United States Department of Agriculture

Improved Understanding of Moisture Effects on Outdoor Wood–Adhesive Bondlines

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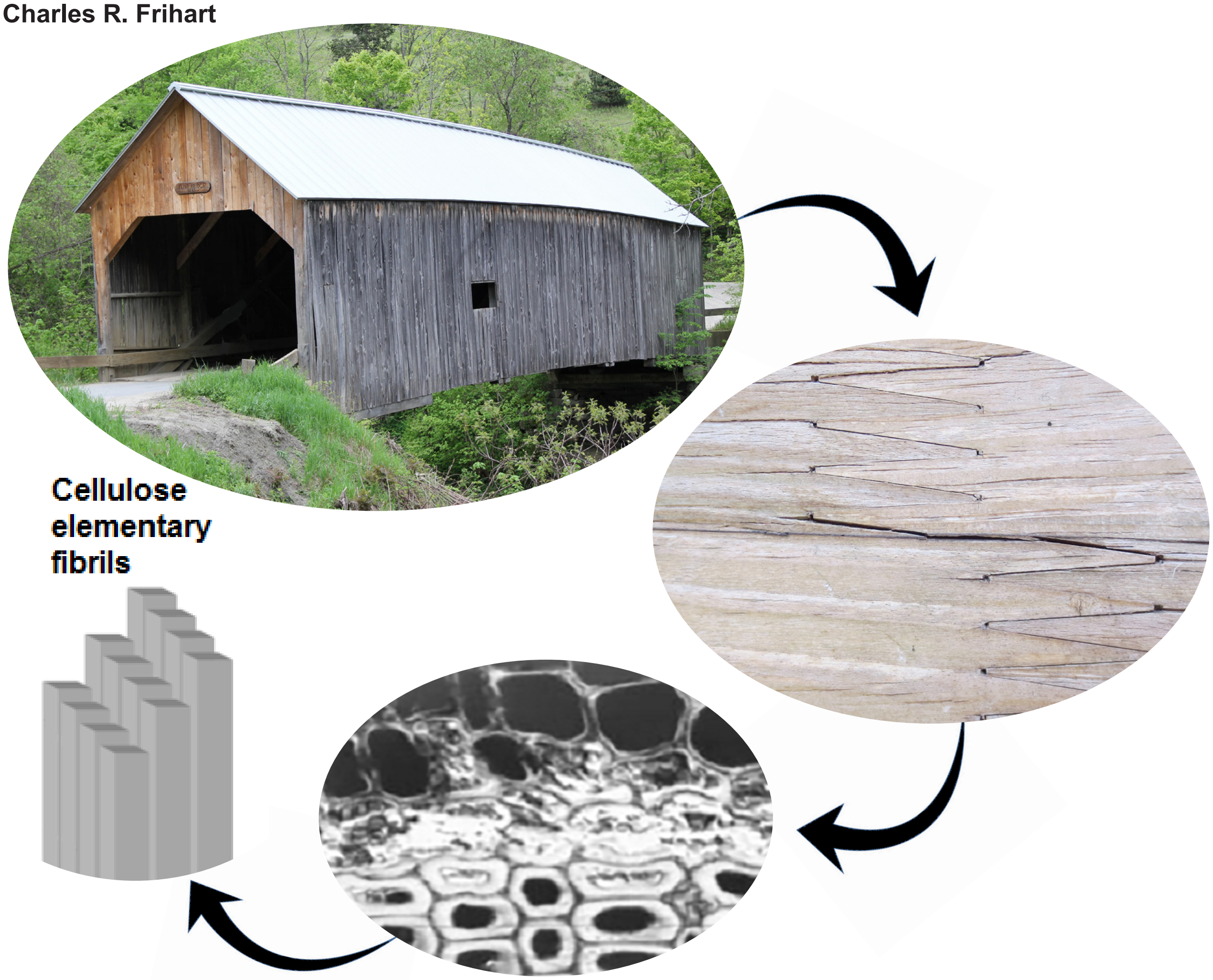

Forest Service
Forest Products Laboratory
General Technical Report
FPL–GTR–246
May 2017

In cooperation with the
United States Department of Transportation
Federal Highway Administration

A FHWA-NHCBP (National Historic Covered Bridge Preservation) publication

Abstract

The development of improved moisture-durable wood adhesives for outdoor applications, such as repairing historic covered bridges, is hindered by an incomplete mechanistic understanding of what makes a wood–adhesive bond moisture-durable. The wood–adhesive bondline is extraordinarily difficult to study because of the chemical, structural, and mechanical complexities and variations of the wood substrate and the many potential interactions that can occur between the wood and adhesive to enhance or degrade the bond performance. Although the literature is filled with bonding information from the bulk level, sufficient experimental tools to study wood–adhesive bondlines and the effects of moisture on bondlines at the cellular and subcellular levels are lacking. Therefore, we recently developed tools to study bondlines at these size scales. We have used synchrotron-based micro x-ray fluorescence microscopy (µXFM) and micro x-ray computed tomography (µXCT) to map the penetration of adhesive into the wood anatomical structure. We also developed nanoindentation into a tool capable of assessing the effects of moisture and adhesive infiltration on wood cell wall properties. Using custom-built in situ humidity chambers with µXCT and small angle neutron scattering, we can now study the moisture-induced swelling in wood across the relevant length scales in bondlines that span from the millimeter to nanometer length scales. Finally, we developed a new approach to study moisture-induced swelling forces using wood slivers. This report gives an overview of these recently developed techniques. The insights these tools provide toward understanding moisture durability in wood adhesive bondlines are also discussed in this report.

Keywords: historic covered bridges, adhesives, moisture durability

May 2017

Jakes, Joseph E.; Plaza, Nayomi Z.; Arzola Villegas, Xavier; Frihart, Charles R. 2017. Improved understanding of moisture effects on outdoor wood–adhesive bondlines. FPL–GTR–246. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 7 p.

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The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin.

Contents

This study is part of the Research, Technology, and Education portion of the National Historic Covered Bridge Preservation (NHCBP) Program administered by the Federal Highway Administration. The NHCBP program includes preservation, rehabilitation, and restoration of covered bridges that are listed or are eligible for listing on the National Register of Historic Places; research for better means of restoring and protecting these bridges; development of educational aids; and technology transfer to disseminate information on covered bridges in order to preserve the Nation's cultural heritage.

This study is conducted under a joint agreement between the Federal Highway Administration–Turner Fairbank Highway Research Center and the Forest Service–Forest Products Laboratory.

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Improved Understanding of Moisture Effects on Outdoor Wood–Adhesive Bondlines

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Introduction

Repairing historic covered bridges may require bonding new wood members to existing wood members or replacing original large solid timbers with glulam beams, which are made by bonding small dimensional lumber together until the glulam beam is large enough to replace the original solid timber. Thus, adhesives with moisture durability are needed to bond these materials. Although the roof structure keeps the heavy timber trusses sheltered and dry enough to survive more than 100 years, the components still experience exposure to water and fluctuating humidity. The effects of moisture play a critical role in the longevity of the adhesive bond's service life. Moisture sorption causes dimensional changes in wood, and if wood–adhesive bondlines cannot accommodate the continuous swelling and shrinking caused by changes in moisture content, then stress can concentrate and bondline failure can occur. Although there are moisture-durable adhesives for making wood products, there are not suitable adhesives for repair of wood products. Epoxy adhesives are often used because they are the best that are available with suitable cure, flow, and gap-filling properties, but they have limited moisture resistance in wood bonds (Frihart 2006, AITC 1994). Most exterior-rated forest products use phenol formaldehyde (PF) adhesives because of their strength and moisture durability, but these adhesives cannot be used for repair of wood structures in the field. However, if we better understood why PF adhesives form a moisture-durable bond with wood, we could use this knowledge to accelerate the development of adhesives that could be used in the field for repairing historic covered bridges.

The majority of research in wood adhesives has concentrated on bulk performance and failure analysis at the bulk level. However, failure begins at the molecular level and continues to propagate until it reaches the bulk level. To develop improved adhesives for repairing covered bridges, research is needed to better understand the effects of moisture on wood and the interactions between wood and adhesives across multiple length scales from molecular to bulk levels. To aid in this research, it is useful to identify the different regions of a typical wood adhesive bondline (Fig. 1). Bulk wood is defined as the wood far enough from the bondline that its properties are not affected by the adhesive's presence. The bulk adhesive is the adhesive layer that separates the two wood adherends. The interface is the exposed surface of the wood adherend that the adhesive is applied to, which typically consists of cut wood cell wall and lumen surfaces. The interphase contains the region of wood modified by adhesive. During ambient humidity fluctuations, the moisture content of both the wood (Glass and Zelinka 2010) and adhesive (Wimmer and others 2013) also fluctuate accordingly, with higher humidity leading to higher moisture contents. As the amount of absorbed water in the wood product changes with changing moisture content, dimensional changes can occur. However, differences in the magnitudes or rates of swelling and shrinking between the different regions in a bondline can result in strain mismatches and stress concentrations that serve as the locus for bondline failure. To produce moisture-durable bondlines, wood adhesives must be able to manage differential swelling and shrinking to prevent failure. One hypothesis is that durable structural wood–adhesive bondlines are formed when the adhesive penetrates into the nearby wood forming a wood–adhesive interphase region that minimizes any stress concentrations that form between the bulk adhesive and wood adherends (Frihart 2009).

At present, the most common moisture-durable wood adhesives typically need to be applied in a mill setting in a controlled environment with carefully prepared wood surfaces, but these conditions are not amendable to making repairs to standing wood structures in the field, such as covered bridges. Of the durable wood adhesives available, PF is one of the best moisture-durable wood adhesives. Although the general consensus is that its durability arises from the penetration of PF into the wood cellular structure

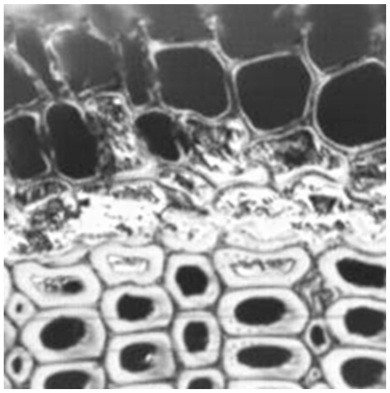

Figure 1—Optical microscopy image representative of a typical wood–adhesive bondline cross section. The image is approximately 0.15 mm per side. The bondline was made using a phenol resorcinol formaldehyde adhesive to bond ponderosa pine (*Pinus ponderosa*). The top and bottom adherends were earlywood and latewood, respectively.

and cell walls to create an interphase region (Kamke and Lee 2007, Frihart 2009, Stamm and Seborg 1936), the underlying molecular- and nano-scale mechanisms that give the PF–wood interphase its favorable properties are still debated. An improved mechanistic understanding of how PF and other moisture-durable adhesives produce moisture-durable bondlines would accelerate the development of new types of wood adhesive systems that could be used in the repair of wood structures in the field. However, the multiscale structural, chemical, and mechanical complexities of the bondline in combination with its small size make wood–adhesive bondlines extraordinarily difficult to study, especially measuring basic parameters such as adhesive penetration, swelling strains, swelling stresses, and mechanical properties of individual components in the bondline.

In this report, an overview is given of recently developed research techniques being used to study wood and wood–adhesive bondlines to improve our mechanistic understanding of how to create moisture-durable wood–adhesive bondlines. To demonstrate their utility, the techniques will be applied in the study of PF bondlines. How synchrotron-based micro x-ray fluorescence microscopy (μXFM) can be used to map the adhesive infiltration into wood cell walls will be shown. Conjointly, nanoindentation can be used to assess moisture-dependent mechanical properties of the same μXFM-mapped cell walls to directly correlate adhesive infiltration of wood cell walls in the interphase to their moisture-dependent mechanical properties. It will also be demonstrated that micro x-ray computed tomography (μXCT) experiments can be used to map adhesive penetration into the wood cellular structure and visualize moisture-induced swelling in wood–adhesive bondlines. We also developed small angle neutron scattering (SANS) techniques to better study how the nanostructures of wood cell walls (1- to 100-nm-length scale) swell with moisture uptake. Finally, a technique will be presented to study moisture sorption and swelling forces in wood slivers, which are composed of a few wood cells that could be excised from wood–adhesive bondlines to assess moisture sorption and swelling stresses in bondline interphases. By combining information from these techniques using the same sample source (wood, adhesive, and bonding conditions), we will learn more about the adhesive interactions with wood that limit the formation and propagation of nano- and microscale failures. Additionally, in the future, the developed research techniques will be used to study and develop other adhesives for making them more moisture-durable and suitable for the in-field repair of outdoor wood structures, such as covered bridges.

Techniques

Mapping Adhesive Infiltration into Wood Cell Walls

Techniques are needed to accurately map and quantify the adhesive infiltration into wood cell walls to better correlate the amount of adhesive cell wall infiltration with changes in cell wall properties and adhesive performance. We developed synchrotron-based μXFM into a tool to accurately map adhesive infiltration into wood cell walls with submicron spatial resolution (Jakes and others 2013, 2015). In μXFM, an x-ray beam is focused to a submicron spot size and then raster scanned over a specimen while an energy dispersive detector system quantifies photons fluoresced from any element inside the x-ray beam interaction volume. Because the energy of fluorescence photons is characteristic for each element, the elemental content and amount of element present at the sample spot can be determined. We used μXFM to map a bromine-labeled phenol formaldehyde adhesive (BrPF) at beamline 2-ID-E at the Advanced Photon Source at Argonne National Laboratory (Argonne, Illinois). The Br maps, which are in direct proportion to the amount of adhesive infiltration into the cell wall, are shown in Figure 2. Wood–adhesive bondlines were made with southern yellow pine (*Pinus taeda*) latewood and five BrPFs with different molecular weight (MW) distributions. From each bondline, 2-μm-thick cross sections were cut and imaged. An increasing MW of BrPF is shown from left to right in Figure 2. With μXFM, we were able to observe that the higher the MW the less the BrPF infiltrated into the cell walls and the less the adhesive penetrated the wood adherend. In some sections, especially at lower MW, individual lumina were filled with adhesives far from the bondline. Subsequently, using μXCT, we will show that the adhesive reached these lumina via ray cells that connected to the bondline in a plane outside of the section cut for μXFM. The red lines in Figure 2 correspond to the rows of cells tested with nanoindentation (next section).

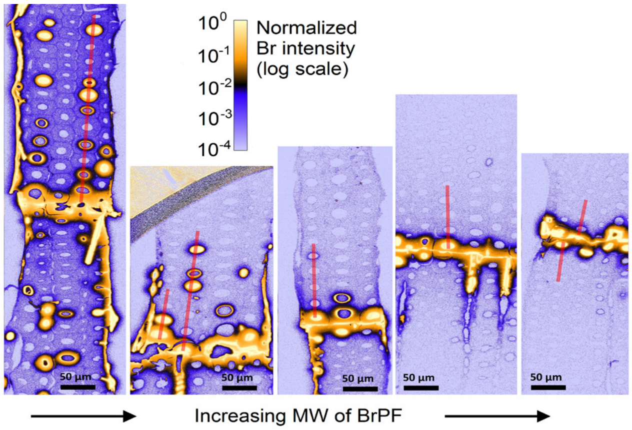

Figure 2—X-ray fluorescence microscopy (XFM) images of bromine-labeled phenol formaldehyde adhesive (BrPF) infiltration into wood cell walls. The Br intensity was normalized to the intensity value of the bulk BrPF in the bondline or BrPF-filled lumina. Red lines indicate rows of cell walls tested with nanoindentation. (MW, molecular weight.)

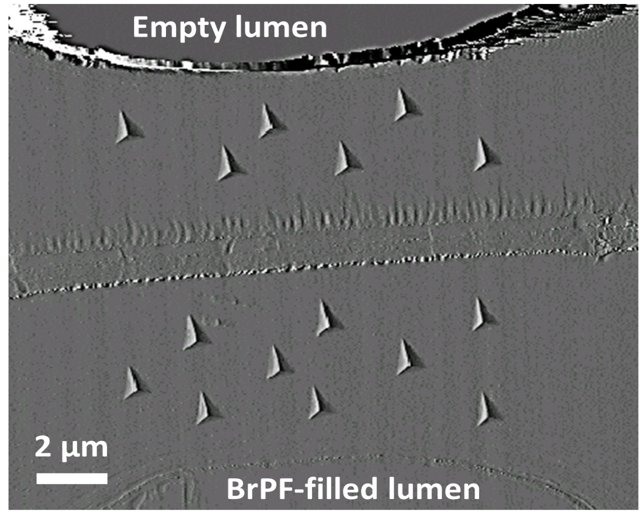

Figure 3—Atomic force microscopy image of nanoindents in the S2 layer of wood cell walls in an adhesive bondline (BrPF, bromine-labeled phenol formaldehyde adhesive).

Moisture-Dependent Mechanical Properties of Wood Cell Walls

Nanoindentation is a technique capable of measuring hardness and elastic modulus of micron-sized volumes of materials. More than a decade ago, this technique began to be used as a tool to assess the hardness and elastic modulus of wood cell walls and adhesive layers in situ in wood–adhesive bondlines (Gindl and Gupta 2002, Gindl and others 2004b). In contrast to conventional macroscopic hardness measurements, such as the Janka hardness test which assesses resistance to deformation in the cellular structure of wood, nanoindentation probes the properties of individual wood cell walls and adhesive layers. We used nanoindentation in experiments on the rows of wood cell walls highlighted by red lines in Figure 2 to quantify the effects of adhesive infiltration on the moisture-dependent mechanical cell wall properties (Jakes and others 2015). Figure 3 shows an atomic force microscopy image of representative nanoindents placed in the S2 cell wall layer. The moisture-dependent cell wall properties were studied by controlling the relative humidity (RH) inside the nanoindenter enclosure, and experiments were performed after conditioning the bondlines in dry air and 78% RH. For the control cell walls without BrPF infiltration, the hardness and elastic modulus decreased by about 50% and 25%, respectively, when conditioned at 78% RH compared with dry air (Jakes and others 2015). The relative effect of BrPF infiltration on cell wall mechanical properties was found to depend on the humidity level. In dry conditions, there was minimal effect of BrPF infiltration on mechanical properties. However, at high humidity, the higher the amount of BrPF infiltration the less the cell wall mechanical properties decreased compared with those for the dry conditions. There was also an effect of BrPF MW on the hygromechanical properties. Interestingly, for the same amount of BrPF infiltration, the lower MW BrPF adhesives were found to be more effective at minimizing mechanical softening at higher humidity by as much as a third (Jakes and others 2015). This greater effectiveness of lower MW BrPF probably resulted from their ability to more intimately associate with water sorption sites in the wood polymers. These results suggest that when designing a moisture-durable wood adhesive, just getting adhesive infiltration into the wood cell walls may not be sufficient. There is also probably specific molecular- and nano-scale interactions between the adhesive and wood that must occur inside the cell wall to create a moisture-durable bondline.

Adhesive Penetration and Moisture-Induced Swelling in the Cellular Structure

Micro x-ray computed tomography (µXCT) is a nondestructive technique useful for creating three-dimensional models with micron spatial resolution of complex solid structures. It has been found to be ideally suited for the study of wood–adhesive bondlines (Paris and others 2013, Kamke and others 2014). In µXCT, a series of two-dimensional x-ray images are taken of an object through a wide range of rotation angles and then used to computationally reconstruct a three-dimensional image of the object. We recently expanded the capabilities of µXCT by developing an in situ RH chamber (Fig. 4a) for beamline 2-BM-B at the Advanced Photon Source at Argonne National Laboratory to visualize the three-dimensional structure of wood–adhesive bondlines and swelling caused by changes in ambient RH. By tagging adhesives with an electron-rich atom, such as Br, the x-ray attenuation of the adhesive increases and, using segmentation software, the adhesive can be visualized separately from the wood cell

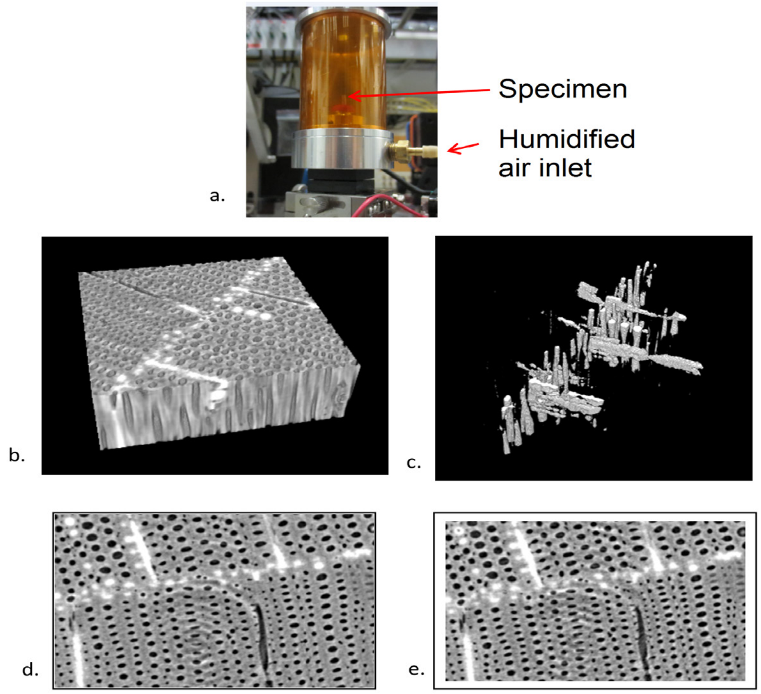

Figure 4—(a) Custom-built in situ relative humidity chamber for beamline 2 BM-B at the Advanced Photon Source at Argonne National Laboratory used to study moisture-induced swelling of wood structure; (b) three-dimensional reconstruction of wood adhesive bondline; (c) the same reconstruction as (b) but with the wood cellular structure computationally removed to reveal the adhesive; (d) tomographic slice of wood adhesive bondline conditioned at 100% RH; and (e) tomographic slice of wood adhesive bondline conditioned in dry air.

walls. This was demonstrated using a specimen cut from a BrPF bondline used in the µXFM study, and the resulting reconstructions are shown in Figure 4b,c. In Figure 4c, adhesive can clearly be observed flowing down rays and into longitudinal tracheid lumina far from the bondline, which explains how the adhesive arrived in the tracheid lumina far from the bondline in some of the bondlines in Figure 2. Figure 4d,e shows an adhesive bondline conditioned at 100% and 0% RH, respectively. Roughly the same cells are shown in Figure 4d,e, and the black box around Figure 4e shows how much the wood structure shrank during drying. Swelling strains of approximately 10% can be observed. Although a more detailed analysis is needed to quantify strains, it is interesting that in the direction parallel to the bondline, the swelling strain is not noticeably different close to and far from this particular bondline. With the in situ RH chamber, µXCT has now been developed into a tool that can be used to study how adhesives accommodate, or conversely fail because of, moisture-induced swelling at the bondline. The swelling in the adhesive, interphase, and bulk wood can now be studied separately, and this information can be used to develop improved wood adhesives.

Moisture-Induced Swelling in Wood Nanostructure

Moisture-induced swelling in wood is caused by the absorption of water molecules in the polymeric structure of wood cell walls. However, it is not well understood how this molecular-scale absorption relates to the swelling observed at larger length scales, such as the cell wall nanostructure or the cellular length scales observed with µXCT (Fig. 4). Therefore, recognizing the ability of SANS to probe nanostructure (1–100 nm) in organic materials such as wood, we developed SANS into a tool to study the swelling in the cell wall nanostructure (Plaza and others 2016). We designed and built an in situ humidity chamber (Fig. 5a) for the Bio-SANS instrument at the High Flux Isotope Reactor and EQ-SANS instrument at the Spallation Neutron Source, which are both located at Oak Ridge National Laboratory (Oak Ridge, Tennessee). In particular, we found SANS useful for quantifying swelling in the nanostructure of cellulose microfibrils in wood cell walls. The microfibril, which is about 15 to 20 nm across, consists of an organized array of cellulose elementary fibrils, each of which is about 3 nm across (Fig. 5b). During moisture sorption, water is absorbed by the less ordered regions between the elementary fibrils and can cause the spacing between the elementary fibrils to increase by as much as 1 nm (Fig. 5c).

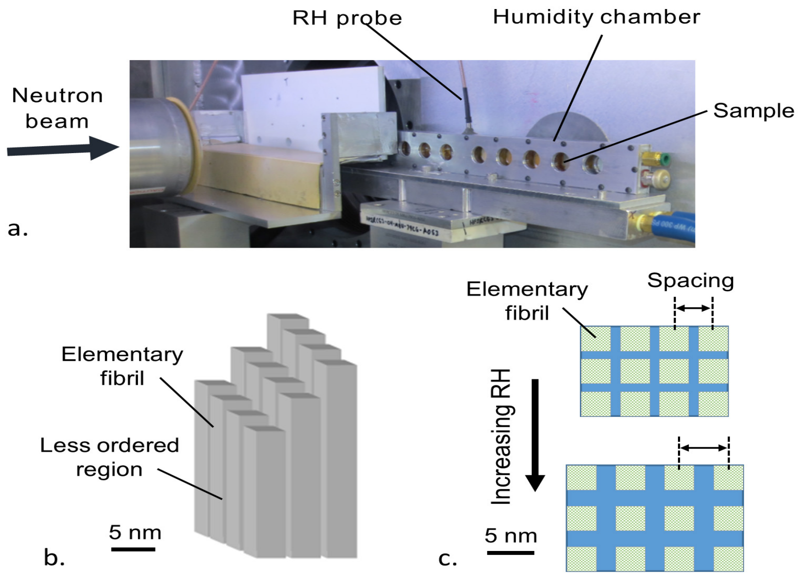

Figure 5—(a) Custom-built in situ relative humidity (RH) chamber for the Bio-SANS instrument at the High Flux Isotope Reactor at Oak Ridge National Laboratory (Oak Ridge, Tennessee). The humidity chamber can also be used with the EQ-SANS instrument at the Spallation Neutron Source at Oak Ridge National Laboratory. The humidity chamber and SANS were used to study moisture-induced swelling in the cellulose microfibril nanostructure, which is illustrated in (b) and (c). The elementary fibrils are semicrystalline cellulose that are not permeable to water. The less ordered regions are areas occupied by amorphous cellulose that can absorb water.

Through simple calculations, we found that in the secondary cell wall, more than half of the moisture swelling can be attributed to the swelling of cellulose microfibrils. This provides new insight to researchers trying to develop adhesives to minimize swelling in interphase wood cell walls. The adhesives must be able to infiltrate and modify the cellulose microfibrils to minimize swelling in wood cell walls.

Measuring Swelling Forces and Moisture Sorption of Interphase Wood Cells

We have found that a wood sliver, consisting of a few intact wood cells (Fig. 6a, b) twists as function of humidity (Plaza and others 2013, Jakes and others 2014). The twist is caused by the moisture swelling of amorphous wood polymers (for example, lignin, hemicelluloses, and amorphous cellulose) in the secondary cell wall and the constraint along the longitudinal direction of the cellulose microfibrils, which are helically wound through the wood cell wall. By attaching a twist indicator to a sliver (Fig. 6c) and conditioning it at different humidity levels, we measured the sliver twist as a function of RH and found it to be directly proportional to the wood moisture content. Furthermore, by tethering the sliver with the twist indicator to a thin tungsten wire (Fig. 6d), we also showed how to assess the specific torque generated during moisture sorption. The sliver torque should be directly proportional to the swelling forces generated by water sorption in the amorphous wood polymers inside the wood cell walls, which are probably the same swelling forces causing bondline failures. We were originally motivated to study wood slivers because they could be extracted from the interphase region of a wood–adhesive bondline. Our developed sliver characterization techniques can now be used to gain new information about how adhesive infiltration into wood cell walls modifies swelling forces and water sorption in these cells as a function of humidity.

Summary and Future Outlook

We have developed innovative research tools that are capable of providing new information about wood–adhesive bondlines at the cellular and subcellular levels and the effects of moisture on the bondlines. These tools should accelerate researchers' efforts to develop a mechanistic understanding of moisture-durable wood–adhesive bondlines and the development of wood adhesives for outdoor use for which moisture is an issue, such as repairing historic covered bridges. Some of the techniques have already been applied to study the effects of moisture in wood and wood–PF bondlines. The combined results from these techniques are providing researchers with new insights. For instance, using µXFM and nanoindentation, we found that for a given level of cell wall infiltration, a lower MW BrPF was more effective than a higher MW BrPF at preventing mechanical softening at high RH. Also, using SANS, we found that more than half of the moisture-induced swelling in a secondary cell wall originates in the cellulose microfibrils. Combining these results leads us to propose that a lower MW BrPF may be better at infiltrating and modifying the cellulose microfibrils than a higher MW BrPF. If so, it may be that targeting and modifying the cellulose microfibrils is a key to dimensionally stabilizing wood cell walls during changes in RH.

The next step includes applying these techniques to study additional bondlines made with different types of wood adhesives that are known to be either moisture durable or not moisture durable to further understand which mechanisms are important. In particular, the adhesive system will probably need to minimize the moisture-induced swelling and shrinking of the wood near the bondline. An example of a system that greatly improves the moisture durability of a variety of adhesive systems, including epoxies, on a variety of wood species is the hydroxylated methylated resorcinol (HMR) primer (Vick and others 1995), but research at many institutes around the world have yet to understand why HMR works so well (Gardner and others 2006; Hosen 2010; Kläusler and others 2014). Other systems for study include melamine formaldehyde (Gindl and others 2004a) and one-component polyurethanes (Kläusler and others 2014), which are both widely used in Europe for exterior applications but not in the United States because they are often insufficiently moisture-durable to pass the required performance standards. After the primary mechanisms are better understood, improved adhesive systems can be designed for bonding new wood members to existing wood members in the repair of historic covered bridges.

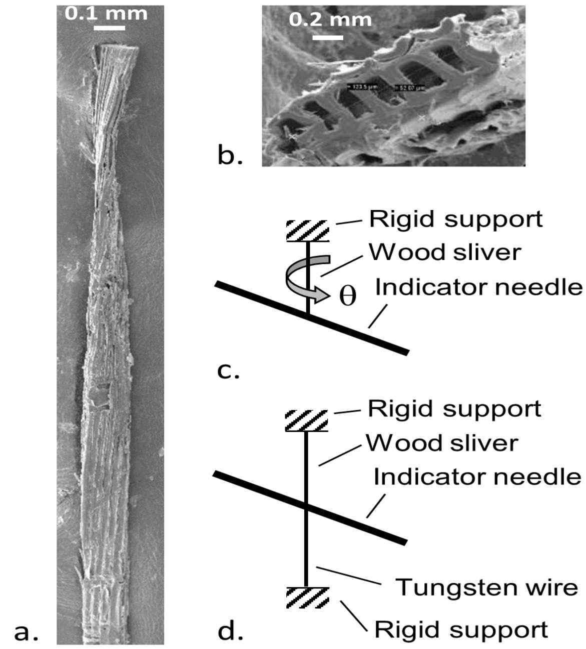

Figure 6—Scanning electron microscopy images of wood slivers cut from latewood loblolly pine (a) from the side and (b) in cross section. Experimental setups have been designed to measure both (c) sliver twist and (d) torque as a function of relative humidity.

Acknowledgments

Support is acknowledged from the Federal Highway Administration Cooperative Research Program for National Historic Covered Bridge Preservation. Nayomi Plaza Rodriguez and Xavier Arzola Villegas acknowledge the Graduate Engineering Research Scholars program at UW-Madison. Plaza Rodriguez acknowledges the 2012 National Science Foundation Graduate Research Fellowship Program and USDA Forest Service Pathways program for support. Joseph E. Jakes acknowledges funding from 2011 USDA PECASE awards. The use of Oak Ridge National Laboratory High Flux Isotope Reactor and Spallation Neutron Source was supported by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. The Bio-SANS beam line is supported by the Office of Biological and Environmental Research (FWP ERKP291), and its facilities are supported by the U.S. Department of Energy and managed by UT-Battelle, LLC, under contract no. DE-AC05-00OR22725. The use of Advanced Photon Source facilities was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under contract number W-31-109-Eng-38. We acknowledge Tom Kuster, FPL Analytical Chemistry and Microscopy Laboratory, for the scanning electron microscopy images in Figure 6a and b and the machine shop at FPL for construction of the in situ relative humidity chambers used in the µXCT experiments (Fig. 4a) and SANS experiments (Fig. 5a). The covered bridge photo on the cover was taken by James P. Wacker of the Forest Products Laboratory. The bridge in the photo is the Flint Bridge in Orange County, Vermont.

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