

# High-Temperature Performance of Soy Adhesives

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## Abstract

We investigated the likelihood of soybean-based adhesives passing the heat resistance requirement for structural adhesives. We evaluated the performance of soy adhesives up to a temperature of 230°C using ASTM 7247 (hot and cold shear blocks), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). We found that pure soy flour performed relatively well at high temperature, and the addition of crosslinking agents generally improved performance. One commercial soy/phenol formaldehyde passed the standard test ASTM D7247.

## Introduction

Soy protein-based adhesives, though used extensively early in the twentieth century, were supplanted by fossil fuel-based adhesives due to cost and durability issues. Renewed interest in bio-based sustainable adhesives has prompted our laboratory and others to develop new, higher performance soy adhesives. One barrier to the use of any adhesive in a structural application or some building products is a relatively recent demand for adhesive heat (fire) resistance, such as ASTM D 5456 and the ICC acceptance criteria for I-Joists (ICC 2007, ASTM International 2009a). In this study we investigated whether it is likely that soy-based adhesives could pass heat resistance standards.

The basic philosophy driving fire resistance certification in the United States is that structural bonded assemblies must perform as well as solid wood in a fire situation. Therefore we compared the performance of soy fractions, soy-based adhesives, and competing adhesives to wood at temperatures where wood loses significant strength, 230°C.

Soy protein adhesives have already shown good fire resistance in at least one application: mixed with casein, a milk protein. "Soybean-casein door glues maintain

strong adhesion in a fire until the gluelines are literally charred away" (Lambuth 2003). It seems likely that the relatively expensive casein in this formulation could be replaced with other adhesive components such as soy flour and phenol formaldehyde (PF) (Wescott and Frihart 2008) or soy flour and polyamidoamine epichlorohydrin (PAE) (Li 2007), to maintain high-temperature performance while imparting other functional properties, such as water resistance.

Standards for heat resistance have changed in United States, with the adoption of ASTM D7247 (ASTM International 2008), the small-scale evaluation of strength at high temperature that is cited in wood product standards (ICC 2007, ASTM International 2009a, ASTM International 2009b). In D7247, solid blocks of wood cut into shear block configuration are heated in an oven until the hot blocks lose a specified fraction of their shear strength. The matching shear blocks bonded with various adhesives are exposed to the same conditions and must not lose a larger fraction of their strength than the solid wood (D7247-06 states: "The mean residual shear-strength ratio for the bonded specimens is recommended to be equal to or higher than the lower 95% confidence interval on the mean residual shear-strength ratio for the solid wood control specimens..."). In this paper, we report shear stress at failure for soy adhesives tested according to D7247 in order to relate our other analyses to a standardized test.

While D7247 is a useful demonstration of heat resistance, it is time consuming and only provides a failure load after heating. Other techniques are much better at probing fundamental properties of adhesives upon heat exposure. Adhesives can lose their strength under fire conditions by either a thermal softening or a thermal decomposition process. The D7247 does not distinguish between these two types of failure. Differential scanning calorimetry (DSC) measures the heat-flow needed

to change the temperature of the sample, telling us if thermal transitions occur in the adhesive polymer whether they are from phase transitions or alteration of the polymers. Thermogravimetric analysis (TGA) measures weight loss, which is indicative of polymer decomposition. Dynamic mechanical analysis (DMA) measures force and displacement on a specimen as a function of temperature, revealing mechanical response as a function of temperature. The DMA data provide good evidence of thermal softening of the polymers. These methods are commonly used when probing fundamental chemical-mechanical relationships in adhesives (Umemura et al. 1998, Umemura and Kawai 2002, Wang et al. 2005, Lei et al. 2008) and other materials.

## Materials and Methods

### Adhesives

Soy flour adhesive was made by mixing 1 part toasted soy flour (ADM Kasoy 20/200; Decatur, IL) in 3 parts water and using directly. The Soy/PF dispersion contains 50% soy and 48% PF, following a literature method (Wescott et al. 2006). The Soy/PAE contains 30.3% toasted soy, 6% PAE, 0.7% additives, and 63% water, and has a viscosity of 20,000 cps with spindle #6 at 10 rpm on a Brookfield Viscometer (Middleboro, MA). The phenol-resorcinol-formaldehyde (PRF) and emulsion polymer isocyanate (EPI) adhesives are from commercial sources. The manufacturer describes the PVAc\* as a non-crosslinked poly(vinyl acetate), but other PVAc's have a  $T_g$  around 50°C, which our tests show to be very different from this material. Since this adhesive differs from expected PVAc behavior, we call this adhesive PVAc\*. The casein protein used was an acid precipitated protein (American Casein Company, BL-330; Burlington, NJ), not a formulated adhesive. Soy flour (ADM Kaysoy 20/200), soy concentrate (ADM Arcon AF) and soy protein isolate (ADM ProFam 974) are commercial products.

### Thermogravimetric Analysis and DSC

Thermogravimetric analysis (TGA) and DSC specimens were ground to fine powders using a dental amalgamator, except for wood, which was Wiley milled to 80 mesh. EPI and PRF were cured at ambient temperature overnight, and 140°C for 1 hr, respectively. All other materials were heated to 120°C for at least 5 min to cure, then were vacuum-dried at 35°C before analysis. DSC specimens were heated from 35 to 240°C at a heating rate of 10°C per min to obtain heat-flow and heat-flow derivative curves. The TGA specimens were held at 120°C for 20 min then raised to 300°C at 2°C per min under a nitrogen atmosphere.

### Dynamic Mechanical Analysis

Solid specimens were prepared from 2.1-mm-thick hard maple peeled veneer, cut to 12 mm wide by 60 mm long (in grain direction), and then machined with an end-mill to  $1.12 \pm 0.02$  mm thickness. Bonded specimens were prepared from two hard maple peeled veneers 57 wide  $\times$  305 mm long (in grain direction)  $\times$  0.6 mm thick. Adhesive was applied to each veneer and cured under the conditions listed in **Table 1**. After curing, the specimens

were held overnight at 21°C/50% RH before cutting to 12 wide  $\times$  60 mm long (in grain direction), then oven-dried overnight and held in a desiccator until tested.

The specimens prepared as above were tested in a Q800 DMA (TA Instruments, New Castle, DE) in the 50-mm span three-point bending fixture. For the low-strain dynamic testing, a sinusoidal load was applied to the specimen that resulted in 0.01% strain (strain control with force track), in addition to a 0.01 N constant preload. The samples were held 60 minutes at 35°C, before the temperature was increased at 5°C per minute to 230°C and held 30 min while recording storage modulus and loss modulus.

Specimens for heat deflection loading were prepared as above and were tested in the Q800 DMA in the same three-point bending fixture. At 35°C, a 2 N load was applied. The temperature was held at 35°C for 60 min, ramped at 5°C per min to 230°C, then held at 230°C for 30 min while collecting strain readings. Initial tests on solid wood with 8 N load found a deflection of 0.35% at 35°C and failure by excessive deflection at 230°C. PVAc\* specimens failed by deflection at ~4 N under the same conditions.

### Hot Shear Block

Hard maple shear-block specimens were prepared according to ASTM D7247 and tested at room temperature (cold), or held with the bondline at 230°C for one hour and immediately tested in shear. The specification calls for the shear test to be completed within 60 s of the oven door opening. We finished most, but not all tests in under 60 s: our time to completion ranged from 45 to 80 s. Under these conditions solid wood retained 30% of its original shear strength. Percent failure in the wood was estimated using ASTM D 5266 (ASTM International 2005).

## Results and Discussion

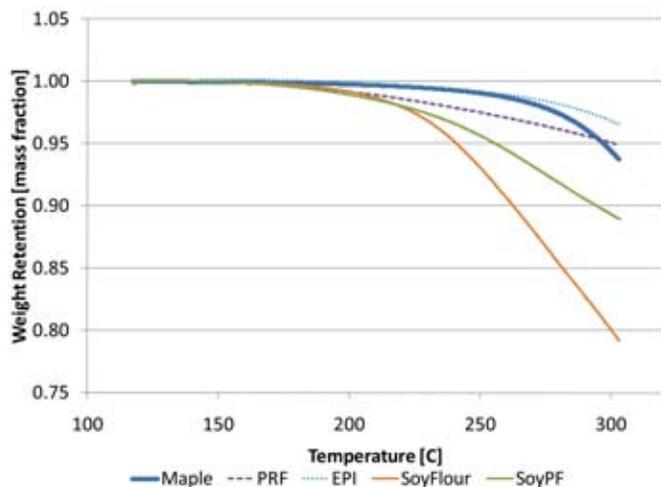
### Thermogravimetric Analysis

TGA gives information relevant to heat stability by measuring weight loss from thermal degradation as a function of temperature. To avoid any confusion about loss of volatiles from the polymer degradation, the sample was first held at 120°C to remove any absorbed water. **Figures 1** and **2** show weight loss of various adhesives and soy fractions vs. temperature. The PRF and EPI show very little weight loss below 230°C. This suggests stability in that no volatiles were formed: maple also shows little weight loss, though we know that 1 hour at 230°C will reduce compression shear-block values by 70% in the D 7247 test discussed later. These data clearly show that some component of the soy flour vaporizes or decomposes much faster than the PRF, EPI, or maple wood at temperatures below 230°. The soy/PF weight loss is proportional to soy flour content (50%).

The poor performance of soy flour in TGA is contrary to our understanding of the thermal stability of proteins. Therefore we compared soy flour to soy concentrate and isolate as well as pure casein (a protein used in heat-resistant applications). Concentrate is made by extracting flour with ethanol (Sun 2005) to remove

**Table 1.** ~ Dynamic mechanical analysis (DMA) sample preparation details.

Adhesive	Spread rate (g/m <sup>2</sup> )	Target bondline temperature (°C)	Time at target temperature (min)
PVAc*	129	Ambient	>8 hr
Soy flour	215	120	10
Soy/PF	215	150	10
Soy/PAE	215	120	10



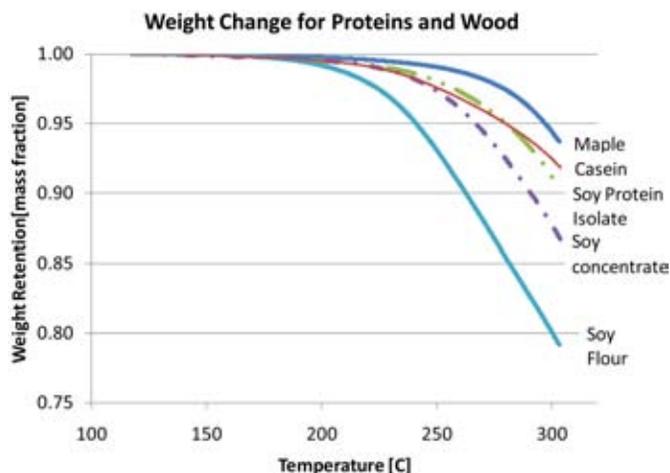
**Figure 1.** ~ Weight retention for several soy-based adhesives, compared to commercial adhesives, tested by TGA.

approximately 15 wt% dimer and trimer sugars, mostly sucrose and raffinose, and some small peptides (Egbert, personal communication, 2008). Soy protein isolate is almost a pure protein, made by dissolving protein to allow filtering out the insoluble carbohydrates followed by precipitating soy protein to allow separation from soluble carbohydrates (Wool and Sun 2005). The results of TGA analysis on these materials are shown in Fig. 2.

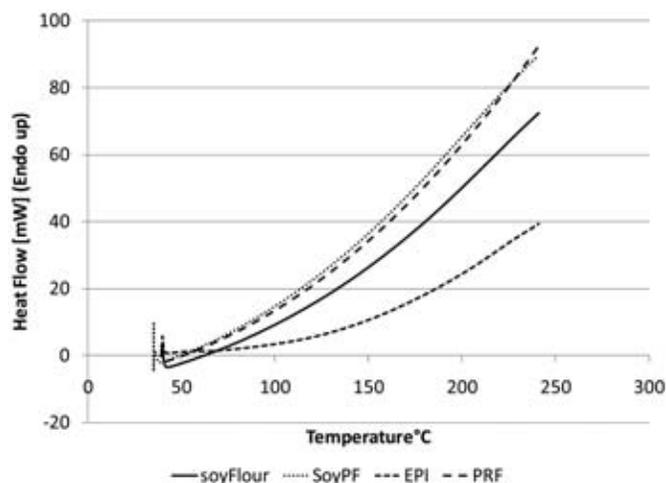
Figure 2 suggests that the portion of soy flour degrading below 230°C is the low molecular-weight carbohydrate and peptides found in flour, but not in concentrate. Because proteins should be stronger contributors to dry/wet bond strength than are the low molecular-weight carbohydrate components, we are not concerned about small carbohydrate degradation. Up to 230°C, the soy protein concentrate and isolate out-perform casein in this analysis, suggesting that, like casein, soy protein has the potential for excellent performance under fire conditions.

### Differential Scanning Calorimetry

Differential scanning calorimetry provides information about changes in the polymer state or polymer stability by changes in the heat capacity of the material as the temperature increases or decreases at a constant rate. Changes in the state of the polymer could be glass or melt transitions or degradation. In Fig. 3, PRF shows no transitions over the temperature range studied. This is consistent with its fully cured thermoset state. A transition is evident in EPI at ~75°C. The soy flour, soy flour/PF, and EPI have a transition to lower heat-flow at 190 to 230°C. This is not a glass or melting transition, as they



**Figure 2.** ~ Weight retention of bio-based materials tested by TGA.



**Figure 3.** ~ Heat flow vs. temperature for four adhesives tested by DSC.

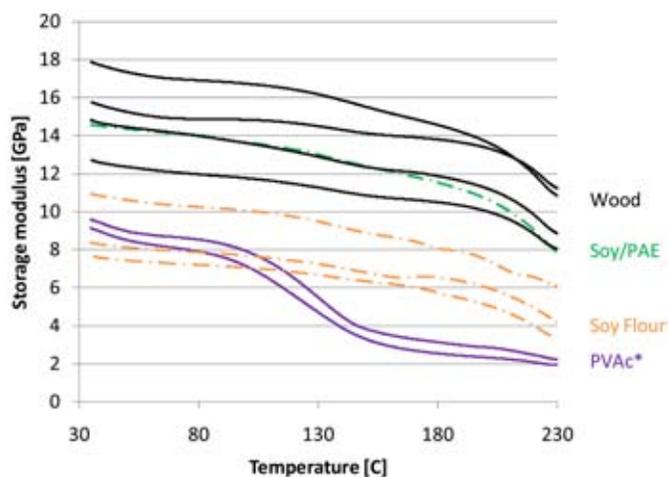
would increase heat-flow. It is more suggestive of an exothermic reaction or lower molecular mobility.

### Dynamic Mechanical Analysis—Temperature Sweep

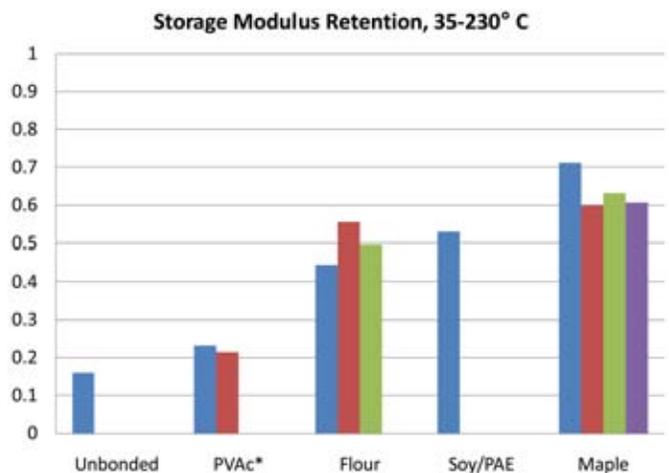
For the samples tested, solid wood and the soy/PAE had the highest adhesive storage modulus (Fig. 4), while solid wood had the smallest reduction in its modulus when heated to 230°C (Fig. 5). PVAc\* shows greatest loss in storage modulus on heating, as it passes through a transition during the heating cycle (maximum tan  $\delta$  at 143°C). Since PVAc typically has a  $T_g$  at ~50°C, we doubt that this commercial material is a pure PVAc.

The pattern of loss of storage modulus with heating is very similar between solid wood, soy flour, and soy/PAE assemblies. The high storage modulus of the soy/PAE complements the observation that the veneers could not be pried apart with a knife without wood failure.

The retention of storage modulus from Fig. 4 is summarized in Fig. 5, where the bar marked “unbonded” represents the theoretical stiffness retention of two unbonded plies of total thickness equal to the bonded specimens [solid wood retained 0.637 of its original strength. A beam of 1/2 thickness has 1/8 stiffness (Forest Products Laboratory 1999), two unbonded veneers therefore have  $2 \times 1/8 = 1/4$  the stiffness. Theoretical stiffness retention of two unbonded veneers is thus  $0.637 \times 0.25 = 0.159$ ]. The severity of the heat treatment is shown by the drop in stiffness of solid wood. Because the soy assemblies retain less storage modulus than solid wood, these adhe-



**Figure 4.** ~ Storage modulus vs. temperature for solid wood and bonded specimens tested by DMA. Separate traces represent replicate runs with separate specimens.



**Figure 5.** ~ Retention of storage modulus as temperature rises from 35 to 230°C. Unbonded is theoretical stiffness of two unbonded plies with the same total thickness as the solid maple specimens. Each bar represents a different replicate.

sives are probably losing stiffness faster than solid wood at these elevated temperatures.

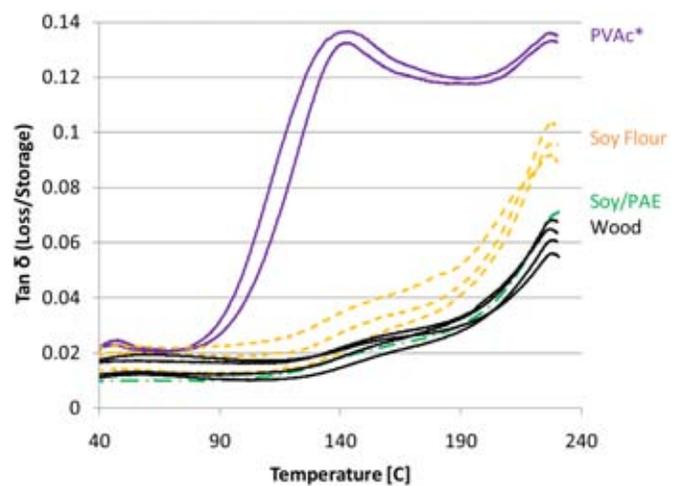
Tan  $\delta$  values (the ratio of loss modulus to storage modulus during deformation) are shown in Fig. 6. The tested PVAc\* shows a peak in tan  $\delta$  near 125°C, consistent with the loss in storage modulus shown in Fig. 4. Soy/PAE has tan  $\delta$  values similar to solid wood, suggesting good mechanical stability at high temperature. Plain soy flour has higher tan  $\delta$  than the soy/PAE at the higher temperatures, which indicates that the PAE crosslinking agent is partially preventing the softening of soy at high temperature. Such crosslinking or other formulation modifications will probably be necessary to pass heat resistance tests with soy flour adhesives.

### Dynamic Mechanical Analysis— Heat Deflection Analysis

We started with the hypothesis that the rate of creep would be greater for polymers that softened at elevated temperatures. To evaluate that hypothesis, strain rates were calculated for the final 25 min at 230°C when specimens were exposed to constant load under heating. Final slopes for PRF and PVAc\* were very similar (Fig. 7). The higher final strain of PVAc\* leads us to the conclusion that final strain magnitude, and the change in strain that occurs during temperature rise, are better indicators of thermal performance of adhesives than final strain rate.

Under constant load and increasing temperature, all laminated beams deflected more during heating than the solid wood (Fig. 8). In addition to some adhesive softening, we attribute a portion of this deflection to the higher stress on bonded specimens, which were 10% thinner than solid specimens but were loaded the same load (2 N). In either case, the two crosslinked soy adhesives have slightly lower creep than soy flour, which is far better than PVAc\*, and approach the values of solid wood.

Throughout these tests, we started from the assumption that the wood was stiffer than the adhesive at all times, in which case, the observed results would indicate



**Figure 6.** ~ Tan  $\delta$  vs. temperature comparison of several soy adhesives, PVAc\*, and solid wood.

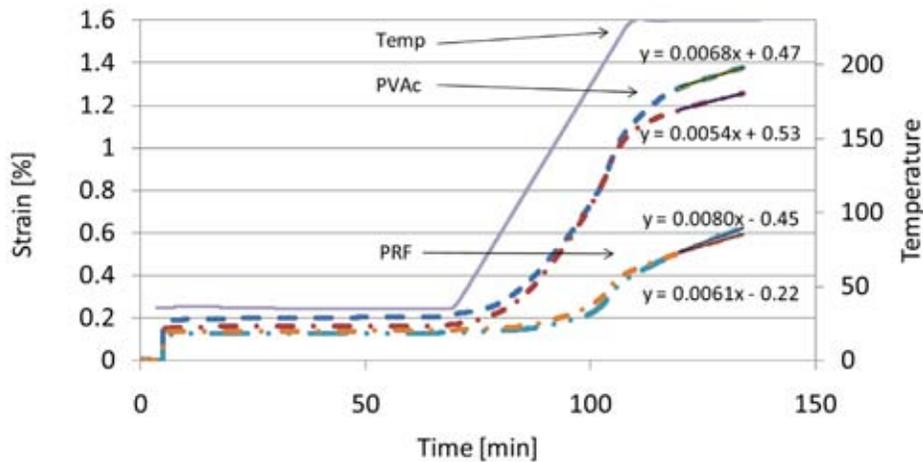


Figure 7. ~ Comparison of heat deflection rates at 230°C. Absolute magnitude of deflection on heating is different for different adhesives, but the final slopes are not a useful measure of difference.

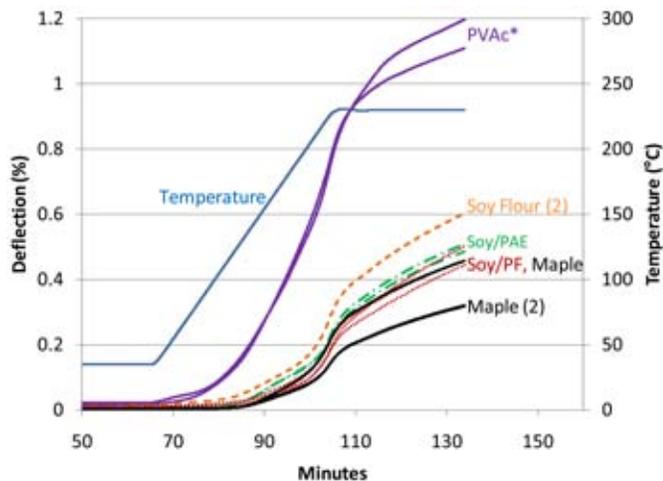


Figure 8. ~ Heat deflection of beams laminated with various adhesives.

the response of the adhesive alone. However, our test system responds as a composite, and what we hope to be a simple measurement of adhesive performance, is complicated by the true condition, namely, that our testing measures the material properties of the weakest link in the wood-adhesive composite. There are other, more rigorous, approaches to elucidating adhesive performance, for example testing the adhesive bonded to a different rigid material (e.g., glass) or supported by a uniform fibrous support (either glass or paper). Each of these has difficulties, with the chief drawback being the lack of interaction with all wood components. This study has presented a first glimpse of the possibilities of soy adhesives in wood composites.

### Shear Block

In addition to understanding the fundamental properties of soy adhesives under heat stress, we wanted to know their performance in the standard test assembly. In the ASTM D 7247 shear-block test, the hot-shear strength of solid maple was 4.4 MPa. Soy/PF and the plain soy flour adhesive had a mean hot-shear strength of 4.9 and 3.1 MPa, respectively (Fig. 9). Soy/PF specimens showed 90 to 100% wood failure, while the soy flour specimens showed wood failure around the edges

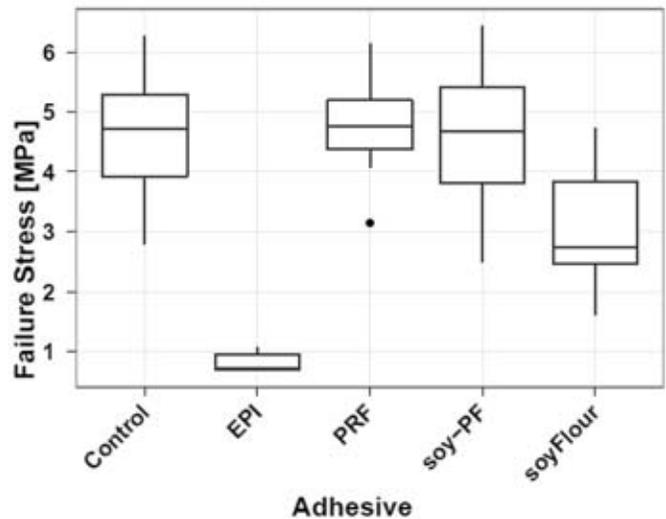


Figure 9. ~ Hot shear blocks tested after 1 hour at 230°C using ASTM D 7247. Horizontal lines represent 25, 50, and 75% quantiles. Outliers are represented as points.

and adhesive failure in the center, suggesting that the time between removal from the oven and completion of the test allowed cooling at the edges which increased the values for the plain soy strength values. The soy/PF system, however, performed just as well as solid wood and had wood failure even in the hot core, so is likely to pass the heat resistance qualification. PRF was also relatively close to the solid wood values, without core/edge differences. We believe the low EPI values may stem from the EPI thermal transition observed at ~75° with DSC. On the basis of the performance of soy/PF and the relatively strong bond with unmodified soy flour, we believe there is a strong possibility that adhesives containing soy could be formulated to meet the heat resistance requirements for structural applications.

### Conclusions

Properties of soy raw material, soy adhesives, and some commercial wood adhesives are compared. TGA suggests that soy proteins have excellent resistance to degradation, while the low molecular-weight fraction of soy flour decomposition begins at ~180°C. The data for the soy concentrate

and isolate indicate that the low molecular-weight carbohydrates are most likely the cause of soy flour degradation. DSC suggests that soy flour and soy/PF have no significant thermal transitions between 50 and 190°C.

Methods were developed to compare stiffness (temperature sweep DMA) and creep under load (heat deflection analysis DMA) for solid wood and veneer laminates. Dynamic testing under a low strain regime showed that the soy/PAE formulation was comparable to solid wood, while plain soy flour lost 14% more stiffness at higher temperatures than solid wood.

In the temperature sweep DMA, total deflection during the heating phase was a better measure of adhesive response to high temperatures than was creep rate at 230°C, since the final rates showed high variability and overlapping ranges compared to the large differences in strain magnitude. Again the soy/PAE performance was very similar to solid wood.

Hot shear blocks adhered with soy/PF, and PRF (ASTM 7247) had essentially the same strength as solid wood, indicating excellent high-temperature performance. Plain soy flour as an adhesive failed at about 60% of the value for solid wood. Considering this was simply the raw flour mixed with water and applied to the wood, we feel this is a very promising result.

The promising results presented here indicate strong possibilities for formulating soy adhesives with the heat resistance necessary for structural applications.

### Acknowledgments

The authors express their appreciation to the United Soybean Board for financial support under grants 8448 and 9448, David Harper from University of Tennessee, Dan Varnell and Tony Allen from Ashland Chemical Co, as well as appreciation to Heartland Resource Technologies, National Starch and Chemical, American Casein Company, Hercules (now Ashland), Cargill, and Archer-Daniels-Midland.

### Literature Cited

ASTM International. 2005. D 5266-99 Standard Practice for Estimating the Percent Wood Failure in Adhesive Joints. Vol. 15.06. ASTM International, West Conshohocken, PA.

- ASTM International. 2008. D-7247-07a Standard Test Method for Evaluating the Shear Strength of Adhesive Bonds in Laminated Wood Products at Elevated Temperatures. Vol. 15.06. ASTM International, West Conshohocken, PA.
- ASTM International. 2009a. D 5456-09a Standard Specification for Evaluation of Structural Composite Lumber Products. Vol 04.10. ASTM International, West Conshohocken, PA.
- ASTM International. 2009b. D 5055-09 Standard Specification for Establishing and Monitoring Structural Capacities of Prefabricated Wood I-Joists. Vol. 04.10. ASTM International, West Conshohocken, PA.
- Forest Products Laboratory. 1999. Wood Handbook: Wood as an Engineering Material. USDA-Forest Products Laboratory, Madison, WI.
- ICC. 2007. Acceptance Criteria for Prefabricated Wood Joists. AC14. ICC Evaluation Service Inc., Whittier, CA.
- Lambuth, A. 2003. Protein adhesives for wood. pp. 457-478. In A. Pizzi and K. L. Mittal (ed.) Handbook of Adhesive Technology. Marcel Dekker, Monticello, NY.
- Lei, H., G.B. Du, A. Pizzi, and A. Celzard. 2008. Influence of nanoclay on urea-formaldehyde resins for wood adhesives and its model. J Appl. Polym. Sci. 109(4):2442-2451.
- Li, K. 2007. Formaldehyde-free lignocellulosic adhesives and composites made from the adhesives USPTO. State of Oregon acting by and through the Oregon State Board of Higher Education on Behalf of Oregon State University 7252735.
- Sun, X. 2005. Isolation and processing of plant materials. pp. 33-55. In R.P. Wool and X. Sun (ed.) Bio-Based Polymers and Composites. Elsevier, New York.
- Umemura, K., and S. Kawai. 2002. Effect of polyol on thermo-oxidative degradation of isocyanate resin for wood adhesives. J. Wood Sci. 48(1):25-31.
- Umemura, K., A. Takahashi, and A. Kawai. 1998. Durability of isocyanate resin adhesives for wood I: Thermal properties of isocyanate resin cured with water. J. Wood Sci. 44(3):204-210.
- Wang, Y., D. Wang, and X.S. Sun. 2005. Thermal properties and adhesiveness of soy protein modified with cationic detergent. J. Am. Oil Chem. Soc. 82(5):357-363.
- Wescott, J.M., and C.R. Frihart. 2008. Water-resistant vegetable protein adhesive dispersion compositions. USPTO. USA, Heartland Resource Technologies. 7345136.
- Wescott, J.M., C.R. Frihart, and A.E. Traska. 2006. High-soy-containing water-durable adhesives. J. Adhes. Sci. Tech. 20(8):859-873.
- Wool, R.P., and X.S. Sun. 2005. Bio-Based Polymers and Composites. Elsevier, New York.

Wood Adhesives 2009 / edited by Charles R. Frihart, Christopher G. Hunt, and Robert J. Moon.  
Madison, WI : Forest Products Society, c2010. 1 CD-ROM.  
ISBN 978-1-892529-57-2. FPS Proceedings no. 7216-09.