

Impact of Hydration and Temperature History on the Structure and Dynamics of Lignin

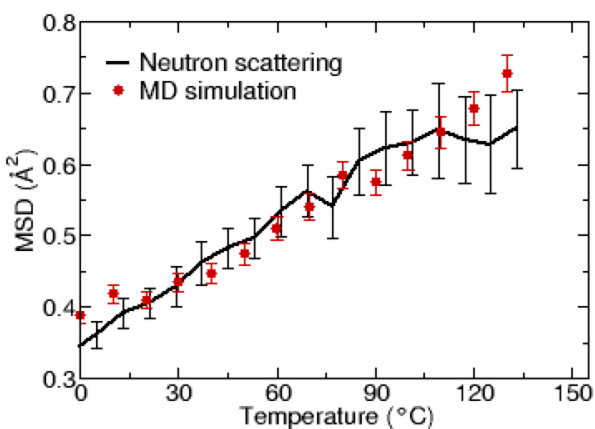
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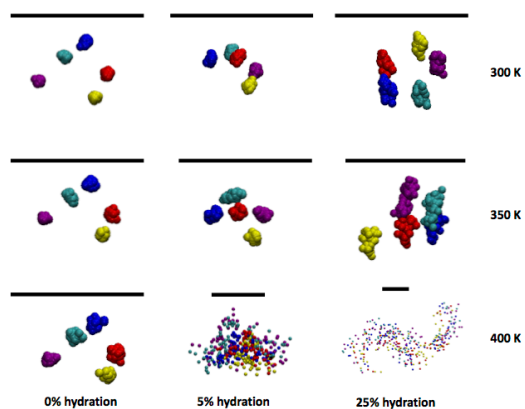
<http://cmb.ornl.gov/research/bioenergy/lignocellulose-dynamics>

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.

The full utilization of plant biomass for the production of energy and novel materials often involves high temperature treatment. Examples include the relocalization of lignin to increase the accessibility of cellulose for production of biofuels and the melt spinning of lignin for manufacturing low-cost carbon fiber. These temperature-induced effects arise from poorly understood changes in lignin flexibility. At the molecular scale this is achieved by enhancing the underlying atomic dynamics. Here, we combine molecular dynamics simulations with neutron scattering and dielectric spectroscopy experiments to probe the dependence of lignin dynamics on hydration and thermal history. Excellent agreement is found between the experiments and the simulations. We find a dynamical and structural hysteresis: at a given temperature, the lignin molecules are more expanded and their dynamics faster when the lignin is cooling than when heating. The structural hysteresis is more pronounced for dry lignin. The difference in dynamics, however, follows a different trend, being more significant at high temperatures and high hydration levels. The simulations also reveal syringyl units to be more dynamic than guaiacyl and the aliphatic chains to be more dynamic than the phenolic rings. The results provide an atomic-detailed description of lignin dynamics and suggest that the lignin glass transition temperature, at which the polymer softens, will be lower in the more hydrated environment of plant biomass than in purified lignin powder. This lignin glass transition is a critical stage in lignin relocalization or in lignin aggregation. Furthermore, the dynamical hysteresis found here implies the softening temperature is lower when the lignin is cooled than when heated, therefore extending the cooling phase of processing may offer ways to lower the processing cost of lignin.



Comparison of lignin mean square displacement measured from quasi-elastic neutron scattering experiments and calculated from molecular dynamics simulations.



Snapshots of the simulations, showing lignin becoming more dynamic with increasing hydration and temperature.

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