

PART 2 BIOBASED ADHESIVES AND NON-CONVENTIONAL BONDING

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INTRODUCTION

Humans have bonded wood for many millennia because it allows greater utilization of the wood. The ancient Egyptians used adhesives for bonding veneer, most likely to allow them to extend the supply of rare wood types (Pearson 2003). Up until the 20th century, adhesives came from biological sources. However, most adhesives today are synthesized from fossil fuel (mainly petroleum and natural gas). These synthetic adhesives often provide products that are more durable, especially for moisture exposure and wet/dry cycling conditions, than do many biomass-based adhesives. The good performance and operability with these adhesives has led to an increase in the volume of adhesives and the number of product types. Despite the success of the synthetic adhesives, some applications have continued to use biomass adhesives.

The interest in biomass-based adhesives is growing for a number of reasons, but there are still challenges in finding the proper chemistry to make these adhesives even more competitive with the synthetic ones. Some of the interest in biomass derives from the desire for greener products, with other interest coming from the biomimicry of natural products for making bonds durable to wet conditions (Lee et al. 2006, Westwood 2007). The emphasis here is for understanding the benefits that these adhesives can provide and to discuss the current needs for improved wood products. The wood adhesives market is very appealing given its large volume, for example, about 2.0 billion pounds of urea-formaldehyde in particleboard and fiberboard, and about 1.7 billion pounds of phenol-formaldehyde used in all wood applications.

Biobased adhesives fall into several major classes based upon their chemical structures. Starches are used in large volume, especially in the paper products industries, but cellulose generally do not have the strength and water resistance needed for most wood products. Several authors have covered cellulose adhesives (Baumann and Conner 2002, Pizzi 2006). However carbohydrate adhesives have not been used in wood bonding and they will not be discussed further here. Biobased adhesive bonding methods covered in this section, include proteins, lignins, tannins, as well as no added adhesive systems. Also not covered are biomass-based adhesive modifiers including fillers like nut shell flours and extenders like wheat gluten.

PROTEIN ADHESIVES

Proteins with their wide variety of functional groups are well suited for making wood adhesives and have been used for this purpose for many centuries. Often, these adhesives are derived from by-products of other industries, for example, hoofs and hides for making hot melt glues, and blood and fish skins for making waterborne adhesives. However, the utility of many proteins is limited due to inconsistencies in composition and performance, limited supply, and high cost compared to many fossil fuel-based adhesives. Compared to other protein sources, soybean flour is more consistent in its composition, is available in large volume, and is reasonably priced; thus, it is the most widely studied and used for biobased adhesives for wood bonding (Frihart 2009). Proteins from sources other than soy are used in limited quantities because of specific performance characteristics for specific applications. However, the main growth has been with soybean flours in interior plywood, engineered wood flooring and other wood composites.

To understand performance of protein, one needs to understand the hierarchical levels of protein structure, especially compared to synthetic adhesives (Frihart 2009). For all polymers, the basic level is the backbone sequence of the polymer. Thermoplastic synthetic adhesives have a secondary level of crystalline domains, while proteins have a secondary level of α -helices and β -sheets. Knowing the primary, secondary levels, and any cross links allow an enhanced understanding of the performance of synthetic adhesives. However, proteins usually fold into globules due to disulfide, acid-base, and hydrogen intrachain bonds, as well as hydrophobic collapse in a water environment; this intrachain folding is classified as the tertiary structure (Pain 2000). The interaction between the surfaces of these individual chain globules provides the quaternary structure. Proteins from different sources have different compositions leading to different solubilities in water, surfactant properties, and bonding abilities. Consequentially, the structure-property relationships for proteins are more complicated than the synthetic adhesives due to their higher ordered structures.

Both the quantity and order of the individual amino acids play an important role in the properties of the proteins. The composition of reactive amino acids and their structures for soy total are protein given in Table 1, but the ratio and sequence of these amino acids varies for individual proteins within the soybean. Thus, knowledge on making an effective adhesive from one protein source may not help with making adhesives from another protein source. Despite this difficulty, ways have been found to use many different proteins as successful adhesives. Most of this discussion is on the increasing technology advances using soybean proteins and is followed by some discussion of the other proteins, which have received little investigation in recent years. Fish scales provide adhesives that are decent, but the supply and market have always been small, and thus, they are not discussed below.

SOY-BASED

Removing the oil (triglycerides) from the soybean leaves grits that is composed of proteins and carbohydrates and can be ground into soy flour (Sun 2005a). Although most laboratory studies have been done on the separated soy protein isolates (about 90% protein) (Sun 2005a), the flour with about 50% protein is the most likely feedstock due to its low cost and ready availability. The properties of the flour are very dependent upon the

processing conditions; for example, increased heat treatment lowers the solubility of the protein but reduces undesired enzymatic activity. The processing conditions used for preparing the flours are chosen to improve their performance in food applications and other industries but not necessarily to make the best flour for wood adhesives. As indicated in the prior section, proteins possess tertiary and quaternary structures that generally need to be disrupted (denatured) to expose the functional groups of the protein for bonding and cross linking, see Figure 1. Advances in both protein denaturation and modification provide new ways to make adhesives from soy flour that are more tailored for different wood bonding applications. Lambuth has covered the traditional processes (Lambuth 2003); thus the emphasis here is on the more recent advances in soy adhesives.

TABLE 1 - Potentially reactive side-chain amino acids in soy protein (Bjorksten 1951).

Amino acid	Structure	Soy protein (%)
Lysine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{NH}_2)\text{COOH}$	6.8
Histidine	$\text{Imidazole ring}-\text{CH}_2-\text{C}(\text{NH}_2)\text{COOH}$	3.4
Arginine	$\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{NHCH}_2\text{CH}_2\text{CH}_2-\text{C}(\text{NH}_2)\text{COOH}$	7.7
Tyrosine	$\text{HO}-\text{C}_6\text{H}_4-\text{CH}(\text{NH}_2)\text{COOH}$	4.2
Tryptophan	$\text{Indole ring}-\text{CH}(\text{NH}_2)\text{COOH}$	1.3
Serine	$\text{HOH}_2\text{C}-\text{CH}(\text{NH}_2)\text{COOH}$	5.4
Cysteine	$\text{HS}-\text{CH}_2-\text{CH}(\text{NH}_2)\text{COOH}$	2.5
Total		31.3

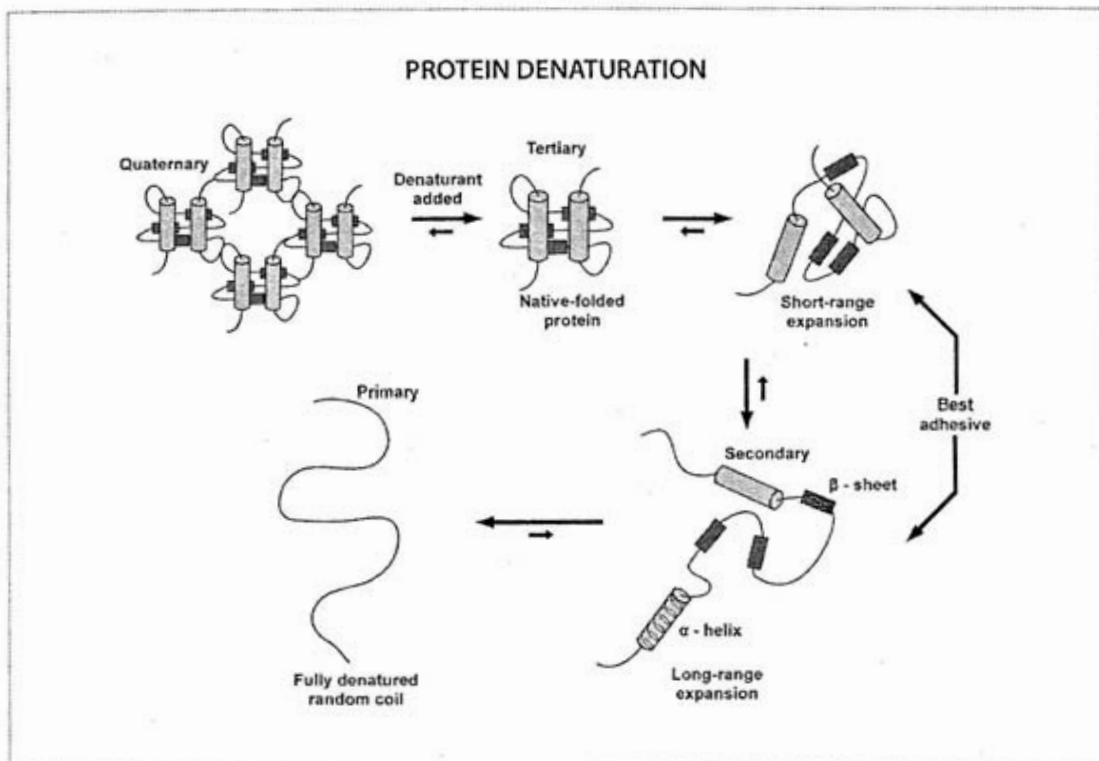


FIGURE 1 -Protein denaturation

NON-CROSSLINKED

Although the traditional soy flour adhesives were not covalently cross-linked, they were useful in establishing plywood as an important wood product (Lambuth 2003). These adhesives for many years were produced at the plywood plants using a caustic and water process for manufacturing interior plywood, with the formulated adhesive being used within a few hours due to pot-life issues. Considerable work was done to try to make these formulations more water resistant, but generally these methods did not involve covalently cross-linked bonds (Wescott et al. 2006a). However, protein adhesives were replaced by urea-formaldehyde (UF) for interior plywood and phenol-formaldehyde (PF) for exterior applications for the following reasons (Wescott et al. 2006a):

- Lower cost
- Better water resistance
- faster setting
- Ease of manufacturing

With the dominance of the UF and PF adhesives, limited research was done on soy adhesives for many years, but recent interest in biobased materials has led to more research on the soy adhesives.

Most of the research has been done with the protein isolates, which are often considered a good model for the behavior of the proteins in the soy flour. Although studies on the behavior of the isolates and its two main fractions, conglycinin and glycinin, has provided useful information on wood bonding (Sun 2005b, Sun 2005c), the information needs to be considered carefully because isolates and flour behave differently in some systems (Wescott et al. 2009). Traditional studies focused on dispersing soy flour using caustic (Lambuth 2003), but more recent studies have used other denaturants, such as surfactants, guanidinium hydrochloride, and urea, to modify the protein for better adhesion (Sun 2005b, Sun 2005c, Wescott and Birkeland 2008, Wescott et al. 2008). These adhesives are usually in the pH range of 5 to 11, in contrast to pH greater than 11 for the caustic processes. Although these adhesives can provide good wood bonds under dry conditions, they have limited wet strength and do not do well in the cyclical wet-dry testing without some type of cross-linking reactions (Wescott et al. 2008).

Liu and Li (2004) were able to obtain increased wet shear strength for soy-bonded plywood by adding cysteamine groups to soy protein isolate compared to the unmodified or ethanolamine-modified soy protein isolate.

COVALENTLY CROSS LINKED

It is generally recognized that to have good water resistance the soy proteins need to be cross linked. A variety of methods have been developed to cross link proteins with aldehydes being important reactants (Bjorksten 1951, Marquie 2001, Means and Feeney 1998). Concern over formaldehyde emissions from adhesives have led to use of aldehydes other than formaldehyde, such as glutaraldehyde (Wang et al. 2007) and glyoxal (Amaral-Labat et al. 2008). A major area of research has been to use soy as partial replacement for phenol-formaldehyde (PF) in adhesives for making oriented strandboard. Formaldehyde emissions are not an issue with PF adhesives, but high costs have been historically an issue. The soy can be added to alkaline PF formulations to provide a durable adhesive bond (Hse and Bryant 2001). Soy-PF formulations with high levels of soy flour are made by changing the order of addition of the components so that the soy is part of the polymer network rather than just a filler (Wescott et al. 2006a, Lorenz et al. 2007). More importantly, it was also found that some of these alkaline soy-PF formulations can be acidified to make dispersions that are even more effective as an adhesive (Wescott et al. 2006b, Wescott and Frihart 2008). Being non-alkaline these adhesives are lighter in color and do not give the caustic burn spots that occur with normal PF formulations, while still giving good bond durability. The stability of these dispersions is surprising given the difficulty in neutralizing alkaline PF products due to precipitation of the PF unless surfactants are used (Broline et al. 2002).

In addition to the previously mentioned performance advantages of soy-PF dispersions over a PF adhesive, they also can be mixed with polymeric diphenylmethane diisocyanate during application (Wescott and Frihart 2008). The soy does not replace the isocyanate but works well with isocyanate. This process shows two advantages in that the diisocyanate provides additional cross-linking of the soy adhesive and that the soy can be a good way to extend an isocyanate. The latter point is an interesting one in that the soy is not so reactive with the isocyanate that the adhesive cures prematurely and soy helps to distribute the isocyanate by serving as a reactive diluent.

Soy adhesives have been cross-linked using poly(amidoamine)-epichlorohydrin (PAE) resins for bonding wood (Li 2007, Li et al. 2004), with proposed reactions given in Figure 2. The mechanism of this reaction with proteins has been studied (Zhoeng et al. 2007). The combinations of different soy dispersion methods with PAE resins have provided soy technology that has water resistance suitable for most wood bonding applications (Wescott and Birkeland 2008, Fong et al. 2008). Significant research and development activities have made these soy-PAE adhesives acceptable for commercial production of interior plywood, wood flooring, and particleboard. These adhesives can cure under similar time temperature and adhesive loading conditions as is used for the urea-formaldehyde adhesives that they replace, although the lower solids level with protein adhesives introduces more moisture into the assembly (Wescott et al. 2009). A driver in the commercial acceptance for changing from urea-formaldehyde adhesives to soy adhesives has been the need to meet the California Air Resource Board's standards for composite wood products (Anonymous 2009). These regulations lowered the permissible formaldehyde emissions from wood composites and products made with wood composites because of health concerns. The soy-PAE products have no added formaldehyde and are a way to meet these standards (Birkeland et al. 2010). These proteins have reasonable biological decay resistance and do not revert like the urea-formaldehyde adhesives under high moisture and heat conditions (Wescott et al. 2009).

Other routes for cross-linking of the soy protein have also been examined. Liu and Li (2002) have grafted dopamine groups onto soy protein isolates so that these groups could cure in a manner similar to that used by mussels. The modified soy provided much better water resistance than the unmodified for bonding maple plywood. Soy protein isolate can be reacted with polyethylenimine (PEI) and maleic anhydride (MA) to make an adhesive with water durability for interior plywood adhesion (Lu and Li 2007). The PEI and MA combination can also be used with the more economical soy flour for interior plywood bonding (Huang and Li 2008).

OTHER PROTEINS

CASEIN

Casein protein comes from milk and was used in the early days of glulam production, but casein is less commonly used now for bonding wood products. The casein is precipitated from milk using either added mineral acid or *in-situ* generated lactic acid formed by the enzymatic conversion of lactose in milk. The precipitated casein are usually dispersed using hydrated lime, and these dispersions provide bonded wood products with better water resistance than those obtained using uncross-linked soy adhesives (Lambuth 2003). Although glulams made with casein are still in service, these adhesives do not provide the durability and good bonding properties that a resorcinol-formaldehyde or phenol-resorcinol-formaldehyde adhesive does for these structural applications. Thus, they are not used in structural products any more. However, the casein adhesives are still used for a few interior applications, especially in bonding door skins for fire doors (Lambuth 2003) because these adhesives do not soften the way that most synthetic adhesives do at high temperatures. Besides being more expensive than soy flour, casein is best dissolved only at very high pH, while the soy is soluble over a much wider pH range (5 to 13).

BLOOD

Blood proteins provide the most natural water-resistant bonds of the uncross-linked protein adhesives (Lambuth 2003). However, blood has varying properties due to the different animal sources (beef, pig, sheep, etc.) and is expensive; thus the use in wood adhesives is small. High solubility blood provides a very slick adhesive, while low solubility blood is granular. Blood does not need highly alkaline conditions to solubilize as does the casein. Blood has often been used as a fortifying agent with other proteins and phenol-formaldehyde resins (Lambuth 2003), and as a foaming agent with urea-formaldehyde glues.

HOOF AND HIDE

In contrast to the other protein adhesives being fluid water-borne adhesives at room temperature, hooves and hides provide hot-melt adhesives (Pearson 2003). These are a very old class of adhesives. Although these adhesives were used in many wood and paper applications, the glue has generally been replaced by synthetic adhesives.

The collagen in the hooves and hides is denatured using acid for bone glues or base for hide glues, and then the protein dispersions are vacuum dried to prepare a solid product (Pearson 2003). Dispersing these solids in water provides a gel at room temperature, but upon heating, it melts to form a liquid. The hot aqueous glue after application initially provides a viscous, tacky film that cools to provide a high green strength bond. The dried adhesives are strong and permanent with good resistance to many solvents (Pearson 2003) but may soften with heat and/or moisture. Among the many uses for these glues is furniture assembly. The relative safety and low cost of the synthetic replacement has not given much impetus to improving the collagen-based adhesives.

BIOMASS AROMATIC ADHESIVES

Aromatic adhesives have found wide utility, especially when polymerized and cross-linked due to their stability under heat and oxidation conditions. For wood bonding, phenolics (aromatic rings containing hydroxyl groups) reacted with formaldehyde produce adhesives that form durable bonds with wood. These adhesives resist the effects of moisture, heat, and biological exposure. Phenolics made from phenol, resorcinol, or their combinations are the main adhesives for most structural and exterior products (Pizzi 2003a). Trees contain aromatic compounds in both the wood and the bark that can be used as adhesives; thus, it is logical to use these natural aromatics to replace the synthetic ones.

TANNIN

Condensed tannins are the most common type of tannin used commercially in adhesive applications (Pizzi 2003b, Pizzi 2006). A number of plant species have useful amounts of tannins, which are functionalized and higher molecular-weight phenols and resorcinols. The hydrolyzable tannins are in smaller supply. These tan-

nins are ester of carbohydrates and phenolic acids, and thus, they are closer in molecular weight to the phenolics used to make phenolic resins. Without unique properties, these monomeric phenolics are of limited use because they are not cost competitive. The condensed tannins are larger multi-ring phenolics that can be used to replace some of the petroleum-derived phenolics. These tannins react in a similar way as do the phenols for making the polymers, although the condensed rings of tannins make them more viscous than are the phenols. The impurities in the tannins cause these adhesives to be weaker in many cases than the synthetic phenolics. This lower performance and limited supply has led the tannins to be a very small part of the adhesive market (Pizzi 2003b). Although many of the studies on tannins have involved formaldehyde for polymerization and cross linking, several non-formaldehyde routes have been examined (Pizzi 2006).

LIGNIN

Lignins have not been used much as an adhesive despite the large quantity existing in nature; trees contain about 28% lignin. Lignin contains mainly aromatic groups, but they are generally not phenolic. Most of the available lignin is that which is removed from wood to make paper products; however, this lignin is normally burned in the recovery boiler or degraded into soluble wastes during the bleaching processes. The limitations for using lignin as a wood adhesive are the lack of phenolics in the native lignin and the difficulty in isolating lignin from wood (Pizzi 2003c, Pizzi 2006).

The large quantity and low value of lignin has led to continuing research in trying to convert isolated lignin into adhesives, but the efforts have resulted in limited success (Pizzi 2003c, Pizzi 2006). In addition to the traditional reaction with phenol and formaldehyde, another route has been to use the polymeric diphenylmethane diisocyanate to cross link the lignin molecules (Stepanou and Pizzi 1993 a and b). A more recent route has been to use glyoxal to replace the formaldehyde for the cross-linking reactions (Mansouri et al. 2007, Lei et al. 2007). Another route is the reaction of polyethylenimine with the lignin for making plywood (Geng and Li 2006).

Lignin is considered an important strengthening polymer for providing wood with its superior strength-to-weight ratio. The cellulose fibrils provide great stiffness to wood, but wood needs the lignin to hold these fibrils together. However, lignin is an easily softened component of wood; thus, it can flow to form bonds under heat, or heat and moisture. The latter condition has been used in hardboard production because the densification is enough to bring the fibers into good direct contact. The former is important in the recently developed processes of wood welding. Wood welding uses friction to fuse wood pieces together, independent of whether it involves vibrational welding to use in side or face seaming applications, or in rotational welding of inserting a dowel into a hole in the wood. This technology is discussed later in this chapter.

WOOD PYROLYSIS OR LIQUEFACTION FOR ADHESIVES

Wood components can serve as the adhesive matrix for bonding wood, but wood itself can also be treated to provide adhesives using pyrolysis or liquefaction processes. The pyrolysis process involves high

temperatures with or without a catalyst to produce a volatile oil and tar. On the other hand, the liquefaction process involves more moderate temperatures and use of phenol or other solvent with and without a catalyst to produce a liquid that is separated from the residue by filtration. The liberated lignin and tannin are natural adhesives, and the cellulose is converted by dehydration and cleavage to provide adhesive components such as the furfural compounds.

The pyrolysis processes use a high temperature to break down the wood polymers and dehydrate the cellulose to make a volatile liquid with the remainder being a tar. The kinetics of converting the cellulose, hemicelluloses, and lignin to pyrolysis oils has been examined (Miller and Bellan 1996). Vacuum pyrolysis of resinous bark produces phenolic-rich oils which represent a potential raw material to replace petroleum-based phenol presently used in the formulation of wood adhesive resins. The performance of pyrolysis oils for substituting up to 50% by weight of the phenol in phenolic adhesives for the face and 25% of the adhesive for the core has been shown to give an acceptable oriented strandboard product (Chant et al. 2002, Amen-Chen 2002). The pyrolysis oils can also be used with polymeric diphenylmethane diisocyanate (pMDI) to replace between 30 and 40% by weight of the pMDI in a 4% adhesive-containing particleboard. The product met performance standards and had reduced adhesion to the metal press platens (Gagnon et al. 2004).

Another way to make adhesives from wood is to use a solvent, such as phenol, and heat to dissolve some of the components in wood; the soluble portion is separated from the residue by filtration and is then made into an adhesive for wood-bonding (Pan et al. 2006, Pan et al. 2007). Commonly these liquefied wood products are reacted with formaldehyde to make adhesives whose properties (Pan et al. 2008) and performance have been investigated. This process has also been examined as a way to make products from creosote-treated wood (Hse et al. 2009). The liquefied product from black wattle bark has been used to replace some of the phenol-formaldehyde adhesive in plywood (Santana et al. 1996). Another liquefying solvent mixture of glycerol/diethylene glycol was used to make an extract that was condensed with melamine-formaldehyde and urea-formaldehyde for bonding particleboard (Kunaver et al. 2010).

NON-ADHESIVE BONDING

Bonding of wood without any added adhesive is another way to produce a high biomass product. If no adhesive is added, then the adjoining wood or fiber surfaces need to be brought into close enough proximity for covalent, hydrogen, or other bonds to be formed between these surfaces. Given the roughness of the solid wood surfaces due to its cellular construction, it is hard to bring enough force onto the bondline without crushing the wood surface cells and forming a weak boundary layer. However, fibers are easier to compress to bring the surfaces into contact, especially if the composite is dense enough. In general, it has been necessary to use adhesives for making wood composites and laminates because they form strong associations with the wood and bridge between the adjoining surfaces. Several processes have been examined to accomplish bonding without added adhesives.

SOLID WOOD BONDING BY WOOD-WELDING

Plastics and metals can be joined by rubbing the surfaces together. This mechanical agitation heats up the materials and can fuse together thermoplastic materials. This technology has recently been examined with wood using several different processes. The concept is that heat can soften wood as well convert some of the celluloses into more thermoplastic components and the friction can fracture some of the rigid, high molecular-weight polymer components. These components can then flow and form bonds between the surfaces. However, the heat does char the wood and fractures the normal wood structure.

Vibrational welding has been used commercially with plastics. This process involves vibrating one material so that its flat surface rubs against another surface under pressure to generate heat that softens the surfaces allow them to fuse together when the vibration is stopped (Leban et al. 2004). The process provides products with good strength under dry conditions (Gfeller et. al. 2003), but wet conditions have been more challenging. The mechanism of mechanically induced vibration wood welding has been shown to be mostly the melting and flowing of the amorphous materials between wood cells, mainly lignin and hemicelluloses (Gfeller et. al. 2003). Control of the temperatures is important because they need to be high enough to get the wood to flow, but not so high that too much charring occurs (Ganne-Chedeville et al. 2006). High frequency and short time process can promote cross linking and reduce oxidation (Omrani 2009, Delmotte et al. 2009). Several European groups have investigated the use of wood welding for applications such as engineered wood flooring.

Another process is rotational welding that involves rotating a wood dowel while pressing it into a hole in the wood surface (Pizzi et al. 2004, Ganne-Chedeville 2008). Since wood dowels have long been used in bonding wood, this is an interesting application of the welding process. The dowel is slightly smaller than the drilled hole so that friction occurs as the two surfaces are mated. This process is not totally different than current manufacturing ones where often a poly(vinyl acetate) glue is used. The force required to pull the dowel from the wood surface is similar to that required for a normal adhesively bonded dowel. For joining scarf, step butt and dovetail joints, the strength of welded and glued dowels were similar and superior to nailed joints (Segovia and Pizzi 2009).

HARDBOARD COMPOSITES

The more dense composites can often be bonded with limited use of adhesives because the moisture, heat, and compaction are sufficient to provide strong interactions between the fibers. Enzymatic treatment can improve the auto adhesion of the fibers sufficiently to make acceptable fiberboard product (Felby et al. 1997, Kharazipour et al. 1997, Muller et al. 2009). An additional study on binderless fiberboard has been done using kenaf (Xu et al. 2009).

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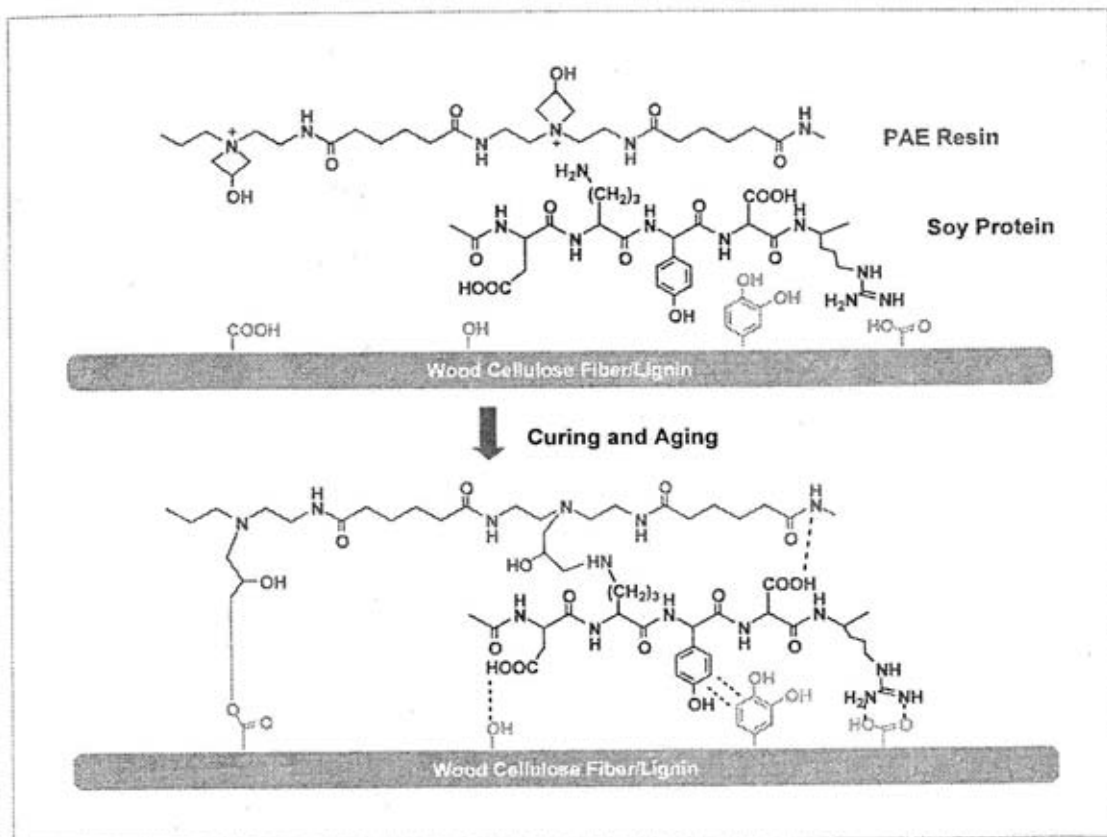


FIGURE 2 - Proposed interactions of soy protein with polyamidoamine-epoxy resin.

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