Chemical Modification of Wood for Improved Adhesion in Composites

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Abstract

Failures in adhesion of wood particles or fiber in a composite board can result from several factors. Poor chemical and physical intetfacial interactions between the wood surface and the resin and dissimilar swelling of resin and wood resulting from moisture sorption are two of the most important mechanisms of bond failure. By changing the chemical nature of the polymers in the wood cell wall, properties such as dimensional stability, moisture sorption, and compatibility with other materials can be modified which may improve adhesion. Three methods for wood modification are presented along with the effects of modification on adhesion properties of acid and alkaline catalyzed phenolic and isocyanate resins.

Introduction

Much of the research that has been done over the years in the area of wood based adhesives has mainly been in bond performance and durability and the development of new adhesives from various resources. These studies focus on the adhesive. A more fundamental approach is not to study adhesives but to study the mechanism of adhesion. Broadly defined, adhesion is a domain involving two adherend interfaces (surfaces) and the development of a matrix between the two (Figure 1). If a penetrating matrix is developed, then the adhesion domain also includes two interphases (the area below the surface that the matrix can reach).

Both physical and chemical factors are involved in the mechanism of adhesion between two similar or dissimilar surfaces. If a resin is used as a bonding agent, physical entanglement of the developed polymer into a porous surface can aid in adhesion. Chemical factors such as dipole interactions, hydrogen bonds, dispersion forces, ionic bonds, and covalent bonds can also play a major role in adhesion. There are many factors to consider when studying the mechanism of adhesion depending on the nature of the surface of the adherend and the adhesive. Assuming the adherend is wood, if the adhesive is a resin, then adhesion will depend mainly on surface wettability, penetration, reaction, polymerization (development of a large molecule), porosity, pH, moisture content, extractives, chemical interactions, surface free energy, surface area, and which surface (radial, tangential or longitudinal) will come in contact with the resin. If the adhesive is a hot melt, then adhesion will depend mainly on porosity, pH, moisture content, extractives, surface area, and, which surface will come in contact with the melt. If the adhesive is a so-called "non-conventional" type, such as enzymatic, free radical, surface activation, crosslinking, etc., adhesion will depend mainly on surface chemistry and proximity of surfaces.

The development of a successful adhesion domain results in what is commonly called a "strong glue line", "high internal bond", or a "durable bond line". Failures in the adhesion domain are usually the result of one or more of several factors: 1) poor chemical and/or physical interactions, 2) dissimilar swelling of adherend and resin when exposed to moisture, 3) poor stress transfer across the domain, or 4) adherend and/or resin failure due to environmental causes.

Wood is a hydroscopic resource and most cured industrial resins vary from somewhat to very hydrophobic. Using dissimilar polarities in the adhesion domain usually results in poor wetting resulting in incomplete resin penetration. The adhesion domain is generally formed in a low moisture content zone. As post-curing moisture enters the domain, both the wood and the resin sorb water but to different extents. The differential swelling which results causes stresses in the domain. Differential shrinking will also cause stress in the domain as moisture is lost. Moisture may also cause hydrolysis of the resin decreasing its molecular weight. This occurs in urea-formaldehyde resins but not in phenol- or resorcinol-formaldehyde resins. Stress transfer from resin to adherend depends on the degree of intimate contact between the two phases. The efficiency of this transfer

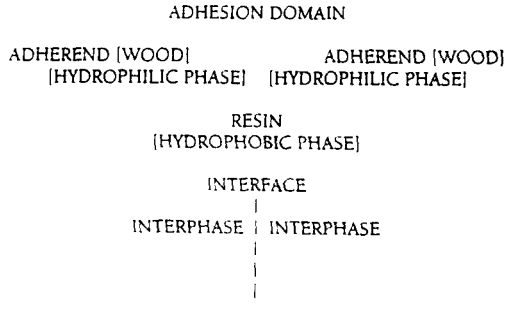

Figure 1. *Adhesion domain of a wood fiber in an adhesive matrix.*

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depends on the nature of the chemical and physical interactions in the vicinity of the interface. This interphase region is very different in morphology from the bulk of the adherend. The mechanical strength of the adhesion domain usually dictates the strength properties of the composite. That is, more wood failure outside the adhesion domain will occur under stress as compared to inside the domain if a successful domain has been developed. Finally, the adhesive domain can fail due to biological or chemical attack (1 ,2). Some resins are very resistant to micro-organisms while others are attacked sooner than the wood. Fire retardant bonded wood can fail in the adhesion domain due to acid catalyzed hydrolysis of the cellulose and hemicelluloses caused by the fire retardant chemicals.

The purpose of this paper is to take a theoretical look at the effects of three types of cell wall modification (reactions with acetic anhydride, propylene and butylene oxides, and formaldehyde) on the adhesion domain of two types of resins (alkaline and acid catalyzed phenolics and isocyanates).

The Resin

The type of resin used in the adhesion domain will influence its effectiveness as an adhesive. The resin usually starts as a low molecular weight pre-polymer and builds the degree of polymerization in the curing process. The resin will always be a resin but at some point it (hopefully) becomes an adhesive. When and how that occurs is an interesting study

The polar nature of the initial resin and developing polymer is critical to the wetting of the wood structure. The more polar the resin, the better the penetration into the wood structure. For phenolic-based resins, penetration of the prepolymer is important as one mechanism in their adhesive function is physical entanglement into the wood structure. Good penetration is also based on wood porosity and cell wall moisture content. Penetration may not be so critical for isocyanate-based resins where physical entanglement seems to play a minor role compared to their covalent bonding role in their effectiveness as an adhesive. The pH of the wood is important for all resin types as wood has a very large capacity as a buffer which can interfere with an acid or base catalyzed system. Wood is also a very effective chromatographic substrate which can result in the separation of two or more critical reactants in a resin system causing the whole system to fail due to an improper mass balance. For all types of resins, reaction with a cell wall hydroxyl group is possible if a favorable reaction condition can be achieved. Polymerization and crosslinking then occurs to build molecular size and stability of the polymer.

Phenolics

In alkaline catalyzed phenol formaldehyde resins (resoles), the addition of formaldehyde to the phenol takes place in *ortho* and *para* positions of the phenol ring giving rise to many possible polymerizing monomers. After formation of these methylol-substituted phenols, reaction takes place with each other and unreacted phenol to give a complex mixture of molecules of different sizes and degrees of branching (13). By controlling the reaction conditions, resoles can be made that are water soluble with a molecular weight below 500. When polymerization (curing) takes place in the wood, a complex, thermoset, crosslinked resin results. Under alkaline conditions, the hydroxyl groups on the phenolics and the wood cell wall polymers do not enter into the reaction, so no covalent bonding to the wood occurs.

In acid catalyzed phenol formaldehyde resins (novolaks), formaldehyde reacts with the phenol in electrophilic substitution in the *ortho* and *para* position of the phenol ring. The methylol groups are unstable under acid conditions and stable methylene bridges are formed. Polymerization proceeds mainly in the formation of a non-crosslinked polymer with a molecular weight of under 2000. Because novolaks are not highly branched, they tend to be water soluble at high molecular weights and tend to be more thermoplastic in nature than resoles.

Under acid conditions, it is theoretically possible for the formaldehyde to crosslink with wood cell wall hydroxyl groups. However, this reaction

$$\text{WOOD-OH} + \text{HCOH} \rightarrow \text{WOOD-O-C(OH)H}_2 + \text{HCOH} \rightarrow \text{WOOD-O-CH}_2\text{-O-WOOD}$$

usually takes place using a very strong acids such as sulfur dioxide or sulfuric or hydrochloric acid. If some crosslinking did take place during acid catalyzed phenol-formaldehyde resin reactions, the hydroxyl groups on the wood polymers would be involved in the reaction.

Isocyanates

Generally, diisocyanates or low molecular weight polyisocyanates are used in the manufacturing of polyurethane resins. Unlike phenolic resins, isocyanates can react with a cell wall hydroxyl group (8). The general reaction is:

$$\text{WOOD-OH} + \text{R-N=C=O} \rightarrow \text{WOOD-O-CO-NH-R}$$

In studies with acetylation, the acetate group was mainly found on the lignin followed by the hemicelluloses (10). It can be assumed that a similar pattern occurs with isocyanate substitution.

Table 1 shows that alkaline catalyzed phenolic resins are more hydrophilic than isocyanate resins. Comparing equilibrium moisture contents (EMC) at different relative humidities (RH), control flakes are higher in moisture

content at a given RH then a phenolic bonded board which is higher than a isocyanate bonded board (11, 16). When acetylated flakes are used, flakeboards made using phenolic resin at both 65 percent and 90 percent relative humidity have a higher moisture content than boards made using isocyanate resin. The isocyanate bonded flakeboards made from acetylated flakes are lower in moisture content at these two relative humidities than the acetylated flakes alone. This means that the isocyanate resin is lower in EMC than the acetylated flakes alone.

The Modified Adherend

Many reagents have been reacted with wood to change properties (4-6). The most studied of all modification is acetylation. The reaction of wood cell wall hydroxyl groups with acetic anhydride is as follows:

$$\text{WOOD-OH} + CH_3\text{-CO-O-CO-}CH_3 \rightarrow \text{WOOD-O-CO-}CH_3 + CH_3\text{-CO-OH}$$

For every molecule of acetic anhydride that reacts, one hydroxyl group is substituted and one molecule of acetic acid is formed. This reaction does not require a catalysis and is usually carried out at reaction temperatures between 120°C to 160°C (8).

The reaction of formaldehyde with wood cell wall hydroxyl groups is given above.

The reaction of epoxides with ceil wall hydroxyl groups is as follows:

$$\text{WOOD-OH} + \text{R-CH}\overset{/O\backslash}{\text{—}}\text{CH2} \rightarrow \text{WOOD-O-}CH_2\text{C(OH)H-R}$$

If R is CH_3, then the reagent is propylene oxide. If R is CH_3CH_2, the reagent is butylene oxide. For every molecule of epoxide that reacts, one wood polymer hydroxyl group is substituted but a new hydroxyl group is formed in the reaction. The reaction is usually catalyzed by an organic base (such as triethyl amine) and carried out at reaction temperatures between 110°C to 135°C (8). The complete epoxide molecule reacts leaving no byproducts.

Table 2 shows the EMC and antishrink efficiencies (ASE) of pine veneers reacted with acetic anhydride, formaldehyde, and propylene and butylene oxides (7). The order of lowest to highest EMC and ASE is formaldehyde, acetic anhydride, butylene oxide, and propylene oxide. Very low levels of formaldehyde are effective in reducing EMC and ASE due to crosslinking of fibrils through a very short -O-C-O- bonds. Acetic anhydride, butylene, and propylene are effective in reducing EMC and ASE by bulking the cell wall with bonded chemical to near the cell wall elastic limit so there is little addition room for water. Since the bonded chemicals are larger than the water molecule, there are still some cell wall hydroxyl groups available for hydrogen bonding with water. Since there are new hydroxyl group generated during the epoxide reactions, the ASE is high due to bulking but the additional hydroxyl groups can hydrogen bond so the EMC values are also higher as compared to acetylation where no new hydroxyl group is generated during reaction.

The Adhesion Domain in Modified Wood

Knowing the chemistry of acid and alkaline catalyzed phenolics and isocyanate resins and of the modified adherend, it is possible to speculate on the adhesion domain when these resins come in contact with a chemi-

Table 1. *Equilibrium moisture content of control and acetylated aspen flakes and flakeboards* at various relative humidities (RH).*

	Equilibrium Moisture Content (%)								
	30% RH			65% RH			90% RH		
	Flakes	Phenolic board	Isocyanate board	Flakes	Phenolic board	Isocyanate board	Flakes	Phenolic board	Isocyanate board
Control	4.9	3.8	4.4	11.1	8.6	8.5	21.5	19.0	17.0
Acetylated	2.0	2.1	2.2	5.2	5.9	4.7	10.7	13.9	8.9

* 5% Phenolic or 3% Isocyanate adhesive resin solids.

Table 2. *Equilibrium moisture content and antishrink efficiency of control and chemically modified pine veneers.*

		Equilibrium Moisture Content at 27°C				
Chemical	Weight Percent Gain	0% RH	35% RH	65% RH	85% RH	ASE
Control	0	1.0	5.0	8.5	16.4	—
Acetic anhydride	20.4	0.7	2.4	4.3	8.4	70.5
Formaldehyde	3.9	0.4	3.0	4.2	6.2	83.2
Propylene oxide	21.9	1.4	3.9	6.1	13.1	62.0
Butylene oxide	18.7	1.3	3.5	5.7	10.7	68.9

cally modified interface and interphase. There is some data in the scientific literature in this area but the information is incomplete.

Blocking hydroxyl groups should have a greater effect on the adhesion domain of an isocyanate resin as compared to a phenolic since the isocyanate resins can react with wood hydroxyl groups. Table 3 shows data on strength properties of aspen control and acetylated flakeboards using both an alkaline catalyzed phenolic and an isocyanate resin (11,16). This data shows that there is a greater effect on strength properties of acetylated wood using a phenolic resin than an isocyanate resin. There is about a 40 percent loss in internal bond using acetylated flakes as compared to control flakes using a phenolic resin but only at 2 percent loss using an isocyanate. There is about a 35 percent reduction in modulus of rupture (MOR) using acetylated flakes as compared to control flakes using a phenolic resin but only a 25 percent loss using isocyanate.

Rudkin showed that acetylation reduced the strength properties of glue joints made with a urea-formaldehyde resin (12). Vick and Rowell also found a reduction in strength properties in acetylated yellow poplar veneer specimens as compared to control (15). Other researchers also found the same trend using both pine and spruce veneers (3, 14).

These results would suggest that the effectiveness of isocyanate resins in the adhesion domain is based on more than just surface chemistry and that the effectiveness of phenolics may have more influence on surface chemistry than once thought. There are certainly other factors to take into account. Looking back at the data in Table 2, the most obvious one is the change in wettability of a modified adherend as compared to a unmodified one. Hydrogen bonding will be greatly reduced due to chemical modification, water repellency will be greatly increased, and, therefore, wettability will be greatly reduced in all water-based resin systems. The available hydroxyl groups will be greatly reduced in acetylated and formaldehyde crosslinked specimens but unchanged in epoxide modified specimens.

Table 3. *Strength properties of aspen flakeboards made from control and acetylated flakes.*

Specimen	Internal Bond (kPa)	Modulus of Rupture (MPa)	Modulus of Elasticity (MPa)
	Phenolic (5%)		
Control	503	29.3	4270
Acetylated	324	19.4	3820
	Isocyanate (3%)		
Control	641	34.4	4475
Acetylated	627	26.6	3785

With the increase in dimensional stability and reduced EMC in acetic anhydride reacted adherends, there should be an increase in wet strength in the adhesion domain of acetylated specimens. Wet and dry shear strength data for pine plywood using acid and alkaline catalyzed phenolics and isocyanate resins is shown in Table 4. The data shows that acid catalyzed phenolics are more effective in the adhesive domain in retaining wet strength than alkaline catalyzed phenolics and isocyanates (15). It is impossible to tell from this data if this is just due to increased dimensional stability and water repellency or changes in surface bonding.

It is theoretically possible that the strong base in alkaline catalyzed phenolic resins could hydrolyze some of the acetyl groups on the cell wall polymer hydroxyls in acetylated wood. The data in Table 4 suggests that this may be happening as retention in wet strength over dry strength is the same for acetylated specimens as for control specimens.

The data in Table 4 on isocyanates suggests that surface bonding is very important in these resin systems as the control specimens retain a higher wet strength over dry strength as compared to acetylated specimens.

Conclusions

It is impossible, from the limited data that exists in the literature, to draw any significant conclusions as to the effect of chemical modification on the adhesion domain of phenolic and isocyanate resin systems. Even with greatly reduced hydroxyl availability in acetic anhydride reacted wood, the isocyanate resin system gave higher internal bond and modulus of rupture values than an alkaline catalyzed phenolic resin. The data also sugests that physical entanglement of isocyanate resins may play a larger role in adhesion than previously thought.

Lower strength values for acetylated wood composites as compared to unmodified wood for both isocyanate and phenolic resins may be due to a lowering in wettability and resin penetration into the modified wood.

Table 4. *Mean values of dry and wet shear strength of control and acetylated pine plywood.*

Specimen	Dry [MPa]	Wet [MPa]	Retained [%]
	Acid Catalyzed Phenolic (5%)		
Control	12.4	6.3	50.1
Acetylated	10.0	7.6	76.0
	Alkaline Catalyzed Phenolic (5%)		
Control	11.0	5.7	51.8
Acetylated	10.7	5.5	51.4
	Isocyanate (3%)		
Control	13	9.0	69
Acetylated	12.2	6.6	54

It would be interesting to look at the adhesive domain of isocyanate resins on epoxide modified wood. In epoxy modified wood, EMC is slightly reduced, dimensional stability is greatly improved, and a new hydroxyl group is generated in the reaction replacing the one involved in bonding. If the adhesion domain of isocyanates requires resin/hydroxyl bonding, this would be a very interesting system to study

It would also be very interesting to study the acid catalyzed phenolic system to determine if a catalyst could be developed to promote formaldehyde crosslinking alone with resin development. This could greatly increase both wet strength and wet stiffness.

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