

Chapter 19

Adhesion Mechanisms of Durable Wood Adhesive Bonds

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Abstract

This chapter presents and discusses the current state of the art regarding adhesion mechanisms in characterizing durable adhesive bonds for wood composites. Particular emphasis is placed on phenol-formaldehyde (PF) and polymeric methylene diphenyl diisocyanate (pMDI) adhesives. An overview of current adhesion mechanisms is presented with an emphasis on categorizing adhesion mechanisms relative to length scale. Characteristics of wood relative to bonding considerations are reviewed, and probable mechanisms for producing durable wood adhesive bonds are discussed.

Keywords: adhesion, bonding, durable, gluing, length scale, mechanisms, wood

Introduction

Gluing or bonding wood has been practiced for many centuries. It has been estimated that 70% of wood is adhesive bonded in industrial practice (Hemingway and Conner 1989). There are a plethora of wood composite products that rely on adhesives in their manufacturing processes. Wood composite products include glulam beams, plywood, oriented strand board, particle board and medium density fiberboard just to mention a few. Studying the mechanisms responsible for wood adhesive bonding has been an important aspect of wood science research over the past 50 years. It is envisioned that improvements in the understanding of wood adhesion mechanisms have the potential to result in better adhesive systems and more efficient and effective processing methods for the wide array of wood composite materials.

Adhesion theories and mechanisms

For wood bonding, studying adhesion mechanisms requires an understanding of wood material characteristics, surface science, polymer characteristics, and the interactions between polymers and surfaces. At present, no practical unifying theory describes all adhesive bonds, although some have proposed a unifying adhesion theory on the subatomic level (Nevolin et al. 1990). The most recent

state of the art for the adhesion science community groups adhesion theories or mechanisms into six models or areas (Schultz and Nardin 1994; Pocius 2002):

1. Mechanical interlocking
2. Electronic or electrostatic theory
3. Adsorption (thermodynamic) or wetting theory
4. Diffusion theory
5. Chemical (covalent) bonding theory
6. Theory of weak boundary layers and interphases

It should be noted that these mechanisms are not self-excluding, and several may be occurring at the same time in a given adhesive bond depending on the particular circumstance. Because of the microcellular characteristics of wood as a material, the mechanical interlocking theory has long been used to describe wood bonding (Browne and Brouse 1929). The electronic or electrostatic theory has been applied in practice to wood in finishing and coating operations, although this adhesion bonding mechanism needs more fundamental research. The adsorption or wetting theory has been exhaustively studied on wood over the past 40 years (Gray 1962; Shi and Gardner 2001). The diffusion theory has also received attention in wood bonding in the area of thermoplastic matrices used in wood plastic composites (Gardner et al. 1994). In addition, the concept of molecular interpenetration via monomer diffusion and subsequent polymerization is an important concept that speaks of monomers that penetrate on a molecular level for thermosetting adhesives (Marcinko et al. 2001). The chemical or covalent bonding theory has long been a focus of study for attempting to understand durable wood bonding with thermosetting adhesives, but this concept has not been realized, and, as is discussed later, it is very likely that covalent bonds between the wood and adhesive are not necessary for durable wood adhesive bonds. The theory of weak boundary layers for wood has also been extensively studied mostly due to the impact of mechanical damage on preparing wood surfaces for bonding and the impact of surface aging on inactivating wood surfaces (Christiansen 1990, 1991; Stehr 1999).

Adhesion interactions as a function of length scale

Grouping the six theories into categories facilitates the description of adhesion interactions. The prevailing adhesion theories can be grouped into two types of interactions: (1) those that rely on interlocking or entanglement and (2) those that rely on charge interactions. Furthermore, it is useful to know the length scales over which the adhesion interactions occur (Table 19.1). It is apparent that

Table 19.1 Comparison of adhesion interactions relative to length scale

Category of Adhesion Mechanism	Type of Interaction	Length Scale
Mechanical	Interlocking or entanglement	0.01–1000 μm
Diffusion	Interlocking or entanglement	10 nm–2 mm
Electrostatic	Charge	0.1–1.0 μm
Covalent bonding	Charge	0.1–0.2 nm
Acid-base interaction	Charge	0.1–0.4 nm
Lifshitz van der Waals	Charge	0.5–1.0 nm

the adhesion interactions relying on interlocking or entanglement (mechanical and diffusion) can occur over larger length scales than the adhesion interactions relying on charge interactions. Most charge interactions require interactions on the molecular level or nano-length scale. Electrostatic interactions are the only exception to this generalization. Electrostatic interactions can occur over wide length scales (Marshall et al. 1998), but for purposes of this discussion, adhesion interactions will be considered to operate from nanoscale to micron-length scales.

Practical length scale of wood composite elements

In researching information about the length scales of adhesion mechanisms, I came across a website that facilitates understanding the orders of magnitude of length scales from the nanoscale range to the astronomical range (<http://www.powersof10.com/powers/space/space.html>). I adapted this methodology for presenting length scale information on wood adhesive bonding interactions.

Approximately 40 years ago, George Marra provided a nonperiodic table of wood elements (Marra 1992) that provided a practical length scale for wood composite elements. The wood elements listed included logs, lumber, veneer, strands, chips, flakes, excelsior, particles, fiber bundles, fibers and wood flour. Marra left a question mark in his table for elements not yet described. Today we could include microcrystalline cellulose and cellulose nanoparticles as well as lignin- and hemicellulose-based preparations used in composite manufacture.

Wood adhesive interaction length scales

The comparison of wood adhesive interactions relative to length scale is listed in Table 19.2. Wood as a porous, cellular material has roughness on the micron scale but can also exhibit roughness on the millimeter scale, depending on how a particular wood element to be bonded is produced. For example, production of rotary-peeled veneer can produce roughness on a millimeter scale due to the creation of lathe checks. Pores or free volume also occur within the amorphous regions of the cell wall material on the molecular level.

Table 19.2 Comparison of wood–adhesive interactions relative to length scale

Component	μm	nm
Adhesive force	0.0002–0.0003	0.2–0.3
Cell wall pore diameter	0.0017–0.002	1.7–2.0
PF resin molecular length	0.0015–0.005	1.5–5.0
Diameter of particles that can pass through a pit	0.2	200
Tracheid lumen diameter	4–25	
Glue line thickness	50–250	

Source: Adapted from Sellers 1994.

Table 19.3 Orders of scale for wood–adhesive interactions

Scale	Wood–Adhesive Interaction
100 meter, 1 meter	Glulam beam laminates
10^{-1} meters, 10 centimeters	ASTM D 2559 Cycle delamination specimen
10^{-2} meters, 1 centimeter	ASTM D 906 Plywood Shear specimen
10^{-3} meters, 1 millimeter	Polymer microdroplet on wood or cellulose fiber
10^{-4} meters, 100 microns	Microscopic evaluation of wood-adhesive bondline
10^{-5} meters, 10 microns	Diameter of bordered pit
10^{-6} meters, 1 micron	Smallest resin droplets on medium density fiberboard furnish
10^{-7} meters, 100 nanometers	Scale of cellulose nanocrystals
10^{-8} – 10^{-9} meters, 1 to 10 nanometers	Scale of wood cell wall polymers

Wood relies on both interlocking and charge interactions to create a proper adhesive bond. Mechanical interlocking occurs on the millimeter and micron length scales, and diffusion entanglement within the cell wall pores occurs on the nanoscale. Charge interactions will occur on the nanoscale level, with the exception of electrostatic interactions. Electrostatic interactions are used practically in the wood industry for coating applications on a macro length scale.

A practical look at the orders of scale for examining wood adhesive interactions from the 1 meter scale down to the 100 nanometer scale are listed in Table 19.3. Evaluations of gross laminate adhesion failure surfaces in glulam beams occur at the 1-m length scale, whereas measurements on ASTM D 2559 cycle delamination specimens occur on the 10-cm length scale. Plywood lap shear specimen percent wood failure measurements are evaluated on the centimeter length scale. Interactions between polymer droplets on individual cellulose fibers are made on the millimeter length scale, and microscopic evaluation of the wood adhesive bondline occurs on the 100-micron length scale. A bordered pit on a softwood tracheid is 10 microns in diameter, and the smallest resin droplets on medium density fiberboard furnish are in the order of 1 micron in diameter. Cellulose nanocrystals are in the scale of 100 nanometers in length (Revol et al. 1992). Higher resolution atomic force microscopy (AFM) measurements offer great promise in elucidating the structure of the wood cell wall polymers on the nanoscale.

Multiscale modeling and simulation of adhesion

Multiscale modeling and simulation of adhesion interactions is being addressed in the materials field, and one practical area is in microelectromechanical systems (MEMS) (Robbins et al. 2002). Adhesion, capillary forces, and other factors can be ignored in most macroscopic machines but often dominate behavior at nanometer scales. Smaller length scales also lead to new physical effects. Flow boundary conditions change qualitatively as dimensions approach the mean free path, and packing effects and surface interactions can stabilize new phases with different structural, mechanical, chemical, and electrical properties. These issues presumably could apply to studying wood adhesion on the nanoscale level. One area that comes to mind is the use of AFM to probe adhesion interactions on wood surfaces.

Choosing the correct adhesive for bonding a material

To create a satisfactory adhesive bond in a composite material, certain criteria must be met (Pocius 2002). Six criteria have been identified:

1. Choose an adhesive that is soluble in the adherends.
2. Choose an adhesive with a critical wetting tension less than the surface energy of the adherend.
3. Choose an adhesive with a viscosity low enough so the equilibrium contact angle can be attained during the assembly time.
4. Provide a microscopic morphology on the adherends.
5. Choose an adhesive compatible with the weak boundary layer or remove the weak boundary layer.
6. For exterior exposure, choose an adhesive that can provide covalent bonding between the adherend and the adhesive.

Wood bonding considerations

Important characteristics of wood germane to adhesion processes are wood's porosity, anisotropy, dimensional instability, and surface properties. Wood as a cellular material is porous and exhibits differing levels of porosity as a function of species. As an anisotropic material, wood exhibits different physical and mechanical properties depending on the orientation of the wood element. Because of its hygroscopic nature, wood swells and shrinks as a function of moisture content, thus contributing to its dimensional instability. Wood surface property issues include chemical heterogeneity, surface inactivation, weak boundary layers, and processing impacts (i.e., machining, drying, and aging). Surface roughness of wood can contribute to better mechanical interlocking and to changes in wettability due to capillary forces. Surface properties of wood fibers may differ depending on the particular process used to isolate the fiber. Mechanically pulped fibers have lignin rich (nonpolar) surfaces, while chemical pulp fibers have carbohydrate-rich surfaces that will have greater polar (acid-base) functionality. Improved wood surface–adhesive/coating interactions can be achieved using coupling agents such as hydroxymethyl resorcinol (HMR) (Gardner et al. 2001).

Measuring wood surface properties

Wood surface properties can be measured by using a variety of analytical techniques, including visual methods, such as microscopy, and chemical methods, such as contact angle analysis, inverse gas chromatography, infrared, Raman and X-ray photoelectron spectroscopies. Microscopy techniques used on wood include conventional optical and fluorescence microscopy, laser scanning confocal microscopy, electron microscopy (scanning and transmission) as well as atomic force microscopy. Contact angle analysis can include sessile drop measurements on lumber and veneer (Liptakova et al. 1995), Wilhelmy plate measurements on veneer, pulp fibers and paper (Gardner et al. 1991), and wicking measurements on particle and pulp fibers (Walinder and Gardner 1999). Data obtained from contact angle analysis measurements can be used to determine wood surface energy, including polar and nonpolar contributions (Gardner et al. 2000).

X-ray photoelectron spectroscopy can be used to monitor the surface elemental analysis of wood, including oxygen/carbon ratios and functional group depth profiling (Gardner et al. 1996). Infrared and Raman spectroscopy can be used to measure surface chemical functional groups, and Raman

spectroscopy has been used to correlate chemical/mechanical properties of fiber surfaces (Tze et al. 2002).

AFM offers promising possibilities for studying wood adhesion interactions on the nanoscale (Groom 2001). AFM can measure fluid dampening on surfaces, electrostatic forces, fluid surface tension forces, van der Waals interactions, and coulombic forces.

Creating a durable wood adhesive bond

Wood wettability

To obtain a proper wood adhesive joint, good adhesive wetting, proper solidification (curing) of the adhesive, and sufficient deformability of the cured adhesive (to reduce the stresses occurring in the formation of the joint) are important (Baier et al. 1968). *Wetting* refers to the manifestations of molecular interaction between liquids and solids in direct contact at the interface (Berg 1993). Adhesion (wettability) requires molecular interaction (0.6 nm or 6 Å) of the liquid resin with the wood surface (Haupt and Sellers 1994).

For adhesive wetting, these manifestations include

- The formation of a contact angle at the solid and adhesive interface
- Spreading of the adhesive over a solid surface
- Adhesive penetration into the porous solid substrate.

Manifestation 1 (contact angle formation) is related to the thermodynamics of the liquid/solid interaction. Manifestation 2 (spreading) is due to the change of energy states on the solid surface, adsorption, and wetting kinetics. Spreading is also related to the droplet shape and solid surface structure. Manifestation 3 (penetration) is mainly related to the surface structure of the solid.

Diffusion into the wood cell wall

Based on work done with polyethylene glycol penetration into wood, data indicate that the effective nanoscale penetration of polymers into the wood cell wall occurs at a molecular weight of 1000 or less (Stamm 1964; Sellers 1994).

Three exterior durable wood adhesives have been shown to have wood cell wall penetration in the formation of a wood adhesive bond. pMDI has been shown to penetrate into the wood substrate and to intimately associate with the wood molecules (Marcinko et al. 1998). For bonding flakeboard with PF resin, both low and high molecular weight resin components are needed to achieve optimum board properties (Stephens and Kutscha 1987). Presumably, low molecular weight PF resin penetrates into the cell wall. Gindl et al. (2002) demonstrated that UV-microscopy is well suited for the investigation of resin diffusion into the wood cell wall. They monitored the diffusion of melamine-urea-formaldehyde into the cell wall. Swelling of the cell wall by the resin components was thought to play a role in diffusion.

Impact of solubility parameters on the wood adhesive bond

For the diffusion mechanism of adhesion to occur, there must be similar solubility parameters between the adhesive and adherend system. This phenomenon is well illustrated by solvent welding

in thermoplastic systems. The adhesive is typically a low molecular weight polymer solution in a compatible solvent that is applied to the adherend, and the solvent-polymer solution will diffuse into the adherend to create molecular entanglement characterizing a diffusion bond.

Recent work suggests that it is important to consider the ultrastructure characteristics of wood from a solubility parameter point of view (Hansen and Bjorkman 1998). It is interesting to note that the thermosetting or cross-linking adhesive systems that promote durable adhesive bonds in wood have molecular structures that are similar to lignin, and they also exhibit strong hydrogen bonding capability. These adhesive systems include phenol-formaldehyde resins, polymeric diphenyl methane diisocyanate (pMDI), and hydroxymethyl resorcinol (HMR). In addition, these systems typically have a range of molecular weights (M_w) that allow diffusion to occur in the wood cell wall, i.e., M_w less than 1000. Because PF, pMDI, and HMR are structurally similar to lignin precursors, they most likely will preferentially associate with the lignin macromolecule in the wood cell wall. It is also possible that these adhesives can associate with the accessible portion of the hemicellulose molecule in the cell wall. However, the mechanism responsible for the production of durable wood bonds is not entirely clear, but several possible explanations are offered here.

Interphase/interpenetrating polymer network

The adhesive systems discussed in the previous section can penetrate the wood cell wall on the molecular level in the amorphous regions where lignin and hemicellulose are present. They can bulk the cell wall by occupying the pore space and/or creating an interpenetrating polymer network (IPN) within the amorphous wood polymers, thus blocking hydrophilic functional groups. The resin system bulking can reduce water uptake in the cell wall, resulting in dimensional stabilization from the reduced swelling stresses. Water sorption experiments on HMR-treated wood indicate reduced water absorption and dimensional stabilization as a result of HMR treatment (Son and Gardner 2004). In addition, with the potential formation of an IPN, the cell wall is mechanically stiffened. Dynamic mechanical thermal analysis (DMTA) data confirms that HMR-treated wood is stiffer than untreated wood and that the lignin glass transition temperature is shifted to a lower temperature, suggesting that either cross-linking and/or polymer segment interactions are occurring in the cell wall between the lignin and the HMR (Son et al. 2005).

Solid-state nuclear magnetic resonance (NMR) experiments have been helpful in elucidating the interactions between PF and pMDI adhesives and wood on the molecular (nanoscale) level. Evidence suggests the formation of an IPN morphology existing at both types of wood-resin interphases. The formation of the IPN morphology is strongly influenced by resin molecular weight, cure temperature, and the presence of solvent. Schmidt and Frazier (2001) reported that ^{13}C NMR relaxation measurements revealed that the wood induces heterogeneity in the cured PF resin (indicating interactions at the molecular level), while neat PF resin is homogenous. Related work indicated homogeneity within the wood-PF interphase on the nanometer scale (Laborie and Frazier 2001). The mechanism of PMDI adhesion in wood is one in which the isocyanate resin form an anchored diffusion interphase. In true diffusion interphases, there is a need for mutual interdiffusion to occur between the two adhering phases. There is evidence that this occurs with the resin diffusing into the wood matrix and at least some wood components diffusing into the adhesive (extractives, moisture) (Marcinko et al. 2001).

It has been demonstrated that combining simple dynamic mechanical analysis (DMA) measurements with cooperativity analysis yields ample sensitivity to the interphase morphology for wood adhesive interactions (Laborie 2002). Cooperativity analysis is a way to measure intermolecular

coupling between polymer chain segments based on relaxations at or around the glass transition temperature (Donth 1996; Ngai 2000). “From simple DMA temperature scans, low molecular weight PF does not influence the lignin glass transition temperature. However, the Ngai coupling model of relaxation indicates that intermolecular coupling is enhanced with the low molecular weight PF. This behavior is ascribed to the low molecular weight PF penetrating lignin on a nanometer scale and polymerizing *in situ*. Furthermore, data from solid-state NMR and DMA studies complement the hypothesis that low molecular weight PF penetrates into the wood cell wall on the nanometer scale. High molecular weight PF resin forms separate domains from wood, although a very small fraction of the high Mw PF is able to penetrate wood polymers on a nanoscale” (Laborie 2002).

Wood adhesive covalent bonds

Over the years there has been considerable speculation whether exterior durable adhesives form covalent bonds with wood. For both PMDI and PF resins, there exists no direct evidence of covalent bonding between the wood and the polymer, although recent NMR studies suggest a possibility of covalent bonding occurring between wood and PMDI (Zhou and Frazier 2001). However, it has been demonstrated that wood contains functional groups that can create strong secondary chemical interactions (acid-base, hydrogen bonding) with adhesives (Gardner et al. 2000).

Dimensional behavior of wood and adhesives

One area of bonding research that continues to receive considerable attention is the durability of wood adhesive bonds to hygro-mechanical and environmental stresses. Indeed, standard tests for evaluating durable wood adhesive bondlines rely on moisture cycling of the bonded assemblies (ASTM 2000). The dimensional behavior of wood as a function of moisture content is well understood, and swelling and shrinkage values for a number of commercially important species in North America are tabulated in the *Wood Handbook* (USDA 1999). However, the dimensional behavior of adhesives used to bond wood is less known because of the inherent difficulty in producing testing specimens based on pure adhesive resins. Some success in studying the hygro-mechanical behavior of adhesive films has been realized (Bolton and Irle 1987; Muszynski et al. 2002). The shrinkage and swelling behavior of phenol-resorcinol-formaldehyde (PRF) resins are similar to wood, which may partially explain the moisture durability of wood bonded with this resin system. Similar dimensional responses to moisture cycling for both wood and adhesive suggest that less mechanical stresses will be experienced in the wood adhesive bondline.

Hydroxymethylated resorcinol (HMR) is a wood surface treatment method that has achieved great success in promoting durable bonding of epoxy resin to wood (Vick 1996; Vick et al. 1995, 1996, 1998). HMR treatment is also effective for enhancing adhesion of wood adhesives, such as phenol-resorcinol-formaldehyde, emulsion polymer/isocyanate, polymeric methylene diphenyl diisocyanate (PMDI), melamine-formaldehyde, and urea-formaldehyde resin as well as vinyl ester resin (Hensley et al. 2000). One hypothesis for the improved durability of adhesives on HMR-treated wood is that the HMR treatment acts as a wood surface stabilizer, i.e., it increases the dimensional stability of the outer wood surface layer. The HMR solution is comprised of low molecular weight molecules that can penetrate into the wood cell wall and chemically react with the cell wall constituents (Vick 1996). Increasing the dimensional stability of the wood surface in contact with an adhesive may help to explain the improved durability of HMR-treated wood composites.

Characteristics of a durable wood adhesive bond

Going back to the six criteria for creating a satisfactory adhesive bond we find that

1. Durable wood adhesives such as PF and pMDI resins have similar solubilities to the lignin in the wood cell wall (*Choose an adhesive that is soluble or diffuses into the adherends*).
2. Most wood adhesives exhibit adequate wetting on properly prepared wood substrates (*Choose an adhesive with a critical wetting tension less than the surface energy of the adherend*).
3. The dynamic behavior of wood adhesive wetting ensures proper contact angles will be obtained during assembly. (*Choose an adhesive with a viscosity low enough so the equilibrium contact angle can be attained during the assembly time*).
4. Inherently, wood has microscopic and nanoscopic morphology. (*Provide a microscopic morphology on the adherends*).
5. In producing a fresh surface for adhesive bonding, the chemical weak boundary layer is removed in wood, and mechanical damage inherent to the machining process may facilitate adhesive bonding in many types of wood composite elements. In addition, adhesives can be formulated to handle extractive contamination of the wood surface. (*Choose an adhesive compatible with the weak boundary layer or remove the weak boundary layer*).
6. Although speculated, covalent bonding between wood and adhesives has not been demonstrated. (*For exterior exposure, choose an adhesive, which can provide covalent bonding between the adherend and the adhesive*).

Durable wood adhesive bonds meet five out of the six criteria described above. In addition, it is very likely that the dimensional behavior of the wood and adhesive is very important in producing an exterior durable adhesive bond. So, for wood bonding the following criteria can be added to the list:

- Similarity in the dimensional behavior of the wood and the adhesive under moisture stress
- Formation of a dimensionally stable wood surface through the use of a coupling agent

Application

In researching the literature for this chapter, several areas of potential research topics became apparent. These include

- Fundamental studies on electrostatic mechanism of adhesion in wood
- Search for the “Holy Grail” of ascertaining whether covalent bonding occurs between wood and any polymer adhesive
- Impact of solubility parameters on wood/adhesive bonding
- Adhesion in wood/cellulose nanocomposites
- Multiscale modeling and simulation of wood adhesion.

Although this is not an exhaustive list of topics, it does point out that there are some potentially fruitful areas for fundamental and applied research in the wood adhesion arena.

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