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Competitive Soybean Flour/ Phenol-Formaldehyde Adhesives for Oriented Strandboard

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Abstract

Soy-based glues were very popular early in the 20th century. These adhesives were low cost and allowed for excellent performance in plywood panels as long as they were kept dry. These adhesives were quickly supplanted by lower cost, better performing petroleum-based resins in the middle half of the century. With the recent increase in the price of petroleum, soy-based resins may again be considered attractive alternatives if some of their previous performance limitations can be overcome. This paper provides a detailed look into a new soy-based adhesive system that offers board manufacturers a lower cost alternative resin system with no drop-off in final board performance or added production cost. The soy/phenol ratio can be as high as 1/1 with no drop-off in performance. The soy-based resin is considered to be a copolymer of soy and phenol formaldehyde. The initial target application is in the face section of oriented strandboard.

Introduction

The use of soy-based adhesives is not new to the chemical world. Traditional soy-based systems were common many years ago. In the late 1920s and 1930s, soybeans were studied extensively for their use as adhesives (Lambuth 2003). Soy flour, produced by grinding the meal after removal of the more valuable oil from the soybean, is high in protein. This protein is considered to be the main adhesive material. Early work mainly included exploring different means of denaturing the soy protein to expose the amide functional groups to maximize adhesion. It was generally believed that the best adhesive resulted if the soy was mixed in a caustic solution (Laucks and Davidson 1931, Davidson 1929, Satow 1930). However, these materials were greatly limited by their very short pot lives (room temperature stability), poor biological stability, low solids, slow press times, and, most importantly, poor water resistance. The latter limited the use of these adhesives to mainly interior applications. Petroleum-based glues entered the market in the 1940s and soon demonstrated that they were far superior to traditional soy-based glues in terms of durability, viscosity, and pot life, and by the 1960s they were even offered at a lower price. Eventually, these factors led to the nearly complete replacement of soy-based glues in the wood-bonding arena **(Fig. 1).**

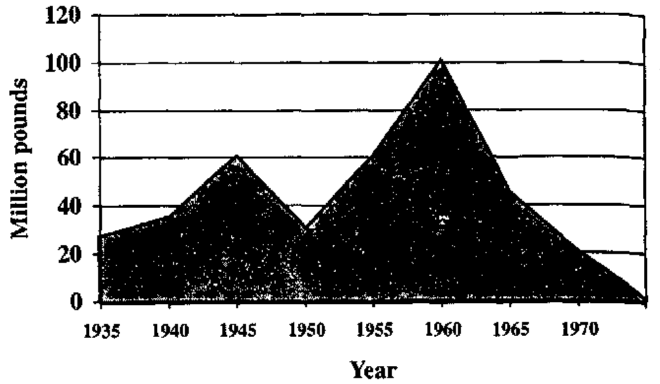

Figure 1.–Soy adhesive usage in the United States.

Today phenol-formaldehyde (PF) resins enjoy a dominate place in the resin market for external applications, and urea-formaldehyde (UF) resins are equally as dominate in the interior wood-bonding market. With recent increases in petroleum prices, along with formaldehyde emission concerns and general phenol safety issues, the use of soy is again being evaluated as a viable exterior grade adhesive.

There have been recent successes in the development of durable soy-based adhesives. Kreibich was able to demonstrate the viability of soy technology in the end jointing of green lumber (Kreibech et al. 1997). This involves the use of the much more costly hydrolyzed soy protein isolate. In this technology, the hydrolyzed soy isolate and a phenol-resorcinol resin are applied to separate "ends" of two boards, which are then joined together in what is now known as the "honeymoon" process. Clay et al. expanded upon this work and demonstrated that soy flour may also be used in this process (Clay et al. 1999). The problem with the honeymoon technology is that it requires keeping the soy portion separate from the phenolic- or resorcinolic-based binder or crosslinking agent. The premise of this technology is the high reactivity between the two components. Thus, a blended one-component resin would offer little pot life. Hse and Bryant demonstrated the viability of using a soy flour/PF system for panel boards (Hse et al. 2001). However, this work involved using large amounts of caustic materials, which resulted in very high pH values, plus they typically employed lower soy levels. Kuo et al. have also worked in this area, but this technology often leads to very high-viscosity, low-solids resins and very short pot lives (Kuo et al. 2001). Most of the other work in this area is dedicated to identifying different methods for soy denaturing and hydrolysis. Conner (1989) offered a general review of some other efforts.

With this new technology, the advantageous properties of soy (low cost, renewable resource, low or no formaldehyde content) have been captured. As much as 70 percent of a traditional PF resin can be replaced with a soy-based product and produce boards of comparable physical properties under comparable pressing conditions (same press time and platen temperature). **Table 1** summarizes the technology advancements over previous soy-based systems.

If soy adhesives are to make a comeback, they must overcome some, if not all, of the performance issues outlined above. Most notably, the water durability issue must be addressed. It is believed that many soy-based adhesives suffer from durability issues primarily due to the limited amount of crosslinking present in the cured resin. Soy protein has been shown to crosslink with formaldehyde, but this reaction is very easily reversed and does not afford a durable bond (Skrzydlewska 1994). Moreover, the primary problem with traditional soy adhesive is very likely that the soy does not lose its water solubility after the curing/drying process has taken place. Thus, when subjected to moisture, the adhesive returns to solution

Table 1. – Advances of this technology compared with traditional soy technology.

Past soy problem	Solution
Biologically unstable	By proper denaturing and copolymerizing with small amounts of reactant, the product is believed to be rendered biologically stable. We are continuing to work in this area.
Low solids	By developing a new method for denaturing and copolymerizing with viable crosslinking agents, the soy resins are offered at solids ranging from 30% to 45%.
Slow press times	By copolymerizing with reactive crosslinking agents, slow press times are not an issue because the cure rate can easily be tailored to meet a variety of applications.
Poor water resistance (durability)	By copolymerizing with reactive crossling agents, the soy resin actually becomes a water-resistant thermoset resin.
Very short pot life	By innovative processing, the shelf life of soy resin ranges from 2 weeks (similar to PF resins) to 1 year.

Table 2. – Physical properties and characteristics of selected soy-based resins[a]

	Control PF	soy 1	soy 2	soy 3	soy 4
Soy/phenol	0	1/1	1/1	1/1	3.411
Viscosity (cps)	244	1,200	1,100	750	1,100
pH	11.2	10.2	11.3	11.3	10.3
Solids (% NVM)	53.3	39.0	34.4	39.5	35
Color	Deep red	Red/brown	Red/brown	Red/brown	Light brown
RT stability	2 to 4 weeks	2 to 4 weeks	2 to 4 weeks	2 to 4 weeks	4 to 6 weeks
Application	ASIS	ASIS	ASIS	ASIS	AS IS/blend
% extractable	24	16	22	22	32

[a] Soy/phenol is wt/wt; viscosity is Brookfield LVT#3 or #2 at 60 rpm; solids is 1 h at 150°C oven method; % extractable is Soxhlet 24-h water after oven method; control is a 100 percent PF commercial OSB face resin.

and bond failure is imminent. When a water-based resin is cured, it must form a water-resistant, highly crosslinked structure to offer much bond durability. This behavior is believed to be responsible for the excellent water resistance offered by commercial PF resins today. This practice is also possible with soy flour. Soy flour contains a large amount of protein. This protein contains many side-chain reactive amino acid groups (25% to 30%) that are believed to have the ability to react with phenolic-type resin systems. It is this reactive nature that provides these soy resin systems with the ability to form thermoset networks with a suitable crosslinking agent. In effect, the soy would be tied into the thermoset network. 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. This may allow the use of soy flour rather than the high-priced protein isolates for the preparation of these novel adhesives. Using this methodology, soy resin, up to 80 wt%, has been successfully incorporated into the PF matrix (extraction results in **Table 2**).

Soy-Based Resin Preparation and Characterization

Soy-based resins are all prepared by a low-temperature process. It is believed that higher temperatures will result in excessive unwanted hydrolysis in addition to the desired denaturing of the soy. In a typical preparation, water, sodium hydroxide (8% to 12% to soy), and a small amount of phase transfer or solubilizing agent (such as ethylene glycol or polyethylene glycol) are combined and heated to 70°C. The soy flour is then added slowly to the solution to afford a homogenous soy solution/dispersion. The resin solution is then subjected to a denaturization step that consists of heating the mixture. The soy is now considered to be denatured and is ready to be used if water durability is not required. To increase the durability of the resin, formaldehyde is then added to "modify" the soy for copolymerization with phenol or formaldehyde-modified phenol. The "modified soy is then reacted with phenol followed by additional formaldehyde to make the final copolymer resin solution. Additional PF resin may be added by either *in situ* preparation (soy 2, 4) or post-reaction blending (soy 1, 3). The final copolymer resin results in a water-durable adhesive with a total soy/phenol ratio of 1/1.

This process is considered to be very manufacturing friendly, with no vacuum processing or high-pressure steps. The resulting adhesives offer gel times and stabilities comparable to those of typical commercial PF resins. Characteristics and physical properties of several prepared soy-based resins are shown in **Table 2.**

The low amount of extractables for these soy-based resins (**Table 2**) is highly indicative that a large amount of soy is incorporated in the final resin matrix. To further prove this, samples of a 40 percent soy (similar to soy 1) containing resin were cured in an oven at 150°C and then subjected to a 24-hour water extraction. Both the initial solids and the extraction residue were analyzed for nitrogen, carbon, and hydrogen content. Because no additional nitrogen was added to this particular soy-based resin, all the detected nitrogen was assumed to be from the soy protein. The results in **Table 3** show the high nitrogen content in the water-insoluble residue. This information leads to the conclusion that the once-soluble soy protein has been rendered water insoluble upon copolymerization with a suitable PF resin. Additionally, it is estimated that more than 60 percent of the other soy flour components (carbohydrates and oil) are also rendered water insoluble upon successful copolymerization. Based on these results and other supporting model studies, it can be concluded that when prepared using this process, the soy protein in soy flour is virtually fully incorporated in a copolymer matrix. It is this process that allows better water-durable bonds to be realized.

Viscosity, Solids, and Stability

Two important property characteristics of soy-based technology that have raised concerns are high viscosity and poor pot life (stability). Although soy-based resins often have higher Brookfield viscosity values than many commercial PF resins, it should be recognized that soy-based resins are thixotropic. This implies that Brookfield viscosity measurements may be misleading with respect to spraying ability. Therefore, a soy-based resin at 700 cps is actually much less viscous than a phenolic resin at 700 cps when subjected to a high shear environment such as a spraying process. In our history of applying these resins either by air or spinning disk atomization, difficulties or problems with adequate resin distribution have not been observed. The solids of the resins are slightly lower than some typical face resin systems. It is felt that as long as this resin is used in the face section of OSB, this additional water is not a serious problem and results in only marginal increases in the total face mat moisture levels.

These soy-based resins also are also well suited with respect to their long-term stability. Many soy-based resins suffer from poor room temperature stability and, thus, have very short useful pot lives. This technology takes into account the importance of room-temperature stability. Comparative examples are shown in **Figures 2 and 3.**

Table 3. – Soy flour incorporation in PF matrix as determined by elemental analysis after extraction.[a]

	N		C		H		Extraction	
	(%)							
Material	Thero.	Exp.	Thero.	Exp.	Thero.	Exp.	Thero.	Exp.
Solids	2.9	2.8	60.5	58.9	5.8	5.4		
Residue	3.1	3.2	65.1	64.6	5.8	5.7	85.7	85.7

[a] Theoretical calculations were made assuming that none of the protein, all of the NaOH, and 40 percent of the carbohydrates and oils were extracted.

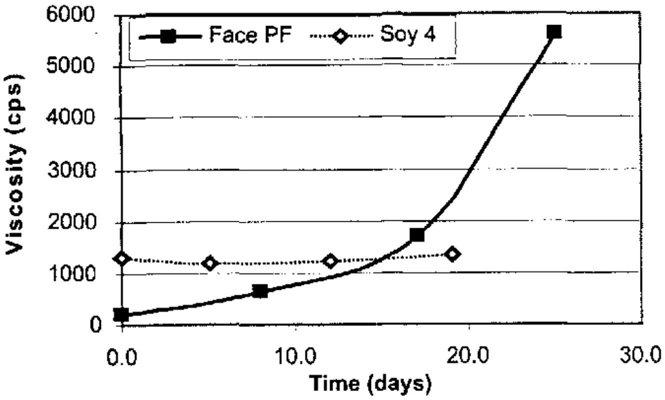

Figure 2. – Stability with time of soy 4 compared with PF resin.

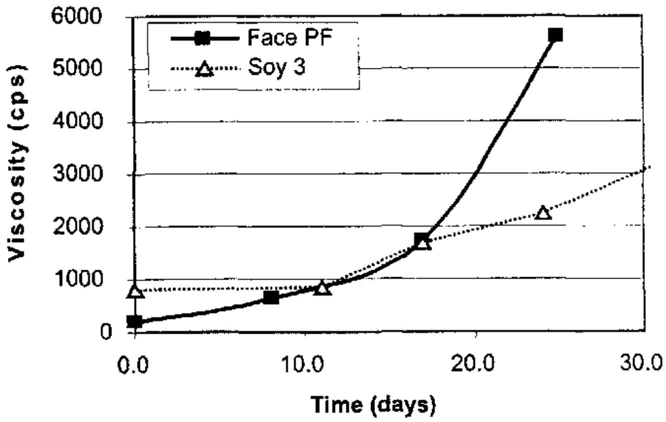

Figure 3. – Stability with time of soy 3 compared with PF resin.

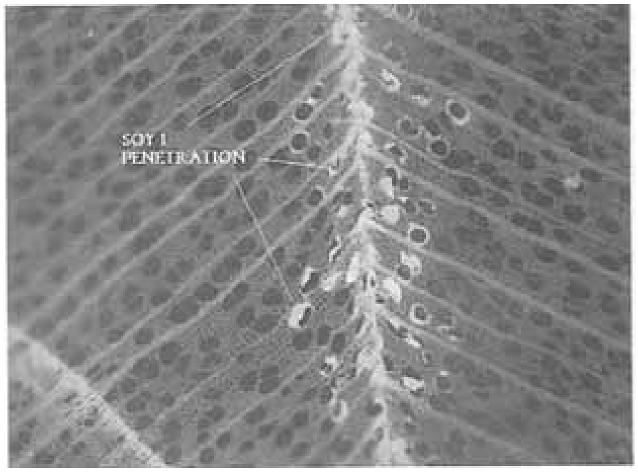

Figure 4. – Micrograph of soy 1 penetration into yellow-poplar.

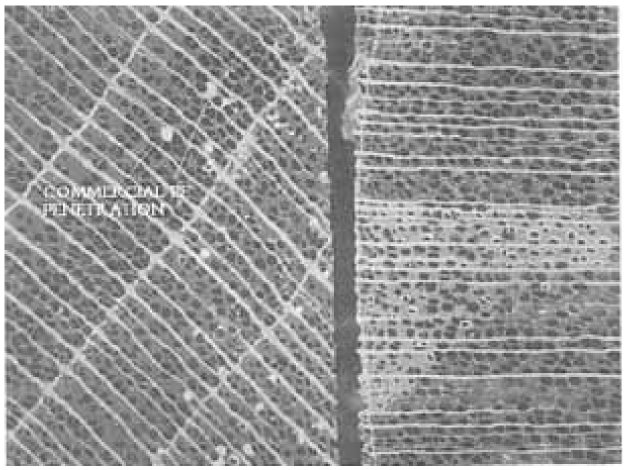

Figure 5. – Micrograph of commercial PF penetration into yellow-poplar (sample tore).

Resin Penetration

The importance of proper resin penetration to achieve the best bonding situation is also well recognized. Thus, optical microscopy to assist in our resin development has been employed. **Figures 4 and 5** show examples of soy 1 and a commercial PF resin applied to yellow-poplar. Note the proper penetration of the soy 1 resin – there is sufficient penetration to allow for good adhesion but not over penetration as is seen with this OSB face PF commercial sample.

Application to Strandboard

These soy-based resins were used as the face resin in random strandboards. Panel preparation parameters are outlined in **Table 4.** Properties of the pressed panels are shown in **Figures 6 to 10.** For all the results shown, the error bars represent one standard deviation of the data. The results are typically obtained from two samples each of two separately pressed boards, from a single resin application to the flakes.

Dry Board Properties

Soy resins are well known for their excellent dry panel properties. Because the primary concern is the water durability of these panels, very little testing was performed on dry panels. Internal bond (IB) strengths were measured to demonstrate that sufficient bonding had taken place. Of most importance is the fact that the boards containing soy 1–3 resins show IB strengths comparable to the control at both press times, suggesting that press time will not be a manufacturing problem and that the samples are comparable prior to entering the wet testing (**Fig. 6**).

Table 4. – Strandboard panel preparation parameters.

Component	Value
Formed mat size (in. (mm))	16 by 16 (406 by 406)
Trimmed board size (in. (mm))	14 by 14 (356 by 356)
Furnish moisture (%)	5.6
Furnish type	Mixed hard/soft
Face/core ratio	55/45
Final thickness (in. (mm))	7/16 (11)
Final target density (lb/ft.^{3} (kg/m^3))	42.0 (673)
Face resin (%)	3.3
Face wax emulsion (Yo)	1.3
Core resin (%)	3.9 (always PF control)
Core was (emulsion) (%)	1.4
Application method	Air atomization
Press temperature (°C)	200
Press soak time (time at thickness) (sec.)	150 and 210
Press close time (sec.)	40 to 50
Total face mat moisture (%)	11.0

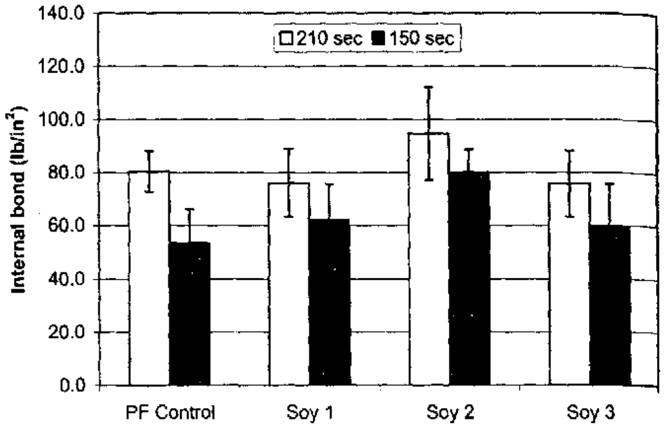

Figure 6.–Dry IB results of soy-based strandboards compared with PF control.

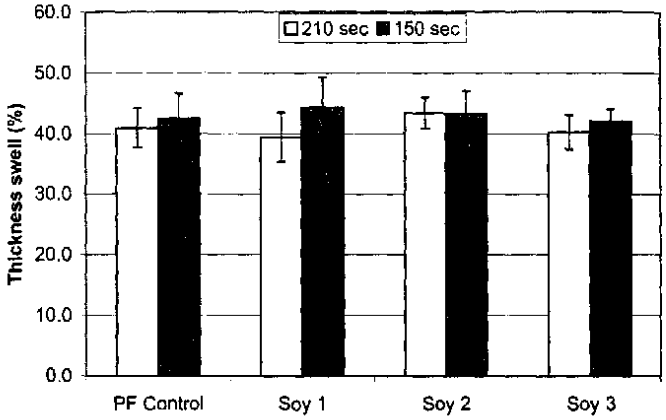

Figure 7.–TS after 24-hour room temperature soak method.

Also of importance is the fact that failures occur mainly in the core, which indicates that even with a soy-based resin on the surface, the weakest section is still the lower density core. Soy 4, with the higher soy content, requires a longer press time to achieve acceptable results due to the low amount of phenol present (soy/phenol = 3.4). However, in recent preliminary work, increases have been achieved in the IB strengths and cure rates of the soy 4 panel by further optimizing the crosslinking agent (results to be reported soon).

Wet Board Properties

Of most importance is the fact that these soy-based resins offer some excellent water-resistance properties. Water durability can be measured by several different means. It is preferred to use both the room temperature 24-hour soak (ASTM D1037) and the very aggressive 2-hour boil methods. Additionally, the 2-hour boil sample is subsequently ovendried and the center is cut and tested for IB strength. This test is designated "wet IB" and is considered to be the most aggressive means of testing resin durability. Data for the 24-hour swell are shown in **Figure 7,** the 2-hour boil swell in **Figure 8,** and the wet IB in **Figure 9.** Due to the strong correlation between board properties and durability, the average board density for each set is also provided (**Fig. 10**).

The results clearly show how resins soy 1–3 all offer comparable final board performances when compared with the 100 percent control, even at the very fast lab press time of 150 seconds. Although values reported for the wet IB strength are much lower than their dry counterpart, it is our experience that unless the resin offers excellent durability, the sample will have no IB strength after the 2-hour boil, ovendry process. Thus, these results clearly demonstrate the excellent durability offered by this soy-based technology. To our knowledge, this level of durability has never been reported for such high soy levels when

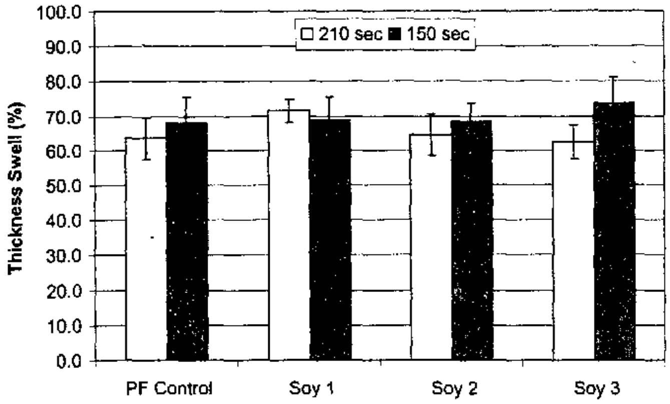

Figure 8. – TS after 2-hour boil method.

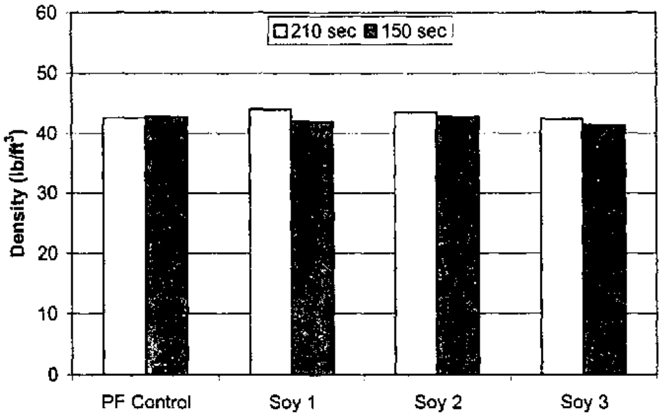

Figure 10. – Board densities of trimmed 14- by 14-inch (356- by 356-mm) panels.

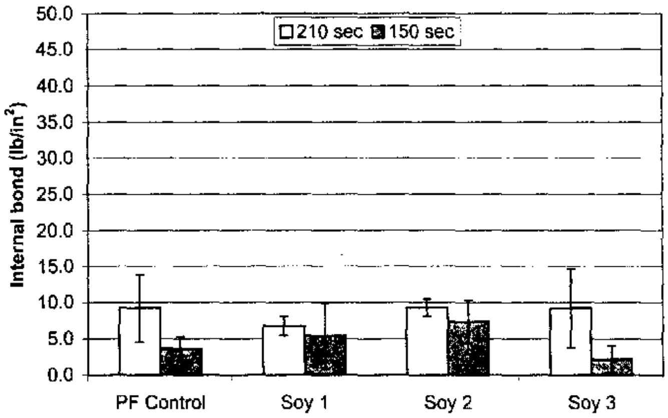

Figure 9. – 18 of ovendried specimens after 2-hour boil method (wet IB).

Table 5. – Cost savings associated with the reduction of phenol in soy-based resins.[a]

Resin type	Soy/ phenol	Phenol	Soy	Total	Savings
		($)			(%)
PF control	0	0.370	0	0.370	
Soy 1	1.0	0.185	0.045	0.230	37.8
Soy 4	3.4	0.081	0.070	0.151	58.5

[a] Cost calculations based on $0.37/1b. and $0.09/lb. for soy flour (solids).

used under commercially required conditions (such as resin load, press time, press temperature).

Summary of Cost Savings

The majority of the cost savings associated with this soy-based technology comes from the replacement of phenol with low-cost soy flour. Comparisons of soy 1, soy 4, and 100 percent PF relative to phenol and soy flour cost are shown in **Table 5.** Based on these estimations, it is believed that a significant cost savings can be realized by using this soy-based technology. Additionally, these formulations allow for an additional savings by offering a 20 to 50 percent reduction in the total formaldehyde in the formula.

Conclusions

The preparation of a novel adhesive with high soy content has been described. These resins have been successfully used as a face resin for the preparation of random strandboards with no significant performance differences compared with a control. Most importantly, these soy-based resins offer cost savings and excellent durability. This technology provides more environmentally friendly products by replacing phenol and formaldehyde with non-hazardous soybean flour. This technology offers a great opportunity for panel manufacturers to reduce their cost for face resin by 20 to 40 percent.

Acknowledgments

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