

SOLID WOOD PROCESSING

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Adhesion and Adhesives

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Introduction

Adhesion science and technology has developed since our earliest ancestors struggled to enhance their conditions. The struggle continues, and as with all modern technologies it is apparent that adhesion has evolved into a highly multi- and interdisciplinary activity. Three disciplines define the foundation of adhesion science and technology: chemistry, materials science, and mechanics of materials. It so happens that wood is a peculiar material with respect to each of these disciplines. The following discussion of wood adhesion touches upon the chemical and material sciences and is intended to direct the reader to the more complete treatments found in the recommendations for further reading. Afterwards, some of the more common wood adhesives are reviewed briefly.

Requirements for Adhesion

Adhesion is the process of 'making things stick.' By this definition, one appreciates that adhesive phenomena are widespread because sticky things and processes are all around us. However, this article focuses on applications in the forest products industry, a more narrow view because typical wood applications not only require 'stickiness,' but also structural integrity and long-term durability. There are three essential requirements for a durable, structurally sound adhesive bond:

1. Surface preparation.
2. Adhesive wetting.
3. Adhesive solidification.

While this seems like a simple plan, and it can be, each step is based upon numerous interacting variables. The highlights of each requirement follow.

Surface Preparation

The preparation of bonding surfaces involves chemical and physical parameters. Physically, a clean bonding surface is required, devoid of loose particles and other weak boundary layers. For wood bonding, most desirable is a well-machined smooth surface with minimal cellular damage and compression. Machining processes such as knife planing and veneer slicing produce smooth surfaces with little damage, when the blades are sharp. In contrast, processes such as abrasive planing and sawing produce more cell damage and a weakened surface layer. Under loading, such defects may concentrate stress and promote bond failure. Understand that all machining processes cause some level of wood surface damage. But again, planing and slicing with sharp blades provides the smoothest and most structurally sound surface; this is generally best. However, contradictory findings exist. For example, there are times when wood surface roughening improves bond test-strengths. However, any benefits from wood surface roughening are difficult to reproduce due to changes in other influential parameters, such as adhesive layer thickness, physical interlocking of wood surfaces, and stress concentrations. Predicting when wood surface roughening may improve bond test-strength is difficult at best. Consequently, a safer approach is to machine a smooth, sound surface with minimal cellular damage.

The chemical aspects of wood surface preparation are also important, and this addresses the concept of surface energy. Surface energy is a chemical manifestation of solids and liquids. It reflects the nature of electrical charges present on the surfaces of all molecules. A higher surface energy reflects a higher

degree of surface charge, lower surface energy, less charge. All molecules have surface charge, positive and negative, and all molecules tend to orient themselves in an attempt to neutralize this charge. This is the essence of adhesion; but these attractive adhesive forces act only over very small distances, under 10 nanometers, or on the order of molecular dimensions. This fact explains why all adhesives must be liquid at some stage, because only liquids can readily achieve intimate molecular contact over large bond areas. When liquid adhesives contact solid surfaces, the force of attraction depends upon the molecular surface charges, the surface energies of the liquid adhesive and the solid wood surface. Wood machining exposes 'fresh wood,' providing the highest possible surface energy which is very desirable for bonding. Unfortunately, there are many factors that tend to reduce the surface energy of wood, producing what is termed a deactivated or aged surface. These include: the simple deposition of airborne organic materials, ultraviolet radiation from the sun, excessive heat over time, and of course, dirt, grime and even oily human hands.

Adhesive Wetting

Wetting is the term used to describe how liquids adhere to solid surfaces. The quality of wetting, be it favorable or unfavorable, is a function of surface energy. This is why we are first concerned with surface preparation, and maximizing the wood surface energy. But we are also interested in the surface energy of the liquid adhesive. A relative measure of solid and liquid surface energy is observed through the 'contact angle,' as depicted in **Figure 1**. Also shown in **Figure 1** is the Young equation, which explains that the contact angle reflects the balance of surface energies (γ), that of the solid, the liquid, and the solid-liquid interface.

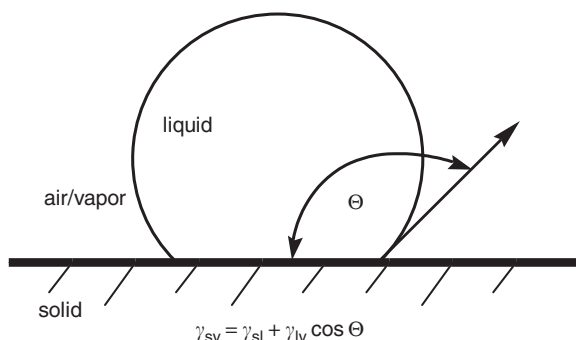


Figure 1 Depiction of the contact angle of a liquid on a solid surface. Also shown is the Young equation which describes the balance of surface energy (γ) between the solid, liquid and vapor phases.

Arbitrarily, 'favorable wetting' is defined by a contact angle less than 90° . When the contact angle exceeds 90° , wetting is 'unfavorable.' When a liquid adhesive favorably wets the bonding surface, the attractive forces at the solid-liquid interface are greater than the cohesive forces acting within the liquid adhesive. Generally, favorable adhesive wetting provides good bonding, but there is no guarantee because good wetting is but one aspect of good bonding. On the other hand and invariably, unfavorable wetting will result in a poor adhesive bond. Consequently, the concepts of surface energy and wetting are critical aspects of adhesion.

Figure 2 depicts two strategies for controlling adhesive wetting. First, let us consider some unchanging solid surface, which is wetted by three different liquids. As the surface energy of the liquid is reduced, wetting becomes more favorable and the contact angle is reduced. For example, consider the wetting properties of two liquids, water and isopropanol (rubbing alcohol). Water is polar and has a high surface energy, whereas, isopropanol is less polar with a lower surface energy. (The term 'polar' also refers to molecular surface charge; polar

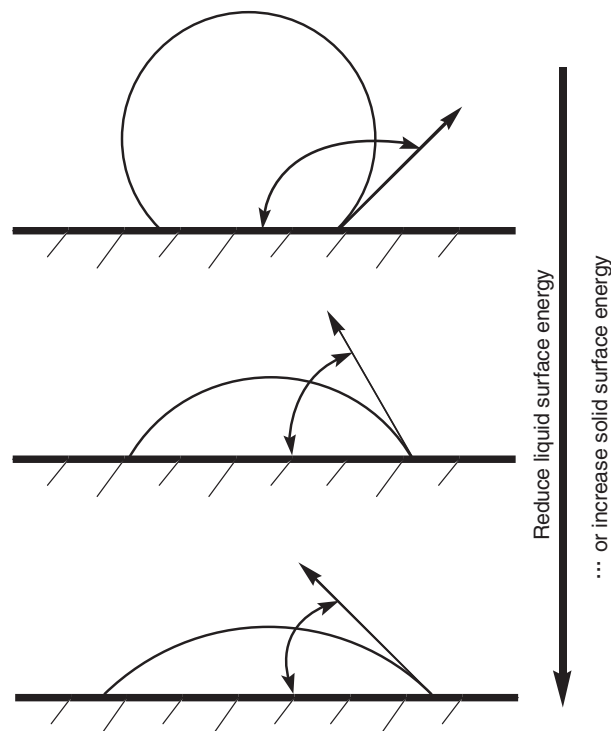


Figure 2 Illustration of two strategies for controlling the contact angle, or the wetting, of liquid adhesives on solid surfaces. Strategy 1: Three identical solid surfaces are contacted by three different liquids; wetting improves as the liquid surface energy is reduced. Strategy 2: Three different solid surfaces contacted by water in each case; water wetting improves as the solid surface energy is increased.

molecules have higher surface charge. Polarity and surface energy are generally related, but the terms should not be interchanged freely.) Isopropanol will wet any particular surface more favorably than will water. In other words, on a given surface the contact angle of isopropanol will be lower than that of water. Furthermore, one can improve the wetting of a liquid adhesive by simply reducing the surface energy of the adhesive. This is commonly achieved by adding wetting agents, chemicals that reduce the surface energy of aqueous solutions. Wetting agents are also referred to as surface active agents, or surfactants. Very small quantities of wetting agents dramatically reduce the surface energy of aqueous adhesives; wetting improves. Now look back at **Figure 2** as we discuss the second strategy to improve wetting.

If we consider a single unchanging liquid, we can improve the wetting of that liquid by increasing the wood surface energy. Imagine that **Figure 2** shows three different wood surfaces, each wetted by a drop of water. The topmost wood surface exhibits a low surface energy because the water contact angle is well over 90° . Likewise, the bottom surface has the highest surface energy, indicated by the lowest contact angle. The best bonds result from favorable wetting that is driven by a high wood surface energy. Unfortunately, we may not always control the wood surface energy. For example, remachining a deactivated wood surface immediately prior to bonding might not be feasible. One may then be forced to improve adhesive wetting by adding wetting agents. If given the choice, one should always achieve and maintain a high wood surface energy.

A simple test reveals differences in wood surface energy. One could measure the water contact angle on wood surfaces, but this is often impractical. However, it is easy to measure the time it takes a water drop to absorb into wood. If a water drop wets favorably, capillary forces rapidly draw the water into the wood. **Figure 3** shows data collected by a group of college students in the author's adhesion class. Water drops ($10\ \mu\text{l}$ in volume) were applied to red oak (*Quercus rubra*) samples having different surface treatments. The water absorption time is fastest on the freshly sanded surface; the sanded surface has the highest surface energy. Samples with the 'old surface' were stored in a plastic bag for 1 year, and they apparently lost surface energy because the absorption time is nearly doubled. The remaining samples were sanded and then heated at 185°C for 5 min, which caused a severe deactivation. Data on the far right of **Figure 3** demonstrate the power of wetting agents. In this case, the water drops contained 10% isopropanol, which causes a remarkable reduction in absorption time; wetting was

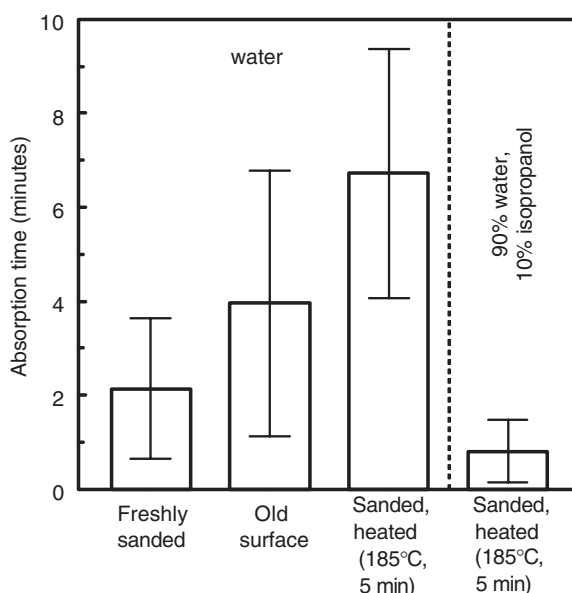


Figure 3 A simple method for comparing wood surface energies involves measuring the time it takes a $10\ \mu\text{l}$ drop of water to absorb into the wood surface. The data shown are for red oak samples exposed to different surface treatments as described in the text.

improved. The broad variation in the absorption times is caused by the natural variability of wood.

Adhesive Solidification

Favorable wetting is required because it ensures strong and intimate molecular contact between wood and adhesive. However, favorable wetting is not enough. After wetting, the adhesive must solidify in order to transmit load. Through wetting we achieve intimate contact and adhesion, but through solidification the adhesive forces are essentially locked into a solid state having mechanical integrity. Small molecules like water do not solidify under convenient conditions. In contrast, the very large polymer molecules solidify into strong solids under desirable circumstances. This is why nearly all adhesives are polymeric. Polymeric molecules, polymers or macromolecules, are extremely large chainlike molecules that may be linear, branched, or crosslinked into network structures. There are three general mechanisms for adhesive solidification: (1) solvent loss, (2) chemical reaction or polymerization, and (3) cooling of a molten adhesive. In all three cases, we are manipulating an important physical parameter of the adhesive, and this is the temperature at which the adhesive changes from a liquid into a solid. For many adhesives, this temperature is referred to as the glass transition temperature, T_g . For other adhesives, hot melt adhesives in particular, this may be the melting temperature, T_m .

Certain adhesives are actually solutions of polymers in organic solvents. While dissolved in the solvent, the polymers are fluid, capable of flow and wetting. Afterwards, the solvent evaporates and/or absorbs into the wood. As the solvent evaporates, the adhesive polymers become less mobile, eventually transforming into a tough, solid adhesive layer (**Figure 4a**). Solvent loss also occurs for another common class of wood adhesive; these are latex adhesives, the water-based 'white glues.' Latex adhesives are actually water dispersions of soft microscopic polymer particles. The fluid latex wets and flows. As water is absorbed into the wood, the particles pack together and deform as they begin to coalesce. When completely dry, the particles have fused into a solid, tough and continuous adhesive film (**Figure 4b**). Adhesives that solidify through solvent loss are typically thermoplastic, meaning they will deform and flow under elevated temperatures. Such thermoplastic adhesives are not designated as

structural adhesives because they may deform, or creep, under loading. Creep is avoided in adhesives that solidify through chemical reaction (polymerization) into rigid network structures. These adhesives are called thermosetting adhesives or resins. During application, thermosetting resins are chemically reactive fluid mixtures. While heated, they react into highly crosslinked, rigid network structures (**Figure 4c**). All wood adhesives that satisfy structural applications are thermosetting. Finally, hotmelt adhesives solidify by simply cooling from the molten state into a tough solid. The polymers in hotmelt adhesives are often semicrystalline. Semicrystalline polymers are typically linear and actually pack into three-dimensional crystal structures, or crystallites. Separate polymer chains pack into the crystallites and become 'physically crosslinked.' The hotmelt adhesive must be heated above the T_m of the crystallites, breaking the physical crosslinks and allowing the polymers to flow and wet. Upon

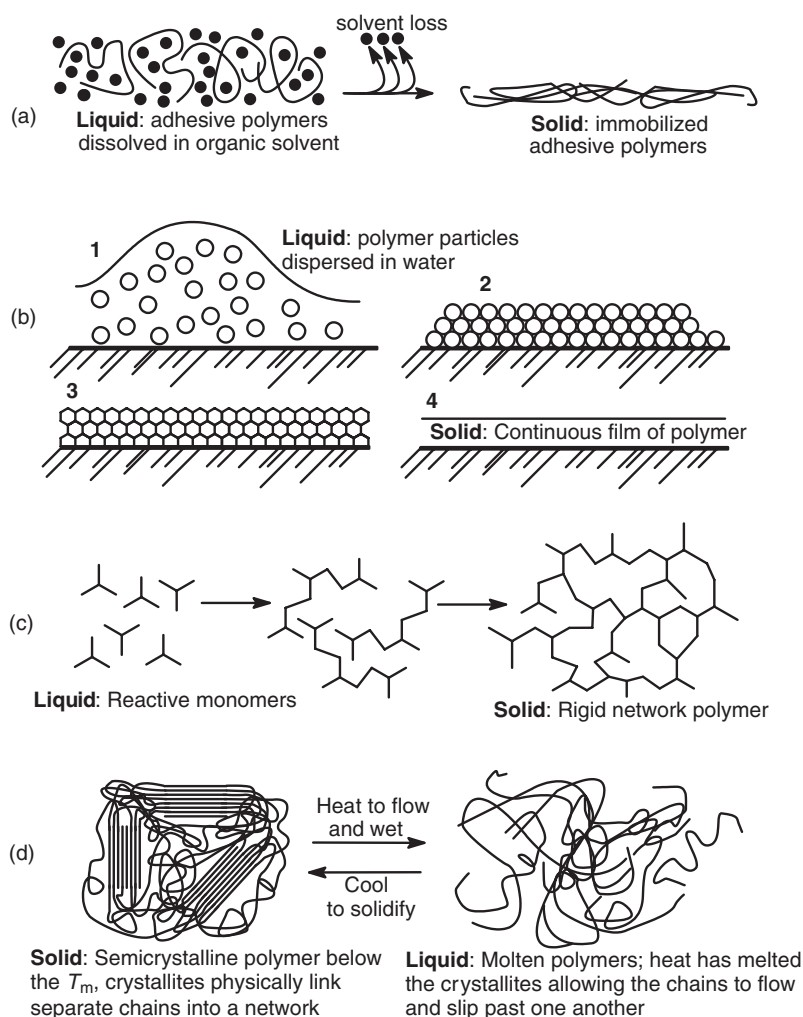


Figure 4 Illustration of four different ways that adhesives solidify to achieve structural integrity.

cooling, the crystallites reform and the adhesive is again a tough solid (Figure 4d).

Theories of Adhesion

There are generally five recognized mechanisms or theories of adhesion: (1) the theory of mechanical interlock, (2) the adsorption theory, (3) the covalent bonding theory, (4) the interdiffusion theory, and (5) the electronic theory. Not all of these theoretical mechanisms are important for wood bonding; we shall limit our attention to those that are. The reader interested in all theories should consult the recommendations for further reading.

Mechanical Interlock

The mechanical interlock theory states that adhesives must flow onto the bonding surfaces and into macro- and microscopic voids. After solidification, the adhesive and bonding surfaces are interlocked, or keyed, and capable of withstanding great shear forces. Of course, wood is porous and experience has shown that ideal performance results from adhesive penetration into the cell layers beneath the bonding surfaces. Consequently, it is clear that mechanical interlock contributes to wood adhesion. In the past some have argued that the interlocking mechanism is most important for wood adhesion. While mechanical interlocking is important, it cannot be described as the primary wood adhesive mechanism, for reasons that we shall discuss. Aside from the interlocking mechanism, one should appreciate that adhesive penetration reinforces the damaged surface cells, preventing crack initiation in the bondline.

Adsorption

We have already touched upon issues related to the adsorption theory; these are the concepts of surface energy and wetting. The adsorption theory states that adhesion results from intermolecular forces, also called secondary forces or secondary bonds, between the adhesive and substrate. The secondary forces are merely electrostatic attractions between complementary charges on molecular surfaces. All molecules possess positive and negative surface charge because atoms and molecules contain charged particles, the negative electrons and the positive protons. Depending upon the atomic elements and their molecular configuration, molecules may have permanent and relatively high-magnitude surface charge (polar molecules), or they may have temporary and lower-magnitude surface charge (nonpolar molecules). The secondary forces described in the adsorption theory

are the simple electrostatic attractions between opposite charges on molecular surfaces. Collectively, these forces are referred to as the Van der Waals forces which includes the weak London, or dispersion, forces and the very strong hydrogen bond. Wood forms strong hydrogen bonds with water, and also with many types of adhesives. The adsorption theory is the most important adhesive mechanism for bonding all materials. So while mechanical interlock is important for wood bonding, adsorption and intermolecular forces are always dominant. Without favorable wetting and secondary forces, adhesive penetration is impaired and mechanical interlock becomes much less effective (Figure 5).

Covalent Bonding

The covalent bonding theory states that adhesion results from covalent, or primary, bonds between adhesive and substrate. Primary bonds are the very strong bonds that hold atoms together as molecules, and are an order of magnitude stronger than secondary bonds. Consequently, adhesion through covalent bonding is highly desirable because such bonds are not easily broken. In contrast, secondary bonds may be disrupted by water and/or elevated temperatures. Covalent bonding could be very important for wood adhesion because wood contains many chemically reactive sites that could provide strong covalent bonds to the adhesive. Not all adhesives possess the chemical properties that promote covalent bonding. Consequently, this adhesive mechanism is relatively specialized, but occasionally important for wood.

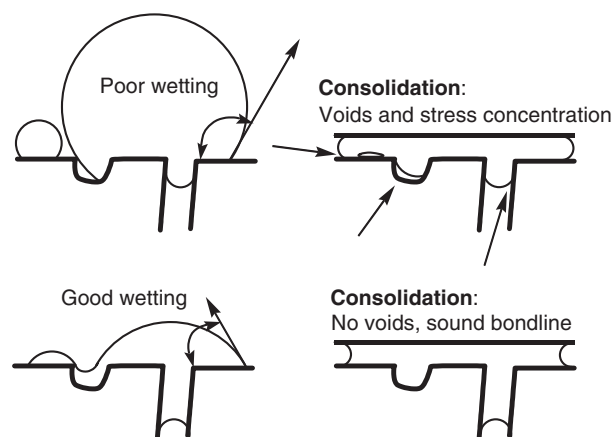


Figure 5 Illustration of the consequences of poor and good adhesive wetting on wood surfaces. Poor wetting promotes void formation by the inefficient coalescence of adjacent adhesive drops, and also by the inability to force air out of small crevices. Also, poor wetting inhibits adhesive penetration and promotes stress concentration. On the other hand, good wetting prevents these problems.

In summary, adsorption and mechanical interlock both contribute to wood bonding, and under special circumstances covalent bonding may also be important. While covalent bonding deserves special consideration, this adhesive mechanism does not improve the tested strength of wood bonds. Adhesion through adsorption and mechanical interlock produces very strong bonds that prove to be stronger than wood (depending upon the test method). However the special case of adhesion through covalent bonding would dramatically improve bond durability.

Wood-Related Factors that Impact Bond Performance

Wood Moisture Content

Wood is a hygroscopic material. Consequently, wood moisture content is determined by the prevailing environmental conditions (*see Wood Formation and Properties: Formation and Structure of Wood; Physical Properties of Wood*). Generally speaking, dry wood is easiest to bond, whereas very wet or green wood is difficult to bond for at least two reasons. The first is that wet wood is essentially encased in a layer of water; this prevents molecular contact. Secondly, as moisture is lost the wood shrinks, creating large bond stresses that may promote delamination. This is particularly troublesome when bonding cross-grain assemblies (**Figure 6**). The moisture-related dimensional change of wood in the longitudinal direction is quite small, whereas the same change in the radial and tangential directions is large. These dimensional changes oppose each other in cross-grain assemblies, creating potentially damaging bond stresses. The solution is to avoid cross-grain joints, use lower-density woods that exhibit less moisture-related

dimensional change, and use compliant adhesives not brittle ones. Of course, each of these solutions entails a peculiar set of trade-offs.

Another important aspect of wood moisture content impacts bond assembly with waterborne adhesives. Optimum bonding requires attention to consolidation pressure, adhesive viscosity and wood porosity; all of this controls penetration and bond thickness. Wood absorbs adhesive moisture, which rapidly changes the viscosity. If the bonded wood is excessively dry or wet, the adhesive will respectively dry out rapidly, or not at all. In either case, this influences how adhesive viscosity interacts with consolidation pressure and wood porosity to achieve the proper penetration and bond thickness.

Wood Density and Porosity

Dense woods have low porosity, and this often impairs adhesive penetration. Similarly, woods with uneven grain (nonuniform density from abrupt earlywood-latewood transitions), typically exhibit nonuniform penetration which can lead to undesirable stress concentrations. Likewise very-high-porosity, low-density woods may promote over penetration if the adhesive and consolidation parameters are not adjusted.

Very-high-density woods may also promote durability problems arising from moisture-related dimensional change, as mentioned previously. Higher-density woods shrink and swell to a greater degree, thus generating larger stresses on the bond. Regarding this point, also note that larger more massive wood components generate greater forces during moisture-related dimensional change, regardless of the wood density.

Extractives

Extractives are nonstructural organic molecules that result from primary and secondary metabolic functions in the living tree (*see Non-wood Products: Chemicals from Wood. Papermaking: Paper Raw Materials and Technology. Wood Formation and Properties: Chemical Properties of Wood*). This general term, extractives, represents a tremendous variety of chemical compounds. Collectively, the extractives are often cited as a major source of bonding problems. The resinous and fatty compounds are particularly troublesome because they may impair wetting by forming a nonpolar film on the wood surface. This process is often referred to as extractives migration, and is accelerated by heat. The loss of wood surface energy, or deactivation, caused by excessive thermal treatment is thought to arise from extractives migration to the wood surface.

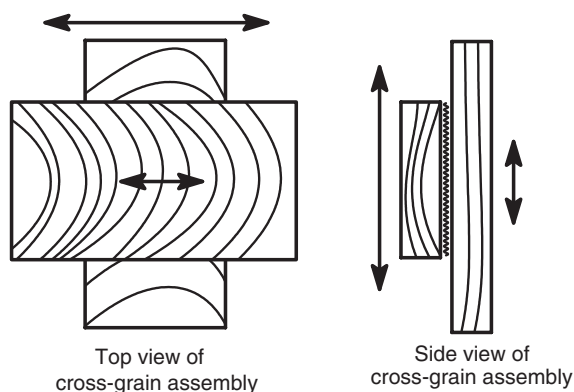


Figure 6 Illustration depicting the stresses that form in cross-grain assemblies, when solid wood is bonded such that the moisture-related dimensional changes in one piece oppose those in the other piece. The size of the double arrows indicates the relative degree of moisture-related dimensional change.

Besides the lipid-like extractives, other extractive compounds may interfere with adhesives that cure under acidic or basic conditions. Certain acid and phenolic extractives influence the buffering capacity of wood, as discussed in the following section.

Wood Buffering Capacity

A buffer, or buffer solution, is an aqueous mixture that resists changes in pH. Different woods often behave as buffers and so may influence the cure of aqueous adhesives that polymerize under acidic or basic conditions. As with most properties, the buffering capacity is highly variable between woods. Within woods, there is often a marked difference between heart- and sapwood. Unfortunately, no commonality exists; in certain woods the heartwood is more buffering, while the sapwood is more so in other trees. When wood buffering is a problem, it either retards or accelerates cure. In the latter case, premature reaction is undesirable if it occurs prior to complete bond consolidation because adhesive flow and penetration may be impaired.

Drying and Surface Aging

This wood-related variable has been touched on previously. The vast majority of wood is dried prior to use, and so there is always an opportunity for surface deactivation. Recall that excessive heating may reduce the wood surface energy to the point that adhesive wetting is harmed. Drying will always reduce wood surface energy below its maximum, which is achieved after machining. However, only severe thermal treatments result in bonding problems. The sensitivity to thermal deactivation is highly variable among different woods.

Common Wood Adhesives

Phenol-Formaldehyde (PF) Resins

Thermosets made from phenol and formaldehyde (PF) are the first synthetic polymers to have been commercialized, which occurred early in the twentieth century. Two classes of PF resins exist: novolaks and resols. Novolaks function under acid conditions, and also require addition of formaldehyde 'hardeners' to cure. Resols operate under alkaline (basic) conditions, and only heat is required for cure. Of resols and novolaks, it is the resols that are preferred in the forest products industry, most commonly in liquid form. They are also prepared as powders and supported films.

PF resols are commonly used for the manufacture of structural composites such as oriented strandboard

(OSB), plywood, parallel strand lumber, and laminated veneer lumber, and for nonstructural composites like hardboard. PF resins are highly durable and are exterior grade, weather-resistant structural thermosets. PF formulations vary widely according to application, i.e., hardboard resins versus plywood resins. PF resols are moderately priced compared to other wood adhesives, but they are probably the least expensive exterior grade wood adhesive.

Since PF resols contain formaldehyde, there is minor concern about the potential health risks of formaldehyde emissions. However, this concern exists only during wood composite manufacture where some free formaldehyde may emit during hotpressing. Any formaldehyde within composite products dissipates rapidly, so long-term formaldehyde emission is absent in PF-bonded wood products.

Urea-Formaldehyde (UF) Resins

Wood-bonding thermosets made from urea and formaldehyde (UF) are the largest production-volume wood adhesives in the world. UF resins are used for interior applications as in the case of particleboard, medium density fiberboard or decorative plywood. In other words, UF resins are not hydrolytically stable; moisture exposure causes adhesive degradation. UF resins are highly versatile and may be synthesized and formulated in many ways for a vast array of applications. Most UF resins are used in water-based liquid form, but they may also be produced as powders and films. In addition to their excellent performance, UF resins are very inexpensive.

While liquid PF resols are stored under alkaline conditions, liquid UF resins are stored very near neutral conditions (pH ~ 7). Liquid UF resins require an acid catalyst which is added immediately prior to cure. UF resin formaldehyde emission has received great research attention and regulation. Atmospheric moisture causes a very slow decomposition of the cured resin that causes long-term formaldehyde emissions in products like particleboard. To its credit, the UF resin industry has drastically reduced formaldehyde emissions while maintaining excellent performance. Formaldehyde emissions are controlled by manipulating the formaldehyde : urea mole ratio. This is accomplished by blending resins made with different mole ratios, or by adding formaldehyde scavengers such as urea.

Melamine-Formaldehyde (MF) Resins

Resins made from melamine and formaldehyde (MF) are similar to UF resins; however, they are superior to UF resins in many respects. MF thermosets are more durable and emit less formaldehyde than UF resins.

MF resins are used to produce plywood and particle-board for exterior or semiexterior applications. Melamine is a very expensive chemical, and so MF resins are commonly prepared with urea (MUF resins) to reduce costs.

A distinguishing characteristic of MF resins is chemical inertness, as well as hardness, lack of porosity and nonabsorbency in the cured state. These traits have provided endless lamination applications for MF resins. For example, paper sheets are impregnated with liquid MF and subsequently dried to produce supported, nontacky films that may be stacked and thermoformed onto various substrates including wood-based panels. Consequently, MF resins are commonly used for low- and high-pressure paper laminates and overlays, producing durable tabletops, industrial bench tops, etc.

Polymeric Methylenediphenyldiisocyanate (pMDI) Resins

Polymeric methylene bis(phenylisocyanate) is commonly referred to as pMDI or MDI, or even just as 'isocyanate.' Its use as a wood binder is relatively recent, growing in importance over the past 30 years. pMDI is commonly used for particulate wood-based composites such as OSB and laminated strand lumber. It is a highly durable, exterior grade structural thermoset. While formaldehyde is used in its preparation, pMDI resin does not emit formaldehyde, not at all. pMDI is more acutely toxic than the adhesives mentioned above. However, very standard precautions allow the safe and routine use of this material.

In a sense, pMDI is a two-part adhesive where the second component is wood moisture. This resin polymerizes by reacting with wood moisture. pMDI is hydrophobic (water insoluble), and therefore moisture tolerant, or insensitive to the steam that forms during hotpressing. This important property explains why pMDI resins are the only wood binders used for steam injection hotpressing. This is the purposeful injection of steam during panel hot compression, accelerating heat transfer in very thick panels, and also providing other product benefits.

Another significant characteristic of pMDI resins is their tendency to adhere to metal surfaces. This causes unacceptable problems during wood-based composite manufacture because the platens will adhere to the panel surface. Release agents (low surface-energy surface active molecules) applied to the platens will prevent this problem. Alternatively, a common practice is to use PF resins in the 'surface layers' and pMDI in the 'core layer,' as in OSB manufacture.

Resorcinol-Formaldehyde (RF) and Phenol-Resorcinol-Formaldehyde (PRF) Resins

Resorcinol-formaldehyde (RF) resins are generally considered to be the most durable and best-performing structural thermosetting wood adhesives. They are not commonly used for the production of wood-based composites such as plywood and OSB because the resin is very expensive. Resorcinol is very costly, and this fact led to the related adhesive in which some of the resorcinol is replaced by the much cheaper phenol molecule, producing the PRF adhesive. Resorcinol is highly reactive and so RF and PRF adhesives are two-part cold-setting resins. Typically, the resorcinolic liquid resin is mixed with a formaldehyde hardener and polymerization begins immediately, followed by solidification in 30–180 min after mixing. These adhesives are particularly well suited for structural wood-bonding applications in which the bonded assembly is not conveniently hotpressed, as in finger-jointed lumber, large laminated timbers, and wood-based I-beams.

Two-Part Isocyanate Curing Latex Adhesives (Emulsion Polymer Isocyanate, EPI)

Emulsion polymer isocyanate (EPI) adhesives are commonly used for the secondary assembly of a vast array of forest products, examples including finger-jointed lumber, furniture and wood lamination. This adhesive has two parts: a water-based latex that visually resembles the common 'white glue,' and pMDI, as in the wood binder mentioned above. As with RF and PRF adhesives, EPI is a cold-setting system that must be applied soon after mixing the latex and pMDI components. EPIs are durable exterior-grade structural thermosets that provide excellent performance.

Poly(vinyl Acetate) Latex (PVA)

Poly(vinyl acetate) latex (PVA) is a nonstructural thermoplastic latex adhesive which is familiar to many as the ubiquitous 'white glue.' PVA technology is extremely versatile because it is prepared in many ways and with a wide variety of monomers besides its namesake, vinyl acetate. PVA adhesives are commonly used for the assembly of many wood products such as furniture, window and door frames, and decorative panels. These waterborne adhesives are not weather durable; however, a common formulation includes comonomers and other additives that provide crosslinking. These more durable systems are referred to as crosslinking-PVAs. The crosslinking-PVAs also serve more demanding industrial applications where additional crosslinking is achieved by adding catalysts.

See also: **Non-wood Products:** Chemicals from Wood. **Papermaking:** Paper Raw Materials and Technology. **Solid Wood Products:** Glued Structural Members; Wood-based Composites and Panel Products. **Wood Formation and Properties:** Chemical Properties of Wood; Formation and Structure of Wood; Physical Properties of Wood. **Wood Use and Trade:** History and Overview of Wood Use.

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Chemical Modification

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Introduction

Wood is a hygroscopic resource that was designed to perform, in nature, in a wet environment. Nature is programmed to recycle wood in a timely way through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. In simple terms, nature builds wood from carbon dioxide and water and has all the tools to recycle it back to the starting chemicals. We harvest a green tree and convert it into dry products, and nature, with its arsenal of degrading reactions, starts to reclaim it at its first opportunity.

The properties of any resource are, in general, a result of the chemistry of the components of that resource. In the case of wood, the cell wall polymers (cellulose, hemicelluloses, and lignin) are the components that, if modified, would change the properties of the resource. If the properties of wood are modified, the performance of wood will be changed. This is the basis of chemical modification of wood to change properties and improve performance.

Wood changes dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose, lignin, and the surface of crystalline cellulose also play major roles. Moisture swells the cell wall, and the fiber expands until the cell wall is saturated with water (fiber saturation point, FSP). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further expansion. This process is reversible, and the fiber shrinks as it loses moisture below the FSP. The swelling pressures exerted when wood swells due to the uptake of water are very large. Stamm estimated these forces to be approximately 24 000 psi (165 MPa) but could only measure a swelling force of 12 000 psi (82.7 MPa). The ancient Egyptians split their large granite stones using the swelling forces of wood. They would chip rectangular holes (approximately 7×15 cm and 10 cm deep) into the rock the desired distance from the face of the mountain. They would then drive dry wooden stakes into the holes and wet them with water. The swelling forces would then split the granite stone from the face of the mountain.

Wood is degraded biologically because organisms recognize the carbohydrate polymers (mainly the hemicelluloses) in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units. Biodegradation of the cell wall matrix and the high molecular weight cellulose weakens the fiber cell. Strength is lost as the cell wall polymers and matrix undergo degradation through oxidation, hydrolysis, and dehydration reactions.

Wood exposed outdoors undergoes photochemical degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes. The lignin acts as an adhesive in the cell walls, holding the cellulose fibers together. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet light degradation. After the lignin has been degraded, the poorly bonded carbohydrate-rich fibers erode easily from the surface, which exposes new lignin to further degradative reactions. In time, this 'weathering' process causes the surface of the composite to become rough and can account for a significant loss in surface fibers.

Wood burns because the cell wall polymers undergo reactions with increasing temperature to give off volatile, flammable gases. The hemicellulose and