Effects of Chemically Modified Wood on Bond Durability

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Abstract

Chemical modification of wood can improve its dimensional stability and resistance to biological degradation and moisture, but modification can also create a new surface for bonding. Acetylation of wood results in the loss of hydroxyl groups, making the wood more hydrophobic and reduces its ability to hydrogen-bond with the adhesive. In contrast, reacting wood with butylene oxide or propylene oxide lowers swelling of wood in water but does not reduce the number of free hydroxyl groups. The hydrogen bonding model of adhesion would favor the oxide-modified wood over the acetylated wood for higher bond strengths. The effectiveness of adhesion to wood modified with acetic anhydride, propylene oxide, or butylene oxides was evaluated by measuring the dry and wet shear strength, and the percentage wood failure of bond specimens. Unmodified and modified wood specimens of yellow-poplar (*Liriodendron tulipifera*) were bonded with four adhesives (epoxy, emulsion polymer isocyanate, melamine formaldehyde, and resorcinol formaldehyde) selected on the basis of their sensitivity in bonding to acetylated wood. The importance of the hydrogen bonding model could not be fully determined in these experiments because even though the propylene oxide and butylene oxide modifications enhanced wood failure percentages, they had made the wood substantially weaker. Except for the emulsion polymer isocyanate, all adhesives gave stronger bonds with the acetylated wood than the untreated wood especially during water-saturated conditions.

Introduction

Wood is a polymer blend made up of cellulose, hemicellulose, and lignin. These polymers make up the cell wall and are responsible for the chemical and physical properties exhibited by wood. Wood is a preferred building material because it is economical, renewable, widely available, strong, aesthetically pleasing, and energy efficient. It has, however, several properties that are disadvantageous, such as biodegradability, flammability, dimensional changes with varying moisture contents, and degradation caused by ultraviolet light, acids, and bases. Because all of these degradative effects are chemical in nature, it is possible to eliminate or greatly reduce the rate of degradation by changing the chemical composition of the cell wall polymers.

Through chemical modification of the cell wall polymers, the highly specific biological enzymatic reactions involved in biodegradation are inhibited because the swelling of the bulk can limit access to the structural polymers and the reactive sites have been altered (7). Modifying the cell wall polymers to make them more hydrophobic not only helps to protect wood from biodegradation by lowering the moisture content but also reduces the tendency of wood to swell and shrink with changes in moisture content.

Acetylation has been researched worldwide since the mid-1940s and has been studied more than all other chemical modifications of wood. (7). Acetylation occurs when hydroxyl groups of wood react with acetic anhydride to form esters of lignin, cellulose, and hemicellulose in addition to the byproduct acetic acid. Acetylation is a single-step reaction where one acetyl group reacts with one hydroxyl group. For every hydroxyl group converted to an acetoxy group, the resulting wood has a lower affinity for water and is potentially swollen. For these reasons, acetylated wood is less permeable to water and less subject to dimensional change with changes in moisture levels.

Reacting wood with propylene oxide or butylene oxide can also modify the properties of the wood (7). Like acetylation, these alkylene oxide-modified woods swell less in water, even though there is no loss of the hydroxyl groups in contrast to the acetylation process. These modifications also increase the bulk of the cell walls so that there is less dimensional change during water soaks.

The modification of wood can alter the adhesive strength in a variety of ways. The changes in the surface tension of the wood should reduce the adsorption of more polar adhesives, especially waterborne ones. Being both proton donors and acceptors, hydroxyl groups form stronger hydrogen bonds than the acetoxy groups that are only hydrogen acceptors. In addition, lowering the swelling of the modified wood during water soaks puts less strain on the bond (6).

The objective of this research was to determine how chemical modification affects adhesion. This was done by chemically modifying wood with acetic anhydride, butylene oxide, or propylene oxide and determining the effect of modification on adhesion by analyzing both shear strength and wood failure values. Four different types of adhesives were selected based upon past experience that showed different responses to moisture exposure and degree of wood acetylation (9). The phenol-formaldehyde (PF) bond was insensitive to changes in moisture or acetylation, whereas the others (epoxy, emulsion polymer isocyanate, or melamine-formaldehyde) showed either a positive or negative response to one or both of these changes.

Experimental

Wood Modifications

Yellow-poplar sapwood was cut into strips (0.6 by 3.2 by 20.3 cm), ovendried for 24 hours at 105°C, cooled 1 hour in a desiccator, and then weighed. Strips were chemically modified with three different chemicals: 1) acetic anhydride, 2) butylene oxide, or 3) propylene oxide.

Acetic Anhydride

Strips were placed in a glass reactor fitted with a reflux condenser. The reactor was filled with enough acetic anhydride to not only cover the strips at the initial filling but also to cover them after absorption of chemical. The acetic anhydride containing the wood was heated to boiling for 4 hours and then cooled. Strips were removed, washed for 4 hours in reverse osmosis water, air-dried overnight, and then ovendried for 24 hours at 105°C. Weight gain from acetylation was determined after ovendrying by calculation as a percent of the original ovendried weight.

Butylene and Propylene Oxide

Strips were placed in a stainless steel reactor with a mixture of propylene oxide or butylene oxide and triethylamine (95:5 (vol.:vol.)) at 120°C and 635 mm of mercury, for 60 minutes for propylene oxide, and 4 hours for butylene oxide. Strips were taken out of the reactor and air-dried under a fume hood overnight, water soaked for 4 hours, air dried, and then ovendried for 24 hours. After ovendrying, percent weight gain was calculated.

All strips, including the untreated controls, were conditioned at 27°C and 65 percent relative humidity prior to bonding.

Specimen Preparation

A joint assembly was prepared by laminating two pre-conditioned strips of wood that have been modified by one of the treatments, as previously described. The untreated wood was planed less than 24 hours before bonding to conform to industry and testing standards. The modified wood was not planed because a previous study indicated planing of acetylated wood reduced the percent wood failure for epoxies (5) and generated additional unmodified hydroxyl groups on the wood surface as shown by x-ray electron photospectroscopy of samples after trifluoroacetic anhydride modification (3).

Four commercial adhesives – resorcinol-formaldehyde (RF), melamine-formaldehyde (MF), polyamide epoxy, emulsion polymer isocyanate – were bonded to the treated strips. Cold-setting adhesives were cured at room temperature under pressure, and the one hot-set adhesive (MF) was cured in a heated press at 175° ± 5°C under a pressure of 862 ± 35 kPa.

Block shear specimens were cut from each joint assembly and randomly assigned to either the dry or wet shear tests. Dry and wet specimens were tested according to ASTM D 905 (1), and wood failure was estimated to the nearest 5 percent on the sheared area according to ASTM D 5266 (2). For each adhesive and each treatment, one standard deviation from the mean value is shown for the 18 samples (two samples from each of nine assemblies).

Results and Discussion

The wood was modified at the highest practical level to the greatest improvement in anti-shrink efficiency (ASE) (7) to maximize the effect of any positive adhesion interaction. Each adhesive reacted differently to the chemical modifications; therefore, the results are given by adhesive. **Figures 1 through 4** depict shear strength and wood failure data results obtained for each adhesive. In most

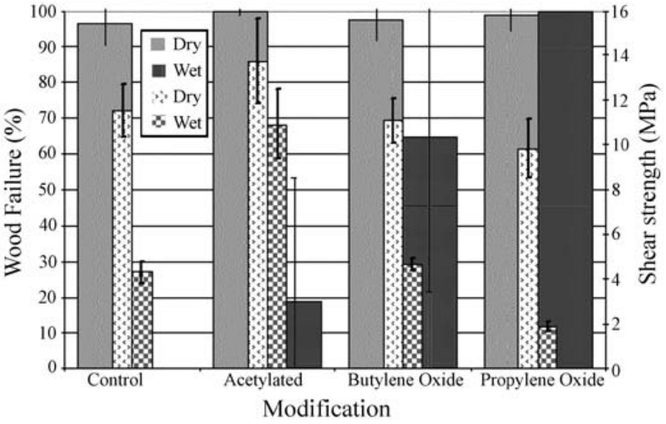

Figure 1. ~ *Epoxy-bonded assemblies of unmodified and modified wood tested as dry and wet ASTM D 905 shear blocks. The wider bars show the percentage of wood failure, and the narrow bars show shear strength. Unmodified wood is the control.*

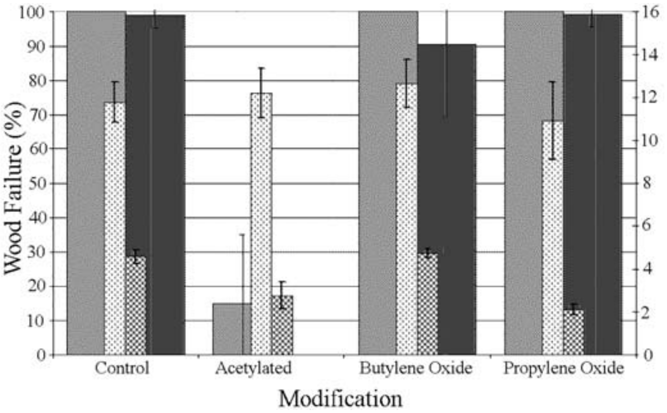

Figure 2. ~ *Emulsion polymer isocyanate-bonded assemblies of unmodified and modified wood tested as both dry and wet ASTM D 905 shear blocks. The wider bars show the percentage of wood failure, and the narrow bars show shear strength. Unmodified wood is the control.*

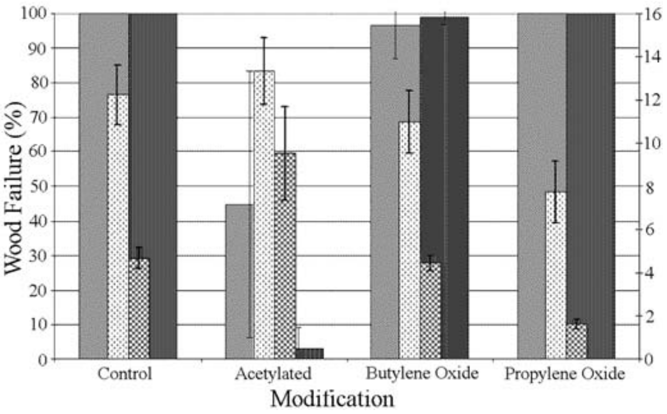

Figure 3. ~ *MF-bonded assemblies of unmodified and modified wood tested as dry and wet ASTM D 905 shear blocks. The wider bars show the percentage of wood failure, and the narrow bars show shear strength. Unmodified wood is the control.*

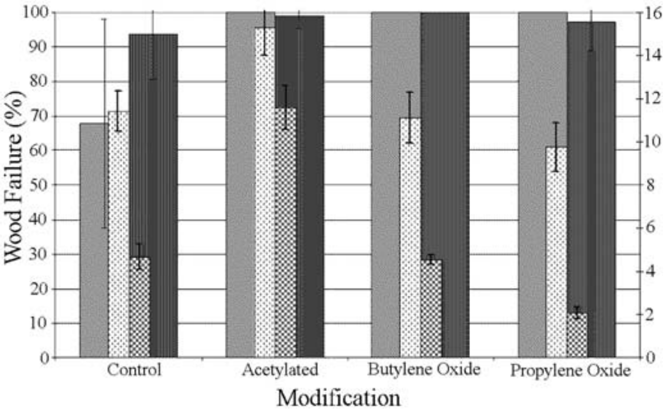

Figure 4. ~ *RF-bonded assemblies of unmodified and modified wood tested as dry and wet ASTM D 905 shear blocks. The wider bars show the percentage of wood failure, and the narrow bars show shear strength. Unmodified wood is the control.*

cases, the acetylated wood produced the strongest bonds, while the propylene oxide-modified wood produced lowest compressive strength values due to some crushing of the wood. Although butylene oxide-modified wood gave similar results in strength and wood failure as the control, it showed some tendency toward crush during the compression tests. The percent wood failure and shear strength need to be considered together. At times weakening the wood can make the percent wood failure higher without making the actual bond any stronger.

Epoxy

Epoxy adhesives with unmodified wood have dry shear strengths that exceed the strength of the wood itself as illustrated by the high wood failure, but upon exposure to water-soaking stresses, epoxy bonds weaken more rapidly giving little wood failure (4,5,8). **Figure 1** illustrates the ability of epoxy to give strong bonds and high wood failure in dry conditions regardless of the modification procedure. Under wet conditions, the epoxy gives the strongest bond with the acetylated wood; this data is in agreement with our earlier study (5). The propylene oxide-modified wood gives acceptable wood failure percentages, but the strength is lower than the control samples because of the weakening of the wood from the treatment. At the level of modification used in these experiments, butylene oxide-modified wood gave similar performance to the unmodified wood, except for higher wood failure when wet.

Despite the improved wood failure over the control, the strength of the bonded assembly was not improved in these compression shear tests.

Emulsion Polymer Isocyanate

Unlike the epoxy adhesive, the emulsion polymer isocyanate did not give good wood failure results with the acetylated wood under the dry conditions; even though the strength value is very comparable with the other treated and untreated wood specimens. **Figure 2** shows that emulsion polymer isocyanate produces a better bond with the untreated wood than with acetylated wood in both wet and dry conditions. Like the epoxy case, the butylene oxide-modification produced assemblies with similar strength and percent wood failure to those that were produced from the control wood, while the propylene oxide-modified wood again yielded the lowest strength assemblies despite high wood failure.

MF

MF is a hot-press adhesive that is well known for its strong and highly durable bonds to wood (9). However, our previous study of bonding to acetylated wood showed lower than expected strength and wood failure due to over-penetration. The addition of low filler levels gave improved bond strength and percent wood failure for the unmodified wood (publication in progress). **Figure 3** demonstrates this bond strength by the high wood failure and shear strength in the control wood under both dry and wet conditions. The strength and percent wood failure for the MF-bonded assemblies were similar to what was observed with the epoxy-bonded samples, except for the acetylated wood. In both dry and wet condition, the MF-bonded samples had good strengths despite the low percent of wood failure. The bonded samples for the buylene-oxide and propylene-oxide modified wood showed higher wood failure but lower strength than those for the acetylated wood.

RF

The RF adhesive produced the strongest and most durable bonds with the acetylated wood. This adhesive gave good wood failure percentages in both dry and wet conditions for all modifications, except for the untreated wood which had wood failure percentages uncommonly low for this adhesive. The somewhat lower percent wood failures for the control sample in **Figure 4** were unexpected from previous results. The shear strength values for the butylene oxide-modification were similar to the control and higher than for the propylene oxide modification. In general, the RF adhesive was the least sensitive in performance to the type of modification.

Conclusions

This study shows that chemical modification of wood can affect adhesion. Acetylation did not always give the highest percent wood failures with all the adhesives; however, it was able to produce the strongest bonds in both dry and wet conditions. The effect of improved adhesion could not be determined for the butylenes- and propylene-oxide modifications because although the treatments produced very high wood failure percentages, the wood was substantially weaker, giving shear strengths comparable or lower than that of the untreated wood. Thus, we were not able to test our hypothesis that the additional hydroxyl groups provided by the oxide modifications could provide superior adhesion over the wood that was acetylated.

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