What does bonding to modified wood tell us about adhesion?

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ABSTRACT

Determining adhesive bond performance for chemically modified wood is important not only in relation to its commercial utility but also because this information helps in understanding wood bond durability. Although wood modification is usually used to improve anti-swell efficiency, the modification can alter adhesive bond performance. Generally, modification is expected to diminish adhesion by making the wood surface less polar and less porous, resulting in poorer adhesive wetting of the wood and fewer chemical bonds between the two surfaces. On the other hand, chemical modification can help the wood bonds to pass water exposure durability tests because modified wood will swell less. Given the great variety of wood adhesives, species, and modification methods, a simple theory does not explain bonding behaviour. However, our model that takes into account the mechanism for dissipating stress induced by moisture-driven dimensional change, as well as general adhesion theories and adhesive-wood interactions, is useful for explaining our observations. Our model is evaluated in relation to bond strengths and percentage wood failure for dry and water-soaked compressive shear blocks of yellow poplar sapwood. The wood was modified with acetic anhydride, butylene oxide, or propylene oxide to provide different polar characteristics for the wood and then bonded with adhesives that belong to both of the main groups in our model, the flexible and the reinforcing adhesives. Thus, we were able to evaluate the validity of this model for explaining our experimental results, and this knowledge should lead to a more systematic design of improved adhesives for bonding wood.

INTRODUCTION

Design of improved adhesives for wood bonding has lagged behind the design of adhesives for metals, plastics, and other substrates in part because of the lack of suitable wood adhesion models. The development of suitable models has been hindered by the great variability between and within wood species, the several modes for adhesive interactions with wood, and the many types of chemistries used for wood adhesives. The ability of adhesives to wet the porous wood substrate allows many adhesives to form strong bonded assemblies for dry or moderate moisture exposure conditions. However, adhesives often fail upon exposure to wet conditions or cycling between dry and wet conditions. Recently a model was developed that divided wood adhesives into two groups based upon the adhesives' interactions with wood and the adhesives' mechanical properties (Frihart 2007). Here we evaluate that model using data obtained in our prior studies on bonding to modified wood.

We treated wood with chemicals that inhibit its swelling by either altering the availability of hydroxyl groups for hydrogen bonding to water, or bulking the wood, or both. These reactions are usually characterized by percentage weight gain of oven-dried specimens and anti-swell efficiency (ASE)-the difference in swelling between the modified and unmodified wood divided by that of the unmodified wood. The most common wood modification technique is acetylation because of its effectiveness in improving ASE, its value in preserving wood strength, and its relative ease to perform (Hill 2006, Rowell 2005, Rowell 2006). Acetylation usually involves reacting the hydroxyl on the carbohydrate and lignin polymers with acetic anhydride to produce an ester that is bulkier and less hydrophilic than a hydroxyl group. Another modification is the reaction of hydroxyl groups with propylene oxide or butylene oxide (Hill 2006, Rowell 2005). This method does not diminish the total number of hydroxyl groups but does bulk the wood cell walls and can produce ASE values similar to those of acetylation. Thus, the comparison of bond performance of wood modified with acetic anhydride to that modified with alkylene oxides could determine the relative effects of loss of hydroxyl groups and decreased swelling on bond strengths. The bonding of 18 different adhesives to acetylated yellow poplar has been studied (Vick and Rowell 1990). Additional studies have been done on bonding of acetylated wood (Vick *et al.* 1993, Frihart *et al.* 2004). We are aware of only one citation regarding bonding to alkylene oxide modified wood (Brandon *et al.* 2006).

Upon analyzing the performance of wood bonds exposed to water, we realized that a single model was not only ineffective but also invalid. This is because the adhesives differ in their ability to interact with the wood and in their mechanical response to internal and external forces. This has led to the development of a new model for analysing wood bond performance. Certainly the need to develop molecular level contacts on the surface is still important; thus, standard adhesion theories involving wetting, development of physical and chemical bonds, and minimizing weak boundary layers are still important (Pocius 1996). However, wood is much more porous than most substrates and exhibits very large dimensional changes as a function of moisture content. Therefore, a durable wood adhesive must avoid stress concentration at the bondline during moisture driven dimensional changes. A wood adhesive model needs to incorporate these factors.

Our model envisions two classes of durable wood adhesives, based on the different mechanisms for minimizing swelling stresses (Frihart 2007). One group of durable adhesives, the reinforcing adhesives, create a swelling gradient by reinforcing the wood adjacent to the bondline. These stiff adhesives do not expand with the wood but avoid a zone of extreme shear concentration by diffusing into and reinforcing the cells adjacent the bondline. This reinforced zone allows for a gradual transition from the bulk swelling of the wood to the non-swelling adhesive layer. Typical reinforcing adhesives are melamine formaldehyde (MF) and resorcinol formaldehyde (RF). The second group, the flexible adhesives, avoid producing a strain gradient by changing dimensionally with the wood. Emulsion polymerized isocyanate (EPI) is an example of this class. Adhesives that do not fall into either of these classes are not durable; they often fail upon exposure to extreme changes in moisture conditions.

Assessing the validity of this model is difficult because of our general dependence upon nature for providing differences in the substrates. However, examining the differences in the performance of bonds for umnodified and different types of modified wood allows us some control over the variables for investigating the validity of our models. In particular, we wanted to examine the validity of our current wood adhesive model in cases where the wood was modified with acetic anhydride, propylene oxide, or butylene oxide and bonded with

different types of wood adhesives. Four adhesives (MF, RF, EPI, and epoxy) from Vick and Rowell's 1990 study were selected for the evaluation, based on their performance. The RF adhesive showed that the degree of wood failure was not greatly affected by either the extent of acetylation or water soaking. The MF lost much of its bonding ability with the acetylation of the wood. In contrast, epoxy bonds gave no wood failure after water soaking but retained some wet bonding performance with acetylated wood. The EPI retained high wood failure in all cases except for water-soaked acetylated wood.

EXPERIMENTAL METHODS

This paper analyses the data from two different planned studies carried out at different times and with different adhesive and wood supplies, and therefore the experimental and discussion sections are separated for each study even though there are some common experiments.

Study 1: Planed and unplaned, acetylated wood

Experimental design

The experiment was originally designed to survey an array of thermosetting adhesives (RF, MF, epoxy, and EPI) for their ability to bond planed and unplaned acetylated wood after modification. Effectiveness of the bonds was determined by measuring shear strength and wood failure in a dry condition and in a wet condition after water soaking under vacuum and then pressure (VPS).

The design was a full factorial arrangement with four adhesives and three treatments (acetylated planed, acetylated unplaned, and an unacetylated planed control) yielding 12 treatment combinations. Each treatment combination was replicated nine times, and four specimens were taken from each replicate, yielding 36 specimens each. After randomly assigning the specimens for dry or wet tests, the 432 total specimens were tested for their shear strength and wood failure in dry and wet test conditions.

Wood modification

Acetic Anhydride

Yellow-poplar (*Liriodendron tulipifera*) sapwood lumber, free of defects, was sawn into strips 6.4 or 7.9 mm thick, 31.8 mm wide, and 229 mm long (see bonding section). After cutting, the strips were placed in an oven and dried at 105°C for 24 h. The strips were then removed from the oven, cooled in a desiccator for 1 h, and weighed,

The strips were acetylated according to the following procedure. Suips were placed in a glass reactor fitted with a reflux condenser. The reactor was filled with enough acetic anhydride to cover them even after absorption of the anhydride. The acetic anhydride and wood were heated to reflux temperature for 4 h and then cooled. Strips were removed, washed for 4 h in reversed osmosis water to remove acetic acid and excess acetic anhydride, air dried overnight, and then oven dried for 24 h at 105°C. Weight gain from modification was determined after oven drying by calculation as a percentage of the original oven-dried weight. The acetylated wood strips had an average of 21.7 ± 0.9 wt% gain.

Specimen preparation and bonding

All strips, including the unmodified controls, were conditioned at 27°C and 65% relative humidity until bonded. If the strips were to be planed, they were 7.9 mm thick and were

planed after treatment and before bonding. If the strips were not to be planed after acetylation, they were planed to be 6.4 mm thick prior to treatment. Specimens were prepared by laminating two strips of wood, 6.4 mm thick, 31.8 mm wide, and 229 mm long.

Cold setting adhesives were spread at an approximate rate of 320-340 g/m^2 and cured at room temperature. Adhesive was spread on both surfaces with a rubber-roll hand spreader. Adhesive spread rate was accurately controlled by automatically tare-weighing the adhesive on the laminates as they were spread. Pressure for the epoxy and emulsion polymer isocyanate was adjusted to provide a small degree of squeeze out. Pressure for the resorcinol formaldehyde was maintained at 690 ± 35 kPa. All nine replicates (joint assemblies) of a single treatment combination were pressed within the same press closure. Closed assembly varied between 15 and 60 min, depending on individual curing characteristics.

The hot setting melamine-formaldehyde was spread at a rate of 240 g/m^2 and was cured in an electrically heated laboratory hot-press maintained at 175 ± 5°C. Pressure was maintained at 862 ± 35 kPa for the recommended curing time. Replicates were pressed in intervals of three sets for not more than 5 min.

After removing material from both sides and ends, four block-shear specimens with a shear area of 25.4 × 25.4 mm were cut from each joint assembly to form shear blocks, as described in ASTM D 905-98 (ASTM 1998) and randomly assigned to either the dry or wet shear tests.

Adhesive testing

Eighteen specimens representative of each treatment combination were subjected to a single vacuum-pressure soak (VPS) and then tested for shear strength and wood failure while in the water-saturated condition. The saturation process procedure consisted of the following events:

1. Submerge specimens in tap water at room temperature in a pressure vessel.
2. Maintain a vacuum of 84.6 kPa for 30 min.
3. Maintain a pressure of 448 ± 35 kPa for 30 min.
4. Submerge in water until tested

Dry and wet specimens were tested in a compression-loading shearing tool as described in ASTM Method D 905-98 (ASTM 1998). Load was applied at a constant rate of 2.54 mm/min until failure. The maximum load at failure was recorded, and then shear strength was computed for each specimen based on the shear area. Wood failure was estimated to the nearest 5% on the sheared area, according to ASTM D 5266-99 (ASTM 1999). The wet-tested specimens were air-dried before estimating wood failure. Estimating is easier after drying because the contrast in color and light reflection between the dry wood fiber and the adhesive is greater.

Study 2: Acetic anhydride, butylene oxide, and propylene oxide modified wood

Experimental design

A similar design and adhesive selection was used as in Study 1, but the wood variables were unmodified, or reacted with acetic anhydride, butylene oxide, or propylene oxide. The wood was not planed after the modification steps.

Wood modifications

Yellow-poplar sapwood was cut into strips (6.0 × 32 × 203 mm), oven-dried for 24 h at 105°C, cooled 1 h in a desiccator, and then weighed. Strips were chemically modified with one of three different chemicals: (1) acetic anhydride, (2) butylene oxide, or (3) propylene oxide.

Acetic anhydride: Acetylation was carried out as described above for Study 1, and the modified wood had a weight gain of 20.9 ± 0.96%.

Butylene oxide and propylene oxide: Strips were placed in a stainless steel reactor with a mixture of either propylene oxide or butylene oxide and urethylamine (95:5 v:v) at 120°C and 84.6kPa for 60 min for propylene oxide, and 4 h for butylene oxide. Strips were taken out of the reactor and air dried overnight, water soaked for 4 h, air dried again, and then oven dried for 24 h. Percentage weight gain was 25.7 ± 1.2% for butylene oxide and 34.1 + 1.9% for propylene oxide.

Specimen preparation and bonding

A joint assembly was prepared as described above. The unmodified wood was planed less than 24 h before bonding to conform to industry and testing standards. The modified wood was not planed. All strips, including the unmodified controls, were conditioned at 27°C and 65% relative humidity prior to bonding.

Four commercial adhesives (resorcinol-formaldehyde, melamine-formaldehyde, epoxy, emulsion polymer isocyanate) were used to bond the modified strips. The bonding procedure was the same as above except that one part walnut shell flour was added per six parts melamine-formaldehyde resin to prevent overpenetration.

Adhesive testing

The samples were tested using the procedure described above for Study 1.

RESULTS AND DISCUSSION

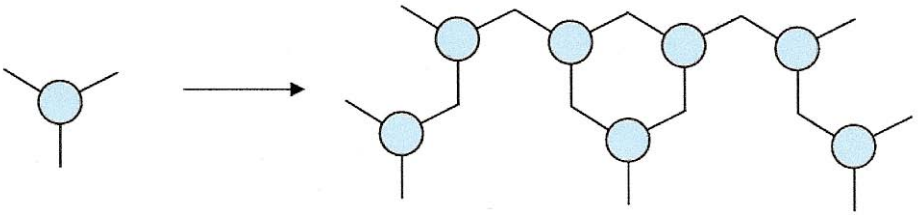
Prior research had shown that acetylation can alter the ability of adhesives to provide wood bonds with high wood failure under wet conditions (Vick and Rowell 1990). Although Vick and Rowell did discuss the performance of each adhesive individually, they tried to look at overall performance based mainly on polarity and concluded that all had reduced adhesion to some degree. Given the concern about the effect of the conversion of hydroxyl sites to esters on adhesion, we suspected that alkylene oxide modified wood could provide reduced water swelling and decay resistance without a decrease in the availability of the important hydroxyl bonding sites. However, prior to doing this study, we realized that Vick and Rowell had followed standard wood preparation procedures for bonding, including planing the surface after acetylation. The concern was that planing of acetylated wood can expose unacetylated hydroxyl groups and confound the test results. Thus, the first study was done looking at the difference between the unplaned and planed acetylated samples in comparison to the standard planed unacetylated wood. The selection of the particular adhesives is discussed in the introduction section.

In trying to rationalize the results of both Vick and Rowell (1990) and our studies with planed vs. unplaned acetylated, as well as alkaline oxide modified wood, the available models on the critical elements for a durable wood bond and the model suggestion that acetylation of

hydroxyl groups reduces wetting and polar interactions were not sufficient in all cases. This led us to develop a better understanding of the critical aspects of wood bonds (Frihart *et al.* 2004, Frihart 2005a, Frihart 2005b, Frihart 2007, Frihart *et al.* 2007). The key aspects of our current model emphases that internal strains generated when the wood gains and loses water need to be dissipated by the adhesive and recognizes that there are two general classes of durable wood adhesives (reinforcing and flexible) based upon their morphology and how they deal with swelling-induced strains.

Our strain model focuses on the fact that wood, but not necessarily the adhesive, undergoes relatively large dimensional changes upon gaining or losing water. It is not surprising that these differences in expansion and contraction lead to large internal strains at the interphases and interfaces that can lead to bond failures. Unless these strains are distributed, they can contribute to an overall lowering of bond strength and less wood failure. This effect explains why wood bonds usually show lower wood failure when wet, even though the wet wood is weaker.

(A) In-situ polymerised—rigid, multifunctional oligomers that highly crosslink but can diffuse into, and reinforce, cell walls



(B) Pre-polymerised—flexible backbone that lightly crosslinks or extends during setting

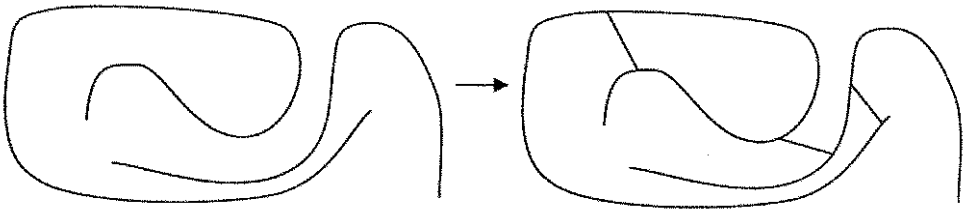


Figure 1. Durable wood adhesives can generally be classified as either (A) those that are in-situ polymerized, where the applied adhesive consists of small molecules that polymerize to form large molecules during the adhesive setting process (reinforcing), or (B) those that are pre-polymerised and are often crosslinked during the adhesive setting process (flexible).

Our model distinguishes two general classes of wood adhesives. One is made up of monomers and oligomers that need to polymerize extensively during the setting process (Frihart 2005a). These *in situ* polymelized adhesives are made of rigid poly-functional oligomers and monomers that lead to even more rigid polymers (Fig. 1). Thus, the differential strain is unlikely to be distributed through the adhesive, but the strain can be dissipated if the adhesive diffuses into the cell walls near the surface, allowing the wood interphase region to distlibute the swelling difference between the bulk wood and bulk adhesive. This is why the resorcinol-formaldehyde resins, despite their brittleness, provide water-resistant bonds in unmodified and acetylated wood (Fig. 2). Epoxies are stiff like RF but are unlikely to alter the wood cell wall structure and do not provide water-resistant bonds

to umnodified wood (Fig. 3). However, when wood swelling is reduced by acetylation, there is less interfacial strain and the epoxy bonds are stronger and show higher wood failure (Fig. 3). The flexible adhesives typically use preformed relatively flexible polymers and are often crosslinked during the setting process. These can distribute swelling volume differences via slight movements through the polymer matrix to avoid strain concentration. EPI fits this model and provides water-resistant bonds to unmodified wood (Fig. 4). However, because of limited penetration, these adhesives may be more susceptible to loss of polar bonding on surfaces such as acetylated wood (Fig. 4). Therefore, the wood failure decreases dramatically under wet conditions. Melamine-formaldehyde data is not shown because even dry untreated wood had low wood failure caused by over-penetration.

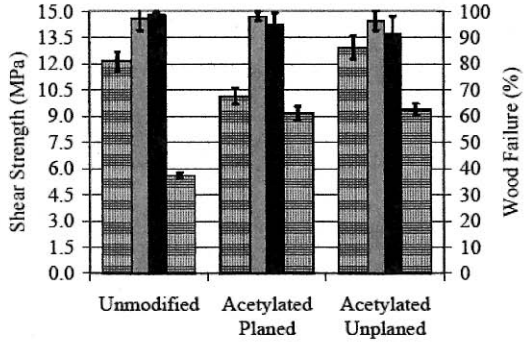


Figure 2: Resorcinol-formaldehyde bonded shear blocks tested dry (left) and wet (right) . Dry shear strength, dry wood failure, wet wood failure, wet shear strength. Error bars show 90% confidence intervals.

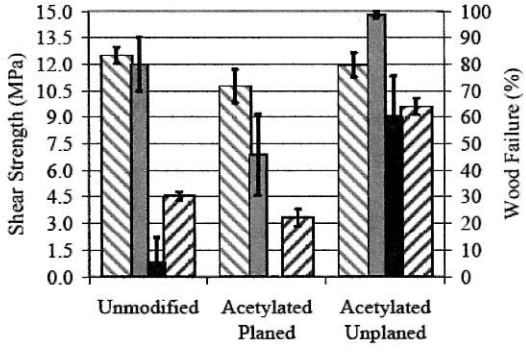


Figure 3: Epoxy bonded shear blocks tested dry and wet. Dry shear strength, dry wood failure, wet wood failure, wet shear strength.

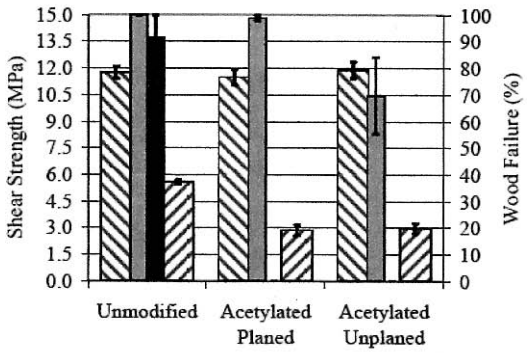


Figure 4: Isocyanate bonded shear blocks tested dry (left) and wet (right). Dry shear strength, dry wood failure, wet wood failure, wet shear strength.

Based upon previous work (Rowell 2005), we expect the butylene oxide and propylene oxide treatments to diminish thickness swelling by 70-75%, similar to the results of acetylation, while maintaining a similar level of hydrophilicity to the unmodified wood. The model predicts that the adhesives that reinforce the cell wall (MF and RF) should behave similarly in alkylene oxide modified wood and the unmodified control. Epoxy, because it cannot reinforce or flex, often fails at the bondline during wood dimensional changes. This adhesive should benefit from the reduction in swelling just as it did with acetylation. EPI could have better bonding to alkylene oxide modified wood than to acetylated wood because of its higher polarity.

We found that in many cases, propylene oxide modified wood crushed at low loads. The propylene oxide modified wood was so weak due to the high modification level (34% versus 25% for the butylene oxide and 21% for the acetic anhydride) that we cannot evaluate the adhesive performance. We saw high wood failures (above 95%) and low shear strength in all cases. Therefore we are not presenting this data.

Butylene oxide modified wood, however, retained enough strength to give us some information. These samples followed the predictions of the model, where RF, MF, and EPI were able to make durable bonds having 90+% wood failure (Fig. 5). The chemical modification, by reducing moisture swelling, reduced bondline stress concentration and therefore raised epoxy bonded wet wood failure from 0% (unmodified) to 65% (butylene modified epoxy, Fig. 5), almost the same as the 60% observed in acetylated epoxy bonded wood (Fig. 3). Results of bonding to acetylated wood are not shown because they are very similar to the results in Figures 2, 3, and 4.

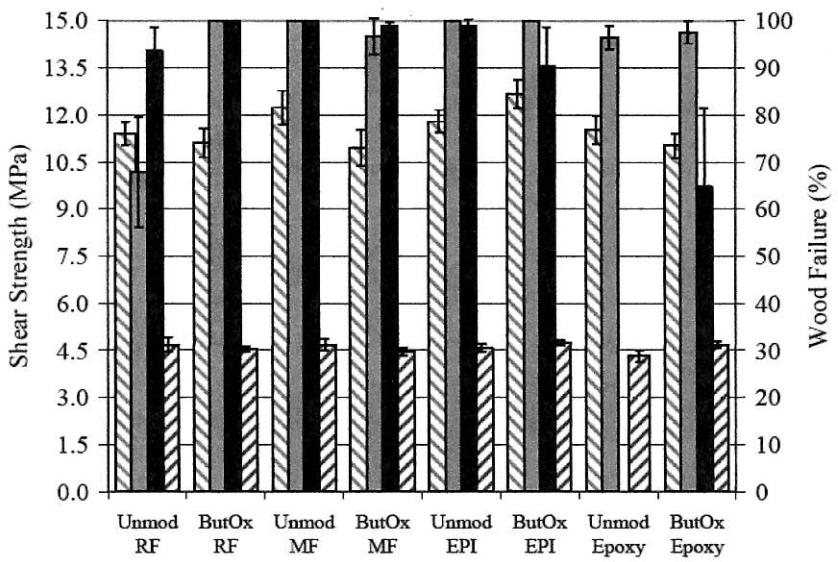


Figure 5: Shear strength and percentage wood failure of dry and wet bonded assemblies. Unmod= unmodified, ButOx = butylene oxide modified wood. Dry shear strength, dry wood failure, wet wood failure, wet shear strength.

These studies have shown that the model, which considers a release mechanism for dimensional changes, is useful in understanding adhesive performance. Investigating bonding of modified wood not only has very practical aspects but offers unique insights into evaluating the critical aspects of making durable wood bonds.

CONCLUSIONS

Although wood adhesion is a very old technology, the understanding of how to design adhesives for applications is limited because of the complexities of wood as a substrate. These complexities include differences in the microscopic surfaces between and within species, many modes of interaction of adhesives with wood, and the variable loss of water and other low molecular weight components into the wood during the setting process. Systematic studies are difficult because we cannot synthesize homogenous wood bonding surfaces, as we can for plastics, metals, ceramics, etc. However, wood modification does offer a way to change the bonding surface and examine the influence of this change on bond performance. Because the modifications also change the bulk properties of the wood, the researcher needs to separate the influence of surface from bulk property changes. Acetylation and alkylene oxide modification of wood are useful because they allow us to change specific wood properties such as thickness swell and polarity. These modifications provide useful insight into the critical aspects of wood bonds because there are cases where modifications do not measurably alter the bond integrity, as well as cases where they can improve or hurt the bond performance under wet conditions. These data can best be understood in light of our current model for durable wood bonds. In addition to standard adhesion, wetting, etc., durable adhesives must minimize strain gradients due to swelling. They can either reinforce the interphase region or be flexible enough to strain with the wood. Adhesives that do not minimize these strain gradients will not make durable bonds to normal, dimensionally unstable wood. This work shows that the proper wood modification can lead to an improved understanding of wood bonds.

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