Small-Angle Neutron Scattering as a New Tool to Evaluate Moisture-Induced Swelling in the Nanostructure of Chemically Modified Wood Cell Walls*

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Abstract

Wood-based products can be a sustainable and more environmentally friendly alternative to traditional construction materials because of their reduced contribution to air and water pollution. An integral component of these products is often an adhesive. Because wood is hygroscopic, moisture-induced swelling in the cell walls near the wood–adhesive bond lines can lead to durability and performance issues. Unfortunately, researchers working toward improving the moisture durability of forest products are hindered by an incomplete understanding of the nanoscale mechanisms that contribute to moisture-induced swelling in wood and how chemical modifications affect the swelling. Therefore, we developed small-angle neutron scattering (SANS) into a tool that can study the 1- to 100-nm structure of unmodified and chemically modified wood cell walls and can measure the effects of moisture in this structure. In this study, SANS was used to reveal the nanostructure of a deuterium-labeled phenol-formaldehyde (dPF) adhesive infiltrated into wood cell walls. The results revealed that the dPF infiltrated the water-accessible regions between the elementary fibrils inside the wood cell walls. These results provide the new insight that adhesive infiltration into the cellulose microfibril (a bundle of elementary fibrils) may be a key to designing moisture-durable wood adhesives.

Most wood-based construction materials, including plywood, particleboard, oriented strand board, and structural wood products, are made of wood components held together by an adhesive. Phenol-formaldehyde (PF) is one of the most moisture-durable wood adhesives, and its durability is thought to originate from its ability to modify the properties of cell walls near the wood–adhesive bond line (Frihart 2009). However, because PF was empirically developed over decades, the mechanisms behind its durability are not well understood. For instance, although it is known that PF with low molecular weight can infiltrate the cell wall, its nanoscale interactions with the wood cell ultrastructure are still an active area of research (Laborie and Frazier 2006, Laborie et al. 2006, Jakes et al. 2015). It is widely debated

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* This article is part of a series of eight selected articles addressing a theme of efficient use of wood resources in wood adhesive bonding research. The research reported in these articles was presented at the International Conference on Wood Adhesives, held on October 25–27, 2017, in Atlanta, Georgia. All eight articles are published in this issue of the *Forest Products Journal* (Vol. 68, No. 4).

Forest Prod. J. 68(4):349–352.
doi:10.13073/FPJ-D-17-00065

whether PF is chemically bonded with the lignocellulosic polymers, although recent studies using solution-state nuclear magnetic resonance have proposed that two competing processes might occur while PF cures inside the cell wall: lignin degradation and formation of methylene bridges between lignin and PF (Yelle and Ralph 2016a, 2016b). The nanostructure of PF-infiltrated cell walls is not known.

Small-angle neutron scattering (SANS) is a powerful technique capable of probing the nanostructure of organic materials like adhesives and wood cell walls. Neutrons are uncharged elementary particles that interact with organic materials via neutron–nuclei interactions. In SANS, a beam of neutrons is focused on a sample and the neutrons that are scattered at small scattering angles are detected on a two-dimensional (2D) detector. The scattered intensity provides information about the size, shape, and orientation of the sample nanostructure. One of the main advantages of neutron scattering is its isotope sensitivity, which allows enhancement of the scattering from nanostructures by selective deuterium labeling (Langan et al. 2012). Moreover, solutions of H_2O and heavy water (D_2O) can be used to match the scattering length density (SLD) of certain nanoscale features and remove their scattering contributions (Hammouda 2010).

SANS has become an increasingly popular tool in lignocellulosic research, particularly to study the pretreatment effects on the nanostructure of isolated wood cell wall polymers (Pingali et al. 2010b, Petridis et al. 2011) as well as native wood cell walls (Ding and Himmel 2006, Pingali et al. 2010a, Nishiyama et al. 2014). SANS also has been found capable of measuring the spacing between elementary fibrils in wood cell walls as a function of moisture content (Fernandes et al. 2011, Plaza et al. 2016). Plaza (2017) and Plaza et al. (2016) recently used the increase in spacing between elementary fibrils measured with SANS to show that more than half of the swelling in the transverse plane of the S2 cell wall layer was caused by swelling between elementary fibrils. This finding is in direct contrast to previous research that attributed the majority of the swelling in the S2 layer to swelling of the lignin–hemicellulosic matrix between concentric lamellae within the S2 layer (Boutelje 1962, Rafsanjani et al. 2014).

The key to minimizing swelling in the wood cell wall is to minimize the swelling between elementary fibrils. Based on this insight, we decided to use SANS to investigate whether the known moisture-durable PF adhesive modifies the microfibrils, which are bundles of elementary fibrils. This study aims to provide further insight into the extent of PF infiltration in the cell wall, particularly at the elementary fibril level. Improving our understanding on the infiltration of PF will benefit researchers developing new and improved moisture-durable adhesives.

Materials and Methods

Tangential–longitudinal latewood samples of loblolly pine (*Pinus taeda*) were cut to 25 by 25 by 0.5 mm from a single growth ring. An unmodified control sample was kept as cut. The sample to be infiltrated was vacuum dried for 30 minutes to remove moisture before adhesive infiltration. Low-molecular-weight deuterium-labeled phenol-formaldehyde (dPF) was synthesized according to Laborie's methods (Laborie 2002). To synthesize the resin, perdeuterated phenol crystals were mixed with 20 percent perdeuterated formaldehyde solution in D_2O and sodium deuteroxide solution in P/F/NaOD molar ratios of 1:2:0.2. Then the reaction flask was immersed in an oil bath and heated at 80°C for 40 minutes. The vacuum-dried samples were immersed into the dPF resin, vacuum treated at room temperature for 30 minutes to infiltrate the samples, and soaked for 24 hours using glass stoppers to keep the wood samples submerged. The samples were removed from the resin, and the excess dPF was wiped off. Residual dPF was removed from the lumina by vacuum treating the samples for 30 minutes. Then the samples were heat treated at 155°C to 160°C for 30 minutes in an oven to cure the dPF. A total weight gain of 29 percent was measured for the sample infiltrated with dPF.

SANS experiments were performed with the EQ-SANS instrument (Zhao et al. 2010) at the Spallation Neutron Source at the Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA). Data were acquired using a sample-to-detector distance of 1.3 m and a minimum wavelength of 2.5 Å. The beam was collimated with aperture diameters of 25 and 12 mm for the source and sample, respectively. Data were recorded using a 2D (1 by 1 m^2) Hellium-3 linear position-sensitive detector with 192 by 256 pixels. Scattering patterns were normalized to the incident beam and monitor counts; corrected for time of flight, pixel sensitivity, dark current, and background contributions; and scaled to absolute units using MantidPlot (Arnold et al. 2014).

The samples were placed in square quartz holders, which were sealed with Kapton (DuPont, Wilmington, Delaware, USA) tape. The 0.5-mm cavity inside the holders was filled with D_2O or a 35:65 D_2O/H_2O solution using a syringe. All air bubbles were removed before the samples were placed in the translation stage at the beam line. The 35:65 D_2O/H_2O solution, for which the SLD corresponded to the cellulose contrast matching point (CCMP), was used to remove the scattering contributions from the wood polymers. Unmodified wood was measured in both pure D_2O and the CCMP solution. The dPF-infiltrated wood was only measured in the CCMP solution to enhance scattering from the dPF. Samples were soaked overnight in D_2O or the CCMP solution before being placed into the holders.

Results and Discussion

The 2D scattering patterns from unmodified wood immersed in pure D_2O, unmodified wood immersed in the CCMP solution, and dPF-infiltrated wood in the CCMP solution are shown in Figures 1a through 1c, respectively. Schematics of the transverse cross section of the microfibrils giving rise to the 2D scattering patterns from unmodified wood in pure D_2O, unmodified wood in the CCMP solution, and dPF-infiltrated wood in the CCMP solution are shown in Figures 1d and 1e, respectively.

In the scattering pattern from the unmodified wood in pure D_2O, lobes along the equatorial axis were observed. These lobes correspond to fiber diffraction peaks that arise from the regular spacing between the elementary fibrils (Fernandes et al. 2011, Plaza et al. 2016). The scattering contrast is provided by the difference in SLDs between the water-inaccessible elementary fibrils and the D_2O (1.9×10^{10} vs. 6.4×10^{10} cm^{-2}) that entered the water-accessible regions between elementary fibrils (Fig. 1d). As expected, the pattern from unmodified wood in the CCMP solution (Fig. 1b) did not have lobes because of the lack of contrast

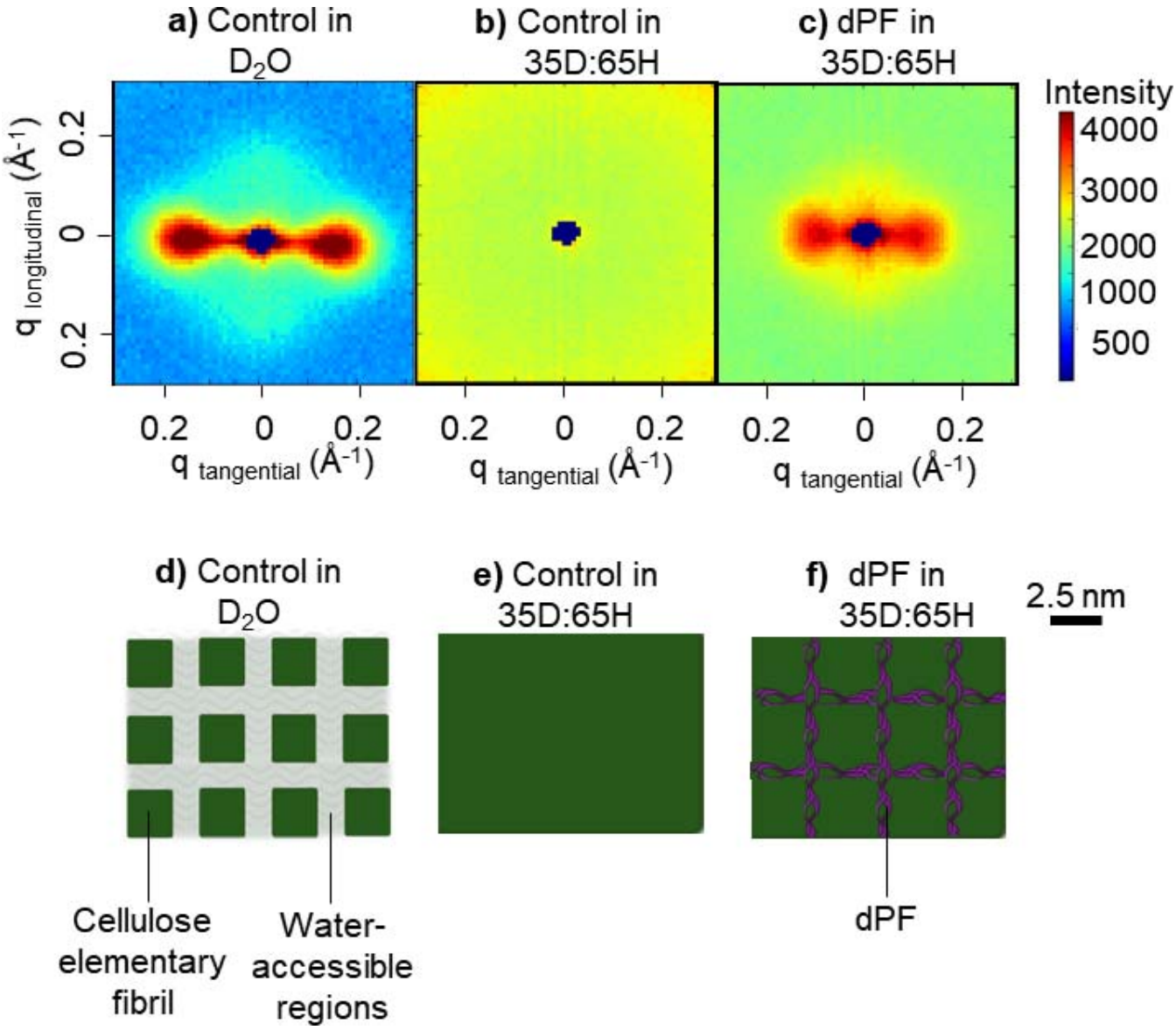

Figure 1.—Small-angle neutron scattering (SANS) patterns from unmodified wood in (a) pure heavy water (D_2O) and (b) cellulose contrast matching point (CCMP) solution. SANS patterns from (c) deuterium-labeled phenol-formaldehyde (dPF)–infiltrated wood in the CCMP solution. Schematics of the scattering length density distribution at the microfibril level that gives rise to the SANS patterns from unmodified wood in (d) pure D_2O and (e) CCMP solution and dPF-infiltrated wood in (f) CCMP solution. A transverse view of the microfibril is shown for simplicity, although SANS patterns were obtained from tangential–longitudinal samples. (Color version is available online.)

between the cellulose elementary fibrils and the CCMP solution (Fig. 1e). However, lobes were observed in the pattern from the dPF-infiltrated wood in the CCMP solution (Fig. 1c). The only explanation for these lobes is that the dPF, for which SLD was comparable with D_2O, was occupying the regularly spaced regions between the elementary fibrils (Fig. 1f).

The SANS results in Figure 1 unambiguously show that the PF adhesive not only infiltrates the wood cell wall but also can infiltrate the cellulose microfibril. More research is needed to fully understand how the microfibril infiltration is related to moisture-induced swelling at larger length scales and the moisture durability of wood–adhesive bond lines. Nevertheless, in this report, we demonstrated the power of SANS to study the nanoscale interactions between adhesives and wood ultrastructure. In the future, we can also use our in situ humidity chamber (Plaza et al. 2016) to measure the effects of PF infiltration on the elementary fibril swelling as a function of humidity.

Conclusions

Using SANS, we discovered that the moisture-durable wood adhesive PF can infiltrate cellulose microfibrils in wood cell walls. This infiltration might affect the moisture-induced swelling in the microfibrils, and further studies could provide insight on whether infiltration of the cellulose microfibrils is necessary to make moisture-durable bonds. We also demonstrated that SANS is a uniquely suited tool to study these types of nanoscale interactions between the adhesive and wood cell wall ultrastructure. In the future,

similar SANS work could be performed to further our understanding of how to make moisture-durable wood adhesives by studying different bonding factors, such as type of adhesive, adhesive molecular weight, and different infiltration conditions. These results should accelerate the development of new and improved wood adhesives.

Acknowledgments

N.Z.P. acknowledges the GERS program at the University of Wisconsin, Madison, 2012 NSF GFRP, US Forest Service Pathways program, and 2016 DOE SCGSR for support. J.E.J. acknowledges funding from 2011 USDA PECASE awards. J.E.J. and N.Z.P. acknowledge support from the FHA Cooperative Research Program for Covered Timber Bridges. The use of Spallation Neutron Source facilities was supported by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. S.V.P. acknowledges the Genomic Science Program, Office of Biological and Environmental Research, US Department of Energy (FWP ERKP752).

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