

Understanding Wood Bonds—Going Beyond What Meets the Eye: A Critical Review

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Abstract: Understanding why wood bonds fail is an excellent route toward understanding how to make them better. Certifying a bonded product usually requires achieving a specific load, percent wood failure, and an ability to withstand some form of moisture exposure without excessive delamination. While these tests protect the public from catastrophic failures, they are not very helpful in understanding why bonds fail. Understanding failure often requires going beyond what meets the naked eye, conducting additional tests, probing the wood surface, the fracture surface, adhesive properties, and the interaction of wood and adhesive during bond formation and service. This review of wood bond analysis methods reviews fundamentals of wood bonding and highlights recent developments in the analyses and understanding of wood bonds. It concludes with a series of challenges facing the wood bonding community.

Keywords: Wood adhesive, wood bond, microscopy, penetration, failure

List of Abbreviations

AFM	Atomic Force Microscopy
AP	Average Penetration
CLSM	Confocal Laser Scanning Microscopy
CV	Collapsed Vessel
CWBL	Chemical Weak Boundary Layer
DCB	Dual Cantilever Beam
DIC	Digital Image Correlation
DMA	Dynamic Mechanical Analysis (also known as DMTA)

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DOI: 10.7569/RAA.2018.097312

DOC	Degree of Condensation
DSC	Differential Scanning Calorimetry
EDXS	Energy Dispersive X-Ray Spectroscopy, also known by EDX, EDXA, and XEDS
EELS	Electron Energy Loss Spectroscopy
EP	Effective Penetration
EPI	Emulsion Polymer Isocyanate
ESPI	Electronic Speckle Pattern Interferometry
FPL	Forest Products Laboratory
FT-IR	Fourier Transform-Infrared
HMR	Hydroxymethylated Resorcinol
LVL	Laminated Veneer Lumber
MC	Moisture Content
MDF	Medium Density Fiberboard
MF	Melamine-Formaldehyde
MIP	Mercury Intrusion Porosimetry
MOE	Modulus of Elasticity
MOR	Modulus of Rupture
MP	Maximum Penetration
MUF	Melamine-Urea-Formaldehyde
MW	Molecular Weight
MWBL	Mechanical Weak Boundary Layer
NIR	Near-Infrared
NMR	Nuclear Magnetic Resonance
OSB	Oriented Strand Board
PB	Particleboard
PF	Phenol-Formaldehyde
pMDI	polymeric Methylene Diphenyl Diisocyanate
PRF	Phenol-Resorcinol-Formaldehyde
PUR	Polyurethane
PVAc	Poly(vinyl acetate)
QENS	Quasi-Elastic Neutron Scattering
SANS	Small Angle Neutron Scattering
SEM	Scanning Electron Microscopy
SThM	Scanning Thermal Microscopy
TEM	Transmission Electron Microscopy
T_g	Glass Transition Temperature
TMA	Thermal Mechanical Analysis
UF	Urea-Formaldehyde
WDS	Wavelength Dispersive Spectroscopy
XCT	X-Ray Computed (Micro)Tomography
XFM	X-Ray Fluorescence Microscopy
XPS	X-ray Photoelectron Spectroscopy, also known as ESCA



1 Introduction: Macroscopic Knowledge for Successful Adhesive Bonding of Wood

Although adhesives have been used for bonding wood products since before recorded history [1], making bonded wood products is a continuous challenge because of the ever-changing wood sources and products, greater performance needs, and desire for lower costs. In recent decades, engineered wood products have mainly replaced solid wood for structural and other wood applications. All these changes and their interacting effects have driven a continuous demand for bonding a wider variety of wood substrates to achieve a higher performance than in the past [2]. These products must perform for decades or even centuries without failing.

Good adhesives and bonding systems have been developed through intelligent empirical approaches and application of the understanding of wood bonds to date. As a result, over 65% of wood products are now bonded [3]. However, this does not mean that adhesive manufacturers and users are done innovating. The continuous change of the market and the unresolved questions addressed in Section 5 of this review present significant challenges [4]. To meet these challenges in a timely and cost-effective way, wood bonding professionals need to understand how bonds work. More importantly, they also need to understand why bonds fail, and this often requires using methods that go beyond standard tests and visual evaluations. They must go beyond what meets the eye.

Studying the mechanisms responsible for wood adhesive bonding has been an important aspect of wood science research over the past 50 years [2, 5]. It has been proposed that a better understanding of wood adhesion mechanisms at the micro and nanoscale has the potential to accelerate development of better adhesive systems using more efficient and effective processing methods for the wide array of wood products [4, 6, 7].

Creating an effective wood bond requires good adhesive wetting, efficient solidification of the adhesive to provide strength, and sufficient deformability of the cured adhesive to reduce the stresses that occur during joint formation and to avoid stress concentrations [8]. This review will first discuss wood properties, the preparation of surfaces, and the application of adhesives. Then we discuss bond performance, followed by examples of investigations that go beyond what meets the naked eye, and a survey of techniques. Finally, we discuss unresolved questions in the field.

The first step in bonding is the preparation of the substrate (wood) surface so that it has minimal surface contamination and, for most products, is smooth. A weak surface layer can lead to bond failure [9–11], but it can be hard to prove the presence of a weak layer because that normally requires techniques beyond simple visualization. Several researchers have emphasized that in wood, such weak boundary layers can be caused by chemical or physical deficiencies, or both [5, 12]. Consequently, a closer examination of the wood surface is needed beyond what can be felt by hand or visualized by eye.

The general theories of adhesion have been intensely studied for a wide variety of substrates [7, 13–17]. For any bonding to take place the adhesive must spread across and wet the wood surface to develop molecular interactions between the adhesive and wood. The maximal surface interactions occur when the surface energy of the adhesive and the wood are nearly equal [18]. Wood is an unusual substrate because of its abundant micrometer scale, interconnected voids. Adhesive flows into these voids and provides better mechanical interlocking with a larger surface area compared to most other substrates [19]. However, just mechanical interlock is not able to provide sufficient strength without intermolecular interactions [20]. These specific interactions are enhanced in those adhesives capable of penetrating wood cell walls at the molecular scale [21]. Some adhesives have components that diffuse into the wood cell wall (cell wall penetration, or infiltration) and polymerize there, potentially providing a continuous chain of covalent bonds from the bulk adhesive into the cell wall. Because wood adhesives penetrate below the surface, it is necessary to differentiate the zone of pure adhesive, which we call the *glueline*, from the entire zone impacted by the presence of adhesive, which we call the *bondline*. In other words, the *bondline* contains both the *glueline* and the *interphase*.

Another unusual property of wood as a substrate is its great variability. Because of the cellular and multilayered composite nature of wood, the bonding surface can vary from the voids of open lumens, the various intercellular pitting patterns, and ends of ray cells to the relatively smooth middle lamella surfaces [22]. The variety of wood cell types and structures serves to increase the types of wood surfaces for bonding [5]. This problem becomes more complex when bonding chips, particles and fibers using a binder adhesive, which can be thought of as spot welding the wood together, as opposed to a continuous *bondline* in a laminated product. Because of the micrometer and molecular level penetration and wood variability, adhesion is highly dependent on a complex interaction of the adhesive formulation, production process, and the wood.

After obtaining adhesion by wetting and penetration, the adhesive must solidify by moisture loss, chemical cure, or both, to develop good cohesive strength. Good internal strength (cohesion) is needed to ensure permanency of the bond and transfer load across the *glueline*, and is controlled by different factors than adhesion to the wood. Most wood adhesives develop cohesive strength through some type of chemical reaction (often condensation) that forms large intertwined polymers and gelled structures [23]. However, strong networks are often difficult to form near an interface with a substrate because the network formation is disrupted at the boundary [11]. Thus, cohesive failure in the adhesive may occur in the weak *interphase* layer while the bulk of the adhesive appears normal. Other causes of weak adhesive *interphase* in wood can be due to interference of cure by extractives from the wood, loss of reactive components to the wood, or alteration of the pH or moisture content by contact with the wood.

Adhesives make possible an efficient use of wood resources to make a wide variety of products, most of which cannot be made out of a solid piece of wood.

The variety of wood products, their performance expectations, and the anatomical variety within wood means that demands on the adhesive vary widely. Comparing the performance of a poly(vinyl acetate) (PVA) adhesive holding a chair together to a phenol-formaldehyde (PF) holding together the layers of structural laminated veneer lumber can seem ridiculous, but both depend on the wood surface, the interaction of the adhesive with the wood, and the demands placed on the bond. Both cases depend on developing molecular level contact between the adhesive and wood substrates and maintaining that contact while the joint is loaded. Obviously, we cannot easily see all molecular level contacts and failures in such a complex environment, but we can certainly determine what makes a good or bad bond at a finer level of examination than what is normally visible to the eye. This review is meant to assist the reader understand the fundamental process of wood bonding and choose from the many methods that have been developed, especially over the past few decades, for understanding wood adhesives at a microscopic level.

2 Bond Formation (Developing Adhesion)

Bond formation is the process of adhesion and cohesion; this means strong adhesion, or attraction between the substrate and the adhesive, as well as sufficient internal (cohesive) strength of the adhesive. Various interactions between substrate and adhesive determine adhesion strength; these interactions can be both physical and chemical in nature. For good adhesion, there must be molecular level contact between the adhesive and the substrate, which includes flow of adhesive over the substrate surface and into the irregularities of the surface to increase the contact area (interface) [14]. For most materials, this involves preparing the surface by solvent wipe, chemical treatment, or ablation to develop good contact between adhesive and substrate, while for wood, sawing, planing, chipping, fibrillation, and sanding are the most common methods.

The problem faced daily by those making wood bonds is not how to make the ideal bond, but rather how to make satisfactory bonds with minimal cost, and with the available equipment and material. This involves balancing many contributing factors. For example, a less expensive wood source, or wood preparation method, might require more adhesive or a different adhesive to bond adequately. The influence of wood anatomy, surface preparation, and other production variables on bond quality have been generally described [5, 22–27]. Therefore, our discussion will briefly survey general principles and focus on recent discoveries.

Because optimizing this balance of economy and quality requires understanding the role of each material in bond formation, the following sections will discuss the role of each component of bond formation in the order: wood properties, surface quality, adhesive penetration, and adhesive properties that influence penetration. Section 3 will then discuss the properties of bonded assemblies and tools for measuring penetration, section 4 discusses some examples of detailed

approaches and methods, and section 5 points out some unresolved questions in the field of wood bonding.

2.1 *Influence of Wood Structure on Bonding*

How an adhesive interacts with the wood surface depends as much on the wood as it does on the adhesive's properties. Wood is a complex material due its multi-layered composite structure and great variability. Wood properties can have important effects on wood bond performance, and these properties vary not only between but also within species and within the tree. Wood properties can influence bond formation primarily through a) adhesive flow (impacted by density, porosity, anisotropy, and grain angle), b) wetting (impacted by wood surface chemistry and extractives), c) rate and extent of adhesive cure (wood moisture content, pH, buffering capacity, and extractives), d) wood mechanical properties, damage and distortions, including those that occur during the bonding process, and e) swelling characteristics, as swelling can create internal stresses.

In practice, the ideal bonding conditions are wood and process dependent. For instance, it is not unusual to find that in production of laminated beams, different pressures or adhesive formulations work better for different species. Therefore, we suggest using caution in drawing conclusions about the relative bond performance across species in a study without detailed evaluation of all the variations. Data within a species are usually more reliable, but still can be confounded by sapwood versus heartwood, the presence of juvenile or reaction wood, or even the age of the tree [5, 26, 28, 29]. For example, the elastic and shear moduli within individual annual rings show considerable variations around the trunk and at different heights [30, 31].

Because of the interaction between wood and adhesive properties, studies often use a single adhesive with different species of wood, or several adhesives with one species of wood. There are fewer studies that involve a matrix effect of different adhesives and wood species. Konnerth et al. showed that the adhesive performance was dependent on the adhesive, wood species, and test method, and that trying to extrapolate the adhesive performance from one wood species to another is risky [32].

Information used to classify wood species into bondability categories has been collected over several decades [33, 34], and has been summarized in Table 1. Though current adhesives or current commercially available wood quality might behave somewhat differently, the basic trends are still helpful.

When encountering a new wood species for wood bonding, it is likely you will look up its properties. Many published wood properties values originated in the Wood Handbook, published by the Forest Products Laboratory (FPL) and is free to the public on their website [35]. Many of the values in those tables were already present in the 1940 edition, meaning that the properties were largely determined using old growth (slow growing, mature) wood. The modern wood supply generally contains more knots, smaller diameters, and significant quantities of juvenile

Table 1 Categories of selected wood species according to ease of bonding.

U.S. hardwoods		U.S. softwoods				Non-U.S. Woods	
Bond easily^a							
Alder	Chestnut, U.S.	Fir	Pine	Balsa	Hura		
Aspen	Magnolia	White	Eastern white	Cativo	Purpleheart		
Basswood	Willow, black	Grand	Western white	Courbaril	Roble		
Cottonwood		Noble	Redcedar, Western	Determa ^e			
		Pacific	Redwood				
			Spruce, Sitka				
Bond well^b							
Butternut	Sweetgum	Douglas-fir	Redcedar, Eastern	Afromosia	Meranti (lauan)		
Elm	Sycamore	Larch, western ^f		Andiroba	Light red		
American	Tupelo	Pine		Angelique	White		
Rock	Walnut, black	Sugar		Avodire	Yellow		
Hackberry	Yellow-poplar	Ponderosa		Banak	Obeche		
Maple, soft				Iroko	Okoume		
				Jarah	Opepe		
				Limba	Peroba rosa		
				Mahogany	Sapele		
				African	Spanish cedar		
				American	Sucupira		
					Wallaba		

(Continued)



Table 1 Cont.

U.S. hardwoods		U.S. softwoods		Non-U.S. Woods	
Bond satisfactorily^c					
Ash, white	Hickory	Yellow cedar		Angelin	Meranti (lauan), dark red
Beech, American	Pecan	Port Orford cedar		Azobe	Pau marfim
Birch	True	Pines, southern		Benge	Parana pine
Sweet	Madrone			Bubinga	Pine
Yellow	Maple, hard			Karri	Caribbean
Cherry	Oak				Radiata
	Red ^e				Ramin
	White ^e				
Bond with difficulty^d					
Osage-orange				Balata	Keruing
Persimmon				Balau	Lapacho
				Greenheart	Lignumvitae
				Kaneelhart	Rosewood
				Kapur	Teak

^aBond very easily with adhesives of a wide range of properties and under a wide range of bonding conditions.

^bBond well with a fairly wide range of adhesives under a moderately wide range of bonding conditions.

^cBond satisfactorily with good-quality adhesives under well-controlled bonding conditions.

^dSatisfactory results require careful selection of adhesives and very close control of bonding conditions; may require special surface treatment.

^eDifficult to bond with some phenol-formaldehyde adhesive formulations.

^fWood from butt logs with high extractive content is difficult to bond.



wood, which has generally inferior mechanical properties relative to mature wood [28, 29]. Reflecting the change in the wood supply over time, the standard mechanical properties values of the most important species group for structural applications in the US, the southern pines, were recently modified to lower values [36]. The user must exercise caution, however, because the southern pines are the only species group where we are aware that the values have been changed, and even if the average value in the Wood Handbook is accurate, there is no indication of the variability within species, which in wood can be quite large [26, 31, 37].

Many people assume that wood from trees that grow fast is inferior to old growth or slow growth wood. Softwood species do tend to have a higher percentage of earlywood with fast growth, resulting in lower density and consequently lower mechanical properties in general [26, 29, 37], as shown in Figure 1. This contributed to the lowering of mechanical properties values for engineering calculations just discussed. In ring porous hardwood species, however, faster growth rates lead to higher density and better mechanical properties [26]. This is because these woods produce a very low density layer of mostly vessels early in the spring, and dense fibers the rest of the year, as shown in Figure 1. Besides density, the larger or smaller number of vessels carrying adhesive away from the bondline might require changes in bonding conditions or adhesive used.

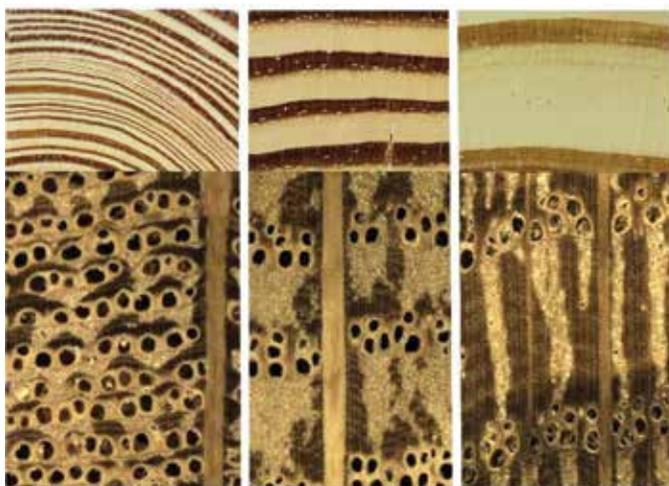


Figure 1 Effect of growth rate on (Top row) softwood, southern pine group and (Lower row) ring porous hardwood, red oak group. Left to right: slow to fast growth. Images courtesy of Alex Wiedenhoef, FPL Center for Wood Anatomy, using surface sanding method described in Section 3.4. Image height: top row 15.6 mm, bottom row 5.2 mm. Color figures online.

While traditional bondability information is useful in general, it does not provide guidance on why specific wood bonds fail and does not help individuals solve their specific bonding problems. In Table 1, the easier to bond species are generally lower in density than those that are harder to bond. Lower density woods have more void space, allowing better adhesive flow into the wood, and also generally swell and shrink less with moisture, resulting in less swelling stress. It should also be noted that low density woods are generally weaker, so there is less stress on the bondline in lower density woods at failure. A major problem encountered with low density species is that it can be difficult to avoid overpenetration, where too much adhesive flows away from the bondline. For example, discussions with particleboard producers reveal that they believe overpenetration causes many problems when low density poplar furnish is used.

In many cases, the reasons for poor bond performance have not been examined in much detail. Was it a wood preparation problem, a bonding problem leading to poor penetration, or a curing issue? An example where the authors tried to understand why failure took place with some adhesives was the use of 18 adhesives for bonding acetylated wood. Their evaluation of why the bonds failed was useful in solving the associated bonding problems [38]. As a follow-up to this study, additional insights into the problems in bonding acetylated wood has been published [39]. However, the literature is still limited in most part to bond strength and percent wood failure with a few analyses of the failure surfaces by microscopic or other techniques.

2.2 Influence of Wood Surface Quality on Bonding

It has long been recognized that the quality of the wood surface has a strong influence on the bond performance properties. Wood surface property issues include chemical heterogeneity, surface inactivation, weak boundary layers, and processing impacts, such as machining, drying, and aging [7]. The influence of wood surface preparation, as well as other production steps, on bond quality has been ably and extensively described elsewhere [5, 22, 24–26]. These references describe how the best bonds are made with freshly prepared, cleanly cut wood surfaces that mate to form uniformly thin bondlines. Here we review recent developments in the understanding of how surface preparation influences bond performance.

2.2.1 Mechanical Damage at the Wood Surface

It did not take sophisticated modern techniques to realize that if the wood surface was damaged, the bond made at that surface was also compromised. The mechanical weak boundary layer (MWBL) is the damaged wood adjacent to the bondline [9, 10, 12], which must be supported or repaired by the adhesive. Even when making “perfect” surfaces, cells can be crushed or torn by planers and veneer peelers. Crushing of surface cells can occur if the surface is mechanically sanded, which is

a major reason why sanding must be used with caution on surfaces to be glued. Sanding tends to crush or gouge out the earlywood on wood surfaces where there is a large density difference between earlywood and latewood. In some cases, this freshly prepared surface is an improvement, as in the case of particleboard and fiberboard where mechanical sanding is used to remove the surface layer that is overdried/overcured and can contain a high wax content. Besides being intuitively straightforward, the MWBL and means to avoid it have been well described [5, 9, 22, 26]. Good wood adhesion is thought to rely on the adhesive penetrating to the depth of solidly attached fibers, i.e., below the MWBL, before cure [40]. Discussion of the MWBL here will focus on developments since those texts were written.

In the production of veneer-based products such as plywood and laminated veneer lumber, lathe checks are invariably formed, but their depth and frequency can be influenced by processing conditions [22]. Lathe checks have long been suspected to lower bond strength and product quality but the literature is conflicting regarding the important parameters and mechanisms [41–45]. Pulling plywood specimens with lathe checks open was known to be detrimental to bond strength but the literature values of checks pulled open are quite varied: lower by 14% to 94% relative to checks pulled closed [42, 43, 45, 46]. Figure 2 shows a veneer in the process of peeling, with evident lathe checks, and the difference between pulling open and closed.

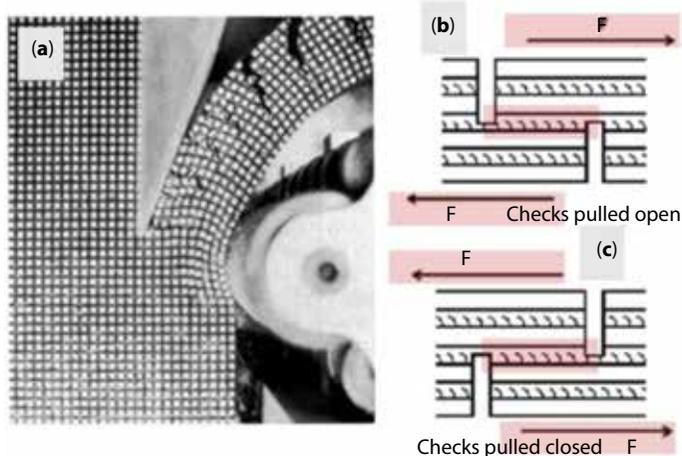


Figure 2 (a) Lathe checks forming during the peeling process are visible on upper side of veneer, top right. The grid was painted on the end grain of the log before peeling (Forest Products Laboratory (FPL) photo). (b) Plywood tested with checks pulled open. (c) Plywood tested with checks pulled closed. Failure zones and applied loads are highlighted in b and c. b and c are adapted from [47].

The effect of lathe checks was greatly clarified by the use of a dye to clearly show (and thus quantify) lathe checks, and by sanding both sides of a veneer to produce veneers that were identical except for lathe check depth. With these innovations, a strong correlation was shown between the depth of lathe checks, as a percent of veneer thickness, and shear strength. The effect on strength was large when the bonds were pulled open, and much smaller when bonds were pulled closed as shown in Figure 3 [47].

The mechanism behind the lathe check effect was further explained by looking beyond the naked eye and closely observing (with magnification and a camera) samples during testing. Figure 4a clearly shows that lathe checks, when pulled open, induced a rolling mode I failure through the veneer instead of the typical mode II failure observed when lathe checks were pulled closed and when checks were shallow (Figure 4b). Another interesting result is that mode I failures propagate very close to the bondline, while mode II failures typically propagate deep in the wood, often from the tip of one check to the tip of a neighboring check [47]. Shallow wood failure is often considered a sign of poor adhesive performance, though in this case the depth of failure appears to be driven by the wood surface preparation far more than by the adhesive. This suggests that the depth of lathe checks and pull direction (open or closed) should be given more attention during bonding studies than they typically had in the past.

The influence of lathe checks on LVL (laminated veneer lumber) properties has also been clarified. Finite element analysis has shown that lathe checks that do not get filled with adhesive are quite detrimental to edgewise shear modulus

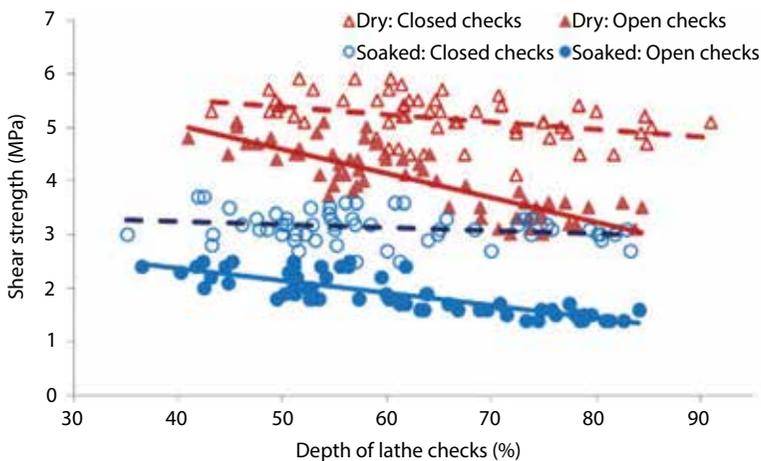


Figure 3 Impact of lathe check depth and direction of testing (pulled open or closed) on observed shear strength of plywood, both soaked and dry samples. % on x axis indicates % of veneer thickness [47].

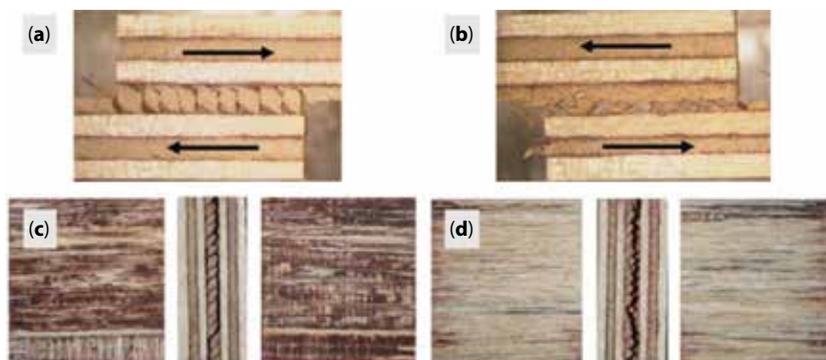


Figure 4 (a) Localized mode I failure of plywood with deep (80% of veneer thickness) lathe checks when pulled open, (b) Mode II failure of plywood with deep lathe checks when pulled closed, (c, d) Typical failure surfaces of samples with deep checks pulled open and closed, respectively [47, 48]. 4a and 4b correspond to Figure 2b and 2c, respectively.

[49], though not to other properties. Other works suggest that lathe checks impact edgewise shear and other LVL properties as well [50, 51].

Surface mechanical preparation, such as sanding, planing or cutting, will produce different surface qualities and will also affect roughness. Generally, the roughening of a surface will improve bonding quality [52] and adhesives often form much stronger bonds to porous than to smooth surfaces [53], though extremely rough wood surfaces contribute to poor adhesive transfer through lack of contact and uneven bondline pressure [5]. Even though the role of topography is unclear [54], roughness parameters have been used to explain adhesive bond formation and quality [55]. The critical roughness values needed for optimal wood bonding are not fully understood and so far no consensus has been found [44, 56–58]. Sellers [59], quoting Walser [60], claimed the maximum roughness depth for acceptable veneer bonding is about 500 μm , while some authors claim that roughness differences of only tens of micrometers are important [55].

Some of these differences in the “optimal” roughness of veneer can be related to adhesive formulation. For instance, fillers can serve to prevent overpenetration (improve holdout) of the adhesives so that they can bridge the gap between surfaces. Different fillers can have very different properties [61]. Also, it has been shown that adhesives with low elastic modulus tolerate thick bondlines much better than adhesives with modulus much higher than the wood being glued [62]. The differences in observed impact of roughness on bond quality might also be explained by the use of different wood species and the diverse measurement techniques used. The conflicting results might also be, in part, due to the fact that different peeling parameters to obtain different roughnesses will also change other surface properties such as the extent of damage to cells at or below the surface, or the frequency and depth of lathe checks.

It is remarkable that there is no easy, widely used technique to assess the presence or severity of a MWBL in wood. To address this deficiency, a new method of quantifying the MWBL, referred to as the surface integrity in the paper, was recently developed [63]. The test consists of attaching a metal tab to a veneer surface with a double sided tape, and tearing the tab off. The tape is then imaged to determine the number and size of wood particles removed from the wood surface. It was shown that veneers with deep lathe checks lost many large fiber bundles, which could easily initiate failure in the product, while shallow lathe checks produced fewer and smaller bundles. On the tight side of veneers, which lack lathe checks, only single fibers or fiber fragments were removed. While this test was developed for veneer, we expect that with an appropriately strong adhesive (tape or otherwise), damaged cells from other types of surface preparations could also be detected.

Another new development was to discover an interaction between the temperature of log soaking and peeling, and the felling season of birch logs. When soaked and peeled at 70 °C, contact angles and bond strengths were only slightly different between logs felled in different seasons. When peeled at 20 °C, however, the logs felled in winter had significantly higher contact angle and lower bond strength than spring or autumn felled logs [64]. While seasonal variation in the density of logs, presumably from extractives stored in the wood, had been documented, it was rather small and the authors did not expect it to impact bonding [65]. Many assumed that the differences in contact angles and bond strengths of veneers peeled at different temperatures originated in the different cutting behaviours of the wood at different temperatures. It was a surprise, then, to learn that birch logs heated to 70 °C and then cooled to 20 °C before peeling had contact angle and bond strength properties closer to veneers peeled at 70 °C than to those soaked and peeled at 20 °C [66]. This suggests that some of the changes in wood that occur at 70 °C soaking temperature are relevant to bonding and are not reversible by cooling. Whether the relevant changes are physical (increased cellulose crystallinity for instance) or chemical is not known.

Moisture weakens wood, and temperature enhances this effect. It has been estimated that with a typical waterborne adhesive loading of 150 g/m², the cells nearest the glueline can reach the fiber saturation point [67]. Therefore, these cells, especially earlywood, are more prone to buckle during pressing, creating a new MWBL, as shown in Figure 5. This is commonly seen in micrographs of solid wood bondlines, as in Figure 5a, and also occurs in composites. In particleboard, the wood structure and orientation on either side of a bond are extremely varied [68, 69], suggesting that conditions favorable for buckling will exist throughout the board. Cell wall buckling appears to be quite common in particleboard but is very seldom described. Thus, the normal macroscopic view of wood surfaces, and lack of attention to this issue, may lead to an underestimation of this source of failures.

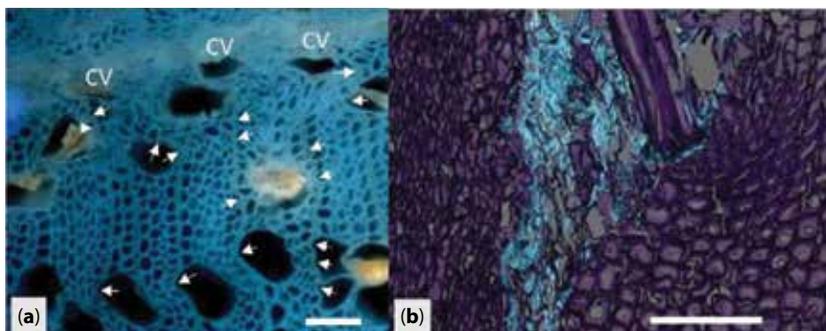


Figure 5 Buckling of cell walls and subsequent MWBL from a combination of moisture, pressure, and heat. (a) bonded poplar radial faces, UF fluorescence emission is yellow, wood is blue. Glueline and collapsed vessels (CV) at top of image, distorted wood structure throughout is evidenced by kinks in ray cells, shown by white arrows. Unpublished image from study reported in [70]. (b) particleboard with light blue UF (urea-formaldehyde) adhesive and purple wood. Method reported in [71]. Color images online. Image from Hogger Elfriede, Wood K plus - Competence Centre for Wood Composites and Wood Chemistry, Linz, Austria. Scale bars: 100 μ m.

2.2.2 Surface Chemistry Barriers to Bonding

In addition to a mechanical weak boundary layer (MWBL) on wood from surface damage, a chemical weak boundary layer (CWBL) can also exist, impeding bond formation [5, 7, 12]. A macroscopic inspection of the wood surface cannot reveal a CWBL: other methods that are sensitive to chemical properties are needed [72]. Wood species with large concentrations of nonpolar extractives are generally more difficult to bond [73]. Wood surfaces tend to become less hydrophilic over time, which impedes the spread of water based adhesives across the wood surface. Freshly planed surfaces had lower contact angles and better wetting, or contact between wood and waterborne adhesives, compared to surfaces that had been stored in the laboratory for only a few hours [74] or longer [75–77]. This is one reason some adhesive standards require planing of the wood surface “just prior to gluing” [78] or “within 24 hours of bonding” [79]. Good manufacturing practice is to apply the adhesive as soon as possible to the freshly cut surface, especially if the wood contains high levels of extractives.

Contact angle with water, polar liquids, or the adhesive of interest is the standard analytical method of assessing surface wettability [80–85]. A low contact angle indicates that surface tension of the solid is high relative to the liquid, as described by Young’s equation. Low contact angles not only indicate adhesive spreading across the wood surface, but also that the adhesive will make molecular scale contact with the wood. The ideal interfacial strength occurs when the

surface energies of the adhesive and wood are equal [18]. Contact angle also influences the rate that adhesive advances through a capillary such as a lumen [86]. Hse supported the utility of contact angle by showing correlation between low contact angle and a thinner bondline (increased void penetration) with 36 different PF formulations [87]. While the phenomenon of lower bond quality with aged surfaces is not disputed, the correlation between contact angle and bond strength is much weaker [80, 81]. Instead of a “lower is always better” relationship, contact angle can be viewed as having a threshold value for a given system. Too high a contact angle can prevent sufficient wetting and spreading and molecular contact between wood and adhesive, but once sufficient wetting is achieved, there is little further improvement by reducing the contact angle. Once an adhesive is able to fully wet the wood, further reduction in contact angle might promote overpenetration and/or distribution of the adhesive over too large an area [87]. Further caution regarding contact angle measurements was advised when Petrič concluded that in most cases it is useless to compare contact angle data on wood obtained in different laboratories with different wood specimens of the same species [88].

There are many factors that are likely to contribute to the gradual loss of surface energy at the wood surface [89–91]. The most likely source is migration of extractives like resin and fatty acids and their esters, waxes, sterols and terpenes to the wood surface. Waterborne adhesives with high pH are often used when high levels of extractives on the surface are suspected to be a problem, whereas neutral or acidic adhesives are typically less effective. There could also be chemical changes to the molecules on the surface, not only those already mentioned but also oligosaccharides, phenols and tannins migrating to the surface. In addition to lowering surface energy, these molecules that dissolve in the adhesive could potentially interfere with the cure of the adhesive [73, 92–94], or influence cure through altering adhesive pH [95–103]. This is especially the case with very acidic woods like oak, which have been known to interfere with cure if the adhesive is not strongly buffered [104]. The surface acidity of many wood species has been documented [105, 106]. In addition, fresh, high energy surfaces attract contaminants from the air which also lowers surface energy. Wiping the wood surface with solvent has also been shown to improve bonding, and is a common practice for small scale woodworkers and very oily woods [107].

An extreme version of surface inactivation comes from overdrying of wood after it has been cut, such as veneer for plywood LVL, or OSB (oriented strandboard) flakes. Surface inactivation by overdrying is likely a combination of many factors [24, 25]. Physical effects include degradation of the mechanical properties of the surface layer, and closing of surface cracks, thus reducing surface area. Chemical changes include migration of hydrophobic wood ingredients to the surface and chemical modification of surface bonding sites, which includes oxidation, molecular rearrangement of various functional groups on the surface, and elimination of hydroxyl sites [24, 25].

It has also been shown that even the time of year that a tree is harvested can impact wettability and bond performance, presumably because of different levels of stored sugars in the stem [64, 108]. Hanetho discussed the influence of seasonal variations on wood quality in particleboard production [109]. Freshly cut wood harvested in winter and used immediately caused problems. The cause was identified as high contact angles from high levels of extractives. Harvesting in different seasons or letting winter felled logs age both had the effect of decreasing contact angle, improving resin contact with the wood, and improving board properties. The lower contact angle achieved by letting logs age must not be confused with the higher contact angle typically experienced when cut surfaces age.

2.3 Adhesive Penetration

Having discussed wood structure and wood surfaces, we now turn to how adhesives penetrate into the wood by considering the following factors [5]:

- i. Wood-related parameters, such as wood species, diameter of the lumens and their exposure on the wood surface due to slope of grain, pit frequency and aspirations, cutting orientation, wood density, and moisture content. Also important is the presence of knots, bark, decay, stain, heartwood, juvenile wood, and occlusions from extractives or tyloses. Wood strength to withstand clamping pressure, wettability of the wood surface and surface energy also play a role.
- ii. The adhesive properties that control penetration such as chemical structure, molecular weight distribution, additives, solids content, viscosity [110] and surface energy, buffering capacity, hardening time and rate of resin curing or solidification [111].
- iii. Processing parameters of bonding such as spread rate, open and closed assembly time, temperature, pressure [70, 112, 113], and moisture profile over time through the material. It should be noted that the temperature and moisture level of the wood surface and of the bondline continuously change the viscosity of the resin (which also depends on the degree of curing). Resin viscosity is also changed by selective loss of some components through cell wall penetration.

Penetration is the ability of an adhesive to enter into the wood structure [5, 19, 110]. Unfortunately, the word penetration has long been used to mean not only wood void penetration (flow into cracks, voids, and lumens in the wood), but also cell wall penetration (molecular scale mixing of adhesive molecules between cell wall polymers) [110]. These are two different phenomena that are controlled by different factors and result in different physical and mechanical properties for the bonded product [6].

Void penetration into wood occurs on the millimeter to sub-micrometer level as a result of the hydrodynamic flow and wetting of the liquid adhesive. The adhesive flows from the glue line (adhesive material between the two wood surfaces) into the porous and capillary structure of wood, mostly filling cell lumens, as well as encapsulating fractures and surface debris caused by wood surface preparation. Also known as adhesive bulk flow, lumen filling, or tissue penetration, void penetration is governed by pore size (wood anatomy), bulk adhesive viscosity, external compression force from pressure applied to the wood, and wetting behavior [6, 110, 114]. Flow through adhesive-filled capillaries is mathematically described by the Washburn equation [86]. The resulting large area of close contact between the adhesive and the internal surface of the substrate plays an important role in developing good adhesion. This is at times discussed strictly in terms of mechanical interlock, but it also includes any type of surface adhesion through dispersion, polar, hydrogen, or ionic bonds [7, 17].

In contrast, cell wall penetration (infiltration, cell wall modification) involves diffusion of low molecular weight adhesive components into the polymer matrix of wood cell walls. Cell wall penetration generally fortifies, increasing strength and lowering cell wall swelling. Whether a given molecule penetrates the cell wall is controlled by its molecular size, shape, and its solubility parameter, as well as the moisture content and chemistry of the wood. In general, polar molecules and especially hydrogen bond donors are good at entering wood cell walls [115], but molecules above MW 1000 are largely excluded from normal wood [116].

Many people have asked “What is the ideal level of penetration for an adhesive bond?” To answer this, consider that an acceptable bond for a given product is determined by the use application. Not every bond has to provide maximal strength, water resistance, loading or moisture cycling, etc. In addition, almost every bonding operation is unique: different species, wood surface properties, adhesives, and bonding processes. Therefore, the question of ideal penetration is only answerable for a particular process and product. Industry experts have confirmed that the amount of flow and infiltration at a particular mill under a particular set of conditions and wood supply do correlate to bond performance, but a general answer to the question does not exist.

2.3.1 Void Penetration (Bulk Flow)

An early discussion of wood bond strength relied on void filling to explain bond strength [19]. However, this strictly mechanical interlock concept was deemed insufficient because there can also be specific adhesion through chemical interactions between the adhesive and the wood surface [20]. Some have indicated that for a strong bond the adhesive must penetrate deep enough into the wood substrate to reinforce weakened cells and to obtain a large contact surface [77]. An emphasis on penetration has continued because of the recognition that mechanical interlock helps to distribute stress, and bond performance is presumed to be significantly

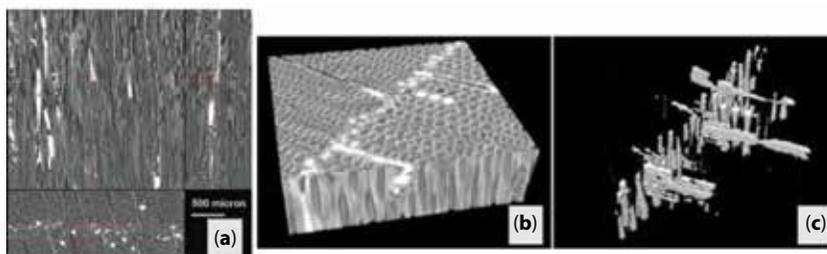


Figure 6 (a) Assembled epi-fluorescence images of a 2-part epoxy bondline in red oak stained with 0.5% Safranin O. Transverse view of horizontal bondline on bottom, flatsawn view in upper left, and radial cut on right side. Bright areas are resin [110]. (b) Tomographic image of bromo-PF bondline in loblolly pine. (c) Same as (b) but wood removed to show void penetration of adhesive [117].

influenced by the degree of adhesive penetration [110]. Improvements have been made in the microscopy techniques and data analyses used to measure the degree of void penetration. However, despite the ease of conducting these tests, there are still many questions around the issue of how much penetration is needed, especially when filling lumens far from the surface.

Wood void penetration is the first step in the formation of the interphase, a three-dimensional zone containing both wood and adhesive on both sides of the glueline. The void filling is clearly visualized in Figure 6a, showing an epoxy adhesive filling the wood voids both in the cross-sectional and transverse sections [110]. This reference is a good review of the techniques to analyze void filling, with detailed discussion. While cross-sectional microscopy has been useful over the years to examine void penetration, it provides only a two-dimensional view that leaves questions on how the adhesive gets to lumens far from the glueline. Images b and c in Figure 6 demonstrate how tomography can help visualize the three-dimensional flow of adhesive into wood structures.

When inspecting cross sections, it is common to observe penetration into a lumen three or more cells deep from the surface where there is no adhesive in the first or second cell. The logical explanation was that deep penetration was due to capillary action of the adhesive up a lumen of a cell cut above or below the plane of the particular cross section. While this explanation was well accepted, there was no way to adequately address the issue with the existing technology. X-ray computed tomography, however, now allows visualization of wood, adhesive, and voids in 3-D using labeled adhesives [118–124]. With this tool it is now possible to investigate the 3-D wood anatomy, bondline, and adhesive distribution on the micrometer scale and to address speculation on adhesive-wood void interactions. The adhesives were shown to flow up open lumens that deviate from the wood surface providing a deeper than expected penetration. Adhesive has also been

observed to flow through pits into longitudinal tracheids away from the bondline [123, 125].

Adequate penetration of the adhesive into the wood surface needs to occur before adhesive curing and solidification to provide a sufficiently large bonding interface. Low bond strengths can result from underpenetration, where the adhesive is not able to move into the wood enough to create a large bonding interface within the wood interphase, or does not extend beyond a weak boundary layer. Weak bonds can also result from so-called starved joints, caused by overpenetration, when an insufficient amount of adhesive remains in the glueline that bridges the wood surfaces [5, 126]. Often the adhesive is applied to only one surface, and thus, transfer to the adjoining piece of wood is a critical process. In open assembly time, the adhesive only penetrates into the applied surface and the solvent evaporates, while closed assembly time allows transfer and penetration into both substrates [59]. Because the adhesive represents a significant cost to the manufacturer, there is a strong incentive to learn how to apply just enough adhesive, and no extra, in every situation.

Adhesive penetrates relatively easily into fiber cells or vessel elements which are physically ruptured, such as during the veneer manufacturing process. SEM images show that adhesives flow predominantly through cut tracheids and rays, simple pits are a minor obstacle, and bordered pits (under these conditions) block the flow of resin from one cell to an adjacent cell [127]. Within a wood species, the penetration can differ greatly between earlywood and latewood and be influenced by the presence of ray cells, grain deviations, and many other factors. Thus, as illustrated in Figure 6, void penetration is not a uniform process, but varies along the bondline.

2.3.2 Cell Wall Penetration (Infiltration)

Although adhesive penetration into the wood voids has long been shown using microscopy of cross sections, penetration into the cell wall (infiltration) was often not assessed in part because it was technically more difficult. Over the years, however, a wide variety of methods capable of demonstrating cell wall penetration have been developed. The migration of phenol-formaldehyde (PF) resins into cell walls has been shown using fluorescence microscopy [128], autoradiography [129], transmission electron microscopy (TEM) [130], scanning electron microscopy with energy dispersive X-ray spectroscopy (EDXS) [131], dynamic mechanical analysis (DMA) [132], and anti-shrink efficiency [133]. For polymeric methylene diphenyl diisocyanate (pMDI), the presence of adhesive in cell walls has been more complicated in that it has been shown to occur by nuclear magnetic resonance (NMR), DMA, atomic force microscopy (AFM), and nanoindentation [134, 135], while other studies using X-ray adsorption spectroscopy, DMA, and solid state NMR spectroscopy found none [136, 137]. These and other techniques such as UV microscopy [138] and nanoindentation [139] have been used to show the presence

of urea-formaldehyde (UF) and melamine-formaldehyde (MF). UF resin penetration in cell walls in particleboards has been visualized with EDX [140], confocal microscopy [141], and others. We refer the reader to Table 2 in section 3.4 for a more extensive list of references and techniques.

The fact that all the adhesives mentioned in the prior paragraph are *in-situ* polymerized and none are prepolymerized supports the concept of an important functional difference between the two adhesive groups in the way they interact with the wood [142]. Prepolymerized adhesives are highly limited by the size of the adhesive molecules as only low molecular weight (MW) portions of an adhesive can infiltrate the cell wall. In the past, determining the size of molecules that will infiltrate was based on the cell wall penetration of poly(ethylene glycol) or dextrans [116, 143]. Today we are able to evaluate cell wall micro- and nano-domains with microscopy, spectroscopy and/or mechanical tests using adhesives as penetrants.

While it is clear that small molecules should infiltrate cell walls better, it is valuable to quantify the relationships between penetrant size, penetration ability, and influence on cell wall properties. Interpretation of dynamic mechanical data pointed out that while a very low MW PF caused stiffening of the cell wall by enhanced intermolecular coupling near the main glass transition of wood lignin, a high MW PF resin did not [132]. Qin *et al.* noted that the first cell row adjacent to the glue-line was more reinforced by UF penetration than cells further from the glue-line [144]. Often, images of cell wall penetration show diminished cell wall penetration with distance from the glue-line, which is likely caused by the depletion of components able to swell cell walls as the adhesive flows away from the glue-line. Examination of brominated PF bondlines with nanoindentation and X-ray fluorescence microscopy (XFM) (Figure 7) showed that a low MW bromo-PF was more effective at maintaining cell wall stiffness under high humidity conditions than an equal quantity of higher MW adhesive [145]. This discovery was only possible through the ability to quantitatively probe essentially the same approximately one-square-micrometer sized area of an individual cell wall with both chemical and mechanical analyses [145, 146]. An additional technique developed to look at the interaction of adhesive components within the cellulose microfibril involved small angle neutron scattering (SANS) [147, 148]. This work showed that deuterated PF entered the cellulose microfibrils and swelled the spaces between cellulose elementary fibrils [117, 147, 149].

Some adhesives have intrinsic differences which differentiate them from wood, and so the amount of cell wall penetration can be directly measured. An example is the distinct UV absorption spectra of wood and UF resin. Quantitative UV absorbance of thin sections in a microscope allowed MUF (melamine-urea-formaldehyde) and MF to be conclusively identified inside the cell wall, supporting the idea that with these resins, cell wall penetration could create an interpenetrating network of adhesive inside the cell wall covalently bonded to the adhesive in the lumen. The small difference in PF and wood UV absorbance has also allowed some

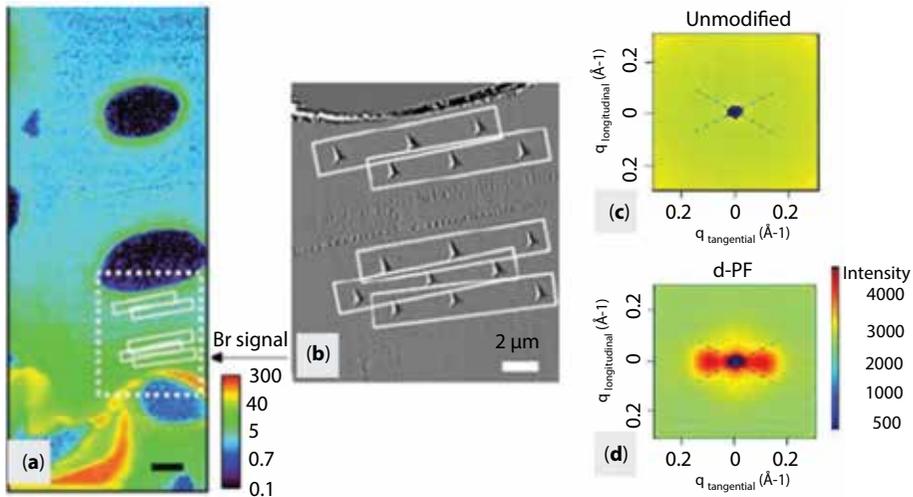


Figure 7 (a) Br signal in X-ray fluorescence of bromophenol-formaldehyde adhesive. The glue line is near the bottom of figure. (b) AFM image after nanoindentation of cell walls with resin content calculated from a [145]. (c) No neutron scattering diffraction pattern is seen from unmodified wood after soaking in 35% H₂O / 65% D₂O solution, but (d) shows diffraction pattern indicating ~4 nm spacing of deuterated PF domains between cellulose “crystals” in the microfibril [147, 149], color images online.

to use the same method to conclude that low molecular weight PF had penetrated the cell walls [151]. Using scanning thermal microscopy (SThM), a PRF was shown to infiltrate while a PUR adhesive did not [152]. Electron energy loss spectroscopy (EELS) has been applied to the detection of partly methylated hydroxymethyl melamine into wood cell walls [153]. After covalently binding a fluorescent dye to the adhesive, confocal laser scanning microscopy was used to determine the amount of UF resin penetration into fibers used for the production of medium density fiberboard (MDF) [141, 154–156]. These examples show that many analytical tools can be used with certain adhesives to ascertain cell wall infiltration, sometimes quantitatively.

The presence of covalent bonds between adhesive components and cell wall polymers has often been theorized but could not be clearly proven until Yelle and coworkers [157, 158] used solution-state two-dimensional NMR. They showed that covalent bonds were present between PF and wood polymers [157] but not between PMDI and wood under typical bonding conditions [158].

After determining that adhesive components have entered the cell wall, the next issue is to determine how they influence the cell wall properties. There is considerable literature in the area of wood modification on the effect of different

levels of infiltration by various chemicals on the changes in wood properties. This has traditionally been done by measuring bulk properties, such as the anti-shrink efficiency and biological decay resistance [159–161].

Nanoindentation, first applied to wood in 1997 [162], allows measurement of mechanical properties of individual cell walls and middle lamella corners. Cell wall hardness, measured by nanoindentation, has been extensively used to observe the effect of cell wall penetration [150, 162, 163]. Gindl *et al.* coupled nanoindentation with UV absorbance spectroscopy to investigate PRF (phenol-resorcinol-formaldehyde) and PUR (polyurethane) bondlines [164, 165]. Significant amounts of PRF resin infiltrated into the cell wall, whereas no PUR could be detected. In both adhesive assemblies examined, cell walls at the immediate surface were damaged during machine planing as shown by a significantly reduced hardness and indentation modulus. The infiltration of the PRF adhesive into cell walls clearly increased the hardness of PRF-impregnated cell walls, but did not significantly change the elastic indentation modulus of sound cells, probably because elastic moduli of sound dry wood cells and PRF are similar.

The standard analysis of nanoindentation data assumes that the substrate being indented is a uniform half-sphere. Because this assumption is never true for wood bondlines, the values obtained using this method contain systematic errors and are only relative numbers. Therefore, methods that allow consistent, absolute measures of hardness and modulus even for a cell wall adjacent to an empty lumen were developed for working with wood bondlines [166, 167]. Methods for obtaining elastic and plastic moduli (broadband nanoindentation spectroscopy) were also developed and used to investigate pMDI-infiltrated cell walls [168, 169]. This series of papers have described nanoindentation on unembedded wood samples obtained from wood bonding, and obtained absolute hardness and modulus instead of just relative values of adhesives penetrating the cell wall. In addition, they have shown pMDI adhesive changed the elastic modulus and hardness of cell walls, and swelled the S2 cell layer, clearly visible in atomic force microprobe (AFM) images [135]. This was interpreted as support for the existence of an interpenetrating network of pMDI and wood polymers originally proposed by Frazier and Ni [137]. Nanoindentation has also been coupled with AFM-IR to study the impact of pMDI penetration [170]. AFM-IR is a promising technique in that it allows IR absorption spectra to be obtained on sub-micrometer sized areas, such as an individual cell wall or compound middle lamella. Further information on the interaction of pMDI with wood and wood cell walls using several other advanced analytical methods can be found elsewhere [171].

The ability of wood cell walls to absorb adhesive components not only involves the reactive components, but can also involve low molecular weight adhesive components or additives. Thus, wood adhesives can contain materials that would normally reduce bond strength, but significant adverse effects are avoided because these materials move from the adhesive into the wood [172]. While this might have no impact on most adhesives [173], this phenomenon seems relevant

to protein-based adhesives and also potentially to those adhesives that contain large quantities of unreacted urea [174].

When Browne and Brouse proposed specific adhesion as an alternative to just mechanical interlocking [20], methodology did not exist to test their concept. Over the years, specific adhesion has been defined by dispersion forces, polar bonds, hydrogen bonds, and covalent bonds [17], all of which, except covalent bonds, are likely relevant to most adhesives.

2.4 Adhesive Properties that Influence Void and Cell Wall Penetration

Although many aspects of the wood influence its bondability, there are also many properties of the adhesive that play a role in controlling bond strength. Molecular weight/molar mass distribution and branching pattern, viscosity, solids content, reactivity, pH, solubility parameter, and surface tension of the liquid phase of the adhesive will all influence penetration. In addition, additives are used to alter some of these characteristics. Consequently, the adhesive formulation has a tremendous influence over the penetration behavior of adhesives into wood. General statements comparing the penetration characteristics of various adhesive types must be offered with the knowledge that specific formulations can have significantly different properties. For example, a PF resin for composite panel faces is usually lower in molecular weight and/or lower in reactivity compared to core resin, because panel faces experience significantly higher temperature, for longer, than cores.

Adhesive specifications generally involve such factors as viscosity, percent solids, pH, and gel time. Although these factors are important for ensuring consistency in production, they do not provide enough data to understand the type and degree of penetration into the wood. While a suitable viscosity is needed for spreading over the surface and into voids, it is influenced by the solids content, temperature, molecular weight distribution, pH, and the presence of additives or fillers in the adhesive. Optimizing an adhesive requires consideration not only of all the adhesive properties but also the details of its formulation as well as the wood and process being used. It should also be remembered that as soon as the adhesive touches the wood, all these properties change because of void and cell wall penetration, moisture movement, wood buffering capacity, temperature changes, etc. Clearly it is not only the initial viscosity, pH, etc. of the adhesive, but also the changes in these properties over the time as they interact with the wood that actually determine adhesive performance. When measuring rheology of adhesives over time, some researchers have replaced the standard aluminum plates with wooden ones, so as to better understand the changes over time [175–177].

Factors influencing void penetration were extensively studied in a recent series of papers with different wood species and different orientations using UF adhesive at three different DOCs (degree of condensation), which resulted in different

viscosities for the three resins [70, 178–181]. In their work, low DOC (lower viscosity due to lower MW, higher polarity due to higher number of remaining methylol groups) adhesive always flowed more deeply (Figure 8). They also showed the expected relationships of higher pressure creating deeper void penetration, cellular collapse at the bondline with higher pressures, and deeper penetration in the radial than the tangential direction, because of the availability of rays to carry adhesive deeply into the wood [182]. It should be noted that wetting properties probably also changed with viscosity [85].

Qin *et al.* [144] selected emulsion polymer isocyanate (EPI) and UF adhesives as typical systems to investigate the microstructure of wood-adhesive interphases by fluorescence microscopy and confocal laser scanning microscopy (CLSM). Further, a quantitative micromechanical analysis of the interphases was conducted using nanoindentation. The results showed that the UF resin penetrated voids to a greater extent than EPI, and that the average penetration depth for these two adhesive systems was higher in the case of earlywood, as is typical. CLSM allowed visualization of the resin distribution with contrasting colors, showing that EPI did not infiltrate the cell wall, whereas UF resin did. The micromechanical properties of the cell walls were almost unaffected by EPI, but were significantly affected by UF infiltration, especially in the first cell wall from the bondline. This further confirmed that resin infiltration can improve the mechanical properties of cells in the interphase regions.

We present only a few of the studies on the effect of adhesive composition on penetration as examples of using multiple newer analytical methods to better

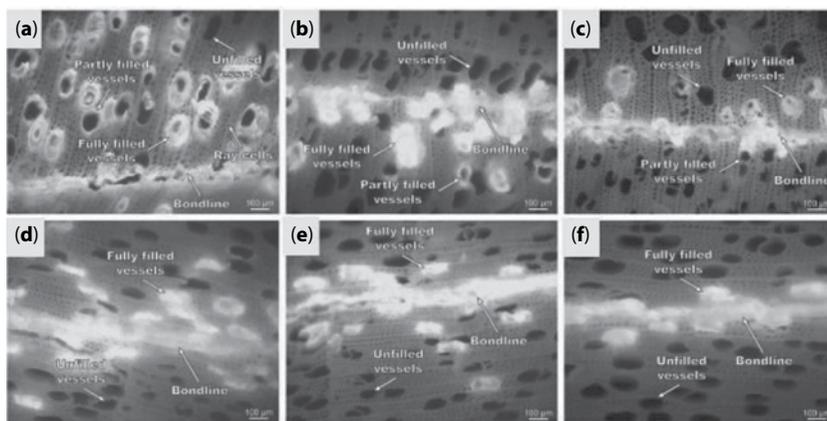


Figure 8 Fluorescence micrographs for three UF resins (mixed with Safranin O as dye) on poplar, using 25 μm thick sections. Left to Right, low, medium and high degree of condensation (viscosity). Upper (a,b,c): bonding of radial faces; Lower (d,e,f): bonding of tangential faces [178].

understand the phenomenon. Many more studies exist in the literature that can provide insight into the formation of strong bonds. A few summaries and textbooks are provided here [23, 27, 67], and many primary references are provided in section 3.4.

Of course, there are many more analytical methods available that are primarily used to study adhesives on their own, which are occasionally applied to bond-lines. Nuclear magnetic resonance (NMR) spectroscopy has been highly useful in determining how formaldehyde reacts with urea, melamine, phenol, and resorcinol to form linear and branched structures depending on reaction conditions with solution state being used for the monomers and oligomers, while solid state can be used after cure. Infrared (IR or Fourier transform FTIR) is useful for functional group determination at all stages of reaction. Thermal properties have been determined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) for the polymeric products as well as for following curing reactions. Molecular weight distribution is measured using size exclusion chromatography. Curing rate can be determined by gel time, dynamic mechanical analysis [183], and small scale mechanical analysis of bonded specimens via the so-called Automated Bonding Evaluation System method [184, 185].

3 Properties of Adhesive-Wood Assemblies

Adhesives are used to hold wood pieces together, whether it is in the structurally strong laminated veneer lumber or the relatively weak particleboard. Without the new methods that let us examine the adhesive-wood interaction zone and the adhesive region in great detail as separate entities, understanding bond performance was mainly limited to speculation. In order to understand and improve adhesive performance, we need tools that let us dissect the bonded assembly to understand what is leading to bond failure. In this section we will discuss models of wood bonds, followed by discussions of methods for analyzing penetration and bond mechanical properties.

3.1 Zones in a Wood Bond

Given that an adhesive needs to hold two substrates together under a variety of conditions, most information about adhesive performance comes from analyzing bond failure. As stated by Marra, a bond fails at its weakest link [5], with the zones (links) illustrated in Figure 9. However, rather than just thinking about a bond with equal stress in all the zones as in the Marra model, it is useful to keep in mind that the failure often occurs where the stress is concentrated the most [186, 187], and that forces are not equally distributed among the different zones. For example, internal strain usually occurs in the adhesive-wood interphase when the adhesive shrinks due to curing reactions and solvent loss, while the substrate dimensions remain unchanged or swell from the absorbed water [22, 187]. Although this

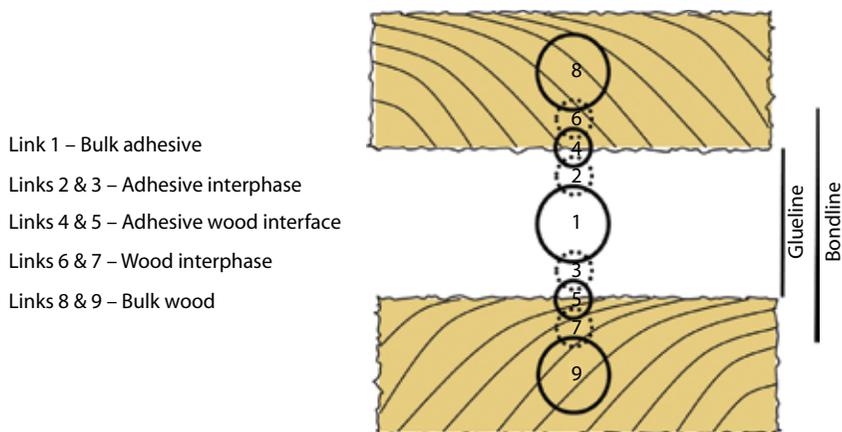


Figure 9 Marra's description of bondline failure zones (links) using the terminology described in this review rather than Marra's original terms [5]. In this review links 1–7 are referred to as the bondline, while links 1–3 are referred to as the glueline.

simple link system is easy to visualize, a real bond has more of a continuum of different states or overlapping zones with dissimilar forces, in both magnitude and direction, in different zones.

3.2 How Adhesives Accommodate Wood Swelling

Besides the requirement that the dry strength of the adhesive bond be greater than the wood strength, another key requirement of the bond is to resist fracture or delamination when exposed to wet conditions. Surprisingly, even though wood loses strength due to plasticization when wet, this exposure often leads to failure in, or close to, the glueline. Therefore, it is often wet testing that differentiates acceptable from unacceptable wood adhesives. Since the failure can even occur in some tests with no applied external load on the bondline [79, 188–191], the swelling and shrinking of the wood is a main source of stress that breaks the adhesive bond [22]. Additional tests involve a load applied to the wet sample [192–194].

Because wood typically swells much more than the adhesive, the constraint imposed by the adhesive leads to complex and sometimes very large stresses on the bondline [22]. The response of a bonded assembly to water exposure is illustrated in Figure 10. Figure 10a shows the dry assembly as formed. Figure 10b illustrates a possible swelling and cupping of the unbonded wood when wetted. For the bonded case, the adhesive resists the dimensional change in wood, resulting in large normal stresses at the interface both perpendicular (Figure 10c) and parallel (Figure 10d) to the bondline. If these stresses are not well distributed, bond rupture can result, even without any external load. Thus, adhesive interactions

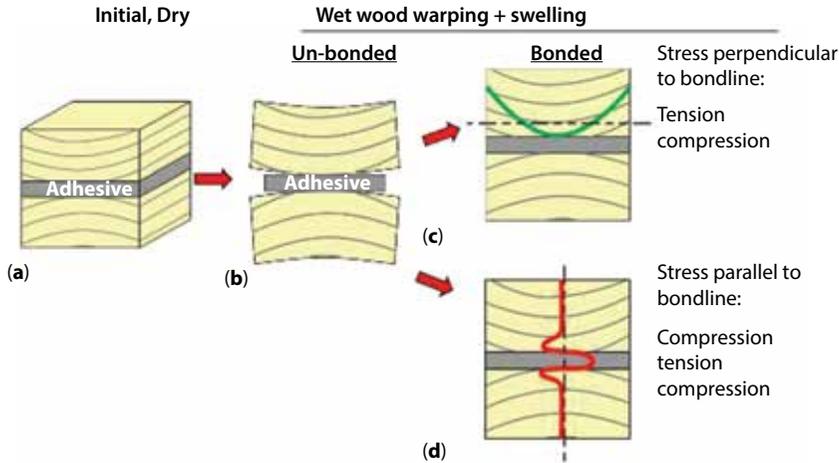


Figure 10 Illustrative swelling stress in two dimensions. (a) dry wood, bonded; (b) wet unbonded, with adhesive in place illustrating swelling and cupping of the wood substrates; (c) image of specimen overlaid with plot of stress perpendicular to bondline (green), expected along the dashed line. In this specimen, cupping pulls edges away from bondline; (d) image of specimen overlaid with plot of stress parallel to bondline (red), expected along the dashed line. When wet wood attempts to expand sideways, adhesive is under tension as it restrains the wood while wood adjacent the bondline is under compression, color images online.

with the wood that minimize stress concentrations in the bondline are important components of bond durability [21, 142]. Recognizing the value of avoiding stress concentrations, many suppliers offer “flexibility modified” condensation resins where the glueline strength, brittleness, toughness and flexibility have been modified, usually using proprietary techniques.

Structural wood-adhesive bonds have to withstand considerable stresses caused by mechanical loads and moisture content changes. Moisture-related durability of such bonds depends on the ability to withstand stresses generated by moisture-induced dimensional changes in the wood.

3.3 Two Classes of Adhesives

While adhesives have been classified using a wide variety of criteria, distinction between *in-situ* polymerized and prepolymerized adhesives seems to be especially useful for wood adhesives. These two adhesive classes generally differ in their chemical curing, morphological, physical, and mechanical properties [16, 142, 195]. The largest group by far in volume sold is the *in-situ* polymerized group, including the aminoplastic and phenolic adhesives that use formaldehyde as a comonomer, epoxies, and pMDI, see Figure 11. These adhesives typically produce rigid polymers on curing [196] and often contain reactive components that are low

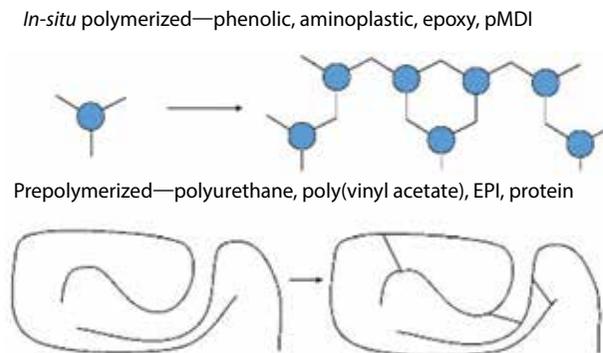


Figure 11 Schematics for the *in-situ* polymerized and prepolymerized classes of adhesives.

enough in MW that they can penetrate cell walls. These polymers are mainly thermoset. The second group of adhesives involves pre-formed polymers that are too large to infiltrate cell walls, and develop adhesive strength by losing water and/or by cross-linking the flexible polymers. These adhesives include PVAc, PUR, and proteins. After physical solidification (coalescence), these are generally more flexible than the *in-situ* polymerized adhesives.

The *in-situ*/prepolymerized categorization is useful for wood adhesives because these two groups appear to have different mechanisms for minimizing water-induced stress [142]. An abrupt change in mechanical properties within a material can result in significant stress concentrations and failure. *In-situ* polymerized adhesives that infiltrate cell walls have been shown repeatedly to modify cell wall properties in the wood interphase region [145, 163, 170, 197], which in addition to void penetration generate a gradual transition of mechanical properties from the stiff glueline to the bulk wood. Infiltrating *in-situ* polymerized adhesives have also been shown to reinforce weak, mechanically damaged cells near the glueline [163]. In addition, cell wall penetration provides the opportunity to have cured adhesive molecules that both interpenetrate cell wall polymers and extend into the bulk adhesive, strengthening the wood-adhesive interphase [21]. Prepolymerized adhesives, on the other hand, are typically not as rigid and so can stretch to accommodate wood swelling, thereby avoiding stress concentrations. *In-situ* polymerized adhesives that are typically durable on nonswelling substrates have failed water soak tests on wood bonds when the adhesive does not have a component that can penetrate cell walls. Examples include PF lacking a low molecular weight component, and epoxy, where bisphenol A is not expected to penetrate cell walls based on its low polarity [21, 142, 198].

Although the two adhesives classes were hypothesized based on many prior studies in the literature, new techniques allow measuring physical and mechanical

properties at the cell wall level and smaller. Instead of relying on a single strain measurement from a traditional strain gage, digital image correlation to measure full-field strains within and near the bondline is now available. Analysis of MUF, PRF, PUR, and EPI adhesives supported the proposal that *in-situ* polymerized adhesives stabilize the wood and the prepolymerized adhesives distribute strain in the adhesives [199].

Minimal creep of the bond is important for structural wood products as evidenced by a wide use of creep tests [200, 201] and minimum performance criteria [79, 202, 203]. The *in-situ* polymerized adhesives typically have very good creep performance because they are thermoset polymers, often with branching and nearly complete polymerization, forming a rigid three-dimensional network. Imparting creep, moisture, and heat resistance to prepolymerized adhesives has been more challenging but the more durable ones are generally lightly crosslinked to maintain some elastomeric properties.

3.4 Methods for Determining Void and Cell Wall Penetration

The essential challenge in measuring penetration is to differentiate between wood and adhesive, on a size scale relevant to the question being addressed. When measuring void penetration only, resolution of up to a few micrometers is often sufficient, while sub-micrometer resolution is needed to quantify cell wall penetration with confidence. Ideally, a natural feature of the adhesive such as color or natural fluorescence allows it to be unambiguously identified. Often the darkness of a phenolic adhesive stands out against the light color or autofluorescence of wood, while isocyanates, proteins, and sometimes other adhesives will naturally fluoresce differently from the wood.

Enhancing contrast between the adhesive and wood is often necessary, however. In many cases, dyes are applied to the sample just before visualization, such as Lugol's iodine (not Povidone iodine) to color PVAc and starch [204]; brilliant sulphaflavine to make amine bearing adhesive fluorescent [205, 206], toluidine blue to suppress the autofluorescence of wood [156], or osmium tetroxide and uranyl acetate to darken oxidizable structures in TEM. Another approach is to add the contrast agent to the adhesive before applying it to the wood. Adding small molecular tracers is attractive because they spread evenly through the adhesive, making every part of it visible. The danger with molecular tracers is that they sometimes migrate independently of the actual adhesive. An example of this was the use of RbOH as the alkali to make a PF: while the Rb did successfully enhance X-ray absorption, it did not stay with the PF [207]. Insoluble tracers like pigment particles are attractive because they do not leave the adhesive, and show up as unmistakable bright specks not only in fluorescence but in element-sensitive mapping such as backscatter SEM, EDX, EELS, TEM, etc. While the concentrated signal from pigment particles are typically more obvious than from a dye, not all the adhesive is visible, just the pigment particles. Because of their size, pigment

particles can be retained by anatomical features like pits or sieve plates when the adhesive passes, defeating their purpose [208]. Also, pigments are too large to penetrate cell walls.

Another approach is to chemically modify the adhesive backbone to integrate the contrast enhancement. Because of the chemical similarity of PF and lignin, it is often difficult to use chemical techniques to distinguish PF and cell walls. To overcome this, Kamke and coworkers made their adhesive from iodophenol and formaldehyde, ensuring one iodine atom stayed attached to each phenolic unit, making the adhesive highly absorbing for X-ray tomography [118, 119, 123, 209–211]. Others similarly used bromophenol with various analytical techniques including SEM-EDX [129, 131], neutron activation analysis [212], and X-ray fluorescence [145]. Grigsby and coworkers [213–218] have made a series of PF and UF adhesives where fluorescent molecules are incorporated into the polymer backbone, typically at ~20% substitution. Grigsby claimed to have done size exclusion chromatography to show that the fluorophore was uniformly present in all the different molecular weights of the applied adhesive [219]. While this approach is sound analytically, care in interpreting results is needed because incorporation of different monomer units (acriflavine, bromophenol) in the polymer means that the adhesive has different molecular size, solubility parameter, branching pattern, etc. than the unlabeled adhesive, which can change the penetration and mechanical properties.

Prepolymerized adhesives are in many ways the easiest to label because the backbone polymers are typically so large that covalently attaching a few heavy atoms or fluorescent dyes is unlikely to significantly change their properties. Also there are typically many functional groups available for covalent reaction with the tracer. While this is a promising technical route, it has been little exploited to date [220].

Visible light is of course not the only technique that can differentiate wood and adhesive: absorption or interactions with radiation of other wavelengths can be exploited by ultraviolet or X-ray absorbance, Raman, IR, NMR, or X-ray fluorescence. Interactions with electrons provide not only simple observation of topography with SEM but a whole collection of analytical techniques from EDXS to EELS. Nanoindentation allows probing the mechanical properties of the compound middle lamella, S2 cell wall, and (resin filled) lumen independently. Often a more complete understanding is only possible by using a variety of methods to examine different properties of the same specimen. Table 2 is provided as a brief overview of methods for measuring void and cell wall penetration, and their relative merits.

Typically, increasing resolution results in a smaller volume or area examined, and this is especially relevant to tomography. It is not unusual to acquire thousands of 2D images for a single 3D reconstruction. Therefore, high intensity radiation (which might cause sample degradation or drying, accompanied by shrinkage), long acquisition times, and small samples are much more the norm

Table 2 Methods of determining void or cell wall penetration in wood.

Method	Characteristics	References
Transmission microscopy; fluorescence microscopy (traditional thin sections)	<ul style="list-style-type: none"> • The traditional thin section method • Visible light transmission or fluorescence emission: fluorescence often has higher contrast • Thin sections provide best samples as light reflects off wood below the image plane making features somewhat fuzzy • Sample preparation can be time consuming and difficult, and one needs to be careful of smearing while cutting • Staining of sections (wood or adhesive) or labelling of adhesive are common • Especially useful if there is natural contrast between wood and adhesive • Fluorescence is especially useful for light colored adhesives that are typically hard to see, especially when failure occurs in the bondline • Fluorescence often uses UV illumination. Wood naturally fluoresces with UV. 	<ul style="list-style-type: none"> • Overviews: [110, 221–225] • Specific studies: [70, 71, 77, 110, 114, 122, 144, 178–181, 198, 199, 205–207, 226–246]
Microscopy of the smooth surface of a thick specimen	<ul style="list-style-type: none"> • Visible light reflection or fluorescence emission from the surface of a block. • The size of surface damage on the sample should be smaller than objects of interest. • Small surfaces can easily be made with a sharp razor blade or microtome; large surfaces are very difficult to produce with a knife. • Sanding can generate large sample areas for observation. 	<ul style="list-style-type: none"> • Efficient method for making smooth surfaces on large areas: [247] • Observing penetration on blocks: [247–250] • Bond and glue line thickness on blocks: [251] • Failure analysis on bulk specimens: [22, 204]



<p>Scanning electron microscopy (SEM)</p>	<ul style="list-style-type: none"> • Images formed from electrons scattered off or ejected from the surface: low contrast between wood and adhesive • Typically imaged under vacuum • 10 cm field of view and nm resolution are possible • Easy to change scan area from cm to μm • With proper detectors, it can be sensitive to topography (secondary ion), or changes in density/ elemental composition (backscatter mode), and several other modes possible • Greater depth of field, resolution, and variable magnification than light microscopy 	<p>[77, 127–129, 131, 207, 226, 227, 236, 246, 252–257]</p>
<p>Transmission electron microscopy (TEM)</p>	<ul style="list-style-type: none"> • Highest resolution (nm scale) • Requires extremely thin sections (~100 nm) and staining with electron-dense materials. • Very small fields of view 	<p>[129, 140, 198, 227, 235, 236, 258–262]</p>
<p>SEM or TEM with analyzers for emitted X-rays (EDXS, EDS, EDX, EDXA, EDAX, XEDS); WDS</p>	<ul style="list-style-type: none"> • SEM or TEM with ability to map location and concentration of near-surface elements based on energy of emitted X-rays 	<p>[123, 129, 131, 140, 156, 172, 207, 227, 235, 253, 254, 259]</p>
<p>Electron energy loss spectroscopy (EELS)</p>	<ul style="list-style-type: none"> • EELS detectors are added on to an SEM, TEM, or ion mill • Sensitive to surface elements (including C, O and N) and their bonding states. • Nanometer resolution possible 	<p>[127, 153]</p>
<p>Interference microscopy</p>	<ul style="list-style-type: none"> • Sensitive to index of refraction, hence whether cell walls are infiltrated 	<p>[263]</p>
<p>Autoradiography</p>	<ul style="list-style-type: none"> • Radioactive atoms (¹⁴C, ³H) are placed in the adhesive, and location of emitted particle from atomic decay is recorded. • Slowly decaying isotopes take long time to image (sometimes months for a single image) 	<p>[198, 264]</p>

(Continued)



Table 2 Cont.

Method	Characteristics	References
Techniques not widely used for penetration before 2000		
Confocal microscopy or Confocal laser scanning microscopy (CLSM); Spinning disk confocal microscopy	<ul style="list-style-type: none"> • Out of focus light is blocked by the optical system, giving much clearer images than standard fluorescence microscopes • Possible to “optically section”, or only collect light from the focal plane, not above or below • Serial optical sections can be used to create 3D images • Multiple fluorescence signals as well as reflected light (for topography information) or transmitted light (if samples are thin) can be simultaneously collected 	[128, 141, 144, 154–156, 163, 205, 215, 216, 220, 226, 227, 238, 265–270]
UV absorbance microscopy	<ul style="list-style-type: none"> • Classical method for wood and lignin studies: measures UV absorbance through thin sections 	[127, 138, 151, 164, 165, 266, 271]
X-ray computed (micro)tomography (XCT, micro-CT); synchrotron x-ray (micro)tomography	<ul style="list-style-type: none"> • 3D image of sample assembled from a series of x-ray absorption images at different angles • Sample size and instrument time limited by desired resolution • Requires different absorption between resin and wood, often achieved by covalently coupling a heavy atom into the adhesive • Would theoretically work for nitrogen-containing adhesives without additional labelling 	[117–123, 125, 207, 209, 210, 272–277]
X-ray fluorescence (XRF) microscopy; XRF-tomography	<ul style="list-style-type: none"> • X-rays passing through a sample excite fluorescence from the (heavy) atoms within the sample. • Resolution from nanometer to millimeter, depending on instrument • Synchrotrons commonly used because of their high X-ray intensity 	[123, 125, 145]
Neutron imaging, tomography	<ul style="list-style-type: none"> • Uses absorption of neutrons by sample to create an image or, by imaging at multiple angles, a tomogram • Highly sensitive to hydrogen, therefore avoids need for labeling 	[256, 274]
Scanning thermal microscopy (SThM)	<ul style="list-style-type: none"> • Observes rate of heat flow from AFM tip to sample 	[152, 278]



IR-AFM	<ul style="list-style-type: none"> • Observes thermal expansion of ~200 nm thick specimen when IR light is absorbed • Traditional IR data with nanometer spatial resolution 	[170, 279, 280]
IR/Raman imaging	<ul style="list-style-type: none"> • Sample is imaged by scanning, IR or Raman spectrum acquired at each spot. • Spot size limited by frequency of excitation, theoretical limit of ~0.5 to 2 μm 	[243, 257, 266, 281]
Nanoindentation stiffness, modulus	<ul style="list-style-type: none"> • Measures the mechanical properties of solids, shows impact of cell wall penetration • Sample volumes of less than $1\mu\text{m}^3$ are possible • Typical values obtained are elastic modulus and hardness. 	<ul style="list-style-type: none"> • Method for eliminating specimen compliance: [167] • Effect of microfibril angle: [282] • Bondline studies: [144, 145, 166, 172, 196, 197, 217, 238, 243, 257, 271, 283–287]
Nanoindentation mechanical spectroscopy	<ul style="list-style-type: none"> • Creep and viscous properties observed with nanoindentation apparatus 	<ul style="list-style-type: none"> • Methods: [168, 169] • Application to wood bondlines: [170]
X-ray microscopy	<ul style="list-style-type: none"> • Analogous to transmission light microscopy, using x-rays • Extremely high spatial resolution possible • Sensitive to nitrogen in the adhesive 	[136]
X-ray photoelectron spectroscopy (XPS) or (ESCA)	<ul style="list-style-type: none"> • Highly sensitive to top few nm but large area illuminated so only mm spatial resolution • Sensitive to all elements except H and He, indicating both their presence and oxidation states 	[156, 281, 288–290]
AFM	<ul style="list-style-type: none"> • Micrometer-scale tip rasters over surface to create map of surface. Topography is most common but many different modes available to enhance sensitivity to particular specimen properties 	[243, 257]
Near-infrared (NIR)	<ul style="list-style-type: none"> • Observes molecular vibrations, difficult to interpret. Has potential for quality control where little variability is expected 	[206, 243]

(Continued)



Table 2 Cont.

Method	Characteristics	References
Mercury intrusion porosimetry (MIP)	<ul style="list-style-type: none"> Quantitative measure of the volume of pores of each diameter Wood samples measured before/after bonding to determine which pores were filled 	[126]
Superresolution infrared (IR) or Raman spectroscopy	<ul style="list-style-type: none"> Chemical bond information at resolution beyond the diffraction limit 	[170]
Methods to investigate interaction of wood and adhesive		
Nuclear magnetic resonance (NMR)	<ul style="list-style-type: none"> Sensitive to the chemical bonds and environment of atomic isotopes with unpaired spins (¹³C, ¹H, ¹⁵N, etc.) Sample can be solid or liquid. Liquid gives better resolution. 	[134, 157, 158, 281, 291–300]
Dynamic mechanical analysis (DMA); Thermal mechanical analysis (TMA)	<ul style="list-style-type: none"> Observes elastic and plastic moduli, which change when adhesive infiltrates wood Typically used for wood-adhesive interaction studies, but cannot provide spatial information 	[134, 137, 237, 298, 301–304]
Differential scanning calorimetry (DSC)	<ul style="list-style-type: none"> Observes heat flow into/out of sample with temperature change: sensitive to chemical and physical changes 	[305]
Small angle neutron scattering (SANS)	<ul style="list-style-type: none"> Change in mean spacing between cellulose nanocrystals is observed when deuterated adhesive or water enters cellulose microfibrils, showing how adhesive impacts swelling inside cell wall nanostructure 	[117, 147–149]
Quasi-elastic neutron scattering (QENS)	<ul style="list-style-type: none"> Measures mobility of hydrogen atoms on picosecond time scale. Provides information on water and polymer mobility inside the cell wall, as affected by resin penetration 	[147]



for tomography than 2D imaging. Because only small volumes are scanned, the volumes being examined need to be carefully selected to ensure that they are representative of the norm.

Traditionally, light microscopy is often used in transmission with thin sections. This provides an excellent view of the wood and bondline, but thin sections can be very time consuming to prepare, and preparation becomes much more difficult as the area becomes larger. Reflection or fluorescence microscopy from the surface of a block of wood can image a large area more quickly, but it has traditionally been challenging to create a surface smooth enough for such images to be useful. Researchers have started polishing large areas with standard sanding equipment and airflow or vacuum to draw debris out of the sanding zone so it does not clog the wood pores [247, 250]. Removal of sanding dust is facilitated by using extremely porous sanding pads rather than traditional sandpaper. Tape can also be used to remove residual dust. This allows much larger areas to be prepared quickly, which can mean multiple samples prepared at once, or much larger areas in a given sample for better statistical reliability. The samples for Figure 1 were prepared by this method. This method is fast and simple enough to be practical for industrial quality control. If near-nanometer smoothness is needed, such as preparation of samples for nanoindentation, an ultramicrotome is typically used [145, 166], but successful sample preparation by polishing with a series of sandpapers and then with a diamond abrasive has also been claimed [306].

It is probably not surprising that the textbooks describing how to cut, mount, and stain thin sections were initially written many decades ago [225, 255, 307]. Because it can be difficult to find resources, we provide some references here. Basic wood anatomy, making wood sections by hand, and using a hand lens is described in English and Spanish in these three book chapters available for free online [308–310]. Hand lens use and making sections by hand are also described by Hoadley [311]. Microscopy, wood specimen preparation, and staining are often described together [224, 312–314]. Collections of wood-related micrographs are also available, and are not only beautiful but also useful for demonstrating how to make extremely informative images [221, 223].

Inspecting bondlines after product failure is discussed, with photos, for an extensive list of potential adhesive problems by Marra [5]. Lukowsky does not address as many adhesive issues but his color photos are easier to interpret and he includes a schematic depicting different types of penetration issues [204], as well as many practical examples of failure analysis of wood products.

3.4.1 Quantifying Depth of Void Penetration

Any measure of void penetration must consider the strong impact wood structure can have on penetration. Differences of earlywood vs latewood, radial vs tangential face, cells parallel to the cut surface vs sloping grain, lathe checks, damaged

surface cells, high or low spots on the wood surface, and the porosity of the wood on the other side of the glueline could all significantly influence penetration depth. Careful attention to these variables, as well as a sufficient number of measurements in appropriate regions of the bondline are necessary to obtain meaningful penetration data.

Perhaps the simplest, and an early-used method of quantifying void penetration was to apply a uniform amount of adhesive and measure the thickness of the cured glueline. A thicker glueline means less adhesive has moved into the wood [87, 241].

Reporting the “Mean Penetrated Adhesive”, or % of an area filled with adhesive, at several different distance increments from the bondline, [114] is simple and extremely informative. With automated image analysis, it is possible to make many segments, resulting in informative histograms of the % of each region filled with adhesive as a function of distance from the glueline; given the variability of adhesive penetration it is important to sample many areas to obtain a representative value.

Probably the most common approach is to quantify the extent of adhesive penetration at each increment of distance along the length of the bondline. The average of these values is termed average penetration (AP) depth [144, 179, 238], or specific penetration.

Effective Penetration (EP) is a commonly used measure of void penetration [119, 122, 144, 205, 238, 244]. Originally proposed by Sernek *et al.*, [205], EP is the sum of area outside the glueline containing adhesive divided by the length of bondline measured. In theory, EP + glueline thickness should be highly correlated to spread rate. One potential uncertainty in this measurement is whether to classify cell walls infiltrated with adhesive as cell wall or adhesive. Paris and Kamke [119] found that two adhesives of very different penetration patterns had indistinguishable EP's, leading them to recommend “Weighted Penetration”, or EP weighted by the distance the adhesive is from the glueline, which did distinguish between their adhesives.

Maximum Penetration (MP), also proposed by Sernek *et al.* [205], needs modification, or at least specific clarification, to be comparable between laboratories and species, and even with that clarification, it has limited utility. MP is the average distance from the glueline to the five most distant resin spots. First, any such measure should be normalized to the length of bondline observed, because as more bondline is measured, more spots will be observed far from the bondline. It has limited utility because it only reflects the most extreme values, which are statistically quite variable. MP has been shown to be highly influenced by a few very efficient flow paths, such as rays or cracks [180]. MP would be valuable, however, in cases where the extreme penetration values are the important information, such as when trying to ensure there is no adhesive bleed-through. Hass and coworkers improved the utility of MP by displaying their tomography results in quartile plots, which are much more informative than single value expressions [272].

At the end of a series of papers on the factors influencing penetration depth, Gavrilović-Grmuša and coworkers settled on six different measurements: AP, MP, MP/AP, total interphase region, I, which is the width of the interphase multiplied by the length of bondline inspected; A or area of filled lumens and rays in the region I; and A/I, the percentage of the interphase filled with adhesive [70]. The percentage of interphase filled with adhesive is essentially the same as Johnson and Kamke's measurement [114], simplified to a single average value.

As an improvement on EP, Hass *et al.* were able to show a good correlation between void penetration and bond strength with PUR, PVAc, and UF resins in beech when penetration was quantified as the degree of saturation of the pore space, specifically excluding cell wall material from the calculation [272]. This is a promising development, and identifying three phases (lumen, wood, and adhesive) instead of just two should be relatively straightforward with data from many techniques.

Edalat and coworkers tallied resin filled areas using the number of cells as their unit rather than micrometers, which has the advantage of capturing the influence of wood anatomy on void penetration [250]. This approach was able to identify different penetration depths for boards made with wood at different moisture contents. If this technique were standardized to the length of bondline inspected (presumably measured in number of cells) there is a chance that numbers could be compared among laboratories. However, it seems more cumbersome than summing the areas using automated analysis methods.

3.5 Shortcomings of Standardized Tests

Standardized tests for wood bonding were developed to allow comparisons of adhesives from different manufacturers, using exactly the same methodology, often with a requirement for testing after exposure to heat or moisture, or even boiling water and/or climatic cycling. However, standard methods seldom cover how the bonded sample is made. Exceptions are ASTM D 2559, which is used for qualifying adhesives for structural products sold in the United States, and is fairly specific on the wood and the bonding conditions used, as is ASTM D7998 [185]. Often it is hard to discern why the test method uses the specified conditions, although the commentaries in versions of D2559 after 2011 are an exception. The problem for industry and academics is that the results from one national standard cannot necessarily be compared to another national standard. A prime example is the many different test methods used by regulators around the world to monitor formaldehyde emissions from wood panels where not only the procedures but also the strategy and aim of the tests vary between jurisdictions [67, 315].

How does one compare the results learned in Europe using an ISO or an EN standard with European wood species to the results from an ASTM test using a North American wood species? An additional complication is that there are no standard adhesive or standard wood specimen, such as the standard epoxy, 316

stainless steel, and pressure-sensitive tape for peel or shear tests. With wood, it is difficult even to obtain consistent samples of a given wood species. In some cases, standards that appear very similar have subtle differences that might have significant impact, such as the requirement in ASTM D906 that half of plywood bonds are pulled open and half pulled closed, while the parallel standard EN314 does not specify how the bonds are pulled [194, 316].

Although the chances of having harmonized international standards are not very likely, the more we understand about wood bond performance beyond the readily visible failure load and percent wood failure, the better we can start to compare studies using different adhesives, wood species and bonding conditions. The increasing level of sophistication of analysis of intact and failed bond samples allows us to better understand bonds from a fundamental perspective.

4 A More Detailed Approach than Standard Wood Failure Analysis

It can be very hard to determine what properties of an adhesive lead to success. The adhesive is considered successful when the bond does not fail and meets other requirements such as cost, fitting the production process, meeting customer's specifications, etc. Improving performance by paying attention to the impact of changes in the wood preparation, adhesive formulation, and bonding conditions has been going on for a long time. Accelerated tests that typically involve changing moisture or temperature, as well as different static loads, or combination of these are helpful and have been used to estimate long term durability [317]. When a product fails in the bondline, however, the researcher can begin to understand what is critically missing from the adhesive's performance. As Marra indicated, all the links between the two wood pieces need to hold together to prevent bond failure [5]. Solving the weak link problem leads to commercial success, but understanding the weak link allows for more effective problem solving in the long term.

Thus, a careful examination of the failure surfaces is useful to understand in what region and why the bond failed. Many traditional and new techniques have been developed to understand the where and why of bond failures. Unfortunately, it is easy to misinterpret the analysis results because wood is such a non-homogeneous material and bonding is complex. At a minimum, the researcher needs to be sure that the area examined is representative of the main failure zone. Below we will look at two examples of studies that used failure analysis to improve understanding of why bonds failed, and then briefly discuss how nonstandard mechanical tests can provide insight.

4.1 *Going Beyond What Meets the Eye to Understand Epoxy Failure*

A study of epoxy failure is a good example of how looking deeper into failure modes using a variety of methods has greatly improved the understanding of a common problem, i.e. water durability of epoxy bonds to wood. Epoxy bonds

often fail water soak tests when bonding wood, but provide strong, durable adhesion to many plastics, metals and concrete [318]. The failure of wood-epoxy bonds has been known for a long time and significant research has been done to find formulations that work well [318–320]. A study was done to explore why water soaking induced failure of epoxy bonds using a commercial epoxy resin [318]. In a typical fashion the bonded products exhibited poor strength during wet testing. Normal naked eye and microscope images showed what looked like a “wood” side and a shiny adhesive side, with a wood-like texture was evident on both sides (Figure 12). This apparent adhesion failure was surprising since cross-sectional analysis of the bonded specimen showed good void penetration of epoxy on both sides of the bond. This reinforces the idea that wood penetration may be a necessary, but it is not a sufficient condition for durable bonds, especially when exposed to water.

Normally at this stage, researchers go to the SEM to obtain more detailed images. The SEM images in some spots appear to show adhesion failure, as illustrated in Figure 13. However, a closer examination showed that most of the lumens on the

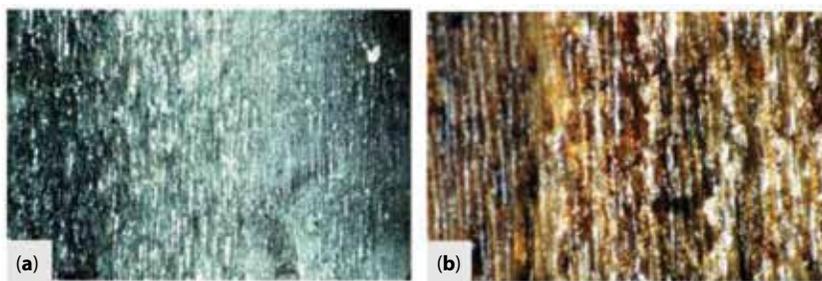


Figure 12 Optical microscopy images of the failure surfaces from ASTM D 905 sample of a commercial epoxy on wood to illustrate the orientation or surface features parallel to the wood longitudinal direction on (a) the side that appears to be epoxy and (b) the side that appears to be bare wood. Approximate image width; 1.2mm.

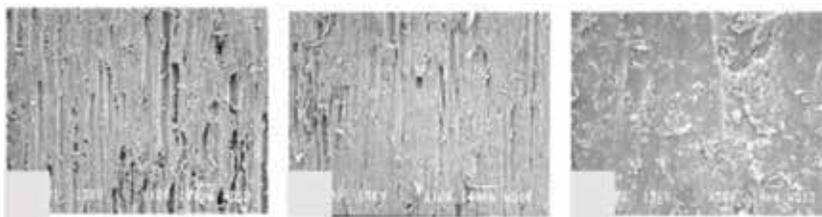


Figure 13 SEM images of the failure surfaces from ASTM D 905 testing of a commercial epoxy on wood to illustrate the difficulty of distinguishing failure (a) unbonded wood, (b) the “wood” side of the failed bond that contrasts with (c) the “epoxy” side of the bond. Approximate image width; a, b 1.2mm; c, 280 μ m.

“wood” side of the bond appeared to be filled with epoxy. Because this analysis can be very subjective, the SEM analysis did not offer any definitive conclusion on failure location.

Attempts to stain the adhesive and the wood showed that there seemed to be an epoxy coating on the wood side, but the results were inconclusive. Fortunately, one of the epoxy adhesives tested happened to provide good fluorescence on curing. The image in Figure 14 shows that the adhesive covers the wood surface even on the wood side, suggesting a combination of failure modes: limited adhesion failure and mainly cohesive failure of the epoxy film very close to the wood surface. Another telling feature was that the fracture planes were oriented parallel to the wood grain and applied load. Fracture planes typically form perpendicular to the main loading direction. This suggests that the primary load was perpendicular to the applied force, as would be expected if failure were induced by wood swelling.

If the “wood” side was generated due to adhesion failure, x-ray photoelectron spectroscopy (XPS, also called ESCA) should show a surface that looks wood-like, not epoxy-like. The XPS data, however, showed epoxy on both failure surfaces [290] as did the FTIR. These different analytical methods showed that what looked like an adhesion issue was really a cohesive failure very close to the wood surface, i.e., in the adhesive interphase. This result led to the idea that internal strain from the swelling of the wood limited the amount of exterior load the bond could withstand. Supporting this result was the observation that the use of certain primers improved the durability of epoxy bonds to wood [321]. The expected inability of bisphenol A in epoxy to penetrate cell walls provided a counter example to most *in-situ* polymerized adhesives, and was critical to Frihart’s development of the idea that stiff, *in-situ* polymerized adhesives must penetrate and modify cell walls in the bondline to be durable [142]. Primers such as hydroxymethylated resorcinol

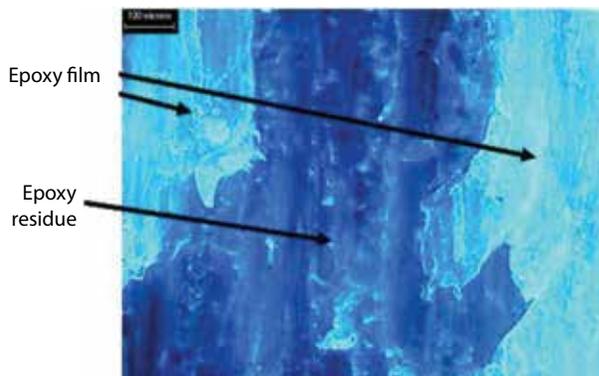


Figure 14 Fluorescent image of the wood side failure surface of epoxy bonded wood. Fractures primarily oriented along the wood grain direction. Scale bar: 100µm.

(HMR) might help epoxy durability by penetrating and modifying the wood cell walls. For more discussion of primers see section 5.

4.2 Using SEM to Detect Brittle Failure in UF

Stress concentration points can initiate failure, which can lead to global failure during mechanical testing, as discussed at length by River [62, 187]. Therefore, the adhesive ductility, or ability to avoid stress concentration in the bondline, can be an important adhesive property [322–325]. UF is a brittle adhesive and fractures on curing due to volume shrinkage from water loss and condensation reactions [326]. Replacing ammonium chloride used for curing the UF with organic ammonium chlorides which are less volatile resulted in higher strength values. Inspecting the failure surfaces with SEM revealed that along with the increased strength came increased signs of ductility such as necking of the adhesive rather than sharp edges [324–326]. The increased ductility appears to explain the improvements in bond strength.

An SEM is commonly used to examine fracture surfaces to identify the difference between adhesion and cohesive failures, and the sharpness of fracture planes on brittle failure surfaces compared to the more distorted surfaces in plastic failure. Because these observations are typically highly magnified, and therefore cover only a small area, it is important that the area selected is typical of the bonded surface area. In addition, the conductive coating traditionally applied has obscured observations. Recent improvements in SEM technology providing higher resolution, better sensitivity, and lower specimen damage are likely to yield better images of fracture surfaces in the future. In addition, advances in techniques that can be added to an SEM, such as EDXS or WDS, allow researchers to simultaneously map the physical structure and the chemical composition of the surface.

4.3 Alternative Mechanical Methods of Testing for More Information

The key requirement of a wood adhesive is that it holds the wood together under normal use conditions. Standard test methods for wood bond strength are numerous depending on the application. In the US, the ASTM methods D905, D906, D1037, D2559, D7247, and D7519 are most commonly used [78, 79, 191, 194, 327, 328]. Europe typically uses the CEN methods EN 205, EN 302, EN 314, EN 391, EN 12765 (formerly EN 204), EN 14080, and EN 15425 [190, 192, 202, 203, 316, 329–331]. These are just the most commonly used standards for bonded wood products. They do not begin to cover specialty applications or other countries.

While standard visual methods are very useful commercially, they rarely provide clear guidance as to why the bond failed. If crack propagation or elongation properties of the cured adhesive between wood substrates are needed, the dual cantilever beam (DCB) method is often used [332, 333]. DCB has been useful in

developing understanding of wood bonding relationships such as the influence of adhesive thickness and plasticity on bond strength [62, 334–339]. In this test, two pieces of wood are glued together, a notch is introduced in the bondline at one end, and the pieces of wood are pulled apart perpendicular to the bondline at the notched end. This procedure enables testing the cohesive strength of an adhesive in a joint. This value is typically used to calculate energy release rate, or energy required for a crack to grow. It has been shown that the energy required to grow a crack in PUR is typically much larger than in PRF or other *in-situ* polymerized wood adhesives [187]. Recently, efforts have been made to use DCB to understand the performance of composite panels, with some success in differentiating adhesives better than the standard internal bond tests [340–342].

Stress concentrations can initiate failure, which can lead to global failure during mechanical testing [187]. Prepolymerized adhesives appear to rely on adhesive ductility to avoid stress concentrations in the bondline, while *in-situ* polymerized adhesives appear to avoid stress concentrations by creating a gradient of properties through the interphase. Digital Image Correlation (DIC) and Electronic Speckle Pattern Interferometry (ESPI) are useful methods for measuring the displacement and strain fields of a bondline during loading. ESPI uses interference between a reference beam and the light reflected off a sample [343, 344]. DIC tracks the motion of high contrast objects, such as specks of spray paint, on the sample surface in a series of images taken as the sample deforms. The work of Kläusler *et al.* [345] shows the striking difference in ductility between two structural adhesives, a PRF and a PUR. PRF strain-at-break ranged from 1% dry to 2.5% wet, while PUR strain-at-break was consistently 25–30%. Figure 15 shows how this difference in ductility manifests in bondline deformation, as

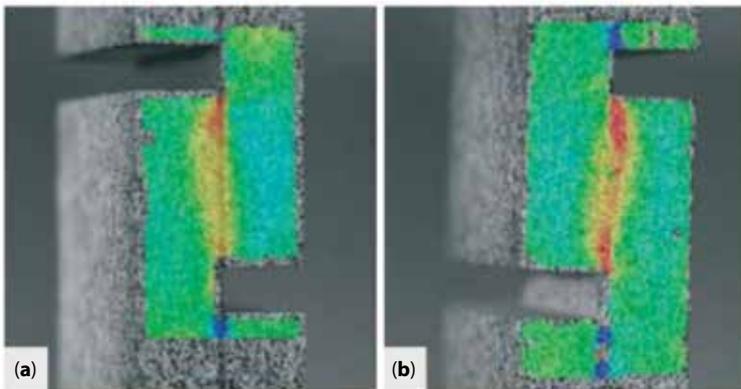


Figure 15 Strain distribution at nominal 10MPa shear stress. Red = high strain. (a) Strain is concentrated at the ends of the joint with brittle PRF adhesive, while (b) ductile PUR distributes strain (and therefore stress or load) more uniformly [346], color images online.

measured with DIC (red = high strain) [346]. The movement and load in brittle PRF (A) are concentrated at the ends of the joint, while the ductile PUR (B) allows movement across the entire joint, which results in more uniform load distribution. A complete discussion of the details of DIC methodology can be found elsewhere [347].

Tracking the displacements of individual elements of a bondline is also possible using tomography, with the advantage of observing all three dimensions of the specimen. Tomography data have led to a micromechanics model of equivalent strain and stress of each volume element of the adhesive bond under load [211]. The experimental lap-shear test results from the same specimens validated the model.

In most tests, it is not possible to extract the mechanical properties of an adhesive independent of the wood due to adhesive-wood interactions or the thin, non-uniform nature of the bondline. Nanoindentation, by contrast, is able to reliably extract mechanical properties of an adhesive in the glue-line or in a single lumen (for references see Table 2).

Dynamic mechanical analysis (DMA), sometimes called dynamic thermal mechanical analysis (DTMA), has been used to probe the changes in mechanical properties of wood pieces with adhesive infiltration. The mechanical response with temperature, moisture, and time scale has provided new insights into the interaction between adhesives and wood polymers [132, 134, 348]. Mechanical properties of cubic micrometer scale volumes, particularly the impact of cell wall penetration, are now commonly probed using nanoindentation (see Table 2). Many interesting discoveries are expected as more labs acquire humidity and temperature control of the specimen chamber, and the practice of dynamic analysis using nanoindentation becomes more common.

5 Unresolved Questions in Wood Bonding Research

Ideally, scientists and engineers should be able to predict bond strength and durability with an adhesive of known composition used for bonding wood of known characteristics under a prescribed set of bonding conditions. While we are still far from this goal, progress in measuring and understanding properties from the macro to the molecular scale is bringing us closer to this goal. Much of this progress in understanding comes from using tools beyond the naked eye for examination of bond properties and bond failure. Even more progress is possible when multiple techniques, measuring complementary properties, are brought together on the same sample set. This approach not only leads to a more thorough understanding of a particular case, but also uncovers inconsistencies and contradictions between the conclusions from different approaches. These contradictions, or conversely, the ability to quantitatively predict properties, are fertile areas for developing our understanding, but often requires a single sample to be studied by multiple, diverse, quantitative methods.

5.1 How Do We Make Wood Surfaces Better for Bonding?

Adhesives need to wet the wood surface. Water drop tests are a quick way of assessing wettability with waterborne adhesives, and a large decrease in contact angle after a solvent wipe suggests that the wipe removed an oily surface that could have caused a chemical weak boundary layer. However, more sophisticated methods are needed beyond these tests. Mechanical weak boundary layers can be identified with cross-sectional microscopy and a tape test can be used to measure loose wood surface pieces [63]. There is no proven test for evaluating the frequency of crushed and buckled cells on the surface or their impact on bond performance. The tests we do analyze small areas and do not give a view of the entire surface. Can large surfaces be quickly and efficiently analyzed before bonding? Macroscopically rough surfaces can easily be judged by their look and feel, finer measurements have not led to consistent comparisons with bonding performance. What techniques can be developed to relate surface properties to bond performance? Could an online monitoring system be developed that would allow dynamic process modifications to account for the quality of the wood surface?

Penetration of the adhesive into the wood is important for developing a strong bond, but how do we assess wood porosity in relation to adhesive penetration? Porosity of the wood is considered important for forming good bonds, but too much porosity can lead to excess costs and starved bonds. Is there a way to judge wood porosity prior to its use so that the adhesive spread rate and/or its formulation can be adjusted prior to production?

The swelling of wood in bonded products is a major problem. Are there ways to measure and reduce stress this swelling causes in the bonded assemblies? How important is the high pH in phenolic resins for promoting good contact between bulk adhesive and the cell wall, as well as cell wall penetration? If the cut-open cells on the surface are important for mechanical interlocking and bonding, does the chemical structure of the surface of wood matter? Does the change in composition of the cell lumen walls between species affect bonding?

5.2 Does the Adhesive Have Good Penetration Into the Wood Structure?

The question is, what does “good penetration” mean? Too little or too much penetration will cause low bond strength and therefore bond failures, especially when the bond is exposed to water. Starved gluelines typically show cohesive failure in the bulk adhesive or in the adhesive interphase. Thick gluelines from low penetration or excessive spread rate are also weak [349] and waste adhesive. Several of the EN standards for testing and classification of bonds require the preparation and testing of thick joints [190, 350]. How do we determine the most important factors for proper adhesive penetration, viscosity of the adhesive, molecular weight of the adhesive components, loss of water to the wood, adhesive cure rate, pressure, temperature of bonding, etc.? How do these factors interact with wood properties?

5.3 *How Does the Adhesive Interact with the Wood at the Nanoscale and Molecular Level?*

Although wood bond formation and fracture seem like macroscopic properties, they are the sum of a multitude of interactions at different length scales. How do we determine the relative contribution of chemical cross-linking vs. secondary chemical bonding (van der Waals, hydrogen bond, etc.) vs. mechanical interlock? Once we begin to understand them, how do we use that information to improve bond performance?

5.4 *Can We Improve the Resistance of Bonds to the Dimensional Changes in Wood with Variation in Moisture?*

The level of moisture-induced stresses in bondlines depends on various factors, such as the geometrical properties of the lamellas and the glued element as well as the wood properties. With increasing density, shrinkage and swelling coefficients as well as stiffness and strength properties generally increase, so moisture changes generate higher stress levels [5]. Durable bonds have been difficult to make with ash (*Fraxinus excelsior* L.) and beech (*Fagus sylvatica* L.), because these wood species have significantly higher densities than other wood species typically used for glulam in Europe, such as spruce (*Picea abies* L. Karst) [241, 245, 351]. An adhesive that expands with the wood as it wets may partially explain the moisture durability of wood bonded with such resin systems. Some success in studying the hygro-mechanical behavior of adhesive films has been realized [173, 287, 343, 352–354]. It has been demonstrated that the mechanical properties of cured adhesives depend on their MC, so this must be considered in modeling and predicting bond performance [345, 355]. PUR and EPI adhesives are more elastic and therefore allow for smoother strain transition, showing less distinct strain peaks than PRF and MUF [199]. How does the bond withstand not only dynamic loading, but also duration of load and fatigue? Which types of loadings are worst for different types of adhesives?

With regard to moisture durability, was Frihart really correct about how the rigid and brittle adhesive layers of *in-situ* polymerized adhesives and the flexible bondlines of prepolymerized adhesives distribute stress [142]? Are there details still to be worked out, such as a gradual reduction in brittleness/increased ductility with *in-situ* polymerized adhesives? Can this theory be turned into predictions of how much void and cell wall penetration are necessary for a given pair of wood surfaces?

5.5 *How do Primers Work?*

Kläusler *et al.* reported that the tensile shear strength and wood failure percentage of wet bonds were substantially lower than the samples that were dried before testing [356]. The microscopic images suggest that the wet samples lose adhesion. Improvement of tensile shear strength and wood failure percentage of 1C PUR

bonded wood joints tested wet was achieved with HMR and dimethylformamide primers. In some cases, the adhesives provide good strength, but a low percentage of wood failure. Primers, in particular HMR, have been found to be effective in improving both wood failure and bond strength for a variety of adhesives and wood species, but the mechanisms of primers is unclear [304, 321, 357–361]. Is it possible that HMR allows the joint to benefit from the dimensional stabilization and reinforcement of the interphase typically afforded by in-situ polymerized adhesives, as well as from the ductility of a prepolymerized adhesive? In what situations do primers help the most? Why? What do primers do, what bond properties are influenced, and when will primers improve bond quality?

5.6 Where Does the Bond Failure Initiate and How Does it Propagate?

One characteristic of failure propagation is the stress concentration at the edge of a defect exceeding the adhesion or cohesive strength at that point. The growth of micro-cracks at stress concentrations results in a gradual loss of mechanical integrity and, hence, weakening of the joint. While bond strength is determined by the weakest link in the adhesive bonding chain, it is currently difficult or impossible to predict whether a crack will remain where it started or move to the glue line, the interphase, or to the wood. In an ideal bond, or one that passes most quality standards, most of the failure occurs in wood, far from the bond line, so the only information obtained is that the bond strength exceeds the wood strength.

Given the complexity of crack propagation, how can we understand the source and propagation of failures? Different failures need to be studied by different, often complementary methods to arrive at firm conclusions. Do the different methods agree? How do we take the understanding of a few observed failures and apply that knowledge to all the possible variations that occur in commercial wood bonds? Even with good information about a particular failure, wood is so varied that a statistical sample of different possible configurations is warranted.

When stresses exceed bond strength, delaminations can develop and affect the remaining service life [362]. How do we consistently determine the effect of an accumulation of micro-delaminations that over time, can lead to macroscopic failure?

5.7 How Do We Optimize the Benefits of Cell Wall Penetration?

It is well known that pMDI is an effective adhesive, but it has been shown not to react with the wood polymers [158]. It is unclear how much the pMDI enters the wood cell walls because sometimes it is observed to penetrate the cell wall [134, 135, 170] and sometimes not [136]. Grigsby and Thumm claimed that either MDI or pMDI (the paper is ambiguous) penetration into MDF fiber was present but very shallow [218]. The question is, how important is pMDI cell wall penetration to bond performance? Do the details of how a bond is made determine whether or

how much cell wall penetration occurs? If pMDI does not enter the cell wall and does not bind to cell wall polymers, how does it develop good bonds?

The literature shows that some adhesives enter the cell wall and others do not usually because of molecular weight limitations for cell wall infiltration. Less well understood is the impact of solubility parameter of the adhesive and moisture content of the wood on wood bonding. Adhesive solubility parameter could determine in what domain of the cell wall the adhesive components will reside, and how the adhesive modifies the properties of that domain. Does cell wall infiltration contribute to adhesive interphase failure in epoxy by allowing the amine monomers to enter the cell wall while excluding bisphenol A, resulting in a depletion of amine? Does this occur in other adhesive systems as well?

5.8 How Does the Adhesive Form a Suitable Polymer Matrix to Bridge Between the Two Wood Surfaces?

The chemical structure of the solid adhesive influences the adhesive's cohesive strength (rigid and brittle vs. ductile and elastic) and the temperature behavior of the glueline, with duroplastic behavior relatively independent of temperature and thermoplastic behavior losing bond strength at the glass transition temperature (T_g) of the solid adhesive. The formation of the solid bondline typically involves shrinkage due to the loss of the water and polymerization or cross-linking of the adhesive molecules. How does the bond deal with this volume reduction without creating too much internal strain? How does the adhesive respond to the strain from external mechanical forces as well as from wood swelling and shrinking? Significant differences have been observed between the properties of adhesives intended for solid wood products compared to adhesives intended for use in composites [196].

Does multiscale modeling and simulation of wood adhesion provide useful insight into bonded wood performance? Does this allow data from standard laminated samples to be used for understanding cross-laminated structures and new types of wood products such as mass timber or plywood?

5.9 Will Adhesives Based on Renewable Resources be the Future in Wood Bonding?

The very first glues were made of natural, renewable raw materials. Today, the great majority of adhesives are derived from fossil fuels because of performance and cost. Nonetheless, there has been great interest in renewable adhesives in recent years driven by concerns about human health and sustainability. The main safety and health concerns have focused on urea-formaldehyde and isocyanates. The biomaterials under investigation include lignin, proteins, bio-oils, hemicelluloses, and others. Several overview and review papers have been published [3, 23, 27, 363–366].

Expressing the renewable content will avoid some confusion about what is a bio-based adhesive, and may promote the use of lignin and proteins both as base adhesives and as extenders, as well as provide a mechanism to give credit to existing bio-based fillers and extenders. There appears to be demand for bio-based wood adhesives in the marketplace, especially in Europe. For example, one of the world's largest furniture retailers, Ikea, has committed to 40% natural raw materials for all their adhesives by 2025 and 80% by 2030 [367].

The broader use of bio-based content in adhesives is hindered by a lack of information and understanding on these bio-based systems. Synthetic adhesives are often more consistent than natural products. In synthetic adhesives, the manufacturer starts with known, well characterized, relatively pure raw materials of consistent quality and properties. Natural materials are often much more complex in composition, structure, and seasonal variability. This leads to the following questions:

- What is the structure of the cured adhesive and how do variations in the cure conditions influence mechanical properties and performance?
- How do these bio-based resins interact with the wood? What components can be added and under what conditions to improve this interaction?
- How does an adhesive manufacturer manage the differences in the growth and extraction of natural materials? How do they deal with variation from season to season, and as the natural material ages after harvest, and geographic differences? How do they ensure a consistent and continuous supply of the raw materials? How do they characterize these extremely complex raw materials for their adhesive properties, when we understand so little about what controls the final bond strength with these materials?

5.10 How Much the Experience with Solid Wood Bonding can be Used to Understand Wood Based Particulate Bonding?

Oriented strandboard (OSB) and particleboard (PB) are assembled from wood particles, while the structure of fiberboard fibers is substantially different from the original wood. As long as solid wood is present (independent of the size of the strands or particles), the basic principles of bonding two wood surfaces remain applicable. In principle, the only difference between solid wood bonding and panel production is the size of an individual bond: several m² for plywood and cross-laminated timber, possibly as much as 2000 mm² for two OSB strands, and finally as small as a few mm² when bonding PB particles. However, the relative importance of various effects will change: some adverse effects that are minor in solid wood bonding become much more common, such as the buckling of cell walls during pressing and the combination of different grain directions. This is especially important in PB, where no consistent grain direction of the particles is present.

The main test methods of mechanical properties for PB, OSB, and MDF are internal bond, bending strength, and bending stiffness; however no evaluation is done concerning proportion of wood failure simply because of the difficulty of the procedure. How do we relate what we find with laminated wood to glued wood products that have spot welds instead of a continuous adhesive layer? Do the test results reflect more the wood particle properties and density profile or the adhesive properties?

5.11 How Do We Compare Results Obtained in Different Laboratories with Different Wood Species with Different Adhesives?

Through the extraordinary work of researchers around the world, we are learning many things about wood bonding. However, it can be hard to know how broadly the results can be extrapolated. How do we know the repeatability of the results, with different researchers and different wood samples, even when they are of the same species? How do we compare work done in Europe on beech or ash with that done in the US using Douglas fir and loblolly pine? How do we relate the work on penetration and bond performance from one set of wood/adhesive/surface preparation/bonding conditions to another?

Summary

Wood bonding is enormously complex given the multitude of variables and unknowns. The intelligent empirical work up to now has led us to bonded wood products that generally meet the customer's need for performance, safety and cost. However, there are always drivers for improvement, whether they are product cost reduction, wood type and quality, new types of bonded wood products, or societal changes. There has been substantial research into why wood bonds fail and what is needed so that they do not. Much of the research discussed in this review has focused on factors that cannot be observed by examination with the naked eye. The factors that contribute to bond performance span several microscopic levels, including the cellular, nano, and even molecular level. This review has tried to summarize the breadth of this work and provides challenges for future research.

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All recent publications authored by USDA Forest Service, Forest Products Laboratory (FPL) employees are freely available to the public and can be found through internet search or downloaded from the FPL website, <https://www.fpl.fs.fed.us/search>. FPL employees referenced include: A.W. Christiansen, C.R. Frihart, C.G. Hunt, J.J. Jakes, N. Plaza, B.H. River, H. Tarkow, C. Vick, A.C. Wiedenhoef, D.J. Yelle, and J. Youngquist.

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DOI: 10.7569/RAA.2018.097312



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