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Soy Products for Wood Bonding

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Abstract

Understanding the structure-property relationships for proteins as adhesives is complicated due to the complex and changeable colloidal nature of most proteins. An abundant source of protein in many parts of the world is the soybean, but the inexpensive soy flour is only 50% protein with the remainder being an approximately equal split of soluble and insoluble carbohydrates. These carbohydrates have been considered the cause of the poor strength under wet conditions for bonded wood products. However, removal of the soluble and/or insoluble carbohydrates did not lead to dramatic improvement in wet bond strength, showing that the native protein is not a great adhesive. In contrast, hydrothermal treatment of the purer proteins provided much higher strength showing the importance of thermal history when considering the use of soy protein in adhesive systems.

Key words: soybean**,** protein, adhesive, wood, viscosity, bond strength

Introduction

Soybeans have been used mainly for their nutritional utility rather than as an industrial product. The soybean is not eaten whole to any great extent, but is converted into other raw materials that are used in many food products. After removal of the protective hull, the bean can be processed to make tofu and soy milk directly. For the most part the crushed beans are solvent extracted to isolate the valuable soy oil. The remaining meal is mainly used as animal feed after heat treatment to make it more digestible; however, the defatted soy is also processed to make a variety of flours, concentrates, and isolates. Each of these classes of soy is not a single product, but a group of products with different properties. Thus, it is important to understand what specific soy material is being used and what specific processing steps were used to obtain a given soy product.

The only commercial soy product that has its proteins in the native state is the defatted (hexane extracted) soy that has not undergone any significant thermal treatment. This

type of product would typically be denoted with a high PDI value of 90, where PDI means protein dispersibility index (measurement of colloidal solubility). However, high PDI does not automatically correlate to a lack of thermal history in other products. All other commercial soy products have proteins in a non-native or denatured state. The proteins in the bean provide a number of biological functions; thus, there is no reason to expect the native state should provide the best adhesive properties. The processing conditions used for other soy products change some or all of the proteins from their native state to a denatured state. To understand this from the aspect of using these products in industrial applications, we have to understand the ways that these products are processed and how these conditions may affect the structures of proteins.

Proteins have four levels of structure: primary (amino acid sequence of the polypeptide backbone), secondary (localized crystalline regions including α-helices and β-sheets), tertiary (whole molecule structure), and quaternary (super structures formed by interaction of multiple protein chains) (Figure 1) (Creighton 1984). The different proteins in soy have unique distribution of the amino acids so there are considerable differences in the resultant higher order structures. These differences include the two types of polypeptide subunits that form the major protein glycinnin and three polypeptides that form the second major protein conglycinnin. A variety of other proteins are also present in the soy. The soy meal and the flour made from it also contain carbohydrates that can be divided into three classes, glycoproteins (covalent carbohydrate-protein structures) as well as soluble and insoluble carbohydrates. About half of he carbohydrates are soluble consisting mainly of sucrose, raffinose, and stachyose, and half insoluble carbohydrate polymers of rahmnose, arabinose, galactose, glucose, xylose, and mannose (Bainy et al. 2008).

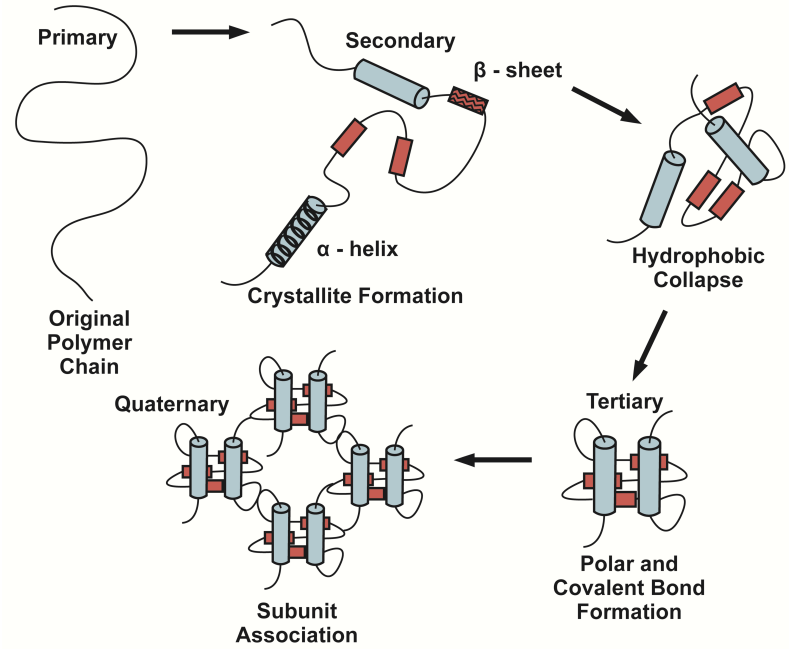

Figure 1. Folding of the proteins as they are synthesized showing all four levels of structure.

In processing soybeans the first step is nearly always a crushing step for hull removal and extraction of the valuable oils with hexane (Sun 2005). The defatted soy is then either dried using the vacuum method to remove the remaining hexane yielding the white flakes used to make the isolate and concentrate or ground into 90 PDI flour, or it is heated to remove the remaining hexane and denature the proteins for improved digestibility of the meal to produce the 20 PDI flour used to as animal feed. There is also an intermediate flour of 70 PDI which is made using the second method albeit with less aggressive heating. These are the three main types of soy flour available commercially.

The next class of soy products is the soy concentrates in which the soluble carbohydrates have been removed. Due to nature of the process required to make concentrates from the defatted white soy flakes, all concentrates contain denatured soy protein. To separate the soluble carbohydrates from the protein fraction involves an aqueous ethanol extraction. The protein content is increased from about 50% to 70% (Sun 2005). This material can then be dried to give a final product after just the extraction step or further modified via jet cooking. Jet cooking involves a rapid heating of the aqueous dispersion of the soy concentrate with high pressure steam in a tube reactor and then cooling and drying it quickly after passing it through an orifice using a vacuum evaporation. The degree of jet cooking plays an important role on the structure/function relationship of the resultant concentrate, producing a variety of products (too numerous to list here) with specific properties for use in the food industry. What is important to note is that each type of concentrate can be expected to contain proteins in various denatured states depending on the conditions of heat and shear that they are subjected to. .

The final class of soy product is soy protein isolates in which the insoluble and soluble carbohydrates have been removed to yield products with greater than 90% protein content. The isolate products require a more complicated process. The first step is to dissolve the majority of the proteins and soluble carbohydrates in water under slightly basic conditions so that they can be centrifuged to remove the insoluble carbohydrates (Sun 2005). The proteins are then precipitated by lowering the pH to the protein isoelectric point and centrifuging to remove the soluble carbohydrates. The precipitate can then be suspended in water, neutralized, and isolated by evaporation of the water. A similar process using a two or three stage lowering of the pH can provide the conglycinnin and glycinnin protein fractions whose crystalline structure has been determined. However, the information on the structure of the native soy protein isolate (NSPI) has limited bearing on the commercial isolate (CSPI) because all the CSPIs are jet cooked to provide greater functionality for food applications (Egbert 2004). Thus attempts to relate the performance of commercial protein isolates to native soy protein structures has provided little value due to the highly denatured state of the jet cooked CSPI. As with the soy concentrates, the degree of jet cooking can alter the level of denatured states in soy isolate yielding a variety of products with specific end use properties. In addition, there are also enzymatic treatments that can further alter the properties.

All commercial soy products can serve as wood adhesives as long as one is interested only in dry adhesive strength. Rarely is this the case, however, because most wood products need some level of water resistance. Thus, the most important aspect for selecting soy products is evaluation of the resultant adhesive bond after exposure to water, typically by prolonged soaking. Two other important aspects for selecting soy products as wood adhesives are the solids content and viscosity. Because hot pressing turns the water to steam that can rupture the composite when the platen pressure is released, minimal water content is valuable. As with any system, higher solids yields higher viscosity which can be especially difficult when using soy products which thicken rapidly even at relatively low solids contents. In order to better illustrate some of the adhesive properties of different soy products, the properties of different soy products are compared under the same bonding and testing conditions. The results are discussed in light of the process conditions used to obtain the soy products.

Materials & Methods

The soy flours used were the following: Prolia™ 200-90, Prolia™ 200-70, and Prolia™ 200-20 (Cargill Inc., Cedar Rapids. IA). The soy concentrates were Arcon® F and SM (ADM, Decatur, IL). The commercial soy protein isolates were PRO-FAM® 646, 781, 875, 891, 955, 974 (ADM)

A Horiba D-47 pH meter was used to measure pH values. Apparent viscosities were measured using a Brookfield Digital Viscometer Model RVTD (Stoughton, MA), with a #6 spindle at 5 rpm. A similar shear history for the samples was ensured by vigorously hand mixing the sample for 30 seconds, allowing it to stand for 10 seconds, inserting the spindle into the sample, switching on the viscometer motor and then recording the viscosity value 10 seconds after the spindle started moving.

The soy dispersions were made by dispersing soy into water at a given solids level. The mixture was then hand stirred for 30 minutes to complete the process. The pH and viscosity of the dispersions were measured.

The various soy dispersions were tested for their wood bonding strength using an Automated Bond Evaluation System (ABES) Model 311c tester (Adhesive Evaluations Systems, Inc., Corvallis, OR) for forming and breaking the bonds to determine strength and wood failure. The wood used for the test was hard maple and the wood samples bonded were 117 mm along the grain × 20 mm across the grain × 0.6 mm thick strips. During processing with the ABES, a 5-mm wide strip of adhesive was applied to one wood specimen and was then immediately overlapped with another. This area was then hot pressed in the ABES unit at 0.2 MPa for 120 seconds at 120°C. After this time period, the platens were retracted and the full specimen was removed from the unit. All samples (7 for dry testing and 7 for wet testing of each formulation) were allowed to re-equilibrate at 22°C and 50% relative humidity at least overnight before testing.

For testing bond strength, half of the specimens were tested dry and the other half were tested wet, after a four-hour water soak at 22°C. Each sample was placed back into the

ABES unit and the grips were engaged. The grips then pulled each sample and the maximum load at failure was recorded. The bond strength was calculated by dividing this load by the adhesive overlap area of 100 mm^2 to give the shear bond strength. The percentage of wood failure was also recorded (not reported herein); the fracture was mainly in the wood outside the bonded area for the dry samples and the failure was in the adhesive for the wet samples. The standard deviations in strength and wood failure were calculated for each combination, and differences were determined by comparing two standard deviation error bars for the different combinations.

Results and Discussion

Solids and viscosity

The adhesive has to be fluid enough to apply in the commercial equipment, which varies from roll coater for plywood to spray applicator particleboard. Soy adhesive viscosities cannot be directly compared to those of phenolics or amino adhesives because the soy adhesives are generally shear thinning while the others are Newtonian. The measured viscosity of soy adhesives can vary greatly depending on the shear history and as well as the selection of spindle and RPM's used during the measurement.

For most soy products, the viscosity increased slowly as a function of solids, then a transition occurred and the viscosity increased very rapidly (Frihart and Satori 2013). This is more typical of a dispersion than a solution. With the molecular weights of subunits being over 20 kD and the aggregates over 150 kD (Kinsella 1979), reaching a viscosity less than 1 Pa·s with a 20% solids would be surprising for a solution (Frihart and Satori, 2013). Thus, the soy is dispersed in water, with some dispersions being more stable than others. The term solubility used with soy does not mean true solubility, but describes how easy the soy is to wet with water. While the term dispersibility is used to describe how stable the protein dispersion is to centrifugation.

Bond strength

For these bond strength comparisons, we used the small scale specimen tests because this test allows for using a wide range of viscosities without a great variation in soy strength and emphasizes cohesive strength of the soy.

Because of economic and availability reasons, the flour is the most widely used soy source for adhesive applications; in particular, the 90 PDI flour with the native proteins is the basis for comparisons of soy performance. The original hypothesis was that the most dispersible protein should result in the best cohesive and adhesive strength, but very little difference and no discernable trend was seen. Both the wet and dry bond strengths were virtually unchanged using 90, 70, and 20 PDI flours with the amount of soy flour at 20%, 25%, 30%, and 35% in water (Frihart and Satori 2013). Thus, there does not seem to be any benefit to having native structure compared to some level of denaturation of the proteins produced during production of the different soy flour types. Not only did the PDI not influence the results, but also the creamy nature of the high PDI flours was not better in these tests than the gritty 20PDI flour. The PDI does play a role in making larger

standard plywood specimens, where the 20 PDI flours were more difficult to spread due to more rapid loss of the water to the wood during sample preparation (Wescott 2008).

One could assume that removing the soluble sugars in making the concentrate would allow a straight-forward comparison of strength compared to the soy flour. However, denaturation of the proteins to insolubilize them for the extraction from the soluble carbohydrates does not allow a direct protein to protein comparison with any of the soy flours. Initial comparisons of high PDI soy flour and Arcon F concentrate showed only a slight increase in dry and wet strength. The low wet strength observed using Arcon® F, led to the conclusion that the soluble sugars do not greatly affect the bond strength as illustrated in Table 1. However, if another concentrate, Arcon® SM is used, the conclusion would be different in that removal of soluble sugars generated a large gain in the wet strength. The difference seems to lie in the fact that the Arcon® SM is jet cooked while the Arcon F™ is not. Thus, we hypothesized that the jet cooking enhances the wet bond strength in the concentrates, and contribution from the removal of the soluble sugars minimal. Other process differences cannot be ruled at this stage since we do not know all the details of the commercial processes.

	% Solids	ABES dry strength		ABES wet strength		pH	Viscosity, cPS
		MPa	SD	MPa	SD		
Prolia™ 200-90	15%	5.4	0.8	0	0	6.25	660
Arcon® F	15%	6.6	0.7	0.7	0.1	6.80	<100
Arcon® SM	15%	6.6	0.5	2.0	0.3	6.75	75,200

Table 1: Bond strength comparison of soy flour and concentrates.

The literature was confusing in that Sun and coworkers published data that the native soy protein isolate (NSPI) had poor wet strength, but we have continually observed very high strengths from the commercial soy protein isolate (CSPI). However the bond strength tests were done differently between the two labs thus generating a need for further investigation. Making our own NSPI showed that it was only slightly better than the soy flour, but much poorer than the CSPI when tested using the same protocol (Table 2). Discussions with a CSPI supplier led to the understanding that all CSPIs were jet cooked for increased functionality in food products (Egbert, personal communication). We tested a variety of CSPIs to determine if most CSPIs provide high bond strength. Table 2 shows that most CSPIs yield enhanced wet strength compared to either soy flour or the NSPI. The major exception is PRO-FAM® 781, which was probably enzymatically cleaved as indicated by the substantially lowered viscosity. This further supports the notion that jet cooking is a way to produce stronger wood adhesives made from soy products. Unfortunately, all the jet cooked samples have much higher viscosities than those not thermally treated. The solids/viscosity ratios of CSPI make these soy products much less practical for use as wood adhesives.

	% Solids	ABES dry strength		ABES wet strength		pH	Viscosity, cPs
		MPa	SD	MPa	SD		
Prolia™ 200-90	15%	5.4	0.8	0	0	6.25	660
NSPI	15%	4.6	0.7	1.1	0.6	7.01	<100
PRO-FAM® 646	15%	8.0	0.5	2.4	0.5	6.36	36000
PRO-FAM® 781	15%	4.1	0.6	0	0	6.90	10
PRO-FAM® 875	15%	7.3	0.8	1.9	0.2	7.06	952
PRO-FAM® 891	15%	7.0	0.4	2.2	0.2	7.16	31300
PRO-FAM® 955	15%	5.1	0.9	1.5	0.2	5.40	<100
PRO-FAM® 974	15%	8.3	0.7	2.1	0.5	7.15	57000

Table 2: Bond strength comparison of soy flour, concentrates, and isolates.

This research shows that drawing conclusions from adhesive research can be misleading if you do not understand how the soy has been processed prior to formulating the adhesive.

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References

Bainy, E M, Tosh, S M, Corredig, M, Poysa, V and Woodrow L (2008) Varietal differences of carbohydrates in defatted soybean flour and soy protein isolate by-products. Carbohydr. Polym. 72: 664–675.

Creighton, T E (1984) Proteins, Structures and Molecular Properties, W. H. Freeman and Company, New York.

Egbert, W R (2004) Isolated soy protein: technology, properties and applications. In: Soybeans as Functional Foods and Ingredients, Liu, K., Ed. AOCS Press: Champaign, IL, 134-162.

Frihart, C. R. and H. Satori (2013) Soy flour dispersibility and performance as wood adhesive, J of Adhes Sci and Tech. 27(18-19): 2043-2052

Kinsella, J E (1979) Functional properties of soy proteins. J. Am. Oil Chem. Soc. 56:242–258.

Sun, X. S. In: Bio-Based Polymers and Composites; Wool R. P.; Sun X. S., Ed.; Elsevier-Academic Press: Burlington, MA, 2005,33-55.

Wescott, J M (2008) Heartland Resource Technologies, unpublished observations

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