Utility of Horioka's and Marra's Models for Adhesive Failure

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Abstract

Bond formation primarily involves adhesive rheology and interface chemistry. Bonded assembly strength, however, primarily involves the viscoelastic dissipation of stress over the entire assembly. Models can aid in the understanding of where and why failure occurs and how to improve the strength of the assembly. Horioka and Marra have both proposed models which define failure zones for wood bonds. Although mechanical property changes from the bulk adhesive to the bulk wood are more of a continuum than the discrete domains used in these models, the location and cause of failure are easier to assess using the domain concept. The suitability of these models is evaluated, and the more applicable Marra model is extended to a failure classification diagram. This diagram is used to discuss the causes of failure and potential solutions, in addition to methods for determining the location of failure. Further development of this classification diagram and improved analytical methods can aid in making more effective bonded wood products.

Introduction

Wood bonding is one of the oldest applications for adhesive assembly of products. Nevertheless, the mechanism of bond failure is not as well understood as are most other adhesive applications. This is not surprising given the complexity of wood; both its structural and chemical complexities hinder the development and evaluation of models for bond formation and fracture. For example, standard adhesion theories, such as surface energetics, chemical bond formation, and mechanical interlock, apply to bond formation with wood, but the unique porosity of wood provides additional aspects for the development of bond strength. These unique aspects of wood need to be considered for the processes of both bonding and fracture.

First, the cellular nature of wood not only provides a significant increase in bondable surface compared with that of most substrates, but considerable surface irregularities may also supply additional sites for crack initiation. Surface roughness is orders of magnitude greater for wood than it is for typical substrates. Lumen walls provide a large surface area for adhesive contact, and swelling of cell walls by aqueous adhesives opens micro-channels, which provide an even larger bonding surface (2). Although wood has very high surface areas, there is limited knowledge about the chemical composition of wood bonding surfaces (7,9,10). The roughness of wood aids in bonding, but it may also promote failure by enhancing interfacial stresses. It is not known how much the fractured wall and normal surface debris serves as stress concentration sites leading to fracture initiation. The images in **Figure 1** show, at different degrees of magnification, the roughness of a wood surface prepared using sharp planer blades. Given the anisotropic nature of wood, stress concentration at the interface between the wood and adhesive may be even greater than anticipated.

Secondly, the porosity of the wood lumens not only provides increased mechanical interlocking but can also lead to "starved" bondlines by soaking up too much adhesive. It is well known that adhesives can flow into lumens through openings on the wood surface, but it is not clear how much this lumen penetration improves bond durability. An unusual aspect of wood is that the adhesive can sometimes penetrate to such an extent that not enough adhesive is left in the bondline to form a strong bridge between the substrates, leading to a starved joint. In addition, if the adhesive fills the lumens without adding sig-

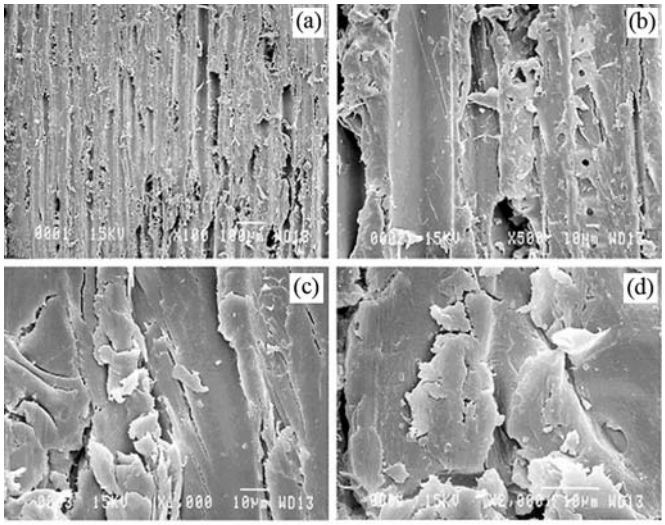

Figure 1. ~ *Scanning microscopy of fragmented surface and surface debris of yellow-poplar resulting from planing: (a) 100×; (b) 500×; (c) 1,000×; and (d) 2,000×.*

nificantly to bond strength, utilization of the adhesive could be inefficient.

The third aspect is that some adhesives can penetrate into wood cell walls, which may increase bonding strength. Many adhesives fall within the 3,000 molecular weight limitation for cell wall penetration (22). This cell wall porosity (6) can provide additional modes for increased adhesion (8). Cell wall penetration has been considered critical for durable bonds between Douglas-fir plywood and phenol-formaldehyde (PF) adhesives (18). However, adhesive penetration into the cell wall does not necessarily add to bond strength. For a two-component system, selective adsorption of one component may lead to off-ratio formulations that reduce the strength of the adhesive, as proposed to explain the lower strength of the epoxy when cured between wood specimens (15).

Fourth are the distinct nanoscale domains (cellulose, hemicellulose, and lignin) within the wood cell walls (4). Each of these domains should behave differently in its interaction with adhesives and water. The high crystallinity of cellulose, the main structural element, limits its ability to interact with water and adhesives. Lignin is the least hydrophilic wood structural element, but it may be the most compatible with some wood adhesives such as phenolics. Limiting lignin modification is its internal crosslinking, which could hinder contact with larger adhesive components. The hemicellulose domains are most likely to swell with water, making them likely to react with adhesive components. It is likely that the hemicelluose domains are the weakest component and may represent a disproportionate amount of the wood surface molecules. Some data indicate that hemicellulose is the main reactive component in wood (20). A better knowledge of wood structure in detail will increase our ability to understand adhesive bonding and bond failure.

In light of this complexity, how can we understand the formation and fracture of wood bonds? One way is to form models for both adhesion and bond failure and to evaluate these in light of the available data. Standard adhesion models certainly apply (19), but they should be expanded to consider the additional aspects of wood porosity, such as lumen penetration (14), and the complex chemistry of wood, including the effect of extractives (3). A number of individual studies have addressed fracture (21), but those results should be analyzed in light of failure models. Both Horioka (13) and Marra (16) proposed models for fracture sites specifically in wood bonds. The value of these models and a preliminary classification relating fracture to bond formation are covered in this paper.

Horioka and Marra Models

Horioka studied the durability of wood bonds (11,12) and developed a nine zone failure model (four zones on either side of the bulk adhesive) (13). The zones are the bulk adhesive (F_C), the adhesive–wood interface ($F_{V\text{-}A}$ and $F_{V\text{-}B}$), the penetrated wood interphase (F_A'' and F_B''), the penetrated wood–unpenetrated wood interface (F_A' and F_B'), and the wood itself (F_A and F_B) (**Fig. 2**). The interphase is the entire transition region of changing properties from the bulk of the substrate to the bulk of the adhesive, while the interface is the abrupt zone between adhesive and wood. The interface is the main concern in the bonding step as the adhesive comes into contact with the substrate. Most adhesion models relate to developing sufficient molecular contact between the adhesive and the substrate, with thermodynamics and rheology being the dominate processes. Bond strength, however, is dependent upon viscoelastic dissipation of energy in the assembly. Thus, interfacial adhesion is one aspect of bond

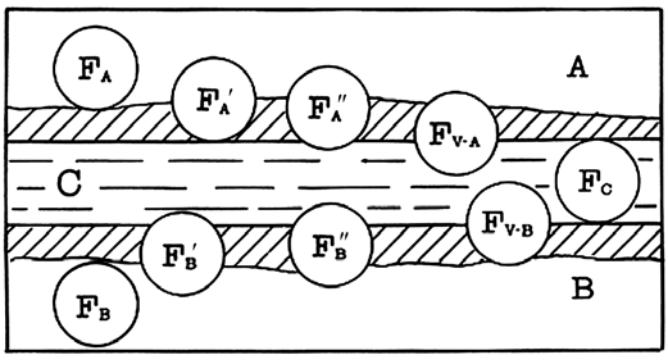

Figure 2. ~ *Horioka's fracture zone model (11), where F_A and F_B are wood failure; F_A' and F_B', penetrated and unpenetrated wood interface; F_A'' and F_B'', penetrated wood; $F_{V\text{-}A}$ and $F_{V\text{-}B}$, wood–adhesive interface; and F_C, adhesive bulk.*

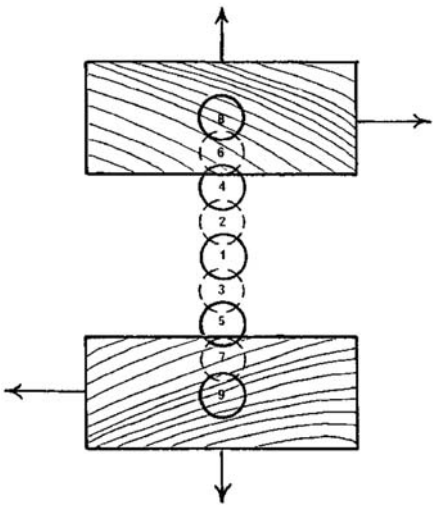

Figure 3. ~ *Marra's model (14) where zones 8 and 9 are bulk wood; 6 and 7, wood interphase; 4 and 5, wood–adhesive interface; 2 and 3, adhesive interphase; and 1, bulk adhesive.*

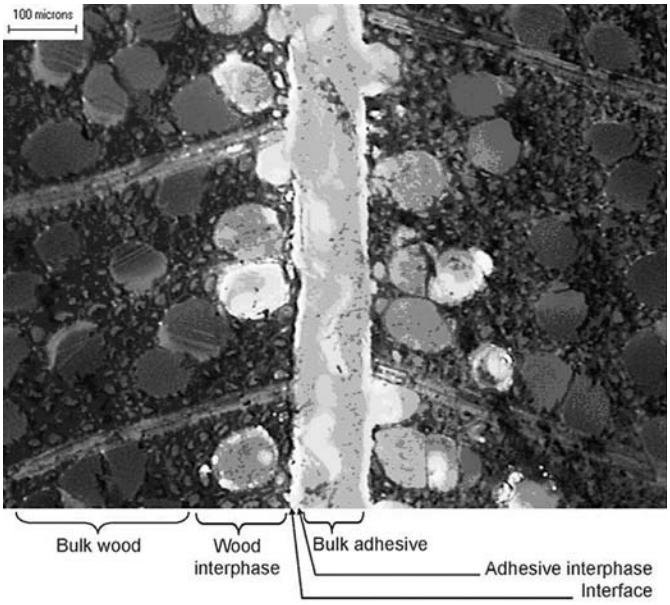

Figure 4. ~ *Zones of bonded assembly in wood bondline of epoxy adhesive according to Marra's model, as shown by fluorescence microscopy.*

strength but so are the substrate and adhesive zones near the interface, because most materials change in chemical and physical properties near interfaces. For example, metals often have a surface oxide layer, and plastics often have low crystalline content near the surface (19).

Marra's nine zone model (16) is similar to Hirioka's model, but the zones farthest from the bulk adhesive (zone 1) are the adhesive interphase (zones 2 and 3), adhesive–wood interface (zones 4 and 5), wood interphase (zones 6 and 7), and bulk wood (zones 8 and 9) (**Fig. 3**). Marra also indicated that the most likely failure zones were the adhesive interphase and wood interphase (17). These zones are identified in an epoxy bonded wood specimen in **Figure 4**. Note that the specimen shown in **Figure 4** has an unusually distinct bulk adhesive layer; the bulk adhesive layer of many bonded specimens is very thin.

From a fundamental mechanical point of view, discrete zones do not exist in bonds because there is a continuum from bulk wood to bulk adhesive to bulk wood. The interface is the most distinct transition, but in some cases the interface is somewhat blurred by the penetration of adhesives into cell walls (7). Despite this limitation, these models at least offer a good framework for understanding bondline forces and failure classification.

Which of these models is better for an understanding of wood failure? For acceptable performance, failure should occur in the wood. An important aspect is to understand failure that takes place in the interphase region. Although both models have some merit, the Marra model is more useful because of its emphasis on failure zones at or near the interface. For example, high stress concentration is expected near the interface as the wood swells and the adhesive tries to resist this swelling. An interesting aspect of Marra's discussion of his model is the emphasis on the wood and adhesive interphase regions as weaker links compared to the interface itself (17). Marra does not give any basis for this proposal, but validation of failure locations with different adhesives is important for developing better adhesives and bonded wood products. The mode of failure may often be adhesive and wood species dependent.

Importance of Failure Analysis

Understanding why bond failure occurs is important for efficiently improving the adhesive or the bonding process for better performance or economics. In some cases, such as double cantilever beam tests, fracture is controlled to be within the adhesive layer, but for most tests, including shear tests and cyclic delamination tests, the fracture location is not controlled. The first step in understanding the cause of failure is to know the location of failure. Marra's model is used in this paper to discuss failure locations and potential causes, as illustrated in **Figure 5**. The location and cause of failure are discussed in this section. Methods for determining this information is discussed in the following section.

The standard division of failure is between cohesive failure in the wood and within the bondline region (1). For adhesively bonded assemblies, it is desirable that failure occur within the substrate because this shows that the adhesive has sufficient strength under the test condition. If deep wood failure occurs under the selected test condition, improving the adhesive and bonding conditions will

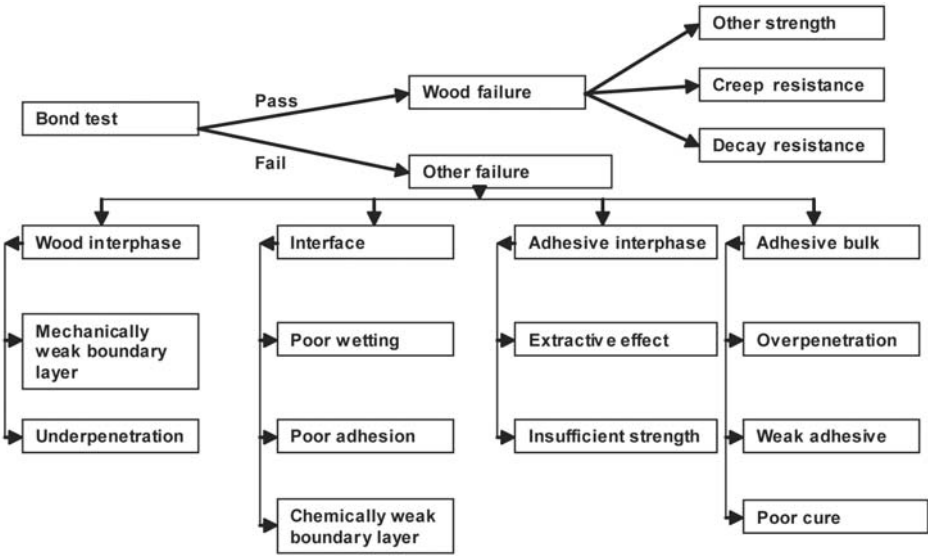

Figure 5. ~ *Analysis of causes of adhesive failure.*

not improve the results of the test. Because many variables influence the integrity of a bond, it is important that the test conditions encompass the range of bonding conditions that are likely to occur in the commercial process, including variation in wood species, wood moisture content, and bonding temperature and time. The wood failure should be distinctly away from the bondline to rule out its classification as shallow wood failure, that is, failure in the wood interphase. Normally, all other failure modes are lumped together, but cohesive adhesive (failure in the bulk adhesive), wood interphase, interfacial, and adhesive interphase failures are examined separately here (zones shown in **Fig. 4**).

While cohesive failure is easy to observe in the wood, it may be harder to observe in the adhesive, especially with colorless adhesives. A common cause of what seems to be cohesive adhesive failure is caused by over-penetration into the wood, leading to a lack of adhesive in the bondline or a "starved" bondline. This problem can be alleviated by increasing the adhesive viscosity, shortening the closed assembly time, increasing the adhesive level, or lowering the bonding temperature. Another possible cause is that the adhesive is too weak in tensile strength. An example is the plastic flow in an uncrosslinked poly (vinyl acetate) under wet or high temperature test conditions. A final cause can be poor cure of the adhesive caused by insufficient time at temperature, too low a temperature, or another factor that retards the cure. For most of these cases, determining the cause of cohesive adhesive failure leads to the necessary modifications for solving the problem.

Failure in one of the three areas (wood interphase, adhesive–wood interface, adhesive interphase) of the entire interphase is more difficult to distinguish from failure in the bulk adhesive or wood. The roughness and inconsistency of wood (e.g., the earlywood and latewood domains) make the characterization of these failure types more difficult.

Failure in the wood interphase often appears as a fuzzy surface after bond fracture. A common cause for this type of failure is damage to the surface cells during surface preparation, such as crushing of cells during abrasive planing. This type of failure has been classified as a weak mechanical interphase. This problem is usually solved by changing the conditions for preparing the bonding surface. Failure in the wood interphase can also occur as a result of underpenetration of the adhesive, which can be caused by insufficient closed assembly time, too low a bonding pressure, too viscous of an adhesive, or improper wood moisture content.

Failure at the interface is an indication of poor adhesion and should be evaluated on the basis of the standard adhesion models. Poor wetting can be caused by the inability of the adhesive to wet the wood; examples are in bonding to dry or over-dried wood. Over-drying causes an irreversible dehydration of the carbohydrate polymers. The condition of dry wood is reversible and increased wood moisture content can improve bondability. Both dry and over-dried wood are hard to wet with aqueous adhesives, as demonstrated by adhesive beads on the wood surface (6). Another cause of failure at the interface can be a low polarity surface, such as the waxy surface layer on straw. A chemically weak layer can look like poor wetting, but it is technically different in that the adhesive bonds to the surface, but the surface layer does not bond well to the underlying wood. It is not clear whether extractives, such as exhibited by the oily surface on teak, are more the result of poor wetting or a chemically weak layer. In any case, improved adhesion is often obtained after the surface is wiped with a solvent. Poor adhesion occurs where

the adhesive wets the surface but there are insufficient adhesive forces to form a strong bond, which may be the case in bonding of heartwood of some species.

Failure within the adhesive interphase can occur because the surface layers of polymers are often weaker than the bulk as a result of incomplete reaction, the presence of low molecular weight components, or low crystallinity. If the wood affects the cure of the adhesive, for example by altering the pH or selective absorption of one component of a two-component system, then this effect should be most strongly manifest in the adhesive zone closest to the wood. Another aspect is that the adhesive interphase may have insufficient strength to support the applied forces, as well as the internal forces. Internal forces can cause shrinkage of the adhesive during curing or the greater swelling of wood compared with the adhesive during water soak treatment.

Evaluation of Location and Causes of Failure

To analyze adhesive failure, the location and the cause of the failure needs to be determined. With wood, even determining the failure location can be difficult given the roughness and inconsistency of the wood surface. Deep wood failure is the easiest to observe because it occurs away from the bondline. Deep wood failure indicates that the adhesive and interphase region is stronger than the bulk adhesive and interphase region. Visual observation is sufficient for determining deep wood failure.

Cohesive failure within the adhesive is often easy to differentiate from other failure modes because of the color or gloss of the adhesive compared to the wood. Overpenetration can be determined by a lack of adhesive on both wood surfaces after fracture or by a very thin bondline prior to fracture as determined by microscopy. A weak or uncured adhesive can also cause cohesive failure. For colored adhesives, the presence of color on both surfaces is a good indication of cohesive failure. For light-colored adhesives, glossiness on both surfaces can often help identify cohesive failure. In microscopic analysis, a failed adhesive has an irregular and distorted appearance compared with the needle-like or fibrous appearance of the wood.

How can we determine the cause of shallow wood failure? Wood interphase failure can often be observed as fuzziness or lack of gloss on the wood surface (1). Microscopically, wood interphase failure is characterized by the presence of oriented needle-like wood cells on the adhesive; the failure can sometimes be enhanced by staining the wood. Some causes of wood failure, such as the crushing of surface cells or lack of penetration, can be determined by microscopic analysis of cross-sectional specimens.

Distinguishing between interfacial failure and adhesive interphase failure is usually very difficult. In general, this evaluation requires very close analysis and the use of multiple techniques. Not only is it difficult to see clear adhesives on a failure surface, but it can also be difficult to see colored adhesives because the color may not be intense enough to reveal a very thin film of adhesive. However, determining the failure location is important because overcoming the failure requires different changes in the adhesive or bonding condition. For example, understanding the failure of epoxy bonds under wet conditions involved the use of optical and scanning electrical microscopy, as well as infrared and x-ray photoelectron spectroscopy (5). This understanding contributed to a better model for the improved adhesion of hydroxymethylated resorcinol primer.

Research Opportunities

Although a number of methods are available for evaluating the failure of wood bonds, the chemical and structural complexity of wood can make it difficult to know where and why wood bonds are failing. Development of improved analytical methods will be useful in better defining the location and cause of bond failures. The knowledge of the cause of failure is critical to a better understanding of bond formation mechanisms and the development of more economically efficient wood bonds. Use of infrared mapping of failed surfaces or fluorescent microscopy examination of these surfaces should be both useful and practical for distinguishing the failure location. Use of nanoscale techniques, such as surface probe microscopy and modulus mapping, can be useful if methods are developed to handle the large topographical differences of a wood surface.

A better understanding of the chemical composition of wood surfaces is important for developing optimized chemical interactions with these surfaces. Knowing whether covalent chemical bonds are taking place can help in improving the adhesive interaction with the wood. Knowing the surface chemistry of wood is challenging, but the use of site-specific fluorescent probes may be useful. Improved infrared and nuclear magnetic resonance techniques may help in determining the amount of covalent chemical bond formation.

Understanding the adhesive–wood interactions that lead to durable bonds is important for learning how to use adhesives efficiently. If stabilizing the cell wall against dimensional change is more critical than filling the lumens, then adhesive development should be placed upon the former rather than the latter. Techniques such as improved microscopic methods, nanoindentation, and durability testing schemes should be valuable in this regard.

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