Chapter 18

Wood Structure and Adhesive Bond Strength

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Abstract

Much of the literature on the bonding of wood and other lignocellulosic materials has concentrated on traditional adhesion theories. This has led to misconceptions because wood is a porous material on both the macroscopic and microscopic levels. A better understanding of wood bonding can be developed by investigating the theories of adhesion and bond strength, taking into consideration the unusual structure of wood. Wood is not uniform in the millimeter, micrometer, and nanometer scales. The interaction of adhesive with wood needs to be considered on these different spatial scales. In addition, emphasis needs to be placed on the stress concentration and dissipation mechanisms that are active in bonded wood.

Because most adhesives bond wood sufficiently to give wood failure under dry conditions, the emphasis is on durable bonds, especially those exposed to moisture and/or heat variations. The new hypothesis emphasizes that for durable bonds, the adhesive needs to give during wood expansion or to restrict wood expansion to lower stress in the interphase regions. Among the experiments that support this hypothesis, one study involves the failure mechanism of epoxy wood bonds. Available information indicates that the fracture occurs near the surface within the epoxy layer. A second study is the bonding of acetylated wood with epoxy adhesives. Under wet conditions, acetylated wood expands less than does untreated wood and less stress thus occurs at the interface. In addition, this hypothesis proposes that the primer, hydroxymethylated resorcinol, is not a coupling agent but stabilizes the wood surface.

Keywords: adhesive, strength, wood, adhesion, failure, epoxy, acetylated, scanning electron microscopy, swelling, bond, durability

Background

Much of the wood bonding literature has addressed standard adhesion bonding mechanisms. There has been limited consideration of how these mechanisms need to be modified when wood is the substrate. Studies have focused on interfacial failure and weak boundary layers. Marra (1980) and Wellons (1977) addressed many aspects of wood-adhesive interactions during the bonding process. River et al. (1991) studied the preparation of wood surfaces in detail. River (1994) also reviewed work on the fracture analysis of bonded wood assemblies.

In discussing the processes of bonding and de-bonding, it is important to emphasize that the unique properties of wood need to be examined on several spatial scales. In discussing adhesion and adhesive
strength, it is important to separate the process of bond formation from tests of bond performance. To form a bond, the adhesive flows into cell lumens and sometimes into cell walls to form an intimate contact with the wood surface. If intimate contact does not occur, the bond is poor since all adhesion requires contact on a molecular level between the adhesive and the substrate.

On the other hand, for an adhesive to have satisfactory strength after solidification, it needs to resist flow and fracture under a given set of conditions. Adhesive strength is a mechanical property because it is defined as the ability to hold two materials together under a given set of conditions. However, the chemical structure determines the mechanical properties of materials. Thus, it doesn’t make sense to separate whether bond strength is strictly mechanical or chemical given the interdependence of these factors. When stress is highly concentrated at a location, some bonds will usually fracture there. On the other hand, if the stress is distributed, then even weaker bonds may not be ruptured.

Adhesive strength is more than adhesion at the interface, although without adhesion there is no bond. Thus, while the process of bond formation is dependent on thermodynamics and rheology, the process of bond fracture is mainly a function of viscoelastic dissipation of energy. The interphase regions of the adhesive and substrate also play an important role, particularly when the substrate is wood.

One useful method for understanding adhesive strength is the chain link analogy (Marra 1980). Different areas of the substrate and adhesive are likened to a series of chain links, with the weakest link being the site of fracture (Figure 18.1). Link 1 is a bulk adhesive layer; this link represents the properties that are normally measured for an adhesive. At the extremes are links 8 and 9, which represent the bulk properties of the wood substrate. The smaller links represent smaller layers of the interphase. Links 4 and 5 are typical interface links, where the adhesive contacts the wood surface.

![Fig. 18.1 Chain analogy for bond strength.](image)
Links 2 and 3 are the adhesive interphase regions, the adhesive layers next to the wood surfaces. These layers are often not fully formed because it is difficult to form a full polymer network in the constrained environment and the curing chemistry can be influenced by the wood. The lack of mobility near the surface limits the molecular collisions needed for a normal curing process. The pH of the wood or adsorption of components can alter the formation of the adhesive structure. Generally, stress is concentrated at the adhesive interphase region when there are differences in expansion and contraction characteristics between the adhesive and the wood.

Links 6 and 7 are the wood interphase regions. These areas are often weaker than the wood itself, because the process of preparing the surface often causes fracture of the normal wood matrix. In addition, as with the adhesive interphase layer, when there are differences in expansion or contraction characteristics, forces are highly concentrated at the wood interphase layers. Ways of preparing the wood surface that lead to a weak surface layer have been discussed by River (1994) and others. Stehr and Johansson (2000) separated the weak interphase layer into two forms: mechanical weakness, caused by fracture of the wood surface from planing, sawing, or sanding, and chemical weakness, caused by the movement of extractives to the surface. I will discuss this model again, but it is important to remember that more than the adhesive-wood interface needs to be considered when thinking about wood adhesion.

**Bond formation**

Bond formation involves several steps. The first is the macroscopic wetting and flow of the adhesive across and into the wood pores. Normally, the main concern is about equilibrium contact angle (q), which determines the wetting of the surface. Everything is fine as long as the adhesive has sufficient time to come to equilibrium. However, in most wood bonding applications, the process is not at equilibrium because some solvent migrates into the wood and polymerization takes place. Both of these factors raise the viscosity of adhesive and therefore reduce penetration. Given these factors, it is more important to be concerned about dynamic wetting \( x(dx/dt) \), which is similar to equilibrium wetting but also has an inverse of the viscosity term (Pocius 1997). Dynamic wetting is important for flow across and into the wood surface. For flow into the pore of distance \( x \), there is an additional term for the pore radius: normal capillary theory would favor flow in smaller capillaries. However, the viscosity factor predominates; thus, larger pores are more easily filled.

An additional aspect, which is unique to wood, is the significant flow of some adhesives into the wood polymer wall. This absorption into the cell walls is different from the adsorption on the cell walls that is usually considered in adhesion theories. Using a variety of techniques, a number of authors have shown that some adhesives end up in the wall (Nearn 1974; Marcinko et al. 2001; Schmidt and Frazier 2001). This flow is obviously controlled by factors on the molecular level, such as solubility parameter, molecular size, and shape. Simple absorption into the cells is probably not sufficient to stabilize the wood because the uncured adhesive can leach out again. Reaction with the cell wall components or polymerization in the cell wall is necessary to provide a stable interphase region.

Polymerization can be inhibited by selective adsorption onto the lignin, hemicellulose, and cellulose components. In a two-component system, the cure could be disrupted by selective adsorption, but this would not affect a single-component adhesive. It is not clear exactly whether the adhesive reacts within the cell wall, but there is substantial evidence, gained by a number of different methods, that many adhesives flow into the cell walls. The adhesives in the wall should reduce dimensional changes with variations in moisture and, consequently, should reduce bondline stress. In summary,
adhesive penetration of the cell walls could play some role in the strength of those walls and the adhesive bond, but that role has not yet been determined.

Most discussions about wood bonding have used general adhesion models; however, these models should be adjusted to reflect the particular characteristics of wood that make it different from most other substrates. The mechanical aspects of adhesion are divided into mechanical interlock and diffusion. For wood, mechanical interlocking could be a significant factor. Certainly, given the porous nature of wood (hollow cells) and the likely fracture of cell walls, mechanical interlock can occur in many places in wood as compared to other types of substrates. Although diffusion of organic adhesives into the substrate does not occur with metals and occurs very infrequently with organic adherends, the wood cell wall is porous enough that some adhesives can penetrate it, as discussed in the previous paragraph. Because a number of adhesives penetrate into the wall, the diffusion of low molecular weight material on a molecular level, followed by polymerization, can generate nanoscale mechanical interlock.

The chemical aspects of adhesion involve interfacial interactions between the adhesive and wood. Van der Waals interactions certainly occur, because for an adhesive to bond, it is necessary to have molecular-level contact. Any chemical that is near another on a molecular level exerts a van der Waals force. The adhesive strength of van der Waals forces has been shown to be significant by the ability of geckos to walk vertically or upside down on almost any solid surface (Autumn et al. 2002). Because most wood adhesives and the wood itself are polar, dipolar interactions should take place between the adhesive and the wood. In addition, because of the polar nature of most adhesives and wood, polar bonds, such as hydrogen bonds, should also take place as well as acid–base interactions in some cases.

The interfacial mechanism that is still open to considerable controversy is the presence of covalent bonds between the adhesive and the wood. A number of people have speculated that covalent bonds occur, but the proof is weak. The other chemical model is electrostatic attraction, which generally does not occur during bond formation but could occur during bond fracture. Thus, electrostatic forces are not really a general aspect of adhesion but are more an aspect of separation. In summary, many adhesion concepts need to be evaluated in consideration of the difference between wood and other substrates, such as metals and plastics.

### Analysis of wood bonds

Wood is an unusual material in that it has many different spatial levels of structure. Therefore, adhesive bonding and de-bonding need to be evaluated at different spatial levels (Frazier 2002). For the purposes of this chapter, I have divided the spatial levels of examination into three tiers: macroscopic, micrometer, and nanometer. The macroscopic tier is at the millimeter or larger level that can be seen with the naked eye. In the bonding process, wood is examined for defects and damage to the surface during preparation, such as the crushing of cells. At this level, wetting is measured and percentage of wood failure is determined after bond fracture (ASTM 1999). On the micrometer level as observed with the scanning electron microscope, the concern is wetting of the lumen walls and failure within the adhesive and wood interphase regions. On the nanoscale level, one area of study is the penetration of adhesives into the cell wall.

On the macroscale level, areas of concern in the de-bonding process are the applied stress, typical fracture analysis, delamination, and visual failure (River and Minutti 1975). The applied stresses are normally macroscopic, but internal stresses are visible on a smaller level. The micrometer scale is
where the fracture is influenced by the cell structure. The nanoscale is the level at which fracture actually begins and is propagated.

One tier that has not been discussed as much as it should for wood bonding and de-bonding is the cellular level. Because wood structure is really based upon cells joined together, it is appropriate that adhesion and adhesive strength are considered at the cellular level. Changes that occur during surface preparation, such as fracture of surface cells and crushing, are important and have been examined in relation to weak mechanical layers (River et al. 1991). The examination of wood has involved transverse wood sections and not the actual bonding surface of the radial or tangential planes. At this level, adhesive penetration into cells near and far from the bondline has been measured. However, it is important for failure analysis to investigate this stress distribution and concentration on the basis of what is happening at the cellular level, as will be discussed later. In addition, the failure within the cell walls after fracture has been examined on only a limited basis (Saki 1984).

The nanoscale level is generally the most difficult to examine. Certainly any adhesive bonding occurs at this level, whether it is van der Waals forces, dipolar interaction, hydrogen bond, or actual chemical bonds. It also should be noted that in the construction of cell walls, the diameter of the cellulose fibers, hemicellulose domains, and lignin domains are generally on the scale of tens of nanometers. This is the level at which fracture propagation and bond breaking actually take place.

To elaborate further on the importance of examination at the micrometer level, a schematic of the structure of wood surface as viewed in the transverse plane is shown in Figure 18.2. This cross-sectional view of surface cells shows that the cells are joined by the middle lamella and are composed of the primary cell wall and the S$_1$, S$_2$, and S$_3$ layers; some surface cells also have a warty layer next to the S$_3$ layer. The bonding surface of wood can be generated by fracturing the middle lamella, fracturing any of the cell wall layers, or fracturing across the cell walls to open the walls of the lumen. In fact, because the earlywood cells of some woods have very thin walls that are easily split in a longitudinal trans-wall mode, the lumen walls can constitute up to 80% of the bonding area. Thus, the chemical structure of the warty layer is very important for understanding bonding.

The literature indicates that the warts consist of highly cross-linked lignin (Baird et al. 1974), but in some cases the S$_3$ wall is also exposed, which is rich in cellulose. A highly lignin-rich surface should provide less hydrogen bonding than does a cellulose or hemicellulose layer. However, if the S$_3$ layer is exposed, then this surface is likely to be highly cellulosic. It is not clear what fractions are exposed in split cell walls. Splitting in the middle lamella exposes a lignin-rich layer. Areas

![Fig. 18.2 Schematic of wood bonding surface from transverse view.](image)
that are worth further exploration are the chemical nature of the wood surface and a more detailed understanding of the morphology at the wood surface. This knowledge is important to be able to characterize how the adhesive interacts with the surface.

Another area that is not clearly understood is how much adhesive bond strength is derived from true interface contact and how much is derived from penetration of the adhesive into the walls and bonding to the wood components. Penetration of adhesive into the cell wall could be either mechanical interlocking at the molecular level or reinforcement of the surface cell wall structure by an intelpenetrating polymer network. Studies have concentrated on interfacial interactions and the role of extractives. Extractives may not play a large role since some adhesives can solubilize extractives, exposing the cell wall for adhesive bonding. Solubilization is less likely in the case of overheating that changes the cell wall itself (Christiansen 1990, 1991).

Another issue is how well the cell wall layers bond to each other compared to the adhesive bond to the wood. If the adhesive bonds to the warty layer, how well is the warty layer attached to the $S_3$ layer or the $S_3$ layer bonded to the $S_2$ layer? It has often been assumed that the adhesive bonds to cellulose. However, isn’t it more likely to bond to the lignin or hemicellulose portion since much of the cellulose is tied up in crystalline domains? To understand why some adhesives are better than others, we need to understand interactions at the molecular level.

**Real bonding surfaces**

The normal appearance of a wood surface is not that of a carefully microtomed scanning electron microscopy (SEM) specimen, but it is important to understand what the real bonding surface looks like (Wellons 1980). Figure 18.3 shows a freshly planed tangential softwood surface. The surface of softwoods has many cells that are split open for good access of the adhesive, but it also has much debris that could serve as failure points. It is not surprising that in normal planing, surface cell walls tend to fracture unevenly and generate debris that can result in a weak bonding area. In the hardwood

![SEM of southern yellow pine tangential surface](image-url)
surface shown in Figure 18.4, the surface is less open for bonding since the ray cells are sealed and the fiber cells are small. Thus, longitudinal surfaces are often not open to adhesive penetration. In fact, most open areas in hardwoods are vessels. Thus, there are areas of poor penetration and good penetration, making stress distribution very uneven.

Next, it is important to consider the sites where failure can occur. True adhesive failure, that is, interfacial failure, occurs along a very contorted path that involves the lumen walls and the edges of the cells. Normally, the percentage of wood failure is determined visually using limited magnification (ASTM 1999). However, cracks in a layer of adhesive near the surface, where stress is concentrated, can appear to be bondline failure. Cell wall failure can also occur by separation of the warty layer from the $S_3$ layer or the $S_3$ layer from the $S_2$ layer, or by failure within the middle lamella. All of these, in a visual observation, would appear to be 0% wood failure, but they are interphase failures, not true adhesion failure. Thus, a number of modes for failure need to be understood. The changes in an adhesive formulation to solve an adhesion failure would be quite different from those needed to solve an interphase failure.

**Examination of epoxy failure modes**

One test that has been used extensively for determining the durability of wood bonds is ASTM D 2559 (ASTM 2004). This test involves repetitive cycles of vacuum pressure soaking followed by rapid heating at 65°C. These cycles cause great stress within the bondlines. First, the soaking cycle can cause greater expansion of the wood than that of the adhesive. Second, the rapid drying does not allow the stress relaxation of the wood, resulting in extensive cracking within the wood. In addition, warping of the wood can cause high normal (Type I) forces on the bondline.

Epoxies do not give highly durable wood bonds (AITC 1992). This is quite surprising given their ability to give durable bonds to metals and plastics. The literature suggests that the failure of epoxy–wood bonds is interfacial, given the low percentage for wood failure values, but we have found otherwise (Frihart 2003). To determine where failure may occur on a finer scale, we have
exposed delamination sections of ASTM D 2559 (ASTM 2004) specimens by cutting laminated pieces vertically to expose the failed surface. Visual examination of the failed bondlines revealed two apparent types of surfaces, one containing a film of the adhesive ("adhesive" surface) and the other containing many characteristics of wood ("wood" surface).

The "wood" surface is different from bare wood in a number of ways. First, when the "wood" surface is held under light at different angles, it is glossier than bare wood; thus, there is likely a thin coating on the wood. Second, the "wood" surface has a more brown character than bare wood, probably from the interaction of the adhesive. Third, the "wood" surface has weak yellow fluorescence under long-wavelength UV light, as compared with bare wood. The fluorescence is typical of the epoxy and suggests the presence of a very thin epoxy coating. Light microscopy of the "wood" surface reveals small beads of adhesive. Staining with para-dimethylaminocinamaldehyde generally shows a reddish characteristic of reaction with amines, while bare wood only acquires a grayish cast within a couple hours after treatment. SEM shows that many lumens are filled with adhesive, indicating that the failure is within the epoxy (see Figure 18.5 compared to Figure 18.3). Although it is hard to clearly identify wood from epoxy components, the "wood" surface apparently has a thin coating of adhesive. This surface is different from wood that has been exposed to water soaking and drying conditions. Many small fragments appear on the epoxy side ("adhesive" surface) of the failure, which are probably fragments from the planed surface.

The top image of Figure 18.6 shows a possible model of the effect of swelling at the cellular level. Exposure of wood to water soaking is expected to cause the cells to expand tangentially and radially. This lateral expansion across the tangential plane causes the wood cell walls to tend to separate from the adhesive, which is not undergoing similar expansion. Thus, high concentrations of stress occur along the wood cell walls and the wood-adhesive interface. This tension can be relieved by fracturing the adhesive, the wood-adhesive interface, or the wood cell walls. It is well known that epoxies have very low tensile elongation; thus, epoxies are likely to fracture from tensile strain.

On the other hand, if the adhesive or primer stabilizes the surface cell walls and so limits expansion, less stress concentration occurs (Figure 18.6, bottom image). Consequentially, the stress may not be great enough to exceed the tensile limit of the adhesive. This raises the question as to how the
adhesive or primer can alter swelling. One idea is that the adhesive or primer penetrates into the cell wall during application when the wood is in a swollen state from the water in the adhesive or primer. If the adhesive displaces the water in the cell wall, the wood surface is unable to shrink. Since the wood is fixed in the expanded state, it does not shrink or swell as much under moisture changes. Another idea is the formation of an interpenetrating polymer network. Cross-linking of the adhesive occurs in the wall to form a grid, which limits cell wall expansion. This dimensional stabilization of the cell walls would allow some adhesives that cannot withstand much dimensional change to pass the durability tests that involve swelling in water, compared to a situation in which cell walls have not been stabilized.

**Bonding to acetylated wood**

In addition to using the epoxy fracture studies for developing an adhesion model, a second program that added support to the concept focused on bonding of acetylated wood. Acetylation converts the exposed hydroxyl groups to acetate groups, which reduce moisture absorption and associated dimensional changes. Acetate groups will form hydrogen bonds with hydrogen donors, but the bonds tend to be weaker than those formed by alcohol groups, which are hydrogen donors and acceptors. Therefore, the theory is that acetylation should decrease adhesion strength. This hypothesis depends on the surface attraction (that is, adhesion) dominating bond strength. However, if the wood or the adhesive
interphases are the weaker links in the chain, then the alteration of the surface functionality may not alter bond strength. Examination of the bond strength of acetylated wood provides insight into the relative importance of thermodynamic adhesion relative to viscoelastic dissipation in bond durability.

These experiments were done under conditions as comparable as possible to those in previous work (Vick and Rowell 1990). We modified yellow-poplar strips by a high level of acetylation and bonded them using bonded, untreated wood as the control. In addition, we tested both planed and unplaned acetylated wood. Unmodified groups may be present on the surface of planed wood, whereas the surface of unplaned wood should be fully acetylated. The specimens were then tested for compressive shear by ASTM D 905, using both dry and wet tests. From the thermodynamic work of adhesion, we expected that the lowest bond strength for the epoxy adhesive should for unplaned acetylated wood. However, the unplaned acetylated wood had higher bond strength and a higher percentage of wood failure than did the planed untreated and acetylated wood samples (Figure 18.7). Thus, the simple act of planing the acetylated surface, which probably freed unmodified hydroxyl

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**Fig. 18.7** Shear strength and percentage of wood failure for epoxy-bonded yellow poplar using ASTM D 905. CE is planed, untreated wood surface; PE, planed acetylated surface; UE, unplaned acetylated surface.
groups, created a weaker interphase that led to a great extent of bondline failure. The wet strength of the control was also low, because this untreated wood expanded and contracted to a greater extent than did the unplaned acetylated wood. These data support the previously proposed model. Expansion causes the wood cell walls to tend to separate from the adhesive, and the strain exceeds the tensile elongation of the epoxy. Thus, viscoelastic energy dissipation plays a significant role in bond durability.

In contrast, our experiments with resorcinol formaldehyde (RF) adhesive showed very little difference in the percentage of wood failure whether the wood was wet or dry, acetylated or unacetylated, or planed or unplaned. All specimens bonded with RF adhesive had a high percentage of wood failure. Thus, variation in shear strength of bonded assemblies is a measure of the strength of the wood itself. The RF adhesive stabilized the wood surface so that water soaking did not overstress the bond. This result could also be due to the fact that the swelling rate of RF adhesive and wood is similar (Muszynski et al. 2002).

The next area to be considered is the role of hydroxymethylated resorcinol primer (HMR), which has been used to improve the durability of bonds in hard-to-bond wood, especially with epoxy adhesives (Vick et al. 1996). The original role of the HMR primer was thought to be one of providing a covalent link between the wood and the adhesive (Vick et al. 1995); thus, it was referred to as a coupling agent. On the other hand, our studies have allowed us to develop another model, in which the HMR serves to stabilize the wood by forming an interpenetrating polymer network or cross-linking of the wood cells (Christiansen 2003). This stabilization of the surface cells reduces their ability to expand and contract and thus reduces the stress on the adhesive. Given the complexity of wood, both morphologically and chemically, this model needs further validation.

Conclusions

The bonding of wood is a complicated process. The particular characteristics of wood surfaces need to be studied in detail and existing models of adhesive bonding and bond failure need to be further elaborated in light of the characteristics of wood. To do this, we need to consider that the adhesive bonding area of wood is greater than that of most substrates as a result of the macroscopic porosity of wood cells. The adhesive can flow into these pores to develop large regions of mechanical interlocking. In addition, fractures in wood surface cells lead to additional penetration of the adhesive and more regions of mechanical interlock. Some adhesives penetrate the cell walls to provide microscopic fingers of adhesive that cross the interface. The adhesive in the cell walls can be characterized as nanoscale mechanical interlocking. Thus, there are many more modes for enhancing the mechanical bond strength at or near the interface for wood than for most other substrates.

Determination of bond strength is not limited to bond formation. It is important to remember that adhesives are defined in a mechanical sense. Bond strength is dependent on the concentration or distribution of internal forces, such as expansion and contraction of the wood in addition to applied forces. Further work is needed to understand the internal forces at work in tests such as ASTM D 2559 and D 905.

From the examination of epoxy wood bond failure as influenced by water soaking and drying cycles, we have determined that the failure mode is most likely within the epoxy layer close to the surface. A proposed model is that expansion of the wood cells causes a tensile strain greater than the epoxy can withstand and causes fracture of the epoxy. One possible explanation for the ability of hydroxymethylated resorcinol (HMR) primer to improve adhesive bond strength is that it reduces this
expansion of the wood. Another hypothesis is that HMR bulks up the wood, altering the selectivity of absorption of the adhesive components and resulting in incomplete cure of the epoxy.

In another set of experiments, we have examined epoxy bonding of acetylated wood. Acetylation results in more wood failure under water soaking conditions compared to failure of unacetylated wood. Planing of acetylated wood resulted in bonds with low wood failure when wet. These results are not easy to understand from a normal surface bonding aspect because acetylation should reduce hydrogen bonding between the adhesive and the wood. However, the data are more consistent with the stress concentration model, where the acetylated wood expands less at the surface than it does in the other two cases.

Application

The results discussed in this chapter have revealed the need for further study of wood bonding on the macroscopic, microscopic, and nanoscale levels to understand how adhesion takes place and how fracture occurs. Given the complexity of wood, this requires the development of more sophisticated techniques to investigate the processes of both bonding and de-bonding. More knowledge about wood and adhesive interactions can lead to the systematic design of improved adhesives.

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Characterization of the Cellulosic Cell Wall

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