

Protein structure and wood adhesives

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ABSTRACT

Interest in biobased adhesives has led to many studies on protein adhesives. Unfortunately, many assume that denatured proteins adopt a permanently extended shape. Neither the properties of the applied soy protein dispersion, properties of the cured adhesive, nor the general protein literature are consistent with proteins being very unfolded or extended. In the presence of water, a compact state (hydrocolloid) is more favorable since it minimizes the number of exposed hydrophobic groups. Each protein chain minimizes contact with water by burying most hydrophobic domains, which is achieved through folding into a compact globular structure and by aggregating with other protein globules to help shield remaining surface hydrophobic domains. Proteins can unfold, but the energy required to mix hydrophobic proteins with water causes them to quickly collapse and aggregate. These globules aggregate with other proteins to form pre-gels (physical bonds) that when heated form a gel during bond formation. Under hot bonding conditions the water is driven from the gel; however, when immersed in water, protein gels can swell again, which weakens the cohesive strength of the adhesive. For plant proteins like soy, addition of chemical reactants to reinforce these gel-forming structures are usually necessary to make bonded wood products that remain strong with water exposure.

1. Introduction

Maintaining bond strength while water saturated is often the most difficult test for wood adhesives and is especially challenging for protein-based adhesives. Most cured wood adhesives are crosslinked polymers that provide wet strength through covalent bonds. The method of strength development for globular protein adhesives has been less clear. Food research has emphasized that proteins form gels in wet environments by surface linking of protein globules through hydrophobic interactions. (Damodaran, 1997). If protein adhesives form gels during bond formation, then understanding this gelation should also be important for adhesive applications

Proteins, such as casein, blood, and hydrolyzed collagen were some of the original wood product adhesives with soy added later (Adhikari et al., 2017; Bye, 1990; Lambuth, 2003). Proteins have been largely displaced by synthetic adhesives, which are more water-resistant, consistent in performance, have faster strength development, and are easier to use. Concerns have been raised with regards to formaldehyde emissions coming from wood products made with urea-formaldehyde (UF) adhesives (Frihart et al., 2012), the dominant adhesive in the wood products market. Additionally, customer demands and regulations

calling for biomaterials and a lower carbon footprint are driving a renewed quest for new adhesives to replace UF (European Commission, 2024). However, success requires that the new adhesive meets existing performance standards, be easy to make and simple to use, while being competitive with the extremely low cost petrochemical incumbent technologies (Dunky, 2020). Soy protein adhesives have been of interest as a replacement in wood panel construction (Adhikari et al., 2017), in addition to other synthetic, non-formaldehyde emitting formaldehyde-containing adhesives (e.g., phenol-formaldehyde) and no formaldehyde-added adhesives (e.g., isocyanates and polyurethanes). Formaldehyde regulations allowed soy-based adhesives to capture the majority of the North American interior plywood market in 2006 (Orr, 2017), but commercial implementation of protein adhesives in other markets has been slow (Dunky 2023c). While strength development in traditional adhesives is fairly well understood (Dunky, 2017), plant storage proteins such as those in adhesives are much larger molecules when applied, and the methods of strength development are less clear.

Although proteins are of considerable interest to wood adhesive researchers (Adhikari et al., 2017; Dunky, 2020; Ma et al., 2023; Sui et al., 2021a), the adhesive literature can be quite confusing due to a lack of their understanding about the physical properties of proteins. While the

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same soy products are used in the food industry and in adhesive research, generally the wood adhesive researchers have not grasped the extensive research carried out for food applications (Damodaran, 1997; Kinsella et al., 1985). The biggest misconception is assuming the unfolded structure of a globular protein is a stable configuration (Cui et al., 2023; Huang et al., 2023; Jiang et al., 2023; Liu et al., 2022; Sun, 2005a, b; Xu et al., 2022) instead of a transient state in the denaturation process (Boye and Harwalkar, 1997; Damodaran, 1988, 1997; Glyakina and Galzitskaya, 2020; Jakubowski and Flatt, 2022c; Pedersen et al., 2020).

Because of the many roles that proteins play in biological systems, an enormous amount of research has been devoted to characterizing their physical and chemical properties. This paper examines why proteins possess the properties that they do and how are they different from the competing synthetic adhesives for wood bonding. These are important issues since much of the soy adhesive literature is often at odds with the general understanding of protein structure, and this problem can inhibit the development of improved protein adhesives.

2. Protein structure

An individual protein chain is a linear polymer, made by condensation of amino acids to provide amide bonds with a set sequence of attached side groups on the amino acids. Steric interactions between adjacent amino acids greatly limit the individual orientations of the amide linkages, as first modelled by Ramachandran (Ramachandran et al., 1963) followed by more sophisticated modelling as the science has progressed (Jakubowski and Flatt, 2022a). The constraints are both steric interactions between neighboring side chain groups and double bond resonance within the amide groups. The Ramachandran plots show that only a small part of the rotational space around the amide linkages are stable structures due to the bulk of the side chains of the amino acids. These factors lead to the secondary structure, in which protein segments are often arranged in α -helices and β -sheets, with reverse turns and random coils in between (Alberts et al., 2015; Damodaran, 1997; Jakubowski and Flatt, 2022d). The α -helices are short continuous stretches of amino acids with hydrogen bonds between adjacent amino acids and should form as amino acids are added to the protein chains. The β -sheets are crystalline regions of hydrogen and hydrophobic bonded non-adjacent segments of the protein chain which can form as the protein is synthesized and, in some cases, depend upon chaperon proteins to facilitate folding. These helices and sheets are amphiphilic in having both polar and non-polar surfaces on opposite sides that allow these helices or sheets to associate with each other and other domains within the protein.

Extended proteins in water under moderate conditions typically undergo hydrophobic collapse as water drives the mostly hydrophobic protein into a globular shape to minimize surface area, i.e. water contact. The steric interactions from primary structure, as well as secondary structures, limit the conformations that the protein can assume when it undergoes hydrophobic collapse. This folding of secondary structures, with reverse turns and random coils between the more restricted segments of helices and sheets, produces the tertiary structure of the protein chain (Damodaran, 1997; Glyakina and Galzitskaya, 2020; Jakubowski and Flatt, 2022c, e; Nassar et al., 2021; Sorokina et al., 2022). The enthalpy energies inducing the protein folding need to be greater than the entropic energy lost through removal of freedom of movement. The α -helices and β -sheets are commonly amphiphilic with the hydrophilic sides facing the aqueous environment surrounding the protein and the hydrophobic sides facing the hydrophobic core of the protein. Although the crystal structure makes the protein look rigid, even native globular proteins with defined secondary structural features have some degree of conformational flexibility that is considered key for their biological functions. For instance, the hexameric structure of the soy 11S has hypervariable regions that behave as intrinsically disordered (Chen et al., 2020). In addition, the energy well of the compact protein is not that

much deeper than some partially unfolded versions that increase the entropy; thus, in solution the protein domains may oscillate between folded and partially unfolded structures. The greater the unfolding, the greater the energy needed to disrupt the internal disulfide, acid-base, hydrogen, polar, and hydrophobic bonds; the unfolding should also disrupt quaternary structures, specific aggregates of individual proteins that minimize water interaction with the hydrophobic domains.

A significant question exists in understanding the tertiary and higher order structure of proteins during alteration. The general concept is that proteins first unfold in sections to a higher energy transition state, and then refold to a lower energy denatured structure or go back to the prior folded state (Fig. 1) (Damodaran, 1997). Changes in the type of ions, ionic strength, temperature, pH, or presence of other molecules nearby can alter the protein structures. A detailed description of configurations one protein adopts as it moves down this energy well is provided in Noé et al. (Noé et al., 2009). It is also possible that during hydrophobic collapse of proteins, a large variety of states that are not the lowest energy become occupied because the large protein molecules, often with limited solvent, become kinetically trapped.

All native proteins have defined tertiary structures due to their unique primary structures and native environmental conditions. Thus, there is not a single pathway to denaturing, especially because of the variety of protein structures and the many different denaturation conditions. A protein needs to lose only some of its native structure to be denatured. Many globular proteins are not just a single chain globule swimming freely in the water but associate with other proteins to form quaternary structures (Jakubowski and Flatt, 2022e). This is certainly true for the main storage proteins in plant seeds or beans. For soybeans the main protein, glycinin, is made up of six individual proteins tied together by covalent disulfide bonds and acid-base bonds. Besides glycinin, the other dominant protein conglycinin, containing 3–4 subunits, also use hydrophobic associations and polar interactions to stabilize quaternary structure (Lawrence 1999; Sun, 2005b; Thanh and Shibasaki, 1976; Utsumi et al., 1997). These quaternary structures are shown in the literature for the glycinin and conglycinin crystal structure (Sui et al., 2021a).

Measuring denaturation is not always straightforward. A large

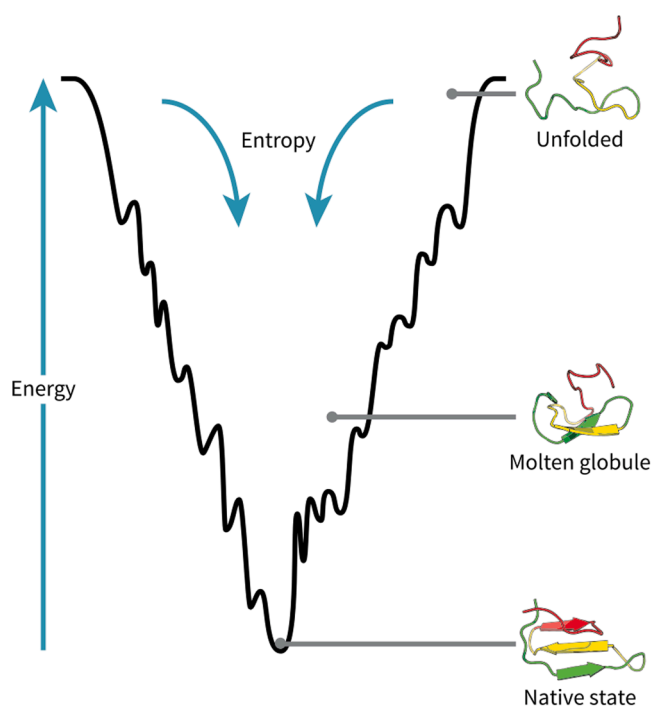


Fig. 1. The hypothetical energy well model for the folding of proteins (Splettstoesser, 2013).

endotherm transition observed during denaturation of soy glycinin and conglycinin makes it possible to estimate extent of denaturation by differential scanning calorimetry (DSC), yet cleavage of disulfide bonds in soy glycinin did not impact the measured enthalpy (Petrucelli and Anon, 1994). Circular dichroism and infrared analyses are also used to quantify alpha helix and beta sheet content, but these structures can be preserved in the unfolded state and reform upon hydrophobic collapse into either native or denatured forms (Boye and Harwalkar, 1997; Damodaran, 1997). The denatured state can be identified by the increase or decrease of helices or sheets. SDS-page reveals the molecular weight of proteins, and if performed without a reducing agent, can reveal disulfide linkages between subunits (Petrucelli and Anon, 1994; Sun, 2005b).

It is sometimes assumed that complete loss of secondary structure is required for denaturation, but this is not needed to change protein properties. In addition, denaturation can be a multiple step process as illustrated in Fig. 1 (Chen et al., 2023). To add to the complexity, proteins are usually studied in water, and the availability of water is important to denaturation (Sun, 2005b). What is less discussed is tightly bound water layers characterized as non-freezing water (Ali and Betzelheim, 1985; Sun, 2005b), whose changes during denaturation have been explored with only a few proteins using advanced instrumentation (Chen et al., 2006; Inoue et al., 2020). Water retention is important in food applications in that retained water is a product criteria (Egbert, 2004). While water retention is valuable for food products, it weakens the adhesive bond by plasticization. There is also little discussion in denaturation literature of the glycosyl groups covalently attached to many of the proteins. Consequentially, the denaturation process is likely more complicated than often discussed.

A main concern with the protein adhesive literature is that some researchers present denaturation as a complete and persistent unfolding, sometimes explicitly but more often implicitly (Huang et al., 2023; Li et al., 2022; Zhang et al., 2022). Complete unfolding requires a large amount of energy, as seen in Fig. 1. In contrast, the process of denaturation only requires that some of the protein segments in the proteins are in an unfolded, extended conformation at any given time, or that the protein is in a slightly expanded transition state. All these transition states quickly collapse to more energetically favorable compact states (Jakubowski and Flatt, 2022c). In contrast to the specificity of the native structure, any change to a new folded structure is called a denatured protein, independent of the chemicals or energy (thermal, mechanical, etc.) used to cause the denaturation (Chen et al., 2023; Damodaran, 1988; Glyakina and Galzitskaya, 2020; Jakubowski and Flatt, 2022c; Schaeffer and Daggett, 2011). What is misleading in the protein-based wood adhesive literature is when the unfolding process is assumed to proceed all the way to a completely unfolded model (spaghetti-like) and stay unfolded. The unfolding probably involves only portions of the protein at a time, and for very short duration, that then refold into a different three-dimensional structure.

This completely unfolded protein model does not fit with the bulk of protein literature, basic energetics, data on rheology of soy dispersions, nor data on cured adhesive properties. The energetics for sustained complete unfolding seem unreasonable since the proteins are mostly hydrophobic polymers of 20–71 kilodaltons (kDa) (Nishinari et al., 2014b). If these polymers were extended, this would lead to a very viscous solution even at very low solids. If complete unfolding occurred, then the resulting soy would have typical polymeric adhesive properties of strong bonds both wet and dry due to the interchain hydrogen, polar and non-polar bonds and chain entanglement. The literature on a wide variety of food proteins show that denatured globular proteins refold to minimize their size and energy state (Damodaran, 1997; De Young et al., 1993; Frihart, Submitted; Jakubowski and Flatt, 2022c; Nishinari et al., 2014a; Oakenfull et al., 1997; Petrucelli and Anon, 1995; Sun et al., 2008; Zayas, 1997). Denaturation has been studied in the medical literature since failure to fold into a native structure generally produces inactive enzymes, and in some instances, misfolded proteins (amyloids)

have toxic functionality. The refolding of the proteins can be unfortunate as in the case of prion diseases that alter brain proteins to yield amyloid structures high in β -sheet content (Jakubowski and Flatt, 2022b).

For a globular protein to stay highly unfolded or extended, it would need to overcome all the intrachain non-covalent bonds between segments of the proteins and replace strong hydrogen bonds between water molecules with water-protein interactions. The globular shape of proteins reduces the viscosity of the dispersion compared to the large viscous drag of a linear molecule. The literature on collagen adhesives shows that these linear helical proteins need to be significantly depolymerized to around 20 kDa before they can be dissolved in water with heating to yield viscous solutions that on cooling become a solid adhesive (Schellmann, 2007). Another biopolymer example is that most gums are highly viscous due to their linear shape and are used as associative thickeners at only a few percent of the mixture. In contrast, the globular gum arabic has a low viscosity even at 35 % solids (Frihart and Beecher, 2022). If the soy protein were to stay completely unfolded, then because of the high molecular weight and the strong interchain interactions, the product would not flow at the solids contents commonly used nor need added crosslinkers for good strength (Alberts et al., 2015).

3. Protein adhesive dispersions

Most wood adhesives contain low molecular weight, water-soluble oligomers that complete their polymerization after application to the wood (Frihart, 2009). This includes the water-borne amino and phenolic resins pre-reacted with formaldehyde, that cure by reaction through the resulting methylol groups (Dunky, 2017). Thus, these materials have been referred to as *in-situ polymerizable* adhesives, and when applied to wood are liquid-like with the loss moduli greater than the storage moduli. Alternatively, the *pre-polymerized adhesives* can also be water-borne but are not entirely water soluble; thus, these waterborne adhesives are produced as dispersions, usually using surfactants to surround the hydrophobic adhesive particle with emulsifiers. Common examples of water-borne adhesive dispersions are poly (vinyl acetate) and emulsion polymer isocyanate. Because of the polar nature of the protein globular surface, surfactant or dispersing aids are not needed.

An important property of adhesives is that they need to spread and wet a wood surface; thus, the fluidity is important for forming molecular level interaction with the wood surface. Dynamic rheology shows the separation of the viscosity (resistance to flow) into the elastic (storage modulus) and flow component (loss modulus) (Mezger, 2014a, b). A common method of obtaining dispersion rheology is to use a cup and bob. Often laboratory tests use a Brookfield viscometer to measure the apparent viscosity, but for non-Newtonian materials a dynamic rheometer that determines both the storage and loss moduli at a variety of shear conditions provides a more complete rheological picture. As an example, Fig. 2 shows the curves for three common household adhesive dispersions and an ovalbumin dispersion (Frihart and Gargulak, 2022). Ovalbumin (an albumin, a family of proteins which are water soluble) is a phosphoglycoprotein that is mainly a monomeric polymer, meaning that the proteins do not tend to agglomerate. The adhesives in Fig. 2 show much higher loss moduli (flow deformation resistance) than storage moduli (elastic deformation resistance), making them liquids (Mezger, 2014a), but they are not Newtonian because the moduli are shear rate dependent. The ovalbumin and the three PVA-based adhesives in Fig. 2 all consist of very stable colloids: globular or spherical polymers with hydrophilic surfaces, dispersed in water.

To better understand protein adhesive dispersions, ovalbumin from egg whites was selected as a model protein adhesive since it is easy to obtain in significant volume with high purity, and has been well studied (Doi and Kitababake, 1997; Huntington and Stein, 2001; Mine, 2007). Ovalbumin dispersions behave similarly to common synthetic adhesive dispersions in dynamic rheology. It is a liquid, having a greater loss modulus than storage modulus even at 40 % solids (Fig. 2). However, it

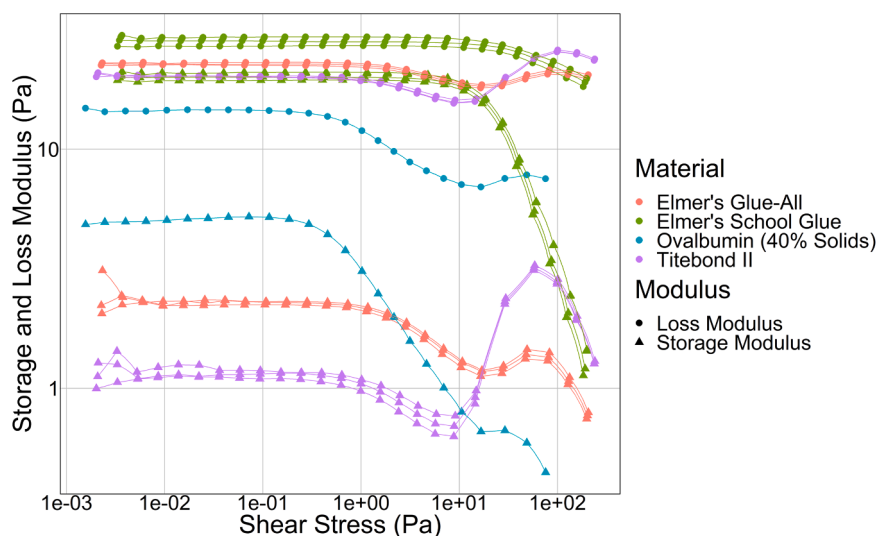


Fig. 2. Shear rheology with increasing shear amplitude of commercial synthetic poly (vinyl acetate) adhesive dispersions: Elmer's Glue-All and School Glue, and Franklin's Titebond II (solids content 41, 20, and 46 % respectively) in comparison with the ovalbumin protein at 40 % solids. Cup and bob geometry, oscillatory strain sweep 0.01–1000 %, 1 Hz. Single scan of ovalbumin, others in triplicate to show variability. Figure adapted from (Frihart and Gargulak, 2022).

is different from synthetic dispersions in that there is more particle-particle interaction as seen by a smaller ratio of loss modulus to storage modulus at low shear. Inter-particle interactions are also evidenced by the shear thinning behavior observed at 0.3 Pa shear stress at the 40 % solids level (Fig. 2), but no shear thinning at 15 % solids (Frihart and Gargulak, 2022). This data supports the conclusion that the ovalbumin particles are mainly monomeric proteins with moderate drag (Doi and Kitababake, 1997; Frihart and Gargulak, 2022; Huntington and Stein, 2001; Tung, 1978) and generally weak interactions between dispersed particles. While ovalbumin dispersions can be a useful model for protein dispersions with weak protein-protein interactions, it is not a good model for globulin plant proteins, which have strong protein-protein interactions and form aggregates in their native state (Amagliani and Schmitt, 2017; Petruccioli and Anon, 1995; Sun et al., 2008; Wang et al., 2017). These strong protein interactions and aggregation tendencies in soy and many other plant proteins are a result of some hydrophobic domains remaining on the folded protein's surface, as indicated in Fig. 3. In an aqueous environment, the remaining hydrophobic domains on the surface lead to interparticle attractions to reduce the interaction with water.

In Fig. 4, the rheological data for the soy flour of 90 PDI (protein dispersibility index) (AOCS, 2017) and the native protein isolate (PPSPI)

are shown. The high storage moduli relative to loss moduli for the soy products are rheologically very different from the ovalbumin despite all being at only 15 % solids (Frihart and Gargulak, 2022). Solid-like behavior for soy (high storage modulus relative to loss modulus) at low shear followed by shear thinning is characteristic of loosely aggregating particles (Mezger, 2014a, b; Parr, 2024). At low shear, they aggregate and form a low-density network. As shear increases, the weak associations between particles are broken, resulting in progressively smaller aggregates and lower viscosity. With soy protein, hydrophobic surfaces attract each other, and at the concentrations relevant to adhesives, can form a semi-continuous network when at rest (Frihart and Gargulak, 2022). As shear increases, the large aggregates of proteins get broken into smaller and smaller aggregates. Thus, the aggregation behavior of soy proteins plays an important role in impeding their flow. More detailed discussions are available (Frihart, accepted; Frihart and Gargulak, 2022). The PPSPI (native soy isolated in our pilot plant (Hunt et al., 2023)) has stronger resistance to flow than does the soy flour, which shows that the purer protein develops greater protein-protein association than when it is diluted by the carbohydrates in the flour.

At 15 % solids, the soy has strong shear thinning while the ovalbumin shows none (Fig. 4). In Fig. 2, the higher moduli and shear thinning of ovalbumin was seen at 40 % solids. This agrees with the model of the ovalbumin being more monomeric, probably due to fewer and smaller hydrophobic patches on the particle surface in its native state compared to the soy proteins.

4. Wood bonding

Wood is an unusual substrate for adhesive bonding in that almost all wood adhesives are waterborne. This water solvent is not a problem for wood adhesives because the water can be transported away from the bondline by the high water-absorption capacity of wood. Low molecular weight components of adhesives can also be absorbed into the wood (Hunt et al., 2015). Proteins are too big to infiltrate the cell walls but components like low molecular-weight sugars in the flour and additives such as urea and glycerol can readily migrate into the wood (Hunt et al., 2015), which is not mentioned by some researchers who use urea as a denaturant of soy protein (Sun, 2005a). Proteins have a wide variety of functional groups on their surface. The fact that many proteins are surfactants, because they have both polar and non-polar surfaces, giving them the ability to form bonds to the various polar and nonpolar components of wood. Our results support this concept because the failure of

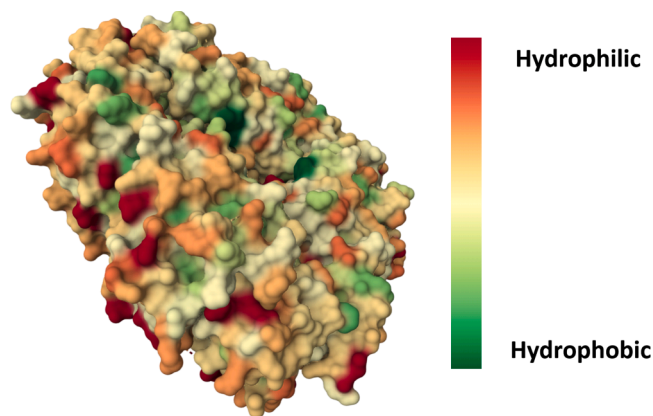


Fig. 3. Soybean protein surface showing polar (red) and non-polar (green) domains. Protein databank model 1FXZ of proglycinin homotrimer (Adachi et al., 2001).

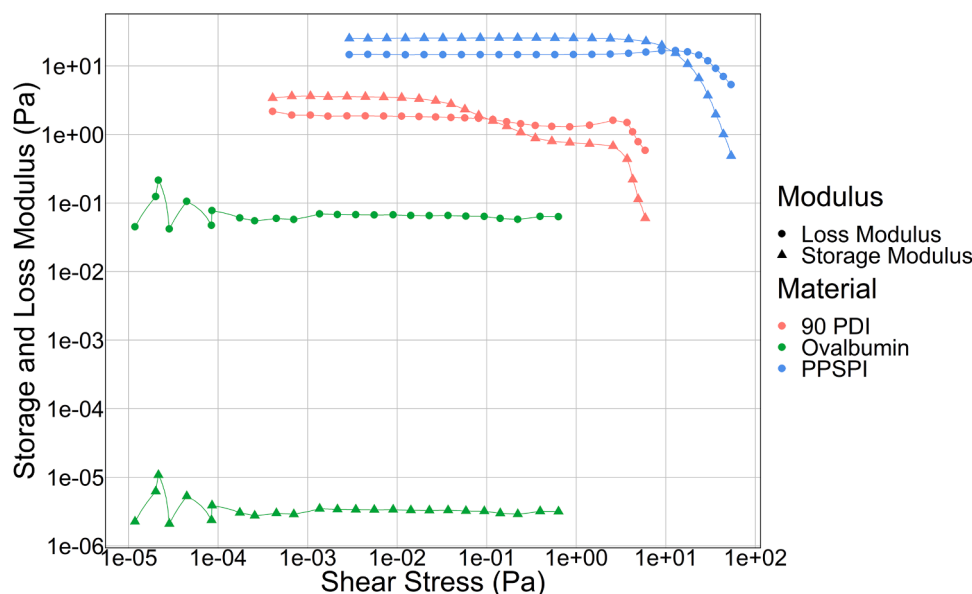


Fig. 4. Shear rheology with increasing amplitude of pilot plant native SPI (PPSPi), 90 PDI soy flour, and ovalbumin, all with 15 % protein content. Cup and bob geometry, oscillatory strain sweep 0.01–1000 %, 1 Hz. Reprinted from (Frihart and Gargulak, 2022).

the water-soaked bond lines made using soy flour without any cross-linking agent is cohesive in the adhesive and not at the soy-wood interface. Thus, the important goal is to build cohesive strength in the adhesive that does not weaken when the bonds are tested wet.

Another important property of wood is that adhesive bonds are subjected to great internal strain due to wood swelling and shrinking as the moisture level changes (Frihart, 2009; River et al., 1991); thus most bonded wood product performance standards include some sort of water exposure test. Although wood loses some strength as the moisture level increases, the failure mode can change from wood to bondline due to the internal strain on the bondline (Frihart, 2009), leading to lower wet bond strength.

Shear tests are a common type of bond evaluation method and both dry and wet strength are often used for product acceptance, but the wet tests are more critical because the wood swells under wet conditions. The use of an Automated Bond Evaluation System (ABES) tester and the related ASTM small scale test method 7998 (ASTM International, 2020; Frihart and Lorenz, 2020) are a rapid way of doing a shear test and have the advantage of good thermal transfer to the bondline by using very smooth thin veneers for testing, both of which leads to good reproducibility (ASTM International, 2020; Frihart et al., 2009; Frihart and Lorenz, 2020). At the FPL, cooperators and staff have used this method for over 15 years to collect a large set of data for comparisons using the hard maple wood specimens, and it has been favorably compared to other test methods (Frihart et al., 2009).

5. Protein bond strength

With the drive to use more biobased adhesives and the concern about formaldehyde release from urea-formaldehyde bonded wood products under heat and humidity, the use of proteins has been studied as a wood adhesive (Adhikari et al., 2017; Dunky, 2020, 2023b; Frihart, 2023; Qi et al., 2017; Shi et al., 2017). Ovalbumin is not only a low viscosity protein adhesive compared to any of the soy products, it also provides high bond strength as shown in Table 1 (Frihart et al., 2014). While it is not available in sufficient volume and low enough cost for commercial wood bonding applications, it shows that the right protein structure can provide good wet strength. For reference, ABES bond strength greater than 3 MPa has been correlated with minimally acceptable interior-grade plywood bonding performance (Frihart et al., 2009; Lorenz and Frihart, 2023). The strength of ovalbumin was attributed to the

Table 1

Properties of soy and ovalbumin adhesives. Viscosity from a Brookfield RTV rotational viscometer. Lap shear strength and standard deviation from ABES (Lorenz and Frihart, 2023); CSPI is a commercial soy protein isolate (ADM ProFam 974) and PPSPi is the native soy protein isolate prepared in the FPL pilot plant. Soy flour is 90PDI (Cargill Prolia 200–90) and ovalbumin is grade II (62–88 % purity, Sigma Aldrich). The viscosity was measured at 10 rpm, at 22.5 ± 2.5 °C, and after 30 sec. mixing, with the spindle size adjusted for the viscosity range after a consistent initial stirring and rest period. Data from (Lorenz and Frihart, 2023).

Adhesive	Viscosity, Pa.s	Bond Strength, MPa	
		Dry	Wet
Soy flour, 30 % solids	6.4	5.8 ± 0.1	0.3 ± 0.1
CSPI, 15 % solids	108	9.4 ± 0.5	2.8 ± 0.3
PPSPi, 15 % solids	5.7	5.2 ± 0.8	1.2 ± 0.2
Ovalbumin, 30 % solids	0.25	7.1 ± 0.4	3.4 ± 0.1
Ovalbumin, 40 % solids	7.2	7.8 ± 0.9	4.6 ± 0.2

transformation of α -helices to β -sheets that exposes a highly hydrophobic surface as measured by ANS (Hu and Du, 2000). The more hydrophobic surface not only causes good gelation of ovalbumin but also makes the adhesive more water resistant. Hydrophobic interactions between neighboring proteins have been previously identified as a source of wet strength in protein adhesives (Wang et al., 2005; Yue et al., 2019).

In contrast to the ovalbumin, soy adhesives have the disadvantage of high viscosities and poor wet strengths. As indicated in a prior section, soy adhesives are more viscous than ovalbumin or synthetic adhesives at low shear. The higher viscosity indicates that soy particles interact more strongly than ovalbumin particles under this condition. The shear thinning indicates that these structures break down, making them fluid enough in the high shear conditions to be used in commercial wood bonding. The high viscosity forces producers to add more water and less adhesive solids to the bondline compared to competing synthetic adhesives. Another problem is that the wet bond strengths are typically low for the soy flour (Table 1 and (Frihart and Satori, 2013)). The SPIs give better wet strengths but require even more water in the bondline due to even higher viscosities. SPIs are also expensive due to the number of processing steps and the loss of material mass in removing the

carbohydrates. Because of these issues it is surprising that the commercial SPIs are used as starting material for many studies on soy adhesive. They cannot be used as model compounds for most studies of soy flour adhesives since the commercial SPIs are highly altered (Hunt et al., 2023; Lorenz et al., 2015).

Although commercial soy-bonded plywood generally has sufficient dry strength, the adhesives often fail cohesively when tested after water soaking. The lower wet strength is likely due to plasticization of the polar bonds between globules, weakening the swollen gel structure (Oakenfull et al., 1997). One advantage of the commercial soy protein isolates (CSPI) is that they are jet cooked and the processing makes larger pre-gel structures in an aqueous environment leading to stronger gels during the adhesive curing. These processing conditions alter the gel strength and the water retention of the SPI (Egbert, 2004; Oakenfull et al., 1997), both of which can be related to the improved wet bond strength of the cured soy adhesives. Outside of the wood adhesive literature, most denaturation of proteins is treated as an agglomeration of protein globules into gel structures rather than a complete opening into an extended linear chain (Nishinari et al., 2014a; Oakenfull et al., 1997), as shown in Fig. 5. Extending protein into linear chains would lead to a typical polymeric adhesive with extensive physical cross-linking between the chains and chain entanglement that would be hard to swell and break even under wet conditions, while an agglomeration of protein globules would be likely to swell and break some of the globular surface interactions. This globular aggregate model makes it easier to understand bond development. Denaturing, pre-aggregating, or pre-gelling the protein before applying it to the wood could generate more of these water-resistant interactions in the final adhesive. In addition, covalent cross-linking agents can improve wet bond strengths (Adhikari et al., 2017; Dunky, 2020) by providing crosslinks both within individual aggregates and between adjacent aggregates. This model is also consistent with the data showing that higher bonding temperatures and times (up to an optimum) generally improve wet bond strength as the proteins have time and mobility to develop stronger gel linkages (Barzegar et al., 2020; Frihart et al., 2016). The hydrogels described by Oakenfull et al. and redrawn in Fig. 5 were made by static cooking soy protein, similar in what occurs during bonding, and also similar to the autoclaving of soy protein which has been shown to increase bond strength of the resulting proto-gel (Hunt et al., 2022). In Hunt's work, even higher bond strength was attained by jet cooking (high shear while at high temperature, followed by flash cooling and desolventization). We suspect the protein molecules in the gel network made during jet cooking were on average, more extended, with more inter-protein interactions, than gels made by static cooking and autoclave treatments depicted in Fig. 5.

Though many crosslinking resins for soy have been explored (Adhikari et al., 2017; Averina et al., 2021; Averina et al., 2022; Dunky, 2020, 2023a, b; Mi et al., 2022), most biobased North American interior

plywood is produced with adhesives made of inexpensive soy flour reacted with polyamidoamine-epichlorohydrin (PAE) resin. Because adhesive application rates are a low fraction of the plywood weight, the low solids content of soy adhesives can be tolerated. Producers must still take care to ensure sufficient bond strength is present when the press opens to resist the pressure from steam inside the panel which can delaminate the bond. The cost of the PAE is a deterrent to a wider soy use, so finding a way to generate more strength from the soy, as well as diminishing its swelling tendencies, could reduce costs and increase competitiveness. A better understanding of soy protein structures is necessary to advance this goal.

Particleboard is another target market for soy adhesives, but it's adaptation there is limited by higher resin loads, and therefore, a need to limit water by using low moisture soy adhesives. The dry soy adhesives that are blended with wood particles do not provide sufficient wet strength nor tack for holding the particleboard mat together prior to hot pressing. Thus, soy particleboard adhesives are not currently a simple drop-in replacement for synthetic adhesives in either their chemical or physical properties, which has limited their commercialization in particleboard production. Solving the performance issues are important since particleboard is the single largest wood adhesive market, and typically requires only modest wet strength compared to structural products.

6. Other plant proteins

Although soy and ovalbumin have been the focus of discussion so far, most oil seed proteins are like soy in that they are globular proteins that disperse well in water because their combination of hydrophobic and hydrophilic surface patches, as illustrated in Fig. 3, provide surfactant properties. One notable exception is the alcohol-soluble zein protein in corn. Much of the literature on protein adhesives with added cross-linkers has been covered in detail (Adhikari et al., 2017; Cheng and He, 2017; Dunky, 2020). Another large volume plant protein is canola that is favored over the soybean in colder climates, such as in Canada and Europe. Research on canola as a wood adhesive has been carried out by a number of groups (Barzegar et al., 2020, 2022; Dunky, 2020; Frihart and Lorenz, 2019; Kord et al., 2016; Li et al., 2020, 2012, 2017; Tene Tayo et al., 2022). Despite the claims in literature that the low yield canola protein isolate gives good wood bonds (Li et al., 2012, 2012c; Li et al., 2012, 2012cc), in FPL testing canola flour performance was similar to soy flour in being water sensitive, but depending on conditions canola flour can be slightly worse or better than soy flour (Barzegar et al., 2020, 2022).

There has been considerable work done on cottonseed flour and isolate (Cheng et al., 2017a; Cheng et al., 2017b; Cheng et al., 2016; Cheng et al., 2019a; Cheng et al., 2019b; He et al., 2014; He et al., 2019; He and Cheng, 2017, 2018; Li et al., 2019; Li et al., 2021). Unreported

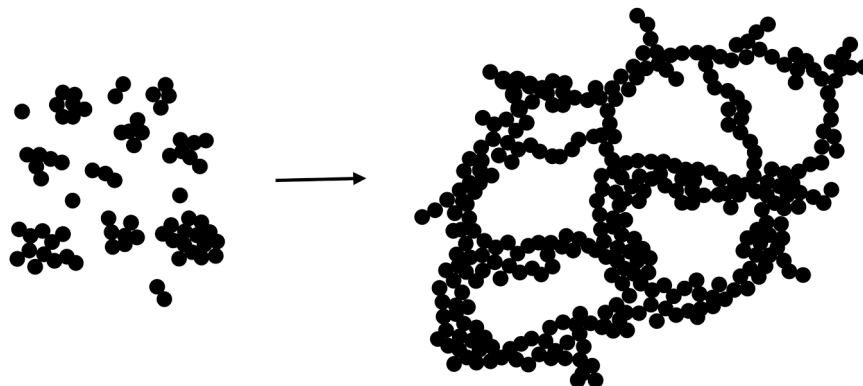


Fig. 5. A hypothesis of soy protein curing. Individual protein subunits (black balls) cluster, and clusters of proteins form a gel during curing. Redrawn from (Oakenfull et al., 1997).

FPL studies showed that cottonseed flour adhesives were not better than the stronger soy isolate products. The literature also reports that lupine flour had a low dispersion viscosity with little loss in wet adhesive strength compared to soy flour (Huang and Li, 2016), but again unreported FPL tests have not supported this claim. So far, the FPL has examined several other plant proteins (four oilseed presscakes; pennycress, lesquerella, cuphea, and camillina, and three tree seed meals; osage orange, black locust, and black mulberry (20 % solids) bonded at 120 °C for 2 min supplied by various other researchers. Since the results were not better than soy flour, which is much more available, has processing infrastructure, and is low in cost, we have not reported the results in the journal literature. It is our understanding, however, that commercial systems based on several protein sources in addition to soy are currently available.

7. Common changes with denaturation

Many researchers have reported that protein denaturation improves wet bond strength, as covered in extensive reviews (Dunky, 2020; Shi et al., 2017). The improved performance is often attributed to protein unfolding and/or exposure of reactive groups. Here we have addressed problems with the protein unfolding rationale, while the rationale of exposing reactive groups is addressed elsewhere (Kallakas et al., 2024). As previously discussed, gel structures often result from hydrophobic surface interactions, and correlations have been reported between adhesive wet strength and protein surface hydrophobicity (Kallakas et al., 2024; Li et al., 2020; Yue et al., 2019). A decrease in protein solubility or dispersibility at neutral pH with heat denaturation is often reported for oilseed proteins such as soy (Palić et al., 2011), rapeseed (Salazar-Villanea et al., 2016), wheat gluten (Mann et al., 2014) and wheat flour (Hong et al., 2023). However, surface hydrophobicity is far from a complete explanation. For example, the very hydrophobic zein protein from corn has poor bonding and film formation when dispersed in water (Zhang and Mittal, 2010). Unfortunately, denaturation induced increases in surface hydrophobicity and aggregation tend to increase viscosity, typically a detriment to commercial systems. Because protein hydrolysis can drastically change protein properties and usually changes protein structures, it is often referred to as a method of denaturation. Though technically not denaturation, protein hydrolysis is common, in part because it can dramatically lower viscosity and therefore allows higher solids content. Limited hydrolysis is used commercially (Spraul and Allen, 2010), but we have observed that beyond a certain point, strength rapidly degrades. For example, a commercial soy protein isolate (SPI) degraded to 20KDa and smaller had no wet strength at all and dry strength approximately half of other SPIs tested, regardless of other denaturation conditions applied or surface hydrophobicity (Kallakas et al., 2024).

8. Discussion

Wood adhesives are a very large market estimated at 17 million tons/yr., dominated by synthetic adhesives (Dunky, 2020; Hunt and Dunky, 2023). Panel products for interior applications seem like a natural fit for protein adhesives because of their ability to make aqueous dispersions, and most wood bonding applications have generally involved aqueous adhesives, but their water sensitivity limits their durability. Unfortunately, many bio-based wood adhesive researchers use an incorrect model for the structure of protein adhesives that is inconsistent with the general protein literature. These researchers have not made use of the very extensive and detailed research done for food applications of plant proteins (Damodaran and Paraf, 1997) as have most reviews of soy proteins (He, 2017; Sun, 2005a). While it is true that the proteins do some unfolding in the denaturation processes, it is unlikely that a highly unfolded protein would be stable in the aqueous dispersion (Frihart, accepted). Since proteins are hydrophobic, keeping the protein in an extended conformation would mean forgoing stabilizing internal bonds,

including the hydrophobic domains, and disulfide, acid-base, and internal hydrogen bonds. Additionally, the water molecules would have to forgo the strong hydrogen bonds between water molecules to accommodate the protein worming its way into water phase (Liu et al., 2009; Nishinari et al., 2014a; Oakenfull et al., 1997; Peters et al., 2017). This clearly would require a large amount of energy (enthalpy). Although entropy favors unfolding, if it was greater than the enthalpy, the protein would not exist as folded molecules. However, the relative ease with which some unfolding occurs, indicates that the energy difference between folding and unfolding is small. In addition, current research at the FPL shows that much of the mass of dilute soy dispersions particles in deionized water are larger than the quaternary crystal structure of the 11S and 7S proteins.

Some argue that adhesives are exposed to high temperatures during the critical moment of bond formation and therefore the extended state model is relevant. However, a careful consideration of the bonding conditions makes extension even during this period questionable. First, the core temperature during wood bonding barely exceeds 100 °C, even though the press is always hotter, because of the cooling effect of water evaporation and the insulating effect of wood. Press times are short because competing formaldehyde adhesives complete cure in much less than 2 min at this temperature. The denaturation temperature of soy glycinin is 93 °C when ample water is present, but increases to 100 °C at ~68 % water content and rises to 110 °C at ~40 % water content (Sun, 2005b). Our unpublished work indicates that by the time the glue is heated, the solids content of the adhesive is at least 50 % and rising quickly, questioning whether denaturation even occurs during the heat-driven adhesive cure. Even if protein is denatured during cure, the high solids content and extremely high viscosity makes it unlikely that the protein polymer would extend substantially.

Determining how to obtain greater wet strength with plant proteins is complicated since the available conformations of globular proteins are limited by their sequence. Thus, making the protein surface more hydrophobic for stronger water-resistant bonds with a cost-effective crosslinker has been a challenge. With ovalbumin as a model, it would be preferable to have a protein that has low interaction with other proteins in the adhesive dispersion, but on heating, transforms into one with high hydrophobic bonding to other proteins (Hu and Du, 2000). The other problem with vegetable proteins is that they form hydrophilic gels. Thus, even if the resulting gel network is a three-dimensional structure, it doesn't stop the swelling with water and subsequent reduction of the bond strength.

Although the food science literature has clarified native soy protein structures, it is not very helpful in suggesting ways to covalently crosslink proteins, because food regulators typically do not allow the use of reactive chemicals. The one route to linking proteins together has been the use of transglutaminase. While FPL has not had success with this approach, others have reported positive results (van Herwijnen et al., 2016; Li et al., 2023a; Li et al., 2023b; Liu et al., 2021).

It is important to point out that while the protein-protein interactions can contribute to bond strength, it is theoretically possible to develop fully functional adhesives relying completely on the crosslinking system for strength. Despite the often-repeated claim that denaturation is necessary to expose reactive groups in adhesives (Huang and Sun, 2000; Adhikari, 2017; Dunky, 2020), there are commercial soy adhesive systems that use 90pdi (i.e. not denatured) soy flour. In these systems, we believe that the abundance of crosslinking agent compensates for the lack of protein-protein interactions. Many reports in the literature report improvements in wet strength with the addition of crosslinking mechanisms (Zhang et al., 2018; Frihart and Lorenz, 2019; Chang et al., 2020; Dunky, 2020; Gu et al., 2020; Li, 2021; Wu et al., 2021; Jiang et al., 2023; Pradyawong et al., 2022; Zheng et al., 2025). We believe that systems using cost-effective proteinaceous flours often rely heavily on crosslinking and little on protein-protein interactions for their wet strength. A better understanding of protein behavior will allow us to visualize our existing systems more accurately and hopefully harness

protein-protein interactions more effectively.

9. Conclusions

Although some proteins serve as adhesives in nature, others not used as adhesives in nature can still serve as a bio-based source of wood adhesives. Like any material it is important to understand its basic physical and chemical properties. Nonstructural proteins are for the most part single protein chains coiled into globules (protein subunits), which aggregate into globular quaternary structures designed to store amino acids in very crowded cellular environments. Minimizing contact between the water solvent and largely hydrophobic polymers lead to their globular structures. Their globular surfaces consist mainly, but not exclusively, of the hydrophilic amino acid components (primary structure). To minimize side chain steric interactions, the protein backbone often adopts helical and sheet structures (secondary structure). These elements minimize, but do not fully eliminate hydrophobic interactions with water which lead to the collapse into three-dimensional tertiary structures, and further quaternary associations of these individual protein globules. Under normal cellular conditions, the native state is the lowest energy state, but during processing and bond formation, other, denatured collapsed states may be low energy or may occur because of kinetic trapping. For soy 7S and 11S proteins the native states are slightly less than 10 nm in diameter (Adachi et al., 2001, Maruyama et al., 2001). Denaturation often leads to even larger aggregates and insolubility, though the difference in width between an individual ~10 nm protein and a common bond thickness (micron scale) is 5 orders of magnitude, suggesting a need for bonding between aggregates during the curing process.

Various conditions can cause unfolding and refolding of proteins to provide other low energy structures that may not be as compact as the native state. The hydrophobic groups on the globular protein surface cause the proteins to form larger structures through aggregation. However, these aggregations are generally not large enough to form highly water-resistant bonds between wood surfaces, with an exception being denatured ovalbumin from egg whites. Thus, plant proteins like those in soy and canola require additional chemical covalent reactants to form good wood bonds that resist disruption by water. Although there is abundant literature on crosslinking of proteins, discussions in the adhesive literature on the curing mechanism often invoke complete unfolding of the protein (Cui et al., 2023; Huang et al., 2023; Jiang et al., 2023; Liu et al., 2021; Sun, 2005a; Xu et al., 2022), which does not make sense considering the energetics of protein structure. This mischaracterization of protein conformation has resulted in the wood adhesive literature being contradictory to the general understanding of protein properties that exist in the food and general plant protein literature. Using of the wrong model of proteins does not negate the findings of improved adhesive performance achieved using various crosslinkers. However a better understanding of these protein structures could lead to faster progress in product development and better use of the protein's natural properties, allowing us to rely less on chemical crosslinking.

Authorship contribution

CRF: Conceptualization, original draft, review & editing. CGH: Visualization, resources, review & editing.

CRediT authorship contribution statement

Christopher G. Hunt: Writing – review & editing, Funding acquisition. **Frihart Charles R.:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

No generative AI or AI-assisted technologies were used in writing this manuscript.

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Data availability

Data will be made available on request.

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