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Chemical Phosphorylation Improves the Moisture Resistance of Soy Flour-Based Wood Adhesive

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ABSTRACT: A green-chemistry approach to improve the moisture resistance of soy flour (SF)-based wood adhesive is described. Chemical phosphorylation of SF (PSF), using $POCl_3$ as the phosphorylating agent, dramatically increased its wet bond strength. The optimum $POCl_3$:SF ratio that produced maximum wet bond strength was about 0.15 (g g^{-1}). The increase in wet bond strength of PSF (PSF0.15) was mostly due to the phosphate groups incorporated into the proteins and carbohydrates, and to a lesser degree to phosphorylation-induced protein denaturation. The attached phosphate groups acted as cross-linking agents, either via covalent esterification with hydroxyl groups on wood chips or via ionic and hydrogen-bonding interactions with functional groups in wood chips. At hot-press temperatures above 160°C the wet bond strength of PSF0.15 was >2.6 MPa, a level that might be acceptable for interior-used hardwood plywood and particleboard. $POCl_3$ is a low cost, general-purpose reagent and therefore PSF-based adhesive is expected to be environmentally friendly. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40451.

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INTRODUCTION

Petroleum-derived urea-formaldehyde adhesives have been widely used in the fabrication of interior-used plywood and particleboards. These synthetic adhesives are cheap, easy to use, and have long pot lives. However, as formaldehyde emissions from these adhesives pose potential hazard to the environment and to human health, the US Congress has passed a law that essentially makes the stringent formaldehyde emission levels set by the California Air Resource Board[1] as a national standard by the year 2013. Thus, there is a critical need to develop environmentally friendly wood adhesives using renewable resources, such as soy flour, as raw materials.

Several chemical modification strategies involving introduction of phenolic,[2,3] thiol,[4] maleyl,[5] amine,[6] hydroxyl[7,8] groups into soy proteins have been attempted to improve adhesive properties of soy protein isolate (SPI). Use of the crosslinking agent polyamidoamine-epichlorohydrin (PAE) as an additive, which reacts both with amino and carboxyl groups, has been shown to produce a soy flour adhesive with acceptable water resistance in hardwood plywood.[9,10] The improved water resistance of soy flour-PAE adhesive virtually arises from PAE only and reaches a maximum strength at 5% PAE (20% of total dry solids) in the formulation.[11] The basic issue with the existing chemical modification methods is that they heavily rely on petroleum-based solvents and chemicals, which may not be environmentally safe. A simpler, nonpetroleum-based "green" chemical modification strategy is needed to transform soy flour with acceptable adhesive properties.

Caseins and marine adhesive proteins (MAP) are known to possess good adhesive properties and acceptable water resistance, whereas soy proteins are not. This suggests that certain structural features and chemical properties of caseins and MAP, which are absent in soy proteins, endow them with good adhesive properties. Caseins are highly disordered phosphoproteins with several phosphate groups attached to serine and threonine residues. MAPs contain anionic and cationic protein fractions: The anionic proteins contain a high mole percent of phosphoserine (>40%), while cationic proteins contain about 20% lysine residues.[12–14] These intrinsic properties of caseins and mussel proteins suggest that a disordered structural state and a copious number of protein-bound phosphate groups might be the two important structural attributes responsible for good adhesive properties of these proteins. Conversely, it can be hypothesized that proteins in general can be transformed into good adhesives through chemical phosphorylation. We tested this hypothesis by studying the effect of chemical phosphorylation on the adhesive strength and water resistance of soy flour-based adhesive.

EXPERIMENTAL

Materials

Defatted soy flour (SF) (Prolia™ 200/90) was obtained from Cargill (Cedar Rapids, IA). The SF contained 51.6% crude protein, 4.5% moisture, 7.2% ash, 0.6% fat, and 36.0% carbohydrates. Phosphorus oxychloride ($POCl_3$, >99.0%), 2,4,6-trinitrobenzenesulfonic acid (TNBS), L-lysine (anhydrous) were purchased from Sigma–Aldrich (Milwaukee, WI). Calcium chloride anhydrates, diethyl ether (anhydrous) was from Fisher Scientific (Pittsburgh, PA). All other chemicals used in this study were of reagent grade. Maple veneer was obtained from Columbia Forest Products (Old Fort, NC).

Phosphorylation of SF

A 15%, w/w, dispersion of SF in water at pH 10.5 was stirred for 60 min at 60°C in order to partially denature the proteins. Phosphorylation was performed at room temperature according to the method described elsewhere.[15,16] Briefly, a calculated amount of $POCl_3$ was added in small aliquots to the pretreated SF dispersion with vigorous stirring. The pH was maintained at 10.0–10.5 by adding 10 N NaOH. The reaction was completed within 1 h. Varying the $POCl_3$ to SF weight ratio from 0 to 0.3 at 0.05 increments (dry weight basis) varied the degree of phosphorylation of SF. The phosphorylated SF was stirred for another hour at room temperature. The pH of the phosphorylated SF (PSF) dispersion was then adjusted to 8.0 and freeze-dried. The extent of phosphorylation at various $POCl_3$ to SF ratios was expressed as the percent of total lysine residues modified in SF. The PSF was stored at room temperature until used.

Lysine Determination

The lysine content of unmodified and phosphorylated SF was determined using the trinitrobenzene-sulfonic acid (TNBS) method.[17] Briefly, to 1 mL of 4% $NaHCO_3$ was added 0.8 mL of a solution containing <5 mg of protein, followed by the addition of 0.2 mL of TNBS solution (12.5 mg mL^{-1}). The mixture was incubated at 40°C for 2 h, and 3.5 mL of concentrated HCl was added. The tube was stoppered and kept at 110°C for 3 h and then, after cooling, the volume was made up to 10 mL with deionized water. The solution was extracted twice with anhydrous diethyl ether. The tube was unstoppered and held at 40°C to allow the residual ether to evaporate. The absorbance of the yellow (ε-TNP lysine) solution was measured at 415 nm against a blank. The amount of reactive lysine residues in the phosphorylated and unphosphorylated soy proteins was determined from the standard curve constructed using lysine. Triplicate measurements were made.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR spectroscopy experiment was performed on Nicolet iN10 (Thermo Scientific, Madison, WI) with liquid N_2 MCT detector. The dried sample (SF and PSF) powders were loaded on a gold plate and pressed by a germanium crystal accessory. The ATR-FTIR spectra were recorded as an average of 64 scans at 4 cm^{-1} resolution at 23°C. The air absorbance background was subtracted from the sample scans.

Preparation of SF and PSF Adhesives

The SF adhesives were prepared by dispersing it in distilled water. The PSF samples contained significant amount of salt (mainly Na_3PO_4 and NaCl) formed during the phosphorylation reaction. The salt content of PSF samples (determined on the basis of ash content of the PSF samples) varied depending on the $POCl_3$ to SF ratio used in the phosphorylation step. Therefore, in order to normalize the salt content, all PSF adhesive formulations were prepared on the basis of soy flour solids content. PSF (and SF) powder was mixed thoroughly into a paste with a calculated amount of deionized water at room temperature and the pH was adjusted to ~8.0. The pH 8 was chosen because the proteins in SF were very soluble at that pH.

Shear Strength Measurement

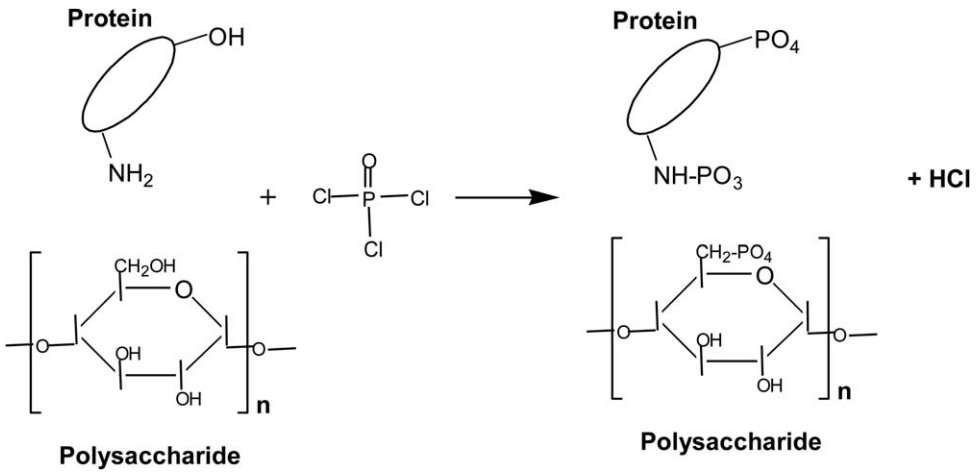
The bonding strength of SF and PSF adhesives with wood was determined by using an Automated Bond Evaluation System[18–20] (ABES) (Model 311c tester, Adhesive Evaluations Systems, Corvallis, OR). Maple veneer (Columbia Forest Products, Old Fort, NC) was used for these tests. The veneers (0.8-mm thick) were equilibrated at 21°C and 50% relative humidity for at least 24 h and cut into 11.7 cm along the grain × 2 cm across the grain strips using a die cutter supplied by Adhesive Evaluation Systems (Corvallis, Oregon). A thin layer of adhesive was applied along the grain to one wood specimen and then immediately overlapped with another veneer so that the overlap area was 0.5 cm × 2.0 cm. The glued area was then hot pressed on the ABES unit at 0.186 MPa air pressure setting (which was equivalent to an actual pressing pressure of 2.43 MPa on 1 cm^2 area on the specimen) at 120–180°C for 2 min. After pressing, the samples were re-equilibrate at 21°C and 50% relative humidity for at least overnight before shear strength testing. To measure dry shear strength, the sample was mounted on the ABES unit and the grips were pulled and the maximum load at failure was recorded. The shear strength (MPa) was calculated by dividing this load by the adhesive overlap area (1.0 cm^2). To measure the wet shear strength, samples were soaked in tap water for 4 h at 21°C prior to testing on the ABES unit.[18] At least five to seven replicate was performed. For good adhesives such as PSF, 5-replicate was found to be enough as the standard deviation was found to be <10%.

Proximate Analysis

Protein content was measured by the Biuret method. Based on this analysis, the true protein content of SF was 48.6% as opposed to 51.6% crude protein. The moisture content was determined by heating samples overnight in an oven at 102°C. The ash content was determined by ashing at 550°C. Crude carbohydrates content was estimated by subtracting all other components from the total mass.

Data Analysis

The data in each figure were the mean value of at least five replicates for shear strength analysis and triplicates for lysine analysis. One-way analysis of variance (ANOVA) was used to analyze the data, and either Tukey–Kramer HSD or Dunnett'S method (JMP Pro10, SAS Institute, Cary, NC) was used to compare the means. The confidence level was 95%.



Scheme 1. Reaction of $POCl_3$ with proteins. The dashed squares denote newly formed bonds.

RESULTS AND DISCUSSIONS

Chemical phosphorylation had been studied to improve functionalities, such as solubility, viscosity, and gelling properties of both proteins and starch.[16,21,22] Phosphorus oxychloride ($POCl_3$) is an economical and practical reagent for protein phosphorylation in a large-scale production. In this phosphorylation reaction, $POCl_3$ reacts with amino groups (lysine, histidine) and hydroxyl groups (serine, threonine, tyrosine) in proteins[22] as shown in Scheme 1. In addition to proteins, SF contains about 35% carbohydrates,[23] which includes, mono and disaccharide, glycans, and cellulose. It is believed that the insoluble carbohydrates (~25% in SF) play a minor role in adhesive properties of SF. The soluble carbohydrates (~10% in SF) are detrimental to adhesive properties as they increase water absorption and thereby decrease the water resistance of soy flour-based adhesives.[24] Carbohydrates such as cellulose, curdlan, and dextran can be phosphorylated using phosphorylating agents, predominantly at the C-6 hydroxyl group.[25] Thus, it can be envisioned that reaction of $POCl_3$ with SF would result in phosphorylation of both proteins and polysaccharides in SF.

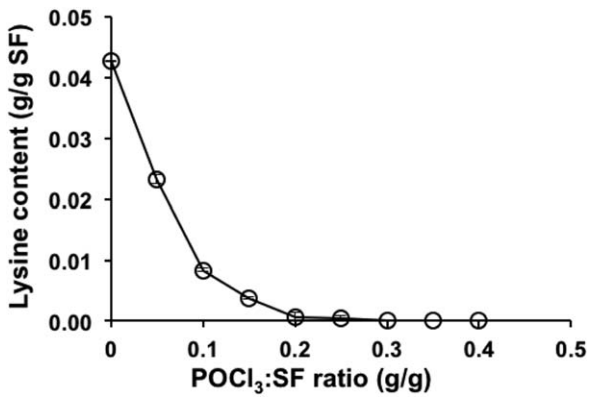


Figure 1. The effects of $POCl_3$:SF ratio on the extent of phosphorylation of lysine residues in soy flour. The concentration of SF used in all these experiments was 15% w/w.

Extent of Phosphorylation

Although several reactive groups in both proteins and polysaccharides in SF may participate in the phosphorylation reaction, the extent of phosphorylation was determined from the percentage loss of the reactive ε-amino group of lysine residues in SF after the phosphorylation reaction. As shown in Figure 1, the reactive lysine content of SF decreased as the ratio of $POCl_3$ to SF (g g^{-1}) was increased in the reaction. More than 91% of lysine residues in SF were phosphorylated at a $POCl_3$:SF ratio of 0.15 (g g^{-1}), and almost 100% of lysine residues were phosphorylated at a $POCl_3$:SF ratio of 0.2 (g g^{-1}). Because the true protein content of SF was 45.8% (Table I), the 0.15 and 0.2 (g g^{-1}) $POCl_3$:SF ratios correspond to 769 and 1025 mol mol^{-1} ratio of $POCl_3$:soy protein (assuming a molecular weight of 360,000 Da for soy proteins), respectively. It has been reported that phosphorylation of soy protein isolate (SPI) by $POCl_3$ reached a plateau at a $POCl_3$:SPI mol/mol ratio of 1000.[21]

The mass balance of $POCl_3$ reaction with SF at various $POCl_3$:SF ratio is shown in Table I. The difference between the final weight of the PSF and the initial weight of SF represents the amount of salts (Na_3PO_4 and NaCl) formed during the reaction at pH 10–10.5. No attempt was made to remove the salt from the final product.

Table I. Compositions of Phosphorylated Soy Flour (PSF)

$POCl_3$: SF ratio (g g^{-1})	Initial mass of SF (g)	Final mass of PSF (g)	Net increase (g)	True protein content (%)
0.00	30.0	30.0	0.0	45.8
0.05	30.0	32.4	2.4	42.4
0.10	30.0	36.0	6.0	38.2
0.15	30.0	38.2	8.2	36.0
0.20	30.0	42.0	12.0	32.7
0.25	30.0	44.0	14.0	31.2
0.30	30.0	47.9	17.9	28.7

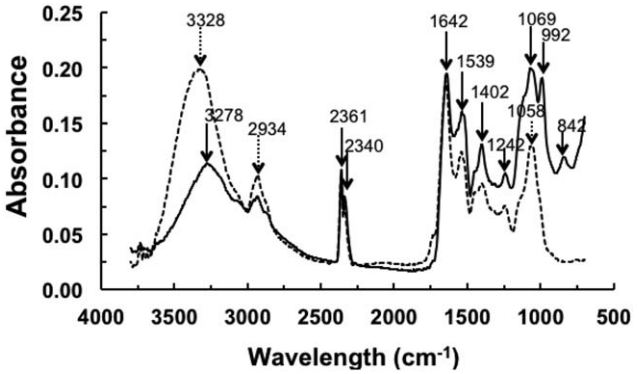


Figure 2. The ATR-FTIR spectra of SF (dot line) and PSF0.15 (solid line) dry samples.

ATR-FTIR Spectra

To identify the groups in SF phosphorylated by $POCl_3$, the ATR-FTIR spectrum of the sample phosphorylated at the $POCl_3$:SF ratio of 0.15 (PSF0.15) was analyzed. Figure 2 shows the ATR-FTIR spectra of SF and PSF0.15 samples. The SF spectrum was characterized by a strong broad band centered at 3328 cm^{-1}, attributed mainly to OH stretching of water and to some extent from N—H (amide A) stretching. The band centered at 2934 cm^{-1} is attributed to CH_2 stretching of carbohydrates and the band centered at 1642 cm^{-1} (Amide I) is due to C=O stretching and N—H bending of peptide bonds and a minor contribution from O—H bending vibration. The band centered at 1539 cm^{-1} is ascribed to the bending of N—H of amide II; the band at 1242 cm^{-1} is C—N stretching of amide III and the band at 1058 cm^{-1} is due to C=O and C—O stretching of the β–(1 → 4)-glucosidic bond (C—O—C) in carbohydrates. The shoulder at 1735 cm^{-1} is due to the C=O stretching vibration of ester groups of carbohydrates.[25–27]

The FTIR spectrum of the PSF0.15 sample was mostly similar to that of SF, but differed at three regions: The OH stretch band of water at 3328 cm^{-1} in SF red-shifted to lower frequency at 3278 cm^{-1}. Such a red shift to lower frequency (higher wavelength) and a reduction in absorption intensity generally occurs when water is tightly bound to polymeric materials.[28] In the PSF0.15 sample, this might be due to water (moisture content = 5.2%) tightly bound to the newly introduced phosphate groups via ion–dipole interactions. Most strikingly, the FTIR spectrum of PSF0.15 contained two new peaks at 992 and 842 cm^{-1}, which were not present in the FTIR spectrum of SF (Figure 2). The peak at 992 cm^{-1} belongs to P—N stretching[29] and the peak at 842 cm^{-1} belongs to P—O—C stretching, which is typically in the neighborhood of 810–861 cm^{-1}, depending on the local environment.[25,30] Undoubtedly, the P—N bond arises from phosphorylated lysine and histidine residues of soy proteins in PSF0.15. Likewise, the P—O—C stretching might be from phosphorylated hydroxyl groups of serine, threonine, and tyrosine residues of soy proteins in PSF0.15 as well as from phosphorylated hydroxyl groups (at the C-6 position) of carbohydrates in PSF0.15.

Bond Strength of the Phosphorylated SF

The effect of phosphorylation of SF on the wet bonding strength of PSF adhesives, as measured by the ABES test, is shown in Figure 3. In all these formulations, the soy flour solids content was maintained at 25% w/w, irrespective of salt content of the samples. The wet bond strength of unmodified SF was typically <0.5 MPa. The wet bond strength progressively increased as the extent of phosphorylation was increased and reached a maximum value of 1.89 MPa at a $POCl_3$:SF ratio of 0.15 g g^{-1} (corresponding to 91% phosphorylation; Figure 1). The wet bond strength decreased at $POCl_3$:SF ratios >0.15, suggesting that either some residual amount of reactive lysine residues was required for better bonding reaction, or excessive phosphorylation of hydroxyl groups of carbohydrates resulted in repulsive electrostatic interactions and/or excessive hydration of the adhesive. To check if the sodium salts formed during the phosphorylation reaction affected the wet strength, the PSF samples prepared at various $POCl_3$:SF ratio conditions were dialyzed using 6–8 kDa nominal molecular weight cut-of dialysis membrane, and the wet bond strength of the desalted PSF adhesives at 25% soy flour solids content was tested and the results are shown in Figure 3. It should be noted that removal of salts from PSF by dialysis significantly increased (about 32% in the case of PSF0.15) the wet bond strength. However, the desalted PSF samples also exhibited maximum wet bond strength at the extent of phosphorylation corresponding to the $POCl_3$: SF ratio 0.15–0.2 (g g^{-1}), indicating that factors other than salts were responsible for the maximum in the wet bond strength verses the extent of phosphorylation profile. As desalting of PSF samples by dialysis or diafiltration is a costly proposition in practical applications, subsequent tests on the wet bond strength were done only on the un-dialyzed PSF0.15 sample. The typical composition of PSF0.15 was 38.2% protein, 34.3% carbohydrates, 0.5% fat, 20.7% ash, and 5.2% moisture.

Bond Strength of PSF0.15

The wet bond strength of PSF0.15 at various concentrations is shown in Figure 4(A). Because the salt content of PSF0.15 was 20.7% on dry basis, for comparative purposes the PSF0.15

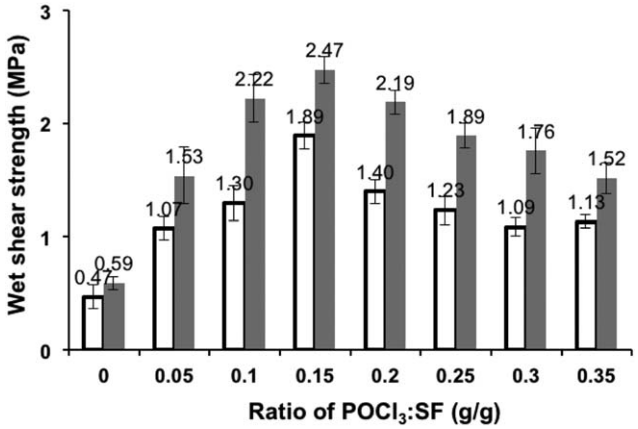


Figure 3. The effects of the extent of phosphorylation on the wet shear strength of soy flour adhesives. The open bars represent wet bond strength of phosphorylated SF (PSF) without desalting, and the filled bars represent wet bond strength after dialysis of PSF to remove salts formed during the phosphorylation reaction. All the samples were hot pressed at 0.186 MPa air pressure setting in the ABES unit (≡2.43 MPa pressure on the wood specimen) at 120°C for 2 min.

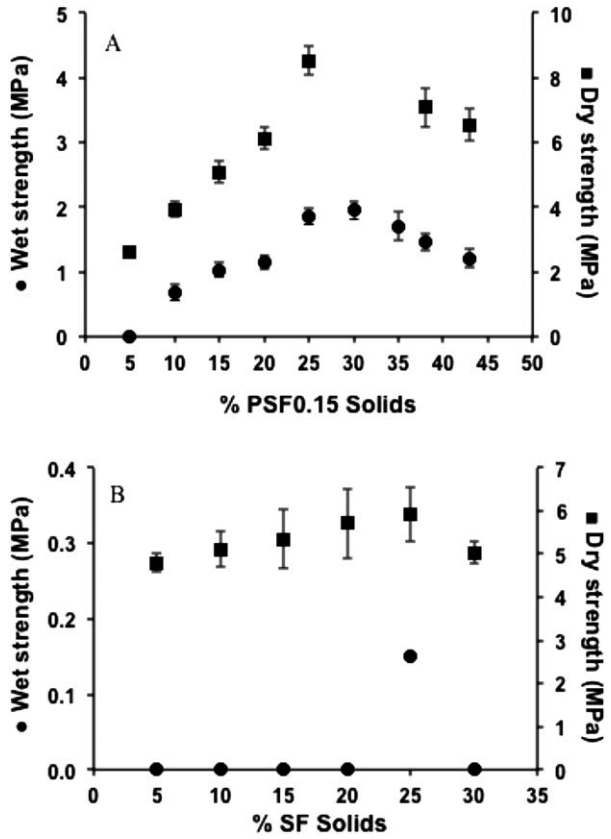


Figure 4. The wet (●) and dry (■) bond strengths of (A) PSF0.15 and (B) SF samples at various soy flour solids content in the adhesive formulation. The true protein content in all the samples was about 12% w/w. All the samples were hot-pressed at 0.186 MPa air pressure setting in the ABES unit (≡2.43 MPa pressure on the wood specimen) at 120°C for 2 min.

concentration in Figure 4(A) is expressed in terms of total SF solids in PSF0.15. The wet bond strength increased almost linearly and reached a plateau value of 1.86 MPa at 25–30% total SF solids of PSF0.15 in the formulation. The wet bond strength decreased at higher PSF0.15 concentrations, which might be due to the high viscosity of the adhesive paste, which might limit penetration of the adhesive into wood fibers. A similar trend was observed for the dry bond strength [Figure 4(A)]. The maximum dry bond strength of PSF0.15 was 8.52 MPa at 25% SF solids [Figure 4(A)].

In contrast, the wet bond strength of unmodified SF adhesive was very poor at all SF solids concentration studied [Figure 4(B)] and in most cases they fell apart after 4 h soaking in tap water. The dry bond strength of unmodified SF adhesive increased with SF solids concentration and reached the highest value of 5.9 MPa at 25% SF solids, and decreased at higher concentrations. The SF sample that had been denatured at alkaline pH 10.5 for 60 min at 60°C had wet bond strength of 0.7 MPa and dry bond strength of 6.4 MPa (data not shown).

The results shown in Figure 4 clearly indicate that introduction of phosphate groups into proteins (and possibly into carbohydrates) in SF dramatically increases the wet strength. The maximum increase in the wet bonding strength occurs at phosphorylation of about 90% of the lysine residues in SF. The fact that alkali denaturation of SF did not significantly improve its wet bond strength suggests that the higher wet bond strength of PSF was primarily due to the phosphate groups attached to the proteins *per se* rather than phosphorylation-induced unfolding of proteins. Depending on the ionized or unionized state of phosphate groups in the glued state in wood, they might interact with wood surfaces either via electrostatic or hydrogen bonding interactions. It is also likely that at high pressure and temperature (0.186 MPa and 120°C for 2 min) employed during pressing in the ABES test, the phosphate groups might be esterified to the hydroxyl groups at the C-6 positions in wood cellulose, forming crosslinks between wood pieces.

Effect of Hot-Press Temperature on Wet Bonding Strength of PSF0.15

The temperature employed during the hot pressing step is an important factor for bio-based adhesives as the extent of unfolding and chemical cross-linking reactions are temperature-dependent. The effect of pressing temperature on the wet bonding strength of SF and PSF0.15 adhesives is shown in Figure 5. The wet bond strength of both SF and PSF0.15 adhesives increased with increase of press temperature from 120 to 180°C. The wet bond strength of PSF0.15 increased from 1.86 MPa at 120°C to about 3.2 MPa at 180°C, whereas the wet bond strength of SF increased from 0.25 MPa at 120°C to about 2.0 MPa at 180°C.

Temperature had a greater net impact on the wet bond strength of SF than PSF0.15. This suggests that the net extent of unfolding was greater for SF than PSF0.15 in the temperature range studied. However, it is also possible that even at 180°C the proteins in SF might not have been fully denatured, because the rapid loss of moisture during the 2-min pressing time might have elevated the denaturation temperature of the proteins. Using differential scanning calorimetry, Kitabatake et al.[31] observed that the denaturation temperature was 118.7°C for 7S and 149°C for 11S globulins of SPI at 47% water content, and only one endothermic peak at 190°C was observed at 11% water content. Thus, dynamic changes in the

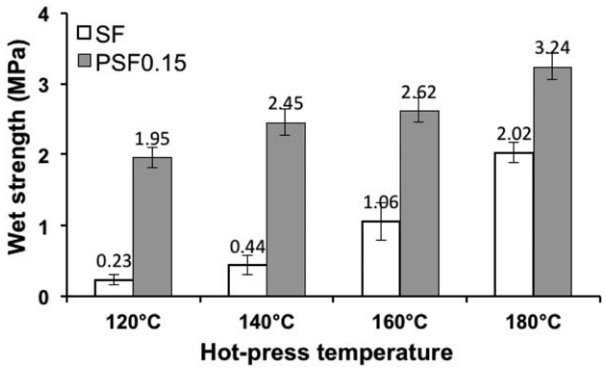


Figure 5. Effect of pressing temperature on the wet bond strength of SF (open bars) and PSF0.15 (filled bars) adhesives formulations. The total soy flour solids content in all the samples was constant at 25%. The samples were hot-pressed at 0.186 MPa air pressure setting in the ABES unit (≡2.43 MPa pressure on the wood specimen) at for 2 min.

water content of the adhesive film during a 2-min hot press at 120°C might affect the extent of denaturation of the proteins in SF and thereby its bonding strength. Regardless of the exact mechanism, the wet strength of SF was still very low even at 180°C pressing temperature compared to the wet bonding strength of PSF0.15.

Simple chemical modification strategies have been used in the past to transform soy proteins into industrial products, such as hydrogels.[32–34] The results of this study demonstrate that the adhesive properties, notably the wet bond strength, of soy flour can be dramatically improved by chemical phosphorylation of proteins (and probably the carbohydrates) in soy flour. Because no organic solvents or petroleum-derived chemicals were used in the modification step, the method offers a green chemistry approach to produce plant protein-based wood adhesives.

It is generally regarded that adhesives displaying a wet bond strength of about 2.0 MPa in the ABES test at hot-press conditions 120°C for 2 min would be acceptable for use in the fabrication of interior-used hardwood plywood and particleboards. For instance, an adhesive formulation containing 25 g SF + 1.25 g PAE + 73.75 g water had a wet bond strength of about 2.3–2.4 MPa in the ABES test under the above hot press conditions.[18] A similar formulation is currently being used in commercial manufacture of interior-used plywood. The PSF0.15 adhesive formulation containing 25% SF solids (~12.5% protein) reported here had wet bond strength of 1.89 MPa in the ABES test. When 1.4% $CaCl_2$ was included in the formulation as an ionic crosslinker, the wet bond strength of PSF0.15 increased to 2.13 MPa (data not shown). This suggests that phosphorylation essentially negated the need for adding PAE. At hot-press temperatures above 160°C, the wet bond strength of PSF0.15 in the ABES test reached 2.6 MPa (Figure 5), which is similar to the SF+PAE formulations. With additional targeted green chemical treatments, it is possible to further improve the wet bond strength of PSF0.15. $POCl_3$ is a low cost, general-purpose reagent and it is used in the production of modified starch (di-starch phosphate) in food applications. Thus, PSF-based adhesive is expected to be low cost and environmentally safe.

CONCLUSIONS

Chemical phosphorylation of SF using $POCl_3$ as a phosphorylating agent dramatically increased the wet adhesive strength of SF. The optimum $POCl_3$: SF ratio that produced maximum wet adhesive strength was about 0.15 (g/g). With further understanding of the type of bonds involved in the bonding mechanism, this chemical phosphorylation approach might be a better alternative to the SF-PAE blends that are currently being used in the plywood industry.

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