PAK LAB Laboratory for Multiscale Modeling of Macromolecular Assembly & Control (LMAC)

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Investigating the effect of water on the mechanical properties of cellulose from multiscale molecular dynamics simulations

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BACKGROUND

Cellulose is a carbohydrate biopolymer composed of linear chains of glucose molecules and is the main skeletal constituent of plant secondary cell walls. The natural abundance, biocompatibility, biodegradability, and mechanical strength of cellulose make it a promising renewable material with a wide range of applications. However, the moisture sensitivity of cellulose poses challenges to engineering high performance cellulosic materials.

The physics of water and cellulose are highly coupled at the nanoscale and contribute to the mechanical properties of cellulosic materials. Previous molecular dynamics (MD) studies have shown that water can influence cellulose self-assembly and the mechanical properties of nanocellulose by disrupting inter-polymer hydrogen bonds at the cellulose surface.[1,2]

Bottom-up coarse-graining provides a means for systematically mapping atomistic information to lower resolution models to increase the length and time scales achievable by simulation, bridging the gap between models and experiment. We present coarse-grained models parametrized using atomistic simulations of cellulose with 0% and 95% moisture content to elucidate the impact of water on the mechanical properties of nanocellulose assemblies.

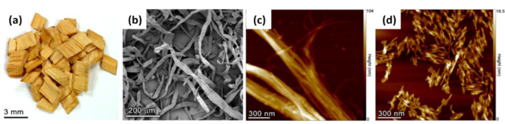


Figure 1. The hierarchical scales of cellulosic materials. Cellulose is naturally found in wood (a), (b) SEM of wood pulp cellulose fiber cells, (c) AFM of cellulose macrofibrils, (d) AFM of cellulose nanocrystals. Reproduced from [3]

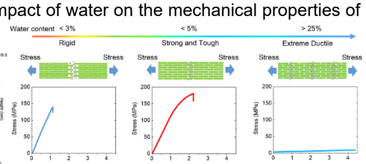
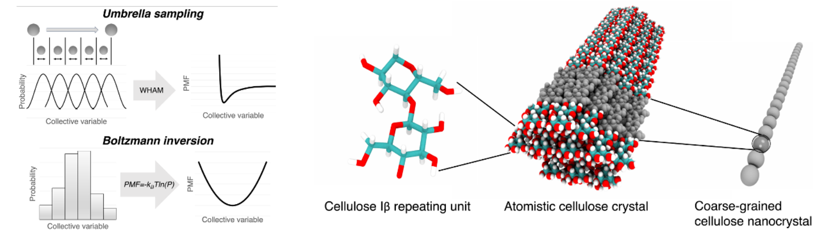


Figure 2. Increasing water content reduces the tensile modulus of nanocellulose films. Reproduced from [4]

APPROACH

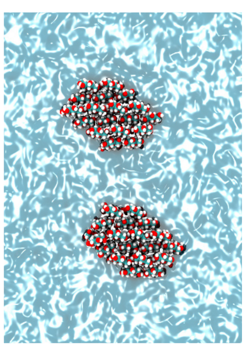
Bottom-up coarse graining for nanocellulose with varying moisture contents



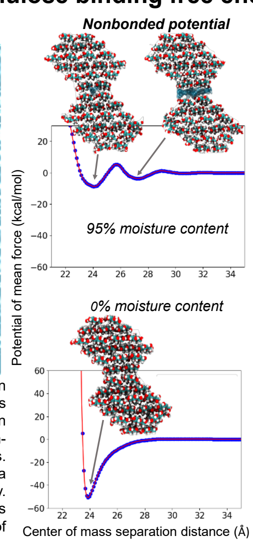
Coarse-grained (CG) force field parameters were derived using atomistic molecular dynamics simulations of cellulose Iβ in vacuum (0% moisture content) and solvated in water (95% moisture content) performed using GROMACS software [5] and the CHARMM force field [6]. 72 glucose residues were mapped to one CG site using a bottom-up coarse-graining approach: non-bonded interactions between the 100 cellulose surfaces in the presence of water were determined using umbrella sampling to calculate the potential of mean force (PMF). The potential energy was taken as an approximation of the PMF in vacuum simulations as the lack of water reduced the entropic contribution to the free energy. Bonded interactions were parametrized using Boltzmann inversion to calculate the PMF from probability distributions of bond lengths and angles between groups of atoms corresponding to CG sites. MD simulations for coarse-grained nanocellulose assemblies were conducted using LAMMPS software [7]. Mechanical stress MD simulations were performed to determine the tensile modulus for CG nanocellulose assemblies with force field parameters corresponding to 0% and 95% moisture content.

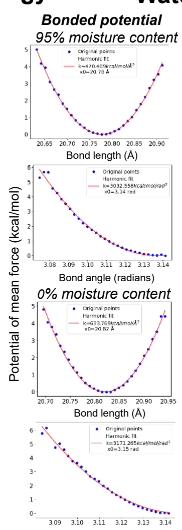
KEY OUTCOMES

Water reduced cellulose binding free energy

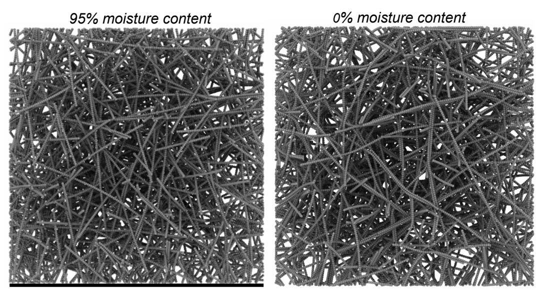


The amount of water in between atomistic cellulose crystals introduced an additional minimum in the free energy profile used for non-bonded CG force field parameters. The lack of water resulted in a stronger binding free energy. Additionally, bonded interactions were less stiff in the presence of water.





Water lowered the tensile modulus of nanocellulose



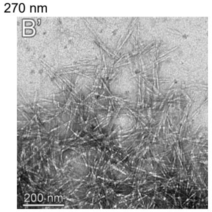
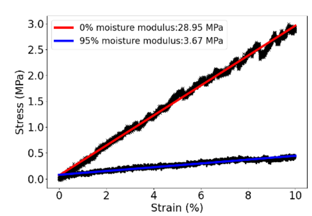


Figure 3. TEM image of nanocellulose reproduced from [8]

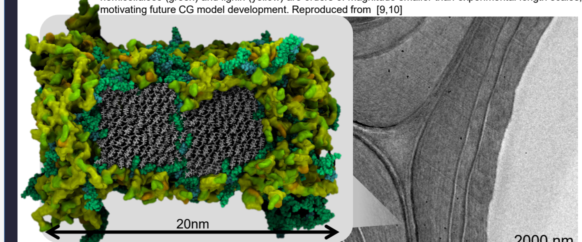


CONCLUSIONS

Water impacted the mechanical properties of nanocellulose by altering bonded and non-bonded interactions: stiffening bonds, allowing cellulose to find thermodynamically stable states at further inter-crystal separation distances, and lowering the free energy of cellulose binding to other cellulose. As a result, increased water content reduced the tensile modulus for CG nanocellulose assemblies.

Future directions include incorporating parameters from interactions of different cellulose surfaces, probing the effect of chemical modifications of the cellulose surface as well as interactions with other biopolymers in the secondary cell wall such as lignin, hemicellulose, pectin; and interactions with other biopolymers such as alginate in composite materials.

Figure 4. Atomistic models of plant cell wall assemblies composed of cellulose (grey) surrounded by hemicellulose (green) and lignin (yellow) are orders of magnitude smaller than experimental length scales, motivating future CG model development. Reproduced from [9,10]



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