

Integrating Multi-Scale 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 used to test and report the bulk level properties of bondlines, such as bondline shear strength and wood failure analysis, sufficient experimental tools to study wood-adhesive bondlines and the effects of moisture at the nm- to mm-length scales are lacking. Here we review recently developed tools that, when combined, are capable of studying bondlines and the effects of moisture across these length scales. The tools include X-ray computed tomography (XCT), X-ray fluorescence microscopy (XFM), nanoindentation, and small angle neutron scattering (SANS). Their utility has been demonstrated by studying model bondline systems using phenol formaldehyde adhesives. The combined results lead to new insights towards understanding moisture durability in wood-adhesive bondlines and a new model to facilitate the discussion of adhesive penetration into the wood nanostructure.

INTRODUCTION

Adhesives are increasingly relied upon to make forest products, such as plywood, oriented strandboard, 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 bondlines. Forest products in service may experience cyclic relative humidity 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 bondline 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 are readily observed and define the transverse, radial-longitudinal, and tangential-longitudinal planes of wood structure (Fig. 1a). Most often adhesives are applied to a longitudinal plane. The cellular structure of wood depends on whether the tree was a hardwood (angiosperm, deciduous) or softwood (gymnosperm, coniferous). Here, we discuss mainly softwood. Therefore, the softwood cellular structure is illustrated in Fig. 1b. In softwood, tracheids aligned with the longitudinal axis are the most common type of cell. A tracheid is essentially a hollow tube with an empty inner space called the lumen. The wall thickness and lumen size depend on whether the tracheid is in the latewood or earlywood portion of the growth ring (Fig. 1b). Generally, the wall is thicker and the lumen smaller in the latewood than in the earlywood. Because in a living tree liquid transport is one of the primary wood functions, cells are connected to allow intercellular transport with small openings called pits, and ray cells are present for radial liquid transport. In an adhesive bondline, 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.

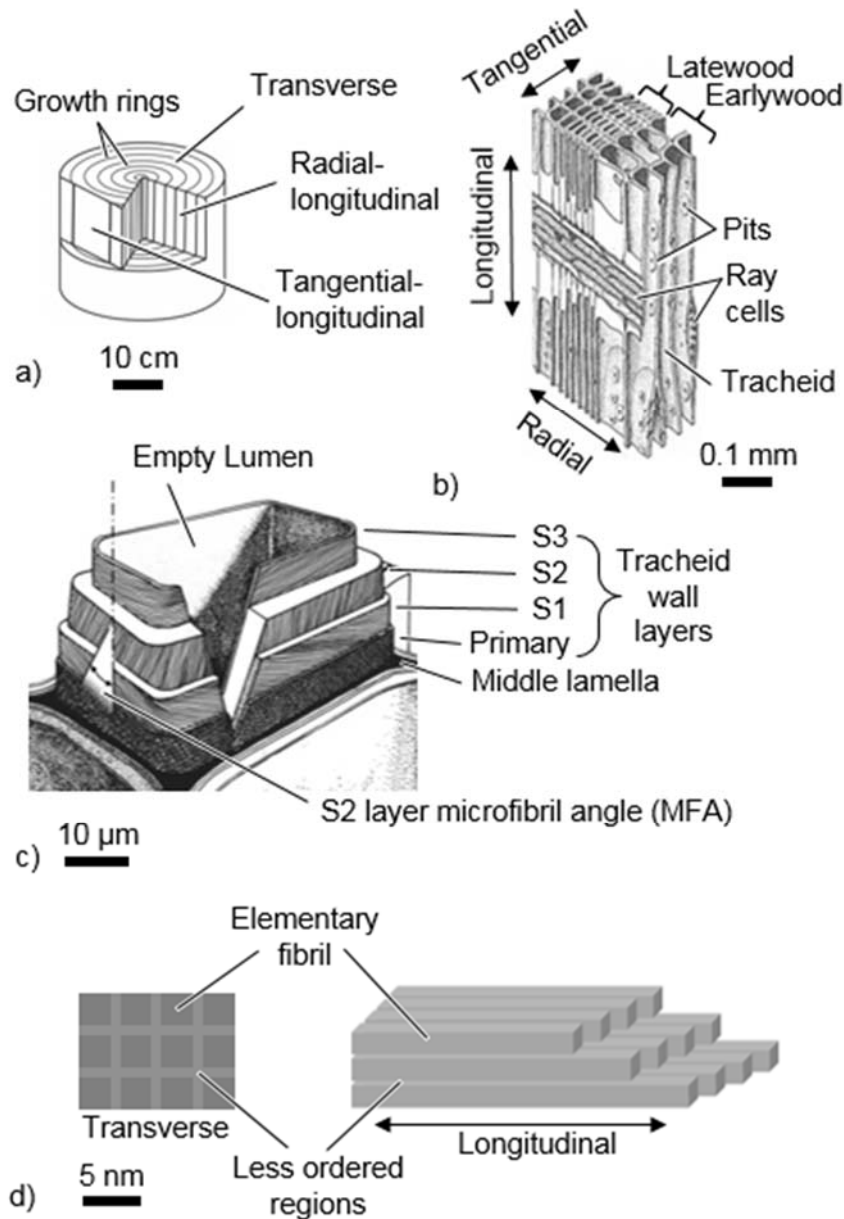


Figure 1: Breakdown of wood structure from the a) bulk to the b) cellular to the c) cell wall to the d) microfibril.

Tracheid walls are highly organized polymeric materials consisting of 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 nano-fiber-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 lamella that run parallel to the lumen surface (Scallan 1974, Kerr and Goring 1975, Ruel et al. 1978, Fahlén and Salmén 2002, 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 Fig. 1d (Terashima et al. 2009). Thin layers of less-ordered structures are integrated into the cellulose microfibrils between the elementary fibrils. The helical angle that the cellulose microfibrils make with the longitudinal tracheid axis is called the microfibril angle (MFA) and in the S2 layer is typically low (5-30°), while it is much higher in the S1 and S3, typically 50-70° and >70°, respectively

(Wiedenhoef 2013). The middle lamella fills in the regions between cells (Fig. 1c) and consists of about 20% hemicelluloses embedded as an irregular, interconnecting network in a matrix of lignin (Hafren et al. 2000, Wiedenhoef 2013). 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 relative humidity (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% MC (depending on definition) (Stamm 1971, Hernández and Bizoñ 1994, Berry and Roderick 2005, Englund 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 bondline 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% 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% from 25% to 85% RH, whereas earlywood swells anisotropically with approximately 3% in the tangential direction and 1% 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% in the direction normal to the lumen surface and 5% in the direction parallel to the lumen surface from 10% to 85% 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 bondlines. 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 bondlines, it is useful to employ models to assist in the discussion. The Marra model (Fig. 2) is a useful tool to break down wood adhesive bondlines into regions for further study (Marra 1992). In the Marra model, the wood-adhesive bondline is conceptualized as a chain where the bondline 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 bondlines. For example, all the adhesive cured in the bondline may have much different properties than the same adhesive cured without wood (Konnerth et al. 2006, Hunt et al. 2015), and therefore the bulk adhesive link may not be present. In the ideal bondline, 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 bondline 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 layers of cells, then 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.

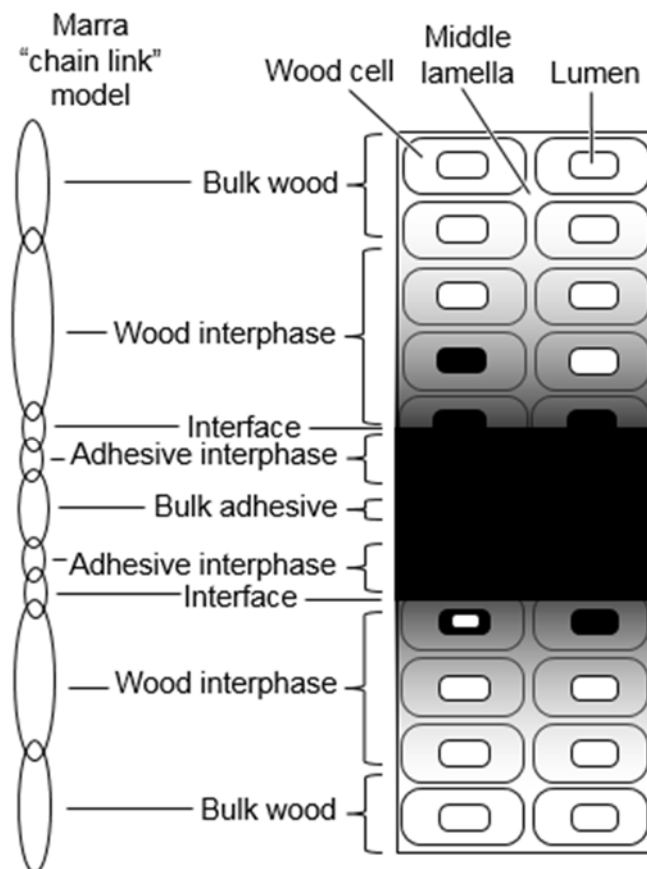


Figure 2: Marra chain link model (Marra 1992) for a wood adhesive bondline together with a cellular-scale schematic of a wood adhesive bondline.

The wood interphase link is proposed to be very important to the performance of a bondline (Kamke and Lee 2007). When discussing this region, it is useful to define a few terms. Here, the term “flow” means 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 Fig. 3, Model A1 shows the unmodified cell wall, A2 shows chemicals only infiltrating the cell wall, A3 shows chemicals 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.

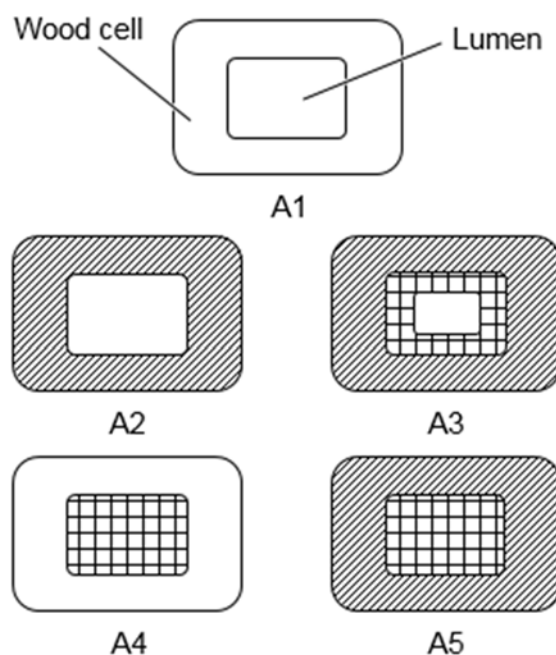


Figure 3: Norimoto cell wall modification models (Norimoto 2001).

To further understand the moisture-durability of bondlines, Frihart proposed grouping adhesives into two groups that have different origins to their durability (Frihart 2009). The pre-polymerized 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 pre-polymerized 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 bondlines (Stamm and Seborg 1936, Kamke and Lee 2007, Frihart 2009). However, the underlying molecular- and nano-scale mechanisms that give PF adhesives their moisture durability are not fully understood. An improved mechanistic understanding of how PF adhesives produce moisture-durable bondlines 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 paper, we review recently developed experimental tools that provide information about the spatial interactions between adhesives, wood, and moisture at the nm to mm 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 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 bondlines. All these techniques have been applied to PF model bondlines, and the results lead to new insights about the wood-adhesive nanoscale interactions in the microfibril and how to design moisture-durable wood adhesive bondlines. We also introduce a new nanoscale model to further aid the discussion of wood-adhesive interactions.

EXPERIMENTAL APPROACHES TO SPAN BONDLINE LENGTH SCALES

X-ray Computed Tomography (XCT)

XCT is a nondestructive technique that can be used to create three-dimensional (3D) visualizations of adhesive flow into wood at bondlines. 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 1000 times larger than the spatial resolution. A spatial resolution of about 1 μm 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, a number of research groups have contributed to developing XCT into a powerful tool for mapping the 3D flow of adhesive into wood, including early work by Evans and coworkers visualizing the distribution of MUF resin in particleboard flakes before and after pressing (Evans et al. 2010), Modzel and coworkers studying PF interphases in numerous wood species (Modzel et al. 2011), Hass and coworkers studying bonding parameters on wood-adhesive bondlines in beech wood (Hass et al. 2012), Paris and coworkers quantitatively measuring flow of multiple adhesives into softwood and hardwood (Paris and Kamke 2015), McKinley and coworkers studying the effects of simulated weathering by imaging bondlines before and after wet-dry cycling (McKinley et al. 2016), and Bastani and coworkers 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, Paris et al. 2015, Paris and Kamke 2015). The 3D models of the adhesive clearly demonstrate 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 bondline. However, care must be taken when interpreting the results because segmentation can be complicated by the heavy atom infiltrating the cell walls near the bondline 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. This, in addition to their penetrating nature, allows the object of interest to be placed in *in situ* mechanical testing devices and different environmental conditions. McKinley and coworkers used an *in situ* mechanical testing device to image the 3D structure of a lap shear specimen before, during, and after loading (McKinley et al. 2016). This work is part of a larger project to utilize XCT in the development and validation of micromechanical numerical models of wood-adhesive bondlines (Kamke et al. 2014). Recently, Jakes and coworkers developed an *in situ* humidity chamber for XCT at the 2-BM beamline at the Advanced Photon Source synchrotron at Argonne National Laboratory (Argonne, IL, USA), and initial work has been performed to study the moisture-induced swelling in the 3D structure of a wood-adhesive bondline (Jakes et al.

2017). 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 bondlines.

X-ray fluorescence Microscopy (XFM)

XFM is a synchrotron-based technique where X-rays are focused on to 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 bondline, the adhesive needs to be tagged with an element in this range. Jakes and coworkers demonstrated the utility of XFM to quantify adhesive infiltration into wood cell walls using a brominated PF (BrPF) adhesive (Jakes et al. 2013, Jakes et al. 2015). Five bondlines were made using southern yellow pine latewood and five different BrPF adhesives with different average molecular weights (M_w). Two- μ m-thick transverse sections of each bondline 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 bondline, the amount of adhesive infiltration was greater for the lower M_w BrPF than 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 bondlines, BrPF was found to fill a lumen far from the bondline. 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 model 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 wood cell wall layers (Wimmer and Lucas 1997). Researchers have therefore utilized nanoindentation to study the properties of wood cell walls 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 bondlines with *in situ* polymerized adhesives are tested, such as PRF (Gindl et al. 2004a, Gindl et al. 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 cell walls in the wood interphase increase compared to control cells. In contrast, for pre-polymerized adhesives, such as PUR (Gindl et al. 2004a, Gindl et al. 2004b, Konnerth and Gindl 2006) and PVAc (Konnerth and Gindl 2006), the cell wall hardness is either unchanged or lowered. These results support Frihart's classification of adhesives (Frihart 2009) 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, Stöckel et al. 2010b).

The temperature and relative humidity of wood cell walls can also be controlled during nanoindentation. Konnerth and Gindl tested the properties of PRF and PUR adhesive inside a bondline and found that the elastic modulus and hardness of the pre-polymerized adhesive PUR decreased with increasing temperature, whereas the *in situ* polymerized PRF properties did not depend on temperature (Konnerth and Gindl 2008). 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 mapped by Jakes and coworkers were also tested with nanoindentation at a low and high RH level in the same study (Jakes et al. 2015). 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 a M_w dependence. Jakes and coworkers 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)

Small-angle neutron scattering (SANS) is a technique that is well suited to study the 1-100 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 and coworkers used SANS to study earlywood at different MCs and found SANS capable of measuring the increase in spacing between elementary fibrils with increasing MC (Fernandes et al. 2011). Similar to X-rays, neutrons do not require restrictive sample environments and are amendable to use with sample environment chambers. Plaza and coworkers built an *in situ* humidity chamber for the BioSANS and EQ-SANS beamlines at Oak Ridge National Laboratory (Oak Ridge, TN, USA) to study moisture-induced anisotropic swelling in the wood nanostructure (Plaza et al. 2016). 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 20-25% between conditioning at 25% 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, Plaza used SANS to study the nanostructure of a deuterium-labeled PF (dPF) infiltrated into loblolly pine latewood (Plaza 2017, Plaza et al. 2017). Plaza found that the dPF infiltrated 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 multi-scale 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 Fig. 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 Fig. 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 are 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 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.

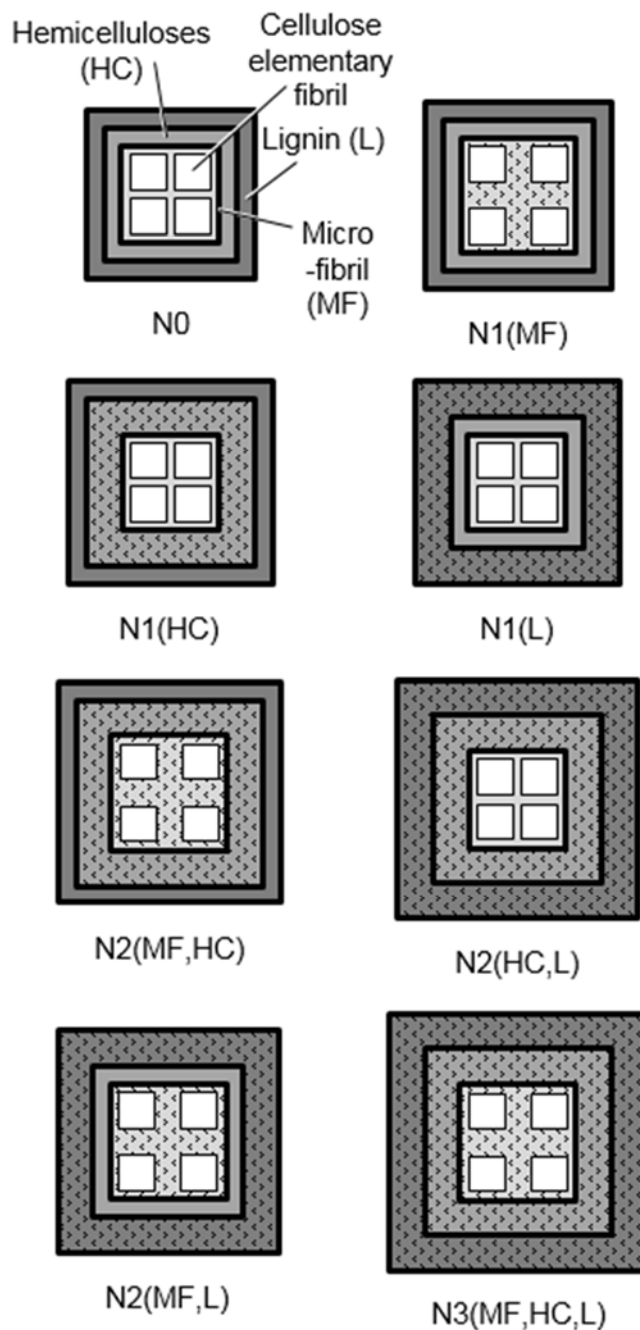


Figure 4: Proposed model to discuss the potential nanoscale interactions between adhesive components and the wood secondary wood cell wall nanostructure.

The nanoscale models proposed in Fig. 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 a M_w dependence on microfibril infiltration.

CONCLUDING REMARKS

A direct path to engineer wood adhesive bondlines with improved moisture durability would be to identify the weakest link in the bondline and modify the wood-adhesive interactions to strengthen the link. The process could then be iterated until an ideal bondline is engineered with the bulk wood as the weakest link. Unfortunately, current researchers are hindered because it is difficult to conclusively identify the adhesive-bondline link responsible for the initial failure mechanism. The combination of *in situ* mechanical testing, RH control, and XCT is progressing researchers towards 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 the paper can play a large role in providing information about these interactions across nm to mm length scales. The results are expected to accelerate research efforts toward develop a mechanistic understanding of moisture-durable wood-adhesive bondlines, such as further understanding of the prepolymerized and *in situ* polymerized groups of adhesives proposed by Frihart (Frihart 2009). The results should also accelerate the development of new and improved wood adhesives.

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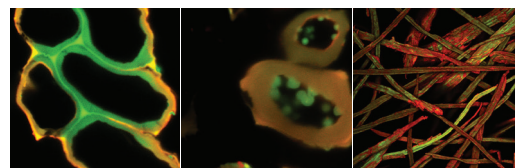
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