



Molecular deformation mechanisms in cellulose allomorphs and the role of hydrogen bonds



Cyrus Djahedi, Lars A. Berglund, Jakob Wohlert*

Wallenberg Wood Science Center, KTH Royal Institute of Technology, Teknikringen 56-58, SE-10044 Stockholm, Sweden

ARTICLE INFO

Article history:

Received 16 March 2015
 Received in revised form 14 April 2015
 Accepted 28 April 2015
 Available online 16 May 2015

Keywords:

Molecular dynamics
 Young's modulus
 Cooperativity
 Energy decomposition

ABSTRACT

Differences in tensile properties between cellulose crystal allomorphs cannot be rationalized by simply counting hydrogen bonds. From molecular dynamics computer simulations the cooperative nature of energy contributions to axial cellulose crystal modulus becomes apparent. Using a decomposition of inter and intramolecular forces as a function of tensile strain, the three allomorphs show dramatic differences in terms of how the contributions to elastic energy are distributed between covalent bonds, angles, dihedrals, electrostatic forces, dispersion and steric forces.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Cellulose is a linear homopolymer of β -1-4 linked anhydroglucopyranose units (Fig. 1). It is synthesized in nature by, e.g., plants, algae, bacteria, and tunicates as more than micrometer-long, semi-crystalline microfibrils with lateral dimensions ranging between a few up to several tens of nanometers depending on synthesizing species (Nishiyama, 2009; Saxena & Brown, 2005). Having extraordinary mechanical properties in combination with a high aspect ratio, being lightweight, thermally stable, renewable, and available in great abundance, cellulose has become important in many technical applications, not the least as the load-bearing component in biocomposites (Berglund & Peijs, 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Thus, knowledge and understanding about the intrinsic mechanical properties of crystalline cellulose is important in order to fully exploit its potential.

Crystalline cellulose exists in several different allomorphs. Crystals in native cellulose, cellulose I, are a combination of two co-existing crystal structures named I_{α} and I_{β} , of which I_{β} is the main constituent in higher plants (Atalla & VanderHart, 1984). Cellulose II, which has the polymer chains organized in an anti-parallel fashion as opposed to the parallel organization of cellulose I, is formed when native cellulose is dissolved and re-precipitated, or regenerated through mercerization. This transition is generally considered to be irreversible, suggesting that cellulose II is lower

in energy than cellulose I (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose III is obtained by liquid ammonia treatment of cellulose I or cellulose II, and is denoted cellulose III_I or III_{II}, accordingly. Finally, cellulose IV is obtained by thermal treatment of cellulose III, but is not considered further in the present manuscript. Interestingly, the different allomorphs of cellulose have been found to possess differences in their respective mechanical properties. Specifically for the case of the Young's modulus, there are several studies, suggesting that it is the highest for cellulose I, typically in the range 130–140 GPa (see Table 1). Values for cellulose II and III are generally 10–40% lower than that of cellulose I, but here experimental results exhibits a larger variability, and furthermore do not agree on which one of those two is the highest. Differences between experimental methods and source materials make comparisons complicated. There is only one study in which cellulose I, II and III was studied under similar conditions (Ishikawa, Okano, & Sugiyama, 1997), and their result with respect to elastic modulus was $II < I_{\beta} \approx III_I$.

Molecular modeling offers almost complete control over molecular details, and has proven to be an invaluable complement to experimental efforts. Consequently, many computational studies have been focused on the mechanical properties of both native and regenerated cellulose (Bergenstråhle, Mazeau, & Berglund, 2007; Cintrón, Johnson, & French, 2011; Eichhorn & Davies, 2006; Kroon-Batenburg & Kroon, 1997; Wu, Moon, & Martini, 2013). Most theoretical estimates of the Young's modulus of cellulose I_{β} agrees well with experimental values, but in the case of cellulose II results are even more scattered than the experiments, ranging from 89 up to 166 GPa.

* Corresponding author. Tel.: +46 087908037.
 E-mail address: jacke@kth.se (J. Wohlert).

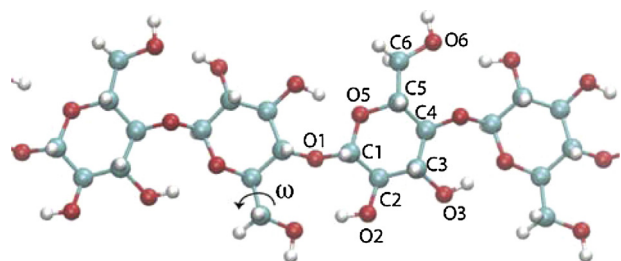


Fig. 1. Cellulose molecule with labels used in this manuscript.

Traditionally, the stiffness of the cellulose crystal has been attributed to its many intra- and intermolecular hydrogen bonds (Moon et al., 2011). It is thus tempting to conclude that the differences between crystal allomorphs is a consequence of them exhibiting different hydrogen bond patterns, as revealed by X-ray crystallography and neutron diffraction. Specifically, as depicted in Fig. 2, cellulose II and III_I both have weaker intramolecular hydrogen bonds oriented in the direction of the chain than cellulose I_β (Langan, Nishiyama, & Chanzy, 1999; Langan, Nishiyama, & Chanzy, 2001; Nishiyama, Langan, & Chanzy, 2002; Wada, Chanzy, Nishiyama, & Langan, 2004), a fact that intuitively would affect the ability of the chain to stretch. Since slight differences in chain packing lead to variations in density, this has been brought forward as a tentative explanation.

However, even though hydrogen bonding clearly does affect the stiffness of the cellulose chain, the mechanisms are not obvious, considering that a hydrogen bond only has a fraction of the intrinsic stiffness of a comparable covalent linkage. This suggests some form of cooperative effect between covalent and hydrogen bonds (Altaner, Thomas, Fernandes, & Jarvis, 2013).

Past descriptions of hydrogen bonding effects on cellulose stiffness have often been simplistic and exaggerated. For example, if hydrogen bonds are artificially removed in simulations, the crystal structure is destabilized and the relevance of the new deformation mechanisms is questionable. Instead, comparison of different allomorphs may be a more fruitful approach. Counting hydrogen bonds is obviously not enough, since it is not clear how changes in the hydrogen bond pattern would affect the overall cellulose crystal stiffness, and the origin of tensile property differences between cellulose allomorphs. In the present work we have used

molecular dynamics (MD) simulations to study the molecular scale deformation mechanisms of three crystalline cellulose allomorphs (I_β, II, and III_I) under tensile stress. The specific aim is to clarify how their structural differences also lead to variations in their mechanical properties. This was done by decomposing the total stiffness into contributions from different degrees of freedom: covalent bonds, angles, and torsions, as well as non-bonded contributions from dispersion interactions and electrostatics.

2. Methods

Molecular Dynamics simulations were run with the GROMACS 4.6.1 (Hess, Kutzner, van der Spoel, & Lindahl, 2008) simulation package, using a leap-frog algorithm with a time step of 2 fs for integrating the equations of motions. The GLYCAM06 force field for cellulose (Kirschner et al., 2008) and the TIP3P model (Jorgensen, Chandrasekhar, Madura, Impey, & Klein, 1983) for water were used for the interactions. A cut-off of 1.2 nm was used for

Lennard–Jones interactions, and electrostatic interactions were handled with PME (Darden, York, & Pedersen, 1993; Essmann et al., 1995) using a cut-off of 1 nm for the real-space part. Temperature was maintained at 300 K using stochastic velocity-rescaling (Bussi, Donadio, & Parrinello, 2007) with a time constant of 2 ps, and pressure was scaled to 1 atm during equilibration using weak coupling (Berendsen, Postma, van Gunsteren, DiNola, & Haak, 1984). The Cellulose-Builder software (Gomes & Skaf, 2012) was used to generate computational models of all crystalline allomorphs based on the published cellulose crystal structures (Nishiyama et al., 2002; Langan et al., 2001; Wada et al., 2004). The ratio of surface chains to core chains was maintained the same in all cases, with models consisting of 16 cellulose chains in a 4 × 4 configuration and 10 cellobiose units in length.

All model nanocrystals were subsequently immersed in water. One may question whether this affects calculated moduli, and if the comparison to experimental data, which usually is obtained at dry conditions, is valid. However, even at dry conditions, there is water bound to the surfaces of cellulose. Moreover, experiments performed at high relative humidity show that moisture has a negligible effect on the stiffness (Mann & Roldan-Gonzalez, 1962; Sakurada, Ito, & Nakamae, 1966). Finally, previous

Table 1
Experimental values of the Young's modulus of cellulose crystal allomorphs.

E [GPa]	Method	Material	Reference
Cellulose I _β			
220	Inelastic X-ray scattering	Flax	Diddens, Murphy, Krisch, and Muller (2008)
105	Raman	CNC/Plant	Rusli and Eichhorn (2008)
151	AFM	CNC/Tunicate	Iwamoto, Kai, Isogai, and Iwata (2009)
138	X-ray	Ramie	Nishino, Takano, and Nakamae (1995)
130–137	X-ray	Ramie	Sakurada, Nukushina, and Ito (1962)
143	Raman	CNC/Tunicate	Sturcova, Davies, and Eichhorn (2005)
122–135	X-ray	Ramie	Matsuo, Sawatari, Iwai, and Ozaki (1990)
114	X-ray	Ramie	Ishikawa, Okano, and Sugiyama (1997)
130	X-ray	Ramie (100% RH)	Sakurada, Ito, and Nakamae (1966)
Cellulose II			
88	X-ray	Ramie	Nishino, Takano, and Nakamae (1995)
106–112	X-ray	Ramie	Matsuo, Sawatari, Iwai, and Ozaki (1990)
89	X-ray	Ramie	Ishikawa, Okano, and Sugiyama (1997)
90	X-ray	Ramie (100% RH)	Sakurada, Ito, and Nakamae (1966)
70–90	X-ray	Fortisan H (92% RH)	Mann and Roldan-Gonzalez (1962)
Cellulose III _I			
87	X-ray	Ramie	Nishino, Takano, and Nakamae (1995)
115–122	X-ray	Ramie	Ishikawa, Kuga, and Okano (1998)
115	X-ray	Ramie	Ishikawa, Okano, and Sugiyama (1997)

Download English Version:

<https://daneshyari.com/en/article/7788044>

Download Persian Version:

<https://daneshyari.com/article/7788044>

[Daneshyari.com](https://daneshyari.com)