Coaxing soy adhesives into living up to their potential

Christopher G. Hunt, Linda L. Lorenz, Eder Valle, Thomas Coolidge, Charles R. Frihart *US Forest Service, Forest Products Laboratory*

ABSTRACT

Although soy flour has been used commercially as an adhesive for interior wood products and recent studies have shown that improved performance can be obtained by adding co-reacting adhesives, improving the performance of soy flour without co-reactants would make soy adhesives more robust and economically attractive. Despite all the research, there is still no clear understanding of soy protein structures and their interaction with other materials in the flour. Prior research showed commercial soy protein isolates, which is jet cooked, out performs isolate made by standard laboratory procedures. This leads to the question addressed here as to whether jet cooking improves the adhesive performance of soy flour adhesives.

INTRODUCTION

Soy and other proteins are of great interest for their potential use as wood adhesives, because of their renewability and potentially low environmental impact. This interest is demonstrated by the presence of several commercial products and an abundance of research papers discussed in some recent reviews of soy adhesives r (Frihart, Hunt et al. 2014; Vnučec, Kutnar et al. 2017).

In the literature, it is common to see statements such as "the protein was denatured to improve bond strength". While there are quite a few papers that discuss the impact of a particular denaturation treatment on bond strength (Hettiarachchy, Kalapathy et al. 1995; Zhong, Sun et al. 2002; Cheng, Sun et al. 2004; Wang, Wang et al. 2005; Chandra, Bura et al. 2007; Zhang and Hua 2007; Luo, Luo et al. 2015; Vnučec, Goršek et al. 2015), we found it difficult to sort out trends from the literature and understand how these denaturation treatments impact wood bond strength. Without this understanding of the state of the proteins being used, the research is not as useful as it could be.

The goal of this paper is to help researchers understand the state of denaturation of commercial soy products and how the commercial denaturation treatments impact adhesive properties. We expect some of these principles will apply to proteins from other sources as well.

Two types of soy product dominate the research literature on adhesives: commercial soy protein isolate and commercial soy flour, especially 90 PDI (protein dispersibility index) flour. Figure 1 is provided to show how dramatically different flour and isolate are. Isolate is a highly processed specialty food ingredient, while flour is a by-product of oil production and primarily used for animal feed. The most common flour grades are 20 and 90PDI, where PDI (AOCS 2005) is a rough indicator of the degree of denaturation: High PDI = more native, low PDI = denatured. For compositional analyses of soy products we referred to Eldridge (Eldridge, Black et al. 1979). Kinsella (Kinsella 1979) provided an excellent overall background on soy products and processing. Another good review was provided by Liu (Liu 1999). A United Nations document (FAO 1992) described soy product production and uses of soy in detail. Egbert focused on, and therefore provides further insight, into isolates and shows that isolates are a family of products that vary in properties rather than a single product. (Egbert 2004).

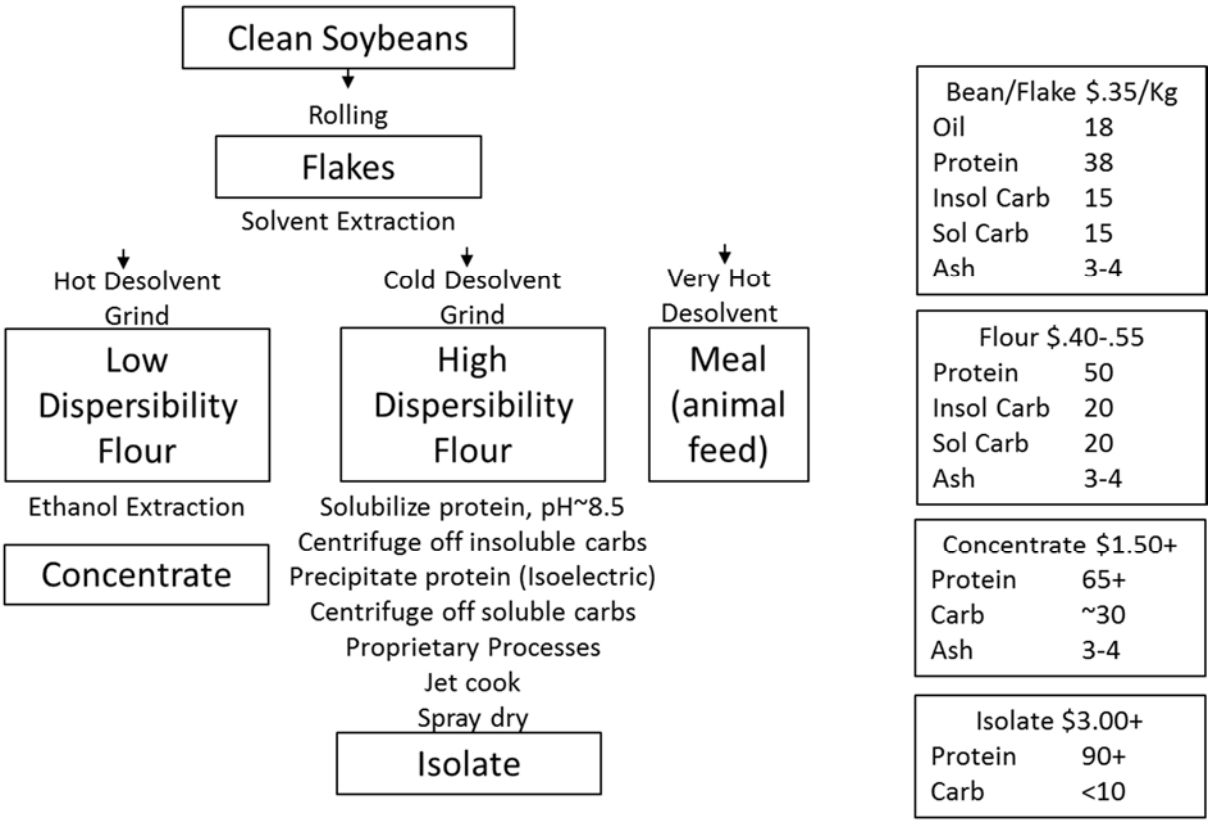

Figure 1: Left, commercial processing of soybeans, products are in boxes. Right, approximate 2014 price, USD/Kg, and content (% dry mass) of soy products (Frihart, Hunt et al. 2014; Lorenz, Birkeland et al. 2015).

MATERIALS AND METHODS

Materials

Soy flour of 20 and 90PDI are Prolia brand products of 200 mesh from Cargill. Commercial SPI is PRO-FAM 974 from ADM. Laboratory SPI (LSPI) followed the standard procedure in Thanh and Shibasaki (Thanh and Shibasaki 1976) with 1.5L batches. Briefly, 90pdi flour is dispersed at pH 8-8.5pH at 10% solids in RO water, and centrifuged to remove insoluble carbohydrates. Then the proteins are precipitated by adding HCl to pH 4.5 and centrifuged to remove the insoluble isolate. We then added water and NaOH to pH 7.6 to resolubilize, and lyophilized for storage. Pilot plant SPI (PPSPI) was produced in a similar process of ~180L batches, but used H_2SO_4 to acidify, and used a Sharpless flow-through centrifuge with capacity of ~4L of solid precipitate.

Testing

It is relatively easy to generate strong bonds when the bonded wood is tested under dry conditions, but wet strength is far more difficult to achieve and is the focus of this research. All reported strength data are wet lap shear strength measured using the ABES (Automatic Bond Evaluation System) Model 311c (Adhesive Evaluations Systems Inc., Corvallis, Oregon) as described previously (Lorenz, Birkeland et al. 2015) and depicted in figure 2. Dry soy was always given at least 30 mins in water, with stirring, to wet out before bonding. Enough

soy:water dispersions of 15-30% solids were placed on the end of one hard maple adherend to allow squeeze-out, and the assembly pressed for 2 min at 120C and 0.2MPa. The bonded samples, 6 per condition, were later soaked in DI water for 4 hours before testing.

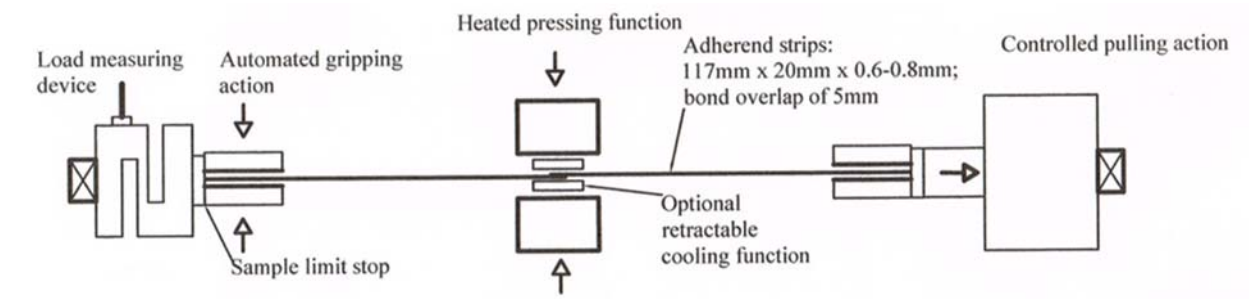

Figure 2: The ABES device for making small adhesive specimens

Viscosity was measured with a Brookfield viscometer. After having time to wet out, the soy dispersion is placed in a 100ml beaker, vigorously stirred with a spatula for 30 seconds, the appropriate spindle (often #6)immediately immersed, and viscosity read 30 seconds later.

Jet Cooking

A stainless steel jet cooking device was constructed to test the impact of high temperature and shear on soy adhesive properties, Figure 3. The soy dispersion was loaded into a 1.5L capacity clear tube and pressurized to 10psi lower than the steam pressure. A gear pump drove the soy dispersion into the tube containing pressurized steam. The pressure of the steam drove the soy dispersion through the adjustable length 8mm ID residence tube and out the small orifice at the end, where it was collected on the walls of rotating stainless steel bucket immersed in ice water to quickly cool the product. Thermocouples along the residence tube and at the end indicated a very small (~2 degree C) temperature drop through the entire system before the restriction. Because of the small volumes, flow through the tube was non-uniform. Residence time was difficult to determine accurately but was on the order of 7-40 seconds (determined by dye injection). Soy dispersion was pumped at 200-250ml min^{-1}. At least 100ml was run through the entire system before sample was collected. Jet cooked material was always tested on the same day it was made. Each replicate in Figure 5 was made on a separate day with new soy dispersion. Gomi et al. (Gomi, Hisa et al. 1980) provided guidance on jet cooking conditions and for changing PDI of the flour.

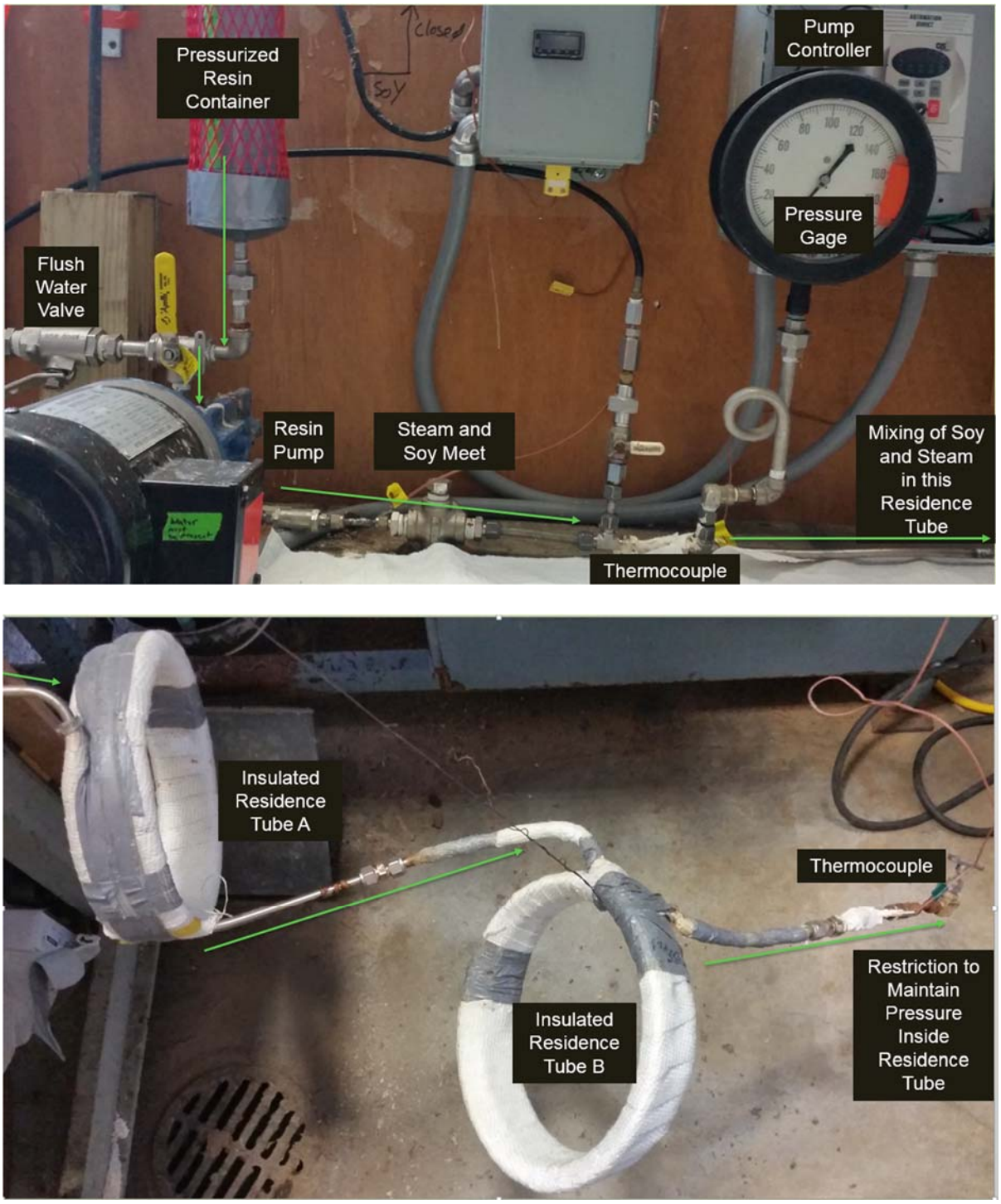

Figure 3: Jet cooking apparatus. Upper, soy dispersion and steam mixing. Lower, residence tubes, thermocouple, and restriction at end to maintain pressure and temperature inside tube. Green arrows indicate flow direction of soy dispersion through the system.

RESULTS AND DISCUSSION

What Does Denaturation Look Like?

Figure 4 is a schematic showing various levels of denaturation of protein and the "ideal denatured state" for a protein adhesive. However these models of "denatured state" are based on studies of proteins in high concentrations of NaOH, urea, or surfactant – not the conditions typically used in soy adhesives. In dispersions dominated by water, expanding the protein would expose hydrophobic residues to water, which is too energetically costly. It may be possible for proteins in the adhesive to exist in this extended conformation if they are buried inside large protein aggregates, where they can have favourable energetic interactions with their neighbouring molecules. The protein, even when denatured, is not delivered as extended proteins in a water matrix. In most cases, we observe a large mass fraction of denatured protein in our soy samples as insoluble precipitates.

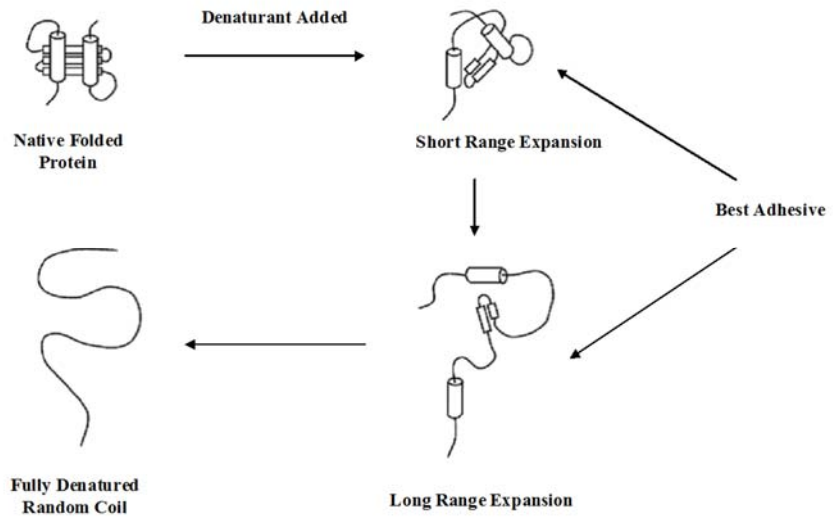

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Figure 4: Concept of ideal state of denatured protein for adhesive use, probably from 1920's pH 12 or higher formulations. The concept persists, even though short range expansion or anything more extended is thermodynamically impossible in water dispersions under typical conditions.

Does Denaturation Help?

While denaturation clearly can improve the bond strength of soy proteins, the details of denaturation are very important. For instance, in our experience, we have never observed an increase in wet strength of soy upon enzymatic hydrolysis (data not shown), despite the appealing reductions in viscosity. Similarly, sodium metabisulfite, which denatures by cleaving thiol linkages, provides appealing viscosity decreases but has never, in our experience, improved strength (data not shown). Because these protein cleaving treatments are often detrimental to wet strength, it is clear that it is not simply denaturation that is important. The details of the denaturation process are critical.

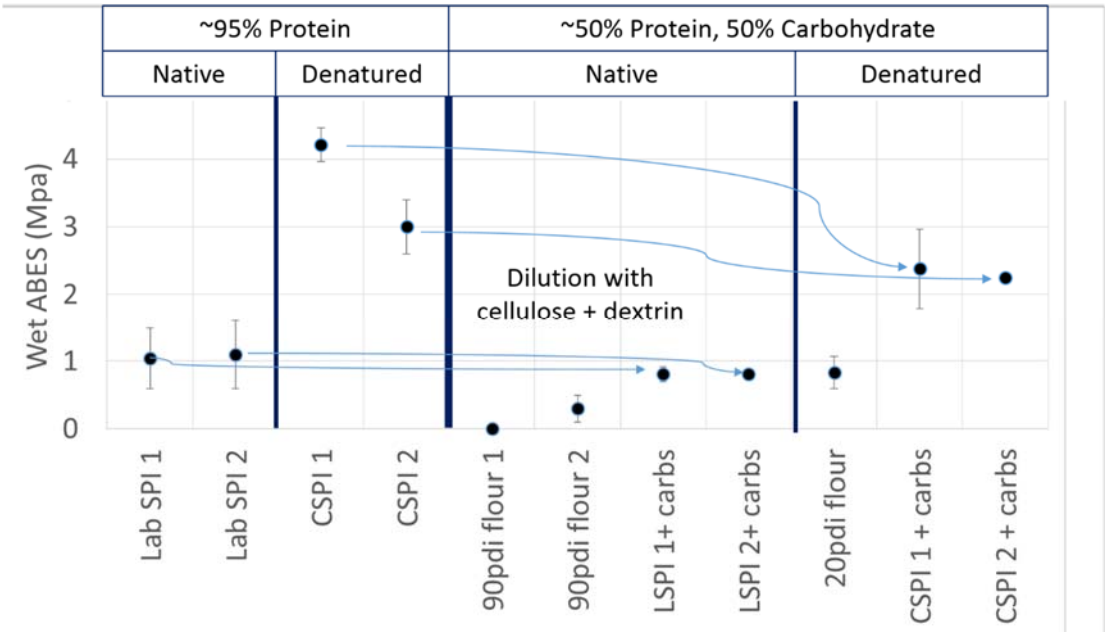

Figure 5: Wet shear strength of soy products. Left half, native and denatured SPI. Middle, ~50/50 native state protein and carbohydrates. Right, ~50/50 denatured protein and carbohydrates. Adapted from (Lorenz, Birkeland et al. 2015)

Note that in Figure 5 the denatured 20PDI flour has higher wet strength than the native 90PDI flours. This is a very consistent observation: the high temperature used in desolventization does generally improve wet strength in the resulting flour. This is also consistent with the observation that soy protein concentrate has generally even better wet strength than 20PDI flour (Hunt, Wescott et al. 2010). Concentrate is made by extracting flour with ethanol, which denatures the protein to allow the extraction of the soluble sugars.

Figure 5 shows the relative impact of both denaturation and dilution of protein with carbohydrate. We made laboratory soy protein isolate (lab SPI) and found that its strength was far below that of the commercial product. In addition, adding carbohydrate to the commercial product decreased strength but still left it far above the 20pdi flour or (lab SPI + carbohydrate) in figure 5. These observations led us to believe that the denaturation that occurs during commercial SPI production contributes significantly to its adhesive properties. Further investigation revealed that all commercial SPI is jet cooked (Egbert 2011); thus, this SPI is probably a poor model for the proteins in soy flours.

		0.4m tube		1.9m tube		6m tube		12m tube		18m tube	
	°C (steam MPa)	Shear (Mpa)	SD(Mpa) ,# reps	Shear (Mpa)	SD(Mpa) ,# reps	Shear (Mpa)	SD(Mpa) ,# reps	Shear (Mpa)	SD(Mpa) ,# reps	Shear (Mpa)	SD(Mpa) ,# reps
Flour	120 (.1)							0.7	NA, 1	0.5	NA, 1
90pdi	155 (.4)	1.2	NA, 1			1.6	NA, 1	1.8	.3, 4	1.7	.3, 4
Cont 0	165 (.6)	1.2	NA, 1			1.3	NA, 1	1.8	NA, 1	2.1	NA, 1
SD 0	185 (1.0)	0.9	NA, 1			1.1	NA, 1	1.5	NA, 1	1.3	NA, 1
Flour	120 (.1)	1.5	0.1, 4	1.4	0.3, 4						
20pdi	145 (.3)	1.6	0.4, 5	1.4	0.2, 4	1.6	NA, 1	1.4	NA, 1		
Cont 1.2	165 (.6)	1.4	0.2, 4	1.6	0.1, 3	1.5					
SD 0.1	185 (1.0)	1.5	0.4, 5								
PPSPI	145 (.3)					3.6	NA, 1				
Cont 0.4,	165 (.6)	3.5	.3, 2			3.2	.2, 2	3.4	NA, 1	2.4	NA, 1
SD 0.4	185 (1.0)	3.5	NA, 1			3.5	.6, 3	2.6	NA, 1	2.3	NA, 1

Figure 6: Wet Shear strength (ABES) of 15% solids soy products after jet cooking. Cont = shear strength (MPa) of soy dispersion without jet cooking, SD = standard deviation.

Figure 6 provides the wet shear strength in ABES of 15% solids adhesives from jet cooked soy materials. Across the top are the length of tube holding the soy at temperature (longer tube = longer retention time), and vertically is listed the temperature, set by steam pressure, for each treatment. Each color highlights the strength data from a different starting material.

First note that the denatured 20pdi flour had some wet strength before jet cooking while the native state 90pdi flour and pilot plant-made SPI (PPSPI) had poor wet strength, consistent with the concept that denaturation improves bond strength. After jet cooking, both flours had similar wood bond strength, suggesting that whatever differences existed before cooking were largely erased by the high energy jet cooking treatment. It also appears that the temperature or residence time do not matter much – for a given starting material, the results were similar for all conditions. That is not to say that the treatment conditions do not matter, however, as the standard deviations were high. The high standard deviations suggest that there may be ways to further influence the strength by jet cooking conditions, but these parameters were either not explored or not well controlled in this system.

The low carbohydrate PPSPI was ~2x stronger after jet cooking than the flour, and was in the general range of commercial SPI data in figure 4, supporting the hypothesis that the jet cooking step in commercial SPI processing is likely responsible for much of the wet strength of commercial SPI relative to flour and laboratory-made SPI. The higher strength of the jet cooked SPI relative to jet cooked flour likely shows the detrimental role of carbohydrates in wet strength, but may also reflect some interaction between carbohydrate and protein during the jet cooking of flour. The difference between our jet cooked SPI and commercial SPI should be expected. A wide variety of commercial SPI are produced with very specific and different properties as food ingredients (water retention, emulsification, gelation, etc.). While they are all jet cooked, there are large differences in their wet strength (data not shown).

Importantly, more denaturation treatment is not always better. We have found that a hot/wet treatment of 1% SMBS on SPI reduces the wet strength of the adhesive by at least 50%. In other

words, performing a thermal treatment could degrade, rather than enhance, wet strength of the protein depending on the state of the starting material.

Flour dispersion viscosity typically increased 7-30x with jet cooking. Observations indicate viscosity increases in isolate were even more, though we were not able to measure viscosity for jet cooked PPSPI because insufficient volumes were produced or viscosities were beyond the range of our instrument. This is consistent with our experience that raising wet soy flour above denaturation temperature always results in extreme jumps in viscosity. The fact that 20PDI flour viscosity increases greatly with jet cooking with little strength increase suggests that viscosity and strength are not intimately coupled. Therefore it may be possible to denature in a way that generates strength without greatly increasing viscosity. Note that extreme caution should be used in interpreting viscosity measurements of soy protein dispersions because of their extreme sensitivity to shear history and therefore the methodology of the viscosity determination.

Our current research program is actively investigating what mechanisms underlie the wet strength of soy proteins, when it is present. It is our intent to discover what particular interactions are facilitated by jet cooking, which will provide guidance on how to improve soy (and possibly other plant) protein adhesives.

CONCLUSIONS

Soy flour is inexpensive enough that it can be economically competitive with other wood adhesives. Soy protein concentrate and isolate generally have better wet strength but are in general too expensive to use in price sensitive commodity adhesives.
Commercial soy protein isolate has little in common with the properties or performance of native protein or to soy flour protein.
Optimal performance requires attention to the denaturation state of the protein. We have not seen any benefit of cleaving proteins, while processes that might reorganize the protein while maintaining molecular weight can be quite beneficial. When starting with a denatured material, further denaturation steps taken by researchers might result in lower bond strength.

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