Insights into Hemicellulose-Cellulose Interactions from Thermochemical Pretreatment of Model Composite Materials

Riddhi Shah,1 Sai Venkatesh Pingali,2 Barbara R. Evans,2 Daisuke Sawada,2 Hugh O’Neill,1,2 and Brian H. Davison2* (davisonbh@ornl.gov)

1Bredesen Center for Interdisciplinary Research and Graduate Education, University of Tennessee, Knoxville; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee

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.

Thermochemical pretreatment of biomass results in structural reorganization of the various cell wall polymers during cell wall deconstruction. However, the underlying molecular level interactions that occur during these processes are poorly understood.1 Model systems of polymers that mimic cell wall structures can potentially help in understanding polymer-polymer interactions that occur during pretreatment.2 In this study, model hemicellulose-cellulose composites were prepared by synthesizing bacterial cellulose in presence of xyloglucan (XG) or glucomannan (GM) dissolved in the growth media. Small-angle neutron scattering (SANS) was used to study the nanoscale structural changes in the composites as a result of dilute acid pretreatment (DAP). By growing deuterium-labeled cellulose3 in the presence of hydrogenated hemicellulose it was possible to deconvolute the scattering signatures of the two components. Changes in crystallite size, crystallinity, and glucan chain packing for the native and DAP-treated cellulose and composites were also studied using X-ray diffraction (XRD).

At the nanoscale, DAP-treated cellulose showed a collapse in structure, as indicated by a decrease in the radius of gyration ($R_g$) from 250 Å to 130 Å that was interpreted as expulsion of water from the space between microfibrils resulting in formation of a tightly packed macrofibril. The change of power law exponent ($\alpha$) from $2.71 \pm 0.26$ to $2.23 \pm 0.048$ showed that the pretreated cellulose microfibril network was less entangled than that of native cellulose. In the case of the xyloglucan-cellulose (XGC) composite, the structure of the cellulose network was relatively unchanged after
pretreatment. Interestingly, in glucomannan-cellulose (GMC) composites, the changes that occurred due to DAP were similar to native cellulose except that $\alpha$ was increased ($\alpha = 2.82 \pm 0.06$) after pretreatment, indicating that the microfibrillar network became more entangled.

XRD analysis showed no significant change in the crystallinity ($69.4 \pm 3.9\%$) and peak positions ($14.47^\circ$, $16.86^\circ$, and $22.72^\circ$) after pretreatment of native cellulose, but an increase in the crystallite size along the (010) plane was evident. The crystallinity of XGC was lower than native cellulose ($36.59 \pm 2.30\%$) but increased to $53.33 \pm 1.72\%$ after DAP. There was a change in the peak positions in XGC compared to native cellulose, but an increase in the crystallite size along the (010) plane was evident. Unlike native cellulose, the crystallite size of the XGC was unchanged after pretreatment. Similar to the SANS data, the structural changes observed in GMC as a result of pretreatment were very similar to native cellulose.

Our results show significant differences between XG and GM interactions with the growing cellulose network. We can propose that XG interacts directly with the cellulose microfibrils as they are formed. This is supported by increased crystalline Iβ content in the cellulose microfibrils and the size of the microfibril remaining unchanged after DAP. On the other hand, GM most likely interacts at the surface of the macrofibrils because it does not change the crystalline form of the cellulose and the macrofibrils collapse as a result of DAP, similar to native cellulose. This study provides insight into cellulose-hemicellulose interactions that may help in studies related to understanding accessibility to enzymes for biofuels, developing cellulosic bioproducts and engineering plants with increased digestibility.

References


*Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract no. DE-AC05-00OR22725. This program is supported by the Office of Biological and Environmental Research in the DOE Office of Science.*