Analysis of Soy Flour/Phenol-Formaldehyde Adhesives for Bonding Wood

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Abstract

The desire to make more environmentally friendly and lower-cost bonded wood products has led to an interest in replacing some phenol and formaldehyde in wood adhesives with soybean flour. It is important to develop tests that relate resin production variables to resin properties before and after wood bonding. The protein needs to be denatured, with minimal hydrolysis, to maximize its incorporation into the final polymerized structure. In this study, the best conditions for denaturing were found to be maintaining the temperature below 100°C and reacting the soy flour with sodium hydroxide for about 1 hour. Gel permeation chromatography was optimized to determine conditions for selectively breaking down the high molecular weight protein fragments that contribute to high adhesive viscosity. This method and extraction data were used to evaluate the reaction of the denatured soy flour protein with formaldehyde and phenol. Results were used to develop more environmentally friendly face adhesives for oriented strandboard.

Introduction

Petroleum-based phenol-formaldehyde (PF) adhesives entered the market in the 1940s and quickly replaced traditional soy-based adhesives because of their superior durability, viscosity, and pot life. By the 1960s, PF adhesives also offered a lower price. Increases in petroleum prices, concerns about formaldehyde emissions, and safety issues with phenol have spurred another look at the use of soy flour for exterior-grade adhesives.

Kreibich demonstrated the viability of soy adhesive technology in the end jointing of green lumber (5). 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. This technology, however, 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 little pot life.

Hse demonstrated the viability of using a soy flour/PF system for panel boards (3). This work involved using large amounts of caustic materials, which resulted in very high pH values, and typically employed soy flour levels of 30 percent substitution for phenol. Kuo et al. have also worked with a soy flour/PF system, but the technology has often led to high viscosity, low-solids adhesives, and short pot life (6). Li developed a soy protein adhesive using the reactivity of a typical paper wet strength additive, such as Kymene (7).

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 soy retains its water solubility after the curing/drying

process. 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 protein in soy flour contains many reactive side-chain amino acid groups (25% to 30% of total amino acids) that are believed to have the ability to react with phenolic adhesives (11). 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 co-polymerization. This allows the use of soy flour rather than high-priced protein isolates for the preparation of these novel adhesives.

Analysis of denatured or hydrolyzed soy flour is necessary for determining the optimum 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. Vijayendran and Clay used gel permeation chromatography (GPC) to analyze denatured/hydrolyzed soy flour that was combined with PRF to bond wood (8), but they reported only peak molecular weight. They hydrolyzed soy flour with sodium carbonate at 100°C for 24 hours and obtained a peak molecular weight of 11,600 dalton. They also hydrolyzed soy protein at 100°C for 14 hours, which resulted in a peak molecular weight of 22,000 dalton. The soy protein adhesives that they formulated were evaluated in finger-jointing Douglas-fir lumber. The strength of the wood bonds was found to increase with peak molecular weight, as expected. Increasing the protein reactivity (higher amine levels) by greater hydrolysis of the protein led to lower, not greater, bond strength.

To further study the relationship between denaturing and modifying conditions and the molecular weight of soy proteins for bonding wood, we modified the GPC procedure used by Vijayendran and Clay for analyzing soy proteins that used phosphate buffered saline at pH 7 (8). Changes included reducing the buffer concentration and increasing the pH to 9 to dissolve more soy protein as well as the phenolic compounds. Our studies also placed emphasis on number and weight average molecular weight rather than peak molecular weight, as well as changes in specific peaks.

GPC Calibration

The denatured soy proteins were analyzed by GPC on a Superose 12 (10/300 GL) column (310 by 10 mm i.d.) (Amersham Bioscience, Piscataway, NJ). The mobile phase was 0.05 M Na2HPO4 (adjusted to pH 9 with NaOH) in HPLC grade water (Milli-Q System; Millipore, Bedford, MA) containing 20 percent acetonitrile at a flow rate of 1.0 mL/min and 25°C. A Hewlett-Packard 1050 series liquid chromatograph (Agilent Technologies, Wilmington, DE) 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. Approximately 7 percent of the denatured soy flour was not soluble in the mobile phase. A calibration curve for the Superose 12 GPC column was obtained using six protein standards (**Fig. 1**).

Analysis of GPC Data

Soy flour samples were analyzed by GPC to determine molecular weight after denaturing under different conditions (90°C or 140°C; sodium bisulfite, sodium hydroxide, or sodium carbonate; soy protein isolate or soy flour). Denaturing soy flour at 140°C compared to 90°C eliminated the higher molecular weight fractions and enhanced the lower molecular weight peaks (**Fig. 2**). The weight-average molecular weight of the sample at 140°C (11,330) was much lower than that of the 90ºC sample (86,370). Lower molecular weight proteins produce adhesives with lower viscosity, but also result in poorer performance in bonding wood because the proteins are not reacted with the PF network (J.M. Wescott, unpublished data, 2002).

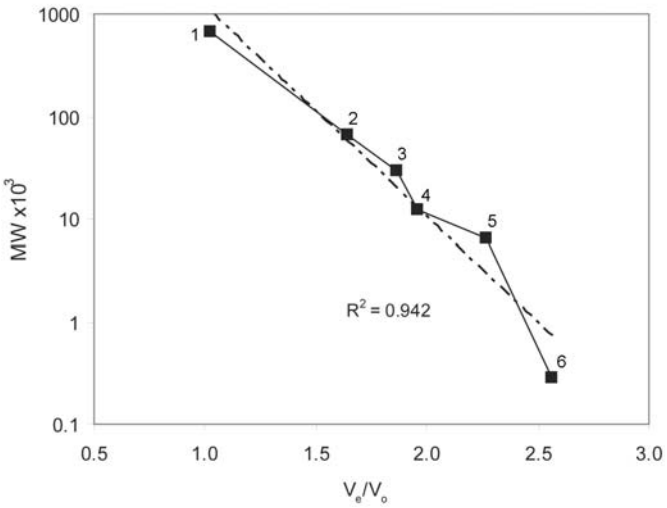

Figure 1. ~ *GPC calibration of Superose 12 column with six protein standards: 1) thyroglobulin; 2) bovine serum albumin; 3) carbonic anhydrase; 4) cytochrome C; 5) aprotinin; and 6) valyltyrosine. MW is molecular weight; V_e/V_0 is elution volume divided by void volume of column.*

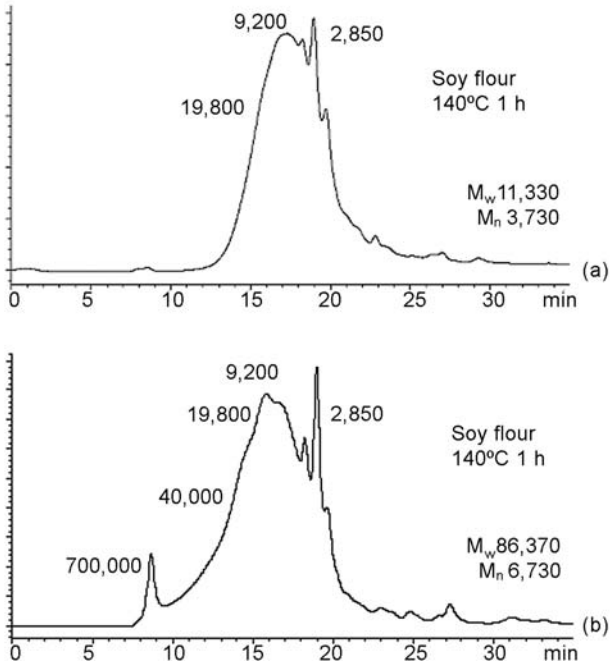

Figure 2. ~ *GPCs of soy flour denatured with sodium hydroxide and sodium bisulfite at a) 140°C and b) 90°C.*

The question is whether the process is denaturing of protein 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 lower viscosity is due more to denaturing than to hydrolysis.

Sodium bisulfite was added in these reactions of soy flour with sodium hydroxide to enhance denaturing by cleaving disulfide bonds (6). The addition of sodium bisulfite (2.5% of soy flour) to the reaction at 90ºC increased denaturing of the higher molecular weight peaks and a lower weight-average molecular weight (86,370, **Fig. 2b**) compared to the reaction at 90°C with only sodium hydroxide (170,000, see **Fig. 4a**). This decrease in higher molecular weight fractions did not reduce the viscosity of the solution, as expected.

The denaturing of a soy protein isolate was studied only for comparison with denatured soy flour, since most work was done with soy flour because of its cost advantage. Soy protein isolate is produced by processing soy flour to remove carbohydrates by dissolving the protein and some carbohydrates, removing the insoluble carbohydrates, and precipitating the higher molecular weight protein fractions, while the lower molecular weight proteins and the soluble carbohydrates remain in solution (4).

The denatured soy protein isolate (**Fig. 3**) had higher peaks at higher molecular weights and a higher weight-average molecular weight (226,490) than that of the soy flour (86,370, **Fig. 2b**).

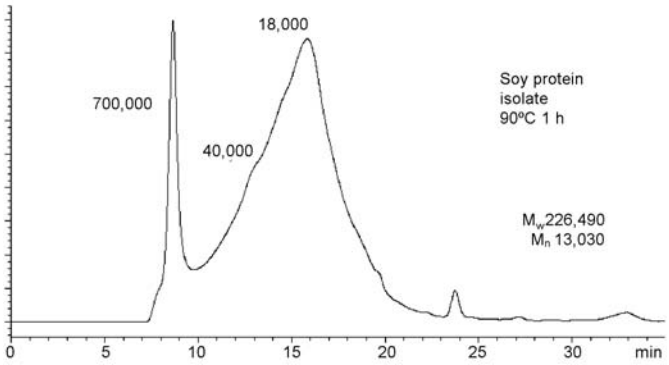

Figure 3. ~ *GPC of soy protein isolate denatured with sodium hydroxide and sodium bisulfite.*

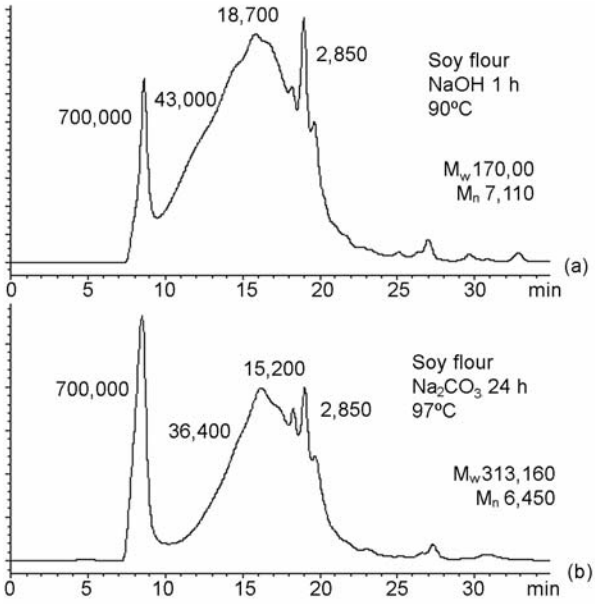

Figure 4. ~ *GPCs of soy flour denatured with a) sodium hydroxide and b) sodium carbonate.*

To compare sodium carbonate with sodium hydroxide, soy flour was denatured with sodium carbonate (8.4% of soy flour) at 97°C for 24 hours (process used in ref. 8) and compared to soy flour denatured with sodium hydroxide (8.0% of soy flour) at 90°C for 1 hour (our process). Much high molecular weight protein remained in the sodium carbonate sample, and the weight-average molecular weight was much higher than that of sodium hydroxide (313,160 vs. 170,000, **Fig. 4**). This suggests that even after reacting for a longer time at a higher temperature, sodium carbonate did not denature the higher molecular weight protein as much as did sodium hydroxide.

After denaturing, an important part of our process was to modify and stabilize the soy flour by adding formaldehyde and phenol (2). The denatured soy protein was first modified with formaldehyde. **Figure 5** compares GPCs of

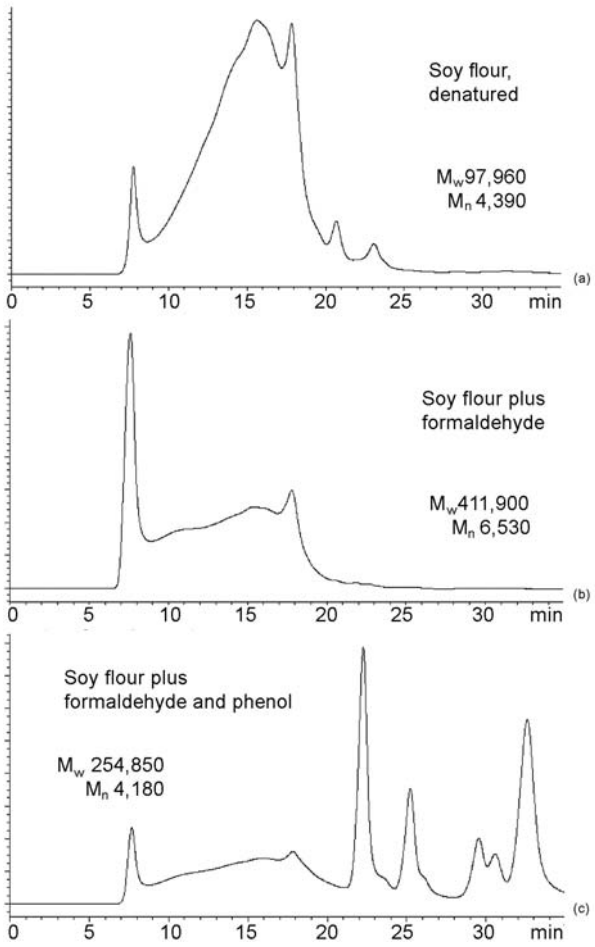

Figure 5. ~ *GPCs of a) denatured, b) formaldehyde-modified, and c) co-polymerized soy flour. (Peaks eluted after 21 min are not included in Mw or Mn).*

denatured 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 (97,960 vs. 411,900) in that the viscosity of the solution did not increase much after the addition of formaldehyde (1,650 vs. 1,690 cP).

The denatured, modified soy protein was then reacted with phenol, followed by additional formaldehyde and sodium hydroxide at 75ºC, to make the final co-polymer adhesive. The GPCs of the final adhesive and the denatured and modified soy flour are compared in **Figure 5**. The weight-average molecular weight of the soy protein in the final adhesive that eluted in the first 20 minutes was lower than that of the formaldehyde-modified soy flour but much higher than that of the denatured soy flour (254,850 vs. 411,900 and 97,960). This comparison suggests that less crosslinking of soy protein occurred in the final adhesive than in the modified soy flour, but more crosslinking occurred in the final adhesive than in the denatured soy flour. The reduction in the weight-average molecular weight in the final adhesive suggests that when phenol is added to the denatured, modified soy protein, some formaldehyde that had reacted reversibly with the soy protein reacts with the phenol, which lowers the molecular weight of the crosslinked soy protein. The peaks that were eluted after 20 minutes (**Fig. 5c**) were low molecular weight hydroxymethyl phenol peaks and were not included in the molecular weight calculations.

The GPC of the final copolymer adhesive was compared at two different wavelengths, 220 and 273 nm. Because phenolic components absorb more at 273 nm than do soy flour components, additional absorption at 273 nm in the high molecular weight components (as indicated by more area under the curve) would indicate the reaction of soy flour with phenol and formaldehyde. No additional absorption occurred, which suggests minimal reaction at 75°C. Since extraction data and tests of wood bonded with the soy flour PF adhesive showed conclusively that the soy flour is co-polymerized with PF, co-polymerization must have occurred at a higher temperature when the adhesive was cured (11).

Extraction Data and Strandboard Properties

To determine if all of the soy flour was reacted into the PF matrix, extraction data were obtained on cured samples of the soy flour PF adhesive. For a sample containing 40 percent soy flour plus 60 percent PF, 14 percent of the solids were extracted compared to 5.4 percent 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. The results showed that essentially none of the nitrogen was extracted from the cured samples and that the soy flour was co-polymerized with PF or irreversibly trapped in the PF network. Since trapping 100 percent of the soy flour is highly unlikely, we strongly believe that the soy flour was co-polymerized with the PF (11).

Strandboards were prepared using a soy flour PF adhesive (40% soy flour) and compared to those prepared using a commercial PF adhesive (**Table 1**). Panel preparation was previously discussed by Wescott et al. (9,10). The quality of boards produced with the soy flour adhesive was equal to that of boards produced with the commercial adhesive; thickness swell of boards made with the soy flour adhesive was excellent at both room temperature and in the very aggressive 2-hour boil test compared to the thickness swell of boards made with the commercial adhesive.

Table 1. ~ *Properties of PF-40% soy flour and commercial PF random strand panels.*[a]

Face resin	Density	Thickness swell (%)		Internal bond strength (MPa)	
		2-hour boil	24-hour room temp.	Dry	Wet
	(g/cm^3)				
PF control	0.679	62.8 (4.8)	15.2 (1.5)	0.60 (0.18)	0.056 (0.01)
PF-40% soy flour	0.672	65.1 (3.6)	14.5 (1.7)	0.62 (0.11)	0.060 (0.04)

[a] ASTM D 1037 (1). Wet internal bond is center cut of panel oven dried after 2-h boil. Values in parentheses represent one standard deviation of data.

To our knowledge, no soy-based adhesives containing such high levels of soy flour have been produced that can withstand a 2-hour 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.

Conclusions

A variety of analytical methods were used to analyze denatured soy flour and its reaction with formaldehyde and phenol to provide more useful information than that currently available and to formulate a durable soy flour PF adhesive. Determination of free formaldehyde by titration and free phenol by HPLC as well as extraction data of the cured soy flour PF adhesives were necessary to optimize the soy flour to PF ratio.

For the GPC analysis of soy proteins using a Superose 12 GPC column, a mobile phase was developed containing a lower concentration of buffer at a higher pH and adding acetonitrile. GPC analysis of the reaction conditions provided useful insight into the denaturing of protein that was not always apparent from the viscosity data.

The different denaturing conditions (sodium hydroxide vs. sodium bicarbonate, 90°C vs. 140°C, and presence or absence of sodium bisulfite) all affected the molecular weight of the product. The addition of formaldehyde to denatured soy resulted in an increase in soy protein molecular weight, but did not increase solution viscosity. Also, GPC showed a significant increase in soy protein molecular weight after the reaction with phenol and formaldehyde.

With this new technology, we have been able to take advantage of soy flour as a low-cost and renewable resource with no formaldehyde content. At the same time, we have extended the previous limitations to the extent that as much as 70 percent of a traditional PF adhesive can be replaced with a soy-based product to produce boards of comparable physical properties under comparable pressing conditions.

Literature Cited

1. American Society of Testing and Materials (ASTM). 2005. Annual book of ASTM standards. Standard test methods for evaluating properties of wood-base fiber and particle panel materials. D 1037-99, vol. 04.10. ASTM International, West Conshohocken, PA.
2. Frihart, C.R. and J.M. Wescott. 2004. Improved water resistance of bio-based adhesives for wood bonding. *In*: Proc. of the 1st International Conf. on Environmentally Compatible Forest Products, Sept. 22-24, Porto, Portugal. pp. 293-302.
3. Hse, C.-Y., F. Fu, and B.S. Bryant. 2001. Development of formaldehyde-based wood adhesives with co-reacted phenol/soybean flour. *In*: Proc. of the Wood Adhesives 2000 Conf. Forest Products Society, Madison, WI.
4. Kinsella, J.E. 1979. Functional properties of soy proteins. J. American Oil Chemists Society. 56: 242-258.
5. Kreibich, R.E., P.J. Steynberg, and R.W. Hemingway. 1997. End jointing green limber with SoyBond. *In*: Proc. of the Residual Wood Conf., Nov. 4-5, Richmond, BC.
6. Kuo, M., D. Myers, H. Heemstram, D. Curry, D.O. Adams, and D.D. Stokke. 2001. Soybean-based adhesive resins and composite products utilizing such adhesives. U.S. Patent 6,306,997 B1.
7. Li, K., S. Peshkova, and X. Geng. 2004. Investigation of soy protein-Kymene adhesive systems for wood composites. J. American Oil Chemists Society. 81(5): 487-491.
8. Vijayendran, B.R. and J. Clay. 2001. Some recent studies on soy protein-based wood adhesives. *In*: Proc. of the Wood Adhesives 2000 Conf. Forest Products Society, Madison, WI. pp. 21-28.
9. Wescott, J.M. and C.R. Frihart. 2004. Competitive soybean flour/phenol-formaldehyde adhesives for oriented strandboard. *In*: Proc. of the 38th International Wood Composites Symp. Washington State Univ., Pullman, WA. pp. 199-206.
10. Wescott, J.M., C.R. Frihart, and A.E Traska. 2006. High soy containing water durable adhesives. J. of Adhesion Sci. and Techn. 20(8): 859-873.

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