16 Soy Proteins as Wood Adhesives

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Protein adhesives allowed the development of bonded wood products such as plywood and glulam in the early 20th century. Petrochemical-based adhesives replaced proteins in most wood bonding applications because of lower cost, improved production efficiencies, and enhanced durability. However, several technological and environmental factors have led to a resurgence of proteins, especially soy flour, as an important adhesive for interior nonstructural wood products. This paper discusses important aspects of protein structure and recent successful advances in higher performance soy flour adhesives for wood bonding. Despite these advances, we believe there is even greater potential for protein adhesives if the reactive groups can be better utilized for bonding and more efficiently cross linked. Protein wood adhesives have recently displaced fossil fuel–based adhesives in some markets and have the potential to replace a significant percentage of fossil fuel–based wood adhesives worldwide.

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16.1 INTRODUCTION

The use of protein-based adhesives has a long history that includes examples of adhesive systems based on several protein sources, such as animal protein, casein from milk, soy flour, and blood [1]. Animal protein–based hot melt glues were used in many applications, including furniture manufacturing, because they set rapidly [2]. Caseins precipitated from skim milk under acidic conditions were used in the development of the glulam industry [3]. Soy flour adhesives were the dominant glue in plywood well into the 20th century [1]. Blood was used mainly with other protein glues to provide improved moisture resistance [4]. The ability of a wide variety of proteins to serve as wood-bonding adhesives indicates a good natural affinity between proteins and wood. The main limitation of protein adhesives is that synthetic, fossil fuel–based adhesives tend to be more durable than protein adhesives. For a widespread resurgence in the use of protein adhesives, new technologies needed to be developed.

Because of the low cost and wide availability of soy flour, soy adhesives have the greatest potential for widespread use in the wood products industry. The original soy flour adhesives used in plywood were made in plywood plants under highly alkaline conditions. They typically had a high viscosity, a low solids content, and a usable pot life of only a few hours [1]. This plywood was adequate for interior applications. However, fossil fuel-based adhesives, such as urea-formaldehyde (UF), replaced soy-based adhesives for interior applications because UF adhesives were cheaper, easier to use, and more water resistant. In recent years, developments in protein adhesive technology [5,6], volatility in petroleum prices, and more stringent regulatory limits on formaldehyde emissions from composite wood panels [7,8] have created a renewed commercial interest in soy adhesive technology. Additionally, these developments have closed the gap in both performance and pricing differences between fossil fuel-based adhesives and soy-based adhesives. Despite these factors, there are still many obstacles in the path to greater usage of soy-based adhesives in composite wood panels. The focus of this chapter is to review these challenges and discuss some of the fundamentals of protein-based adhesives, focusing mainly on soy-based adhesives, to provide an understanding of current technology and a background for future improvements to protein adhesive technologies.

16.2 DEMANDS OF AN INDUSTRIAL-SCALE WOOD ADHESIVE

For a new adhesive to be successful on a large scale, it must meet certain minimum requirements. First, it must be relatively inexpensive and abundant and have consistent properties. Second, given the great expense associated with changing process designs and equipment capabilities in the wood products industry, a new adhesive should preferably work with current process equipment and conditions.

One very important aspect of these demands is the adhesive's fluid properties. Adhesives are typically pumped through pipes and applied to wood by a variety of processes, including atomization, shear blending, and roll or curtain coating. Any new adhesive technologies must be produced with a suitable viscosity needed for them to flow through existing equipment for a specific process.

Another highly important process parameter in wood product manufacturing is moisture content. Adhesives must not greatly raise the moisture content of the wood product during processing or in the final product. Current composite products are heat-cured, and excess water in the processing of a product results in problems in production speed or quality. In end products, changes to moisture content can alter the working properties of the panel, such as machining, or lead to problems with dimensional stability.

The final requirement for a new adhesive is to provide finished products with sufficient strength and stiffness properties as defined by the appropriate industry standards. In the wood products industry, there are three main classes of materials: interior nonstructural, exterior nonstructural, and structural. Each class has its own set of standards and testing requirements, but in general, all three classes require some level of both dry and wet strengths. Interior products are judged mostly by dry strength and stiffness properties; however, wet strength and dimensional stability are also used to gauge product quality. Adhesives for exterior products must have great water resistance, while structural adhesives must be resistant to water, extreme heat (fire), and creep. An adhesive that promotes mildew, mold, or insect infestations is not acceptable, so these issues must also be considered.

In recent years, low formaldehyde emissions have become a major performance criterion for interior composite wood products in North America, Europe, and Japan. With the change in the classification of formaldehyde from a suspected to a known carcinogen, the California Air Resources Board (CARB) was required to consider setting new standards for formaldehyde emissions [7,9]. However, CARB could not act unless technology was available that could meet a new standard. A soy-based adhesive system was one way to meet the new standard and had been demonstrated to be commercially viable for decorative (interior) plywood. CARB ultimately set regulations that apply to decorative plywood, particleboard, fiberboard, and products made using these materials [9], and recently, a national standard was passed based on the CARB limits for formaldehyde emission in wood products [8].

The low formaldehyde emissions requirement has spurred commercial interest in protein-based adhesive technology, especially as a replacement for UF, which may have difficulty achieving consistent compliance with CARB formaldehyde emissions limits in all composite wood panels. Although protein-based adhesives have continued to be used in several niche applications for wood products, now soy-based adhesives are again being used at increasing levels in the interior plywood industry, even though the processes and properties of wood products have been designed and defined for use with synthetic adhesives. Synthetic adhesives have high productivity in composite or engineered wood product manufacturing processes because of their design; thus, natural adhesives need to perform equally well. For the protein adhesives to effectively displace the synthetic adhesives, they need to be of low cost and in large enough supply, to fit with the current manufacturing processes, and to produce products that meet all the relevant specifications.

16.3 PROTEIN FUNDAMENTALS

Proteins have long been used for bonding wood because of their strong adhesion to wood surfaces. Proteins have many of the characteristics of good adhesives, such as having surfactant character, both polar and nonpolar domains, and good cohesive strength. Surfactant character means that proteins can wet surfaces well. Once the surface has been effectively wetted, the polar and nonpolar domains can interact with the polysaccharide and lignin domains, respectively, in wood. The long history of proteins used as adhesives, as well as their ability to form gels, demonstrates that proteins also adhere well to themselves.

16.3.1 CHANGES IN PROTEIN ADHESIVE TECHNOLOGY

Compared to the early 1900s, when proteins were used widely in wood products, the knowledge about protein structure and properties has advanced tremendously. The driving force has been to better understand the biological function of proteins (enzymatic processes, pharmaceutical interactions, cellular adhesion) and how they behave in food products. For food applications, many properties of proteins have been studied extensively, including the following [10,11]:

- Primary, secondary, tertiary, and quaternary structures
- · Gel properties, especially under heating
- · Foaming ability and water retention
- · Interaction with other proteins, carbohydrates, and salts
- Thermal transitions for characterizing protein structure

Despite the tremendous advances and sophisticated analytical methods, many aspects of proteins are still not well understood. For instance, the effect of the common denaturant urea is still debated [12]. One reason for the lack of progress in research is that crude protein products are mixtures of proteins with different compositions, structures, and properties. Another reason is that the energy difference between one folded conformation and another is often so small that changes in the environment can affect the protein's tertiary conformation [13]. Given the heterogeneity of most protein sources, understanding structure–property relationships on a fundamental level as they relate to adhesion is a daunting task made more difficult by the myriad of complex interactions and influences.

16.3.2 PROTEIN STRUCTURE

Proteins are linear polypeptides made from α -amino acids, whose sequence is determined by the genetic code. Amino acids are distinguished by their side chains, which, in addition to steric differences, can be categorized as hydrophobic or hydrophilic. Depending on the pH of the medium as well as the immediate environment of a given side chain, the hydrophilic residues can also exhibit various states of charge. This backbone sequence is referred to as the primary structure (see Figure 16.1). As the polypeptide is synthesized, certain sections have the proper sequence for forming



FIGURE 16.1 The formation of secondary and tertiary structures where each chain folds and coils in specific ways into a relatively compact structure with a characteristic three-dimensional shape. These folded chains can interact to form a quaternary structure.

 α -helices or β -sheets. These sections constitute the secondary structure resulting from hydrogen bonds joining the atoms of the peptides along the polypeptide chain [10]. The α -helix involves a single chain of adjacent amino acids that require certain sequences in order to form a stable helix. The β -sheets contain a series of adjacent amino acids as well as segments from other parts of the same chain. The fraction of a protein in helices and sheets can be determined by several methods, including infrared spectroscopy and optical rotation [11].

Whereas most polymers depend primarily on interchain interactions to provide structure, proteins use intrachain interactions extensively to form a tertiary structure. Therefore, understanding the properties of protein begins with the intrachain properties and how the molten globular structure is influenced by the external environment. The term "molten globule" has been used by protein scientists to reflect the ease with which the tertiary structure rearranges as a result of changes in the surrounding environment and the small energy differences between different folded conformations. In a normal aqueous environment, nonpolar amino acid side chains want to minimize the amount of surface area exposed to water. This aversion results in a "hydrophobic collapse," with more of the nonpolar groups ending up on the inside of the molten globule and more of the polar groups residing on the outside [13]. Intrachain stabilization is provided by van der Waals interactions of the hydrophobic groups, hydrogen bonding of polar groups, ionic bonding between acids and bases, and disulfide bonds between thiols.

Protein interchain interactions result in a quaternary structure, made up of two or more kinds of protein subunits, and offer a significant level of additional structure and stability. Interchain associations involve the same kinds of hydrophobic, polar, ionic, and disulfide interactions as the secondary and tertiary structures. Although it is energetically favorable to have all nonpolar side chains buried inside the globule and all polar groups on the outside, the backbone sequence does not allow this. This is especially true for proteins like soy with a high proportion of hydrophobic residues. As a result, proteins often have nonpolar groups on the surface. This leads to interchain associations to reduce the interaction of surface hydrophobic groups with water.

Most proteins serve a structural, enzymatic, or storage role in their native biological system. Storage proteins (e.g., soy, casein, wheat gluten) [14] supply the amino acids that are needed to make the structural or enzymatic proteins of the growing organism and can also be used as adhesives with little modification. In contrast, structural proteins (e.g., bone, hide, blood, skin) often need to be treated to make them useable as adhesives [2,4,15]. Interestingly, there is no clear difference in wood adhesion properties between storage and structural proteins, with both having been used for wood bonding. However, there are substantial differences in their structures and other properties [14]. In addition, protein adhesives are not equal in their wood adhesion durability [1–4], the general order being animal, soy, casein, and blood, from least to greatest water resistance.

16.3.3 PROTEIN DISPERSION AND MODIFICATION

Proteins as they exist in living organisms are referred to as being in their native state. In their native state, many proteins are water dispersible so that they can migrate from their synthesis site to where they are used or stored. Either intentionally or unintentionally, processing of the proteins can denature (change from native state) them in a reversible or nonreversible fashion. Proteins may be intentionally altered to make them more digestible; destroy enzymes that can cause food degradation; precipitate them (e.g., casein); or alter water retention properties, dispersibility, swelling characteristics, or accessibility of functional groups. Common ways to denature proteins are to change the pH, apply heat, and add denaturants such as urea.

Proteins can also be modified by chemical reactions, especially if cross-linking is desired [16,17]. Often, primary amino groups, such as the side chain of a lysine amino acid, are used as reactive sites. Amino groups can be alkylated, acylated, hydroxymethylated, and so forth. These reactions can be done either to reduce water solubility (such as a reaction with acetic anhydride) or increase water solubility (such as a reaction with succinic anhydride). Reactions with aldehydes, such as formaldehyde, usually decrease the water solubility of proteins by causing gelation. Other groups that are relatively easily modified include carboxylic acids, thiols, hydroxyls, and a variety of nitrogen-containing groups.

16.3.4 CURRENT SOY PROTEIN ADHESIVES

Soybeans are a major crop in the United States and are noted for having high protein content. For adhesive applications, the most common raw material is soy flour ground from defatted meal. Defatted meal is the residue after the oil has been pressed or extracted from the dehulled soybean [18]. If mild conditions are used to process the flour, it has a high protein dispersibility index (PDI). PDI is the ratio of protein content in the supernatant to the total protein in the flour after dispersion of the flour and centrifugation. Greater heat treatment gives a lower PDI, which is desirable for a number of applications [19]. As shown in Figure 16.2, soy flour has slightly more protein than carbohydrates. The carbohydrate contains a variety of insoluble and soluble components [20]. Extraction with aqueous ethanol removes many of the soluble carbohydrates to produce soy concentrate [18]. The purest commercial soy protein product is the soy protein isolate (SPI), which has almost all of the insoluble and soluble carbohydrates removed [18].

With over 90% protein content, SPI is the commercial soy product used in many soy reaction studies. SPIs have been altered using a variety of denaturants, including surfactants, amino-containing agents, alkali, and enzymes, in efforts to improve adhesive properties. For example, addition of 1% of the anionic surfactant sodium dodecyl sulfate (SDS) resulted in the maximum improvement of SPI adhesion to plywood [21]; cationic surfactants had a similar effect [22]. Urea at 1 and 3 molar concentrations provided improved bond strength and water resistance for SPI over 0.5 and 8 molar concentrations [23]. Studies have also investigated the effect of alkali and enzyme treatments [24–26]. Much of the recent work on modifying the performance of SPI and soy protein fractions without curing chemicals has been discussed in terms of mechanical and adhesive properties [27–29].

While soy contains a number of proteins, the two that account for most of the mass are glycinin (11S) and conglycinin (7S) [30]. *S* is the Svedberg number, an expression of the sedimentation rate, and larger numbers signify higher molecular weights. These two proteins have distinctive differences in tertiary and quaternary structures. The subunits in 11S are either acidic or basic and are held in their quaternary structure by acid–base interactions, disulfide bonds, and hydrophobic interactions [30]. On the other hand, the 7S subunits are more neutral and are held together mainly by hydrophobic interactions. Although the 7S and 11S proteins are very different structurally, this difference has not resulted in observation of any large differences in their wood-bonding properties [27].

Although most of the recent adhesive research has been with soy proteins, other proteins have also been studied. The concentration on soy research in the United

- Whole soybeans
- \approx 16–17¢/lb, 36% protein, 18% oil, 36% carbohydrates, 10% moisture Defatted meal
- ≈ 15¢/lb, 48% protein, 0% oil, 44% carbohydrates, <10% moisture
- Soy flour
- \approx 18–25¢/lb, 50% protein, 0% oil, 40% carbohydrates, <10% moisture high (90%) to low (20%) PDI (dispersible protein)
- Soy protein concentrate

 ≈ 50-90¢/lb, 65+% protein, 0% oil, up to 35% carbohydrates
 Soy protein isolate
- \approx \$1.50–2.00+/lb, 90+% protein, 0% oil, up to 10% carbohydrates

FIGURE 16.2 Soybean products with their 2010 prices and composition, with the flour and isolate highlighted because they are the most commonly investigated products for adhesives.

States has been due to the availability of soy flour in large quantities at reasonable prices, along with financial support of the United Soybean Board and similar producer-based organizations. However, in other countries, especially in Europe, soybeans are not a major crop. Thus, research in Europe tends to use wheat gluten and other protein sources [31,32].

16.3.5 PROTEIN ADHESIVE CROSS-LINKING AGENTS

Traditional methods of making protein adhesives have not provided as much water resistance as their competing synthetic adhesives. Un–cross-linked soy proteins are good adhesives for wood under dry conditions, but their water resistance is typically poor. Older soy or casein formulations, made under alkaline conditions and using calcium compounds, had good water resistance [1,3]. The problem is that none of these methods makes products that can fully meet current performance standards, such as ANSI/HPVA HP1-2009 4.6 three-cycle soak test for decorative plywood. Thus, in the past dozen years, more emphasis has been placed upon covalent cross-linking.

Some recent research has emphasized using soy as a part of a phenol-formaldehyde (PF) adhesive matrix in contrast to earlier work that treated soy as a filler. Several programs attempted to keep the soy-PF viscosity at the same low level as typical PF adhesives. This limited the level of soy incorporation [33-36]. However, viscosity limits are more flexible for soy adhesives because soy is shear thinning, whereas PF adhesives are Newtonian. Thus, a soy adhesive of higher apparent viscosity can perform just as well as a PF with a much lower viscosity with current process equipment without significantly altering adhesive distribution on the wood. This has allowed a higher incorporation of soy into soy-PF adhesives [36,37]. An interesting aspect of these alkaline soy-PF adhesives is that they can be acidified to provide stable dispersions [38,39]. Both the alkaline-dispersion and acid-dispersion soy-PFs have shown good performance as adhesives for oriented strand board (OSB) face layers. The acid-dispersion adhesives are lighter in color and do not give the caustic burn spots in OSB that occur with normal PF formulations, while still giving good bond durability. The stability of these dispersions is surprisingly good, as it is usually difficult to neutralize alkaline PF products without precipitation of the PF unless surfactants are used [40].

Formaldehyde is well known for cross-linking proteins [16,17], but there are concerns about the safety of formaldehyde. This has led to the examination of other types of aldehydes. Among the other aldehydes are glyoxal, glutaraldehyde, and starch dialdehyde. Improved properties have been reported when using glutaraldehyde and glyoxal with soy flour or SPI [41–43].

The biggest commercial success in water-resistant soy adhesives has been achieved with the addition of polyamidoamine-epichlorohydrin (PAE) resin. Kaichang Li [5,6] developed the PAE cross-linked soy technology, and others have studied PAE–soy interactions [44]. This technology has been licensed and is currently used by several major North American plywood manufacturers. Soy–PAE resins have been demonstrated to make products that meet the standards for interior (decorative) plywood, engineered wood flooring, particleboard, and fiberboard [45–47]. It has also been tested commercially on all these products. A main advantage of these products

is that, because they contain no added formaldehyde (NAF), the formaldehyde emissions of these products are well below all of the standards [46–48]. The reaction mechanism of PAE with soy proteins has been investigated [44], but many of the details are still unknown.

Other technologies have also been developed to make soy-based adhesives that have good water resistance. Liu and Li [49] have grafted dopamine groups onto SPIs so that they could cure in a manner similar to that used by mussels. The modified soy provided much better water resistance than the unmodified soy for bonding maple plywood. SPI can be reacted with polyethylenimine (PEI) and maleic anhydride (MA) to make an adhesive with suitable water durability for interior plywood bonding [50]. The PEI and MA combinations can also be used with the more economical soy flour for interior plywood bonding [51]. Cysteamine has been grafted onto SPI by amide linkages to increase the mercapto content; this provides improved strength and water resistance of plywood [52].

16.4 PROPERTIES OF SOY ADHESIVES

16.4.1 RHEOLOGY

Although proteins have good adhesion to wood, their rheological properties cause complications. Most proteins make water dispersions of high apparent viscosities, with both the words *dispersions* and *apparent* being important. Proteins, under most conditions, do not make true solutions. Globular proteins have enough hydrophobic domains to prevent them from forming a true solution. Even though many of the hydrophobic groups are located inside the globule because of the hydrophobic collapse, not all these groups can be buried [19]. Thus, there are hydrophobic patches on the surface of folded protein chains (tertiary structure). To minimize the energy involved, the individual proteins associate with each other in the hydrophobic regions to form quaternary structures. The hydrophobic attraction of the chains is balanced by the electrostatic repulsion because each of the chains is negatively charged above a pH of about 4.5. Thus, understanding the colloidal properties of the protein is important to understanding how these dispersions behave. The native tertiary and quaternary structures of the protein can be disturbed by a variety of conditions such as heat, pH changes, or added chemicals. The tendency of proteins to fold into globules, and the tendency of these globules to associate with one another, cannot be avoided because of the hydrophobic side chains [19]. These disruptions often result in permanent changes. Thus, heating soy flour causes the dispersibility of the protein to decrease. For example, heating the 90 PDI flour results in a 20 PDI flour. It has been determined that upon heating, the 11S and 7S subunits can separate and recombine to form combinatorial versions of both 11S and 7S subunits [53].

The associations of proteins also result in the need to refer to apparent viscosities, because the shear conditions and history of the dispersions greatly influence the measured viscosity. Protein dispersions are shear thinning (Figure 16.3); thus, the apparent viscosity measured using a Brookfield viscometer with a low shear rate does not represent the fluidity under the high-shear-rate environment found in most mixing, pumping, and application equipment. Consequently, incorporating low



FIGURE 16.3 Viscosity (Pa/s) vs. frequency for soy flour measured on a Paar Physica UDS 200 with a 25 mm serrated parallel plate [54], with the TS5525 using Prolia 100-90 flour from Cargill at different pH values.

amounts of soy in a PF adhesive or the enzymatic degradation of the protein to obtain a low Brookfield viscosity is unnecessary and often counterproductive. Considerable education of wood adhesive users is necessary, because they are used to Newtoniantype adhesives, in which high viscosity means difficulty in pumping and applying the adhesive. Often, protein adhesives can be in the range of 2 to 75 Pa/s apparent viscosity and still work in typical application equipment, with the lower end for spray application and the higher end for roll coaters.

In spite of the shear-thinning nature of protein adhesives, workable viscosities are usually found at lower solids content than with synthetic adhesives. This causes a problem in many wood applications because of excessive steam pressure during the making of composite panels or in having a bonded product at a low enough moisture content to meet its standards. Most wood composite panels are produced by hot pressing the wood–adhesive combination under heat. In products such as OSB, particleboard, and fiberboard, this heating generates an internal steam pressure that the adhesive bonds need to withstand to prevent blows in the composite when the pressure is released. More water in the adhesive produces greater steam pressure and requires high adhesion under wet conditions to withstand the internal forces.

16.4.2 BOND STRENGTH

Protein adhesives have been used with wood because they give good bond strength under dry conditions, but wet strength has been an issue. Some proteins, like casein and blood, have been able to provide more water-resistant adhesive bonds than soy proteins [1,4], but they have tended not to be as resistant as most synthetic adhesives. Good synthetic adhesives have a curing mechanism that generates covalent bond formations between the polymer chains. The newer soy adhesive technologies do incorporate some type of covalent bond formations. Even though not all cured soy products provide good water resistance, the soy–PF products [36–39] and soy–PAE products [45–47,54] discussed above have been shown to produce wood products

using standard production techniques with sufficient water resistance to meet normal product standards for the specific application.

Heat resistance has also been important in structural applications and has become more of an issue in some of these areas. The ability to withstand load at elevated temperatures has been important for many years for engineered wood products because of the concern about creep, especially for products used in floor and roof supports. In recent years, the ability of adhesives to hold up under fire conditions has become important [55]. In the past, protein adhesives have shown good heat resistance at higher temperatures; however, the ability of soy flour-based adhesives to withstand more extreme heat treatment was unclear. Recent work has shown that properly formulated soy flour adhesives maintain strength at elevated temperatures [56].

16.4.3 Environmental Impact

Although ultra-low-emitting urea-formaldehyde (ULE-UF) adhesives can meet the current regulations, the soy–PAE products are much lower in formaldehyde emissions using current tests [48]. Furthermore, unlike UF and ULE-UF formulations, soy–PAE formulations are not susceptible to long-term emissions by hydrolysis under conditions of increased heat and humidity (Figure 16.4a and b) [54,57].



FIGURE 16.4 (a) Formaldehyde (CH₂O) emissions at various relative humidity levels at 25°C (4-day samples) using modified EN-317 with commercially produced hardwood plywood with NAF (soy–PAE) and ULE-UF (ultra-low-emitting urea-formaldehyde). (b) Formaldehyde emissions at various relative humidity levels at 35°C (4-day samples) using the same testing and hardwood plywood as in Figure 14.4a. Note different scale on *y*-axis.

Additional reasons for using soy proteins as wood adhesives are their strong woodbonding ability, their excellent heat resistance, a desire to be more environmentally friendly, and the increasing price of fossil fuel. All of the proteins are derived from natural, renewable resources. Most of the proteins are available in large quantities, and even though the wood adhesive market is large, many of the proteins are available in much larger quantities, making them different from tannins, which are in limited supply. Thus, soy proteins are environmentally friendly and offer long-term sustainability. For a long time, the price of fossil fuels was decreasing compared with agricultural feedstocks. Increasing competition for and limited supplies of fossil fuels coupled with improvements in the agricultural yields have led to a shift in petroleum versus agricultural economics. These trends are expected to continue in the future. The advantage of soy protein is the availability of a very large supply of soy flour that can readily meet the needs of even a large market, such as wood adhesives.

16.4.4 OPPORTUNITIES

Although performance of soy adhesives has vastly improved, there is still a need for better products to make them more competitive with synthetic adhesives. One area of focus is the properties of soy itself. Generally, proteins in water at high concentrations generate high viscosities and are very shear thinning. Making higher percent solids soy formulations at equivalent or lower viscosities is an important goal in order to compete more effectively with fossil fuel–based adhesives. This involves understanding what contributes to the high viscosity and designing processes to reduce this effect. Perhaps alterations of processes are available to control the viscosity through avoiding denaturation in some cases or by selectively denaturing the proteins in others.

In soy flour, about half the material is carbohydrates. These are likely to be a detriment to adhesive performance due to their hygroscopic nature. This portion is relatively unstudied in adhesives and is simply assumed to contribute little to bonding and/or rheological properties. Understanding the role of these carbohydrates may provide further insight into the use of soy flour as a protein-based adhesive. Other questions for consideration include the following: Can the carbohydrates be removed from soy flour at low cost so that the product contains more of the higher-bond-strength proteins? Can the carbohydrates in the flour be reacted so that they contribute to the strength of the adhesive network?

In general, proteins need to be cross-linked to provide good wet strength. Are there types of chemicals, in addition to those already investigated, that can be incorporated to provide greater wet strength? Are there ways to denature the protein to expose additional functional groups for increased cross-linking? Can soy protein adhesive be made less water sensitive like the naturally water-resistant hair, collagen, or mussel protein adhesives?

16.5 CONCLUSIONS

The bonded wood products were originally based on proteins from various sources, but fossil fuel-based adhesives have generally displaced these protein adhesives over the past 60 years. The need to make wood composite panels with lower formaldehyde emissions for interior uses and the desire for bio-based adhesives have opened an opportunity for a resurgence in protein adhesives. New technology for cross-linking soy adhesives has shown the ability to make composite products that meet current product specifications. Proteins differ from most other polymers in that intrachain interactions play a very important role in influencing interchain interactions and adhesion. To develop better protein-based adhesives, more of the fundamental structure–property relationships, as they relate to adhesion, must be understood. Although the push toward green technology and some environmental factors have provided a renewed level of commercial interest in protein adhesives, it is clear that to gain more widespread use and acceptance, advances are still needed. This review hopefully has provided some of the basic background information to spark the research necessary to achieve the goal of using a renewable adhesive source with the lowest long-term environmental impact.

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