Specific Oxidants Improve the Wood Bonding Strength of Soy and Other Plant Flours

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ABSTRACT: To meet newer environmental standards, modified plant proteins have been studied as no-added formaldehyde wood adhesives for interior applications. Many methods have been developed to increase the wet strength of wood products bonded with soy adhesives. These methods involve modifying the soy in separate steps prior to formulating the adhesive or adding a polymerizable co-reactant to the soy. We show that adding periodate, permanganate, or iodate to soy flour improved the strength of soy adhesive bonds in small-scale testing and in plywood shear, especially when tested under wet conditions. Periodate improved the bond strength of other plant materials (lupine, canola, and cottonseed) but none of these produced as high of a wet strength as the soy flour. We investigated other oxidants with plant proteins. Permanganate was quite effective and iodate was somewhat effective, whereas nitric acid, chlorate, perchlorate, and bromate were not effective in increasing wet strength. The available data are consistent with oxidation of the carbohydrate–protein mixture in plant flours to provide adhesives with increased wet strength in wood bonds. This mechanism was also supported by the improved wet strength with the addition of dialdehydes (glyoxal and glutaraldehyde). The purified soy protein also gave strength improvement with periodate. Published 2019. This article is a U.S. Government work and is in the public domain in the USA. J. Polym. Sci., Part A: Polym. Chem. **2019**

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INTRODUCTION Protein adhesives were the main raw material used in bonding wood products from the earliest times until the commercialization of fossil fuel adhesives in the middle of the 20th century. The increased demand for bonded wood products in World Wars I and II for aircraft, ships, military buildings, and shipping containers led to the development of higher performing bonded wood products. Aircraft needs resulted in the highest performing protein adhesives (casein plus blood) in World War I and led the movement to synthetic adhesives in World War II.[1] However, even the most advanced protein adhesives generally could not compete with fossil fuel adhesives, especially the phenol- and amino-formaldehyde adhesives. This deficiency led to almost complete disappearance of research on protein adhesives with the exception of research on soy as a partial phenol replacement in phenol-formaldehyde adhesives to lower costs.[2,3] The only new commercial soy adhesive during this time was as a fast-setting honeymoon adhesive involving soy on one side and a phenol-resorcinol formaldehyde on the other for finger jointing green studs,[4,5] but this formulation was later replaced by a reformulation of the phenolic adhesive.

Interest in bio-based products and limits on formaldehyde emissions from wood products[3,6,7] has led to renewed interest in protein-based adhesives. Many of the formerly used animal-derived proteins (casein, collagen, and blood) are no longer available in useful volumes and prices for general wood adhesive applications and are used only in more specialty products that command higher prices. However, plant-derived proteins are still available in sufficient volumes and at reasonable prices. Given that plant proteins are mainly used in animal feed,[8] it is economical for them to be used as wood adhesives, and this use will not diminish the human food supply.

Of the many plant materials, most of the research has been with soy because of its ready availability as a low-cost flour with acceptably consistent composition. Most recent research has focused on addition of co-reacting adhesives, such as phenolics,[2,9–14] polyamidoamine-epichlorohydrin,[15–17] isocyanates,[18] and epoxies,[19,20] but other research has used aldehydes, or added reactive functionality to the protein.[2,3,12,21,22] Often, this research has used commercial soy protein isolate, which is readily available but can be a poor model compound for the native proteins in soy flour because of the processing involved in commercial isolate production, especially jet-cooking for increased performance in food applications.[23] Thus, it is important to test any improvement in adhesive strength not only with the non-jet-cooked soy isolate but also with the concentrate, and especially the low-cost flour.

Although good adhesives can be achieved using soy with a coreacting adhesive or separate modification steps, there is also a need for soy that is modified chemically *in situ* to improve the adhesive's strength and water resistance. The carbohydrates (about 45% of the soy flour composition) may help the adhesive's dry strength, but they most likely decrease its wet strength, given the propensity of carbohydrates to absorb moisture.[24] Half of these carbohydrates are soluble, such as sucrose, raffinose, and stachyose, and half are insoluble, such as polymers containing rhamnose, arabinose, galactose, galacturonic acid, glucose, xylose, and mannose.[25–28] As illustrated in Figure 1, carbohydrates can bridge between the protein globules, which provides good strength under dry conditions, but these bonds most likely break down with the addition of water.[29] If the carbohydrates were removed, there would be better coalescence of the protein globules, which is an important property of the soy protein isolate (and is measured by gel strength).[25]

Because the carbohydrates decrease soy flour wet bond strength,[30] removing them or converting them into more reactive compounds are likely paths for improving soy flour wet strength.

Commercial concentrates and isolates are available with lower carbohydrate contents (about 20% and less than 5%, respectively), but they are much more expensive because of mass loss in the carbohydrate removal steps and processing costs.

Conversely, oxidizing the carbohydrates in the soy flour causing them to react with the protein appeared to be a better way to improve the bond strength under wet conditions; this would turn a detriment into an asset without separating and discarding components. A specific oxidant for carbohydrates is periodate, which reacts with adjacent hydroxyl groups to form dialdehydes.[31] Aldehydes are known to react with proteins,[2,12,32] but they have not been used in an *in situ* process without adding other reactive chemicals. Hypothetically, these periodate-generated dialdehydes could tie together the soy protein globules to form a stronger network between two wood surfaces. Additionally, the carbohydrates may also react with other oxidants and similarly tie the proteins together rather than be an interference in the protein–protein interactions necessary for wet bond strength. Thus, in this study, a variety of plant sources containing proteins and carbohydrates were reacted with periodate and other oxidants to determine whether the wood bond strength could be improved when tested wet.

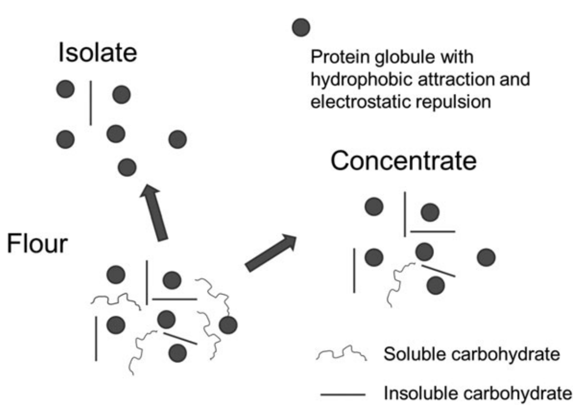

FIGURE 1 Schematic representation of soy flour with its protein globules (circles), insoluble carbohydrates (straight lines), and soluble carbohydrates (squiggly lines).

EXPERIMENTAL

Materials

Soy flour (ProliaR 200/20, 200/70, 200/90) was obtained from Cargill (Cedar Rapids, IA). Isolate (Pro-Fam 974R) was obtained from ADM (Decatur, IL). Canola flour (Behpak Industrial Company, Iran), lupine flour (Lopino Foods, Mt. Shasta, CA), cottonseed flour (Planters Cotton Oil Mill, Inc., Pine Bluff, AR), sodium periodate, potassium bromate, hydrogen peroxide (Sigma, St. Louis, MO), potassium iodate (Mallinckrodt Chemical Co., New York, NY), and potassium permanganate (Baker Chemical Co., Phillipsburg, NJ) were used as received.

Adhesive Formulations

The plant material for testing was mixed with water at 25% solids. Lower concentrations were used with commercial soy protein isolate (CSPI, 15%) to avoid the adhesive being so viscous that it could not be mixed and spread. The oxidant was added at 8.7–15% relative to the plant material solids and was well mixed. When the pH was adjusted, less water was initially added, the pH was adjusted after oxidant addition, and water was added to obtain the final concentration of 25% plant material solids. Viscosities were measured with a Brookfield Engineering DV viscometer (Middleboro, MA) at 20 °C using the method of rapidly hand mixing the sample for 30 s, immediately plunging in the spindle #4, waiting 10 s, then turning on the motor at 12 rpm and taking the reading after 10 s.

Small-Scale Bonding

An automated bonding evaluation system (ABES), Model 2010-14 (Adhesive Evaluations Systems Inc., Corvallis, OR), was used for bonding and testing the shear strength of the adhesives in ASTM D7998-15.[32] The adhesive formulation was applied to 5 mm on the end of one piece of maple veneer (117 × 20 × 0.6 mm), which was overlapped by 5 mm with another piece of veneer. The amount of adhesive applied was enough for a small amount to be squeezed out. Samples were immediately hot pressed in the ABES at 0.2 MPa for 120 s at 120 °C. The bonded wood samples were equilibrated at 21 °C and 50% relative humidity at least overnight before testing dry and after soaking in water for 4 h at room temperature for wet testing. Four specimens were tested in tensile shear for the dry and wet conditions. Error bars represent one standard deviation.

Plywood

Poplar and Douglas-fir 3-ply plywood panels (3.2-mm veneer ply) were bonded with 90 protein dispersibility index (PDI) soy flour at 25% solids plus 15% periodate and tested for delamination, shear strength, and wood failure (ASTM D906-98). The panels were bonded for 5 min at 150 °C at 0.86 MPa after a closed assembly time of 15 min. The spread rate was 215 g/m^2. The panels were conditioned at 26.7 °C and 30% RH for 1 week before being cut into samples. The delamination (127 × 51 mm)

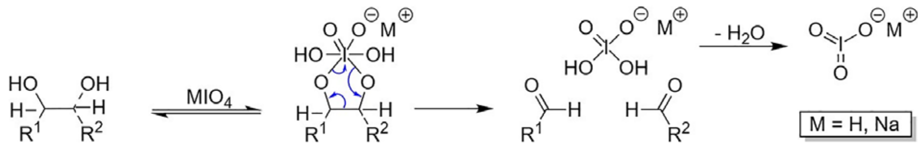

FIGURE 2 Periodate cleavage of vicinal diols to yield aldehydes. [Color figure can be viewed at wileyonlinelibrary.com]

samples were soaked for 4 h in room temperature water and then dried for 19 h at 50 °C. The soaking and drying were repeated for the second and third cycles. The delamination was measured within 15 min of removal from the oven, according to ANSI/HPVA HP-1.[27] For testing shear strength, the panels were cut into 82.6 × 25.4-mm samples according to ASTM D906-98[33] with half of the samples being tested dry and half tested wet after soaking in room temperature water for 24 h. In a modification of D906, all samples were pulled with the lathe checks closed to obtain more consistent data.

RESULTS AND DISCUSSION

Soy Flour Oxidations Using ABES Evaluations

Periodate readily reacts with adjacent hydroxyl groups in carbohydrates to form dialdehydes, as illustrated in Figure 2.[31,34] These dialdehydes can react with amine-containing amino acids such as lysine in the protein to form a Schiff base.[32,35] This initial Schiff base is usually reduced to form a secondary amine, which is a more stable chemical bond than the Schiff base. When sodium periodate (15% of the soy solids) was added to a 25% solids dispersion of the 90 PDI soy flour in water, the mixture turned pink and became slightly warm, going from 20 °C to 28 °C. This unusual change in the dispersion indicated that periodate was reacting with something in the flour. Although the periodate appeared to modify the soy at room temperature, additional changes could also be taking place during the bonding step at 120 °C.

To evaluate adhesive performance of the modified soy, we used a variation of ASTM D7998-15,[36] which forms and tests bonds under carefully controlled pressure, time, and temperature with a wide range of adhesive viscosities. With the ABES and smooth maple veneer, the measured cohesive strength for moderate-strength adhesives is less sensitive to effects of viscosity, spread rate, pressure, and so on than other shear tests. The periodate-oxidized 90 PDI soy flour at 120 °C had an average wet (4-h water soaking) strength of 2.89 MPa compared with 0.40 MPa for the unmodified 90 PDI soy flour and 2.80 MPa for the expensive, unmodified CSPI. Another advantage is that the soy flour plus periodate adhesive has only about twice the viscosity of the soy flour (40,000 mPa·s vs 18,000 mPa·s, respectively), compared with the CSPI, which has a high viscosity (90,000 mPa·s) at just 15% solids. The lower solids and resulting higher water content of the CSPI is detrimental to the commercial bonding process. Because the periodate–flour reaction and the resulting improved wet bond strength have not been covered in the plant flour literature, this promising *in situ* alteration of the soy flour led to a number of questions. What is the optimum pH, periodate to soy ratio, and PDI of soy flour? Does the periodate react with soy isolate or other kinds of plant proteins? Consequently, a number of factors were examined to determine the optimum conditions for the periodate reaction.

The pH of the soy dispersions is often important, because it determines the charge and solubility of proteins[37] and could influence the reaction of periodate with the carbohydrates.[31] As shown in Figure 3, we determined that a pH range of 4.6–8 was the most effective for the 90 PDI flour (25% dispersion and 15% periodate based on flour weight). Adhesives below pH 4 are undesirable because of acid degradation of the wood. Conversely, pHs above 8 cannot be used because of gelation of the soy flour with periodate. This gelation is additional evidence that periodate is changing the soy because soy flour does not generally gel at a pH above 8. In all cases, the pH of the soy dispersion was adjusted after sodium periodate addition.

A low ratio of periodate to soy flour is important for two reasons: to minimize the cost of periodate and to avoid breaking the carbohydrates into pieces too small to be effective for protein cross-linking. Figure 4 shows that the wet strength increases up to 15% periodate based on weight of soy flour. The effect of

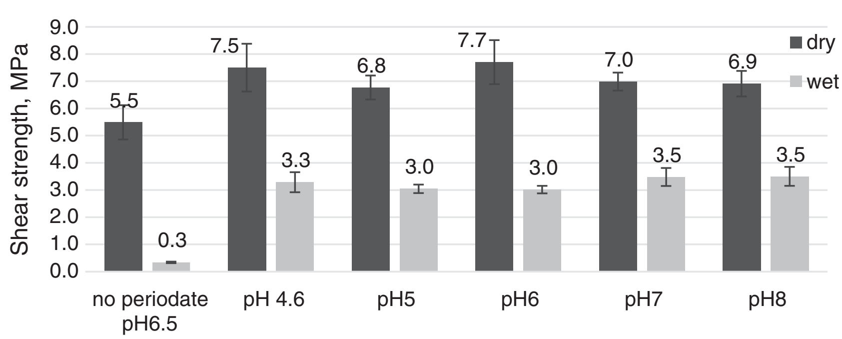

FIGURE 3 Effect of pH on dry and wet ABES bond strength for periodate-reacted 90 PDI soy flour, compared with soy flour with no periodate added.

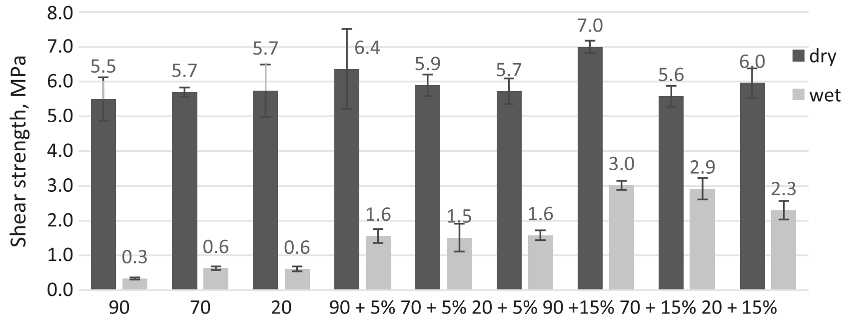

FIGURE 4 Effect of periodate concentration on dry and wet ABES bond strength of periodate-reacted soy flour; 90, 70, and 20 are the PDIs of the soy flours, 5% and 15% are the amounts of periodate added based on weight of flour added.

periodate on wet strength was investigated using low heat (when removing the residual hexane from oil extraction) native 90 PDI flour, lightly heated 70 PDI, and heavily heated and highly denatured 20 PDI flour. Although the effect of periodate was very similar between flours at 5% periodate, the native 90 PDI flour gave higher wet shear strength than denatured flours at 15% periodate.

Compared with other oxidants, periodate is relatively expensive (>$22/kg on a commercial scale), leading to the question of whether other oxidants can be equally effective but at a lower cost. Thus, we investigated other oxidants, such as permanganate, iodate, chlorine oxides, and peroxide. As illustrated in Figure 2, iodate is the byproduct of periodate oxidation of vicinal diols and is usually not considered a strong oxidant. However, as shown in Figure 5, the iodate improved the wet strength of the wood bonds but did not provide the heat or color change in the initial mixing that was observed with periodate. It may be that the iodate was only able to react at 120 °C during bonding. Permanganate is known to oxidize alcohols, and it provided good adhesive strength with a maximum increase in wet strength at 8.7% of the 90 PDI flour. The smaller increase may have been caused by permanganate not being as selective in vicinal diol oxidation[38] as is periodate[31] or by the fact that the optimum reaction conditions were not selected. In contrast, the higher oxidation state of other halides of perchlorate, chlorate, and bromate, similar to periodate, did not provide any substantial increase in wet shear strength. Other oxidants, such as hydrogen peroxide, alone or with copper or iron salts, nitrate, persulfate, or perborate gave little to no improvement.Thus, only certain oxidants improved the soy flour adhesive wet strength under the conditions tested. Some of the oxidants did improve dry strength somewhat, but the key issue is improving the wet strength.

Oxidation of Other Plant Materials Using ABES Evaluations

Given the increase in wet strength of periodate-reacted soy flour, the question arose whether there is something specific about the proteins and carbohydrates in soy or would periodate react with other plant materials containing carbohydrates and proteins to increase the wet bond strength. We found that periodate increased the wet bond strength of canola, lupine, and cottonseed flour, but none of them outperformed the soy flour in wet bond strength (Figure 6). The higher dry and wet bond strengths were probably caused by soy flour having about twice as much protein as canola or cottonseed to react with the periodate-produced dialdehydes (Table 1).

Because periodate improved the wet bond strength of canola, lupine, and cottonseed flour, they were also tested with permanganate and iodate. Compared with the unmodified data in Figure 6, permanganate improved the wet bond strength of all of them, but none had wet strength as high as soy flour (Fig. 7). Iodate also improved the wet bond strength of all except lupine.

The response of a variety of natural products to the different oxidants is quite interesting. However, without understanding the detailed structural information of both the proteins and carbohydrates of these materials and what the exact mechanisms are of the improved strength with these oxidants, it is

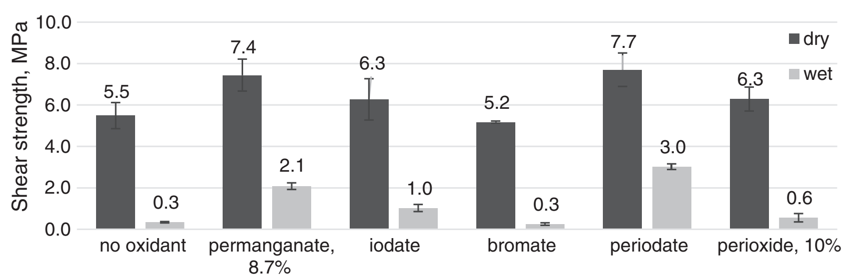

FIGURE 5 Effect of various oxidants (permanganate: 8.7%; hydrogen peroxide: 10%; rest: 15%) on dry and wet ABES bond strength of 90 PDI soy flour.

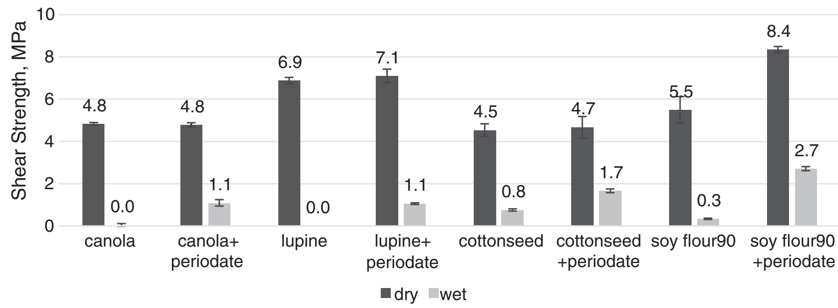

FIGURE 6 Effect of 15% periodate on dry and wet ABES bond strength of canola, lupine, cottonseed, and 90 PDI soy flour.

TABLE 1 Composition of Plant Seeds (Carbohydrate Refers to High-Molecular-Weight Carbohydrate)

Flour	Protein (%)	Oil (%)	Carbohydrate (%)	Carbohydrate type	Reference
Soy	51	20	6	Fiber	39
Canola	22	41	22 + 10	Starch + fiber	40
Lupine	55	10	35	Starch + fiber	41,42
Cottonseed	22	20	35 + 19	Starch + fiber	43

hard at this point to explain these data in any detail. The ability of periodate to oxidize carbohydrates to dialdehydes that react with the proteins is a logical mechanism, but it does not explain the effect of the iodate and why different plant sources provide such varying results with the permanganate and iodate. Research is continuing to try to determine the chemical reactions in the very complicated mixtures present in these unpurified biomaterials.

Related Experiments

The presented data support our hypothesis that plant materials with significant levels of carbohydrates can be made into better adhesives using periodate to oxidize the vicinal diols to dialdehydes. Because soy flour is a complex mixture of proteins and carbohydrates, we decided to examine the effect of periodate addition to the CSPI, which is about 95% protein. If the reaction was mainly with the carbohydrates, then one might not expect much improvement with CSPI, which is an effective adhesive in its own right.[30] However, the wet bond strength of CSPI improved from 2.8 to 3.5 MPa with periodate addition (at 15% of soy solids). This suggests that periodate is able to act with the protein directly, although it must be noted that CSPI does contain some (<5%) carbohydrate in the form of glycoproteins and residual carbohydrate.[44] Although most of the literature on periodate discusses reaction with carbohydrates, there is also mention of reaction with proteins.[35] Reaction of periodate with proteins will be addressed in another paper.

If the main reaction with periodate is to convert the carbohydrates to dialdehydes, then the addition of dialdehydes to soy flour might give similar results. Consistent with the findings of others,[45,46] Figure 8 shows that glyoxal and glutaraldehyde both significantly improved the wet strength of 90 PDI soy flour adhesive. Glyoxal added at 10% and glutaraldehyde at 0.5% of soy flour solids were determined to be the optimal amounts for increased wet strength while still avoiding gelation. Glyoxal and glutaraldehyde did not increase wet strength as much as periodate, which may suggest that the proteins are not as accessible to aldehyde reaction as when periodate was

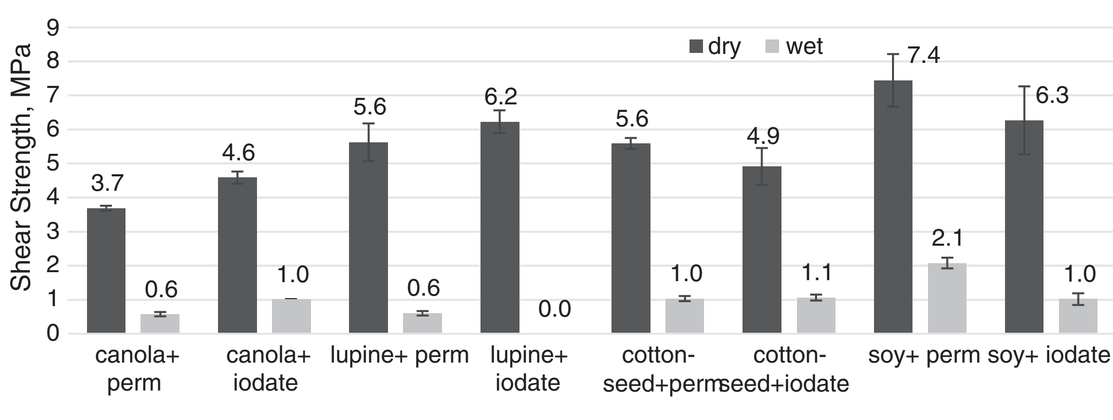

FIGURE 7 Effect of 8.7% permanganate (perm) and 15% iodate on dry and wet ABES bond strength of canola, lupine, and cottonseed.

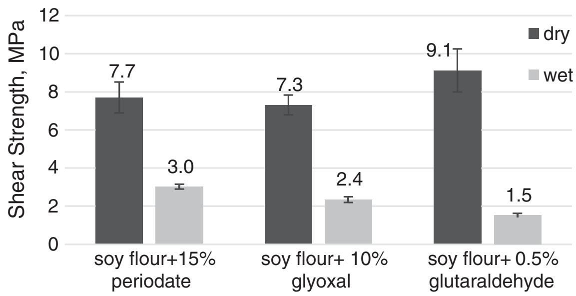

FIGURE 8 Effect of glyoxal (10%) and glutaraldehyde (0.5%) on dry and wet ABES bond strength of soy flour compared with periodate (15%).

used, that the formation of dialdehydes specifically on carbohydrates and proteins was a significant contributor to strength, or that the unreacted carbohydrates significantly interfered with bond strength.

Plywood Test Results

The results from ABES testing were very promising as a screening tool, but the situation can be quite different when bonding plywood because of greater surface roughness, cross-laminated plies, different wood species, and many other factors. An important property of interior plywood is resistance to delamination from water soaking and drying. The poplar samples bonded with 25% soy flour plus 15% periodate passed three soak and dry cycles, but the Douglas-fir samples failed after the first cycle.

The results of plywood shear testing according to ASTM D906-98 are shown in Figure 9A. Dry and wet strengths of both poplar and Douglas-fir were increased with periodate added to the soy flour and compared favorably with CSPI-bonded plywood. As shown in Figure 9(B), both the poplar and Douglas-fir bonded with soy flour plus periodate had good wood failure compared with the CSPI. These results show that soy flour plus periodate provides increased dry and wet strength and wood failure in plywood panels compared with CSPI, but the results were very dependent on wood species. Because the ABES results showed that soy flour alone had minimal dry strength and very little wet strength, soy flour plus periodate was compared with CSPI in bonding plywood because the comparison would be more informative.

CONCLUSIONS

Periodate reaction with soy flour *in situ* provides adhesives with unexpectedly high wet strengths for bonded wood products compared with wet strengths of unmodified soy flour using the small-scale shear tests. The mechanism most likely involves oxidation of the carbohydrates to provide dialdehydes that can react to tie together the protein globules into a strong water-resistant network. This reaction turns the carbohydrates from a detriment into an asset. Not only did the reaction increase the strength of native-state soy flour, but it also increased the strength of heat-treated (denatured) soy flour. Under the conditions of 120 °C bonding temperature with 120-s press time, 15% periodate based on soy flour weight and a pH of 5–8 gave the best strength.

Permanganate and iodate also improved wet strength, but many other oxidants did not. Periodate, iodate, and permanganate also generally increased the wet strength of bonds when added to other plant flours, such as canola, lupine, and cottonseed, but the strength was usually not as high as with soy flour. The hypothesis

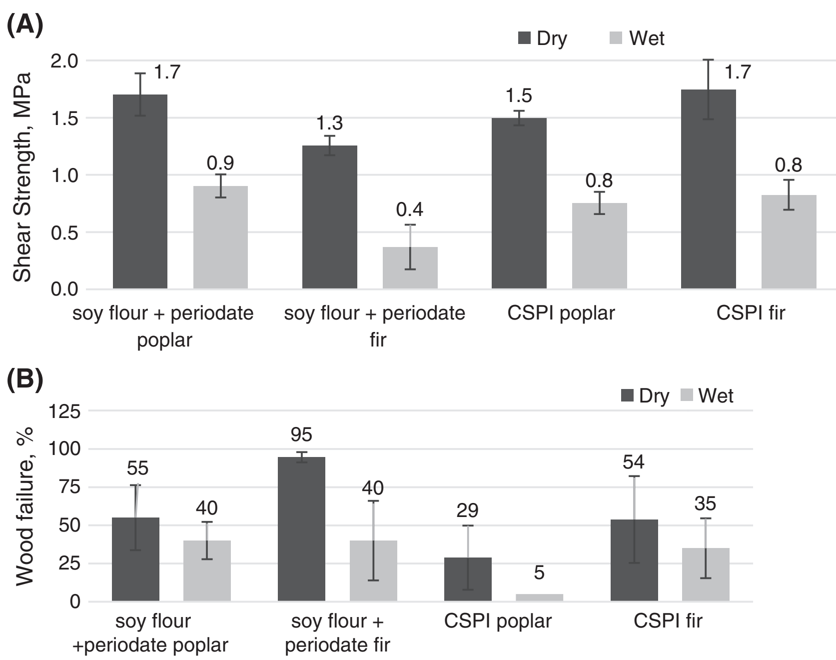

FIGURE 9 (A) Shear strength of 3-ply poplar and Douglas-fir plywood bonded with soy flour plus periodate. fir = Douglas-fir; (B) Wood failure of 3-ply poplar and Douglas-fir plywood.

that dialdehydes react with protein to improve wet strength was supported by increases in wet strength when two other dialdehydes, glyoxal, and glutaraldehyde, were added to the soy flour. However, the processes may be more complicated because periodate improved the wet strength of commercial soy protein isolate (3.5 MPa commercial isolate with periodate vs 2.4 without) and the iodate improved wet strength of the flour despite its unknown ability to produce aldehydes from carbohydrates. The reaction of periodate with proteins is being further studied for future publication.

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