

High temperature performance of soy-based adhesives

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We studied the high temperature performance of soy meal processed to different protein concentrations (flour, concentrate, and isolate), as well as formulated soy-based adhesives, and commercial nonsoy adhesives for comparison. No thermal transitions were seen in phenol-resorcinol-formaldehyde (PRF) or soy-phenol-formaldehyde (SoyPF) or in as-received soy flour adhesive during differential scanning calorimetry scans heating at 10 °C/min between 35 and 235 °C. Heat flow rates decreased in the order soy flour (as received) > SoyPF > PRF > emulsion polymer isocyanate (EPI). In thermogravimetric analysis (TGA) scans from 110 to 300 °C at 2 °C/min, total weight loss decreased in the order soy flour (as-received) > SoyPF > PRF > casein > maple > EPI. For bio-based materials, the total weight loss (TGA) decreased in the order soy flour (as-received) > concentrate, casein > isolate. Dynamic mechanical analysis from 35 to 235 °C at 5 °C/min of two veneers bonded by cured adhesive showed 30–40% decline in storage modulus for maple compared to 45–55% for the adhesive made from soy flour in water (Soy Flour) and 70–80% for a commercial poly(vinyl acetate) modified for heat resistance. DMA on glass fiber mats showed thermal softening temperatures increasing in the order Soy Flour < casein < isolate < concentrate. We suggest that the low molecular weight carbohydrates plasticize the flour product. When soy-based adhesives were tested in real bondlines in DMA and creep tests in shear, they showed less decrease in storage modulus than the glass fiber-supported specimens. This suggests that interaction with the wood substrate improved the heat resistance property of the adhesive. Average hot shear strengths (ASTM D7247) were 4.6 and 3.1 MPa for SoyPF and Soy Flour compared to 4.7 and 0.8 MPa for PRF and EPI and 4.7 for solid maple. As a whole, these data suggest that despite indications of heat sensitivity when tested neat, soy-based adhesives are likely to pass the heat resistance criterion required for structural adhesives.

Keywords: soy; wood; structural adhesive; heat resistance; fire resistance

1. Introduction

Adhesives based on proteins from plants and animals were at one time the main wood adhesives. Soy adhesives for plywood were used early in the twentieth century until low-cost, water-resistant fossil fuel-based adhesives took a dominant position in wood-based composites in the 1950s. The largest adhesive types currently used are based on urea-formaldehyde (UF) and phenol-formaldehyde (PF). Concerns about formaldehyde emissions during manufacture and after installation of panel products using UF adhesives, as well as price volatility of fossil fuel-based chemicals, have led to renewed interest in sustainable adhesives from biological sources, such as soybeans. Soybeans processed for oil production result in abundant quantities of low-cost defatted soy meal and flour. Soy flour and other soy protein products are

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bio-based, renewable, have very good wood bonding properties under dry conditions and can be formulated as no added formaldehyde adhesives with increased durability.

Water resistance and high temperature survivability are two areas that are of major concern in structural wood adhesives. In this study, we investigated whether soy products had the intrinsic properties needed to meet heat resistance requirements for structural adhesives. Water resistance has already been demonstrated by adhesives containing 50% or more soy flour [1]. Our ongoing research is focused on whether methods to achieve water resistance with soy using different cure chemistries hold the potential for future soy-based structural grade adhesives. Whereas requirements for wood adhesive performance at elevated temperatures, such as for use in attics, have been in place since at least the 1980s [2], additional standards have recently been implemented for structural wood adhesives requiring performance testing at high temperature, i.e. the ability to maintain structural integrity during a fire [3–6]. We wanted to know whether it was reasonable to expect that soy-based adhesives would be able to pass the heat resistance tests required for structural adhesives. The maximum temperature of current testing is 232 °C because at this temperature, severe and rapid strength loss occurs in solid wood [6,7]. Several articles show examples where commonly used adhesives (polyurethane, emulsion polymer isocyanate, and epoxy) have lost significant strength at or below this temperature [6,8]. On the other hand, formulated adhesives based on the milk protein casein have good performance in fire door applications, with one article even reporting wood degradation before adhesive decomposition [9]. We hypothesize that if soy protein is resistant to decomposition and retains mechanical properties at high temperatures, soy-based adhesives have a reasonable chance of achieving the performance necessary to meet heat resistance standards.

Several different commercially available soy products were investigated in this study. Soy flour is typically ground from hexane-extracted soy meal after drying and contains 4–13% of the soluble di- and trisaccharides sucrose, stachyose, and raffinose [10]. Soy concentrate is generally produced by ethanol extraction of soy meal, which removes low molecular weight soluble carbohydrates and peptides. Soy protein isolate is produced by aqueous extraction of soy flour from the nondispersible carbohydrates and proteins followed by precipitation of the main protein from the soluble fraction by pH adjustment to 4.2–4.5. Typical protein contents of soy flour, concentrate, and isolate are 57, 69, and 91% of dry weight, respectively [10].

One goal of our research is to extend fundamental understanding of wood adhesives and adhesion, while providing information valuable to industry. To this end, our goals in this study were to determine the effects of high temperatures on chemical and mechanical properties of soy, both as isolated protein and as less-processed fractions (concentrate and flour). A second goal was to compare the results to adhesives commonly used in the forest products industry using both approved test methods and other tests that provided additional insight.

2. Materials and methods

2.1. Materials

The soy adhesives selected were soy flour reacted with phenol-formaldehyde (designated Soy-PF) [1], soy flour cured with polyamidoamine-epichlorohydrin (SoyPAE) based on the patent of Li [11], and soy flour simply mixed with water (hereafter referred to as Soy Flour). Both SoyPF and SoyPAE had shown improved water resistance [1,11] compared to Soy Flour and we were interested in their high-temperature physical properties compared to commercially available adhesives. For comparison, we tested several commercially available adhesives: a modified poly(vinyl acetate), labeled heat resistant (PVAH), emulsion polymer isocyanate

(EPI), and a structural phenol-resorcinol-formaldehyde (PRF). In addition, we also tested casein, soy concentrate (Concentrate), soy protein isolate (Isolate), and isolate with polyamidoamine-epichlorohydrin curing agent (IsolatePAE).

The soy products were defatted, heat-treated soy flour (ADM Kaysoy 20/200), soy concentrate (ADM Arcon AF), and soy protein isolate (ADM ProFam 974) (Archer Daniels Midland, Decatur, IL, USA). The Soy Flour adhesive was one part soy flour mixed with three parts water, blended with a high shear mixer for 1 min, and held for 1 h prior to use. The SoyPF adhesive was described in example eight of US Patent 7345136 [12], which is a hybrid of 48% defatted soy flour and 50% phenol and formaldehyde that has shown good water resistance on strand-board test panels [1,13]. The casein protein was an acid-precipitated protein, casein protein polymer powder (BL330, American Casein Co., Burlington, NJ, USA), and not a formulated casein adhesive. The IsolatePAE contained 3.8 g PAE per 100 g isolate diluted in water to 5% solids. The SoyPAE adhesive is a plywood formulation that contains 37% total solids (solids ratio approximately five parts soy flour and one part polyamidoamine-epichlorohydrin [PAE]) (CA1300, Ashland-Hercules, Wilmington, DE, USA) on a solids basis.

The conventional adhesives were chosen to represent heat-sensitive adhesives (EPI and PVAH) and a heat-resistant adhesive (PRF). The EPI was a commercial product originally intended for structural applications but now targeted toward nonstructural uses. The PVAH was Franklin Titebond Original (Franklin International, Columbus, OH, USA). The PRF was 2.5 parts Cascophen LT-5210 resin to one part slurry of Cascoset FM-6210 paraformaldehyde hardener (slurry is 1:2, FM-6210:water) (Momentive, Columbus, OH, USA), mixed by hand for 1 min just prior to use. PRF was the only adhesive in this study recommended by the manufacturer for heat-resistant applications. Cascophen LT 5210 with a different catalyst has been approved as heat resistant [14] and thereby is allowed in structural finger-jointed lumber applications.

For tests using wood, our interest was in measuring adhesive properties. Thus, we used solid hard maple (*Acer saccharum*) or rotary-peeled hard maple veneer (except for the CSA 112.09 creep specimens see Section 2.5.) [15]. Given the high strength of hard maple, our tests would be more likely to measure adhesive properties rather than wood failure.

2.2. Evaluation of properties

We used both high-temperature standard qualification tests that provide a pass-fail criterion (ASTM D7247-hot shear [16] and CSA 0112.9-creep [15]) and other laboratory tests, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) [17], and automated bond evaluation system (ABES) shear test [18,19]. Compared to the standard qualification tests, these other laboratory tests are useful because they require smaller amounts of material and take less total technician and testing time, while providing more information about thermal and mechanical properties of the adhesive.

2.2.1. ABES, DSC, and TGA

The ABES (Adhesive Evaluation Systems, Corvallis, OR, USA) test samples were prepared from two rotary-peeled hard maple veneers (117 mm × 20 mm × 0.6 mm) with an overlapped and bonded area of 5 mm × 20 mm. Eighteen specimens for each adhesive were cold-pressed at 21 °C overnight (PRF, EPI) or hot-pressed at 120 °C for 2 min (Soy Flour) or at 160 °C for 4 min (SoyPF), then conditioned at 21 °C, 50% RH for a minimum of 1 week. Six specimens were tested at each of the three exposure conditions: 21 °C, 35 s at 230 °C to demonstrate the thermal softening just after reaching the target temperature, or 600 s (10 min) at 230 °C to show the degradation from heat after a longer exposure, without complete charring of the

wood. The specimens were loaded in tension to failure within 1 s of opening the hot platens. The peak load was recorded.

Neat adhesives for DSC and TGA were cured at the following temperatures before scanning: EPI at ambient overnight, PRF at 140 °C 1 h, SoyPAE at 120 °C 1 h, and SoyPF at 150 °C 1 h. Adhesives as well as neat soy flour were vacuum dried at 35 °C before scanning on a PerkinElmer DSC 7 (PerkinElmer, Waltham, MA, USA). The data were acquired and analyzed with Pyris™ Version 3.80 software (PerkinElmer, Waltham, MA, USA). Specimens were heated from 35 to 240 °C under nitrogen at a heating rate of 10 °C/min to obtain the heat flow and heat flow derivative curves.

TGA specimens (cured adhesives as well as neat soy flour, concentrate, isolate, casein, and 0.42-mm (40-mesh) ground maple) were dried at 105 °C for 1 h. Adhesives were then pulverized in a dental amalgamator. Heating profiles were collected on a PerkinElmer TGA-7 (PerkinElmer, Waltham, MA, USA) with Pyris software V3.5 using 5–10 mg specimens in a nitrogen environment. Specimens were held at 110 °C for 20 min and then ramped to 300 °C at 2 °C per min while recording the weight change.

2.2.2. DMA: 3-point veneer sandwich

Adhesives were applied between two rotary-peeled maple veneers, each approximately 0.6 mm thick. The selected adhesive was applied to one face of each veneer, rolled to distribute adhesive uniformly, and then pressed at 1.0 MPa. Table 1 shows the adhesive, spread rate, and press time and temperature for the tested samples. After conditioning for at least 24 h at 21 °C and 50% RH, the bonded veneers were cut to test specimens sized 12 (transverse) × 60 mm (longitudinal). Solid wood specimens were machined with an end mill to 1.2 mm and loaded on the tangential face. All DMA specimens were dried at 105 °C for at least one day, then stored in a desiccator over CaSO₄ until testing.

Storage and loss moduli profiles were collected using a Q800 DMA (TA Instruments, New Castle, DE, USA), fitted with the 3-point bend fixture with a 50-mm span. For the low-strain dynamic testing, a sinusoidally varying load was applied to the specimen that resulted in 0.01% strain at 1 Hz and static force automatically controlled to always exceed the dynamic load by 25%. This instrument mode is designated strain control with force track and is designed to ensure that the sample is always under load. The samples were held for 30–60 min at 35 °C before the temperature was increased at 5 °C per min to 230 °C and held for 30 min while recording storage modulus and loss modulus. The DMA test chamber was purged with dry air during testing. The number of specimens was limited because, despite many attempts, it was very difficult to produce bonded specimens without a natural curl or twist. Each trace in Figures 5–9 represents a replicate run (1–4 replicates per sample).

Table 1. Sample curing parameters for DMA and ASTM D 7247 tests.

Adhesive	Spread rate (g/m ²)	Target oven or bondline temperature (°C)	Time at target temperature (min)
Soy Flour	215	120	10
SoyPF	215	150	10
SoyPAE	215	120	10
PVAH ^a or EPI	215	21	480

^aCommercial product formulated for 'heat resistance,' includes poly(vinyl acetate).

2.2.3. DMA: impregnated glass fiber

Whatman glass fiber filter disks (type GFC, Whatman International, Maidstone, England) were cut into 50-mm-wide strips. These strips were saturated with a solution of the selected adhesive diluted to 5% solids, gently rolled with a rubber roller to remove excess solution, and then hung to air-dry overnight. Test specimens, approximately 6 mm × 30 mm, were cut with a razor blade from the treated strips, oven cured at 120 °C, and then stored in sealed bags. Specimens were tested in the Q800 DMA film tension fixture at 0.005% strain, 1 Hz (strain control with force track) and static force in excess of dynamic load by 25%. The specimens were equilibrated at 35 °C and held for 5 min to collect initial storage and loss moduli. The temperature was then increased at 5 °C/min to 230 °C and held for 30 min at 230 °C. The $\tan \delta$ data (Figure 8) were smoothed between 35 and 100 °C for presentation.

2.3. D7247: hot block shear test

Samples were prepared according to the ASTM D7247 method [16], using hard maple as the substrate and PRF, EPI, SoyPF, and Soy Flour as the adhesives for the bonded specimens, with curing parameters as shown in Table 1. Bondline target temperature during the heat resistance test was 230 °C. The specimens were held for 60 min after reaching the target temperature, removed from the oven, and immediately tested in block shear at 5 mm/min to failure. Ultimate load and percentage of wood failure were recorded. Time from opening oven door to failure was between 60 and 75 s. We found it physically impossible to move the samples from oven to test fixture, accurately position the samples, and complete the test in the 60 s as specified in the standard. ASTM D7247 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.' The standard leaves acceptance criteria to be established by the structural product manufacturer and code or qualification agencies. The interested reader is referred to the standard [16] for a discussion of the detailed calculations required.

2.4. CSA 0112.9: creep

Lodgepole pine (*Pinus contorta*) blocks were cut according to CSA 0112.9-04 Section 5.7 [15] and bonded with SoyPAE. Lodgepole pine is one of three standard softwood substrates specified for this test (Per CSA 0112.9 Appendix C, hard maple is not required because 'creep test results are not as dependent as block shear test results on a test's wood substrate.'). Assemblies were pressed at a platen temperature of 160 °C and 0.86 MPa until the bondline reached 120 °C, then held for 10 min to complete the adhesive cure. The four bonded assemblies were trimmed and cut into a total of 16 partial length specimens. After conditioning at 20 °C and 30% RH, four specimens were randomly selected for each test condition, then loaded (static load is applied by a spring) and heated to the temperature specified for the test. Conditions in Table 3 represent the temperature and load for each test. These conditions were under consideration for inclusion in future versions of the CSA standard. Time to collapse was recorded. In the specimen, the test load passes through multiple bondlines in shear. A specimen fails if it collapses or the total displacement is more than 0.6 mm for all the bondlines on a full-length specimen in 2 h of exposure.

3. Results and discussion

3.1. DSC/TGA/DMA

DSC and TGA have been used in the polymer industry for decades to characterize thermal transitions (DSC) and thermal decomposition (TGA). For wood adhesives, DMA has been particularly useful to describe bond strength development either in a veneer sandwich tested in bending [20–22] or on a glass fiber support (either torsion or tension) [23,24]. The veneer sandwich DMA technique is well suited for adhesive layers whose stiffness is much less than that of wood, for example, during curing or to detect softening of the adhesive relative to the wood veneer. The veneer sandwich technique also tests an adhesive bondline formed in contact with wood – the real condition in use. We found that for the stiffer adhesives, it was difficult to determine if the changes seen at high temperatures were caused by the adhesive or the thermal response of the veneer. Therefore, we also used glass fiber support to compare cured soy adhesives because, in this method, the glass fiber retains its original modulus, while the mat is weak enough that only the material response of the adhesive is measured. This test is suitable for adhesives that are fluid enough to penetrate into the structure of the mat and are relatively stiff during testing, such as PF [23,25]. We also attempted to form films of the soy products without support, but the films fractured or crumbled.

3.1.1. Differential scanning calorimetry

The heat flow profiles in Figure 1 and the derivative heat flow profiles in Figure 2 suggest that both as-received soy flour and SoyPF show steady increases in heat flow up to $\sim 200^\circ\text{C}$ and steady or declining rates of heat flow at higher temperatures. The constant heat capacity in as-received soy flour and SoyPF below 200°C suggests that no thermal transitions exist that would lead to softening in this region. There is a small peak in the derivative curve for heat-sensitive EPI around 75°C (Figure 2), suggesting a thermal transition, whereas there is no change at all in the heat-stable PRF across the entire temperature range.

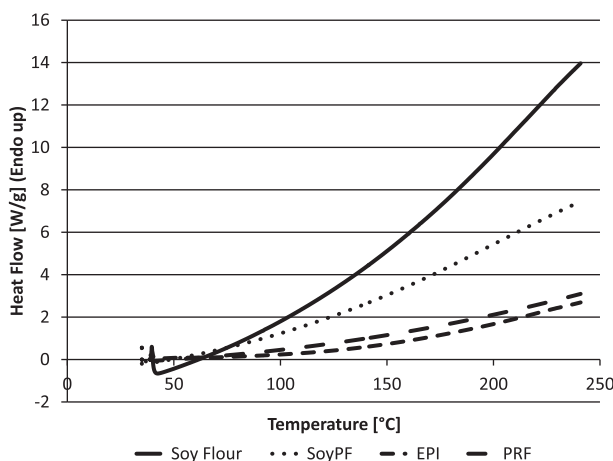


Figure 1. DSC heat flow for soy flour (as-received) and SoyPF adhesive compared to conventional adhesives: EPI and PRF.

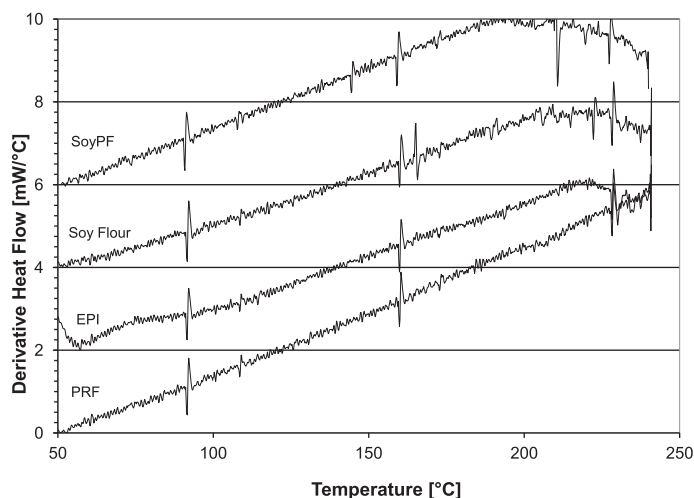


Figure 2. Comparison of derivative heat flow for soy flour (as-received), SoyPF, EPI, and PRF adhesives.

3.1.2. Thermogravimetric analysis

Figures 3 and 4 show the TGA weight vs. temperature profiles of casein, soy-based adhesives, and several commercial adhesives. In Figure 3, below 230 °C, Soy Flour and SoyPF weight losses were less than 4% but still greater than PRF, casein, or solid wood (maple). Further testing (Figure 4) showed that the relative weight retention increased in the order flour $\ll$ concentrate $\approx$ casein $<$ isolate, indicating that the soluble, lower molecular weight carbohydrates found in flour (which are removed in concentrate and isolate) are more susceptible to thermal decomposition than are the insoluble, presumably higher molecular weight carbohydrates in concentrate. The higher relative weight retention throughout the temperature profile for protein compared to concentrate and flour also showed that soy protein itself (isolate) is more heat stable than either the flour or concentrate. It also shows that the heat stabilities (toward

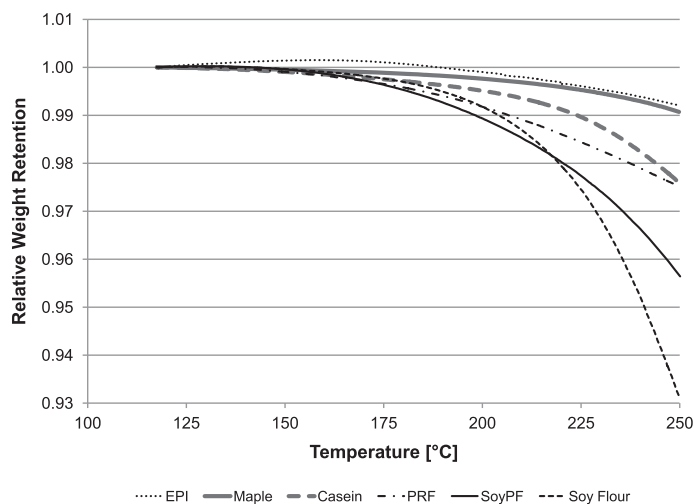


Figure 3. TGA: relative weight retention ($\text{mass}_t/\text{mass}_0$) for soy-based materials and commercial resins.

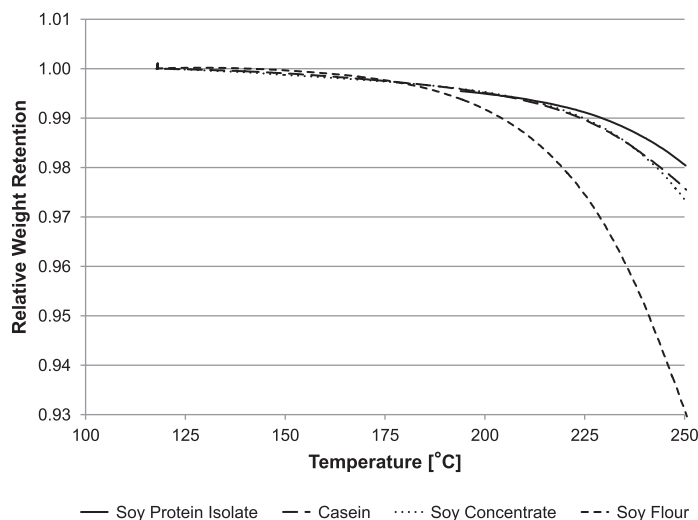


Figure 4. TGA: relative weight retention for soy fractions and casein protein.

decomposition) of soy concentrate and casein protein are very similar. Because of the observed sample darkening, we suspect carbohydrate dehydration and/or Maillard reactions may be causing the weight loss.

3.1.3. DMA: pre-cured veneer sandwich 3-point bend method

To make the change in properties with temperature more clear, and because wood is naturally variable, we present storage modulus data in the following figures as relative storage modulus (modulus at time t divided by modulus at time 0). The absolute storage moduli of the assemblies in Figure 5 were 13, 10, 9, and 14 GPa at 35°C with standard deviations 4, 2, 0.3, and

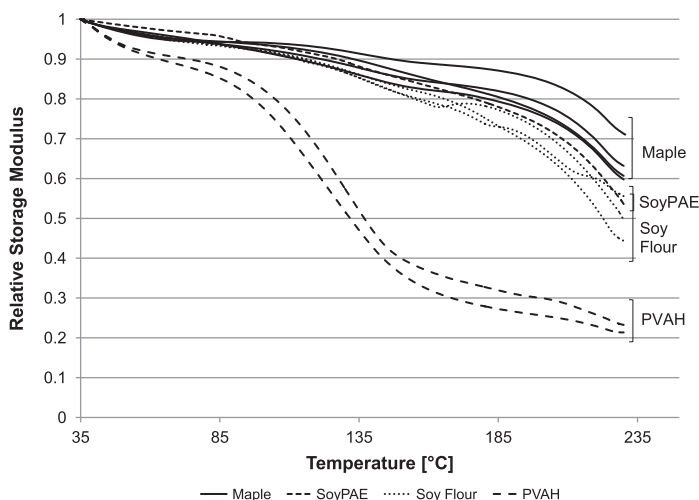


Figure 5. DMA relative storage modulus ($E'(t)/E'(t=0)$) vs. temperature for 2-ply maple veneer-adhesive assemblies and solid maple, heating rate 5°C/min. Multiple curves are shown for each adhesive type to indicate variability.

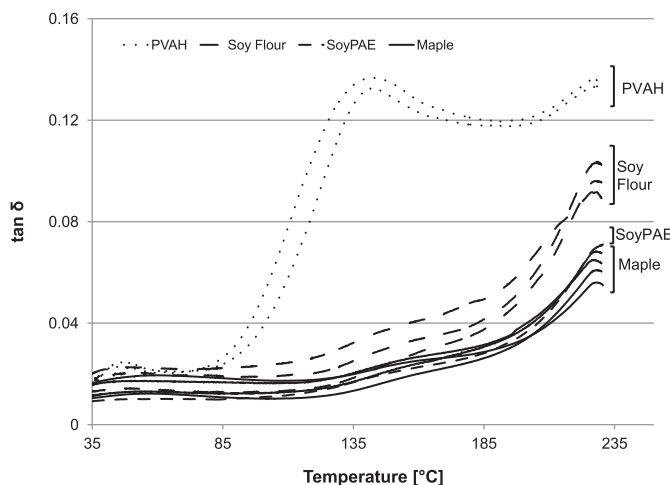


Figure 6. DMA $\tan \delta$ vs. temperature for 2-ply maple veneer-adhesive assemblies and solid maple, heating rate 5 °C/min. Multiple curves are shown for each adhesive type to indicate variability.

undetermined, respectively, for solid wood, Soy Flour, PVAH, and SoyPAE. Note that only one specimen of SoyPAE was testable.

PVAH is a reference material presented to evaluate the sensitivity of the DMA veneer 3-point bend method. In Figure 5, a large decrease in storage modulus is visible at 135 °C. At 160 °C, the assemblies glued with PVAH retained, on average, 34% of their original stiffness, higher than would be expected if the PVAH had lost all structural integrity. Because the stiffness of a solid beam is proportional to the thickness cubed, the stiffness of the two unbonded veneers with no adhesive contribution would be 21% of original stiffness (two beams each with $(1/2)^3$ of the full beam stiffness or 1/4 of the solid wood stiffness retention). This theoretical calculation assumes that two beams would have no interaction at the interface, yet real materials have at least surface asperities and a frictional interaction, as well as any residual strength left in the PVAH.

The storage modulus of Soy Flour- and SoyPAE-bonded specimens appears to decline more than solid wood, particularly above 180 °C. While solid wood at 230 °C retained 64% of its original modulus, SoyPAE, Soy Flour, and PVAH retained 53, 50, and 22%, respectively. This suggests softening of the Soy Flour in this region. While the $\tan \delta$ (i.e. damping or energy dissipation in the DMA test) of Soy Flour is also greater than wood at temperatures above 160 °C, it is nowhere near the values observed for PVAH in Figure 6. The $\tan \delta$ of the SoyPAE laminated specimen is very similar to solid wood throughout the entire curve. The steeper rise in $\tan \delta$ of SoyPAE above 210 °C suggests that the SoyPAE plasticizes more quickly than wood in this region, though the evidence is limited.

3.1.4. DMA: impregnated glass fiber

Adhesives were also tested while being supported on glass fiber mats, intended to allow measurement of pure adhesive properties without wood–adhesive interactions. Figures 7 and 8 show the storage modulus and $\tan \delta$ profiles, respectively, for Soy Flour, concentrate, and isolate, as well as casein. We deposited a dilute adhesive solution on a glass fiber mat. When the solution dries, the polymer molecules connect the glass fibers at fiber crossings. The benefit of this approach is that the applied load transfers from fiber to fiber either through the

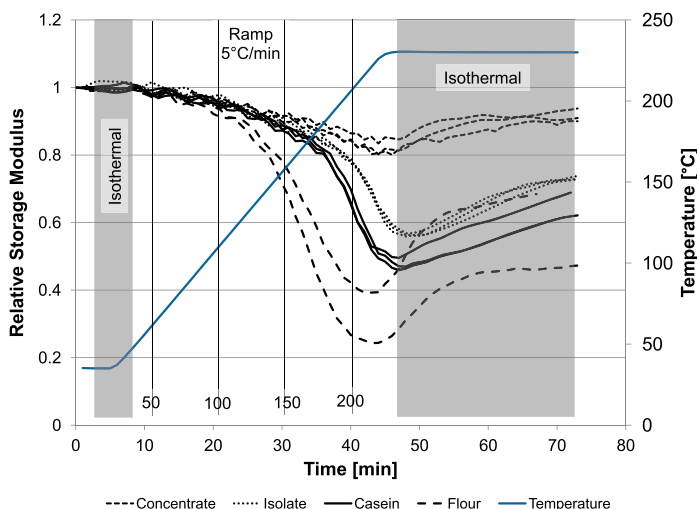


Figure 7. DMA relative storage modulus ($E'(t)/E'(t=0)$) of casein protein and various soy fractions supported on glass fiber filter paper, tested in tension, during 5 °C/min ramp and 30-min hold. Relative storage modulus vs. time is plotted to show the changes that occur during the temperature rise and hold at 230 °C. Multiple curves are shown for each adhesive type to indicate variability.

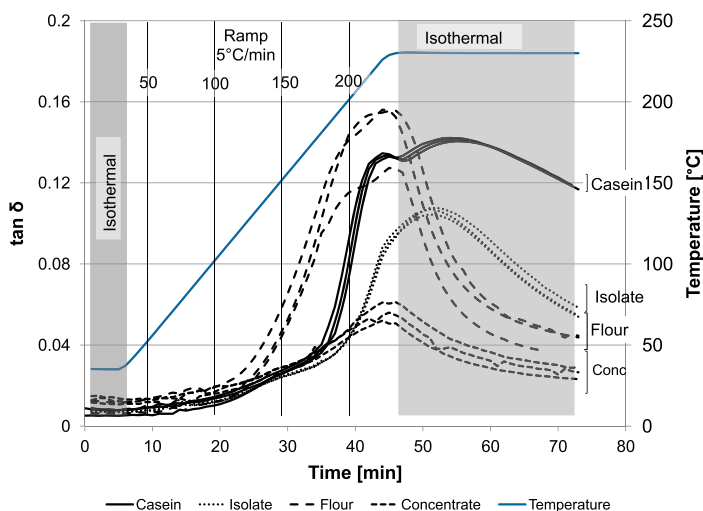


Figure 8. DMA $\tan \delta$ of casein protein and various soy fractions supported on glass fiber filter paper, tested in tension, for 5 °C/min ramp and 30 min hold. Multiple curves indicate variability.

adhesive layer or through glass fiber entanglements. This allows the method to measure the response of adhesive independently from the response of the wood (as seen in the veneer sandwich DMA). We note that the glass mat is very weak on its own (storage modulus of 100 MPa, constant throughout the temperature ramp). A drawback of this method is that the cross-sectional area of the adhesive bonds with the glass fiber matrix is poorly defined (varies from specimen to specimen); thus, the storage modulus, which is dependent on cross-sectional area, is also variable. As $\tan \delta$ and modulus relative to initial modulus at 35 °C are dimen-

sionless, we expect them to be less affected by variations in amount of adhesive deposited and, therefore, more reproducible from sample to sample.

We noted a small periodic oscillation in the mechanical properties shown in Figures 7 and 9. This was determined to be caused by the high heating rate and low mass of the specimen. The manufacturer recommends placing a fine mesh screen around the sample to reduce this effect.

Because of the high temperatures, as well as the dark and brittle nature of Soy Flour specimens at completion of these experiments, we suspect that the tested material underwent irreversible thermal change. We attribute the increasing modulus and decreasing $\tan \delta$ during the final isothermal portion of Figures 7 and 8 to Maillard and dehydration reactions. We also note that the Soy Flour exhibits the largest recovery of stiffness at high temperatures and also has the largest mass loss in TGA (Figures 3 and 4), suggesting again that the easily extractable carbohydrates in soy are more sensitive to thermal degradation than proteins.

The loss in storage modulus for soy isolate at 200 °C (Figure 7) is consistent with the softening of plastic made from extruded soy protein at ~200 °C reported previously [26]. We saw a smaller change in modulus at this temperature than is reported for soy protein plastics, as would be expected from the large volume fraction of stiff glass fibers in our samples. Another way to compare our data to the literature is to look at the denaturation temperature of soy proteins. Since both denaturation temperature and T_g represent the onset of coordinated motion of polymer segments, they should have similar values. Literature values of soy protein denaturation temperature vary from 83 °C when water saturated to 190 °C at 1% moisture [26].

In comparing the performance of soy flour, concentrate, and isolate, it is important to note that the protein conformation is likely being altered in addition to changes in composition during the purification processes for the concentrate and isolate. The ethanol extraction used for making the concentrate not only removes the low molecular weight sugars and proteins, but is also known to denature the protein. Removal of these sugars can provide greater stability, but we also observed that concentrate had lower initial stiffness. The isolate has most of the carbohydrate removed and this may reduce the Maillard reaction that can provide greater heat resistance. The softening temperature of the soy (Figure 7) decreases in the same order as the protein content: isolate > concentrate > flour. It seems reasonable that the Soy Flour has the lowest softening temperature, as it contains approximately 10% low molecular weight sugars [10] that could act as plasticizers. Similar effects have been observed before: for instance, the T_g of wheat gluten protein dropped 30° upon addition of 9% sorbitol, a glucose derivative [27].

The magnitudes of the $\tan \delta$ peaks (Figure 8) are in the same order as the relative drop in modulus (Figure 7): concentrate > isolate > casein > flour. Concentrate had a very small change in modulus and a correspondingly small $\tan \delta$ peak, whereas Soy Flour and casein had the largest change in modulus and $\tan \delta$. In addition to information about the transition itself, the height of the $\tan \delta$ peak in a composite such as these glass mats is, in part, dependent on the volume fraction of material undergoing transition [28]. Therefore, some of the difference in $\tan \delta$ peak intensity would be expected from variations in adhesive application rates on the glass fiber.

Figure 9 shows the effect of 3.8% PAE addition on isolate and 20% PAE and formulation additives on flour. Typically, the T_g of a miscible blend of polymers follows the Flory-Fox equation, which is essentially a rule of mixtures taking into account the T_g of the individual polymers [29]. Whereas the T_g of cured PAE is dependent on curing conditions, 60 °C is a typical value [30]. Therefore, we should expect addition of PAE to shift the thermal softening to lower temperatures. In a comparison of Figures 7 and 9, the onset of thermal softening is

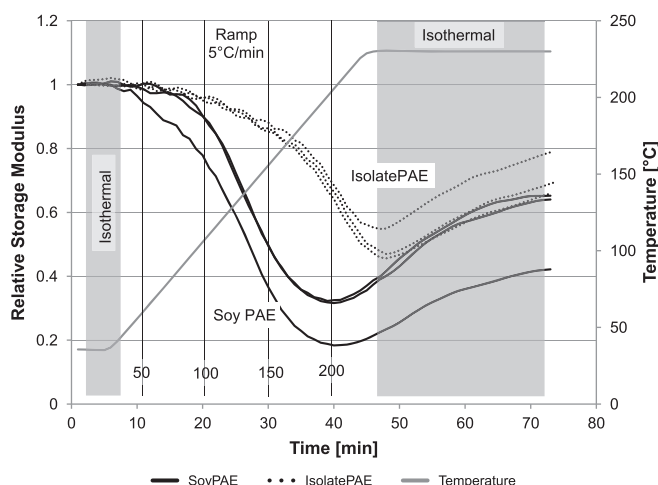


Figure 9. DMA relative storage modulus profiles ($E'(t)/E'(t=0)$) for SoyPAE and IsolatePAE during 5 °C/min ramp and 30 min hold. Multiple curves indicate variability.

clearly earlier in SoyPAE vs. Soy Flour, but not so in IsolatePAE vs. Isolate. This is consistent with the low (3.8%) PAE content in IsolatePAE.

It is interesting to note the differences in behavior of SoyPAE when supported on glass vs. in an actual bondline (Figures 9 vs. 5 and 6). SoyPAE exhibited nearly a 70% decrease in relative storage modulus around 150 °C on glass and then stabilized. In an actual bondline (Figures 5 and 6), there was very little apparent loss in modulus: SoyPAE assemblies softened slightly more than solid maple around 180–220 °C. Polymers can have a depressed T_g as a result of interactions with the substrate, but this only occurs within nanometers of the substrate [31]. Small changes in T_g have been reported; for instance, a 5 °C increase in T_g has been observed in a cross-linked PVAc when tested on wood as opposed to neat adhesive [32]. In our case, we suspect that the actual chemistry of the adhesive in the bondline may be different than the neat adhesive because of differential migration of low molecular weight components from adhesive into the wood, effectively removing the plasticizer from the adhesive. This highlights the original reason we chose the sandwich technique, i.e. to measure the properties of the adhesive as they appear in a real bondline. If the difference between SoyPAE modulus retention on glass vs. wood (Figures 9 vs. 5) is real, then we would expect this adhesive to perform much better in practice than the data in Figure 9 would suggest.

Before completing the discussion of properties as measured by DMA, it is important to note that stiffness is not the same as strength. Stiffness is measured at very low loads, and whether the loss in stiffness affects load-bearing capacity depends on whether the polymer segmental interactions freed at a thermal transition, such as T_g , are critical to carrying the load. It may be that load bearing is dominated by the long chain segments that are still frozen. The DMA gives information about the molecular structure of the adhesive, which increases understanding of the system, but whether the adhesive will bear a load at a given condition must be determined by actual testing at high loads, which we will now address.

3.2. Hot ABES

ABES uses bonded overlapping veneer specimens pulled in tension along the grain of the veneer and parallel to the short dimension of the bond [19]. Originally designed for studying

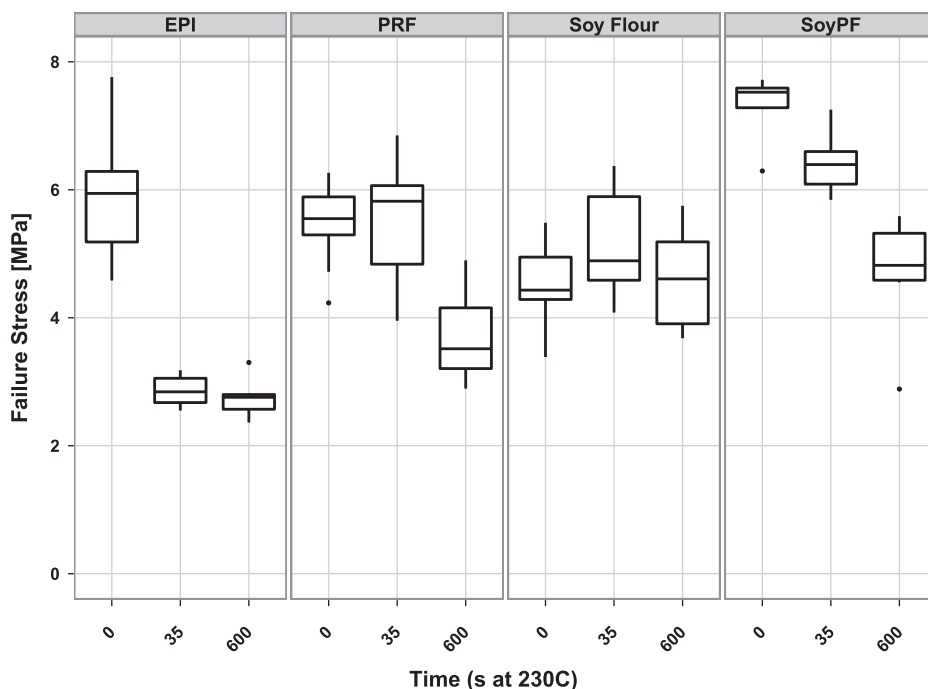


Figure 10. ABES results for several commercial and soy adhesives: boxplot of failure stress for samples unheated (0) and heated for 35 and 600 s at 230 °C.

cure kinetics, we used it as an accelerated test for high temperature bond performance. ABES showed good performance of soy-containing adhesives (Soy Flour and SoyPF) at 0, 35, and 600 s exposure to 230 °C when compared to PRF, a heat-resistant adhesive (Figure 10). EPI showed a dramatic drop in strength at 35 s exposure, long before the wood degraded, highlighting the heat sensitivity of this material. PRF showed a drop in performance at 600 s but little change at 35 s. At 600 s exposure, the wood failures for PRF and SoyPF were 100% and the wood was scorched. This suggests that these data points were dominated by wood strength rather than adhesive strength and the wood was losing strength faster than these adhesives.

3.3. D7247: hot block shear test

Shear strength results from the D7247 test are summarized in Table 2. The severity of the test is indicated by the fact that solid wood retained only 25% of its unheated strength. As

Table 2. Shear strengths of various soy-based and commercial wood adhesives (ASTM D7247).

Shear strength (MPa)	Maple		PRF		EPI		Soy Flour		SoyPF	
	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
Average	18.8	4.7	19.6	4.7	14.5	0.8	15.6	3.1	15.6	4.6
SD	3.5	0.9	2.2	0.8	2.0	0.2	4.4	1.0	4.4	1.2
<i>n</i> *	37	33	10	10	5	5	10	10	10	10
% of cold strength		25		24		5.6		20		38

**n*: number of specimens.

expected, PRF performed well and EPI failed badly. SoyPF, the soy adhesive closest to one likely to be tried in structural applications, passed the test easily with 38% strength retention. It should be noted that when the specimen is moved from the oven to the test machine, it begins to cool immediately from the outside in. Soy Flour failed the test (20% strength retention), yet its retention was close enough to passing to indicate promise for future improvements. Some of these Soy Flour failures were observed to have wood failure at the perimeter of the failed region and cohesive failure in the core. As it took 60–75 s between opening the oven door and failure, some cooling must have occurred at the edges of the specimen (and the bondline) before failure. This observation is consistent with a suggestion of Soy Flour plasticity in Figure 6 where the Soy Flour $\tan \delta$ value was higher than both solid wood and SoyPAE at 230 °C.

3.4. Hot creep test

In this creep test, specimens rarely fail by excessive creep: specimens either pass or collapse from cohesive or interfacial failure. Therefore only time to collapse was recorded for these specimens. The results presented in Table 3 show that the time to collapse for the SoyPAE specimens exceeded the 2-h survival criterion of the current test and showed promising performance even under more severe conditions.

The contrast between creep performance (Table 3) and DMA of SoyPAE on glass fiber (Figure 9) is interesting. Figure 9 shows a 70% decline in stiffness between room temperature and 200 °C, yet the bonded assemblies performed very well under high loads at 180, 200, and even 220 °C. We suspect that this is because the chemistry of the actual bondline is somewhat different from the neat adhesive chemistry. Possibly, low molecular weight components of the adhesive migrate into the wood because bondlines are thin and wood is porous, leaving behind high molecular weight components to carry the load and better resist softening at high temperatures. Another reason could be that the SoyPAE softened in the creep test at the same temperature as in the glass fiber DMA, but the adhesive had enough strength to carry load even after the softening event. Whatever the reason, the performance of real bondlines at high temperatures was considerably better than expected based on softening observed for a neat adhesive in DMA.

Under the most taxing conditions proposed, 220 °C and 1.6 MPa load, three of the four SoyPAE specimens lasted between 1.66 and 1.92 h, very close to the 2 h needed to pass. Because the D7247 bondlines typically took ~1 h to reach target temperature and the creep specimen geometry allows better heat transfer to the bondlines, we conclude that the creep specimens were able to carry these loads at, or very close to, 220 °C for an extended period before collapsing. We expect that because the SoyPAE carried the load for an extended period, it is not unreasonable to believe that formulation technology could be used to make soy adhesives pass even the most stringent proposed test condition, 220 °C and 1.6 MPa.

Table 3. Time to collapse for creep test specimens (CSA 0112.9 Section 5.7 using SoyPAE).

Oven temperature (°C)	Load (MPa)	<i>n</i> *	Time to collapse (h)
180	2.1	4	>3 (all)
180	2.5	4	<i>0.75, 1.57, 2.17, >3</i>
200	2.1	4	<i>1.40, 2.17, >3, >3</i>
220	1.6	4	<i>1.35, 1.72, 1.77, 1.88</i>

Notes: Bold=pass (collapse in >2 h), italics=fail (collapse in <2 h).

**n*: number of specimens.

4. Summary and conclusions

Knowledge about the high temperature (i.e. fire) performance of soy adhesives is important if soy-based adhesives are ever to be used in structural applications. Since our goal was to add to the fundamental knowledge of bio-based adhesives, we tested soy flour and its derivatives, soy concentrate and isolate, as well as formulated soy-based adhesives and casein. This allowed us some insight into how different soy flour components and different processing might affect heat resistance properties. In addition to standardized product performance tests, we developed or extended several small-scale tests to allow more rapid testing and provide information beyond pass-fail.

Soy protein isolate shows similar thermal decomposition in TGA and thermal softening in DMA when compared to casein, which is used as an adhesive for fire-resistant doors. Higher weight loss at high temperatures and lower softening temperatures were associated with the presence of low molecular weight carbohydrate in the soy. Whereas Soy Flour and a formulated soy flour-based adhesive show thermal softening at around 150–160 °C when tested using glass fiber-supported DMA, the formulated adhesive in real wood bonds performed quite well in DMA tests and under creep conditions (static load at high temperature), maintaining 2.1 MPa of shear stress at 180 °C for over 2 h. This suggests that the adhesive in a wood bond is physically or chemically different from the adhesive tested on glass fiber. We suspect low molecular weight components of soy flour migrate into the wood, but not into glass.

SoyPF, the 50% soy flour adhesive similar to what might be used for structural applications, easily passed ASTM D7247. This confirmed (with a different soy flour formulation) the conclusions from creep testing: high soy content adhesives can deliver excellent performance. The PRF performed well and the EPI performed poorly, as expected. Whereas unmodified Soy Flour adhesive did not pass, we find it encouraging that it gave performance so close to solid wood results. We believe our findings show that with proper adhesive formulation, soy protein, flour, and concentrate are viable materials for use as a fire-resistant adhesive.

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References

- [1] Wescott JM, Frihart CR, Traska AE. *Journal of Adhesion Science and Technology*. 2006;20:859–73.
- [2] ASTM Standard D4502-92. Standard test method for heat and moisture resistance of wood-adhesive joints. West Conshohocken, PA: ASTM international. 2004;Vol. 15.06.
- [3] ASTM Standard D7470-08. Standard practice for evaluating elevated temperature performance of end-jointed lumber studs. West Conshohocken, PA: ASTM International. 2008;Vol. 04.10.
- [4] ASTM Standard D5456-09a. Standard specification for evaluation of structural composite lumber products. West Conshohocken, PA: ASTM International. 2009;Vol. 04.10.
- [5] ICC. Acceptance criteria for prefabricated wood joists-AC14. Whittier, CA: ICC Evaluation Service; 2007.
- [6] Yeh B, Herzog B, Ipsen P, Brooks R. In: Frihart C, editor. *Proceedings of the International Conference on Wood Adhesives 2005*. Madison (WI): Forest Products Society; 2005. 195–201.
- [7] Milner HR. *Journal of Adhesion Science and Technology*. 2006;20:897.

- [8] Frangi A, Fontana M, Mischler A. *Wood Science and Technology*. 2004;38:119.
- [9] Lambuth A. In: Pizzi A, Mittal KL, editors. *Handbook of Adhesive Technology*. 2nd ed. New York (NY): Marcel Dekker; 2003. 457–77.
- [10] Liu K. *Soybeans Chemistry, Technology and Utilization*. Gaithersburg, MD: Aspen; 1999.
- [11] Li KC. US Pat. 7252735. 2007.
- [12] Wescott JM, Frihart CR. US Pat. 7345136. 2005.
- [13] Wescott JM, Traska AE, Frihart CR, Lorenz LF. In: Frihart C, editor. *Proceedings of the International Conference on Wood Adhesives*. Madison (WI): Forest Products Society; 2005. 263–9.
- [14] American Lumber Standards Committee, Summary of HRA Approvals by BOR. Available from: http://www.alsc.org/greenbook%20collection/LumberProgram_Approved_Heat_Resistant_Adhesives.pdf [Accessed July 15, 2011].
- [15] Canadian Standards Association, CSA O112.9-Evaluation of adhesives for structural wood products (exterior exposure), Canadian Standards Association, Mississauga, Ontario, Canada, 2004.
- [16] ASTM Standard D-7247-07a. Standard test method for evaluating the shear strength of adhesive bonds in laminated wood products at elevated temperatures. West Conshohocken, PA: ASTM International. 2008;Vol. 15.06.
- [17] Menard KP. *Dynamic mechanical analysis: a practical introduction*. Boca Raton, FL: CRC Press; 1999.
- [18] Chowdhury MJA, Humphrey PE. *Wood and Fiber Science*. 1999;31:293–9.
- [19] Humphrey PE. In: Frihart C. editor. *Proceedings of the International Conference on Wood Adhesives 2009*. Madison (WI): Forest Products Society; 2010. 203–13.
- [20] Laigle Y, Kamoun C, Pizzi A. *Holz als Roh-und Werkstoff*. 1998;56:154–4.
- [21] Pizzi A. *Journal of Applied Polymer Science*. 1997;63:603–17.
- [22] Wang JW, Laborie MPG, Wolcott MP. *Thermochimica Acta*. 2007;465:18–24.
- [23] Follensbee RA, Koutsky JA, Christiansen AW, Myers GE, Geimer RL. *Journal of Applied Polymer Science*. 1993;47:1481–96.
- [24] Steiner PR, Warren SR. *Holzforschung*. 1981;35:273–8.
- [25] Christiansen AW, Follensbee RA, Geimer RL, Koutsky JA, Myers GE. *Holzforschung*. 1993;47:76–82.
- [26] Wool RP, Sun XS. *Bio-based Polymers and Composites*. Amsterdam: Elsevier Academic Press; 2005. 292–326.
- [27] Pouplin M, Redl A, Gontard N. *Journal of Agriculture and Food Chemistry*. 1999;47:538–43.
- [28] Wetton R. In: Dawkins JV, editor. *Developments in Polymer Characterization*. Amsterdam: Elsevier Science Publishers; 1986. 179.
- [29] Hiemenz P, Lodge T. *Polymer Chemistry*. Boca Raton, FL: CRC Press; 2007.
- [30] Allen A. Research Chemist, Ashland Water Technologies. Personal communication. 2011.
- [31] Tsui OKC, Russell TP, Hawker CJ. *Macromolecules*. 2001;34:5535–9.
- [32] Lopez-Suevos F, Frazier CE. *Holzforschung*. 2005;59:435–40.