Heat Resistant Soy Adhesives for Structural Wood Products
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Introduction
Because load-bearing bonded wood assemblies must support the structure during a fire, the limited softening and depolymerization of biobased polymers at elevated temperatures should be an advantage of biobased adhesives compared to fossil fuel-based adhesives. This study aimed at: 1) advancing biobased adhesive technology using renewable soy, and 2) better understanding the mechanisms of adhesion and failure of bonded materials. We evaluated several adhesives using differential scanning calorimetry and thermogravimetric analysis, as well as testing bonded specimens using ASTM D7247 [1] and a new method involving the Automated Bond Evaluation System (ABES) apparatus. The data indicated good heat resistance for some soy adhesives and that the thermal softening can be separated from thermal degradation for understanding adhesive performance.

Experimental

Adhesives
We two commercial and three soy-based adhesives. The commercial adhesives were an emulsion polymer isocyanate (EPI) and a phenol resorcinol formaldehyde (PRF). One soy flour adhesive was unmodified defatted soy flour and water, blended with a high shear mixer just prior to use. The soyPF is a hybrid of defatted soy flour and phenol-formaldehyde (PF) that has shown good water resistance on strandboard test panels [2]. The 1:1 SoyUrea/PRF is a mimic of the soybond honeymoon system, a two-component adhesive for finger jointed studs, using one part soy-urea on one face and one part PRF on the opposite face of the joint [3, 4].

DSC and TGA
Thermogravimetric analysis was performed on a Perkin Elmer TGA-7 using 5-10mg specimens of pulverized, oven dry cured adhesive or maple wood. Specimens were held at 110° for 20 min, then ramped up to 300° at 2° per min. Derivative spectra were calculated using Pyris software V3.5 (Perkin Elmer).

DSC samples were run on a Perkin-Elmer DSC 7 and the data was acquired and analyzed with Pyris™ Version 3.80 software. The DSC was calibrated with a standard indium sample. Aluminum capsules containing cured samples were heated from 35 to 240C at a heating rate of 10C/min to obtain the heat flow and heat flow derivative curves.

ASTM D7247
Hard maple shear block specimens were prepared according to ASTM D7247 and tested at room temperature (cold), or held at 230C for one hour and tested hot as specified in the heat resistance standard [5]. Percent failure in the wood was estimated using ASTM D-5266 [6]. Only soy flour and hybrid soyPF have been tested at time of publication.

ABES
The ABES (Adhesive Evaluation Systems, Corvallis, WA) test uses bonded overlapping veneer specimens pulled in tension along the grain of the veneer and parallel to the short dimension of the bond. Samples were prepared from two maple veneers with an overlapped and bonded area of 5x20 mm. Six specimens were prepared for each of 3 temperature conditions: room temperature, 35 seconds at 230C to demonstrate the loss in properties just after reaching the target temperature, and 10 min at...
230C to show the degradation from heat possible before a fire might char the wood.

Results and Discussion

**DSC and TGA**

In Figure 1, of the five adhesives tested, PRF shows no transitions over the temperature range studied. This is consistent with its full cured thermoset state. Other adhesives show similar behavior up to at least 190C. The Soy/PRF adhesive shows multiple transitions that may be related to decomposition or evaporation of urea.

Figure 2 shows the TGA results of the adhesives and maple wood. We can see that, as we expect, the PRF is stable across the temperature range, as is EPI and wood until temperatures exceed 250C. Hybrid SoyPF weight loss is proportional to soy content. SoyPRF adhesive has a high urea content, and shows a similar profile to the soy/urea adhesive. We attribute this weight loss to the vaporization/or decomposition of the urea. While soy flour isn’t as stable as wood, weight loss in TGA alone does not necessarily indicate failure under fire conditions. Weight loss is moderate up to 200C – In real fire there is often less than 10 minutes between attaining 200C and charring of the wood.

**Figure 2: TGA: Derivative of mass loss for 1:2 soy/urea(y axis * 0.5), maple wood, and 5 adhesives**

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After 1 hour at 230C, plain soy flour adhesive, maple, and soyPF had hot shear strength of 3.1, 4.4, and 4.9 MPa, respectively. The hot tested, SoyPF specimens showed 90-100% wood failure, while the soy flour specimens showed wood failure around the edges and adhesive failure in the center. This data data indicates that the soyPF system performed just as well as solid wood and so are very likely to qualify any heat resistance standard. The unmodified soy did not match solid wood performance, but was relatively close. We believe that it is reasonable to hope that adhesives containing soy could match solid wood in high temperature performance.

**ABES**

Figure 3 below summarizes the failure load for each adhesive at room temperature, upon reaching 230C, and after 600 seconds of thermal degradation.

The room temperature specimens showed PRF, EPI and SoyPF failed in wood away from the bonded area, while the soy flour specimens failed in the adhesive layer.

In the short hot exposure, EPI failure moved into the adhesive layer, suggesting thermal softening. Failure in soy flour specimens was was either in the adhesive or in the wood at the edge of the
bonded area, an improvement over room temperature performance. PRF and SoyPF failed at the edge of the bonded area or in the wood away from the bond. After 10 min of heat exposure, PRF, SoyPF and soy flour bonded specimens all failed in the wood adjacent to the bonded area, indicating that the adhesive was withstanding the heat at least as well as the wood. EPI again failed in the adhesive layer.

Conclusions
Our results are promising for the use of soy in adhesives for heat-resistant applications. A hybrid SoyPF showed equivalent shear strength to solid wood in the ASTM D7247 shear block test, and even a simple soy flour-water adhesive was only somewhat lower in strength than solid wood. Compared to a commercial PRF, both SoyPF and soy flour showed similar performance in the ABES test. We are continuing to study the high temperature degradation and polymer behavior of soy adhesives. Considering the years of optimization that have gone into the commercial PRF adhesive, we are optimistic about the potential for development of heat-resistant adhesives from renewable soy materials.

References

Figure 3: ABES: Failure load for soy-based adhesives compared to EPI and PRF adhesives over 3 exposure times to 230C