Potential for Biobased Adhesives in Wood Bonding

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Abstract

There has been a resurgence of interest and research on using bio-based materials as wood adhesives; however, they have achieved only limited market acceptance. To better understand this low level of replacement, it is important to understand why adhesives work or fail in moisture durability tests. A holistic model for wood adhesives has been developed that clarifies many issues of wood bond durability. This model addresses performance challenges that bio-based adhesives must overcome to compete with synthetic adhesives. Additionally, bio-based adhesives face challenges on economic and process requirements in order to fit into current wood products manufacturing environments. Despite these challenges, bio-based adhesives continue to show great potential for wider acceptance in wood bonding.

Key words: *wood, adhesives, protein, lignin, tannin, durability, moisture*

Introduction

Wood is a renewable resource, but environmental concerns exist about the use of adhesives made from fossil fuels lowering the bio-content of the bonded wood products. Most wood products are adhesively bonded composites and laminates, and there is a strong desire to use more renewable resources in the adhesives. With so many biological materials available, it can be difficult to select the right chemistry for making suitable adhesives. Some biopolymers have proven less useful as wood adhesives; for example, carbohydrate adhesives usually absorb so much water that the adhesive is weakened and the wet bond strength is poor. Though there are a variety of cellulose derivatives that may have enhanced wet strength, it is not clear if any of these are currently used or could be used in wood adhesives. Several routes have been investigated, but none of these systems has been commercialized (Pizzi 2013). If this problem could be solved in a cost effective manner, it could provide an outlet for the abundant carbohydrates, which are low in cost and relatively consistent in composition. Nanocellulose provides a new opportunity for using carbohydrates in adhesives, but this is in its early stages.

Interestingly, biopolymer adhesives have been used as wood adhesives for centuries long before the introduction fossil fuel-based adhesives in the 20th century. Mainly these were proteins from a variety of animal or plant sources.

Before individual biomaterials are discussed in further detail, it is important to understand what properties make a suitable wood adhesive. Wood is typically used for its strength, requiring that the adhesive needs to have strength that is equal to or preferably greater than that of the wood, thus, minimizing failure within the adhesive. Wood products need to bear loads for a long time; therefore an adhesive needs creep resistance so the wood product doesn't distort with time. The typical way to meet both the strength and creep requirements is for the adhesive to be a thermoset that forms a strong interlocking network during the bonding process. The roles of adhesion (adhesive to wood) and cohesion (within to itself) are very important, but determining these aspects is complex given the porous nature of wood. The proper rheology of the adhesive is important for getting the right degree of penetration. If the adhesive does not flow into the wood enough, there is not enough mechanical interlock via the lumens and in some cases infiltration of the wood cell walls for stabilizing the wood surface (Frihart 2009, Kamke 2007). However, too much penetration will leave too little adhesive in the glueline and insufficient cohesive adhesive strength between the wood surfaces.

Durable Wood Bonds

Most adhesives will bond wood and give high wood failure if the sample is kept at a constant moisture content and temperature as when initially bonded. However, this is an unrealistic expectation because wood bonds need to perform for decades if not for centuries under a wide variety of moisture and temperature conditions.

Temperature effects are straightforward in that wood is fairly stable until above 200° C before wood starts to degrade. Structural wood products must not deform or collapse too quickly in a fire, and so the adhesive should not soften or degrade until well above 200C. Therefore an adhesive like an uncrosslinked poly(vinyl acetate) is not good for structural applications due to its thermal softening. Polymers such as those made from isocyanates, can often depolymerize at higher temperatures; thus they may not resist fires as well as phenolic adhesives.

Moisture changes are a far bigger problem for bonded wood products because while wood swells and shrinks with changing moisture levels, most thermoset adhesives tend to have a very small change in dimensions with moisture changes. Thus the adhesive needs to accommodate this increased strain from the differential volume change so that the internal stress at the interface does not exceed the adhesive's strength (case a in Figure 1). There are two ways to minimize the localization of the strain. Case b has adhesive components enter the cell wall to minimize the amount of swelling and shrinking due to bulking of the wall, reacting with the cell wall components, or forming an interpenetrating polymer network in the cell wall (Frihart 2009). Monomeric or oligomeric adhesives that complete their network formation during the bonding step are referred to as *in situ* polymerized. These adhesives often have components that enter into

and stabilize the cell wall. This cell wall stabilization is critical for these polymers in that they are inflexible due to their rigid monomers and highly crosslinked structure, and cannot accommodate the wood swelling by movement in the adhesive layer. Thus, amino resins and phenolics, which are known to enter cell wood walls and reduce their swelling, typically survive wet conditions, while epoxies that are also rigid are less able to enter and reinforce cell walls, and are not able to withstand the wood swelling unless a primer is used with them (Frihart 2006).
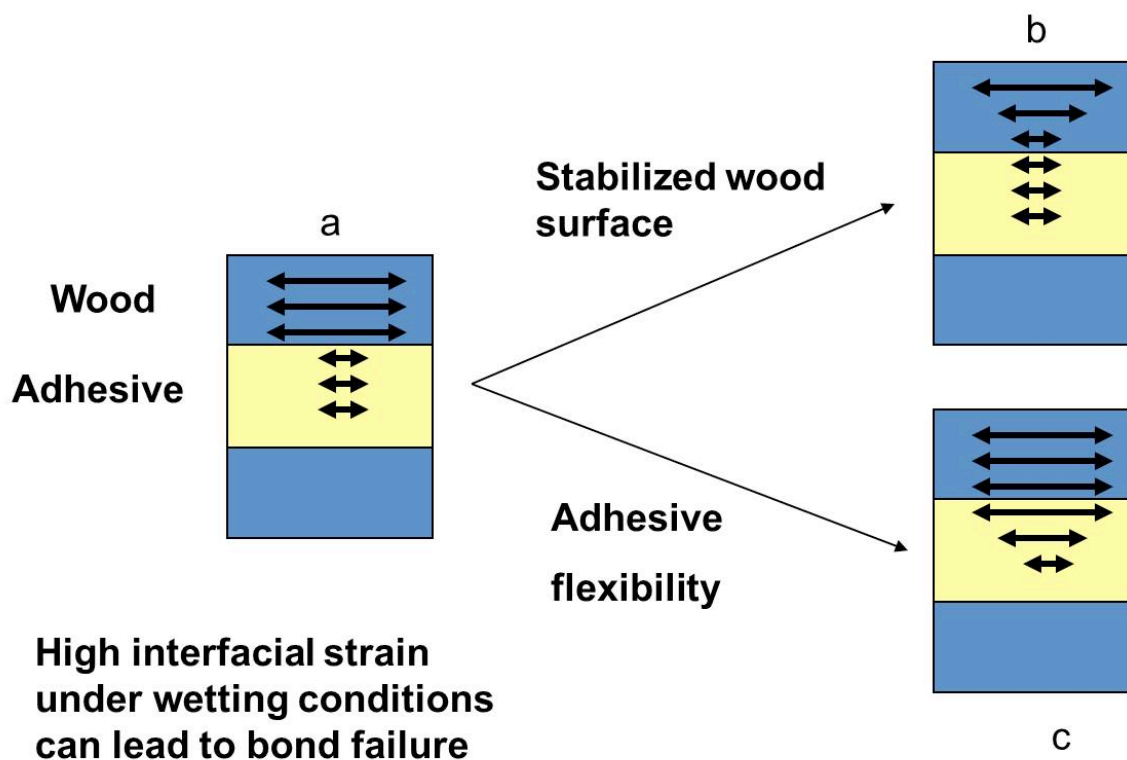
Figure 1. Models for how the adhesives can minimize interfacial strain in a by either stabilizing the cell wall (b), or being able to distort themselves near the interface (c)

In contrast, the other group (case c) of adhesives is the prepolymerized adhesives that undergo light crosslinking, such as polyurethanes, during the adhesive curing. These adhesives are too high in molecular weight to enter and stabilize the wood cell wall, but have a flexible backbone that allows the adhesive to deform, minimizing the bondline stress bondline caused by wood swelling. Because of their high molecular weights, biopolymers usually fit in this case.

Biopolymer Adhesives

Proteins
Although proteins were the dominant choice in wood adhesives for centuries, the previously used technology is for the most part not competitive in today's manufacturing environment. In many cases, the formulations were sensitive to the specific source of the

protein requiring a lot of time consuming adjustments and low production rates in the bonding process. Also, the sourcing from various locations as well as long term storage were additional problems; this was especially true for adhesives using blood and fish scales.

Although casein adhesives used in glulam construction have not had a problem with durability during use, including one building at the Forest Products Laboratory that stood for 75 years before deconstruction (Rammer 2014), these adhesives are unlikely to pass the current adhesive standards for glulam durability. Currently casein is more expensive because it is isolated from milk in New Zealand for example, where milk production exceeds what is needed for food applications. The casein is still used for products like fire-resistant wood doors, which is probably made using casein-soy combinations.

Many of the protein glues once widely used now have very limited application for wood bonding Animal glues from the hydrolysis of collagen from hooves and hides were used for paper products more than wood products. The animal glues are currently used in only a small quantities for historic restoration because poly(vinyl acetate) and other synthetic polymer adhesives are easier to use and lower in cost while providing superior performance. Likewise, glues from fish scales are used in small amounts for restoration and artistic products. Blood glues were often used to fortify other protein glues and give tack to phenol-formaldehyde adhesives, but they are probably not used now in wood adhesive applications.

Recently, the main research for using bio-polymers in the wood adhesive field has been on the use of vegetable proteins because they can be produced in sufficient volume for wood adhesive applications and are reasonable in cost. Although most of the research has been on proteins from soybeans, some work has also been done on other sources, such as canola (rapeseed), wheat gluten, lupin flour, and zein using similar types of chemistry to that being used with soy adhesives.

Soy has been the most studied protein adhesive (Frihart and Birkeland 2014), especially in the United States due to its low cost, wide availability, and research support from the United Soybean Board. Although soy was used in large volumes for making interior plywood until the 1960's, this highly alkaline adhesive is no longer competitive with other adhesives in performance or cost. Of the many soy products that have been examined for wood bonding in the literature, most commercial applications use soy flours due their low cost relative other soy products (Frihart et al. 2014). However, there is some commercial exploration of soy protein isolates as binders for magnesium oxide adhesives. The largest commercial market currently employing soy adhesives is decorative (interior) plywood, although soy adhesives are also used for engineered wood flooring and particleboard using the polyamidoamine-epichlorohydrin coreactant technology (Li 2007). A major appeal of these adhesives is that they are in the category of no added formaldehyde, so the bonded wood products are well below the California Air Resources Board standards for formaldehyde emissions. A wide variety of other approaches have been developed for soy adhesives (Frihart and Birkeland 2014), but none of these are used commercially. In the protein adhesive literature, some of the data

interpretation on the role of the protein is incorrect due to an unclear understanding of terminology, such as solubility, dispersibility, and uncoiling of the protein, and how the proteins have been altered in making a variety of commercial products (Frihart and Birkeland 2016). It is important to know that soy proteins are colloids so protein-protein interaction is critical for forming strong bonds.

There is still a tremendous opportunity for soy and other vegetable adhesives since they give good dry adhesive strength, are low cost, and can be significantly modified by a variety of means. Some chemists, such as Prof. Kaichang Li, have been examining some innovative ways to improve the wet strength of soy adhesives. The other challenge with vegetable adhesives is that, being prepolymerized adhesives, they need the strength and flexibility to accommodate wood swelling and shrinking, and produce wood failure. This challenge has largely been unmet for making low cost soy adhesives with sufficient cohesive strength.

Lignins
Lignins are the second most abundant renewable resource and in their crude form are low in cost. It has been estimated that there are 78 million tons/year available from Kraft pulping of wood and 60 million tons/year from cellulosic ethanol production (Lake and Scouten 2014). It is important to realize that the lignins are a family of materials instead of a single material. The ratios of the lignin monomers used in nature to construct the lignin polymers is very dependent upon whether the lignocellulosics are from softwoods, hardwoods, and other plants. The lignin polymerizes in many different ways leading to a distribution on the types of linkages between the monomeric units (i.e., lignin precursors). Additionally in the separation of the lignins from the cellulosic plant materials (as well as other non-cellulosics, such as ash), the lignins undergo a variety of reactions that can alter their functionality, depolymerize the lignin and repolymerize the degraded units. Thus, the lignin is characterized by its molecular weight, spectroscopic methods and its chemical reactivity rather than specific structures since its native structure remains a mystery (Stark et al. 2015). Major problems in using lignin as wood adhesives include its high molecular weight, limited number of reactive sites that are often sterically hindered, and a significantly higher cost for purer lignins.

The most often considered approach is to use lignin as a partial replacement for phenol in phenol-formaldehyde (PF) adhesives. Although PF adhesives are a very large market, the high viscosity of the lignin precludes any significant use of it in many applications, such as with oriented strandboard, where the adhesive needs to have a low viscosity for spray or spinning disc atomizer application methods. This still leaves the exterior plywood industry and some other laminating applications for lignin-phenol-formaldehyde (LPF) adhesives. There has been a lot of research touting that lignins can be used up to a 40% replacement of phenol while making products that meet the performance specifications (Nimz 1983, Pizzi 2003a, Pizzi 2013). Problems are that on an industrial scale a fast cure rate and a low cure temperature are economically important. Unfortunately, addition of lignin diminishes the PF adhesive performance in both of these properties. The slow curing of the LPF compared to the PF is a negative for the industry because when too much lignin is added, the lignin becomes more of a filler than a coreactant in the

formulation due to lignin's slow cure rate. The addition of cure accelerators allows PF adhesives to cure quicker and at lower temperatures, but more powerful accelerators would need to be used with the lignin. Lignin can be used in the adhesive formulation by either adding it from the beginning of the PF reaction, or by blending in methyolated lignin (product of reacting formaldehyde with lignin) (Gardner and Sellers 1986). Furthermore, if the PF adhesive needs oligomers to stabilize the cell wall and repair surface damage (Frihart 2009), then adding lignin, which has too high of a molecular weight to enter the cell wall, will require that the formulation be readjusted to have more low molecular weight PF components and require the lignin to bridge the two surfaces.

Given the large amount of isolated lignin available in the future, more research should be done to find uses for the lignins in adhesives. However, in order to be successful, this research is likely going to need dedicated development, not just a few experiments here and there as is evident in most of the literature. Furthermore, it will need more market pull because currently there is little incentive for adhesive companies to add the lignin to the PF resins. The development cost and manufacturing risk will outweigh any raw materials saving unless the price spread between phenol and the lignin source is large, limiting how much purification or modification can be done to the lignin.

Tannins

Tannins are very different from lignins in supply, cost, and reactivity, although both are aromatics. Of the two types of tannins, most of the research has been done on the one most commercially available, the condensed tannins. The tannin availability is about 200,000 tons per year from a variety of different plant species, including bushes and trees. Tannins are very reactive due the high content of phenolic groups, and can be compared more to resorcinol in reactivity than to phenol (Pizzi 2003b, Pizzi 2013). Like lignin, condensed tannins are higher in molecular weight so the PF formulation needs to be adjusted to obtain the proper flow and cell wall infiltration characteristics. The high reactivity of tannins has allowed them to be cured without the use of formaldehyde (Pizzi 2013). Another key difference is that commercial lignin is a by-product of other processes (pulping for papermaking and cellulosic ethanol), while tannins are the main product of extraction of plant materials. Thus, the tannin has to bear more of the production costs than does lignin. Consequently tannins are higher in price and more of a localized product compared to PF resins. In the right circumstance, they have been used commercially with good success (Pizzi 2013, Pizzi 2014).

Unsaturated Oils
Many plants make unsaturated oils that are processed for human food applications, but their reactive unsaturated bonds make them useful for wood products. Traditionally they have been used as coatings, such as the catalyzed oxidative curing of linseed oil finishes. However, the unsaturated carbon bond is available for many transformations into other functional groups. One that has been vigorously pursued is the conversion into polyols that can then be converted into polyurethanes (Li 2015). Polyurethanes are widely used as adhesives because they can cure at moderate temperatures using the moisture from the wood and are able to bond wood with higher moisture contents than are phenolic and

amino resins adhesives. The research into using this route for wood adhesives has been limited so far, but it would not be surprising if this was more actively pursued in the future. Fatty oils for non-polyurethane routes are also being pursued for making adhesives (Pizzi 2013). It is not clear if this research has led to commercial products because it is important for industry to maintain trade secrets on formulations.

Summary and Conclusions

Bonded wood products have been around for thousands of years, and the original adhesives were biobased. The renewed interest in biobased materials have led to the exploration of incorporating cellulose, proteins, lignin, tannins, and fatty oils. into many innovative adhesives. There is plenty of opportunity to develop new chemistries to make these even better adhesives. The biggest challenge is providing high reactivity and/or wet bond strength while keeping costs low. Currently proteins and tannins are used in wood bonding, but continued research on improved products should expand the wood adhesive market for biobased adhesives.

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