Why Do Some Wood-Adhesive Bonds Respond Poorly To Accelerated Moisture-Resistant Tests?

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Abstract
The most challenging part of developing acceptable adhesives for wood bonding often is to create a bond that will withstand exposure to wet conditions or wet/dry cycles. Products that pass these tests have been developed empirically, but the aspects that make it difficult for adhesives to pass these tests and systematically ways to develop more durable adhesive bonds have not been researched. The first aspect is that the swelling strain of wood can impart sufficient force to contribute to the bond fracture if interfacial strain between the adhesive and wood is not dissipated through the interphase regions. The second aspect is that adhesives for wood bonding fall into two groups (*in-situ* polymerized and pre-polymerized) based upon their chemical–structure–property relationships and their abilities to interact with wood cell walls. The *in-situ* polymerized adhesives are typically rigid monomers/oligomers that form the polymer backbone and numerous crosslinks after application to wood. Some of these adhesives can enter into cell walls and stabilize the wood interphase region to decrease interfacial strain. Pre-polymerized adhesives usually have only a low degree of reaction after application as well as flexibility in the backbone. Because these polymeric adhesives are generally too large to stabilize wood cell walls, they need to dissipate interfacial strain between the wood and adhesive through the adhesive interphase region. If adhesives do not form interphases that distribute strain, they are more likely to fail as wood swells upon absorbing moisture.

Keywords: wood, adhesives, durability, strain, stress, models

Background

For most wood bonding applications, the assembly needs to pass some test involving large changes in moisture content (1, 2). Although the literature contains considerable performance data, our understanding of how moisture changes influence bond performance is more limited (1). Usually, the emphasis has been on bond failure when wood shrinks as the wood moisture content is decreased because this is when delamination and wood cracks are easy to observe (2). However, wood swelling under increasing moisture conditions often leads to poor integrity of the bond (3, 4). In fact, most existing tests have only a wood swelling step as part of the wood bond performance criteria and those tests are typically administered when the failure is initiated. Thus, we wanted to better understand the failure mechanism and to determine if various adhesive types respond differently. Examination of the literature and the results of our studies led to the aspects that define the failure mechanism and allows grouping of adhesives.

The first aspect relates to the importance of appreciating that the greater swelling of wood compared with adhesive leads to a strain at the adhesive–wood interface. The second aspect is the knowledge that adhesives have different ways to distribute this strain so as to decrease the interfacial stress. Understanding details of the swelling of bonded assemblies helps to explain the results observed with different adhesives and wood species under different test conditions.

Aspect #1: Stress from Differences in Swelling Strain

Research demonstrates that as wood swells and shrinks, these dimensional changes can decrease the integrity of adhesive bonds (1), but these effects have generally not been examined to determine how and why these changes alter bond strengths. For this paper, we discuss only the wood swelling process because this can be the hardest on the bondline. Mankind has found that drying wood increases its lifespan and strength, making it especially useful as a building material. However, wood shrinkage during drying is mainly reversible if the wood is exposed to higher moisture conditions. Wood is generally bonded in a low moisture state (< 8%). Thus, when exposed to higher moisture levels, wood expands. Given the anisotropic nature of wood, this expansion is directionally dependent. On the other hand, adhesives for wood bonding have very limited swelling ability and are usually relatively rigid to resist bond creep. Most importantly, an adhesive needs to resist the wood swelling force or bond failure will result (Figure 1).

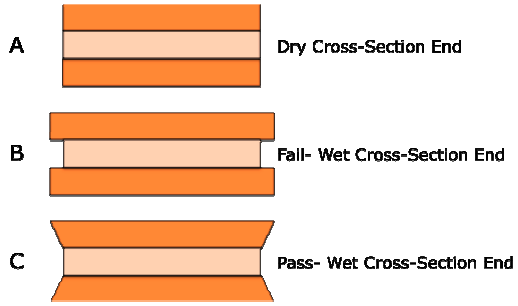

Figure 1. When a bonded assembly **A** of an adhesive layer between two wood layers is exposed to moisture, the wood expands more than the adhesive. If the wood can not deal with this expansion difference, the bond fails as in **B**. Successful adhesives **C** withstand the expansion difference

Thus, the difference in hygroexpansion causes wood to exert a pulling force (tensile strain) on the adhesive, while the adhesive exerts a restricting force (compressive strain) on the wood at the interface, where the adhesive is adjacent to the wood cell walls. The interphase also includes areas adjacent to the interface where properties of either the wood or adhesive are different than the bulk wood (1, 5). Figure 2 gives an illustration of different domains where we distinguish between the adhesive and wood portions of the interphase. If this strain differential is concentrated at the adhesive–wood interface, a considerable and often harmful stress develops.

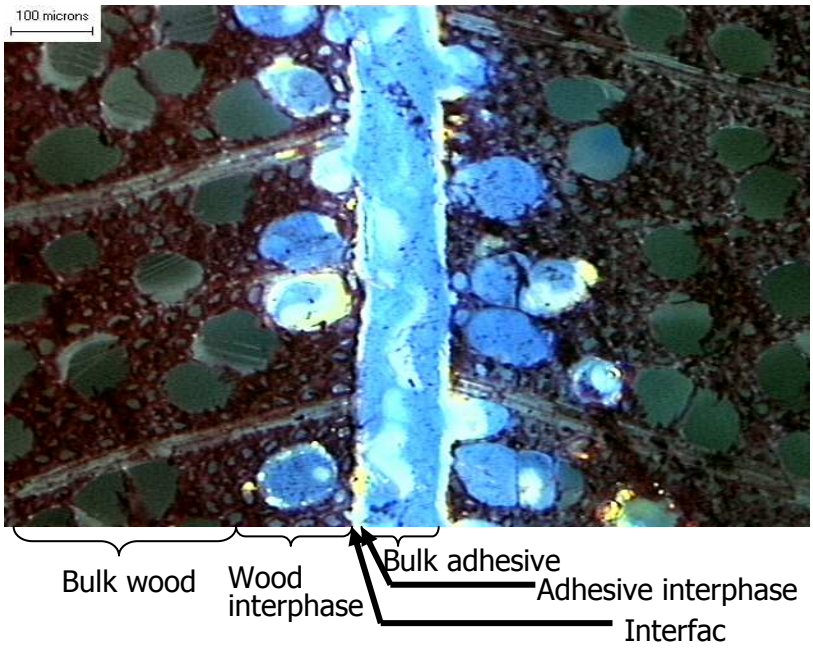

Figure 2. Epoxy /yellow-poplar bondline cross-sectional view using fluorescence spectroscopy showing the different regions of the bondline.

Although wood swelling stresses exist, the forces have been difficult to quantify. To measure the force of the swelling of wood, the wood needs to be restrained. A wood swelling force as high as 8 MPa for beech has been claimed (6), although a more recent study reported a much lower value (1.2 MPa) for spruce (7). Despite these differences, the swelling stress adds to the initial internal stress created by adhesive shrinkage during bond formation because of loss of solvent and polymerization by chain extension and crosslinking. Determining this internal stress is also difficult. One study was been aimed at measuring the wood swelling force on an epoxy adhesive (8). In work with new soy adhesives using 8-mm maple veneer with a 20-mm lap shear bond area, Wescott and others found that adhesives with a wet shear strength for a bonded assembly below 1.4 MPa always failed a three-cycle wet-dry test, whereas adhesives bonds stronger than 2.0 MPa always passed the three-cycle wet-dry test (9). Those with in-between values sometimes passed and sometimes ruptured during the three-cycle soak. Gillespie has shown that seven adhesives [poly(vinyl acetate), crosslinked poly(vinyl acetate), phenol–resorcinol–formaldehyde, gap-filling phenol–resorcinol–formaldehyde, casein, urea–formaldehyde, and epoxy] were adversely influenced by the wood swelling from 10 to 30% equilibrium moisture content for sugar maple and eastern white pine (3). We have found that with an epoxy adhesive, wood species with greater swelling tendencies gave more bond failure (4). Although determining actual internal stresses on the bond is difficult, many studies have shown that enough stress exists from swelling to decrease the bond integrity (1–4).

Although wood swelling is well known to put internal stresses on the bondline (3), the location and concentration of these stresses have not been fully appreciated. Normally, the expansion difference between two bonded materials is concentrated at the interface between two materials, unless some means can distribute it elsewhere. Although the adhesive–wood interphase is complicated because of the cellular structure of wood and the ability of adhesives to penetrate into the wood, there is still an interface where the adhesive bonds to the cell wall. This swelling can produce a large strain on the adhesive near the wood surface, whether examined on a macroscopic (Figure 1) or cellular level (Figure 3).

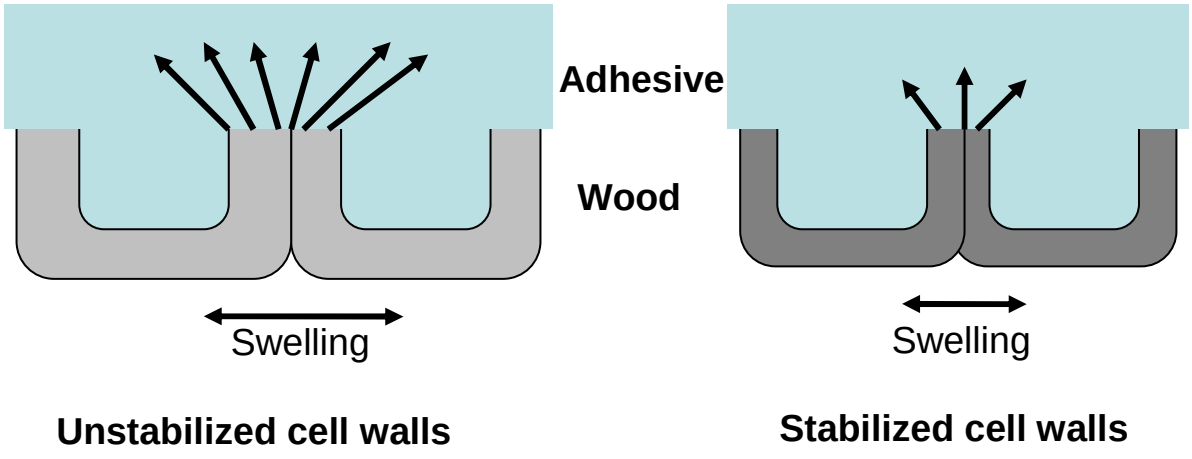

Figure 3. On the left, the unaltered (unstabilized) cell walls expand greatly at higher moisture levels and put high localized stress on the adhesive. On the right, the cell walls are altered (stabilized) to minimize this expansion and the localized stresses are lower.

As is illustrated in Figure 3, one way to decrease interfacial stress is to restrict the swelling of the wall near the interface. As will be discussed in the next section, some adhesives are known to infiltrate into cell walls and decrease their swelling. With other adhesives, this is not likely because

they are too high in molecular weight or too large in hydrodynamic volume to infiltrate into cell walls.

This first aspect emphasizes the importance of interfacial strain caused by moisture swelling the wood much more than the adhesive; the more the wood swells, the greater the bondline strain. This strain, if localized at the interface, can lead to adhesive bond failure; however, distribution of the strain as a gradient in either the wood or adhesive interphase can improve bond durability as will be discussed in the next section.

Aspect #2: Adhesive Groups and Bondline Properties

Wood adhesive literature either tends to lump wood adhesives as a single group or treats every adhesive individually. Does this make sense based upon what we know about them? The similarities and dissimilarities of these adhesives need to be examined. Do they all have comparable molecular weights or distributions? No, many of the more common adhesives are applied as monomers or oligomers that then polymerize after application. The others are generally applied as highly formed polymers that then undergo a limited number of reactions (generally crosslinking or chain extension) after application. Do all of these adhesives interact with wood in the same way? With sufficient pressure and time prior to curing, all these adhesives are expected to flow into the available lumina. However, some adhesives contain components that can also infiltrate into the cell walls. Research has shown that some of these adhesives will alter the cell wall properties as a result of this penetration. Do adhesives all have similar mechanical properties? Many of the common polymers have a rigid backbone and are highly crosslinked. Others have a more flexible backbone and are lightly crosslinked, if at all. The interesting aspect is that all these issues can be addressed by combining adhesives into two groups (10). Group 1: The *in-situ* polymerized adhesives, which are made up of monomers and oligomers, can penetrate and may modify cell walls and are generally rigid polymers with a high degree of crosslinking. Group 2: Pre-polymerized adhesives are mainly preformed prior to application, are too big to infiltrate cell walls, and have flexibility in the backbone with light crosslinking.

Group 1: In-situ polymerized adhesives

Many of the larger volume wood adhesives fall into this group of wood bonding. Phenolics (phenol–formaldehyde, resorcinol–formaldehyde, and phenol–resorcinol–formaldehyde) and amino resins (urea–formaldehyde, melamine–formaldehyde, and combinations of these) are the main adhesive types in this group. The group also includes the polymeric diphenylmethane diisocyanate (pMDI) and epoxy adhesives. These adhesives are mainly used for making primary wood-bonded products, such plywood, oriented strandboard, medium density fiberboard, and particleboard. Detailed discussion of phenolics and epoxies is covered elsewhere (1).

Amino resins involve three raw materials: urea, melamine, and formaldehyde, which provide a rigid backbone and a high degree of crosslinking. The rigidity of melamine is clear with the reactive amino groups attached to an aromatic ring containing three nitrogen groups (11). With three exocyclic primary amine groups that can each react with two formaldehyde molecules, melamine has ample opportunity for providing a crosslinked adhesive. Urea can also form highly crosslinked structures by adding multiple formaldehydes to its two nitrogen groups. Their stiffness is increased because there is limited rotation around the carbon-nitrogen bonds, a result of resonance interactions with the carbonyl of urea. These polymer backbones and crosslinks involve reaction of formaldehyde to generate methylene bridges that have limited flexibility. In fact, research has been done on making urea–formaldehyde adhesives less brittle to limit adhesive fractures (12, 13). Thus, these adhesives are unlikely to distribute much of the interfacial strain though the adhesive

interphase. On the other hand, these adhesives are generally low enough in molecular weight to infiltrate into the cell wall, prior to crosslinking, and to change cell wall properties in the wood interphase region after curing. Studies have shown that melamine–formaldehyde resins do stabilize the wood cell wall both by lowering the swelling tendency and by improving mechanical strength (14, 15). Thus, the amino resin can have enhanced water durability, because the wood interphase region distributes the swelling strain.

Polymeric diphenylmethane diisocyanate (pMDI) is another member of the *in-situ* polymerized adhesive group. The name is somewhat confusing because the adhesive contains mainly monomeric and oligomeric components. These adhesives polymerize by reacting with water to form urea and other linkages (11). Given the aromatic rings and the short chains linking these aromatic rings, it is expected that these adhesives would be quite rigid if the reaction goes to a high conversion. However, an incomplete polymerization, along with the foamed structure caused by carbon dioxide released from the reaction of the isocyanate group with water, could make these adhesives more flexible than expected based upon the polymer structure. Frazier and Ni have proposed that pMDI adhesives form an interpenetrating polymer network (IPN) within the wood cell wall (16); this IPN should stabilize the cell wall to decrease the swelling.

It is valuable to briefly mention epoxy adhesives because, with some exceptions, they usually do not create durable wood bonds (17). Epoxies have been shown to fail in the adhesive interphase (18), which was an important aspect in developing the model of interfacial strain because epoxies are not likely to stabilize wood cell walls. The marginally polar epoxy resin is expected to have low solubility in the cell wall. However, Gardner and others have demonstrated that a hydroxymethylated resorcinol (HMR) wood primer (similar to a resorcinol–formaldehyde adhesive) can dramatically improve the durability of epoxy-bonded wood (19). Frihart and Chandler have found that melamine–formaldehyde primers can also provide a similar improvement in the durability of wood bonds (20). The best information to date is that HMR primer stabilizes wood surfaces, limiting the effect of the swelling stain (21), and we assume that the melamine–formaldehyde primer acts by the same mechanism.

Group 2: Pre-polymerized adhesives

The other group of adhesives used for wood bonding involves mainly pre-formed polymers and, therefore, is grouped as pre-polymerized. These adhesives have high enough molecular weight that penetration into the cell walls is very limited. If the normal criteria of 2000 Dalton molecular weight is considered the upper limit for penetration (22), these adhesives have little chance of entering the cell wall and stabilizing it. Thus, the interfacial strain is high unless it can be distributed through the adhesive interphase. These adhesives are often crosslinked to provide the needed creep resistance, but the degree of crosslinking is low so that there can still be important localized mobility, and therefore the ability to accommodate swelling strains. This group includes polyurethanes and poly(vinyl acetate) covered elsewhere (1), as well as proteins and emulsion polymer isocyanates.

Proteins were the original wood adhesives and are still used today; mainly, where the moisture level changes are small. Because uncrosslinked protein adhesives lose strength and are plasticized at high moisture levels, they have been used in low moisture applications. Soy is considered the most dominant player in the protein adhesive arena and the newer crosslinked soy adhesives are much more moisture tolerant than the older soy adhesives. The protein isolates are very high in molecular weight and even the high-carbohydrate-containing soy flours contain very little low molecular weight compounds. Thus, proteins are unlikely to stabilize wood. However, these adhesives can

absorb some water and increase sufficiently in flexibility to spread the strain through the adhesive interphase; thus, they do have potential of good durability. These adhesives need to have sufficient crosslinking to avoid bulk deformation that would lead to unacceptable creep under load at high moisture levels but sufficient localized flexibility to allow the strain to be distributed into the adhesive. We have found this concept of interfacial strain to be useful for understanding adhesive performance in bonding to different wood species that have different swelling characteristics.

Emulsion polymer isocyanates (EPI) are two-component adhesives based on the reaction of a mixture of water-based emulsions of styrene–butadiene rubber, ethylene vinyl acetate and/or poly(vinyl acetate) with an isocyanate hardener (crosslinker) forming water-resistant bonds. Additionally, isocyanate may provide some reaction with wood, but most likely not enough to suppress wood swelling. However, the water-based emulsion portion certainly provides a localized flexibility to distribute the strain within the adhesive interphase.

Thus knowing the strain induced by the first aspect (the swelling strain of wood contributing to the bond fracture), the researcher needs to consider the type of adhesive that is being used. The second aspect (that adhesives have different ways to distribute this strain so as to decrease the interfacial stress) divides wood adhesives into two groups based upon how they can respond to the swelling-induced strain. To improve adhesive performance, different strategies need to be used depending upon whether the adhesive falls into group 1 or 2.

Evaluation and Use of These Aspects of Wood Bonds

To move to a more systematic development of new adhesive systems, or efficient use of current wood adhesives, the critical aspects of wood adhesive bonds, especially for durability, need to be determined. Thus, we feel that a sequence of steps can help to better understand the adhesive performance and lead to more specific recommendations on improving performance.

The first step is to determine where failure occurs for more adhesive systems. The ASTM method 5266 can be a starting point (23), but it is important to move beyond this to determine where failure takes place in the bondline. Marra developed a system of breaking the bondline into nine domains (both bulk wood, both wood interphases, both interfaces, both adhesive interphases and bulk adhesive) (24). Close examination of failure surfaces using microscopy (light, fluorescence, or electron, with or without stains or dyes) and spectroscopy (infrared, Raman, x-ray photoelectron) are often needed to better understand the main location of failure.

The second step is to understand adhesive properties and adhesive interactions with wood. This can be done by examining the effect of wood species, wood modification, and adhesive formulation on bondline failure. Another approach is to better understand adhesive mechanical properties and whether the adhesive modifies wood at the wood interphase. This can be done using standard mechanical measurements, dynamic mechanical analysis, and nanoindentation.

We have found determining the location of bond failure and adhesive–wood properties useful in planning future experiments both for fundamental and applied programs. We have been comparing results expected from these evaluations to those expected for the durability of bonds for both modified wood and different wood species with a select group of adhesives (4, 25). We have used the concepts of the model to develop new methods for faster screening of new adhesives (9). We have used these models to understand the bonding of different wood species with soy adhesives. In some recent work with developing new soy adhesives for the engineered wood flooring market, we were able to use this model to produce finished panels with excellent moisture resistant properties.

Summary
Given that we have wood adhesives that perform well, it is easy to assume that a more detailed understanding of their performance may not seem necessary. However, the lack of generalized methods to evaluate wood adhesives means we must empirically test adhesives for each application and wood species. Optimization often requires a large amount of reformulation. This paper presents aspects that need to be evaluated and that will help to guide and streamline the process of choosing the proper adhesive for each application.

The first aspect emphasizes the nature of interfacial strain moisture causes the wood to swell much more than the adhesive. The more the wood swells, the greater is the bondline strain. This strain, if localized at the interface, can lead to adhesive bond failure; however, distribution of the strain as a gradient in either the wood or adhesive interphase can improve bond durability.

The second aspect proposes that wood adhesives can be divided into two groups based upon their structure-property relationships and their interactions with the wood. The *in-situ* polymerized adhesives are made up of the monomers and oligomers, can penetrate and may modify the cell walls, and are rigid polymers with a high degree of crosslinking. The pre-polymerized adhesives are mainly preformed prior to application, are too big to infiltrate the cell walls, and have flexibility in the backbone with light crosslinking.

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