Probing the Nanostructural Mechanisms Behind Decay Resistance of Chemically Modified Wood Using Small Angle Neutron Scattering

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Abstract

While it is known that modifying the hydroxyls in wood can improve the decay resistance; what is often missing in the literature is whether these modifications alter wood nanostructure, and how these changes correlate to the improved decay resistance. Here, we used SANS to probe the effects of alkylene oxide modification on wood nanostructure. Southern pine wood samples were chemically modified to various weight percentage gains (WPG) using four different alkylene oxides: propylene oxide (PO), butylene oxide (BO), epichlorohydrin (EpH) and epoxybutene (EpB). After modification, the samples were water leached for two weeks to remove any unreacted reagents. Then, we conducted laboratory soil block decay evaluations against the brown rot fungus *Gloeophyllum trabeum* to determine weight loss and biological efficacy of the modifications. To assist in understanding the mechanism, we used SANS to study samples that were fully immersed in D_2O. These measurements revealed that the modifications altered the water distribution inside the cell wall, and the most effective modifications reduced the microfibril swelling. Likewise, we observed that these modifications were also able to preserve the microfibril structure even after being subject to 12 weeks of brown-rot decay.

Introduction

Outdoor exposure of low naturally durable wood often results in wood decay. Brown rot fungi, in particular, are responsible for a large part of the timber decayed in service and these affect all wood polymers but target primarily the wood carbohydrates[1]. While the mechanisms behind brown rot degradation are still being actively investigated, most evidence suggests that reducing the moisture content of the wood is key to prevent and/or delay the onset of decay[2,3]. One way to reduce the moisture content of the wood is to modify it with chemical reagents that can react with the available hydroxyls to form stable, covalent bonds[4]. However, since most chemical modifications have been developed empirically over decades, the development of new chemistries is hindered by an incomplete understanding of the nanoscale interactions that lead to decay resistance.

While probing wood nanostructure continues to be difficult, small angle neutron scattering (SANS) has become a valuable tool in lignocellulosic research thanks to its ability to study wood nanostructure with minimal sample preparation. Using SANS, researchers have measured the structure of cellulose microfibrils in wood cell walls[5-10] and even, how the wood nanostructure is degraded by brown-rot fungi[11,12]. Yet, despite its potential to provide new insights on how modification alters the wood nanostructure, the technique is underutilized in this research area.

Here, we use SANS to determine how chemical modifications meant to impart decay resistance modifies wood nanostructure, and how these changes affect the nanostructural degradation of the cell wall. Our findings show that those modifications effective at preventing weight loss due to degradation were also effective at keeping the moisture outside of the cellulose microfibrils and preserved the wood nanostructure from decay.

Materials and methods

Southern pine (*Pinus spp.*) sapwood blocks (25.4 mm wide x 25.4 mm long (transverse plane) x 6.4 mm thick along the longitudinal axis) were modified with one of the following alkylene oxides: butylene oxide (BO), propylene oxide (PO), epicholorohydrine (EpH) and epoxybutene (EpB). All reagents were obtained from Sigma Aldrich (Milwaukee, WI). All reactions were performed inside a Parr reactor using a mixture consisting of 95% alkylene

oxide, 5% triethylamine catalyst under nitrogen at 120 °C and 150 psi[13,14]. Blocks were reacted (up to 6 hours) to achieve different weight gain percentages (WPG). Specimens were air-dried under a fume hood overnight prior to oven drying at 105 °C for 24 hours. The samples were then water leached for two weeks to remove any unreacted reagents[15]. The average weight gain caused by the chemical modification was determined from the dried weights. For the SANS measurements, the blocks soaked in water and then cut across the wood grain to expose long longitudinal surfaces from which thin longitudinal sections (less than 1mm thick) were obtained. Thin samples were cut from the unmodified wood as well as the wood blocks modified with EpB (5 and 30WPG), EpH (7 and 12 WPG), PO (6 and 30 WPG) and BO (4 and 19 WPG). These sections were then air-dried at room temperature under a fume hood over two days and inspected for curling prior to being shipped to ORNL for the SANS remote experiments.

The ASTM D 1413 standard soil block test was performed on oven dried solid wood southern pine specimens[16]. Five soil bottles each of unmodified controls and modified specimens were exposed to the brown-rot fungus *Gloeophyllum trabeum*. Two soil bottles each with no fungus were run to monitor leaching of any chemicals. Specimens were removed from the test following the standard 12 weeks. The extent of decay was determined as oven dry weight loss (WL). To prepare the specimens for SANS, the decayed blocks were first soaked in water and then cut across the wood grain to expose long longitudinal from which thin sections were obtained. Thin sections less than 1mm thick were cut from the following decayed specimens: unmodified (66% WL), EpB (25% and 0% WL), EpH (23% and 5% WL), PO (46% and 30% WL) and BO (50% and 22% WL). These sections were then air-dried at room temperature under a fume hood over two days, and then inspected for curling before being shipped to ORNL for the SANS remote experiments.

SANS measurements were conducted at the Bio-SANS instrument at the High Flux Isotope Reactor in the Oak Ridge National Laboratory (ORNL), Oak Ridge, TN, USA[17]. First, the thin samples were immersed in D_2O for over 12 hours to exchange all exchangeable sites. Then, the samples were loaded into 1mm path length titanium cells filled with D_2O. The neutron incident wavelength was 6Å, with a relative wavelength spread of 15%. A single configuration was employed with the main detector at 15.5m, and the wing detector at 1.4°. The effective q range accessible was 0.003–0.85$Å^{-1}$. The 2D SANS patterns were normalized by monitor counts and corrected for dark current, pixel sensitivity, solid angle, and background. Then, SANS data were anisotropically reduced and merged using the ORNL drtsans reduction package, a common reduction software for all ORNL SANS instruments. The reduced data were fitted to a model consisting of two power laws and a Gaussian diffraction peak. For some of the heavily modified samples a second diffraction peak was needed. For the decayed samples, a mid-q Guinier feature, previously assigned to the formation of repolymerized lignin[11], was also included. All data analyses were performed in IgorPro8 using the Modelling II tools included in the Irena package[18].

Results and Discussion

All alkylene oxide modifications prevented brown rot decay to different degrees except for PO, which did not significantly reduce the weight loss due to fungal decay. In general, the weight loss was reduced with increasing WPG. Using SANS, we studied samples with different degrees of modification and decay to further understand the nanostructural origins of the differences observed.

For unmodified wood (UW) samples immersed in D_2O, the contrast between water-accessible regions and non-water accessible regions inside the wood cell walls give rise to a distinct scattering pattern that typically includes power law scattering from the bundles of cellulose microfibrils, as well as a diffraction peak caused by the regular packing of the cellulose elementary fibrils (**Figure 1a**). After the sample has been decayed by brown-rot, the structural integrity of the sample is compromised (**Figure 1b**), and the small angle diffraction peak is lost. However, when the sample is modified with EpB (30WPG) we observe that the diffraction peak ($q \sim 0.14Å^{-1}$ for UW) shifts to higher q ($q \sim 0.18Å^{-1}$ For EpB), meaning that the microfibril is swelling less in the modified wood compared to the unmodified one. Modifying the wood with EpB also gave rise to a small but detectable mid-q scattering feature ($q \sim 0.03Å^{-1}$), whose size is comparable to the diameter of cellulose microfibrils observed in secondary cell walls from softwoods using scanning electron microscopy[19,20], atomic force microscopy[21] and SANS[9,12]. Interestingly, this mid-q feature was not observed in all the alkylene oxide modified wood studied; and it was more prevalent at the higher weight gains evaluated. By comparing the SANS profiles from the decay resistant EpB modified wood before and after exposure to brown rot, we observe that both the mid-q scattering feature and the high-q diffraction peak are still visible, indicating that the nanostructure of the cellulose microfibril was preserved during fungal exposure.

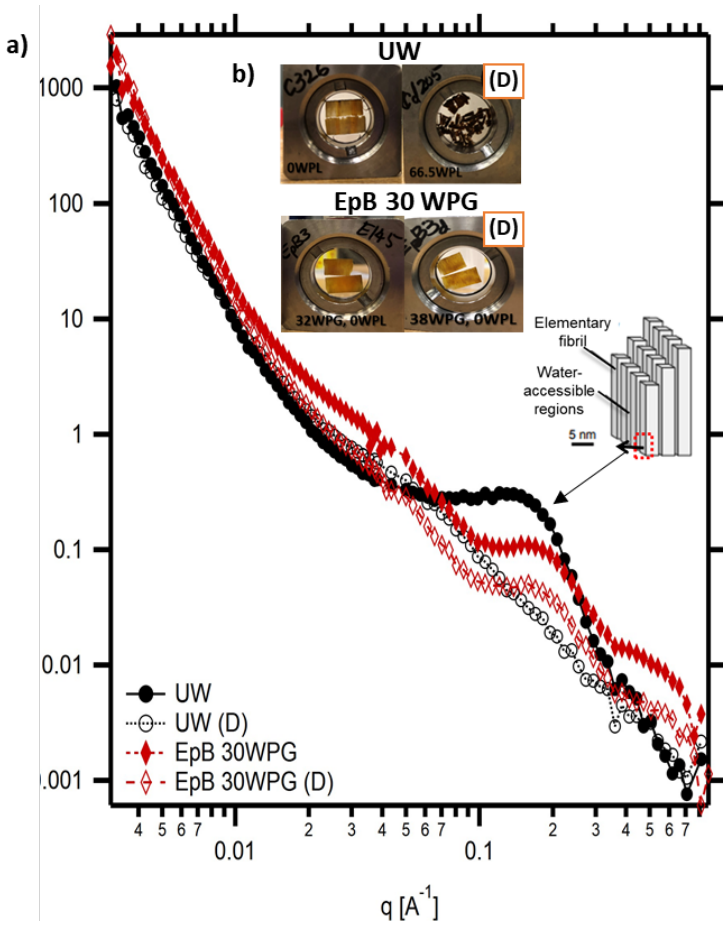

Figure 1. Effects of epoxybutene modification and decay on wood nanostructure. (a) Anisotropic scattering profiles from unmodified wood (UW) and wood modified with epoxybutene (30WPG) with and without weight loss caused by decay (D). (b) Titanium cells loaded with the samples whose scattering profiles are shown in (a). Insert: Schematic showing the cellulose microfibril structure, which gives rise to the diffraction peak, consisting of well-ordered elementary fibrils and water accessible regions in between the fibrils.

By tracking the changes in the diffraction peak position as a function of both chemical modification and subsequent brown rot decay, we were able to determine the combined effects of these parameters in terms of the elementary fibril spacing inside cellulose microfibrils (**Figure 2**). The chemical modifications affected the swelling of the cellulose microfibrils before and after decay differently, suggesting different mechanisms for achieving biological efficacy. All modifications except for PO, reduced the microfibril swelling with increasing WPG, which was also the only modification that did not provide biological efficacy. After decay, for most samples the intensity of the diffraction peak decreased, which increased the uncertainty of the associated peak position in the decayed samples compared to the non-decayed ones. Nevertheless, we observe some differences between the different modifications. For the BO and EpB modified woods the spacing between fibrils was slightly smaller, suggesting that the cross-section of the cellulose microfibrils decreased. Conversely, for the EpH and PO decayed wood, the spacing between fibrils increased suggesting that the cellulose microfibrils were not as constrained and could swell more.

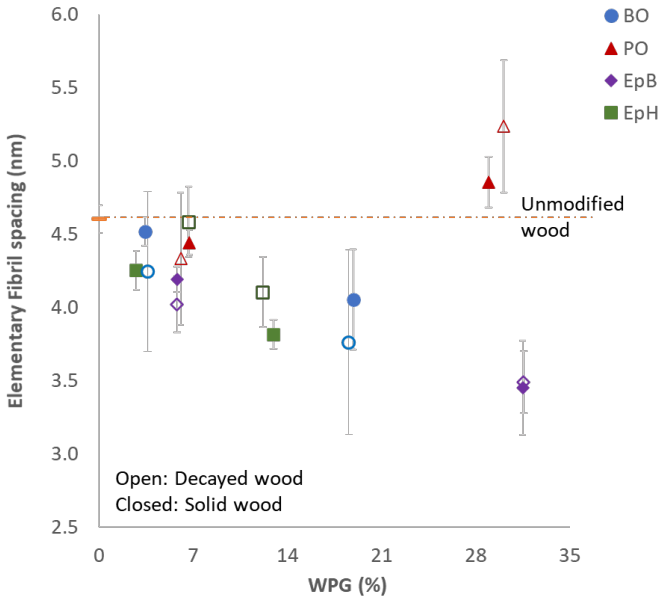

Figure 2. Combined effects of alkylene oxide modification and brown rot decay on the elementary fibril spacing. Error bars corresponds to the uncertainty in the diffraction peak position based on all modelling parameters, so the peak position of weaker diffraction peaks will have larger error bars.

Conclusions

Using SANS, we discovered that alkylene oxide modifications that impart brown rot decay resistance also minimize the swelling of the cellulose microfibrils and preserve the overall cellulose microfibril nanostructure. These findings suggest that the moisture distribution inside cell wall plays a key role in fungal degradation, and that keeping water from entering the cellulose microfibrils can prevent and/or delay decay. SANS can provide valuable insights on the nanostructural mechanisms behind the effectiveness of different wood chemical modifications.

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