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ORIGINAL PAPER

Chromatographic Analysis of the Reaction of Soy Flour with Formaldehyde and Phenol for Wood Adhesives

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Abstract The desire to make more biobased and lower-cost bonded wood products has led to an interest in replacing some phenol and formaldehyde in wood adhesives with soybean flour. Improved knowledge of the soy protein properties is needed to relate resin chemistry to resin performance before and after wood bonding. To expose the soy protein's functional groups, it needs to be disrupted, with minimal hydrolysis, to maximize its incorporation into the final polymerized adhesive lattice. The best conditions for alkali soy protein disruption were to maintain the temperature below 100 °C and react the soy flour with sodium hydroxide at pH 9–12 for about 1 hour. A gel permeation chromatography procedure was optimized to determine conditions for selectively breaking down the high molecular weight soy protein fragments that contribute to high adhesive viscosity. This method and extraction data were used to evaluate the reaction of the disrupted soy flour protein with formaldehyde and phenol to provide a stable adhesive. The results were used to develop more economical adhesives that are ideally suited for the face section of oriented strandboard.

Keywords GPC · HPLC · Phenol–formaldehyde · Soy flour · Wood adhesive

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Introduction

Although soybean oil has many non-food uses, the remaining flour (ground meal) has fewer non-food uses. With the advent of biodiesel consuming large quantities of soy oil the need for value added soy flour products is at an all time high. Soy flour use as a wood adhesive has actually declined over the years. It has been displaced by petroleum-based phenol–formaldehyde (PF) and urea-formaldehyde (UF) adhesives starting in the 1940s because of their superior durability, viscosity, and pot life. By the 1960s, PF and UF adhesives also offered a lower price. Increases in petroleum prices, concerns about formaldehyde emissions, and safety issues with phenol, in general, have spurred new chemistry studies to use soy flour for producing more water-resistant adhesives that can be used with current manufacturing practices.

Kreibich demonstrated the viability of soy adhesive technology in the end jointing of green lumber [1]. In this technology, the hydrolyzed soy protein isolate and a phenol–resorcinol–formaldehyde (PRF) adhesive are applied to separate ends of two finger-jointed boards, which are then joined together in what is now known as the "honeymoon" process. However, this technology requires keeping the soy portion separate from the PRF adhesive, because of high reactivity between the two components. Thus, pre-blending these two components would provide an adhesive with a short potlife (time that an adhesive maintains its useful properties prior to application).

Hse demonstrated the viability of using a soy flour/PF system for panel boards [2], using large amounts of caustic materials, which resulted in very high pH values, and typically employing soy flour levels of 30% substitution for phenol. Kuo and others have also developed a new soy flour/PF system, but this technology is somewhat limited

due to its high viscosity and low-solids adhesives, with a short potlife [3]. Li developed a plywood adhesive containing soy protein reacted with a typical paper wet-strength additive, such as the poly(amidoepichlorohydrin) (PAE) Kymene® [4]. Despite these advances, there is a need for a higher soy content adhesive using alkali disruption of low cost soy flour that has the stability and sprayability to be used with current oriented strandboard (OSB) production technology.

If soy adhesives are to make a comeback, they must overcome some, if not all, of these performance issues. The primary problem with traditional soy adhesives is that alkali-disrupted soy flour retains its water solubility after the curing/drying process [5]. Thus, the adhesive weakens when subjected to moisture, leading to bond failure. The poor water durability of many soy-based adhesives is primarily due to a limited amount of crosslinking in the cured adhesive. A more crosslinked structure should improve bond durability under wet conditions.

Bond durability is possible with soy flour-based adhesives. The first stage in all these processes is to disrupt the native protein structure usually by using caustic and heat. This opens up the side chain groups to make the side chains available for bonding to the wood or crosslinking chemicals. The term disruption is used because with our process it is not clear whether the protein is just being denatured or if some actual hydrolysis takes place. It is well known that at higher temperatures, hydrolysis does take place during the caustic treatment [6]. The protein in soy flour contains many reactive side-chain amino acid groups (25% to 30% of total amino acids) that have the potential to react with phenolic adhesives [5]. It is this reactive nature that provides soy flour adhesive systems with the ability to form thermoset networks with a suitable crosslinking agent. Furthermore, not only can the protein fraction of soy flour react with PF crosslinking agents, the carbohydrate fraction may also contribute to additional durability through copolymerization. This allows the use of soy flour rather than high-priced protein isolates for the preparation of these novel adhesives.

Analysis of the soy flour protein is necessary for understanding the reaction of soy flour with caustic and other components to produce a durable adhesive. Most analyses of soy flour adhesives have been limited to viscosity and gel time, which do not give enough useful information about the chemistry of the processes. Vijayendran and Clay [6] used gel permeation chromatography (GPC) to analyze disrupted/hydrolyzed soy flour that was combined with PRF to bond wood, but they reported only peak molecular weight. They hydrolyzed soy flour with sodium carbonate at 100 °C for 24 h and obtained a peak molecular weight of 11.6 kDa. They also hydrolyzed soy protein at 100 °C for 14 h, which resulted in a peak molecular weight of 22.0 kDa. The soy protein adhesives that they formulated were evaluated in finger jointing Douglas-fir lumber. Bond strength was found to increase with peak molecular weight, as expected. Increasing the protein reactivity (higher amine levels) through further hydrolysis of the protein led to lower, not higher, bond strength, probably due to a decrease in the final resin crosslink density.

The proteins in soy flour are complex mixtures of four characteristic fractions, illustrated by the ultracentrifuge pattern (2S, 7S, 11S, and 15S) and range in molecular weight from 8 to 700 kDa. The range in molecular weight and approximate distribution (%) of these fractions are as follows: 2S, 8–50 kDa, 8%; 7S, 100–180 kDa, 35%; 11S, 300–350 kDa, 52%; and 15S, 600–700 kDa, 5%. The 7S and 11S fractions consist of several subunits each with molecular weights from 22 to 70 kDa [7]. Complete disruption breaks these fractions into individual protein chains and alters the three-dimensional structure of the proteins. Caustic disruption can also lead to some hydrolysis of the proteins. In this paper, mild conditions will be referred to as disruption and more severe conditions will be referred to as hydrolysis, to correspond to the extent of each process.

To further study the relationship between disrupting and modifying conditions and the molecular weight of soy proteins for bonding wood, we modified the GPC procedure used by Vijayendran and Clay [6] for analyzing soy proteins that used phosphate buffered saline at pH 7. Our changes were to make the chromatography conditions closer to the reaction conditions to minimize changes in the protein during the analysis and keep the phenolic components solubilized during the analysis. The changes included reducing the buffer concentration and increasing the pH to 9. Our studies also emphasized number and weight average molecular weight rather than peak molecular weight, as well as changes in specific peaks. The development of the new HPLC method and its use for understanding the differences in the disruption of soy flour using our methods compared to those in the literature are discussed.

Experimental Procedures

Materials

Soy flour produced by an extrusion process was supplied by Oelwein Custom Commodities (Oelwein, Iowa). It contained 44% protein, 10% residual oil, and 5% ash, and was ground such that 90% passed through a 100-mesh (149 μm) screen. Although not reported here, we have found that the type of soy flour is not a highly critical factor in this process.

Phenol, formaldehyde, and sodium hydrogen phosphate were purchased from Aldrich Chemicals (Milwaukee, Wisconsin). Sodium hydroxide, sodium carbonate, and sodium bisulfite were purchased from Fisher Scientific Co. (Fair Lawn, New Jersey). The protein standards were purchased from Sigma (St. Louis, Missouri). Commercial PF and wood strands were donated by an oriented strandboard (OSB) manufacturer. Our analysis showed the wood was composed of black gum, southern yellow pine, and soft maple, with trace amounts of red oak. Strand size was approximately 7.5 by 1.5 by 0.08 cm. Strand size was typical of a commercial product, except that fines were removed.

GPC of Soy Proteins

The disrupted soy proteins were analyzed by GPC on a Superose 12 (10/300 GL) column (310 × 10 mm i.d.) (Amersham Bioscience, Piscataway, New Jersey) [8]. The mobile phase was 0.05 M Na_2HPO_4 (adjusted to pH 9 with 50% NaOH) in HPLC grade water (Milli-Q System; Millipore, Bedford, Massachusetts) containing 20% acetonitrile at a flow rate of 1.0 mL/min and 25 °C. A Hewlett–Packard 1050 series HPLC (Agilent Technologies, Wilmington, Delaware) with autosampler and variable wavelength detector modules was used for analysis. Hewlett–Packard 2D ChemStation plus GPC analysis software was used for data acquisition and determination of molecular weight. The eluted compounds were detected by UV absorbance at 220 nm. Samples of soy–PF adhesives were weighed into vials and dissolved in the mobile phase. Sample solutions were filtered through 0.2-μm disposable PTFE membrane filters (Supelco, Bellefonte, Pennsylvania) before injection. Using the external standard method, the chromatographic system was calibrated with the following protein standards, dissolved in the buffer solution: thyroglobulin, 669 kDa; bovine serum albumin, 66 kDa; carbonic anhydrase, 29 kDa; cytochrome C, 12.4 kDa; aprotinin, 6.5 kDa; and valyltyrosine, 280 Da. The peak times of the standard compounds divided by the void time of the column were plotted versus the logs of the molecular weights (Fig. 1). The R-squared value for this relationship was obtained by exponential regression.

HPLC of Soy Flour–PF Adhesives

A Hewlett–Packard 1050 Series HPLC (Agilent Technologies, Wilmington, Delaware) with autosampler, variable wavelength detector, and 2D ChemStation software was used for analysis of phenolic components [9]. Twenty microliters of each sample was filtered through a 0.2-μm PTFE filter and analyzed on an Inertsil ODS-3 column (250 × 4.6 mm, 5 μm particle size) (Alltech Associates, Deerfield, Illinois) using 10% acetonitrile in water (containing 0.1 % H_3PO_4) for 3 min, with a gradient from 10% to 80% acetonitrile in 23 min at 1.0 mL/min. The eluted compounds were detected by UV absorbance at 273 nm. The phenol was quantified by adding a known amount of 3-hydroxybenzyl alcohol as an internal standard. The relative response factors for phenol and 3-hydroxybenzyl alcohol were calculated with solutions of known composition.

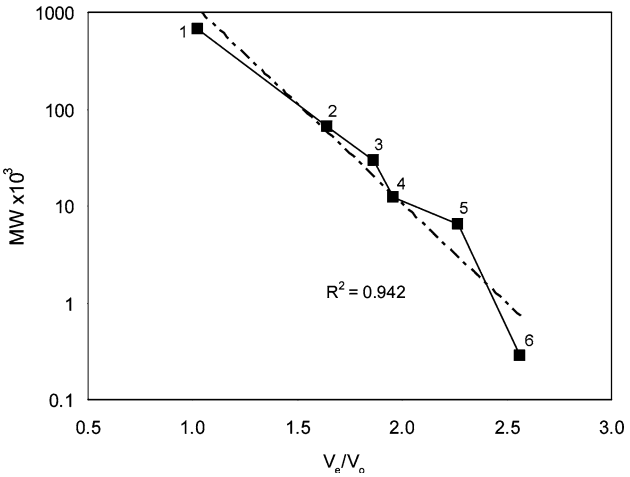

Fig. 1 GPC calibration of Superose 12 column with six protein standards: (1) thyroglobulin, (2) bovine serum albumin, (3) carbonic anhydrase, (4) cytochrome C, (5) aprotinin, and (6) valyltyrosine. MW is molecular weight; V_e/V_0 is elution volume divided by void volume of column

Determination of Free Formaldehyde

Determination of free formaldehyde was a modification of the hydroxylamine hydrochloride method described in Walker [10]. A 1- to 2-g sample of the modified soy flour or soy flour PF adhesive was weighed into a small beaker, and 10 mL of distilled water was added with stirring. The sample was titrated to pH 4.0 with standardized 0.1 N hydrochloric acid. Ten mL of 0.50 N hydroxylamine hydrochloride, previously adjusted to pH 4.0, was added and the solution was stirred for at least 10 min. It was then titrated to pH 4.0 with standardized 0.10 N sodium hydroxide. The percentage of free formaldehyde was calculated from the following equation:

$$\%\ \text{free formaldehyde} = 100(\text{mL} \times \text{N NaOH}) \times 0.030/\text{g sample}$$

Extraction of Cured Soy Flour PF Adhesives

A 3- to 5-g sample of liquid soy flour PF adhesive in a small aluminum pan was cured in an oven at 150 °C for 1 h.

The cured sample was then lightly ground with a mortar and pestle and extracted with water for 24 h in a Soxhlet extractor. The residue was oven dried for at least 2 h at 150 °C and weighed.

Viscosity Determination of the Disrupted Soy Solutions

The viscosity of the solutions was measured using a spindle #3 at 60 rpm on a Brookfield Viscometer LVTD viscometer (Stoughton, Massachusetts) at room temperature. The relatively low shear process was used to reduce the sensitivity to shear rate that occurs with these thixotropic solutions under high shear rates.

Preparation of Disrupted, Modified, and Co-Polymerized Soy Flour

To prepare disrupted soy flour, water, sodium hydroxide (8% of soy flour by weight), and a small amount of phase transfer or solubilizing agent (such as ethylene glycol or polyethylene glycol, 1.5% of soy flour by weight) were combined and heated to 70 °C. The soy flour was then added slowly to the solution with stirring to form a homogenous mixture containing 32% soy flour solids. The soy protein was disrupted by heating the mixture at 90 °C for 1 h. Formaldehyde (15% of soy flour by weight, added as a 37% aqueous solution) was then added to modify the disrupted soy protein with heating at 90 °C for another 1 h. The modified soy protein was then reacted at 75 °C with phenol and additional formaldehyde (at a 3.4/1 mole ratio of F/P) for another 2 h to make the final adhesive solution containing the desired amount of soy flour [5]. The soy protein isolate was also disrupted and reacted by the same method.

For the higher temperature process, the same process of dispersing the soy flour with solubilizing agent and caustic in water at 70 °C was used. Then the mixture was transferred to a 2-L autoclave and heated at 140 °C for two hours.

For the sodium carbonate process, the literature procedure was followed [6].

Results and Discussion

GPC and HPLC Methods

For the GPC analysis of disrupted soy protein using a Superose 12 column, we developed a more suitable mobile phase than the phosphate buffered saline that was previously used [6]. Because protein solubility and association are dependent upon pH and ionic composition, using a low buffer content at a pH close to the adhesive pH is important in providing an accurate analysis of the protein molecular weight. To aid in solubilizing the hydroxymethyl phenol components, acetonitrile was also part of the solvent phase. The column was calibrated with proteins of known molecular weight (Fig. 1). Thus, the chromatograms provided accurate weight-average and number-average molecular weights of the soy proteins after disrupting and reacting with formaldehyde and phenol. With our flour approximately 7% of the disrupted soy flour, mostly carbohydrates, was not soluble in the mobile phase. In calibrating the column, blue dextran was tried as a void volume marker because it has a molecular weight of 2,000 kDa, but it did not produce a detectable peak. Because both the column and blue dextran are composed of carbohydrate polymers, the blue dextran was probably absorbed on the column and not eluted by the mobile phase. Therefore, the soluble carbohydrates could not be analyzed with this column. We did not establish any additional method for analyzing the carbohydrates. Although the presence of soluble carbohydrates in the soy flour can possibly hurt water resistance of the bond, the flour is usually preferred over the soy protein isolates due to the flour's much lower cost and low molecular weight protein content that allows for lower viscosities and better bond formation compared to that of the isolate.

The reactions of soy flour with formaldehyde and phenol were also characterized by separating the individual hydroxymethyl phenol components by HPLC, as shown in Fig. 2 [9]. This method was used because it was important to understand the phenolic chemistry as well as the protein chemistry. The amount of free phenol in the soy flour PF was quantified by HPLC using 3-hydroxybenzyl alcohol as an internal standard. This method was used to determine the actual amount of formaldehyde needed to react with the phenol at a >2/1 F/P level.

Analysis of Disrupted, Modified, and Co-Polymerized Soy Flour

Samples of soy flour were analyzed by GPC to determine the resulting molecular weights after disrupting under different conditions (90 °C compared to 140 °C; addition of sodium bisulfite, sodium hydroxide, or sodium carbonate; soy protein isolate compared to soy flour). Disrupting soy flour at 140 °C compared to 90 °C (by the same method except for the final temperature) resulted in virtually eliminating the higher molecular weight fractions and enhancing the lower molecular weight peaks (Fig. 3). The weight-average molecular weight of the sample at 140 °C (11.33 kDa) was much lower than that of the 90 °C sample (86.37 kDa). These lower molecular weight proteins produce adhesives with lower viscosity, but also result in poorer performance in bonding wood because the proteins

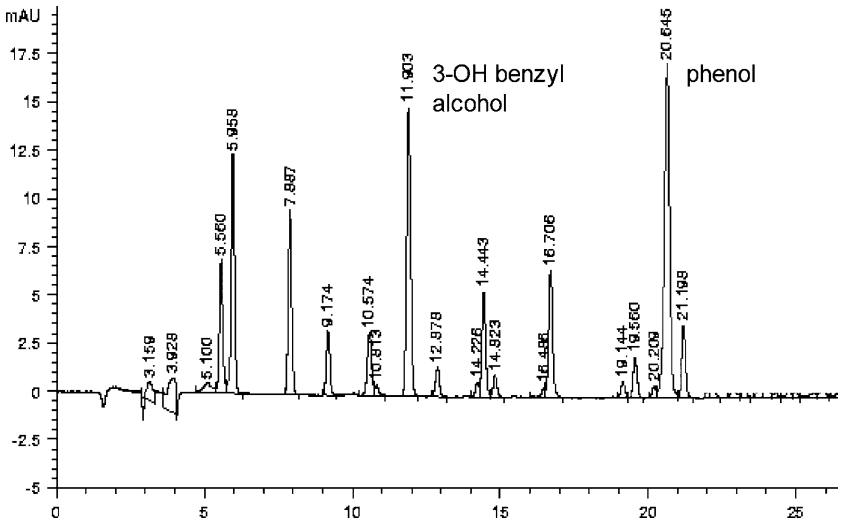

Fig. 2 HPLC chromatogram for determining free phenol of soy flour PF adhesives using 3-hydroxybenzyl alcohol as internal standard

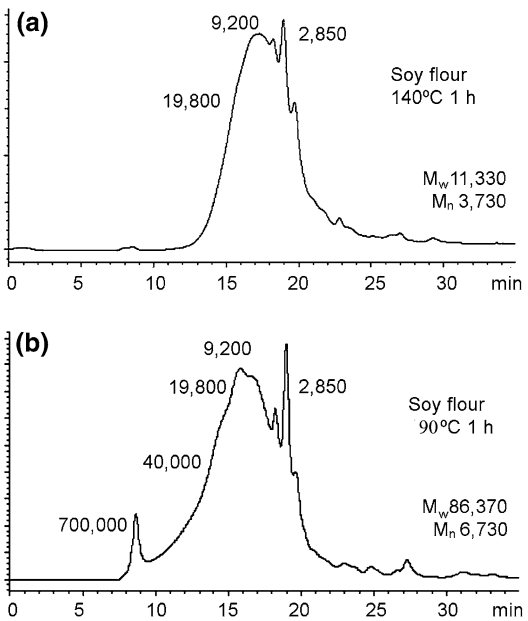

Fig. 3 GPCs of soy flour disrupted with sodium hydroxide and sodium bisulfite at (a) 140 °C and (b) 90 °C

are not incorporated completely within the PF network (J.M. Wescott, unpublished data). The question is whether the process is a denaturing of protein by breaking the agglomerates into smaller fractions or actual hydrolysis of the protein. The GPC showed very small amounts of individual amino acids or small peptides, which would indicate that the lowering of the viscosity is due more to disrupting than to hydrolysis.

Sodium bisulfite was added in these reactions of soy flour with sodium hydroxide to try to enhance disrupting by cleaving disulfide bonds [3]. As expected, the addition of sodium bisulfite (2.5% of soy flour) to the reaction at 90 °C increased disrupting of the higher molecular weight peaks and led to a lower weight-average molecular weight (86.37 kDa, Fig. 3b) compared to the reaction at 90 °C with only sodium hydroxide (170 kDa, Fig. 5a). This decrease in higher molecular weight fractions did not reduce the viscosity of the solution, as expected.

The use of a soy protein isolate was studied only for comparison with disrupted soy flour, since most of the work was done with the economically attractive soy flour. Soy protein isolate is produced by processing soy flour to remove carbohydrates by dissolving the protein and some carbohydrates in dilute alkali (pH ~ 8), removing the insoluble carbohydrates, and precipitating the higher molecular weight protein fractions at pH 4.5, while the lower molecular weight proteins and the soluble carbohydrates remain in solution [7]. The disrupted soy protein isolate (using a similar process as the soy flour) had larger peaks at higher molecular weights and a higher weight-average molecular weight (226.49 kDa, Fig. 4) than the soy flour (86.37 kDa, Fig. 3). This shows that the lower molecular weight proteins are lost in preparation of the protein isolate from the soy flour, probably due to their greater solubility in the precipitation step.

To compare sodium carbonate with sodium hydroxide, soy flour was disrupted with sodium carbonate (8.4% of soy flour) at 97 °C for 24 h (process used in reference 1) and compared to soy flour disrupted with sodium hydroxide (8.0% of soy flour) at 90 °C for one h (our process). More high molecular weight protein remained in the sodium carbonate sample, and its weight-average molecular weight was much higher than that of the sodium hydroxide sample (313.16 vs. 170 kDa, Fig. 5). This suggests that even after reacting for a longer time at a higher temperature, sodium carbonate did not disrupt the higher molecular weight protein as much as did sodium hydroxide. The viscosity of the sodium carbonate sample was also much higher than that of the sodium hydroxide sample (>10,000 vs. 1650

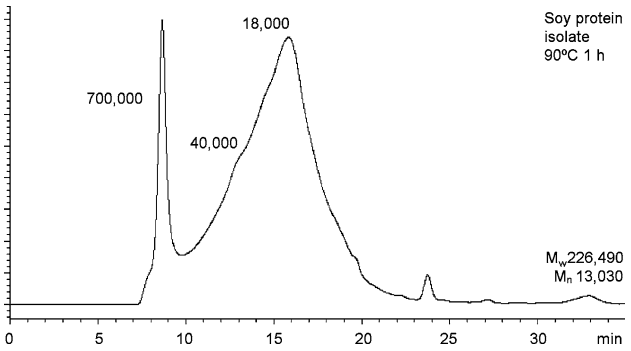

Fig. 4 GPC of soy protein isolate disrupted with sodium hydroxide and sodium bisulfite

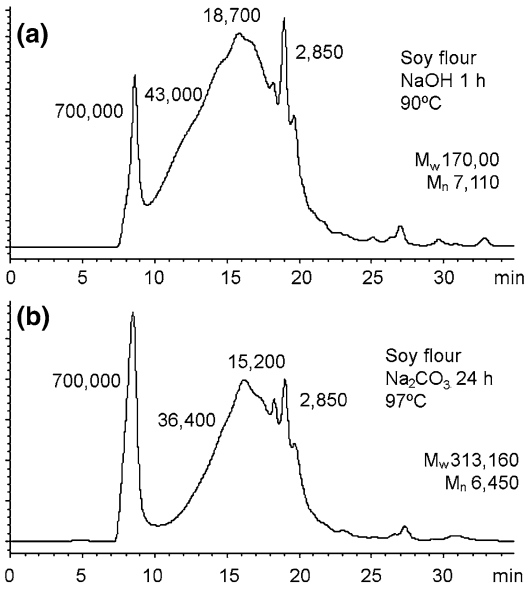

Fig. 5 GPCs of soy flour disrupted with (a) sodium hydroxide and (b) sodium carbonate

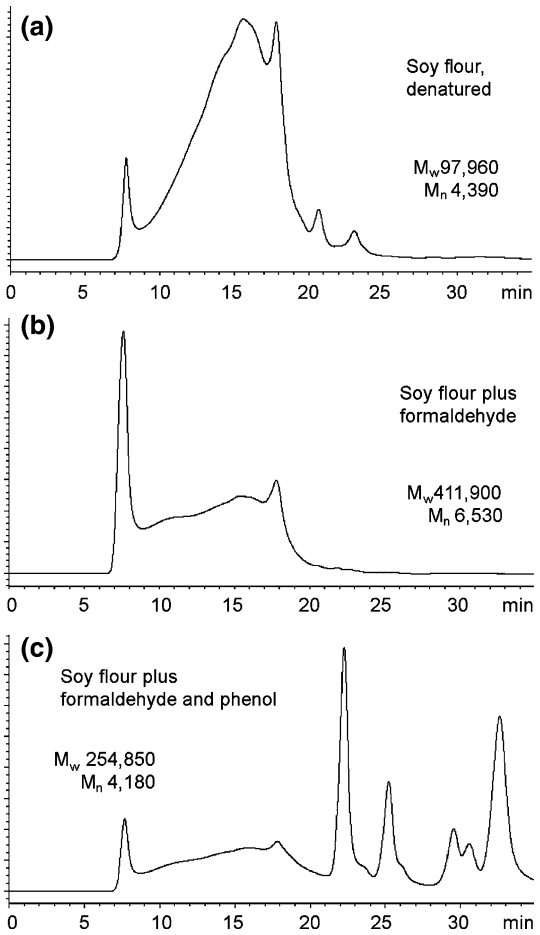

Fig. 6 GPCs of (a) disrupted, (b) formaldehyde-modified, and (c) co-polymerized soy flour. (Peaks eluted after 21 min not included in M_w or M_n)

cPs,), as might be expected from the larger amount of high molecular weight protein fractions as shown in the chromatography data.

After disrupting, an important part of our process was to modify and stabilize the soy flour by adding formaldehyde before reacting with phenol and additional formaldehyde [11]. The disrupted soy protein was first modified with formaldehyde to stabilize the protein from extensive refolding. Figure 6 compares GPCs of disrupted soy flour before and after the addition of formaldehyde. The result was an increase in the higher molecular weight peaks after formaldehyde addition, probably due to some crosslinking of the soy proteins. The increase in the weight-average molecular weight is surprising (97.96 vs. 411.9 kDa) in that the viscosity of the solution did not increase much after the formaldehyde addition (1,650 vs. 1,690 cPs).

After the reaction of the soy flour with formaldehyde, the amount of free formaldehyde was measured by the hydroxylamine hydrochloride method. Knowing how much formaldehyde would react with the soy flour made it possible to add the amount of phenol and additional formaldehyde that would react to produce a soy flour PF adhesive with the desired percentage of soy flour with the functionality to produce a highly crosslinked network [5].

The disrupted, modified soy protein was then reacted with phenol followed by additional formaldehyde and sodium hydroxide at 75 °C to make the final co-polymer adhesive. The formaldehyde links the protein molecules with each other and with the phenol molecules, as well as linking together the phenol molecules. Figure 6 compares the GPC of the final adhesive with the GPCs of the disrupted and modified soy flour. The weight-average molecular weight of the soy flour protein in the final adhesive that eluted in the first 20 min was lower than that of the formaldehyde-modified soy flour but much higher than that of the disrupted soy flour (254.85 vs. 411.9 and

97.96 kDa). This comparison suggests that there is less crosslinking of the soy flour protein in the final adhesive compared to the modified soy flour but more crosslinking compared to the disrupted soy flour. The reduction in the weight-average molecular weight in the final adhesive suggests that when phenol is added to the disrupted, modified soy flour protein, some of the formaldehyde that had reacted reversibly to crosslink the soy flour proteins reacts with the phenol, which lowers the molecular weight of the soy flour proteins. The peaks that were eluted after 20 min (Fig. 6c) are low molecular weight hydroxymethyl phenol peaks and were not included in the molecular weight calculations of the soy proteins.

The GPC results of the final copolymer adhesive were compared at two different wavelengths, 220 and 273 nm. Although 220 nm is used for monitoring the soy protein fractions, it cannot be used to distinguish between soy proteins and phenol-modified soy proteins. Because the phenolic components absorb more at 273 nm than do the soy flour components, additional absorption at 273 nm in the high molecular weight components (indicated by more area under the curve) would indicate reaction of the soy flour with the phenol and formaldehyde. No additional absorption occurred, which suggests minimal reaction at 75 °C. However, since extraction data and tests of wood bonded with the soy flour PF adhesive showed conclusively that the soy flour was co-polymerized with the phenol formaldehyde, the co-polymerization must have occurred at a higher temperature when the adhesive was cured [5]. This is similar to the reaction of phenolic resins with themselves and was expected. The fact that we were able to quantify and separate the phenolic fraction from the soy fraction is very useful in formulating new adhesives.

Extraction Data and Strandboard Properties

To determine if all the soy flour was reacted into the PF matrix, extraction data were obtained on cured samples of the soy flour PF adhesive. For the sample containing 40% soy flour plus 60% PF, 14% of the solids were extracted compared to 5.4% of the PF without added soy flour, which is consistent with the amount of sodium hydroxide in the PF adhesive. The extracted and un-extracted soy flour PF samples were also analyzed for elemental composition. Because the only source of nitrogen in the soy flour PF was from the soy protein, elemental analysis was used to determine the relative levels of elemental nitrogen [12]. The results showed that essentially none of the nitrogen was extracted from the cured samples and that 100% of the protein fractions of the soy flour was co-polymerized with the phenol formaldehyde or irreversibly trapped in the PF network. Since trapping 100% of the protein is highly unlikely, we strongly believe that the soy proteins were co-polymerized with the PF [5].

Strandboards were prepared using a soy flour PF adhesive, containing 40% soy flour, and compared to those prepared using a commercial PF adhesive. Panel preparation was previously described [12]. The soy flour adhesive produced boards of the same quality compared to boards produced with the commercial adhesive (Table 1). Thickness swell was excellent at both room temperature and in the very aggressive 2-h boil compared to thickness swell with the commercial adhesive. To our knowledge, no soy-PF adhesives have been produced with such high levels of soy flour that can withstand a 2-h boil test. These results are consistent with the fact that soy flour can be used to produce durable adhesives when it is sufficiently modified and co-polymerized to convert it into water-insoluble material.

The biomass content of wood products can be increased by adding high levels of soy flour to an adhesive provided that the soy structure can be disrupted to expose the functional groups bonding to the wood and reacted with the other reactive components in the adhesive. Given the complexity of the protein structure and the chemistry of the protein reactions, knowing the change in molecular weight in each step is useful for understanding the process. Most gel permeation chromatography methods are run under near physiological conditions to minimize protein alteration during the analysis. However, the chemistry of these protein disruptions is under much different conditions, requiring the development of a GPC method that is closer to the reaction conditions. This method allowed an analysis of the change in soy protein molecular weight in each step and was useful in developing a soy flour-formaldehyde-phenol

Table 1 Properties of PF–40% soy flour and commercial PF random strand panels[a]

Face resin	Density (g/cm^3)	Thickness swell (%)		Internal bond strength (kPa)	
		2-h boil	24-h room temp	Dry	Wet
PF control	0.678	62.8 (4.8)	15.2 (1.5)	600 (56)	56 (10)
PF–40% soy flour	0.671	65.1 (3.6)	14.5 (1.7)	620 (60)	60 (40)

[a] ASTM D 1037 (13). Wet internal bond is center cut of panel oven dried after 2-h boil. Values in parentheses represent one standard deviation of the data

adhesive with much higher levels of soy flour in the formulation compared to prior methods. This soy flour-formaldehyde-phenol adhesive has given good performance as the face resin in bonding oriented strandboard (OSB).

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