184. Hydration Control of Cellulose Surface Structure and Dynamics

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Project Goals: Lignocellulosic biomass comprises the vast majority of biomass on Earth and has the potential to play a major role in generation of renewable biofuels if cost-effective conversion can be achieved. Largely composed of plant cell walls, it is a complex biological composite material that is recalcitrant to the structural deconstruction and enzymatic hydrolysis into sugars that is necessary for fermentation to bioethanol. The Scientific Focus Area in Biofuels is developing “Dynamic Visualization of Lignocellulose Degradation by Integration of Neutron Scattering Imaging and Computer Simulation” for multiple-length scale, real-time imaging of biomass during pretreatment and enzymatic hydrolysis. This is providing fundamental information about the structure and deconstruction of plant cell walls that is needed to drive improvements in the conversion of renewable lignocellulosic biomass to biofuels.

Cellulose recalcitrance to enzymatic hydrolysis is determined in part by the structural features of cellulose surface, which influence the binding of hydrolytic enzymes, and the mechanical work needed to pull apart cellulose strands for catalytic cleavage. Cellulose in biomass is found in a hydrated state, and it is therefore important to understand how hydration influences its surface structure and dynamics. By combining neutron scattering experiments and molecular dynamics simulations we characterized the nanosecond motions in cellulose, their dependence on temperature and hydration, and how they affect the surface order of the microfibril.1 The experiments reveal that samples hydrated to 20% w/w exhibit a higher average mean-square displacement above \( \sim 240K \) than dry samples do. The molecular dynamics (MD) simulation reveals hydroxymethyl groups on the surface of the fibril have the highest fluctuations, and these increase significantly when cellulose is hydrated due to faster relaxation of the hydroxymethyl/water hydrogen bond network. Although in the MD simulations the hydroxymethyl groups in the cellulose core are always found in the crystallographically determined trans-gauge conformations, hydration leads to increased disorder in the hydroxymethyl conformation at the cellulose surface. The detailed characterization obtained describes how hydration-dependent increased fluctuations are connected with hydroxymethyl disorder that disrupts the cellulose hydrogen- bond network and makes cellulose more susceptible to enzymatic attack.

Reference

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