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Stiff as a Board: Perspectives on the Crystalline Modulus of Cellulose

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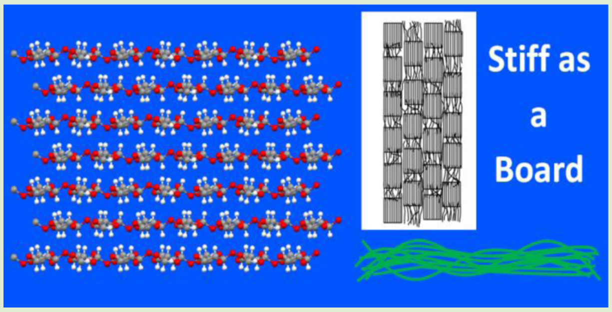
Supporting Information

ABSTRACT: A viewpoint on the importance of the accurate determination of the crystal modulus of cellulose is given with respect to recent advances in extracting high modulus nanofibrils/fibers from plants and production by bacteria and animals. Often the modulus of these nanofibrils/fibers is assumed to be the same as the crystal modulus of cellulose. Both experimental and theoretical calculations of the crystal modulus of cellulose are discussed and put in context of the use of cellulose nanofibers for high stiffness composites. New research into the exact nature of the structure of cellulose nanofibers is suggested, with a view to better processing routes for realizing high modulus/low density materials.



The English language contains notions of stiffness and inflexibility associated with our most used material: that of wood. To be "stiff as a board" is to be inflexible, formal, or unbending, where the "board" is in effect a simile for a piece of wood (some say "stick"). Despite our general conceptual appreciation of the stiffness of wood, there has been great debate over the maximum stiffness of cellulose or the crystal modulus. One possible reason why this debate has ensued stems from the fact that cellulose, being the main structural component of plant material, is the most common organic polymer.[1] In engineering applications, to minimize the mass of a beam undergoing deflection, the key parameter that also has to be minimized is $(\rho^3/E)^{1/2}$, where ρ is the density of the material, and E is Young's modulus.[2] Cellulose, in the form of wood, has a particularly low value of this parameter (0.13 $\mathrm{Ns^3\ m^{-5}}$).[2] Only carbon fiber reinforced plastic (0.11 $\mathrm{Ns^3\ m^{-5}}$) and foamed polyurethane (0.13 $\mathrm{Ns^3\ m^{-5}}$) compete and, respectively, equal wood on this basis.[2] Increasing the effective modulus of cellulose by extraction of stiff high-modulus crystals and nanofibers will further decrease $(\rho^3/E)^{1/2}$ by increasing E, while maintaining a competitive density to other materials. Here I define the "effective modulus" as being the value achieved when all other factors that reduce this value have been removed (e.g., fibril angle, defects/amorphous material).

Plant tissue is hierarchical, and cellulose is only part of the overall structure.[1] The basic building blocks of plant cell walls are called "microfibrils", which is a misnomer as they typically have lateral dimensions on the nanoscale.[3] These microfibrils have a semicrystalline polymeric structure, with the crystalline domains being the stiff or high modulus component. If this stiff cellulosic component can in some way be extracted from the cell wall then there is potential to effectively increase E and, therefore, reduce $(\rho^3/E)^{1/2}$ and reinforce composite materials at low weight.

For the reasons above, there has been a lot of interest recently in the ways in which cellulose nanofibers can be extracted from the plant cell wall via mechanical means.[4] This extraction is usually achieved by homgenisation and/or grinding methods.[5] The resultant fibers produced during this process are typically in a reticulated network of what has been termed microfibrillated cellulose (MFC).[4] Cellulose nanofibers can also be produced via acid hydrolysis of plant tissue, removing a large proportion of the amorphous material.[5] This process results in rod-like "crystals" that have been called, cellulose nanocrystals (CNCs) or cellulose nanowhiskers (CNWs).[6] It has been made clear that there is great potential for these nanofibers/nanofibrils and nanowhiskers/nanocrystals for a wide variety of applications where high stiffness is required. It is not clear though that the ultimate modulus of cellulose is, and indeed has been, realized when they are extracted from the cell wall, either by mechanical or chemical approaches. It is important therefore to firmly establish the upper limit of modulus and to then see where our existing materials sit in relation to this. Given this challenge, we could then alter processing and production methods to better extract nanofibers to fully utilize the inherent stiffness of cellulose.

Sakurada et al. published a paper in 1962 reporting a value of 137 GPa for the crystal modulus of cellulose.[7] The "crystal modulus" is representative of the 3-dimensional periodic chain structure, as distinct from the "chain modulus", which is simply the stiffness of a single molecular chain. This value reported by Sakurada et al.[7] is widely reported in the literature, often without justification, as being representative of the modulus of nanofibers of all types. The approach assumed that the fibers

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have a uniform stress microstructure, where the stress in the crystals is the same as in the amorphous regions. Of course, this may indeed be true, but nevertheless no concrete evidence for this has ever, to the author's knowledge, been presented. The question then arises, what are the implications of the microstructure not being uniform stress? If the structure is not uniform stress, then we must assume that there is some averaging of stress across the microstructure. It is presumed that the stress will be higher in the crystals than in the amorphous regions of the material. This would comply with our current understanding of a composite microstructure, with stress being transferred to the stiffer phase. We should therefore expect that the modulus of the former could be underestimated by assuming a uniform stress microstructure. High values of the crystal modulus have been reported in the literature; Diddens et al. report a value of 220 GPa for instance.[8] The vast majority of molecular modeling studies on the crystal modulus of cellulose, however, give values in the range 100−150 GPa.[9−14] Unless these calculations vastly underestimate the modulus then it is probably best to assume that they represent our most accurate upper limit to the modulus of cellulose. Unfortunately (and this includes one of the author's own papers[13]), some forcefields have been used to calculate crystal modulus that do not have an explicit function for the hydrogen bonds and so may overestimate their stiffness contribution. The use of different forcefields and approaches in itself is also a source of confusion in the literature, so good experiments are required. Other potentially important interactions, such as hydrophobic and van der Waal forces, are generally not considered.

Recent AFM (atomic force microscope) cantilever measurements of the bending stiffness of tunicate cellulose microfibrils has yielded values of ∼145 and ∼150 GPa for TEMPO oxidized and acid hydrolyzed fibrils, respectively.[15] This is probably our best yet experimentally determined value of the modulus of highly crystalline cellulose. Less direct measurements, with some possibly flawed assumptions, using Raman spectroscopy have yielded similar values to these (∼143 GPa).[16] This is encouraging, providing some consistency across experimental methods. Another recent determination of the modulus of nanofibrils contained within MFC sheets, using a better basis for the Raman approach, has yielded values in the range 29−36 GPa,[16] which are not especially high compared to say even an intact plant fiber (values of 20−40 GPa are not untypical). In the same study bacterial cellulose (BC) fibrils were found to have moduli in the range 79−88 GPa,[17] similar to values reported using an AFM cantilever method.[18] There appears to be a mechanical difference then between nanofibrils/fibers extracted from the cell wall and bacterial and nanocrystal forms of cellulose.

All this leads to important questions. Do MFC nanofibrils/nanofibers have moduli of the same order as the crystal modulus of cellulose? Also, what is the structural form of cellulose nanofibers extracted from the cell wall? Do they comprise amorphous and crystalline domains? How does this microstructure affect their mechanical stiffness? How might things like the orientation of molecular chains play a role in the determination of the stiffness of cellulose nanofibers?

Very little is known about the exact fine structure of cellulose nanofibers. It is perhaps true that more is known about the structure of native crystals in the plant cell walls before extraction takes place. Some recently published high resolution TEM images of TEMPO oxidized and then mechanically treated nanofibrils/fibers appear (on inspection by the present author) to contain highly misoriented chains with little apparent crystalline order at this resolution (see Figure 1).[19]

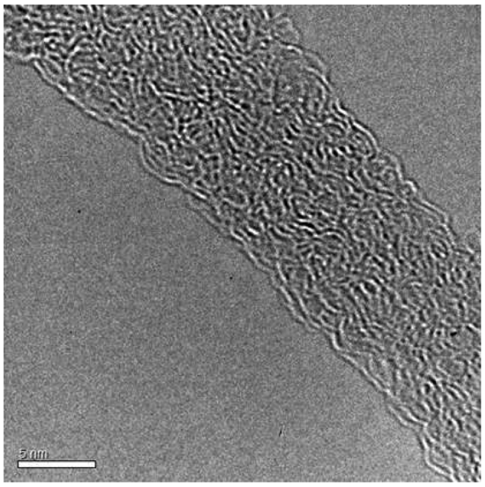

Figure 1. High resolution transmission electron microscope (TEM) image of a cellulose nanofibril/fiber extracted using the TEMPO oxidation method. Image courtesy of Professor B.S. Hsiao (Stony-Brook University). Adapted with permission from *ACS Macro Letters* **2012**, *1*, 213−216. Copyright 2012 American Chemical Society.

It may be, therefore, that this highly disordered structure is a reason for the low modulus of nanofibrils/fibers. Orientation of molecular chains along the axis of a fibril will significantly affect the mechanical properties of the nanofibrils/fibers; the less oriented the molecular chains, the lower the nanofibril/fiber modulus. A simple relationship can be found (see Supporting Information) for the nanofibril/fiber modulus (E_f) based on misoriented molecular chains, assuming they have a modulus E_m equal to the crystal or chain modulus of cellulose, at a mean angle of θ to the axis of the nanofibril/fiber, as $E_f = E_m(\cos^2\theta - \nu\sin^2\theta)$, where ν is Poisson's ratio. Assuming ν to be 0.3, as has been previously reported,[20] and E_m to be 150 GPa (to account for upper values of the modulus, but excluding very high values) then a plot of this function can be obtained, as shown in Figure 2. The equation is valid in the range ∼0−61°, after which E_f becomes negative.

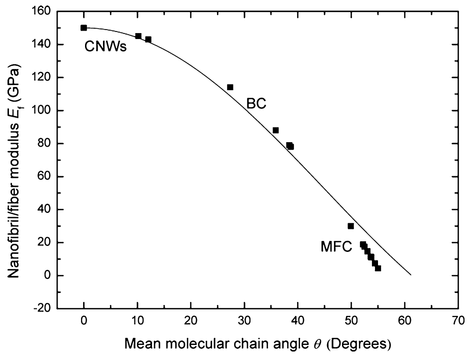

Figure 2. Fibril modulus E_f as a function of mean molecular chain angle θ. The solid line is the equation $E_f = E_m(\cos^2\theta - \nu\sin^2\theta)$, where ν is Poisson's ratio (=0.3) and E_m is the modulus of the molecular chains (=150 GPa). Data points are values of the modulus of cellulose nanowhiskers (CNWs), bacterial cellulose (BC), and microfibrillated cellulose (MFC) taken from the literature.[15−18,21−27]

The solid line represents the equation, and data are plotted from known values of the modulus of various forms of cellulose nanofibrils/fibers and nanocrystals/whiskers, with their predicted mean molecular chain angles calculated using the equation for E_f. Of course we have no information about the mean molecular chain angle. Image analysis of Figure 1 (using Image J, see Supporting Information), however, suggests a mean angle of ~45°, which is consistent with these data. In the noncrystalline (or amorphous) regions of a nanofiber, orientation of molecular chains may deviate from the main axis, and so a correlation could be made between θ and crystallinity. Given that it is well-known that MFC can exhibit a very low crystallinty (sometimes as low as ~8–50%),[28] and nanocrystals/whiskers exhibit the highest (~90%),[29] with BC intermediate between these two values, this could form a good correlation. As can be seen, this relationship could account for the differences seen in nanofibril/fiber moduli, although more work has to be done to fully characterize the subfibrillar form of these nanofiber types. Very recent data published[30] on disordered material present in cellulose nanocrystals seems to offer a new and promising approach to a better understanding of these materials.

To summarize, there has been a great deal of debate on the exact value of the crystal modulus of cellulose. It is important to establish what the modulus of crystalline cellulose is, perhaps most importantly by simulation, as it represents what is potentially achievable from an experimental point of view. It is not enough, in my view, to simply assume that nanofibrils/fibers, nanocrystals/whiskers extracted from the cell walls of plants, or produced by bacteria and sea creatures have the same value as the crystal modulus of cellulose. Ultimately, only the structure *within* these nanofibrils/fibers will have this property. It is, however, conceivable that better processing of nanofibers may lead us to achieve increased modulus of our nanofibers and ultimately to engineering applications for our materials. To achieve this, we need better understanding of sub-nanofibril/fiber structure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A derivation of the equation used to predict the fibril modulus as a function of molecular chain angle is reported along with the details of the image analysis method used to calculate the mean molecular chain angle in Figure 1. Details on how the TEM image in Figure 1 was obtained are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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