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ADHESIVE-WOOD INTERACTIONS IN RELATION TO FAILURE IN BONDED WOOD PRODUCTS FROM THE CENTIMETER TO NANOMETER SCALE

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To maximize the use of forest resources and to minimize wood product costs, most wood products use adhesives in their processes. Bonding wood not only requires fulfilling normal adhesion criteria, but also needs to deal with the porosity, composite nature, and anisotropic character of wood. Most adhesives will develop good wood bonds, but few hold up to the dimensional changes caused by moisture changes in the wood. Although the durability of wood products has met most of the market needs, the adhesive is a large part of the cost of the bonded product and lower cost, greener adhesives are desired. However, the complexity of wood–adhesive interactions across length scales hinders efforts. Our work involves applying new tools to study the interactions of adhesives with wood at the centimeter to nanometer scale and using a wide variety of methods to understand the where and why of failure.

Most wood products involve at least one, if not several, adhesive bonding steps in order to make the most efficient use of wood resources and to develop the strongest and most durable products needed for a particular application. The usual criteria is for the bonded assembly to be stronger than the wood. With weak wood species this is less of a challenge than with very strong wood species. However, passing room temperature tests of a bonded assembly is insufficient for wood products that have to survive variable moisture exposure, and in the case of structural products, also fire exposure.

In many cases, it is difficult to separate the performance of the wood bond from the performance of the wood itself. Normal structural design criteria involves testing the bonded assembly to failure and then adding safety margins because failures can be catastrophic and lead to the loss of life. Thus, understanding the initial locus of failure is very important, but can be difficult to sort out, such as in the case of the failed beam in Figure 1. Because of the multiple failure zones, one might expect that failure started in the bottom member and cascaded to the other sites, but it is clear that very little adhesive failure occurred.

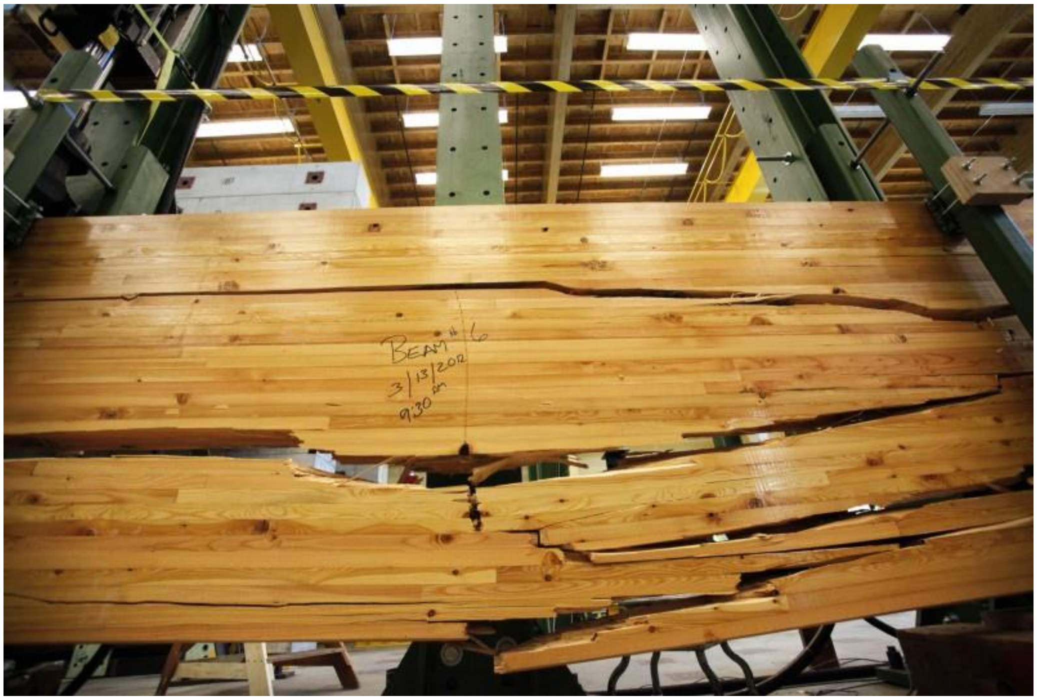
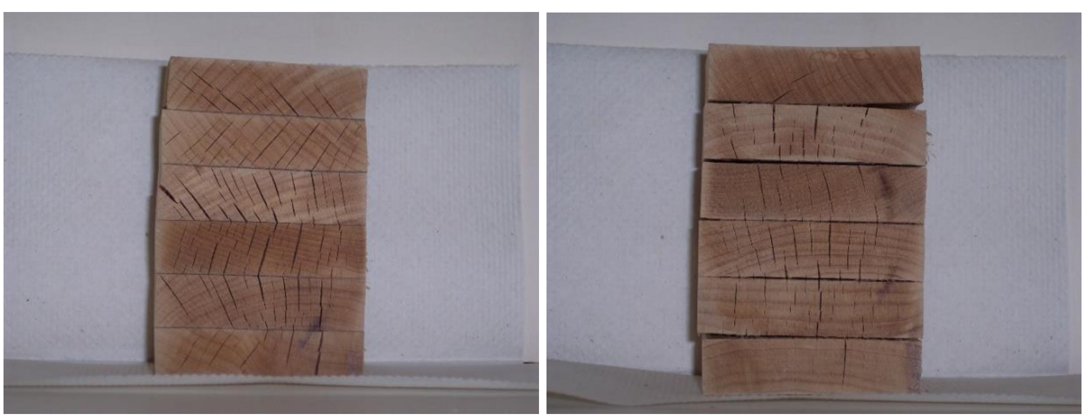


Figure 1. Failure of one of twelve 72-foot glulam beams that failed under loads between 69,000 and 95,800 pounds after up to a 13 inch deflection (Posted on January 28, 2013 by James T. Spartz https://www.fpl.fs.fed.us/labnotes/?p=72).

To understand specifically adhesive bond failure, organizations such as ASTM wood and adhesive committees have developed tests to measure bond performance when exposed to heat and changes in wood moisture content. As an example, Figure 2 shows what happens to a bonded sample that was exposed to water soaking and drying using the ASTM 2559 delamination test, which is often cited in US building codes. In Figure 2A, the adhesive bonds held up quite well while the wood suffered damage, whereas in Figure 2B failure was almost completely in the adhesive bondline, along with considerable cracking in the wood.



A B

Figure 2. Samples tested using D 2559 exhibiting low (A) and high adhesive failure (B).

As useful as these types of tests are in helping to develop better adhesives and determine acceptable adhesive performance, they do not determine why adhesives do or do not form strong and durable bonds. One way to understand bond performance is to test different types of adhesives with different species of wood [1], but this is only empirical data, not fundamental information., Fundamentally it is important to understand that wood adhesive performance depends not only on the properties of the adhesive glueline between the two surfaces, but also on the entire bondline that also includes the adhesive penetration of the wood surface due to the porosity of wood [2, 3]. A model to explain adhesive interaction with wood during the bonding process and water-induced failure has been developed [4]. This model depends not only on considering bulk adhesive performance, but also on the interaction of the adhesive with the wood cells and cell walls [5, 6]. One problem with the standard testing for wood failure is that one needs to look closely at the failure since the problem can be in the wood, for example deep checking in veneers [7], or can involve failure in the adhesive adjacent to the wood surface that may be assigned as adhesion failure without close examination [8].

It is important to understand that adhesive penetration involves not only flow into lumens, but also infiltration of cell walls [9]. Flow into lumens is easier to analyze [3, 9] than infiltration of cell walls [10-12]. In addition, flow into lumens while useful, has been shown not to be sufficient for durable adhesion, making cell wall infiltration an important issue for study [8]. Analyzing adhesive infiltration of cell walls has required going beyond simple light microscopy and using other types of analysis methods [12-15]. The most active groups in research on adhesive-wood interactions are BOKU in Vienna, Austria, Oregon State University in Corvallis, Oregon, and the Forest Products Laboratory in Madison, Wisconsin. The rest of this manuscript will highlight the work being done at the last place.

A model for durable wood adhesives under variable wood moisture contents divides durable adhesives into two groups [4]. The *in situ* polymerized adhesive group involves highly cross-linked polymers with a rigid backbone that limits the swelling of the wood surface to provide a durable bond. The pre-polymerized adhesive group includes polymers with backbone flexibility and limited cross-linking so that they can thus distribute the swelling strain within the adhesive. In general, the *in-situ* polymerized adhesives have better moisture resistance than the pre-polymerized due to former's stabilization of the cell walls [4]. Because of our interest in how adhesives interact with the cell wall, our work has concentrated on the *in-situ* adhesives and the effect of moisture on that interaction.

The first aspect investigated was mapping the adhesive penetration of the cell wall and comparing this with change in the cell wall mechanical properties. A bromine-labeled phenol-formaldehyde (Br-PF) adhesive was used because the PFs are very durable adhesives, are known to penetrate cell walls, and with the bromine label, can be visualized using synchrotron-based µX-ray fluorescence microscopy (µXFM). The effect of PF infiltration on the hardness and elastic modulus of the cell walls can be measured using nanoindentation [16, 17]. In Figure 3, the left hand µXFM image shows the adhesive penetration into the cell lumens (orange or light color) and cell wall structure (green or darker color walls), and the right hand picture shows the indents made by the nanoindenter to measure the mechanical properties. The humidity of the nanoindentation chambers could be controlled to determine the effect of moisture on the wood cell wall mechanical properties. By varying the molecular weight of the Br-PF, the combined results of µXFM and nanoindentation revealed new insights into the interactions between adhesives and wood at the cell wall length scale. Compared to the higher molecular weight Br-PF, the lower molecular weight Br-PF flows deeper into the wood substrate and infiltrates to a higher weight percent gain in the cell walls near the bondline. For a specific amount of cell wall weight percent gain, the low molecular weight Br-PF was more effective at minimizing the moisture-induced softening of the wood cell walls, which suggests adhesive molecular weight plays a role in determining the moisture-durability of the adhesive.

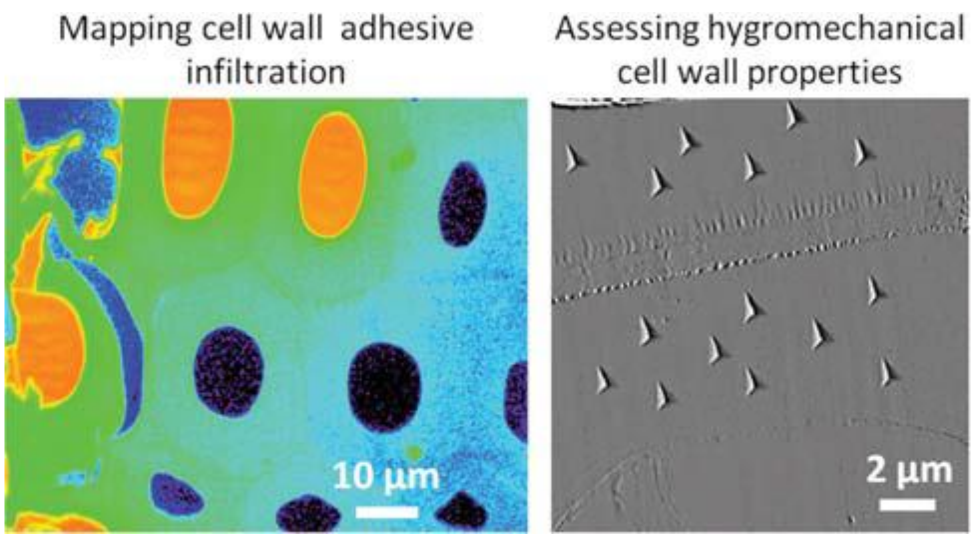


Figure 3. Use of Br-labeled phenol-formaldehyde to study the penetration of cell walls and the effect on its mechanical properties [16].

Having shown that the Br-PF adhesives migrate into the cell wall preventing moisture-induced softening of the cell wall matrix for a specific percentage weight uptake of adhesive [16], the question then arose in what domain of the cell wall does the adhesive appear. This required developing an additional technique that can explore even smaller cell wall length scales. A technique has been developed to examine changes in the ordered part of the cellulose domains using small angle neutron scattering (SANS) for its ability to probe at 1-100 nm. In this case, instead of bromine labelled PF, a deuterated PF (dPF) was used to examine the effect of the adhesive at the elementary cellulose fibril level [18].

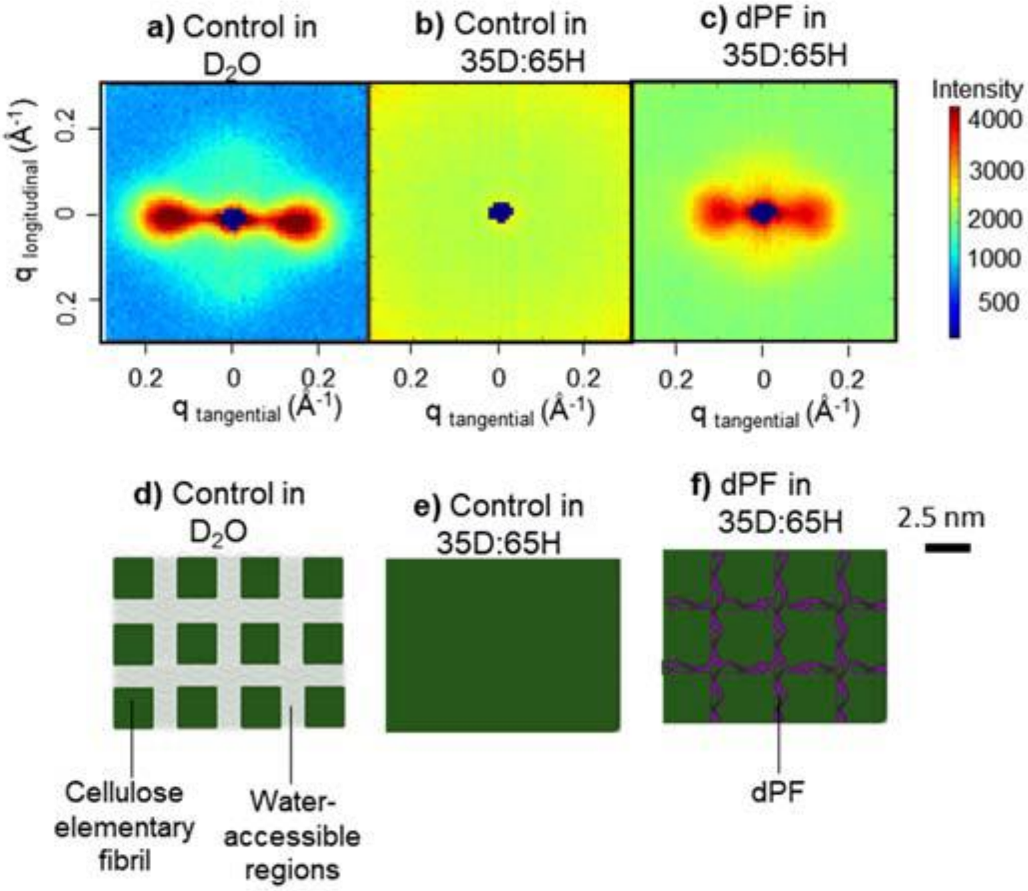


Figure 4. Small angle neutron scattering (SANS) patterns from unmodified wood in (a) pure D_2O and (b) CCMP (cellulose contrast matching point) solution. SANS patterns from (c) dPF-infiltrated wood in the CCMP solution. Schematics of the scattering length density distribution at the microfibril level that results in the SANS patterns from unmodified wood in (d) pure D2O and (e) CCMP solution and dPF-infiltrated wood in (f) CCMP solution. A transverse view of the microfibril, which is a bundle of cellulose elementary fibrils, is shown for simplicity, although SANS patterns were obtained from tangential–longitudinal latewood samples.

In Figure 4, the scattering contrast is provided by the difference in scattering length density (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. 4d). As expected, the pattern from unmodified wood in the cellulose contrast matching point (CCMP) solution (Fig. 4b) did not have lobes because of the lack of contrast between the cellulose elementary fibrils and the CCMP solution (Fig. 4e). However, lobes were observed in the pattern from the dPF-infiltrated wood in the CCMP solution (Fig. 4c). 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. 4f). Using SANS, we discovered that the moisture-durable wood adhesive PF can infiltrate cellulose microfibrils in wood cell walls. Other research has shown that the swelling of wood involved separation of the elementary fibrils [19]; thus some of the PF is forming an interpenetrating network in areas that are involved in water swelling.

Research is continuing to understand the adhesive failures and successes in bonding wood products. This information will be useful as less common wood species are being used and with the use of more bio-based materials as wood adhesives.

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References

[1] J. Konnerth et al., "Survey of Selected Adhesive Bonding Properties of Nine European Softwood and Hardwood Species," *European Journal of Wood and Wood Products,* 74 (2016) 809-819.

[2] A. A. Marra, *Technology of Wood Bonding: Principles in Practice,* (New York, NY: Van Nostrand Reinhold, 1992).

[3] F. A. Kamke et al., "Methodology for Micromechanical Analysis of Wood Adhesive Bonds Using X-Ray Computed Tomography and Numerical Modeling," *Wood and Fiber Science*, 46 (2014) 15-28.

[4] C. R. Frihart, "Adhesive Groups and How They Relate to the Durability of Bonded Wood," *Journal of Adhesion Science and Technology*, 23 (2009) 601-617.

[5] C. R. Frihart, "Adhesive Bonding and Performance Testing of Bonded Wood Products," *Journal of ASTM International,* 2 (7) (2005) 1-12.

[6] C. R. Frihart, "Adhesive Interactions with Wood," (Report GTR-FPL-149, USDA FS Forest Products Laboratory, Madison, WI, 2004).

[7] A. Rohumaa et al., "The Influence of Lathe Check Depth and Orientation on the Bond Quality of Phenol-Formaldehyde - Bonded Birch Plywood," *Holzforschung,* 67 (2013) 779-786.

[8] C. R. Frihart and J. F. Beecher, "Factors That Lead to Failure with Wood Adhesive Bonds" (Paper presented at World Conference on Timber Engineering, Vienna, Austria, 22 August 2016), 7.

[9] F. A. Kamke and J. N. Lee, "Adhesive Penetration in Wood - a Review," *Wood and Fiber Science*, 39 (2007) 205-220.

[10] A. J. Allen, B. K. Spraul, and J. M. Wescott, "Improved CARB II-Compliant Soy Adhesives for Laminates", *Proceeedings of Wood Adhesives* 2009, ed. C. R. Frihart, C. G. Hunt, R. J. Moon (Lake Tahoe, NV: Forest Products Society, 2010), 176–184.

[11] C. Hunt et al., "Wood as Polar Size Exclusion Chromatography Media: Implications to Adhesive Performance," *Forest Products Journal*, 65 (2015) 9-14.

[12] C. G. Hunt et al., "Understanding Wood Bonds: Going Beyond What Meets the Eye," *Reviews of Adhesives and Adhesion*, 6 (2018) 369-440.

[13] J. E. Jakes et al., "Improved Understanding of Moisture Effects on Outdoor Wood–Adhesive Bondlines" (Report FPL–GTR–246, USDA FS Forest Products Laboratory, Madison, WI, 2017).

[14] N. Gierlinger et al., "Comparison of UV and Confocal Raman Microscopy to Measure the Melamine-Formaldehyde Resin Content within Cell Walls of Impregnated Spruce Wood," *Holzforschung*, 59 (2005) 210-213.

[15] J. Konnerth et al., "Adhesive Penetration of Wood Cell Walls Investigated by Scanning Thermal Microscopy (Sthm)," *Holzforschung*, 62 (2008) 91-98.

[16] J. E. Jakes et al., "Synchrotron-Based X-Ray Fluorescence Microscopy in Conjunction with Nanoindentation to Study Molecular-Scale Interactions of Phenol-Formaldehyde in Wood Cell Walls," *ACS Applied Materials & Interfaces*, 7 (2015) 6584-6589.

[17] J. E. Jakes et al., "X-Ray Methods to Observe and Quantify Adhesive Penetration into Wood," *Journal of Materials Science*, 54 (2019) 705-718.

[18] N. Z. Plaza et al., "Small Angle Neutron Scattering as a New Tool to Evaluate Moisture-Induced Swelling in the Nanostructure of Chemically Modified Wood Cell Walls," *Proceedings 2017 International Conference On Wood Adhesives*, ed. C. G. Hunt, G. D. Smith, N. Yan (Peachtree Corners, GA: Forest Products Society, 2017) 5.

[19] N. Z. Plaza, "Neutron Scattering Studies of Nano-Scale Wood-Water Interactions" (Ph.D. thesis, University of Wisconsin – Madison, WI, 2017). https://www.fpl.fs.fed.us/documnts/pdf2017/fpl_2017_rodriguez002thesis.pdf

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