Durable Soy-Based Adhesive Dispersions

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Abstract

Soybean flour-based adhesive dispersions were prepared by the acidification of alkaline-denatured, formaldehyde-modified soybean-phenol formaldehyde (PF) coresin systems. The resultant dispersions, which contained 50 to 66 percent soybean flour, demonstrated room temperature viscosity stability in excess of 100 days with no observed separation or settling. The pH range was 4 to 4.5, and typical viscosity ranged from 300 to 600 cP. Randomly oriented strandboard panels prepared from the dispersions demonstrated excellent durability comparable to that of a commercial PF control resin. The addition of 10 percent polymeric methylene diisocyanate (pMDI) resulted in a resin capable of producing strandboard panels with 50 percent lower thickness swell (24-h water soak) compared with panels prepared with a commercial PF resin. Furthermore, the low pH of the dispersion resins resulted in lighter colored gluelines in the finished product. With as much as a 77 percent reduction in total phenol, the raw material cost savings of these resin systems is estimated to be 20 to 40 percent when compared that of commercial PF resins.

Introduction

The use of soy-based adhesives is not new to the chemical world. Traditional soy-based adhesives were studied extensively in the late 1920s and 1930s and used to develop the plywood industry (8). Soy flour, produced by grinding the meal after removing the more valuable oil from the soybean, is high in protein. This protein is considered to be the main adhesive material, although carbohydrates and the carbohydrate-protein Maillard reaction should not be overlooked for their contributions (1). Early work primarily involved exploring different means of denaturing the soy protein to expose the amide functional groups for maximizing adhesion. It was generally believed that the best adhesive resulted if the soy flour was mixed with a caustic solution (5,9,12,14). However, these adhesives were greatly limited by their very short pot life (room temperature stability), poor biological stability, low solids content, slow press times, and, most importantly, poor water resistance. The last characteristic narrowed the use of these adhesives to interior applications for the most part. Petroleum-based adhesives entered the market in the 1940s and soon demonstrated their superiority over traditional soy-based adhesives in terms of durability, viscosity, and pot life. Moreover, by the 1960s, petroleum-based adhesives were even offered at a lower cost. Eventually, these factors led to the nearly complete replacement of soy-based adhesives by petroleum-based adhesives in the wood-bonding arena (Trocino, F. Personal communication, Heartland Resource Technologies, Oelwein, Iowa) (**Fig. 1**).

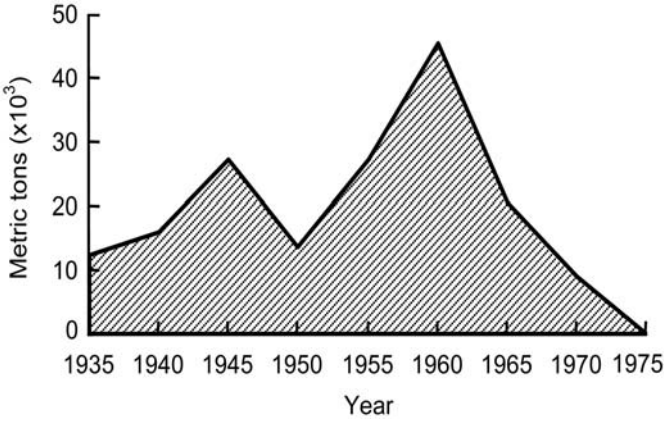

Figure 1. ~ *Usage of soy-based adhesive in the United States.*

Today, phenol-formaldehyde (PF) resins enjoy a dominant place in the resin market for exterior wood composites, and urea-formaldehyde (UF) resins are equally dominant in the interior wood composites market. With recent increases in petroleum prices, along with formaldehyde emission concerns and general phenol safety issues, the use of naturally renewable soy is again being evaluated as a viable exterior-grade adhesive. Although soy-based adhesives can be used for interior applications, the very low cost and fast-curing properties of UF resins suggest that they will likely be displaced only by a drive for a formaldehyde-free product.

One point of connection in all previous work on soy-based adhesives has been the importance of denaturing the soy flour to expose the polar backbone amide and polar side-chain groups that are believed to be essential in developing the physical bonds required for adhesion to the substrate. Denaturation of soy flour has been well studied (6,15) and is generally recognized as the most critical step in producing protein adhesives capable of producing strong bonds with wood – mainly by exposing hydrophilic groups during the uncoiling of the protein.

Denaturation is the first step in the process of making soy-based adhesives. The second step can be classified as protein modification. Formaldehyde is used to prepare the soy flour for the third step of copolymerization with suitable crosslinkers; in this study, mainly PF resole-type resins. Soy protein has been shown to crosslink with formaldehyde, but this reaction is often very easily reversed and does not result in the formation of a durable bond unless a large excess of formaldehyde is utilized (2). Non-copolymerized soy adhesive formulations typically do not form water-stable or insoluble "cured" adhesives. Thus, a suitable water-resistant copolymer is required, at least in small quantities, to obtain any degree of durability.

Since soy flour contains an appreciable amount of proteins that have many potentially reactive side-chain amino acid groups (10), crosslinking with condensation-type resins presents a viable path toward producing durable soy-based resins. Additionally, many soy protein amino acids have been shown to react with formaldehyde and to undergo further condensation (13,16). It is this reactive potential that provides soy resin with the ability to form thermosetting networks with suitable crosslinking agents. Notably, a condensation reaction is believed to occur between the side chains of lysine and tyrosine (11), and it is expected that a similar reaction can be realized with lysine (from soy) and phenol (from PF). Furthermore, not only can the protein fraction of soy flour react with PF-type crosslinking agents, but the carbohydrate fraction may also contribute to additional durability through copolymerization, by either a Maillard-type reaction or a direct reaction with phenol. This possibility is important as it allows for the use of soy flour rather than the higher-priced protein isolates for the preparation of these novel durable adhesives. The mechanisms for many amino acid-formaldehyde reactions are believed to proceed at a faster rate as the pH is lowered. This is perhaps due to the formation of Schiff base intermediates which could allow for a faster rate or higher degree of condensation with suitable nucleophiles.

Liquid PF resins are typically of the alkaline resole variety. Alkalinity is deemed important for controlling the solubility, viscosity, reactivity, and stability of the resins. Typical room temperature stability is around 30 days, before excessive viscosity build-up occurs. Additionally, the high pH causes what is commonly referred to as an "alkali burn" (dark color) in the final product. Several attempts to produce PF resin acidic dispersions have been attempted with mixed results (3,4,7,17), but none has gained any great commercial success to date.

Two important properties of both soy-based technology and PF resins that have been areas for concern are high viscosity and short pot life (stability). An acid dispersion of either type of resin, or in our case of a combination resin, should improve both of these properties. It is well known that alkaline resole-type PF resins have limited water solubility in slightly acidic aqueous solutions, which leads to the formation of a precipitate. It is also well known that soy flour has limited solubility in slightly acidic aqueous solutions and also precipitates out of solution. However, the combination of the two types of resins can be used fortuitously to produce a highly stable dispersion that is not provided by either component alone. As a result, we recently discovered that alkaline denatured, modified soy flour in combination with an alkaline resole-type phenolic resin can be phase inverted with the addition of acid into a very stable, lightly colored, highly durable wood adhesive that is suitable for exterior applications. This paper provides an overview of the process

for preparing this adhesive and highlights some final properties of laboratory-prepared randomly oriented strandboards.

Experimental

Materials

Soy flour was supplied by Oelwein Custom Commodities (Oelwein, Iowa). The flour was ground such that 80 weight percentage (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 to 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) by Dow Chemical Company (Midland, Michigan). Commercial PF was donated by an oriented strandboard (OSB) manufacturer.

Furnish

The furnish used for the strandboard study consisted of black gum, southern yellow pine, and soft maple, with trace amounts of red oak. Strand size was nominally 7.5 cm long by 1.5 cm wide by 0.08 cm high, with a standard deviation of around 20 percent.

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 charged to the rapidly stirring solution at an average rate of 5 percent/min, or as rapidly as possible while ensuring proper dispersion and no clumping. The mixture was then heated to 90°C over 15 minutes, with rapid agitation, and held between 88°C and 92°C for 1 hour. Formaldehyde 37 percent (268.0 g) was added to the hot mixture over a 5-minute period, less the heat source. The mixture was allowed to stir and maintained between 88°C and 92°C for an additional 55 minutes, followed by the addition of phenol (205.8 g) while cooling to 75°C over a 10-minute period. NaOH (17.5 g) was then added, followed by a second addition of formaldehyde 37 percent (335.2 g) and two more NaOH charges (8.8 g each). The mixture was held at 75°C for an additional 1.5 hours, at which time the vessel was cooled to 35°C with an ice bath and filtered through a course 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 drop-wise addition of concentrated sulfuric acid (3.5 to 100 g Soy-66A) to the rapidly stirring mixture. The temperature was kept below 25°C during the inversion to prevent grit formation. After being inverted, the dispersion was stirred rapidly for 15 minutes, filtered through a course screen (35 mesh), and stored in the refrigerator.

Soy-50 (50% soy/50% PF wt/wt). — A higher phenolic-resin-containing dispersion, Soy-50, was prepared in a similar manner as was 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 inversion step.

Soy-66-Iso (66% soy/34% PF wt/wt with 10% pMDI added post-dispersion). — 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 hour. 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 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. Using water as the solvent, the extraction was allowed to proceed for 24 hours. The residue in the thimble was then ovendried for at least 2 hours at 150°C, removed from the thimble, and weighed.

Results and Discussion

Properties of Prepared Resins

Table 1 compares the properties of the soy-PF alkaline resin and slightly acidic dispersion resins along with the properties of a commercial PF control resin. The results clearly demonstrate a substantial decrease in viscosity (from 1,030 to 606 cP) upon conversion of the alkaline resin (Soy-66A) to the acidic dispersion (Soy-66). The color of the dispersion was off-white and virtually no grits were formed. The alkaline and acidic dispersion resins are shown in **Figure 2**. Because the resins were prepared as dispersions and not solutions, accurate gel time measurements could not be made. Dispersions do not have a tendency to settle as long as the soy flour is properly alkali-denatured prior to inversion. When the slightly

Table 1. ~ *Physical properties and characteristics of soy-PF alkaline and acidic dispersion resins.*

Face resin	Soy	PF	pMDI	pH	Solids[a]	Viscosity[b]	Gel time[c]	Insoluble[d]
	- - - - - - - - - - - - (wt %) - - - - - - - - - - - -				(wt %)	(Cp)	(min)	(%)
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.

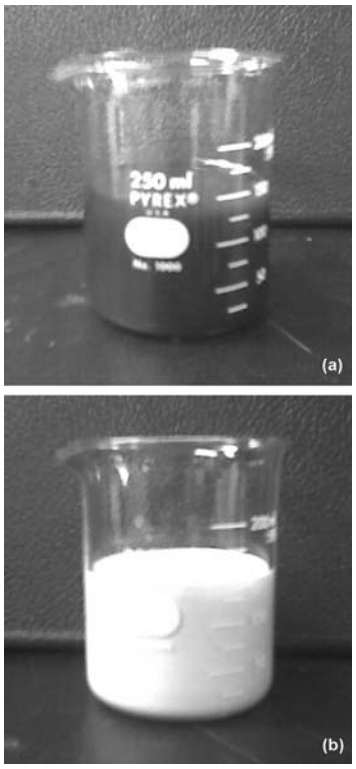

Figure 2. ~ *(a) Alkaline soy-phenol formaldehyde dispersion resin and (b) acidic dispersion resin.*

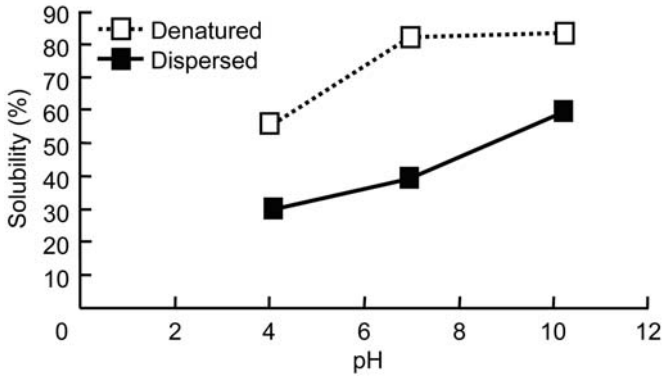

Figure 3. ~ *Water solubility of dispersed and denatured soy flour as a function of pH.*

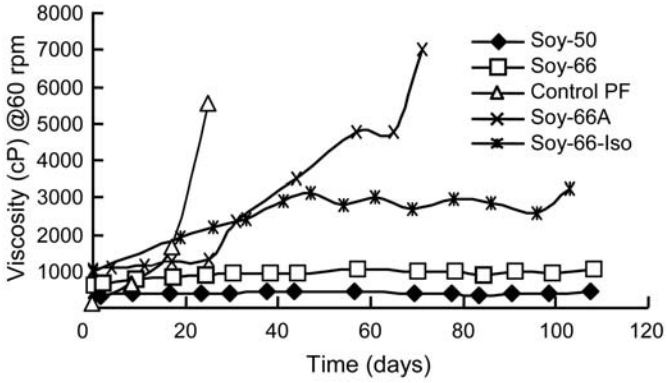

Figure 4. ~ *Room temperature viscosity stability profiles of resins.*

acidic dispersion was prepared with non-denatured soy flour, the resulting dispersion had a tendency to settle and have viscosity instability. This is attributed to the increased solubility of the denatured soy flour. The viscosity stability of test and control resins at room temperature is shown in **Figure 3**.

The slightly acidic soy-PF resin dispersions offer a tremendous advantage over the typical alkaline resole PF or alkaline soy-PF resins in terms of viscosity stability at room temperature. As **Figure 4** demonstrates, the viscosity of the two dispersion resins (Soy-66 and Soy-50) did not essentially change after more than 100 days. Conversely, the viscosity of both the commercial PF control resins, as well as that of the alkaline Soy-66A resin, increased rapidly after only a few days/weeks. The isocyanate-containing resin dispersion (Soy-66-Iso) showed an unexpected increase in viscosity stability initially; viscosity stability then leveled off, as expected. This profile of viscosity stability can perhaps be attributed to the fact that some isocyanate reaction took place in an aqueous dispersion. In spite of this, even the isocyanate-modified dispersion was able to offer a more stable

product than could the alkaline resins over a time frame of several weeks to months. Additionally, none of the dispersions exhibited any apparent settling or phase separation at any time.

One objective of this research was to develop a water-durable soy-based resin. To properly assess our candidate resins, their properties and performance were evaluated as both neat resin as well as in composite panels, namely strandboard. To determine the percentage of water-insoluble material within the final cured resin, a sample of the neat resin was placed in an oven, cured, and then subjected to a 24-hour Soxhlet extraction with water. This technique has been used previously to relate final board durability to neat resin properties (17). The data in **Table 1** show that all the soy-based resins are comparable to or better than a commercial PF resin, with typical values of around 70 percent.

Adhesive Performance

To evaluate the performance of the adhesives in composite panels, random OSBs were prepared using the resins (**Table 1**) in the face section of the panel only. The parameters used for preparing the boards are outlined in **Table 2** and are considered to be reasonable simulations of a commercial operation. We recognize that other variables, such as resin distribution, resin penetration, flake orientation, and press closing/opening conditions, are also of great importance in preparing quality wood composites, and we understand that these too would need to be evaluated in the future for a more complete analysis. However, our objective in this study was not to optimize any one variable, but rather to hold as many process variables constant as possible to provide a vehicle for comparing the different resins to each other and to a control. A direct comparison of these acidic soy resin dispersions to a commercial resin for this type of composite panel was considered the most important measurement of performance.

Table 2. ~ *Parameters for preparation of strandboard panels.*

Component	Value
Formed mat size	55.9 by 55.9 cm (22 by 22 in.)
Trimmed board size	50.8 by 50.8 cm (20 by 20 in.)
Starting furnish moisture wt% (face + core)	4.5%
Furnish type (size)	Mixed softwood/hardwood (75 by 23 by 1.0 mm, 2.9 by 0.9 by 0.04 in.)
Face/core ratio	55/45
Final thickness	11 mm (7/16 in.)
Final target density	673 kg/m^3 (42 lb/ft^3)
Face resin	3.26%
Face wax (emulsion)	1.31%
Core resin	3.89% (always PF control)
Core wax (emulsion)	1.39%
Application method	Air atomization
Press temperature	200°C (392°F)
Press soak times (time at target thickness)	210 and 330 s
Press close time (mat contact to thickness)	40 to 50 s

Table 3 and **Figures 5, 6, and 7** summarize the results. The results are consistent with our belief that soy resins can produce durable adhesives when they are properly modified and copolymerized to convert them into a water-insoluble material. The data show that the Soy-66 and Soy-66A resins performed comparably to the commercial PF control resin in all regards, except that the soy-based resins required slightly more press time. This is believed to be largely due to laboratory-scale heat transfer issues and is not expected to be a commercial liability. The fact that the performance of the panels showed no statistically

Table 3. ~ *Properties of strandboard panels produced from soy-PF alkaline and acidic dispersion resins.*[a]

Face resin	Press time	Density	Thickness swell[b]		H_2O uptake	Internal bond strength
			2-hour boil	24-hour RT soak		
	(s)	(lb/ft^3)			(%)	(lb/in^2)
Control PF	150	40.2	56.6 (9.3)	33.5 (4.5)	84.6 (7.1)	83.7 (20.8)
	210	40.5	53.7 (8.1)	31.0 (2.9)	86.0 (4.6)	94.6 (26.7)
Soy-50	210	43.4	64.6 (10.0)	38.1 (0.7)	84.1 (7.5)	95.4 (20.2)
	330	42.8	55.6 (7.1)	33.6 (2.5)	86.1 (8.3)	89.1 (26.5)
Soy-66	210	42.8	76.0 (9.9)	38.0 (1.4)	85.4 (6.5)	88.4 (27.5)
	330	42.5	60.6 (3.4)	33.7 (2.3)	83.2 (7.2)	77.0 (27.8)
Soy-66A	210	40.9	71.5 (10.7)	38.9 (3.5)	89.2 (6.2)	67.6 (18.5)
	330	40.8	58.4 (11.5)	36.3 (2.8)	89.0 (5.7)	71.0 (15.6)
Soy-66-Iso	210	41.7	76.9 (6.4)	17.3 (1.4)	38.3 (6.2)	84.8 (11.1)
	330	41.1	63.0 (8.6)	15.8 (0.8)	35.6 (3.6)	64.1 (17.6)

[a] Values in parentheses represent one standard deviation. 1 lb/ft^3 = 16 kg/m^3, 1 lb/in^2 = 6.89 kPa.
[b] ASTM 1037 soak procedure also applied to 2-hour boil. RT = room temperature.

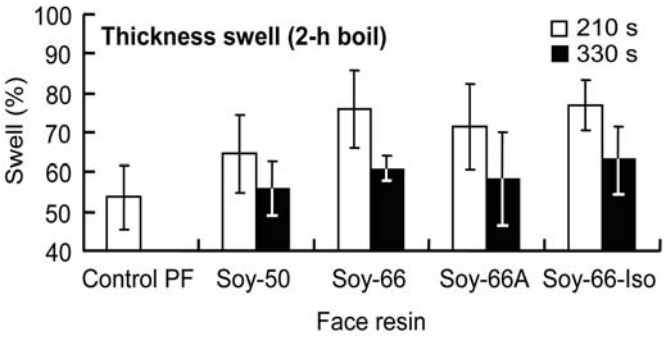

Figure 5. ~ *Thickness swell in 2-hour boil test by press time (210 and 330 s) and resin type.*

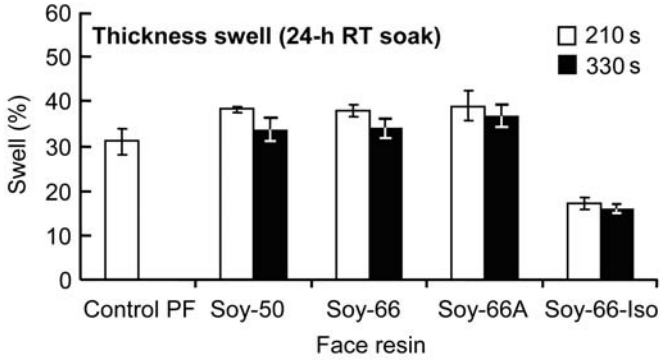

Figure 6. ~ *Thickness swell in 24-hour room temperature (RT) soak by press time and resin type.*

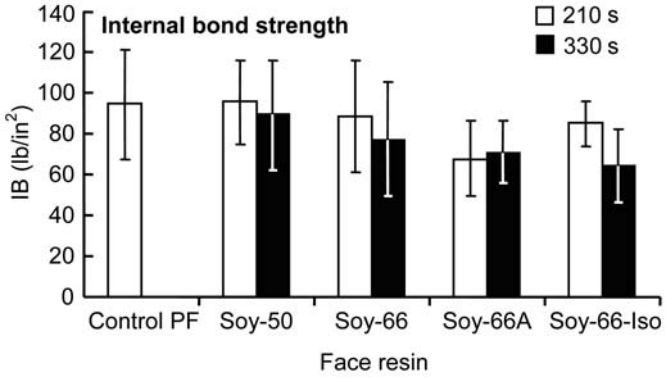

Figure 7. ~ *Dry internal bond strength by press time and resin type.*

significant change in the transition from the alkaline to the dispersion soy-based resins is encouraging, especially considering the improved color, improved stability, and lower viscosity of the dispersed resin. The significantly lowered room temperature thickness swell associated with the isocyanate-modified dispersion was a surprising and highly encouraging result for the potential of this technology to simultaneously save costs and enhance performance. Considering the fact that this resin still contains a very high level of soy (59%), we did not expect that its thickness swell would be around 50 percent less than that of the control PF. It is interesting to note, however, that the improvement in room temperature thickness swell did not translate to superior 2-hour boil results. Nonetheless, the raw material cost of a soy-PF resin is estimated to be 20 to 40 percent less than that of a commercial PF resin. These slightly acidic soy-PF dispersions could offer a huge opportunity to panel manufacturers to reduce resin cost without compromising quality.

Conclusions

The preparation of novel, slightly acidic soy-phenol formaldehyde (PF) adhesive dispersions with 50 to 66 percent soy content has been described. When compared to a commercial alkaline PF resin and also to an alkaline soy-PF resin, the dispersion resins offer greatly improved viscosity stability (in excess of 100 days) as well as lighter color, ultimately producing a more natural looking panel. The soy-PF resins were successfully used as a face resin for random strandboards with no significant difference in performance compared to that of a control commercial PF resin. The addition of 10 percent pMDI produced boards with 50 percent less water swell at room temperature compared to that of a control PF panel.

The results indicate that the slightly acidic soy-PF dispersion resins are viable candidates for the manufacture of durable composite panels. These resins also provide the possibility of increased performance or elimination of the dark alkali burn common in other currently used resins. Moreover, the soy-based resins offer substantial cost savings without the sacrifice of performance. This technology offers a great opportunity for panel manufactures to reduce the cost of face resin by 20 to 40 percent by replacing most of the phenol and formaldehyde with nonhazardous and fully renewable soybean flour.

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