaccharide cellulose models. Because hydrogen bonds have only 10% of the strength of C - O covalent bonds, it is initially surprising that intramolecular hydrogen bonding can increase the stiffness of a covalently bonded glucose backbone.

# **References**

Azizi Samir, M. A. S., Alloin, F. and Dufresne, A. 2005. Review of recent research into cellulosic whiskers, their properties and their Application in nanocomposite field. Biomacromol. 6:612-626.

Eichhorn, S. J., Young, R. J. and Davies, G. R. 2005. Modeling crystal and molecular deformation in regenerated cellulose fibers. Biomacromol. 6:507-513.

Eichhorn, S. J. and Davies, G. R. 2006. Modelling the crystalline deformation of native and regenerated cellulose. Cellulose 13:291-307.

Tashiro, K. and Kobayashi, M. 1991. Theoretical evaluation of three-dimensional elastic constants of native and regenerated celluloses: Role of hydrogen bonds. Polymer. 32:1516-1526.

Nishiyama, Y., Langan, P. and Chanzy, H. 2002. Crystal structure and hydrogen-bonding system in cellulose Iß from synchrotron x-ray and neutron fiber diffraction. J. Am. Chem. Soc. 124:9074-9082.