MODEL FOR UNDERSTANDING THE DURABILITY PERFORMANCE OF WOOD ADHESIVES

Charles R Frihart
cfrihart@fs.fed.us
USDA Forest Service, Forest Products Laboratory
Madison, Wisconsin U.S.A.

Introduction

Wood has been bonded for thousands of years, but it has been only for the past 100 years that structural wood bonds have been obtainable. Furthermore, structural wood bonds with exterior durability have been available for about 60 years. The development of new or improved adhesives for these applications has been hindered by having only limited wood bonding models that encompass both chemical and mechanical aspects. Developing a general wood bond model has been difficult because of the structural and chemical complexity of wood across the spatial scales from nanometers to meters and the wide variety of adhesive chemistries. Most adhesives readily form strong wood bonds, but few adhesive bonds are able to withstand accelerated aging tests involving water exposure. The specific tests depend upon the product; however, water saturation of the bonded assembly has been generally considered important to determining bond integrity over the useful life of the product. Some tests involve placing the assembly in room-temperature or boiling water, followed by oven drying to look for delamination in the bondline. Others involve testing of wet samples for shear strength and area percentage failure in the wood or measuring internal bond strength. These tests were developed because the swelling and shrinking of wood with changes in moisture content lead to strong forces on the bondline. These forces are usually a shear mode in the bondline plane but can also involve normal forces (perpendicular to the bondline) due to warping of wood as it dries (Figure 1).

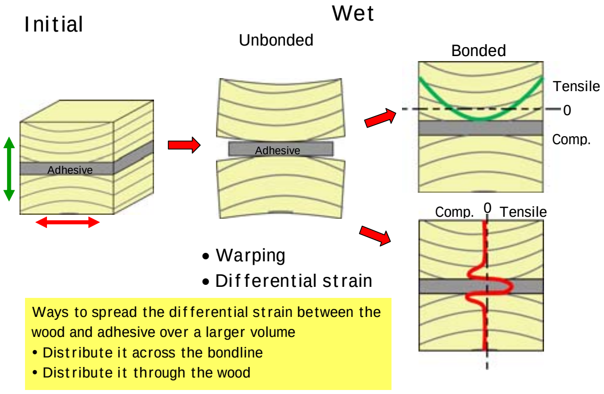

Figure 1. Swelling bondline stress. Wet conditions cause wood to swell and deform, but when restrained by an adhesive bond, they cause shear and normal stresses to occur in both the wood and adhesive.

When dry wood is placed in water, the water not only fills the lumen (void in the cells) but also diffuses into the cell walls, causing them to expand. Although the wood becomes weaker via this cell wall plasticization, failure generally increases in the bondline rather than in the wood under wet conditions. Thus, the question is why water exposure often causes a greater decrease in bondline strength than in wood strength. In a few cases, such as uncrosslinked poly(vinyl acetate), bondline failure comes from the adhesive's decreased structural integrity because of plasticization under wet conditions . For others, such as epoxies, an explanation for bond durability had not been determined prior to our recent study (1). An important aspect of our work was to determine the main failure location within the bondline and the main reason for the failure (Figure 2). This study showed that epoxy failure was mainly in the epoxy interphase adjacent to the wood surface (Figure 3). This and other studies using chemically modified wood (2) and a hydroxymethyl resorcinol primer (3) have led to the model of high interfacial strain between wood and adhesive being a critical parameter for bond durability. Wood swells going from dry to wet conditions, whereas most adhesives do not; therefore large internal stress can be generated at the bondline (4). How well wood adhesives deal with this stress caused by differential expansion and contraction has led to part of a more comprehensive chemical–mechanical wood adhesion model. An aspect of this model is in understanding how adhesives successfully deal with this difference in strain under wet conditions

Discussion

Developing a more comprehensive wood adhesion model requires an understanding of why wood has unique aspects as a substrate for bonding. Normal bonding mechanisms, such as mechanical interlocks with surface roughness and chemical interactions, apply to adhesively bonded wood. Surface roughness and exposed lumens allow for greater mechanical interlocking and more chemical bonds than are available for a typical bonding surface. Hydrogen bonding should be common, given the hydroxyl functionality of both cellulosics and lignin in the wood and the polar groups present in most wood adhesives. In addition, these adhesives interact below the exposed wood surface because of adhesive flow into the empty cells (lumens) and pits connecting these lumens. In some cases, adhesives are known to also diffuse into the cell wall

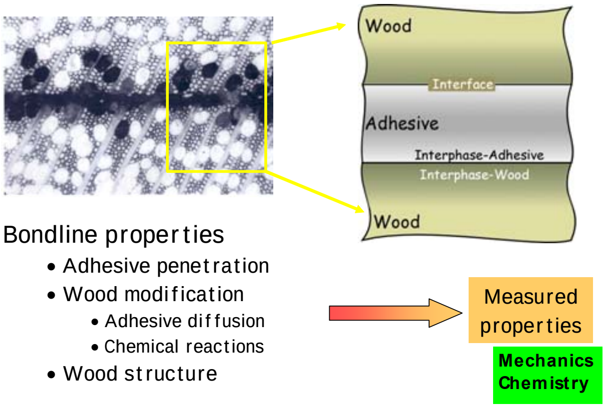

Figure 2. The wood bondline needs to be divided into zones of failure, and the causes of failures in these zones need to be understood from both chemical and mechanical bases.

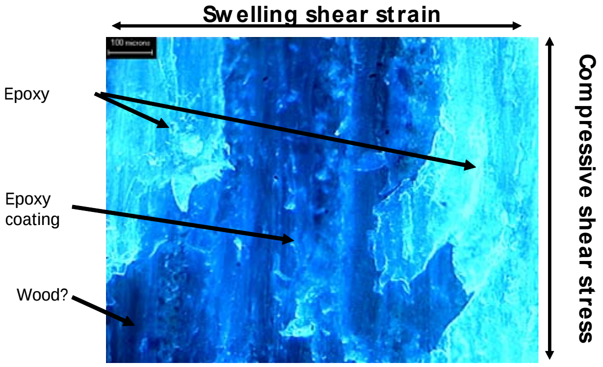

Figure 3. Failure of an epoxy bond looking at the failure surface, showing different failure locations, with the bondline. Swelling stress develops from the wood absorbing water, and compressive shear is the externally applied force.

polymer matrix (4). Thus, many modes are available for adhesives to interact well with wood, compared with other substrates such as metals and plastics.

If these adhesives have so many ways to interact with the wood, why do wood bonds fail? As moisture levels change, cell walls expand or contract. Thus, in addition to normal internal stress from setting of the adhesive, large additional internal stresses can result from the dimensional change of the wood, as illustrated in Figure 1. Absorbed water may also disrupt hydrogen bonding between the wood and adhesive, especially if these bonds are weakened from the differential swelling pulling the bonds apart. Consequently, the difference in swelling and shrinking between the wood and the adhesive will cause high interfacial stress if the assembly cannot find a way to distribute this strain.

Given the wide variety of adhesives used in wood bonding and the wide variety of ways that they can interact with the wood, a single factor model to explain the difference between a durable and non-durable bond is not likely to be successful. Thus, a more comprehensive model of wood bonds is needed to encompass different adhesives, especially in the evaluation of durability. As part of this model development, the question arose as to whether all adhesives respond in a similar fashion to differential swelling strain. I believe that wood adhesives can be classified into two main groups based upon their mode of setting and the polymer topology and morphology of the cured resin: (a) those that polymerize *in situ* from monomers or oligomers and (b) those that are pre-polymerized (polymerized prior to application) and may be crosslinked during setting.

The *in situ* polymerized resins consist mainly of phenolics [phenol formaldehyde (PF) and resorcinol formaldehyde (RF)], aminoplastics [urea formaldehyde (UF) and melamine formaldehyde (MF)], epoxies, and isocyanates, such as polymeric diphenylmethane diisocyanate (pMDI). The PF, MF, and UF groups also include all the combinations of formaldehyde adhesives, such as PRF and MUF. These adhesives are generally aromatic and multifunctional, leading to extensive crosslinked networks. Given the stiff backbone structures and the high crosslinked density, these adhesives are generally rigid and brittle, with glass transition temperatures above room temperature. They make good structural wood adhesives because their rigidity limits creep. Given their lack of flexibility, how do these materials respond to the strain differential between wood and adhesive? Many of these, in particular the phenol-formaldehyde and melamine-formaldehyde resins, dimensionally stabilize the wood interphase (5,6). Thus, the wood surface does not swell much compared with the bulk, so the strain gradient is spread across the wood interphase, which is often millimeters thick. The thick and stabilized wood interphase can contribute to low stress at the interface between the wood surface and the adhesive. It should also be considered that when these adhesives make bonds that bridge the adhesive–wood interface, factors such as water weakening of wood–adhesive hydrogen bonds and extractives on the surface are less likely to play an important role in bond durability. However, not all *in situ* polymerized wood adhesives may stabilize a wood surface. In particular, consider epoxies. Even if the epoxy enters the cell walls, it may not stabilize the walls because of their composition: they are made of two components having quite different solubility parameters and can phase separate. However, epoxies form more durable bonds if a wood-stabilizing primer is used (3) or the epoxies contain flexible segments (7). Additionally, using flexible components in UF resins has also been reported to give more durable bonds (8).

The pre-polymerized adhesives consist mainly of poly(vinyl acetate), polyurethanes, emulsion polymer isocyanates, and proteins. These adhesives generally have flexible, aliphatic backbones that may be crosslinked but have long segments between crosslinks. The pre-polymerized adhesives are very different in their topology and morphology when compared with the *in situ* polymerized adhesives. These polymers are generally too large to diffuse into the wood cell walls and therefore cannot stabilize the wood. However, the flexibility of these adhesives allows the strain differential to be distributed more evenly across the adhesive rather than being concentrated at the wood surface–adhesive interface. As these adhesives are made more rigid to develop improved creep and heat resistance, they may lose some of their ability to dissipate the interfacial strain on the macroscopic scale. These adhesives often provide good shear strength when wet, but they often fail in the bondline rather than in the wood. Compared with *in situ* polymerized adhesives, these adhesives have fewer modes of bond formation. There is mechanical interlock on the surface, but not all the adhesives flow well enough to fill the lumens deep in the wood. Some may not even be able to bond to the microscopic roughness of the wood surface, and certainly none of these are likely to penetrate cell walls. Thus, one would expect that these adhesives would be more sensitive to extractives on the surface than are the *in situ* polymerized adhesives; however, this has yet to be shown.

Conclusions

In general, much of the literature on wood adhesives has used a single-aspect model, such as wetting or lumen penetration, to analyze adhesive performance. This approach has little chance of success given the many modes of adhesion, the complexity of the wood substrate, and the wide variety of wood adhesives. Our work in trying to understand the durability of wood bonds has led to a differential swelling strain model that fits well with the literature data (1,4). In understanding how durable adhesives respond to this strain, we need to understand how an adhesive's topology and morphology and its interaction with wood can dissipate the strain to minimize internal stress. As part of developing a more comprehensive wood model, the most common wood adhesives have been divided into two classes, the *in situ* polymerized and the pre-polymerized. Their setting processes, topologies, and morphologies provide different mechanisms for responding to interfacial strain concentration. The differences in these two classes require different routes for improving the performance of an adhesive, depending on which class it belongs to. Furthermore, a more complete understanding of these mechanisms could lead to better ways for developing adhesives that provide durable wood bonds.

Acknowledgments

I thank Al Christiansen, Chip Frazier, and Jim Wescott for their valuable criticisms in developing this more comprehensive model of wood adhesives and Robert Moon for his input and drawings.

References

1. C.R. Frihart, *in* Wood Adhesives 2005 Proceedings, Forest Products Society, Madison, Wisconsin, 2006, pp 241-246.
2. C.R. Frihart, R. Brandon, and R.E. Ibach, *in* Wood Adhesives 2005 Proceedings, Forest Products Society, Madison, Wisconsin, 2006, pp 111-114.
3. D.J. Gardner, C.E. Frazier, and A.W. Christiansen, *in* Wood Adhesives 2005 Proceedings, Forest Products Society, Madison, Wisconsin, 2006, pp 93-97.
4. C.R. Frihart, J. ASTM International, July/August 2005, 2(7), Paper ID JAI12952 (at www.astm.org).
5. W.T. Nearn, Official Digest, Federal Society of Paint Technology, 1965, 37, pp 720–733.
6. F. Miroy, P. Eymard, and A. Pizzi, Holz als Roh und Werkstoff, 1995, 53, p 276.
7 W.Z. Olson and R.F Blomquist, Forest Products J., 1962,12(2), pp 74–80.
8. R.O. Ebewele, G.E. Myers, B.H. River, and J.A. Koutsky, J. Appl. Polym. Sci., 1991, 42, pp 2997-3012.

PROCEEDINGS

30th Annual Meeting

of

The Adhesion Society, Inc.

February 18-21, 2007
Tampa Bay, FL

Anand Jagota, Program Chair

ISSN 1086-9506