

DISPERSION ADHESIVES FROM SOY FLOUR AND PHENOL FORMALDEHYDE

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Introduction

Higher petroleum prices and greater interest in bio-based adhesives have stimulated a considerable amount of research on incorporating soybean flour into wood adhesives in recent years. In some cases, soy was used at low levels as an extender for phenol-formaldehyde (PF) adhesives; in other cases, highly hydrolyzed soy flour was used. Although progress was made in getting soy to react with PF, incorporation of the soy was still fairly low. Addition of the flour to hot aqueous caustic, followed by stabilization of the alkaline soy mixture by reaction with formaldehyde, was a recent key step toward higher incorporation of soy flour in PF adhesives (1). These conditions provided an ideal protein structure to allow the reaction of phenol and formaldehyde with functional groups on the protein while minimizing undesired hydrolysis of the protein backbone. Good performance was obtained using nearly equal quantities of soy flour and phenol-formaldehyde resin for the face adhesive in producing strandboard (1). A ratio of 40% soy to 60% PF resulted in an adhesive with performance equal to that of a commercial PF face adhesive in both cure speed and final properties of the resultant strandboard (2). A limitation on soy flour incorporation in these adhesives may be caused by the slow curing reactions of the hydroxymethylamine groups on the protein under basic conditions. Amino resins cure slowly under alkaline conditions but work well under acid cure conditions (3). Therefore, the question was whether an acidic soy-PF resin can be made and whether this would allow for higher soy contents in the adhesive.

Soy flour consists mainly of proteins (41–48%) and soluble and insoluble carbohydrates (30–40%), along with some other minor components. The protein in its native state is only moderately soluble, but treatment with caustic is known to increase the solubility of soy protein by increasing the net charge of the proteins. Acidification to pH 4–6, near the isoelectric point of many soy proteins, generally leads to precipitation of much of the protein. Likewise, the phenolic resins are usually soluble in aqueous caustic and precipitate out upon acidification to pH 4–6. This research was aimed at trying to make stable acidic mixtures

of soy-PF resins with high soy contents that could be readily applied to and bond wood flakes to make strandboard.

Experimental

Materials

Soy flour was supplied by Oelwein Custom Commodities (Oelwein, Iowa). The flour was ground such that 80% by weight (wt%) passed through a 100-mesh screen. The composition of the flour was 44 wt% protein, 10 wt% oil, and 5 wt% ash on a dry basis, with the remainder being mainly carbohydrates. Phenol (99 wt%) and formaldehyde (37 wt%, 8%–9 wt% methanol) were purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin). Sodium hydroxide (99 wt%) was purchased from Fisher Scientific Co. (Fair Lawn, New Jersey). Antifoam 1500 was donated by Dow Corning (Midland, Michigan), and polymeric diphenylmethane diisocyanate (pMDI) was provided by Dow Chemical Company (Midland, Michigan). Commercial PF was donated by an oriented strandboard (OSB) manufacturer.

Preparation of Resins

Soy-66A (66% soy/34% PF wt/wt) alkaline solution—In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and condenser, tap water (1,418 g), NaOH (56.0 g), a phase transfer agent ethylene glycol (10.5 g), and Antifoam 1500 (19 drops) were added while mixing and heated to 70°C. Soy flour (700.0 g) was then added to the rapidly stirring solution at an average rate of 5% per minute, or as rapidly as possible while ensuring proper dispersion and no clumping. The mixture was then heated to 90°C over 15 min, with rapid agitation, and held between 88°C and 92°C for 1 h. Formaldehyde 37% (268.0 g) was added to the hot mixture over a 5-min period, without heating. The mixture was allowed to stir and maintained between 88°C and 92°C for an additional 55 min, followed by the addition of phenol (205.8 g) while cooling to 75°C over a 10-min period. NaOH (17.5 g) was then added, followed by a second addition of formaldehyde 37% (335.2 g) and two more NaOH charges (8.8 g each), separated by about 5 min. The mixture was held at

75°C for an additional 1.5 h, at which time the vessel was cooled to 35°C with an ice bath and filtered through a coarse screen (35 mesh). The final resin was labeled Soy-66A and was stored in the refrigerator.

Soy-66 (66% soy/34% PF wt/wt)—The resin Soy-66A was used to prepare an acidic soy–PF dispersion by the dropwise addition of concentrated sulfuric acid (3.5 g to 100 g Soy-66A) to the rapidly stirred mixture. The temperature was kept below 25°C during the acidification to prevent grit formation. After being acidified, the dispersion was stirred rapidly for 15 min, filtered through a coarse screen (35 mesh), and stored in the refrigerator.

Soy-50 (50% soy/50% PF wt/wt)—A dispersion with higher phenolic resin content, Soy-50, was prepared in a manner similar to that for Soy-66 by adding an additional amount of laboratory-prepared PF resin (F/P = 2.08, NaOH/P = 0.2) to Soy-66A prior to the acidification step.

Soy-66-Iso (66% soy/34% PF wt/wt with 10% pMDI added post-dispersion)—Polymeric diphenylmethane diisocyanate (pMDI) was combined with the Soy-66 dispersion at a level of 10 parts pMDI to 100 parts Soy-66 solids to produce an isocyanate-modified soy–PF dispersion.

Analysis

The percentage of non-volatile solids was measured by heating a 1- to 2-g sample of the resin solution in a small aluminum pan in an oven at 150°C for 1 h. Viscosity was measured at 25°C using a Brookfield LVT viscometer (Middleboro, Massachusetts) with No. 2 to No. 4 spindles at both 60 and 30 rpm. The specific spindle selections were based on the recommended viscosity ranges for each spindle. Multiple speed measurements were conducted to properly evaluate the shear-thinning (thixotropic) properties of the soy–PF resins. Extraction of the neat resins was conducted as follows. Neat cured resin was prepared via the same procedure used to measure the percentage of non-volatile solids. A Soxhlet extraction was performed using 2.5 to 3.0 g of lightly ground, cured resin solids and water as the solvent for 24 h. The residue in the thimble was then oven dried for at least 2 h at 150°C, removed from the thimble, and weighed.

Results and Discussion

Soy flour/phenol-formaldehyde technology has been developed that provided homogenous alkaline solutions with stability equal to or better than that of a typical phenol-formaldehyde resin (1,2). The key steps involved (a) adding soy flour to hot aqueous caustic to solubilize and denature the protein, (b) after sufficient equilibration time, adding formaldehyde to react with exposed lysine and tyrosine groups and stabilize the open protein conformation, and (c) reacting with phenol and additional formaldehyde to produce coreactive soy protein/phenol-formaldehyde adhesive. This technology disrupted the soy flour to expose the reactive groups on the protein without developing the high viscosities encountered with typical

alkaline solvation methods for soy flour. This technology provided good base solutions of stabilized soy flour that could be coreacted with phenol and formaldehyde or blended with preformed phenol-formaldehyde resins. Thus, our studies entailed ways to lower the pH to make a stable dispersion because it was expected that both the soy protein and phenolic resin would become insoluble.

Surprisingly, lowering the pH of these alkaline soy-PF solutions to PH 4–6 generated light-colored stable dispersions if the acid was added slowly and good agitation was used. Only a small amount of grit (larger sized particles) was observed after filtration of the product through a 35-mesh screen. The filtered product had a smooth texture. For our dispersion, not only are the dispersed particles fine but these dispersions have little tendency to settle over months of storage. Faster lowering of the pH or slow agitation resulted in more grit, probably caused by localized agglomeration. Dispersion processes like this often require use of surfactants with the proper hydrophilic–lipophilic balance to form a stable dispersion. In fact, prior research on phenol-formaldehyde dispersions indicated the need to use surfactants (4). Although surfactants can aid in the wetting of the bonding surfaces, they can cause poor adhesion because of weak boundary layers.

The properties of the dispersion are very promising. Table 1 data show that the dispersion has a lower viscosity than the alkaline solution from which it is made; this effect is attributed to some of the higher molecular weight molecules ending up in the dispersed phase and contributing less to the solution viscosity. This makes the viscosity of the soy adhesive closer to that of the PF control, although it is still thixotropic, as indicated by the difference in viscosities at 30 and 60 rpm. The dispersions do not show a gel point, because much of the reaction takes place within the dispersed phase. In fact, we have determined that heating does cause increased polymerization in the dispersed phase because after heating, the viscosity of the dispersion did not increase appreciably, but after adding caustic to the dispersion, the solution viscosity of the heated sample was much higher than the unheated sample. Thus, more advanced resins can be made through dispersions of lower molecular weight PF, followed by heating to increase the polymerization. This is a more effective process than trying to make dispersions of the higher molecular weight PFs. In general the percentage insoluble after curing was the same for the dispersion (Soy-66) as the base solution (Soy-66A); thus, we did not see the increase in curing by making the dispersion as we had initially anticipated, although we may have increased the crosslink density of the final cured adhesive.

Viscosity stability is an issue with PF resins because of a slow increase in cure under ambient conditions (advancement of the resin), leading to a limited storage life of the adhesives. Our alkaline soy-PF resins are more stable than the PF resins with time (Figure 1). We believe this is a result of both a lower molecular weight PF resin and a decrease in the PF amount. Moreover, the dispersions were much more viscosity-stable than were the alkaline resins.

With the PF in the soy dispersed phase at the lower pH, the greater stability is not totally unexpected.

Polymeric diphenylmethane diisocyanate (pMDI) is a good but expensive wood adhesive. It is hard to lower the adhesive cost by blending it with other wood adhesives because of its high reactivity with hydroxyl and primary and secondary amine groups present in most wood adhesives, mainly hydroxide under alkaline conditions. The pMDI can readily be blended with these soy-PF dispersions to generate a sufficiently stable dispersion. Surprisingly, the soy-PF dispersion is able to successfully distribute and stabilize the organic pMDI within the aqueous environment. The viscosity data in Figure 1 showed that after an initial rise, the soy-66-iso (10% pMDI on a solids basis) resin was quite stable. The pMDI addition did not have any effect on the percentage insolubles as determined in cured extraction test. In data from other studies, we found that although soy-66 and soy-66A made strandboard of similar swell resistance, strandboard made using soy-66-iso had improved swell resistance after room-temperature water soaking (5).

Conclusions

In prior research, we developed a process for making improved soy flour/phenol-formaldehyde alkaline adhesives that have good utility in bonding wood strandboard. The crosslinking of the soy protein was most likely through the amine groups of the lysine and aromatic groups of the tyrosine amino acids, with additional contributions likely coming from several of the other reactive side groups. Because amino resins are known to cure with formaldehyde better under acidic conditions, the conversion of our alkaline resins into slightly acidic dispersions might be a way to increase the cure and therefore allow for an increase in soy flour levels in the final adhesive. Alkaline solutions containing soy flour/phenol-formaldehyde combinations give surprisingly stable dispersions upon acidification to pH 4–6 without the use of additional surfactants. Although these dispersions did not result in greater cure as determined by percentage insolubles on the cured product, they were lower in viscosity and much more viscosity stable. In addition, the dispersion allowed greater flexibility in making wood adhesives because the polymerization can be advanced without raising the adhesive viscosity and pMDI can be added to the formulation and still provide a stable adhesive. Thus, this technology allows higher incorporation of biobased soy flour into wood adhesives and additional flexibility in making new adhesives at lower costs.

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Table 1. Physical properties and characteristics of soy–PF alkaline and acidic dispersion resins

Face resin	Soy (wt %)	PF (wt %)	pMDI (wt %)	pH	Solids (wt %) ^a	Viscosity (Cp) ^b	Gel time (min) ^c	Insoluble (%) ^d
Control PF	0	100	0	11.0	53.8	184	25	71
Soy-50	50	50	0	4.3	38.1	300/364	—	77
Soy-66	66	34	0	4.3	36	606/764	—	69
Soy-66A	66	34	0	10.4	35.2	1030/1284	51	72
Soy-66-Iso	59	31	10	4.2	38.0	982/1236	—	73

^a Solids are from 150°C 1-h oven pan method.

^b Viscosity was measured at 60/30 rpm.

^c Gel time was measured at 100°C.

^d Water-insoluble material after 24-h Soxhlet water extraction of prepared oven solids samples.

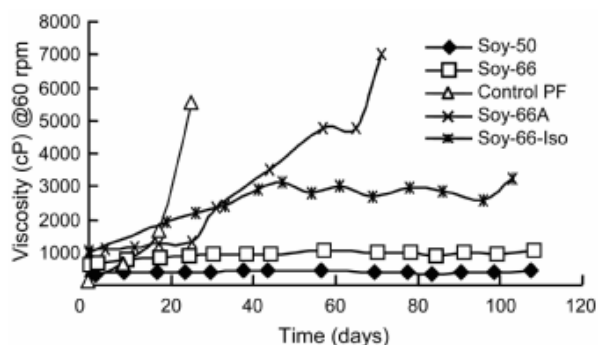


Figure 1—Room-temperature viscosity stability profiles of resins.

PROCEEDINGS

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