Chapter 8

Soy Properties and Soy Wood Adhesives

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Soy flour has been used for many years as a wood adhesive. Rapid development of petroleum-based infrastructure coupled with advancement of synthetic resin technology resulted in waning usage since the early 1960s. Discovery of using polyamidoamine–epichlorohydrin (PAE) resin as a co-reactant has been effective in increasing the wet bond strength of soy adhesives and led to a resurgence in soy-based adhesive consumption. Technology for making wood adhesives from soy is reviewed in this chapter. It is clear from this review that commercial processing technology used to make various soy protein-containing products influences protein adhesive properties. Thermal denaturation of soy flour does not influence the dry or wet bond strength either without or with added PAE. However, in case of soy protein isolate, the hydrothermal process used to provide proteins with more functionality for food applications make these proteins much better wood adhesives, especially in wet bond strength both without and with added PAE.

History of Protein Adhesives

Proteins as chemicals have been an important material to humans dating as far back as 6000 BC when Neanderthals used animal protein to waterproof works on cave walls (1). It is well known that ancient Egyptians used protein adhesives for a variety of substrates with written formulas dating back to 2000 BC. Animal glues from collagen, blood glues, and casein glues from milk have been used for a
very long time, while fish glues originated in the 1800s and soy glues in the 1900s. All of these adhesives are derived from naturally occurring proteins.

Animal glues are made by hydrolysis of collagen either from hides or bones (2). After hydrolysis and purification, glues are then dried to provide ease of shipment and resistance to decay. They can be dissolved for use by heating in water and provide instant bonds upon cooling and loss of water. They are mainly used in woodworking, gummed tape, and coated abrasives and can develop good wood bonds of up to 3 MPa of dry strength. Currently, these adhesives are not in general use because of the advancement of synthetic adhesives, such as poly(vinyl acetate), polyurethanes, and acrylic emulsions, which offer greater ease of use and enhanced performance.

Blood glues were used for a long time by themselves or mixed with other materials (3). Natural clotting properties of blood made these glues a popular adhesive for exterior plywood, such as in wooden aircraft. Proper drying conditions for blood adhesives are important to maintaining their solubility, but blood from different sources had quite different properties. Even after blood glue was replaced by phenol–formaldehyde adhesives for plywood applications, it still continued to be used to modify properties of other adhesives.

Fish glues replaced some animal glues because they did not need to be heated for application (4). The glue is prepared by heating fish skins in water, then filtering and concentrating the resultant material. The glue can be made insoluble in water by addition of certain salts or reaction with aldehydes. Although they had certain advantages over other animal glues, availability and enhanced performance of synthetic adhesives led to their replacement.

Casein glue was the most utilized protein adhesive from strength and supply perspectives as a structural wood adhesive and was used in production of glulam beams (5, 6). Casein is isolated from milk either by direct acidification with hydrochloric or sulfuric acid or by lactic acid formed from lactose and a bacterial culture. This solid is dispersed in water using a mixture of sodium and calcium hydroxide to balance dispersibility and water resistance of the bonded product. Although they have been used to make glulam beams that have a long life span (7), casein glues have generally faded from the market replaced by better performing phenol–(resorcinol)–formaldehyde, melamine–formaldehyde, and polyurethane adhesives. In the remaining specialized applications that use casein glues, these are often mixed with soy products to keep cost down (6).

Soy flour adhesives were developed early in the 20th century and aided development of the interior plywood industry. Although laminated wood products go back to the early Egyptians and Chinese, the concept of cross-ply plywood dates from 1865 (8). Production of modern interior plywood was limited until discovery of effective soybean adhesives. For these adhesives, soybeans are first de-hulled and extracted with hexane to remove the valuable oil, leaving soy meal that is ground to a fine flour and then dispersed in water using pH conditions greater than 11 (9, 10). This soy adhesive could be pressed cold or hot to bond the plywood. The soy adhesive formulation was altered to give better water resistance by adding casein or blood proteins, incorporating divalent salts instead of just sodium hydroxide for making the solution basic, adding sulfur compounds such as carbon disulfide, or using other additives such as borax, sodium silicates,
or preservatives. Soy continued to be used in interior plywood for many years, but was eventually replaced, mainly by urea–formaldehyde, because of the latter’s ease of use, low cost, and enhanced water soak resistance. Some of the soy, casein, or blood proteins continued to be used in synthetic adhesives for modifying properties, such as tack or foaming.

Adhesive Needs

General Adhesive Properties

An adhesive needs to be a liquid, or at least have sufficient flow under conditions of bonding so that it can come into good contact with the two substrates. The adhesive must then solidify to hold the substrates together, either by cooling and/or loss of water in the case of thermoplastics, or by chemical reaction to cross-link the material or build molecular weight in the case of thermoset adhesives. Chemical properties are important in bonding substrates for developing adhesive and cohesive strength, while bond performance is measured as the mechanical strength for holding substrates together under various exposure conditions. Emphasis for bonding has been placed on the interaction at the interface between two surfaces (adhesive and substrate); these include adsorption (thermodynamic) or wetting, acid-base, chemical (covalent) bonding, and electrostatic interactions. These interactions can be fairly well evaluated by various studies of adhesion and measurement of surface properties (11, 12). Additional bond strength comes from mechanical interlocking and its molecular-level equivalent of diffusion where interactions go beyond the planar interface. Surface roughness can be measured to understand the amount of typical mechanical interlock assuming good wetting of the surface. Diffusion is harder to measure, but can provide durable bonds if the adhesive is compatible with the substrate.

Adhesion to many substrates has been well understood because the substrates are generally quite uniform, allowing extrapolation of results from studying small areas to performance over the entire area. Thus a range of methods from measuring surface energetics to bond-breaking force tests have been used (11, 12). As will be discussed in a later section, high viscosity and therefore reduced flow is often a problem with soy adhesives. However, proteins have many side chain groups allowing adhesion to many surfaces.

The above discussion assumes that the surface is sound enough that surface layers of the substrate are firm layers, well attached to the bulk substrate material. Surface preparation can be an important part of forming a strong bond. This is illustrated particularly well in the case of bonding of aluminum airplanes. The thermodynamically stable aluminum oxide layer on the surface of exposed aluminum is mechanically weak, resulting in bond failure (13). Rather than making modifications to the adhesive, this problem was addressed by developing a more stable surface layer using the FPL etch and then forming the adhesive bond soon after (13).
Another cause of a weak boundary layer is presence of oils or other low molecular weight materials on the surface; this can usually be solved by chemical or mechanical cleaning of the surface just prior to bonding.

In addition to cleaning the surface, primers can be used to form a strong link between the substrate and adhesive (14), or the surface can be treated by some type of chemical, such as acid/base or oxidant, or with irradiation to make a more active bonding surface (14). Wood can have weak surface layers (15) and these techniques have been used to solve specific adhesion issues (16, 17).

The ultimate purpose of an adhesive is to hold two substrates together under the desired end-use conditions. Thus, a key test of adhesive performance is to subject the bonded assembly to some type of mechanical force until failure occurs. Certainly the magnitude of the force required for failure is an important characteristic of an adhesive. However, examining the location of the fracture is also important to fully understand performance of an adhesive. Substrate failure is usually desired to ensure that the adhesive’s cohesion and adhesion to the substrate are not the weakest link of the assembly. Failure within the adhesive itself usually leads to developing a stronger adhesive. Adhesion failures are harder to analyze and solve, plus is the uncertainty of how sensitive the substrates are to bonding and testing conditions.

Additional Wood Bonding Aspects

Although the focus of this chapter is dedicated to soy materials as adhesives, nearly all the commercially relevant applications of soy adhesives are with wood products. Thus, some relevant background material on wood bonding is included.

i. General Performance Criteria

Adhesives have allowed efficient use of wood to make a wide variety of structural and non-structural products from all types of wood material from solid lumber and veneer to sawdust and wood fiber (Figure 1). In fact, over 80% of wood products are adhesively bonded (18). Although many applications involve a layer of adhesive between the two substrates, many panel products use binder adhesives that are like spot welds. Some of the products are only made for interior use, while others need to be resistant to outdoor environments. Thus, the different adhesive bonds are subjected to many types of forces and conditions preventing a single type of evaluation. However, there are some common requirements for different adhesive applications. A main one is permanence in that adhesives should last the lifespan of the product, which is usually decades, if not centuries, for wood products. The second is that wood is usually used for its rigidity, and thus the adhesive needs to be fairly rigid. The product has a defined shape so adhesive must not flow over time (i.e., creep), which would allow the product to deform. An unusual property of wood compared to other materials is that it swells and shrinks significantly with moisture changes (19). Although this problem is more severe for exterior applications, it is important for interior applications as well. Thus, the adhesive needs to accommodate these changes.
Also, wood products are unique because of the wide variety of species that can have drastically different properties, which greatly influence bonding process and strength measurements.

![Figure 1](image-url)

**Figure 1.** Some wood products from top to bottom, engineered wood flooring (soy), hardboard, fiberboard (UF), particleboard (UF-soy), OSB (soy-PF), interior plywood (soy), glulam (casein).

### ii. Wood Structure

Wood in trees has to perform many functions to survive (20). Not only does it need good structural strength, especially in vertical compression, but it also has to have some flexibility to withstand wind that generates a high force when the tree is fully leaved. The wood must also transport water up to the leaves and bring chemicals for growth back down. It has to support heavy branches and try to grow vertically when external forces make that difficult. Thus, the structure of wood is very complex to accommodate all these functions and this complexity exists at many different length scales. This complex structure has made wood adhesion with soy and other adhesives difficult to fully understand and improve.

A unique feature of wood compared to most substrates is that it is porous, and thus adhesive can penetrate the wood, moving adhesion bonding beyond just a surface phenomenon. However, this porosity varies greatly from species to species and even within a single piece of wood itself. This can lead to a situation where mechanical interlock is sometimes an important strength contributor, and other times it is difficult to obtain. Dense wood can be hard to bond because porosity of the wood is low and the adhesive has to depend more on surface bonding than on mechanical interlocking. Given that dense woods are generally much stronger...
than less dense species, higher forces can be applied to the bondline because the wood is less likely to break. Higher density woods also swell and shrink more with changes in humidity. Thus, it is not surprising that the greater the density of a wood species, the harder it is to bond (27).

Wood has many features that complicate adhesive bonds besides density differences of the different species. Other factors relate to high orientation in the grain direction, ray cells that run perpendicular to the grain and growth rings, and rings with differences between cells in spring and later in the year. The tree also possesses juvenile wood, heartwood, sapwood, and reaction wood, as well as knots (20). A successful adhesive needs to bond equally well to all these different wood surfaces. Adhesive interaction with wood surfaces follows along with general adhesion theory (22) and weak boundary layers are also a factor in wood bonding (15), but additional complications caused by the wood structure also must be considered.

Given the great variation in bonding surfaces, synthetic adhesives with the ability to precisely control composition and molecular weights of the polymers often have an advantage over biobased adhesives where these are controlled by nature, such as soybeans.

iii. Bonding Methods and Testing

Lamination applications are a common type of wood bonding, covering plywood, engineered wood flooring, surface veneers on fiberboard (FB) and particleboard (PB), glulam, laminated veneer lumber, finger joints, and web to flange bonding in wooden I-joists (23–25). Usually adhesive is applied to just one surface, introducing the issue of transfer efficiency. All of these applications are bonded under pressure not only to bring the adhesive and other substrate into contact, but also to enhance adhesive penetration into the wood. Depending upon the cure conditions, these applications can be bonded at room temperature, but more often at elevated temperatures, typically at 110 to 160 °C.

The other type of application uses binder adhesives in making composites where adhesive bonds the wood in spots instead of as a continuous film. Adhesive is usually sprayed onto the wood pieces (flakes, particles or fibers) with the specific application and mixing equipment depending upon the type of pieces (26). These resin-coated pieces are then formed into a panel by pressing with heated platens or belts at 120 to 205 °C. Moisture from the wood and adhesive softens the wood to allow wood particles to deform for better bonding and carries heat to the center of the panel for a more thorough cure. It is important for adhesive to develop enough strength so that when pressing is completed, adhesive can resist delamination by force of the internal steam pressure.

Besides outside force on the bonded assembly, the biggest factor affecting durability of a bond is the change of the wood moisture content. As wood absorbs water, it expands considerably tangentially and across the growth rings, but very little parallel to the grain. Given that different species of wood expand differently and that adhesive needs to be quite rigid to resist external forces, adhesive has to withstand many internal and external forces (27, 28).
A typical test for lamination applications is to apply a shear force to a specimen and measure shear strength and percentage of wood failure (26). Specimens are tested dry and after water soaking or water soaking and drying. Other tests look at delamination after water soaking and oven drying. To increase the water effect, the specimen may be placed in boiling water or subjected to vacuum to remove air in the wood and then pressure soaked to force water into the wood.

For composite products, key tests are the internal bond strength when a block of material is pulled apart holding onto the faces, and how much the composite swells when it is soaked in water (28). Strong adhesion between the wood pieces will resist pulling and swelling force.

Especially for water-borne adhesives, adhesive needs to cure sufficiently during the bonding process to have low water sensitivity for withstanding these moisture resistance tests. This is an important aspect in developing and testing soy adhesives.

Another key test can involve measuring creep as static loads are applied to the wood product (28). It is preferred that the adhesive does not contribute to creep that would distort the bonded wood product. Adhesives used in bonded wood products should also be able to resist the effect of heat in a manner similar to the wood substrate.

**Protein Structure**

Proteins are biological polymers consisting of specific sequences of amino acids. There are 20 biologically relevant amino acids, each with a common backbone, but a different side chain (29). Figure 2 shows the amino acids found in proteins and categorizes them into groups based on polarity and charge. This wide variety of amino acids provides the protein with non-polar, polar, basic and acidic groups for both internal and external interactions. There are four levels of structure in proteins: 1) primary – the sequence of amino acid residues, 2) secondary – specific structural units called α-helix and β-sheet, 3) tertiary structure – the globular, stabilized structure of a protein polymer strand and 4) quaternary, the superstructure of more than one protein forming a stabilized unit. Each layer is important to a protein’s overall properties.

As proteins are synthesized on the RNA template to form the primary structure, specific sequences cause proteins to fold into α-helices or β-sheets to provide the secondary structure (29), see Figure 3. As it is formed, protein undergoes a hydrophobic collapse wherein the hydrophobic surface area of the non-polar side chains comes together at the core of the globular structure. Many polar groups are trapped inside during this process. These can associate with other polar groups that further stabilize the tertiary structure. There is typically one biologically active tertiary structure for a protein, known as the native state of the protein. Protein can be transformed into other tertiary structures of nearly similar energy that are all considered denatured states (30). This coiled structure has hydrophilic and hydrophobic domains both inside and on outside of the globule. Thus, interaction properties of proteins tend to be dominated by groups on the surface and not by the entire sequence. This includes the propensity of proteins

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to aggregate or form quaternary structure based on shielding hydrophobic surface patches and specific polar interactions. This folding of protein and subsequent aggregation of individual proteins mean that many potentially reactive groups are buried. These processes also make it harder for protein to interact with rough wood surfaces.

![Amino acid diagram](attachment:image.png)

Figure 2. Amino acids grouped as hydrophobic, hydrophilic, or polar vs. non-polar as well as acidic or basic.
Figure 3. Folding of proteins.

The combination of polar and non-polar groups explains why proteins are good adhesives for a wide variety of surfaces. Although soy proteins provide reasonable strength for wood bonds, it is necessary to modify proteins to make them even stronger to compete with synthetic adhesives. Many ways have been developed to chemically modify these proteins for improved adhesive properties (31, 32). However, because of the globular structure, it is unreasonable to look at the amino acid composition of soy flour (Figure 4) and assume that all potentially reactive sites are accessible under normal conditions. In fact, many of these polar groups may be stabilized inside the molecule by internal hydrogen bonding or salt bridges within the hydrophobic domains (33, 34). With soy, the difficulty in reacting with protein functional groups is even more complex in that individual protein chains are aggregated with other protein chains. Seed proteins represent between 30 and 50% of seed mass with storage proteins accounting for 65–80% of the seed protein (35). The two main storage proteins in soy, glycginin and conglycinin, are made up of a number of individual proteins that are held together by hydrophobic surface patches, salt bridges, and even intermolecular disulfide bonds (33–36).
**Figure 4.** Reactive amino acids in soy flour from data provided by Cargill. Approximately 53% of these are amides rather than carboxylic acids.

### Commercially Available Soy Products

Raw soybeans are delivered to a processing facility direct from the farmer’s field. Hulls of the beans are removed by cracking them into a number of pieces and aspirating the light hulls away to leave raw soy meal. After de-hulling, the soybean is crushed and extracted with hexane to remove valuable oil. The remaining fraction, called defatted soy meal, can then be converted to meal for animal feed or to flakes, flour, or texturized products for food and industrial uses (37). Although some of the material is left with protein in its native state, much of it is heated to make the product more digestible. Thus, flour comes in three forms characterized by the protein dispersibility index (PDI), relating directly to “solubility” of proteins within a given material, the highly dispersible native state soy (90 PDI), the low dispersible, denatured soy (20 PDI), and the in-between soy (70 PDI).

Soy flour is the least expensive of the refined soy materials examined as adhesives, but is also the most complex, containing about half protein and one third carbohydrate, as shown in Table I. Half of these carbohydrates are soluble, such as sucrose, raffinose, and stachyose, and half are insoluble, such as containing rhamnose, arabinose, galactose, galacturonic acid, glucose, xylose, and mannose (38, 39). Despite lower purity, soy flour is the only soy material being used in wood adhesives because of the low cost of competing synthetic adhesives for wood bonding.

Soy protein concentrate is produced by removing soluble carbohydrates and some low molecular weight proteins using an ethanol/water wash. The process to remove these components denatures proteins (37). This material can be used as is or hydrothermally treated to enhance some of the properties (39, 40). Limited work has been reported on comparing soy flour and concentrate for adhesives (41).
Table I. Typical soy products with approximate analysis and relative costs to soybeans.a

<table>
<thead>
<tr>
<th>Soy product</th>
<th>Protein content (%)</th>
<th>Carbohydrate content (%)</th>
<th>Oil content (%)</th>
<th>Moisture/Other content (%)</th>
<th>Relative cost (Soybeans = 1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole beans</td>
<td>36</td>
<td>32</td>
<td>20</td>
<td>12</td>
<td>1.0</td>
</tr>
<tr>
<td>Defatted meal</td>
<td>48</td>
<td>42</td>
<td>&lt;1</td>
<td>10</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Soy flour</td>
<td>51</td>
<td>34</td>
<td>&lt;1</td>
<td>&lt;10</td>
<td>~ 1.3</td>
</tr>
<tr>
<td>Soy protein concentrate</td>
<td>66</td>
<td>24</td>
<td>&lt;1</td>
<td>10</td>
<td>~ 4.0</td>
</tr>
<tr>
<td>Soy protein isolate</td>
<td>91</td>
<td>&lt;3</td>
<td>0</td>
<td>6</td>
<td>~ 8.0</td>
</tr>
</tbody>
</table>

a The price of whole soybeans fluctuates with world supply. Meal is typically less expensive than whole soybeans on average, but may be equal or greater in price on a regional basis. Soy flour, soy protein concentrate, and soy protein isolate are sold as proprietary products, primarily in the food market. Their prices relative to whole soybeans given here are approximate and fluctuate much less than commodity soybeans or soy meal. There are significant differences in processing and functional properties of these products for the food industry, and prices reflect these differences.

High protein content soy products can be made by removing both insoluble and soluble carbohydrates along with some protein through a series of steps. Generally, soy flour is dispersed in water and centrifuged to remove insoluble carbohydrates and proteins. The supernatant is acidified to precipitate proteins (37, 39) and soluble carbohydrates are discarded. Separated protein is finally solubilized, neutralized, and dried. Under mild conditions, this process is considered to give native state proteins. However, these proteins can be made more functional for many applications by hydrothermal treatment (39, 40). These functionalized proteins are commonly what has been used in the literature for studying adhesive and food use properties.

Current Commercial Soy Technology

There has been renewed interest in biobased adhesives, partially for reducing the level of dependence on fossil fuels used in wood adhesives, but especially for replacing urea–formaldehyde adhesives to reduce formaldehyde emissions from interior wood products. Along with many other products, there is an interest in replacing phenol derived from petroleum and urea and formaldehyde from natural gas. Although natural gas is now more plentiful, petroleum is still imported and increasingly expensive. However, the urea–formaldehyde commonly used in interior products has been of concern for a long time because of its formaldehyde emissions (42). With development of the California Air Resources Board (CARB) standard on formaldehyde emissions from bonded interior wood products (43,
no-added formaldehyde soy adhesives have received additional market acceptance. Lowering of formaldehyde emissions from products as set in the CARB standard has become accepted by the wood products industry and has been incorporated into U.S. national law (45). Other countries have their own formaldehyde emission standards (46). Although urea–formaldehyde is a low cost and effective wood adhesive, with heat and humidity it breaks down to give off formaldehyde (47, 48). Thus, emissions can continue for the life of the products and become much worse under certain environmental conditions (47–52).

Technology of using a polyamidoamine-epichlorohydrin (PAE) resin co-reactant for soy was developed by Li at Oregon State (53, 54) and has become widely used for interior plywood and engineered wood flooring with some limited acceptance in particleboard (55, 56). Variations in this technology have been covered by a number of patent applications (57–62). Limited work has been done to understand the mechanism of this reaction (63, 64); however, a hypothesized mechanism is shown in Figure 5. PAE is expected to react with wood because the reaction of PAE with paper is practiced commercially to make the paper more water resistant (65, 66). In fact, PAE can bond wood itself (3.8 dry and 1.0 MPa wet shear strength using ABES test method, see below). Exposed amino and carboxylic acid groups of protein can readily react with PAE. Thus, the hypothesized mechanism is well supported by available data.

**Soy Adhesives without and with PAE Co-Reactant**

Understanding performance of different soy adhesives has been difficult as various researchers have used a variety of soy products with different modifications, wood species, and test conditions. Work reported in this section has used hard maple veneer with a similar set of bonding and testing conditions. Work was done using an Automated Bond Evaluation System - ABES (67–69) because it provides more uniform bonds, is less sensitive to viscosity differences in the adhesives, and can provide similar information to other test methods (68).

Soy and PAE combinations are being used to replace urea–formaldehyde adhesives; thus, a standard curing temperature selected was 120 °C with a 120-second curing time to allow complete cure. These tests were carried out using soy with no PAE co-reactant and with PAE co-reactant at a low level so it can react with protein but does not dominate bond-strength values. PAE can react with wood, as it is known to react with carboxylic acid groups of paper pulp to produce water-resistant paper towels (65, 66). Samples were tested dry as well as wet following a four-hour room temperature water soak. Although dry strength data are valuable information about protein and carbohydrate bond strength, wet strength tells more about protein strength because carbohydrates lose most of their strength under wet conditions. Although it is not possible to eliminate adhesion factors in testing bonded assemblies, these tests emphasize cohesive properties of soy adhesives, especially for tests under wet conditions. Dried soy adhesive is too brittle to test by itself, leaving the bonded assembly with a strong veneer as the best option for understanding soy cohesive strength.
Soy Flour Adhesives

Soy flour comes in three grades of protein dispersibility from the most dispersible, native structure (90 PDI) to the least dispersible and highly denatured protein (20 PDI) with an in-between grade (70 PDI). Researchers assumed that the most dispersible protein 90 PDI flour, with a creamy texture when dispersed in water, should make the best contact with wood and other proteins, whereas 20 PDI flour adhesive with a gritty texture should give a weaker bond. However, there was no significant difference in bond strength either for dry samples or saturated samples after four hours of water soaking using ABES testing with these three soy flours (69). Results were similar at the 20, 25, and 30% solids and whether the flour had a 200- or 100-mesh size.

Researchers assumed that the more dispersible flour (90 PDI) should be better able to react with PAE than the less dispersible flour (20 PDI). At 5% PAE (solids per soy solids), shear bond strength was improved for dry samples and even more so for wet shear samples. However, there was not a significant difference observed in dry or wet strength of PAE plus soy adhesives on the basis of PDI (69). This again supports the theory that aggregation of protein limits the ability of protein to form stronger bonds.

Figure 5. Proposed reaction of PAE with soy protein and wood.
Why does dispersibility of flour not make a difference in these tests? First, even when proteins are dispersed, individual protein chains that average 20 to 72 kDa join in the native soy to form the main glycinin and conglycinin globulins of 150 to 360 kDa (70). These globulins can go on to form even larger aggregates (71). Thus, although proteins may be dispersible, it does not mean that they are individual protein chains with great mobility. Aggregation can be a problem with wood bonding in that even wood that seems smooth has a rough surface at the cellular level. This can make it difficult for soy protein agglomerates to interact well with the wood surface. The size and deformability aggregates and porosity all play a role in the interaction between adhesive and wood. Another way to form stronger bonds with wood would be to break up the soy protein aggregates and/or open up the coiled protein structure.

Can soy protein structures be altered to increase their adhesive strength? Previous researchers showed that denaturation of soy proteins with caustic increased their adhesive bonding strength and water resistance for concentrate and isolate as well as for soy flour (9, 10, 71–73). One concept is that caustic enhances electrostatic repulsion between the chains sufficiently to overcome hydrophobic attraction and provides sufficient negative charge to help open the protein structure. Unfortunately, this process cannot be combined with PAE chemistry because PAE rapidly self-reacts under basic conditions.

Apart from this caustic transformation of soy flour, other methods for disrupting soy flour have been examined. Studies, especially by Sun’s group, have shown that chaotropic agents, like urea and guanidine, and surfactants, like sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB), alter properties of native soy protein isolate (SPI) so that more water resistant bonds can be formed (74–76). This work was done with SPI, glycinin and conglycinin proteins in their native states; thus we expected that the same effect would be seen with the 90 PDI flour. Chaotropic agents help swell protein so the structure is more accessible, leading to expectation of similar behavior, given that both this SPI and the 90 PDI flour are in their native states. However, no significant improvement was seen with any of the chaotropic agents tested, urea, guanidine, or dicyandiamide, in terms of ABES wet shear strength (77). Possibly the high viscosity of soy flour prevented these chaotropic agents from swelling protein to make it more reactive, or the carbohydrates prevented these agents from interacting with proteins through steric hindrance. The surfactants SDS and CTAB also did not have any effect on the dry or wet shear strength (77).

Carbohydrates may be closely associated with protein that surfactants could not interact with proteins. Protein isolates, including soy, are also known to be influenced by the salt type and content of the solution as the salt influences the swelling of protein, with some shrinking and some swelling the protein (34). However, little effect was seen on the bond strength of soy flour adhesives (77, 78). Another concept was to use a co-solvent to increase the solubilization of the hydrophobic regions to aid in swelling of soy proteins to make them easier to interact with wood, each other and PAE. However, no improvement in ABES bond strength was seen with propylene glycol (77).

In summary, many methods that are known to alter the properties of native state SPI were shown not to significantly alter the soy flour’s ABES shear strength.
under either dry or wet conditions. It seems likely that the proteins are being stabilized either by the presence of carbohydrates or just not having the ability to change confirmations through steric hindrance as shown by the high viscosity of the flour in water.

Although the ABES tests for soy are very good at determining changes in the cohesive strength of soy in that the bonding zone is uniform in temperature and moisture content and the veneer is quite uniform and smooth, it does not reflect all parameters that are critical in commercial use of soy adhesives. As an example, 90 PDI and 20 PDI flour gave similar dry and wet shear strength in the ABES test, but the property differences of the wet adhesives make a large difference in actual commercial applications. The 90 PDI flour makes a creamy dispersion that wets the wood well, while the 20 PDI flour makes a gritty dispersion that is difficult to spread because of its lack of fluidity and tendency to lose water too quickly into the wood (79). Thus, some of these parameters can be important in having the proper flow and wetting characteristics needed for bonding in commercial processes where the veneers can be inconsistent and rough.

A key to the resurgence of soy adhesives is not alteration of soy flour, but use of polyamidoamine-epichlorohydrin (PAE) resin co-reactant. Even low levels of PAE (5% solids based upon dry weight soy flour) improve water resistance of all soy flour adhesives. As expected, addition of more PAE gives an even greater improvement in strength as there is more PAE co-reactant to react with the wood and proteins. Although the reactions between protein and PAE have not been fully elucidated, it has been shown that PAE does interact with SPI (63, 64). Knowing that PAE reacts with carboxylate groups in paper (65, 66) to increase its water resistance, it is certainly to be expected that the PAE should bond to wood, which also contains carboxylic acid groups.

**Soy Concentrate Adhesives**

As noted in an earlier section, technology for separating soluble carbohydrates requires denaturation of proteins to reduce their solubility; thus, soy concentrates do not have native state proteins (39, 40). Although the native state is mainly one biologically active structure, denaturation of a protein can create a multitude of different structures. This makes comparing soy concentrate performance to that of soy flour that has been heat denatured rather tenuous. Furthermore, many of the soy concentrates are hydrothermally treated (jet cooked) to improve their functionality, i.e., their ability to function in certain food products. The jet-cooked concentrates also do not represent the native state or any other states in available soy flour products (39, 40). Some wood adhesion studies have involved use of soy concentrate to make composite products, but given different applications and conditions (70, 74, 80–82), it can be difficult to understand their performance in relation to soy flour or soy isolate.

Some research on soy concentrate adhesives has been done using similar bonding and test conditions to those using soy flour adhesives discussed above (82). However, this was just done on the product after extraction, whereas many other concentrates on the market have also been jet-cooked to improve functionality. Table II shows the comparison of two non-hydrothermally
treated soy flours having different PDI with two concentrates, Arcon AF (non-hydrothermally treated) and Arcon SM (hydrothermally treated) and a soy protein isolate, ProFam 974 (hydrothermally treated), all commercially available. Although the two very different flours give fairly similar results in bond strength and viscosity, the two concentrates are very different with Arcon SM showing greatly enhanced bonding both in dry and wet shear strength as well as significantly increased viscosity. Studies using the Arcon AF have shown that it does not have much better adhesive strength than soy flour, but when blended with 5% PAE solids based upon soy solids, Arcon AF provided much better wet strength than soy flour with a similar PAE addition (82). The data in Table II show that it is easy to draw incorrect conclusions without understanding the history of the soy concentrate product. If Arcon AF is used to look at the effect of removing the soluble carbohydrates, one can conclude that their removal did not improve soy performance. On the other hand, use of hydrothermally treated soy concentrate would indicate that soluble carbohydrate removal improved soy adhesive shear strength. The net result is that changes in proteins that occur while making soy concentrate prevents learning much about the performance of native proteins.

<table>
<thead>
<tr>
<th>Soy/Property</th>
<th>ABES, dry</th>
<th>ABES, wet</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 PDI, 25% solids</td>
<td>4.9</td>
<td>0.3</td>
<td>16,200</td>
</tr>
<tr>
<td>20 PDI, 25% solids</td>
<td>4.4</td>
<td>0.9</td>
<td>2,080</td>
</tr>
<tr>
<td>Arcon AF, 20% solids</td>
<td>6.5</td>
<td>0.9</td>
<td>2,600</td>
</tr>
<tr>
<td>Arcon SM, 20% solids</td>
<td>8.2</td>
<td>1.8</td>
<td>&gt;200,000</td>
</tr>
<tr>
<td>ProFam 974, 15% solids</td>
<td>9.0</td>
<td>4.2</td>
<td>&gt;200,000</td>
</tr>
</tbody>
</table>

**Soy Protein Isolate Adhesives**

Much of the literature uses commercial soy protein isolate (CSPI) to investigate adhesive properties of soy proteins because of its availability. Thus, it is important to understand performance of CSPI relative to performance of soy flour and concentrate. The original work on PAE co-reactant was done using CSPI and showed improvement in wood adhesive strength by adding PAE (53, 54). In Table III, data show that CSPI is much better than soy flour and jet-cooked concentrate without and with added PAE in both dry and wet strength.
Table III. Strength values (MPa) for soy flour, concentrate, and isolate

<table>
<thead>
<tr>
<th>Co-reactant ⇒</th>
<th>Without PAE</th>
<th>With PAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soy product</td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>Flour, 30% of 90 PDI</td>
<td>5.0 ± 1.2</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>Arcon SM, 20%</td>
<td>8.2 ± 0.2</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>Commercial isolate, 15%</td>
<td>7.2 ± 1.3</td>
<td>3.0 ± 0.4</td>
</tr>
<tr>
<td>Laboratory isolate, 30%</td>
<td>4.6 ± 0.4</td>
<td>1.1 ± 0.5</td>
</tr>
</tbody>
</table>

a Too much wood failure to obtain an accurate value.

In Table III, CSPI has high dry and wet bond strength even though high viscosity limits solids to 15% compared to 30% for soy flour, but this 15% isolate has the same protein content as 30% solids soy flour dispersion (82). Addition of a small amount of PAE improves both dry and wet bond shear strength of CSPI, but not as much as that for soy flour (1.7 times versus 7.3 in wet strength, respectively).

The CSPI is functionalized to give it better aqueous gel properties in food products (39, 40), but it was not obvious that this material denatured by jet cooking would improve adhesive properties once the material was taken to dryness in forming a wood bond. It is worth noting that although jet cooking is important for obtaining improved properties, there are other manipulations that CSPI producers use to obtain different products optimized not only for gel properties, but also other properties, such as foaming and water retention (32, 33). Several groups have bonded different wood species under different conditions with laboratory-prepared SPI (LSPI), glycinin, and conglycinin and have not found exceptionally high bond strengths (51, 61, 63). Recent work has shown that LSPI does indeed have much lower bond strength than CSPI, as indicated by data in Table III (69). This indicates that although it can be valuable to use CSPI for developing new protein modification methods for wood bonding, it may not clearly indicate how proteins in soy flour are going to be modified.

Another big property difference of various products is viscosity. All soy products are shear thinning; thus, they may appear to be too thick compared to more Newtonian synthetic adhesives. However, because general application processes involve significant shear forces, “thick” soy adhesives actually apply well using typical application equipment. Viscosity is important in that wood adhesives should be of high solids to minimize steam generation during the bonding process. Lab isolate has a much lower viscosity compared to most commercial isolates (8,500 vs. >200,000 cP, measured at 5 rpm using a #6 spindle on a Brookfield viscometer for 15% solids at pH 7). In fact, for isolates and concentrates, higher viscosity soy products tend to have higher strength, as is illustrate by comparing Arcon AF and SM in Table II and the discussion about soy protein isolate adhesives section. It is not clear whether this is because of greater swelling of protein, uncoiling of the tertiary structure, altering the structure so that more hydrophobic groups are exposed, or changing the aggregation of proteins.
Effect of Carbohydrates

As noted above, inexpensive soy flour is about half carbohydrate, and it is natural to assume that carbohydrates are a main contributor to poor water resistance of bonded wood products. Testing this out by purification is not straightforward because in removing carbohydrates to make SPI, some insoluble and soluble proteins are removed. However, adding carbohydrates to SPI should answer the question of whether the presence of carbohydrates interferes with protein–protein interactions and consequently lowers bond strength, especially under wet test conditions. Soy flours contain about 34% carbohydrates, half soluble and half insoluble, compared to less than 5% for the CSPI. As illustrated in Figure 3, isolate proteins should readily aggregate through polar and hydrophobic interactions that can provide strength under both dry and wet conditions. However, for concentrate, insoluble carbohydrates present should interject themselves between protein molecules. Under dry conditions, carbohydrates can form chemical bridges between protein molecules. However, given weakening of hydrogen bonds under wet conditions, and thus, this bridging effect should decrease significantly. This effect should be even more pronounced with soy flour that also contains soluble carbohydrates. As mentioned before, protein structure is altered in going from flour to concentrate to commercial isolate; thus, the difference in bond strength cannot be solely attributed to differences in carbohydrate content. Given the ready availability of CSPI, a study shows that adding some carbohydrates (soluble and/or insoluble) initially causes a reduction in bond strength, but the effect levels out at higher levels of carbohydrates (83). The carbohydrate effect was similar with most carbohydrates tested. As shown in Table IV, addition of carbohydrates to laboratory SPI at the level present in flour causes reduction in wet ABES shear strength, but strengths do not drop to the level seen with soy flour. Thus, either other components are causing the difference or just the disassembly of the natural matrix can cause some changes in proteins.

<table>
<thead>
<tr>
<th></th>
<th>Wet strength (MPa)</th>
<th>Wet strength with dextrin and cellulose (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial isolate, 15%</td>
<td>3.0</td>
<td>2.25</td>
</tr>
<tr>
<td>Laboratory isolate, 30%</td>
<td>1.1</td>
<td>0.81</td>
</tr>
<tr>
<td>Soy flour, 30%</td>
<td>0.3</td>
<td>Not applicable</td>
</tr>
</tbody>
</table>

Thus, although it can be convenient to use commercial SPI to study protein modification, the resulting data may be misleading when attempting to extrapolate these results to what might be obtained using soy flour. This is because commercial SPIs are usually jet-cooked to improve their functionality (30, 32, 33), thereby
changing proteins from the native state present in soy flour. Additionally, this modification may make better proteins for bonding wood than exist in flour and so methods that improve soy flour may not have the same effect when using SPI.

Soy-PF

Traditional soy flour adhesives used alkaline conditions to improve the soy bonding performance (6, 9, 10, 71, 73–75). Because resole phenolic wood adhesives are also used under basic conditions, combining soy with phenol-formaldehyde (PF) adhesives was a logical combination for making PF adhesive more biobased and reducing its cost, as soy flour is lower in cost than PF (84). The first application used soy and phenolic resin as separate components applied to opposite surfaces that are brought into contact (85, 86). This technology was used commercially for finger-jointing green studs (87), until a phenolic adhesive was developed that could accomplish this type of bonding without the use of soy.

A major complication is that soy dispersed in water can be quite viscous, especially under alkaline conditions. This caused researchers to either add less soy or to depolymerize the soy through enzymatic or caustic hydrolysis (88, 89). The assumption is that soy adhesives need the same low viscosity that PF adhesives have when measured at low shear. However, given that most adhesive application systems involve high shear and that soy adhesives are shear thinning, soy–PF adhesive viscosity at low shear can be higher than that for a PF adhesive as long as the material can be pumped. This logic was used to develop alkaline soy–PF adhesives with soy contents as high as 50% (90–92). Three major problems with alkaline PF and soy-PF adhesives are poor stability, caustic burn of composites, and dark color. Acidification of alkaline PF adhesives causes them to precipitate out of solution, but acidifying soy–PF formulations led to formation of stable acidic dispersions (93, 94). This type of product has been shown to make an acceptable product in commercial production of oriented strandboard, but has not been commercialized.

Soy with Other Modifications

A variety of other routes have been demonstrated to modify soy proteins to make improved adhesives for wood bonding. There are no indications that any of these have been commercialized.

Besides treatment with base mentioned previously, soy has been altered in other ways. One way is to make protein acidic to reduce its solubility, generally by treating it with citric acid (71, 75). Soy protein modified by proteolytic enzymes (such as papain, trypsin, chymotrypsin, etc.) have been shown to exhibit greater shear strength and enhanced water-resistance (95).

Reaction with aldehydes is a common way to modify proteins (31, 32, 96). Certainly formaldehyde is a common and inexpensive way, but because of concerns about emissions, the desire is to minimize use of formaldehyde in wood adhesives used in interior wood products. One method
is to use melamine–urea–formaldehyde or melamine–formaldehyde with soy (97–100). These formulations were mainly a soy matrix using formaldehyde resin as a co-reactant in contrast to formulations where soy is added at lower levels to reduce formaldehyde emissions of urea–formaldehyde and melamine–urea–formaldehyde adhesives (100, 101). However, other aldehydes can be used and they are less likely to present as much of an emission issue. Glyoxal and glutaraldehyde are examples of other aldehydes that can modify soy (102).

Research has also involved modification of the soy polymer for improved adhesion through a variety of chemical reactions. Lei et al. (103) indicated that wood adhesives based on hydroxymethylated or glyoxalated hydrolyzed gluten protein were shown to have satisfactory results that can meet the relevant standard specifications for interior particleboard. Liu and Li (104) reported grafting a dopamine molecule onto SPI to make a product similar in behavior to mussel adhesives. Cystamine has been grafted onto soy protein isolate to give improved wood adhesion (105). Reaction of soy with epoxy resin (106) and with combined epoxy resin and melamine-formaldehyde resins (107) have been reported. Gu and Li (108) reported a novel adhesive based on soy protein, maleic anhydride, and polyethyleneimine that can yield an adhesive with good bonding potential. Li has also developed a soy-magnesium oxide adhesive for wood bonding (109).

**Heat Resistance of Soy Adhesives**

One use for casein adhesive has been in fire doors because proteins are non-melting. However, it was not clear how soy proteins would behave, especially with soy flour having a high carbohydrate content that is not present in casein. Heat resistance is important in some wood bonding applications because many synthetic adhesives soften or depolymerize in fire situations, which can cause significant weakening or delamination of bonded wood products.

Recent work has investigated both chemical and mechanical degradation of different soy products. As expected, CSPI did well in both aspects, being quite similar to results obtained with very stable PF adhesives (110). On the other hand, soy flour showed considerable weight loss during heating at 220 °C; most likely that weight loss was due to the carbohydrate fraction. Interestingly, this chemical change did not cause an observed loss in bond strength. Thus, soy adhesives are good in wood-bonding applications that may require significant heat resistance.

**Summary**

Adhesive bonding always involves good wetting and adhesion to the substrate surface. Because of wood’s porosity, adhesives can penetrate beyond the surface and into cell lumens. However, for this to take place effectively, viscosity of the adhesive and the hydrodynamic volume of its components need to be small enough for the wood species that is being used.

Soy proteins have some very beneficial properties, such as both polar and non-polar components for bonding to a variety of surfaces, most notably, wood.
Although the tendency for proteins to aggregate probably adds to the strength of soy adhesives, it can be problematic for wetting the three-dimensional surface of wood. In addition, economically viable soy flour has much lower strength under wet conditions compared to commercial soy protein isolate (CSPI).

Because of processing conditions, soy proteins in CSPI and soy concentrates have been denatured. Thus, studies with these materials may not well represent what is obtainable with highly dispersible flour, which contains proteins in their native state. Thus, caution needs to be exercised in drawing conclusions from using only CSPI.

The high shear strength of both native and commercial SPI compared to what can be obtained with soy flour shows that much better properties can be obtained if the proper soy treatments are used.

Acknowledgments

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References


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