

Characteristics of the Wood Adhesion Bonding Mechanism Using Hydroxymethyl Resorcinol

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Abstract

A recent collaborative effort among the U.S. Forest Products Laboratory, Virginia Tech, and the University of Maine has explored the possible bonding mechanisms contributing to durable wood adhesive bonding using hydroxymethyl resorcinol (HMR) surface treatment. Current adhesive bonding mechanisms include: mechanical interlocking, electronic or electrostatic theory, adsorption, thermodynamic or wetting theory, diffusion theory, chemical (covalent) bonding theory, theory of weak boundary layers and interphases. In this paper, the findings of the research project will be presented and categorized relative to current adhesion bonding mechanism theories. In addition, consideration will be given to HMR's impact on adhesion bonding relative to interactions across different length scales from molecular to macroscopic. HMR has been shown to diffuse into the wood cell wall on the molecular scale and appears to associate with lignin based on similar solubility behavior. Within the cell wall, HMR chemically crosslinks contributing both to an increased stiffness of the wood material and improved dimensional stabilization on a macroscopic scale.

Introduction

Hydroxymethyl resorcinol (HMR) has generated interest in the wood adhesion community since its introduction as a wood coupling agent in the mid-1990s. Much of this interest stems from the fact that HMR has been shown to be effective in producing durable adhesive bonds in an exterior environment for a number of diverse resin-adhesive systems. Thermosetting adhesives whose adhesion to wood is improved by HMR treatments include epoxy, emulsion polymer isocyanate, polymeric diphenylmethane diisocyanate (pMDI) (24), and phenol-resorcinol-formaldehyde (PRF) resin (23,24). For bonding wood to fiber-reinforced plastics (FRP), HMR promotes the exterior durability of the joints bonded with adhesives such as epoxy, PRF resin (24), and vinyl ester (10).

Despite the effectiveness of HMR treatment, the mechanism of wood adhesive bond enhancement remained unclear, providing impetus for the research presented in this paper. The original bonding mechanism proposed by Vick (24) describes the coupling action of HMR where ether linkages are formed between hydroxymethyl groups of the HMR and the primary alcohols (hydroxyls) of both the wood and a thermosetting adhe-

sive (epoxy). This proposed bonding mechanism, although conceptually plausible based on organic chemistry reactions, focuses on only a single adhesion bonding theory (covalent bonding), and only on the molecular length scale. To test a hypothesis that crosslinking is necessary for the positive action of HMR on durable bonds, increasingly higher amounts of 2-methylresorcinol were substituted for resorcinol in HMR formulations, their reactivities being much the same (5). Increasing substitution of 2-methylresorcinol progressively deteriorated the ability of HMR-type treatments to produce durable bonds between wood and epoxy resin. This is interpreted as indicating that crosslinking, not just higher molecular weight, is necessary to produce more durable bonds.

Objective

The purpose of this paper is to describe characteristics of the wood adhesion bonding mechanism using HMR. This work is a collaborative effort of the University of Maine, Virginia Tech, and the U.S. Forest Products Laboratory and was funded in part by the USDA National Research Initiative Competitive Grants Program. In describing the HMR bonding mechanism, fundamentals of wood adhesion bonding theories are reviewed with an emphasis on wood material behavior over length scales ranging from molecular to macroscopic. Material properties of HMR-treated wood are discussed with an emphasis on material behavior contributing to durable wood adhesive bonds.

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 wood adhesive bonds. The most recent state of the art, for the adhesion science community, groups adhesion theories or mechanisms into six models or areas (14,15). These are:

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

It should be noted that these mechanisms are not mutually exclusive 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 (2). The electronic or electrostatic theory has been applied in practice to process wood in finishing and coating operations, although this adhesion bonding mechanism has

not received much attention in scientific literature. The adsorption or wetting theory has been exhaustively studied over the past 40 years (9,17). Diffusion theory has also received attention in the area of thermoplastic matrices used in wood-plastic composites (7). In addition, the concept of molecular interpenetration via monomer diffusion and subsequent polymerization is an important concept which speaks of monomers that penetrate on a molecular level for thermosetting adhesives (11,13). 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, although 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 because of the impact of mechanical damage on preparing wood surfaces for bonding and the impact of surface aging on inactivating wood surfaces (3,4,20).

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 scale(s) over which the adhesion interactions occur. The comparisons of adhesion interactions relative to length scale are listed in **Table 1**. It is apparent that 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. Diffusion interactions (entanglement) occur primarily on the nano-length scale up to several millimeters depending on the size of the bond interphase. Mechanical interlocking occurs over several orders of length scale from sub-micron to several millimeters.

Wood-Adhesive Interaction Length Scales

The comparison of wood-adhesive interactions relative to length scale is listed in **Table 2** (16). 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. Free volume also occurs within the amorphous regions of the cell wall material on the molecular level. 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 of reactive adhesive monomers to

Table 1. ~ Comparison of adhesion interactions relative to length scale.

Category of adhesion mechanism	Type of interaction	Length scale
Mechanical	Interlocking or entanglement	0.01 to 2000 μm
Diffusion	Interlocking or entanglement	10 nm to 2 mm ^a
Electrostatic	Charge	0.1 to 1 μm
Covalent bonding	Charge	0.1 to 0.2 nm
Acid-base interaction	Charge	0.1 to 0.4 nm
Lifshitz van der Waals	Charge	0.5 to 1 nm

^a Dependent of size of the interphase.

Table 2. ~ Comparison of wood–adhesive interactions relative to length scale.^a

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

^a Adapted from Sellers 1994 (16).

form an interpenetrating polymer network 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 more in-depth discussion of wood–adhesive interaction length scales can be found in Gardner (6).

Material Properties of HMR and HMR-Treated Wood

The material properties of HMR and HMR-treated wood to be discussed are listed in **Table 3** along with associated measurement techniques and reference citations. Material properties examined include polymer properties, surface chemistry, adhesive wettability, thermal properties, and physical and mechanical properties.

Polymer Properties

HMR was designed to be a low solids content, low molecular weight coupling agent that could penetrate the wood cell wall at the molecular level. The low molecular weight nature of HMR solution was confirmed by Vick et al. (25). HMR in its reactive, application state mostly occurs as monomers, dimers, and trimers that can penetrate the wood cell wall because the molecular weight of these HMR molecules are less than 1,000.

Table 3. ~ References discussing material properties of HMR and HMR-treated wood.

Material property	Measurement technique	Reference
Polymer properties	Solubility parameter	Son et al. 2005 (19)
	HMR molecular weight	Vick et al. 1998 (25)
	HMR crosslinking	Christiansen 2005 (5)
Surface chemistry	XPS	Tze et al. 2005 (22)
Adhesive wettability	Contact angle analysis	Gardner et al. 2000 (8)
Thermal properties	DMA	Son et al. 2005 (19)
Mechanical properties	Stress relaxation via DMA	Sun and Frazier 2005 (21)
Physical properties	Dimensional stability via Wilhelmy Plate Measurement	Son and Gardner 2004 (18)

Based on theoretical calculations of solubility parameters for wood cell wall components and HMR, it is postulated that HMR most likely will associate with lignin because of their similar solubility parameters (19). Protonated HMR has a solubility parameter of 27.5 ($\text{J}^{1/2} \text{cm}^{3/2}$) while lignin, hemicellulose, and cellulose have solubility parameters of 31.1, 36.3, and 38.6 ($\text{J}^{1/2} \text{cm}^{3/2}$), respectively. Further support for the preference of HMR for lignin is the impact of HMR on possibly lowering the glass transition temperature (Tg) of lignin in dynamic mechanical analysis (DMA) experiments on HMR soaked wood veneers (19).

As a thermosetting chemical, HMR needs to form a crosslinked network in the cell wall to impart a durable wood adhesive bond. This HMR crosslinking nature was explored by Christiansen (5) who substituted resorcinol in HMR with progressively greater amounts of 2-methylresorcinol to lower the crosslinking ability. This substitution resulted in decreased wood–epoxy bond durability. The overall HMR polymer property results suggest that HMR will diffuse into the wood cell wall to form an interpenetrating polymer network (IPN) most likely in association with the lignin.

Surface Chemistry

Two primary means to measure surface chemical characteristics of wood are X-ray photoelectron spectroscopy (XPS) and contact angle analysis. XPS provides a measure of the elemental composition of the wood surface including carbon and oxygen percentages as well as the carbon oxidation state. Contact angle analysis can be used to probe the surface energetics (polar and dispersive character) as well as adhesive wettability of wood (8,22).

Upon treatment with HMR, treated wood surfaces exhibit an increase in non-oxidized carbons and a decrease in carbon-oxygen bonds (22). Any carbonyl or carboxyl functionality remains unaltered or slightly decreased

compared to untreated wood. However, despite the increase in non-oxidized carbon and the decrease in carbon-oxygen ratios, the oxygen/carbon (O/C) ratios either remain unaffected or become higher. This XPS result correlates well with the surface energetics, where it was found that HMR-treated wood reduced the dispersive (nonpolar) character, but increased the polar character of the wood surface (8). The enhanced polar interaction can be attributed to the hydroxymethyl groups of the HMR. Overall, the total surface energy of HMR-treated wood is similar to that of untreated wood.

Adhesive Wettability

A study examining the dynamic adhesive wettability of HMR-treated wood with phenol-formaldehyde (PF) and polymeric diphenylmethane diisocyanate (pMDI) resin indicated that HMR treatment decreased both adhesive wettability and the rate of adhesive wettability (8). The surface energetics' contribution to this decreased adhesive wettability behavior was initially correlated to the dispersive surface free energy, which decreased as a result of the HMR treatment. This result, however, may be better explained by the earlier discussion that HMR penetrates the wood cell wall on the molecular level and occupies free volume, thus contributing to limiting the rate of adhesive diffusion and penetration into the wood substrate.

Thermal Behavior of HMR-Treated Wood

The thermal behavior of HMR-treated wood was explored using DMA and differential scanning calorimetry (DSC) (19). It was found that HMR possibly lowers the glass transition temperature of lignin and, to a lesser degree, hemicellulose. Based on this data, HMR is postulated to act as a plasticizer, so that a flexible interphase (glueline and adjacent wood surface) could exist upon adhesive bonding. This flexibility would delay damages induced by hygro-thermal stresses during cyclic delamination testing via ASTM D 2559.

Mechanical Behavior of HMR-Treated Wood

The mechanical behavior of HMR-treated wood was also explored using DMA in both conventional DMA measurements and stress relaxation experiments. Depending on the drying conditions for HMR-treatment, the storage moduli of wood can be unaltered or reduced as a response to HMR soaking time (19). In a related DMA study, HMR significantly improved wood's resistance to stress relaxation (21). The earlier discussion on HMR crosslinking also indicated that mechanical aspects of the primer are important (5).

It is fascinating that HMR induces stiffness to wood, but such an effect is opposite to that of plasticization postulated in the preceding section. This material behavior might hypothetically be explained in the context of

antiplasticization. Antiplasticization is a known phenomenon where plasticizers, in a low concentration, improve stiffness and reduce fluid permeability of the host polymer (12). Plasticizers in small quantities (or low weight percent gain values) were shown to form small-sized domains, which preferentially fill the small voids in the free volume instead of larger voids (1). The smaller voids are usually located in the vicinity of the polymer chain ends which, upon association with plasticizers, would undergo mobility restraint. The restraint leads to a decrease in stress relaxation and free volume to result in the stiffness that was observed by Sun and Frazier (21). More work is needed to explore this antiplasticization hypothesis on HMR-treated wood.

Physical Properties of HMR-Treated Wood

On the macroscopic scale, HMR was shown to improve the dimensional stability of veneer as evidenced by smaller perimeter changes in water immersion tests using the Wilhelmy plate method (18). These tests also show dimensional stabilization efficiencies approached 80 percent. HMR treatment resulted in a highly efficient decrease in veneer swelling from 7.8 to 1.6 percent for untreated veneers. This dimensional stabilization result along with the stress relaxation results suggests that one aspect of the HMR coupling mechanism may involve covalent crosslinking and stabilization of amorphous regions against water swelling and other mechanical stresses. The stiffness and water resistance, according to the antiplasticization model of Anderson et al. (1) are expected to drop upon addition of large quantities of plasticizers, which fill the larger free-volume voids located along the polymer chains to favor plasticization effects.

Characteristics of the HMR-Treated Wood

Adhesive Bond

According to fundamental adhesion theories and the material properties of HMR-treated wood, the following characteristics of the HMR-treated wood adhesive bond can be listed:

- Mechanical interlocking should be similar to untreated wood.
- The diffusion of HMR into the wood cell wall and association with lignin based on solubility parameters, lowered lignin T_g as well as probable formation of an IPN is consistent with the diffusion theory of adhesion
- Enhanced surface chemistry (polar functionalities), weak boundary layer is positively impacted.
- Wood wettability is shown to be partially reduced but is still adequate.
- Covalent bonding between an adhesive and HMR-treated wood still needs to be explored, but may not be necessary to produce a durable adhesive bond.

Other attributes of HMR-treated wood that contribute to durable adhesive bonds, and should potentially be investigated as wood adhesion mechanisms, include:

- Lignin plasticization contributing to a more compliant wood surface layer and
- Improved wood surface dimensional stability.

Conclusions

Based on a synopsis of the material properties of HMR-treated wood and their relationship to fundamental adhesion theories, the bonding mechanisms of HMR-treated wood and the mechanisms responsible for durable wood adhesive bonds are better understood. This understanding required ascertaining the material characteristics of HMR-treated wood over length scales ranging from molecular to macroscopic and applying fundamental adhesion principles to this understanding. The results of this work should help provide a framework for researchers interested in developing adhesives and/or wood treatments to create durable wood adhesive bonds.

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