Cohesion and Adhesion with Proteins

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Introduction

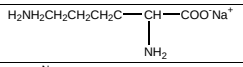
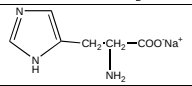
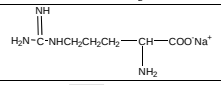
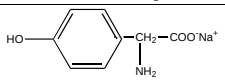
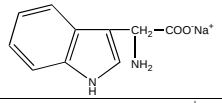
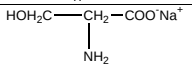
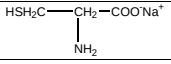
With increasing interest in bio-based adhesives, research on proteins has expanded because historically they have been used by both nature and humans as adhesives. A wide variety of proteins have been used as wood adhesives. Ancient Egyptians most likely used collagens to bond veneer to wood furniture, then came casein (milk), blood, fish scales, and soy adhesives, with soybeans and caseins being important for the development of the plywood and glulam industries. Despite many years of research on developing adhesive products, it is not clear how the proteins provide good adhesive strength, but some thoughts are expressed here.

Protein Structure

Understanding protein macromolecular structure is a prerequisite for understanding properties because protein structure is so different from that of other adhesives. Except for structural proteins, such as silk, collagen, and keratin, proteins mainly form globular shapes due to the hydrophobicity of their protein sequences. As amino acids are linked together to form a polyamide (primary structure), certain sequences can lead to formation of either α-helices or β-sheets (secondary structure) (1). This intrachain formation of secondary structure is very different from most polymers that have interchain crystallites or crosslinks to provide strength. Given the hydrophobicity of the protein, as it is synthesized it undergoes hydrophobic collapse. During this collapse, it is energetically favorable for polar groups to be on the surface and hydrophobic groups in the interior. However, this is not totally possible due to sequence restrictions. The polar groups on the inside try to minimize their energies by associating with other polar groups through formation of hydrogen bonds and acid-base interactions. The hydrophobic groups on the surface minimize their energy by associating with nonpolar groups on other protein globules. Thus, the protein globules associate, providing the quaternary structure. Although this association is mainly driven by hydrophobic interactions, specific polar interactions can also hold the protein globules together.

Thus, although proteins may have many functional groups that could react with other chemicals (as illustrated by the soy flour composition given in Table 1), these groups are not readily available for reaction because they are buried inside the individually coiled protein chains and these chains are often part of larger protein aggregates. These aggregates can be broken up and may be somewhat uncoiled at pH extremes, especially at high pH conditions, when electrostatic repulsion overcomes hydrophobic attraction. Additions of chaotropic agents, some surfactants, and certain salts are also used to disaggregate and maybe somewhat uncoil the protein structure.

Table 1. Important reactive components in soy proteins as percent of total protein weight.

Amino Acid	Structure	% Soy Protein
Lysine		6.4
Histidine		2.6
Arginine		7.3
Tyrosine		3.8
Tryptophan		1.4
Serine		5.5
Cysteine		1.4
TOTAL		28.4

The best way to visualize proteins is as soft balls whose main interaction is via hydrophobic patches on their surfaces. Certainly in some cases hydrogen bonds, acid-base interactions, and disulfide bridges play an additional role in stabilizing these agglomerates. Moreover, carbohydrates can be involved because some are covalently bound (glycosylated) or complexed with the proteins. Increased aggregation should occur in the heat-dried films of an adhesive bond compared to the aqueous dispersions of the adhesives. Much of the literature for agricultural proteins is related to food applications, with emphasis on aqueous gelation and surfactant properties. Gels are formed by heating aqueous dispersions to disrupt the protein, and then cooling. The ability to form gels in water means that much of the protein interactions are due to protein-protein association by hydrophobic rather than hydrophilic interactions on the proteins' surfaces, or a reconfiguration of the protein to put polar groups on the outside and hydrophobic groups on the inside. The ability to break up these gels

with urea and salts supports the view that the gels are not mainly supported by covalent interactions. In fact, it has been recently shown that products, like cooked egg whites, can be reconverted back into their original form by urea denaturation and shearing steps (2). Because each protein chain is a separate globule, an understanding of colloid properties is as important as understanding organic and polymer chemistry.

Protein Adhesives

A major problem in studying proteins is that their amino acid sequences and properties are so diverse that it is hard to relate the performance of one protein to another. There are few similarities between the proteins that have been used commercially for wood bonding, such as casein, blood, and soy flour. For example, soy proteins have a typical quantity of secondary structure, but the two main proteins have very different compositions and quaternary structures. Casein, the other common protein for wood adhesives, has very little secondary structure but is phosphorylated and has very different subunits compared to soy. Blood proteins have three different types in the native state: serum that is elongated and water soluble with a high negative charge at pH 7.4, globulin that is globular and not soluble, and fibrogen that is a soluble, complex glycoprotein. Each of these varies depending upon blood source and processing conditions. Although finding a specific factor that defines the performance of protein adhesives is not possible, we have learned a considerable amount about what factors are important and which ones are not for soy proteins.

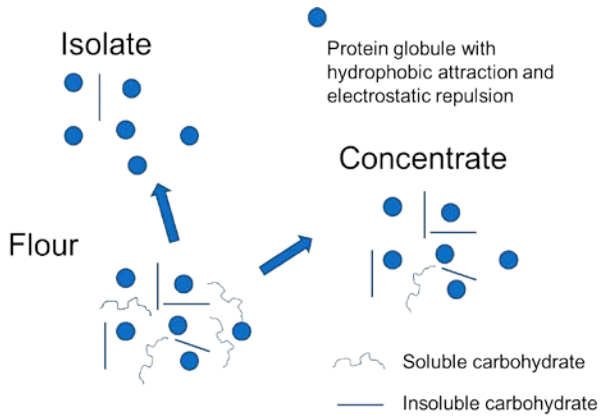


Figure 1. Schematic of soy flour with proteins, soluble and insoluble carbohydrates.

The main question is why do commercial soy protein isolates (CSPI) provide about 10 times greater wet bond strength than soy flour adhesives. We and others felt that it was due to the carbohydrates (both soluble and insoluble) that constitute about half the weight in flour but only a few percent in the isolates (Figure 1). However adding carbohydrates to CSPI caused less than a 50% drop in wet strength (3). The limited effect of carbohydrates was also demonstrated by using purification conditions that provided the native isolate (NSPI), which has greater wet strength than the flour but provides only 1/3 of the strength of CSPI. This leads to questions as to why CSPI is more viscous and has higher strength than the NSPI, and why NSPI and flour have the same DSC transitions but CSPI transitions are missing. The answer is that CSPIs are jet cooked (rapid heating of an aqueous soy dispersion of soy using steam in a tube reactor followed by rapid cooling) to improve their performance in food applications (4). Thus, the transformed proteins are much better adhesives than the native proteins. We also found that jet cooked soy concentrates (soluble carbohydrate and proteins removed) have much better wet strength than uncooked concentrates (unpublished).

We have also found that all the soy adhesives gave better wet strength when bonded at 150 °C than at 120 °C, and even better when bonded at 180 °C. This is not true of many wood adhesives but was true for all the soy flours, concentrates, and isolates tested. A higher strength with the flour could be due to Maillard reactions between the carbohydrates and the proteins, but to get a similar effect with isolates that have less than 5% carbohydrates would be very unusual. This does not rule out some covalent bond formation. However, in another test the higher bonding temperature gave a higher modulus at ambient conditions when the NSPI was adsorbed onto glass cloth using DMA analysis, but a lower modulus when tested at high humidity (unpublished). This result is not consistent with a product that is developing more crosslinks at the higher temperature. The best model for the available data is that jet cooking causes more coalescence of the proteins, probably though hydrophobic interactions and some polar bonds.

Conclusions

Remembering that proteins are normally colloids in water, the improved wet strength of soy protein bonds after jet cooking or bonding at high temperatures is most likely because of increased coalescence of the proteins. Although a number of aspects of soy proteins have been well studied (5), there are still areas that are not fully understood. The higher viscosity and only partial dispersity of the jet cooked soy is probably due to increased hydrophobic interactions with some contribution from polar interactions to form larger aggregates (6). The better wet strengths of the higher bonding temperatures are more likely due to increased hydrophobic coalescence than polar coalescence, which should be water sensitive. A recent publication indicated that a cooked egg yolk could be converted to its original proteins by mechanical means (4). Thus, it is not very likely that the change in properties from a liquid to a solid in the cooking process involves substantial covalent bond formation.

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