

# Integrating Multiscale Studies of Adhesive Penetration into Wood\*

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## Abstract

The development of new and improved wood adhesives is hindered by an incomplete mechanistic understanding of what makes a wood–adhesive bond able to withstand changes in moisture levels. Although common methods are established to test and report the bulk-level properties of bond lines, such as bond-line shear strength and wood failure analysis, the development of experimental tools to study wood–adhesive bond lines and the effects of moisture at the nanometer to millimeter length scales remains an active area of research. Here we introduce and briefly review four recently developed tools that, when combined, we have found capable to facilitate the study of bond lines and the effects of moisture across these length scales. The tools are X-ray computed tomography, X-ray fluorescence microscopy, nanoindentation, and small-angle neutron scattering. Their combined utility has been demonstrated by studying model bond-line systems made using loblolly pine and phenol-formaldehyde adhesives. The results led to a new insight that adhesive infiltration into cellulose microfibrils at nanometer length scales likely plays an important role in the moisture durability of wood–adhesive bond lines. A new model to facilitate the discussion of potential interactions between adhesive and wood nanostructure was also developed.

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Adhesives are increasingly relied upon to make forest products such as plywood, oriented strand board, laminated veneer lumber, wooden I-joists, and cross-laminated timber. For these products to be structural building materials, the adhesive must transfer load between pieces of wood without failing. A major challenge facing researchers is understanding and improving the moisture durability of wood–adhesive bond lines. Forest products in service may experience cyclic relative humidity (RH) conditions, or even inadvertent wet–dry cycles, that modify the moisture content of the wood. Changes in the wood’s moisture content cause swelling and shrinking of the wood, and adhesives that produce durable bonds must be able to deal with these dimensional changes. If not, stress may concentrate in the wood–adhesive bond line and failure may occur. Replacing failed products is not cost effective, and it is an inefficient utilization of the forest resource.

Wood, which is an anisotropic cellular material with multiple levels of structure (Wiedenhoeft 2013), is a much more complex substrate than other commonly bonded materials, such as plastics and metals. This is because of the many structural, chemical, and mechanical interactions that may occur between the wood and adhesive across many length scales. At the bulk level, the tree growth rings define the transverse, radial–longitudinal, and tangential–longitudinal planes of wood structure (Fig. 1a). Most often adhesives are applied to a longitudinal plane. In softwood cellular structure (Fig. 1b), longitudinal tracheids are the most common type of cell, and intercellular transport is facilitated by ray cells and pits. In an adhesive bond line, the adhesive may flow into the lumina exposed on the prepared surface and into the wood cellular structure through the pits and lumina of connected ray and tracheid cells. Tracheid walls are highly organized polymeric materials consisting of

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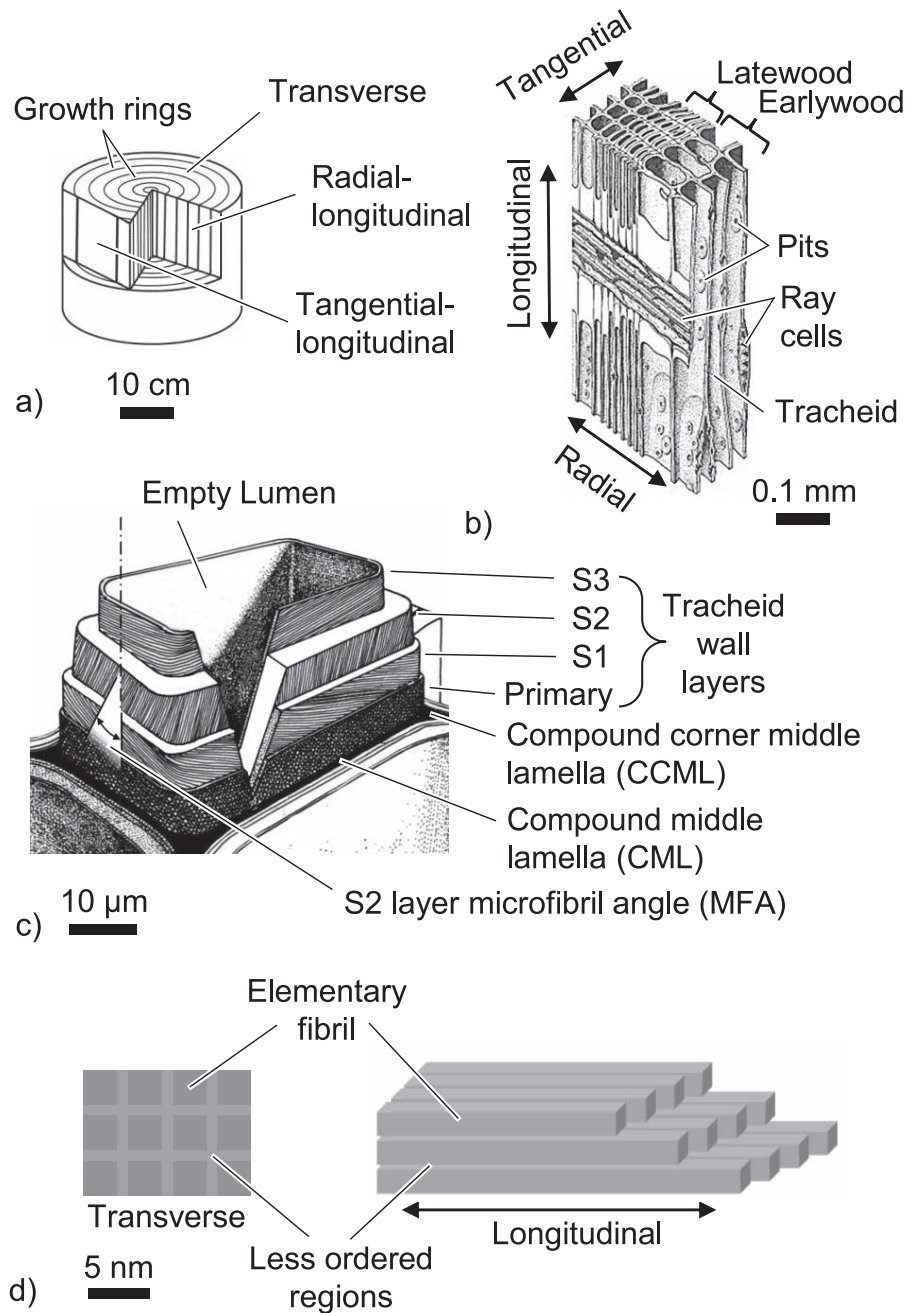


Figure 1.—Breakdown of wood structure from the (a) bulk to the (b) cellular to the (c) cell wall to the (d) microfibril.

three secondary cell wall layers (S1, S2, and S3), the primary wall layer, and the middle lamella (Fig. 1c). The S2 layer is much thicker than the S1 and S3 layers and therefore has the largest influence on bulk wood properties. The secondary cell walls are nanofiber-reinforced composites of highly oriented, semicrystalline cellulose microfibrils embedded in a matrix of amorphous cellulose, hemicelluloses, and lignin (Rowell et al. 2013). Although still debated, the general consensus is that the microfibrils in secondary cell wall layers are organized in concentric lamellae that run parallel to the lumen surface (Scallan 1974, Kerr and Goring 1975, Ruel et al. 1978, Salmen and Fahlen 2006). A microfibril is composed of cellulose elementary fibrils, such as the 12 elementary fibrils in a 3 by 4 array proposed by

Terashima and coworkers shown in Figure 1d (Terashima et al. 2009). Thin layers of less-ordered structures are integrated into the cellulose microfibrils between the elementary fibrils. The middle lamella fills in the regions between cells (Fig. 1c) and consists of about 20 percent hemicelluloses embedded as an irregular, interconnecting network in a matrix of lignin (Hafren et al. 2000, Wiedenhoef 2013). The middle lamella and primary cell wall layer are considered indistinguishable in wood, and typically grouped into a layer called the compound middle lamella (CML). At the corner between multiple tracheids, the larger-volume CML is called the corner CML (CCML). At least some adhesives can infiltrate and modify the cell walls (Kamke and Lee 2007, Frihart 2009). However, there

is no information about how adhesives spatially interact with the nanoscale features of the cell wall, such as the microfibril.

Water is another important component of wood. The moisture content (MC) in wood is defined as the mass of water divided by the oven-dried mass of wood and depends on the ambient temperature and RH. The absorption of water in the wood polymers occurs at the accessible hydroxyl and other polar chemical groups and causes complex swelling stresses and strains in the wood structure. The maximum capacity for bound water is reached at the fiber saturation point, which is between 30 and 40 percent MC (depending on definition; Stamm 1971, Hernández and Bizoñ 1994, Berry and Roderick 2005, Engelund and Thygesen 2013, Zelinka et al. 2016). At higher MCs, free water forms in wood cavities like lumina and pits. The swelling stresses in wood have been estimated to be 90 MPa (Tarkow and Turner 1958). These swelling stresses are so high that simply wetting a dry wood wedge placed in a groove can produce forces large enough to split a boulder (Rowell 2013). A wood–adhesive bond line must be able to accommodate these high stresses. The swelling strains of wood depend on the length scale of observation. At the bulk level, wood swelling is anisotropic, with about 0.1, 5, and 10 percent swelling in the longitudinal, radial, and tangential directions, respectively. The low longitudinal swelling is attributed to the predominately longitudinal orientation of the stiff cellulose microfibrils. At the cellular scale, swelling depends on whether latewood or earlywood is observed. The cellular structure of thick-walled latewood in softwood has been observed to swell isotropically in the transverse plane approximately 3 percent from 25 to 85 percent RH, whereas earlywood swells anisotropically, with approximately 3 percent in the tangential direction and 1 percent in the radial direction over the same range of RH (Derome et al. 2011). At the S2 cell wall layer, swelling is also observed to be anisotropic, with strains of approximately 20 percent in the direction normal to the lumen surface and 5 percent in the direction parallel to the lumen surface from 10 to 85 percent RH (Rafsanjani et al. 2014). Swelling in the microfibril has also been observed, with moisture uptake by the less ordered regions within the microfibril increasing the distance between elementary fibrils (Fernandes et al. 2011, Leppänen et al. 2011, Plaza et al. 2016). Wood adhesives must be able to accommodate or minimize these swelling forces and strains near wood–adhesive bond lines. However, it is unclear which length scales are most influential and what adhesive interactions are needed for moisture durability.

Because of the complexity of wood–adhesive bond lines, models are useful to assist in the discussion. The Marra model (Fig. 2) is a useful tool to break down wood–adhesive bond lines into regions for further study (Marra 1992). In the Marra model, the wood–adhesive bond line is conceptualized as a chain where the bond line is only as strong as its weakest link. The links consist of the bulk wood (wood not affected by the adhesive), wood interphase (wood modified by the adhesive), interface (boundary between wood and adhesive), adhesive interphase (adhesive affected by wood), and bulk adhesive (adhesive with same properties as adhesive not cured between wood). All the links may not be present in all bond lines. For example, all the adhesive cured in the bond line may have much different properties from the same adhesive cured without wood (Konnerth et al. 2006, Hunt et al. 2015), and therefore the bulk adhesive link

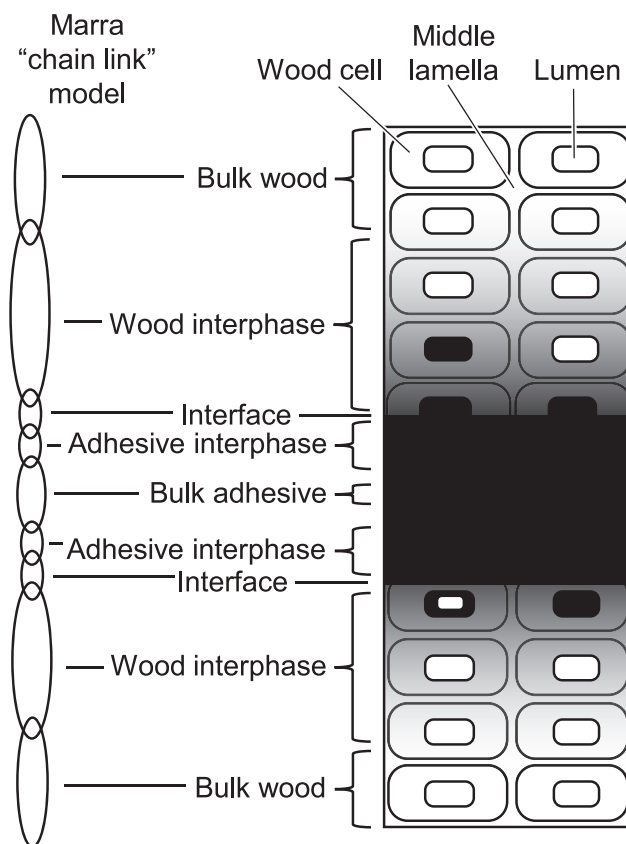


Figure 2.—Marra chain link model (Marra 1992) for a wood–adhesive bond line together with a cellular-scale schematic of a wood–adhesive bond line.

may not be present. In the ideal bond line, the weakest link is the bulk wood. However, often another link is the weakest and successfully identifying the weak link is key to improving the adhesive. For instance, if the adhesive bond line is “starved” and all the adhesive flows into the wood structure, the adhesive links will likely be the weakest, or if the surface preparation causes damage to the first couple of layers of cells, the wood interphase can be the weakest. Wet–dry cycles may also cause debonding at an interface. Researchers typically attempt to identify the weakest link by visual analysis of a failure surface. However, accurately identifying the weakest link can be very difficult because the analysis of a failure surface may be only providing information about the propagation of failure, and not about the weakest link at the onset of failure.

The wood interphase link is proposed to be very important to the performance of a bond line (Kamke and Lee 2007). When discussing this region, it is useful to define a few terms (Frihart 2009). Here, the term *flow* means that adhesive components are entering the micron-scale voids in the wood structure, such as lumina and pits, and the term *infiltrate* means specifically that adhesive components are entering the cell wall. To refer to the unspecific case of chemicals entering the cell walls or lumina, the term *penetration* is used. Norimoto cell models are also useful to discuss the different types of interactions that can occur in the wood interphase (Norimoto 2001). In Figure 3, Model A1 shows the unmodified cell wall, A2 shows chemicals only infiltrating the cell wall, A3 shows chemicals

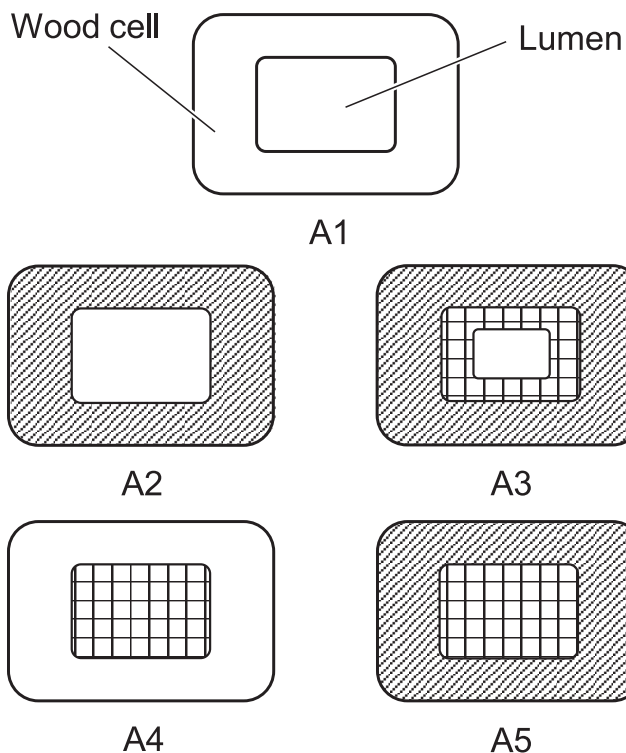


Figure 3.—Norimoto cell wall modification models (Norimoto 2001).

infiltrating the cell wall and flowing into the lumen to partially fill it, A4 shows adhesive chemicals flowing to completely fill the lumen but not infiltrating the cell wall, and A5 shows chemicals infiltrating the cell wall and flowing into the lumen to completely fill it.

To further understand the moisture durability of bond lines, Frihart (2009) proposed grouping adhesives into two groups that have different origins to their durability. The prepolymerized adhesive group, which includes polyurethane (PUR) and polyvinyl acetate (PVAc), consists of polymers with flexible backbones that can accommodate the swelling strains of the wood substrates. Because of their large molecular weight, they are not expected to infiltrate cell walls and so likely interact by Norimoto cell Model A4. However, the same flexibility that allows the adhesive to accommodate the moisture-induced swelling may also creep under loading, making prepolymerized adhesive inappropriate to use in load-bearing applications. The second group of adhesives identified by Frihart is the in situ polymerized group of adhesives, which includes epoxy, polymeric diphenylmethane diisocyanate (pMDI), phenol-formaldehyde (PF), phenol resorcinol-formaldehyde (PRF), melamine-formaldehyde (MF), melamine-urea-formaldehyde (MUF), and urea-formaldehyde (UF) adhesives. This group of adhesives consists of highly cross-linked rigid polymers that are typically resistant to creep and suitable for structural applications. However, their rigidity also makes them less capable of accommodating moisture-swelling strains of wood in the adhesive link. It is therefore proposed that moisture durability in the in situ polymerized group of adhesives derives from the adhesive infiltrating and modifying the wood near the surface (Norimoto cell Models A2, A3, and A5) to create a wood interphase link that

minimizes the swelling stresses and strains in the interface and adhesive links.

One of the most common moisture-durable wood adhesives available is PF adhesives. PF adhesives have been largely developed through decades of empirical research. The general consensus is that flow of PF into the wood cellular structure and infiltration into the cell walls creates a wood interphase that leads to moisture-durable bond lines (Stamm and Seborg 1936, Kamke and Lee 2007, Frihart 2009). However, the underlying molecular- and nanoscale mechanisms that give PF adhesives their moisture durability are not fully understood. An improved mechanistic understanding of how PF adhesives produce moisture-durable bond lines would accelerate the development of improved and new types of wood adhesives, such as adhesives from renewable resources to replace those derived from petroleum, and formaldehyde-free adhesives to replace adhesives that use formaldehyde.

In this article, we introduce and briefly review four recently developed experimental tools that provide information about the spatial interactions between adhesives, wood, and moisture at the nanometer to millimeter length scales. The techniques include X-ray computed tomography (XCT) and X-ray fluorescence microscopy (XFM) to map the penetration of adhesives into wood, nanoindentation to assess the effects of moisture and adhesive infiltration on wood cell wall mechanical properties, and small-angle neutron scattering (SANS) to observe the nanostructure of adhesive infiltrated inside cell walls. Using custom-built in situ humidity chambers with XCT and SANS, the moisture-induced swelling in wood can now also be studied across the cellular and subcellular length scales in bond lines. We chose these four tools because we have experience using them to study PF model bond lines. By using all of the tools to study similar bond lines, the combined results have led us to new insights about the wood-adhesive nanoscale interactions in the microfibril and how to design moisture-durable wood-adhesive bond lines. We also introduce a new nanoscale model to further aid the discussion of wood-adhesive interactions.

## Experimental Approaches to Span Bond-Line Length Scales

### X-ray computed tomography

XCT is a nondestructive technique that can be used to create three-dimensional (3D) visualizations of adhesive flow into wood at bond lines. With XCT, a series of two-dimensional (2D) X-ray images are taken of an object over a wide range of rotation angles. Then, these images are used to computationally reconstruct a 3D image of the object. An advantage of using X-rays for imaging is their ability to penetrate through an object and provide information about its internal structure not accessible to other types of microscopy, such as optical and electron. Although spatial resolution lower than 100 nm is possible in XCT (Rafsanjani et al. 2014), there is a general trade-off between spatial resolution and field of view. The field of view is generally about 1,000 times larger than the spatial resolution. A spatial resolution of about 1  $\mu\text{m}$  with a specimen on the order of 1 mm across is typically sufficient to characterize the flow of adhesives into the cellular structure of wood.

Over the past decade, several research groups have contributed to developing XCT into a powerful tool for

mapping the 3D flow of adhesive into wood, including early work visualizing the distribution of MUF resin in particle-board flakes before and after pressing (Evans et al. 2010), studying PF interphases in numerous wood species (Modzel et al. 2011), studying bonding parameters on wood–adhesive bond lines in beech wood (Hass et al. 2012), quantitatively measuring flow of multiple adhesives into softwood and hardwood (Paris and Kamke 2015), studying the effects of simulated weathering by imaging bond lines before and after wet–dry cycling (McKinley et al. 2016), and observing the effects of wood modifications on adhesive flow into wood (Bastani et al. 2016). Because of the large amount of contrast between air and adhesive, XCT can readily be used to see cell lumina filled with adhesive (Norimoto cell Models A3, A4, and A5) and the extent of adhesive flow.

A further advantage of XCT is that the X-ray attenuation of the adhesive can be increased by including a heavy atom in the adhesive. The increased attenuation results in contrast between the adhesive and wood cell walls that can be exploited using segmentation software to create 3D models of the adhesive separate from the wood. In the first attempts, atoms such as Cu and Rb were included in the adhesive formulations, but they were not covalently bonded to the adhesive polymers and there was concern that these heavy atoms migrated away from the adhesive (Evans et al. 2010, Modzel et al. 2011). To minimize the potential migration of the heavy atom, Paris and coworkers developed model PF, pMDI, and PVAc adhesive systems with the halide atom I covalently bonded to adhesive polymers (Paris et al. 2014, 2015; Paris and Kamke 2015). The 3D models of the adhesive clearly demonstrate that XCT is capable of mapping the flow of adhesives from the application surface through the radial and longitudinal cells of wood and the pits that connect the cells. The segmentation results also allow the quantification of the adhesive flow into the wood cellular structure as a function of distance from the bond line. However, care must be taken when interpreting the results because segmentation can be complicated by the heavy atom infiltrating the cell walls near the bond line and phase-contrast effects (Paris et al. 2015).

Another advantage of using X-rays for imaging is that they do not require the imaged object to be in a restrictive environment, like a vacuum in electron microscopy. Thus, in addition to their penetrating nature, X-rays allow the object of interest to be placed in situ mechanical testing devices and different environmental conditions. McKinley et al. (2016) used an in situ mechanical testing device to image the 3D structure of a lap shear specimen before, during, and after loading. This work is part of a larger project to utilize XCT in the development and validation of micromechanical numerical models of wood–adhesive bond lines (Kamke et al. 2014). Recently, Jakes et al. (2017) developed an in situ humidity chamber for XCT at the 2-BM beamline at the Advanced Photon Source synchrotron at Argonne National Laboratory (Argonne, Illinois), and initial work has been performed to study the moisture-induced swelling in the 3D structure of a bond line made using loblolly pine (*Pinus taeda*) and a brominated PF (BrPF). One advantage of using synchrotron X-rays is that the extremely bright source allows experiments to be performed very quickly. An entire data set can be collected in a matter of seconds. This makes time-lapse XCT imaging possible,

which in the future will facilitate study of the dynamics of swelling and shrinking in wood–adhesive bond lines.

## X-ray fluorescence microscopy

XFM is a synchrotron-based technique where X-rays are focused onto a spot on a specimen while an energy-dispersive detector system quantifies photons fluoresced from the specimen. The fluoresced photons can be analyzed to determine the amount and type of elements in a given spot. By raster scanning the specimen, 2D maps of ions can be built. Analogous to XCT, it is also possible to create 3D maps of elements by collecting 2D maps at multiple rotation angles and performing a computational reconstruction. The spatial resolution of XFM depends on the size of the spot illuminated by the X-ray beam. Typically with hard X-rays, elements with mid- to high atomic numbers (Si and higher) can readily be mapped with XFM. Therefore, to utilize XFM to study the wood–adhesive bond line, the adhesive needs to be tagged with an element in this range. Jakes et al. (2013, 2015) demonstrated the utility of XFM to quantify adhesive infiltration into wood cell walls using a BrPF adhesive. Five bond lines were made using southern yellow pine latewood and five different BrPF adhesives with different average molecular weights ( $M_w$ s). Two-micrometer-thick transverse sections of each bond line were prepared and used for imaging. The XFM maps show Br inside the adhesives and some of the wood cell walls. The Br signal inside the wood cell walls is representative of adhesive infiltration into the wood cell walls because the Br was covalently bonded to the adhesive. The wood interphase link could be clearly identified with cells exhibiting Norimoto cell Models A2, A3, and A5. The XFM maps allowed the quantification of BrPF infiltration and showed that in the cell walls immediately adjacent to the bond line, the amount of adhesive infiltration was greater for the lower- $M_w$  BrPF than for the higher- $M_w$  BrPF. The wood interphase link also extended farther from the adhesive link in the lower- $M_w$  BrPF. In the cell walls with infiltration, gradients in the adhesive could also be observed across the thickness of the cell walls, with the highest amount of infiltration nearest the interface between the adhesive and cell wall. Within a whole cell with an adhesive in the lumen (Model A3 or A5), the infiltration was found to be radially distributed from the lumen. In other words, the amount of adhesive was the same at a given distance from the lumen surface. In some sections, especially the lower- $M_w$  bond lines, BrPF was found to fill a lumen far from the bond line. The adhesive must have traveled through ray and tracheid cells outside of the plane of the section. Even in these cells, infiltration could be observed in the cell walls, similar to Models A3 and A5.

## Nanoindentation

In nanoindentation, a carefully shaped probe is pressed into a material while both the load and depth of penetration are continuously assessed. From the resulting load–depth trace, mechanical properties, most often hardness and elastic modulus, are calculated. An advantage of nanoindentation is its ability to probe small volumes of materials, such as the wood cell wall layers S2 and CCML (Wimmer and Lucas 1997). Researchers have therefore utilized nanoindentation to study the properties of wood cell wall and adhesive layers in the wood interphase region. Often, changes in cell wall

layer mechanical properties are interpreted as an indication that the adhesive infiltrated the cell wall. It is interesting to note that when bond lines with in situ polymerized adhesives are tested, such as PRF (Gindl et al. 2004a, 2004b; Konnerth and Gindl 2006), MUF (Konnerth and Gindl 2006, Stöckel et al. 2010a), UF (Stöckel et al. 2010a), and pMDI (Jakes et al. 2009), the hardness of the S2 cell wall layers in the wood interphase increase compared with control cells. In contrast, for prepolymerized adhesives, such as PUR (Gindl et al. 2004a, 2004b; Konnerth and Gindl 2006) and PVAc (Konnerth and Gindl 2006), the S2 cell wall layer hardness is either unchanged or lowered. These results support Frihart's (2009) classification of adhesives that successful in situ polymerized adhesives infiltrate and modify the cell walls in the wood interphase. In addition to probing the cell wall layer properties, nanoindentation can also be used to assess the mechanical properties of the bulk and adhesive interphase links (Konnerth et al. 2006; Stöckel et al. 2010a, 2010b; Wang et al. 2017b). Additionally, the CCML and S2 cell wall layers can be probed individually in bond lines (Liang et al. 2011, Liu et al. 2014).

The temperature and RH of wood cell walls can also be controlled during nanoindentation. Konnerth and Gindl (2008) tested the properties of PRF and PUR adhesive inside a bond line and found that the elastic modulus and hardness of the prepolymerized adhesive PUR decreased with increasing temperature, whereas the in situ polymerized PRF properties did not depend on temperature. More recently, Wang et al. (2015, 2017a) reported that the in situ polymerized PF, UF, and pMDI mechanical properties increased with temperature, which they attributed to additional curing during the high-temperature nanoindentation experiments. The humidity can also be controlled to measure hygromechanical properties of cell walls (Yu et al. 2010, Bertinetti et al. 2014, Youssefian et al. 2017). The same cell wall layers infiltrated with BrPF and mapped with XFM by Jakes et al. (2015) were also tested with nanoindentation at a low and high RH level in the same study. This allows a direct comparison of the amount of moisture-induced mechanical softening as a function of adhesive infiltration. An interesting finding of the study is that for a given amount of BrPF infiltration, the lower- $M_w$  BrPF adhesives were more effective at minimizing the mechanical softening. This suggests that the interactions between the adhesive and cell wall had an  $M_w$  dependence. Jakes et al. (2015) suggested that the lower- $M_w$  BrPF adhesives could more intimately associate with the water sorption sites on the wood polymers to prevent moisture-induced softening.

### Small-angle neutron scattering

SANS is a technique that is well suited to study the 1- to 100-nm structure of organic materials like wood. With SANS, a beam of neutrons is passed through a sample and the elastic scattering of neutrons at small angles is measured and analyzed to determine the internal nanostructure of the sample. The scattering arises from differences in neutron contrast between nanoscale structures. Fernandes et al. (2011) used SANS to study earlywood at different MCs and found SANS capable of measuring the increase in spacing between elementary fibrils with increasing MC. Similar to X-rays, neutrons do not require restrictive sample environments and are amendable to use with sample environment chambers. Plaza et al. (2016) built an in situ humidity

chamber for the BioSANS and EQ-SANS beamlines at Oak Ridge National Laboratory (Oak Ridge, Tennessee) to study moisture-induced anisotropic swelling in the wood nanostructure. The anisotropic scattering observed was consistent with a lamellar structure of the S2 cell wall layer. They measured strains at the elementary fibril level that increased about 20 to 25 percent between conditioning at 25 percent RH and water saturation. Through simple calculations, they also found that in the transverse plane of the S2 secondary cell wall layer, over half of the moisture-induced swelling could be attributed to the swelling between elementary fibrils inside the microfibrils. This calculation goes against the previous assertions by researchers that most of the swelling occurs in the lignin-hemicelluloses matrix between the concentric lamellae composed of the microfibrils (Boutelje 1962, Rafsanjani et al. 2014). In terms of wood adhesives, this also provides the new insight that to minimize moisture-induced swelling at the nanoscale, the adhesive should modify and prevent swelling in the cellulose microfibril.

Another advantage of SANS is that the neutron contrast can be controlled by isotope labeling, such as using deuterium to replace hydrogen in adhesives. This would facilitate the study of the adhesive nanostructure in wood cell walls. Recently, SANS was used to study the nanostructure of a deuterium-labeled PF (dPF) infiltrated into loblolly pine latewood (Plaza 2017; Plaza et al. 2017, 2018). dPF was found to infiltrate the microfibril in the less ordered regions between the elementary fibrils. This suggests that for PF one of the nanoscale mechanisms contributing to the moisture durability is its ability to not only infiltrate the wood cell wall, but also the microfibril.

### Nanoscale Wood-Chemical Interaction Model

The combined results of these multiscale studies of PF-wood interactions suggest that current models are not adequate to describe all the potential interactions between an adhesive and the wood substrate. Models to describe the potential interactions at the nanoscale are missing. Therefore, we propose a nanoscale wood-chemical interaction model in Figure 4. The model has three components. At the center of the model is a microfibril (MF) composed of a two-by-two array of elementary fibrils. It is assumed the elementary fibrils consist of highly organized cellulose chains that cannot be infiltrated by water, wood-modifying chemical, or adhesive. The less ordered regions outside the elementary fibrils in the microfibril are accessible. Surrounding the microfibril are the second component, hemicelluloses (HC), and outside of the hemicelluloses is the third component, lignin (L). The model is not meant to accurately represent the actual nanostructure of a wood cell wall, but rather to schematically represent different nanoscale components in the wood cell walls that could be infiltrated and modified by chemicals. The eight models in Figure 4 represent all the potential types of interactions. In the model labeling, the "N" stands for "nanoscale," the number represents the number of components modified, and the acronyms in parentheses indicate which components were modified. For example, N0 is the unmodified model and N2(MF,L) is the model with microfibril and lignin modifications. Although it currently may not be feasible to selectively infiltrate chemicals into the wood cell wall with respect to all the proposed nanoscale models, they are included here for completeness. It is also possible that in the

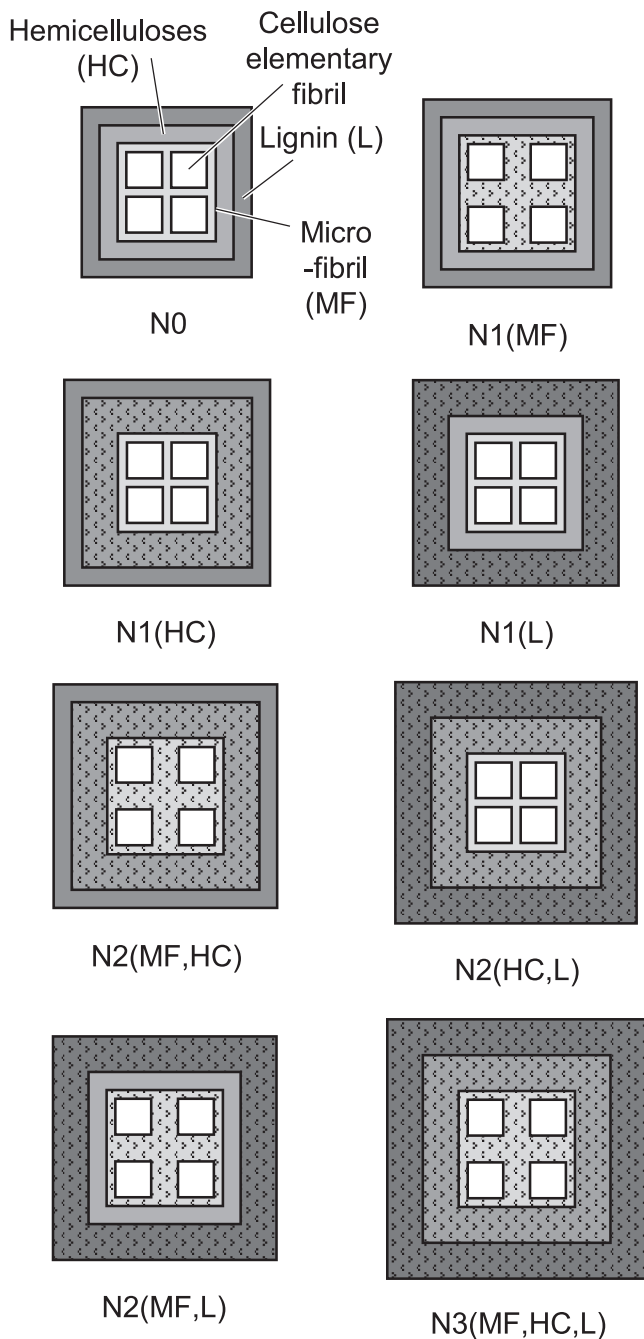


Figure 4.—Proposed model to discuss the potential nanoscale interactions between adhesive components and the wood secondary wood cell wall nanostructure.

future different types of modifications, such as genetically modifying a growing tree to selectively modify lignin (Wilkerson et al. 2014) or hemicelluloses (Busse-Wicher et al. 2016), will become available and can utilize these models.

The nanoscale models proposed in Figure 4 give us new context to discuss the hygromechanical BrPF nanoindentation results (Jakes et al. 2015). We propose that the high- $M_w$  BrPF samples had a nanoscale interaction of N2(HC,L) and the low- $M_w$  BrPF had an interaction of N3(MF,HC,L). The microfibril is the primary structural component in the S2 secondary cell wall layer. It may be that the high- $M_w$

BrPF could not infiltrate the microfibril, and thus the microfibril was softened more by the uptake of moisture. In contrast, the low- $M_w$  BrPF could infiltrate the microfibril and minimized the water entering and softening the microfibril. This could be why, for a given amount of BrPF infiltration, the lower- $M_w$  BrPF adhesives are more effective at minimizing the mechanical softening. In the future, SANS can be used to test this conjecture and whether or not there is an  $M_w$  dependence on microfibril infiltration.

### Concluding Remarks

A direct path to engineer wood–adhesive bond lines with improved moisture durability would be to identify the weakest link in the bond line and modify the wood–adhesive interactions to strengthen the link. The process could then be iterated until an ideal bond line is engineered with the bulk wood as the weakest link. Unfortunately, current researchers are hindered because it is difficult to conclusively identify the adhesive–bond-line link responsible for the initial failure mechanism. The combination of in situ mechanical testing, RH control, and XCT is progressing researchers toward the ability to observe the initiation of failure, and therefore the weakest link, in situ. However, even after identifying the weakest link, researchers still need to be able to specify how the wood–adhesive interactions need to be modified to strengthen the link. Furthermore, they also need to identify interactions between the unsatisfactory adhesive and wood, as well as how those interactions change as the adhesive and bonding process are modified. The recently developed innovative research tools reviewed in this article can play a large role in providing information about these interactions across nanometer to millimeter length scales. The results are expected to accelerate research efforts toward developing a mechanistic understanding of moisture-durable wood–adhesive bond lines, such as further understanding of the prepolymerized and in situ polymerized groups of adhesives proposed by Frihart (2009). The results should also accelerate the development of new and improved wood adhesives.

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