Mechanical properties of cellulose nanofibrils determined through atomistic molecular dynamics simulations

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SUMMARY: We have carried out atomistic molecular dynamics simulations to study the mechanical properties of cellulose nanofibrils in water and ethanol. The studied elementary fibrils consisted of regions having 34 or 36 cellulose chains whose cross-sectional diameter across the fibril was roughly 3.4 nm. The models used in simulations included both crystalline and non-crystalline regions, where the latter were designed to describe the essentials parts of amorphous cellulose nanofibrils. We examined different numbers of connecting chains between the crystallites, and found out that the elastic constants, inelastic deformations, and strength of the fibril depend on this number. For example, the elastic modulus for the whole fibril can be estimated to increase by 4 GPa for each additional connecting chain.

The strength and stiffness of cellulose crystals underlies vast technological uses of wood and wood fibres including traditional paper making. In recent years, there has been an increasing interest in cellulose nanofibrils due to their excellent mechanical properties and their ability to form strongly bonded networks (Moon et al. 2011). Potential applications are based on hierarchies of such structures from nano to micro and macro scale. However, experimental studies (Henriksson et al. 2008) have mainly focused on its crystal structure (Moon et al. 2011; Mazeau, Heux 2003; Eichhorn, Davies 2006; Bergenstråhle et al. 2009; Matthews et al. 2011; Zhang et al. 2011; Paavilainen et al. 2011). In this paper, we extend this approach to non-crystalline regions formed within the fibril in zones where a large part of the cellulose chains is broken. X-ray diffraction data suggests such regions to be common in cellulose fibrils, sometimes even 50% of the material being in the amorphous state (Leppänen et al. 2010).

The studied fibrils consist of crystallites having about 36 cellulose chains that correspond to the average elementary fibril size in wood. The simulations were carried out both in water and ethanol. The observed elastic modulus for crystal cellulose compares well with the values obtained experimentally. However, non-crystalline regions were found to decrease the modulus significantly. Moreover, these regions were observed to introduce non-uniform stress in cellulose chains. At high tensile stress, this can lead to relative sliding of the chains and finally to the breakup of the fibril. The deformation behaviour couples to opening up of the characteristic twist in individual chains and in the whole fibril.

Atomistic model of cellulose nanofibrils

The atomistic molecular dynamics simulations were performed using the GROMACS software package, version 4.0.7 (Lindahl et al. 2001; van der Spoel et al. 2005). To parameterize cellulose molecules we used the all-atom OPLS force field (Jorgensen, Tirado-Rives 1988; Rizzo, Jorgensen 1999; Price et al. 2001; Kaminski et al. 2001) extended for carbohydrate simulations (Damm et al. 1997). For water, we used the TIP3 model, which is compatible with OPLS. The bonds within a cellulose chain were described by quadratic potentials, thus they did not break during the simulations. Meanwhile, hydrogen bonds were dynamic and allowed spontaneous formation of transient hydrogen bonding networks.

Periodic boundary conditions with the usual minimum image convention were used in all three directions. The time step was set to 2 fs. Simulations were performed in NVT conditions at a temperature of 293 K. More details have been presented by Paavilainen et al. (2011).

The studied systems can be divided into three categories:

1) Bare crystalline fibrils having 36 chains, which corresponds roughly to 3.4 nm cross diameter of the fibril. The length of the crystal is about 10 nm (20 residues in each chain).

2) Fibrils with a non-crystalline region, in which there are two 10 nm long crystalline regions with 36 chains in each. The non-crystalline region breaking the order along the fibril has 10 chains, which connect the crystalline
regions together, and the remaining 26 chains are broken in random positions (see Fig 1 for visualization of the structure).

3) Fibrils with a non-crystalline region, in which there are two 10 nm long crystalline regions with 34 chains in each (two corner chains were removed as compared to the previous case with 36 chains). The non-crystalline region has only 3 chains connecting crystalline parts together.

The length of the non-crystalline region was about 5 nm in both cases 2 and 3.

The simulations for elastic properties were carried out using the code for steered molecular dynamics (Park, Schulten 2004) that is implemented in GROMACS (van der Spoel et al. 2005). A constant force was applied between centres of mass (COM) of two groups in the fibril. The groups were selected either as sections (about 3-4 residues from each chain) close to the non-crystalline regions, or at the far ends of the fibril. In the cases involving non-crystalline regions, one of the groups was frozen and the force was only applied to the other group. For the bare crystalline fibrils neither of the groups was frozen.

The bare crystalline structures were studied previously by Paavilainen et al. (2011). In brief, in these studies we took advantage of recent wide-angle X-ray data for commercial nanocellulose (Leppänen et al. 2010) and used the results with previous studies of crystal (cellulose Iβ) structure (Nishiyama et al. 2002) to construct initial configurations for the fibrils. In the simulations, the fibrils developed clearly visible overall twisting. The simulations showed two different stages of twisting of the model fibrils: rapid initial twisting with no clear temperature dependence and a slower twisting whose rate of relaxation is strongly temperature dependent. No significant bending or stretching was discovered but the individual chains are also twisted along their long axis. The number of intra-chain hydrogen bonds was decreased due to twisting but the number of inter-sheet bonds and bonding with water was increased.

The twisting of individual molecular chains and fibrils starts a hierarchy of twisting structures, extending to cellulose nanofibers, macrofibrils (not studied here) and finally to wood fibres. On the other hand, it is known that this twisting behaviour is important to many macroscopic properties of fibres and paper, including strength and dimensional stability. Thus, the observed characteristic twisting on the molecular level may have far-reaching consequences on product properties, e.g., when moisture content is varied. However, one has to be careful in analyzing the results related to twisting in molecular dynamics simulations, since its stability has been recently questioned (Matthews et al. 2012).

In order to calculate the stress imposed in fibrils we need to know the cross-sectional area of fibrils. In the fibril including 6×6 cellulose chains, the separation of chains is 0.53 nm in the 110-crystal direction, and 0.60 nm in the 1-10 crystal direction (Nishiyama et al. 2002; Nishiyama 2009). The angle between these crystal directions is 93.5 degrees. Thus, the cross-sectional area can be estimated to be \((6 \times 0.53 \text{ nm}) \times (6 \times 0.60 \text{ nm}) \times \sin(93.5^\circ) = 11.4 \text{ nm}^2\). This estimate is used in all underlying calculations of the stress.

**Fig 1.** Atomistic model of a cellulose nanofibril of type 2) used in simulations. The fibril consists of two 10 nm long crystalline parts connected by 10 chains in the non-crystalline part. The crystalline part on the left is not shown completely. For clarity, water/ethanol is not shown.

**Fig 2.** a) Strain response of the crystal region in water for varied force levels (1 kJ mol\(^{-1}\)nm\(^{-1}\) = 1.86054 MPa). b) Resulting stress-strain behaviour obtained by averaging the strain over the time period 3-1000 ps, after the force applied at time zero. When calculating the modulus, we used the cross-sectional area of the full single crystal with 36 chains.

**Mechanical testing in nano scale**

Elasticity of the modelled fibrils was determined by applying a tensile force on them and looking at the strain response. The magnitude of the constant force was varied between 2500-15000 kJmol\(^{-1}\)nm\(^{-1}\), corresponding to 0.415-2.491 GPa for the studied fibril. The strain behaviour for pure crystal region in water is shown in Fig 2. The main strain component appeared very quickly after the force was applied. In addition, a small gradual increase in strain with time was observed in most cases. When plotting the strain versus stress, we observe an offset at vanishing stress. Despite the offset, the value of elastic modulus can be determined. The obtained value 157±4 GPa compares well with experimental values 120-150 GPa for crystal cellulose (Moon et al. 2011).

The offset and the initial rapid increase in strain are, at least partly, a consequence of untwisting of the crystalline structure under the applied force. In all cases the twisting decreased from the value of 2.3 degrees/nm obtained without the applied force (Paavilainen et al. 2011). For the smallest force 2500 kJmol\(^{-1}\)nm\(^{-1}\) the twisting decreases to about 2.0 degrees/nm, and for the largest force 15000 kJmol\(^{-1}\)nm\(^{-1}\) to about 1.0 degrees/nm.
We also studied the elasticity of the amorphous-like regions with 3 and 10 connecting chains attached to the neighbouring crystallites. Now the force was varied between 500 and 5000 kJmol⁻¹nm⁻¹. An example of the effect of the relatively large applied force on the fibril structure is shown in Fig 3. The strain response of the whole fibril was very close to that of the disordered region (see Fig 4). However, it is easier to calculate strain for the latter due to the small bending of the fibril under applied force.

When calculating the modulus, we assumed the same cross-sectional area as for the full single crystal with 36 chains. As expected, the elastic modulus decreased with reduced number of connected chains. As indicated in Table 1, it is possible to crudely estimate the total elastic modulus by assuming that each connecting chain adds 4 GPa to the overall value. However, there are refinements to this rule coming from the hydrogen bonding. The true elastic modulus can be either bigger or smaller than this simple estimate.

It is interesting to notice that the surrounding liquid also plays some role in determining the elasticity of fibrils. The results for water can be compared with those for ethanol, see Fig 5. For the same 10 connecting chains as for water, the value of elastic modulus for the disordered region is 41.0 ± 0.5 GPa when estimated by averaging strain in the time interval 6-500 ps. This value is clearly smaller than the value 54 ± 2 GPa for water. This result may reflect the reduced hydrogen bonding in ethanol. The strain/force curve is characterized by a strong power-law increase with time for ethanol, and the estimated value of the modulus slightly decreases with time. By estimating the modulus from the three largest forces in the interval 1300-1500 ps, we obtain the value of 39.7 GPa. The initial strain offset (0.008 ± 0.025%) practically vanishes in Fig 5b, which means that a similar initial power-law increase of strain is found with all stress levels. The strain averages later at 1300-1500 ps, and the offset becomes finite as in water.

The larger value of modulus in water compared to ethanol may be somewhat counter-intuitive, as for wood fibres the absorption of water generally lowers elastic modulus. However, for fibres the main effect of water is likely to open up pores between fibrils, thus softening their collective behaviour under stress.

Another curiosity is the relatively large “initial strain” obtained in water in the limit of vanishing stress. It looks

Table 1. Elastic properties of the cellulose crystal with 36 chains and fibrils with non-crystalline regions with reduced number of connecting chains. In these estimates, the relative strain was calculated over the disordered region only. Strain at F = 0 refers to the linearly extrapolated value of strain at vanishing stress. In each case, the results (including error estimates) are for one connecting chain configuration only.

<table>
<thead>
<tr>
<th>Number of connecting chains</th>
<th>E_mod (GPa)</th>
<th>E_mod/chain (GPa)</th>
<th>Strain at F = 0 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>11.9±0.2</td>
<td>4.0±0.1</td>
<td>0.29±0.06</td>
</tr>
<tr>
<td>10</td>
<td>54±2</td>
<td>5.4±0.2</td>
<td>0.16±0.04</td>
</tr>
<tr>
<td>36</td>
<td>157±4</td>
<td>4.4±0.1</td>
<td>0.10±0.04</td>
</tr>
</tbody>
</table>

Fig 3. The effect of tensional force 15000 kJmol⁻¹nm⁻¹ on elementary fibril with 10 connecting chains. The initial structure is the same as in Fig 1.

Fig 4. The strain calculated over the total length of the fibril follows closely to the strain over non-crystalline part for 3 connecting chains at 5000 kJmol⁻¹nm⁻¹ stress level.

Fig 5. a) Strain response of the crystal region in ethanol for varied force levels. For short times, strain increases like a power-law in time. b) Resulting stress-strain behaviour obtained by averaging the strain over a time period of 6-500 ps after the force was applied at time zero.
Fig 6. Snapshots of fibril structure during straining. a) Initial structure, b) at the point where hydrogen bonds begin to open up, and c) after the connecting chains have been partly pulled out from the crystal.

like the lower the number of connecting chains is, the more these chains (or their bond angles) have freedom to straighten up when the load is turned on. On the other hand, in ethanol a statistically significant offset appears only after some straining in the case of 10 connecting chains.

When the stress is increased sufficiently, hydrogen bonds between cellulose chains begin to open and the sliding of chains with respect to one another becomes possible. Snapshots of a broken structure are shown in Fig 6. For the case of 3-connecting chains with 10 nm long crystals, the tensile strength of the fibril is about 0.8 GPa in water. Beyond this level of stress, the pulling of the fibril causes sliding of the three connecting chains with respect to the rest of the crystal. This is combined with enhanced untwisting of the three chains.

In Fig 7, we show the strain development for three different force levels. The force application induces elastic longitudinal oscillations in the fibril that decay rapidly. After this, the strain increases almost linearly with time. A change in the slope of the strain curve is noticed when the opening of hydrogen bonds begins. For the two higher forces, hydrogen bonds begin to open quite soon after application of the stress. Still, the turning point is visible roughly at the same strain level 0.53 as for the lowest force. This behaviour can be compared with the snapshots of the fibril structure at various moments of the straining as shown in Fig 6.

It is very interesting that beyond the turning point, the strain rate remains roughly constant even when the pulled chains have shorter and shorter parts within the crystallite. Such behaviour is possible, if due to stress concentration, the chain is detached from the rest of the crystallite essentially one residue at a time. An analogous fracture mechanism has been suggested earlier for paper where inter-fibre bonds open up near a stress concentration point during fracture (Alava, Niskanen 2006). It would be intriguing if a similar mechanism applied on molecular scale as well. This would imply that the strength would be rather independent of the total amount of hydrogen bonds between the pulled chains and the crystal part. In other words, the strength of fibril would be rather insensitive to the length of the crystalline.

Linear increase in strain with time is in agreement with the simple Eyring model (Caulfield 1985) that has been earlier used as a simple illustration when discussing creep of paper. Unfortunately, the current simulations are not sufficient to conclude the form by which the strain rate depends on stress. We hope that future simulations will shed more light on the exact breaking mechanism and on the effects of various factors on strain rate.

Discussion

We have shown that it is possible to study the mechanical properties of cellulose nanofibres on an atomic level by atomistic molecular dynamics simulations. In addition to elasticity of crystalline regions, it is important to study imperfect fibrils with non-crystalline (amorphous) regions where only a few connecting cellulose chains glue different crystal regions together. Such regions have earlier been indicated by X-ray diffraction experiments. The amorphous regions are expected to cause the stiffness of fibrils to be significantly lower than the stiffness of pure cellulose crystals.

Our simulations indicate that each connecting chain contributes roughly 4 GPa to the elastic modulus. This can be compared with measured elastic moduli below 20 GPa (Henriksson et al. 2008) for nanocellulose sheets. Even though this value is affected by finite porosity and orientational distribution of fibrils, the moduli of the fibrils most likely are not far from this level. Thus, this suggests that the number of connecting chains is typically less than 10. In order to estimate this number more accurately, the effect of network structure should be analysed systematically and the crystallinity of fibrils should be known more accurately. Especially it would be critical to know how much of the amorphous cellulose is along the fibrils (as in non-crystalline parts) compared to...
the amorphous parts in between the fibrils. Moreover, analysis of complete nanocellulose fibrils instead of elementary ones together with analysis of network elasticity would be important to do in the future.

Our current simulations indicate an intriguing constant strain rate in the “supercritical” region where cellulose chains begin to slide with respect to one another. This behaviour suggests stress to be distributed in a manner where the resisting force becomes rather independent of the total amount of hydrogen bonds between sliding chains and crystallite. We hope future simulations on varying crystal lengths will clarify the exact mechanisms underlying the strength behaviour of elementary fibrils.

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Literature