Adhesion properties of soy protein adhesives enhanced by biomass lignin

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ABSTRACT

Soy protein adhesives have great potential as sustainable eco-friendly adhesives. However, low adhesion under wet conditions hinders its applications. The objective of this research was to enhance the water resistance of soy protein adhesives. The focus of this research was to understand the effect of protein to lignin ratio and lignin particle size i.e. (large (35.66 μm), medium (19.13 μm), and small (10.26 μm) on the adhesion performance of soy protein adhesives as well as to characterize its rheological and thermal properties. Results showed that the lignin particle size and the protein to lignin ratio greatly affected the adhesion performance of soy protein adhesives. The addition of lignin slightly increased the viscosity, spreadability, and thermostability of soy protein adhesives. The wet strength of soy protein adhesives increased as lignin particle size decreased. Soy protein mixed with small size lignin at a protein to lignin ratio of 10:2 (w/w) at 12% concentration presented the lowest contact angle and the highest wet adhesion strength of 4.66 MPa., which is 53.3% higher than that of 10% pure soy protein adhesive. The improvements in adhesion performance and physicochemical properties of soy protein adhesives by lignin were ascribed to the interactions between protein and lignin. Lignin with smaller particle size increased the wet shear strength of soy protein adhesives because a larger surface area of lignin was available to interact with the protein.

Key words: *Lignin, Protein, Particle size, Adhesives*

1. Introduction

Approximately 8 million pounds of formaldehyde-based adhesives are supplied to the wood-based products industry annually [1]. Since formaldehyde-based adhesives provide durable adhesion performance, it is widely applied in pressed wood products, such as particleboard, plywood and fiber board. However, formaldehyde causes negative effects on the environment and human health because it induces high carcinogenic and chronic toxic risks [2]. The United States Environment Protection Agency (EPA) proposed a regulation for formaldehyde emission standards for composite wood products [3]. In addition, petroleum demand is increasing while petroleum shortage has been a topic of concern. Therefore, there are strong demands for safe, environmentally friendly, and sustainable wood adhesives.

Soybean seed, a potential eco-friendly adhesive source, contains approximately 40% protein and is readily available and reasonably priced [4, 5]. Recently, most studies have focused on soy protein-based adhesives [6]. Commercially, the soy protein-based adhesive has been a successful replacement for urea formaldehyde-based adhesives due to its excellent adhesion performance on wood and other materials [7]. Nevertheless, the water resistance of soy protein-based adhesive is not comparable with formaldehyde-based resin for exterior applications [8].

Lignin, the most abundant aromatic polymer is readily available as an industrial residue from pulping and biofuel production [9]. Lignin is traditionally known as a low value byproduct and is usually burned to generate energy [9, 10]. Lignin provides basic aromatic subunits that can be utilized as building blocks for many monomers and polymers, which are currently obtained by synthetic chemistry from petroleum-based products [11, 12]. Since only a few percentages of

lignin from pulping liquors are utilized for specialty applications, such as epoxy resins, and wood panel products [10, 13], there is a high demand for lignin-based value-added research [11].

The phenolic group in the lignin is an excellent hydrogen donor that can interact with functional groups of proteins such as carboxyl, hydroxyl, and amino, and forms covalent and hydrogen bonds with these carboxyl groups. Lignin reacts with protein to form a protein-lignin complex or network by hydrophobic interactions, and ionic and hydrogen bonds which are similar to the interaction between protein and polyphenol [14] (Fig. 1). The mechanism of this interaction is still not yet fully elucidated [15]. However, a cross-couple interaction, as a result of nucleophilic attack of amino acid polar side chains (Nu), was found between coniferyl alcohol, a major lignin subunit, and amino acids [16]. Lignin and soy protein interaction studies were reported. The adsorption of both glycinin (11S) and β -conglycinin (7S), soybean protein subunits, on the lignin surface occurred by non-specific interactions, hydrophobic and electrostatic force, and hydrogen bonding [17]. The sorghum lignin and lignin-based resin improved the wet strength of soy protein adhesive contributed to the increased wettability of adhesive to wood surface and cross-linking between lignin-based resin and reactive group on soy protein [17-19]. By cross-linking with protein, lignin enhanced the tensile strength, thermal stability, and Young's modulus while decreasing water absorption of soy protein [20].

Lignin is more hydrophobic than protein. Therefore, bio-based adhesives, derived from lignin and soy proteins, could improve water resistance as well as reduce the cost because lignin is inexpensive and inexhaustible. Among all lignins, kraft lignin with hydrophobic property [20] showed the highest content of aliphatic hydroxyl, more reactive toward modification, and was an excellent substrate for lignin derivatives, especially for wood adhesives [21]. Therefore, the

objective of this research was to study the effects of kraft lignin on adhesion performance of soy protein, and protein and lignin interaction through rheological and thermal properties.

2. Materials and methods

2.1. Materials

Kraft Lignin (no. 370959) was purchased from Sigma-Aldrich, Inc. (St. Louis, MO). Defatted soy flour with a dispersion index of 90 was obtained from Cargill (Cedar Rapids, IA). Hydrochloric acid and sodium hydroxide were acquired from Fisher Scientific (Fair Lawn, NJ). Cherry wood veneers were supplied by Veneer One (Oceanside, NY).

2.2. Preparation of kraft lignin

The kraft lignin was ground using a planetary ball miller ND 0.4L (Torrey Hills Technologies, LLC, CA) at 500 rpm. Samples were collected and particle size was measured by a laser scattering particle size distribution analyzer, LA-910 (Hiroba Scientific, NJ). Three particle sizes of 35.66 ± 21.42 , 19.13 ± 22.90 , and 10.26 ± 9.98 μm labeled as large (L), medium (M), and small size (S), respectively, were used for this study. The particle size distribution of these 3 samples is shown in Fig. 2. All samples were kept at room temperature for future experiments.

2.3. Soy protein isolation

Soy flour was mixed with distilled water at a ratio of 1:15 (w/w), and the pH was adjusted with NaOH (10N) to 8.5. Soy protein was precipitated and extracted at pH 4.2 then neutralized to pH 7.0 with NaOH (10N) [22]. The soy protein was freeze-dried and ground with

a cyclone miller with 1 mm screen (Udy Corp., Fort Collins, Colo.) and was stored at 4 °C for further testing.

2.4. Preparation of adhesives

Soy protein and lignin were mixed in distilled water to meet the designed protein to lignin ratios. In the first experiment, soy protein solution at 10% (w/w) was blended with 20% of large, medium, and small size lignin (based on w/w of soy protein), respectively. Adhesive with 12% soy protein only was used as a control. In the second experiment, soy protein and lignin were mixed at ratios of 12:0, 10:2, 8:4, 6:6 (w/w) of the total solid content of 12%. For the third and fourth experiments, 10% and 12% of soy protein solutions were mixed with 10%, 20%, 30%, 40%, and 50% small size lignin (based on w/w of soy protein), respectively. The pH of all slurries were adjusted to 4.5 by 3N HCl, and then stirred at 300 rpm for 2 hours.

2.5. Preparation of plywood specimen and shear strength testing

Approximately 0.6 ml of adhesives were brushed on the surface of cherry wood veneer panels with dimensions of 2 × 12 cm (width × length). The two panels were rested at room temperature for 15 minutes before being assembled and hot-pressed (Model 3890; Auto 'M', Carver Inc., Wabash, IN) at 170 °C, for 10 min under a pressure of 2 MPa. The assembled panels were conditioned at 23 °C and 50% relative humidity for 7 days. Plywood specimens were cut to 20 mm length. The samples for wet strength test were soaked in water for 48 hr. The dry strength samples were conditioned in a controlled environment for 48 hr according to ASTM standard method (ASTM D1183-03). An Instron testing machine (Model 4465; Canton, MA) was used to measure the tensile strength with crosshead speed of 1.6 mm/min. 10 replications for wet tensile strength and 5 replications for dry tensile strength were evaluated, respectively.

2.6. Rheological properties

A Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA, USA) was used to measure apparent viscosity of the adhesive samples. The gap between a plate and a 20 mm-diameter parallel plate head was set to 500 μm . The apparent viscosity was measured at 23 °C at a shear rate range of 0.01-100 s^{-1} . Silicone oil was applied to prevent water evaporation.

2.7. Contact angle measurement

Contact angles were observed by an optical contact angle meter on glass (CAM100, KSV Instruments, Helsinki, Finland) (plain microscope slides, Fisher Scientific, Fair Lawn, NJ). The polar surface energy, which is highly related to contact angle, of glass and cherry wood were reported as 38.9 and 35.1-38.1 mJ/m^2 , respectively [23, 24]. Thus, the spreadability of adhesives on glass could be similar to a cherry wood surface. Contact angles of 10 replications for each sample were measured every 1 s for 32 s.

2.8. Fourier transform infrared analysis

The samples were dried at 170 °C which is the curing temperature for samples in this study. Then dry samples were ground to 100 mesh. The Fourier transform infrared (FTIR) data was collected in the region of 400–4000 cm^{-1} with a PerkinElmer SpectrumTM 400 FTIR/FT-NIR spectrophotometer (Shelton, CT, USA). The transmission spectra of 32 scans of each sample were collected at a resolution of 4 cm^{-1} .

2.9. Thermogravimetric analysis

The thermostability of dried samples was measured by a thermogravimetric analyzer (TGA) (Perkin-Elmer TGA 7, Norwalk, CT). Approximately 5 mg of samples were scanned

from 25 °C to 700 °C with a heating rate of 10 °C/min. Nitrogen gas was flushed to provide an inert atmosphere.

2.10. Differential scanning calorimetry

The thermal properties of lignin-soy protein adhesives were analyzed by a differential scanning calorimeter (DSC) (Q200, TA instrument, Schaumburg, IL, USA). 20 mg of adhesives were placed in a Tzero aluminum hermetic pan. The samples were set at 25 °C for 1 min, then heated to 120 °C at a heating rate of 10 °C/min. Universal Analysis 2000 software was used to calculate peak temperatures and denaturation enthalpies.

2.11. Microstructural properties

The fracture plane on the wood surface was observed by Stereo Microscope (SMZ1000, Nikon, Japan)

2.12. Statistical analysis

The shear strength and contact angle were analyzed through analysis of variance by statistical software (SAS Institute, Inc., Cary, N.C.). Pairwise comparisons were performed for the means using the Tukey adjustment at a significance level of 0.05.

3. Results and discussion

3.1. Viscosity

According to the findings shown in Fig. 3, the apparent viscosity of soy protein and soy protein- lignin samples presented a shear thinning behavior, the viscosity decreased as shear rate increased. All the samples showed low viscosity compared to other soy protein based adhesives [18, 25], which indicates good flowability. All lignin blended samples resulted in higher viscosity than the soy protein, which agrees with a previous study [18]. Soy protein with small

particle size lignin showed the highest viscosity, attributed to the increased surface area of small particle size lignin and the more interaction between lignin and soy protein (Fig. 3a). The ratio of soy protein and lignin also affected the viscosity of the soy protein adhesive (Fig. 3b). In particular, the ratios of soy protein and lignin at 10:2 and 8:4 presented greater viscosity than that of 12:0 and 6:6. This is because at the ratios of 10:2 and 8:4, the soy protein and lignin exhibited the optimum interaction, resulting in slightly increased viscosity, than at ratio of 6:6. Excessive lignin interrupted the interaction of soy protein and lignin, leading to decreased viscosity. Samples that were 10% soy protein blended with 20% small size lignin showed the highest shear thinning properties at low shear rate (Fig. 3c). The higher viscosity was likely related to the high solid content and lignin particle size for 12% soy protein samples (Fig. 2d).

3.2. Contact angle

Contact angle indicating the ability of adhesives to wet or spread on solid surfaces is presented in Fig. 4. The lower contact angle implies low surface tension and better adhesive spreadability. The contact angle of adhesives significantly reduced as lignin particle size decreased (Fig. 4a) because there was more surface area available for lignin with smaller particle size for the soy protein-lignin interaction. The ratios of soy protein and small size lignin affected the contact angle significantly. Soy protein adhesives with small particle size lignin at 10:2 ratio and 12% total solid content exhibited the lowest contact angle of 43.64° compared to 54.44° and 48.43° at ratios of 12:0, and 6:6, respectively (Fig. 4b), indicating lignin improved the wettability of soy protein adhesives at the proper ratios of soy protein and lignin as reflected by the decrease of contact angle. However, excessive amounts of lignin in higher solid content could significantly increase in contact angle (Fig. 4d).

3.3. Fourier transform infrared spectroscopy

Neither the grinding process nor particle size of lignin affected the chemical structure of lignin as large particle size and small particle size lignin showed similar spectral patterns (Fig. 5a). The wide absorption band of aromatic and aliphatic OH groups was presented at 3400 cm^{-1} . The peaks at 2973 , 2939 , 2837 , and 1457 cm^{-1} were related to the C-H vibration of CH_2 and CH_3 [26]. The aromatic ring skeleton vibrations and stretching could be identified at 1594 , 1509 , and 1423 cm^{-1} [27]. The lignin contained the main absorption bands of guaiacyl (G) at 1268 , 1129 , 858 , and 813 cm^{-1} and the non-esterified phenolic OH group at 1366 cm^{-1} which is also found elsewhere in literature [28].

The broad peak at 3281 cm^{-1} refers to N-H stretching and the sharp absorption peaks at 2957 , 2929 and 2873 (Fig. 6b) are assigned to the antisymmetric and symmetric C-H stretching of protein [29]. The absorption bands of protein and the amide group, are at 1642 , 1515 and 1231 cm^{-1} which are attributed to C=O stretching (amide I), N-H bending (amide II), and C-N stretching and N-H vibration (amide III), receptively [18]. The COO^- and $-\text{C-NH}_2$ groups absorbed at 1391 and 1067 cm^{-1} , respectively [30].

In Fig. 5b, the amide I and II peak shapes slightly changed and presented a peak shoulder. The shoulders became more obvious with increasing S content (Fig 5c and d). These might be caused by the interactions between the -NH group in soy protein and lignin or an overlap between lignin and soy protein peaks. The $-\text{COO}^-$ peak intensity at 1391 cm^{-1} gradually decreased with the more lignin added. Hence, the $-\text{COO}^-$ of soy protein possibly acted as an active group and interacted with L.

3.4. Thermogravimetric analysis

The slight weight loss below 200 °C was ascribed to moisture evaporation in the samples (Fig. 5). At 210-280 °C, the initial degradation was related to the breakage of unstable bonds of small molecule fractions [18]. The mid-degradation of the cross-links and skeleton structure of soy protein and lignin occurred at high temperatures (280-360 °C). Finally, the C-O, C-C, and C-N bonds and the peptide bond of soy protein were destroyed and H₂S, NH₃, CO, and CO₂ were released with the further increase of temperature [18]. According to Fig. 6, degradation of soy protein started above 200 °C and peaked when the temperature was in the range of 342-347 °C. The weight loss rate of lignin slowed as particle size increased, indicating lignin with smaller particle sizes thermally stabilize the soy protein adhesives (Fig. 6a) as indicated by approximately 3% less weight loss at 700 °C compared to pure protein adhesive. The peak areas of derivative thermogravimetric analysis were decreased as the soy protein to lignin ratios decreased due to the decrease of protein content in the soy protein adhesives (Fig. 6b).

3.5. Differential scanning calorimetry

The T_d of 7S and 11S, and heat flow/g protein are shown in Table 1. The DSC endothermic thermograms of the samples displayed 2 major peaks at temperatures of approximately 77-78 and 93-95 °C, which are assigned to the denaturation behaviors of 7S and 11S protein subunits [25]. The 11S peak became flatter with adhesives with small particle size lignin at low protein/lignin ratios. All samples showed insignificant difference of 7S T_d, whereas a protein/lignin ratio of 10:2 presented a significantly higher 11S T_d than pure SP but insignificantly different from others. The lignin content affected the ΔH_d of protein/lignin significantly. Addition of lignin, especially to protein-lignin adhesives at solid content higher than 12%, required significantly more energy to denature the structure of protein-lignin complex. To Table 1, the 12% soy protein with 50% lignin adhesive showed significant difference of ΔH_d

(6.717 J/g) compared to pure protein (4.1209 J/g). It is possible that the formation of soy protein-lignin networks strengthened the soy protein structure, therefore, enhancing the denaturation temperature of soy protein-lignin blends.

3.6. Shear strength

Preliminary tests were conducted to find the best pH to improve the wet strength of the adhesive. As a result, lignin-protein adhesives at pH 4.5 gave the highest stability under wet conditions. Moreover, the highest wet strength was reported at pH 4.6, caused by the exposure of the buried hydrophobic group to the protein surface at pI, which contributes to water resistance improvement [25]. Therefore, the experiment was conducted at pH 4.5. Our result showed that the 12% pure soy protein dry strength was 6.4 MPa. The particle size did not affect dry strength at all (Fig. 7a) whereas, reduction of protein to lignin ratio caused weaker dry strength. The lowest ratio (6:6) showed significantly lower dry strength to 5.0 MPa (Fig. 7b). An additional lignin at 10 and 12% did not significantly change or reduce dry strength (Figures 7c and d). On the other hand, the wet shear strength of soy protein adhesives increased with the decrease of lignin particle size. The increase in wet shear strength was significant to soy protein adhesives with medium and small particle size lignin compared to pure soy protein adhesives. This increase in wet shear strength was due to the larger surface area of medium and small lignin particle sizes that were available to interact with protein (Fig. 7a). The wet strength of soy protein to lignin with a small particle size ratio of 10:2 adhesive was 4.7 MPa, which is about 53.3% greater than that of 10% soy protein adhesive only. The wet strength did not improve with the further decrease of protein to lignin ratio, but reduced the wet strength to approximately the same as the pure soy protein adhesive (Fig. 7b). In addition, the wet strength of protein adhesive with 40 and 50% lignin was reduced to 4.2 MPa, which is about a 9% decrease compared to that of soy

protein adhesive with 20% lignin (Fig. 7c). On the other hand, adding small size lignin to 12% soy protein slightly increased the wet strength. Wood cohesion failure presented in all conditions of dry samples, whereas partial wood failures were found in most soy protein adhesives with lignin during wet strength testing. Significant partial wood failures were also observed in the soy protein to small lignin ratio of 10:2.

Adhesion mechanisms have been discussed in several theories. Mechanical bonding theory explains how the adhesive wets the wood surface, penetrates into the wood pore, and forms a complex matrix during the curing process. Flow behavior and covalent bonds between protein and cellulose are important factors affecting adhesion performance [31]. In this study, the 10% soy protein mixed with lignin at the ratio of 10:2 showed the highest wet strength because of four major reasons. First, as discussed, the lowest contact angle offered the best spreadability leading to good penetration into wood surfaces. Second, the entrapment of soy protein and lignin enhanced water resistance [19, 32]. Third, the interactions of active groups between lignin and protein or in lignin itself and the formation of the cross-linked network of soy protein and lignin led to a stronger adhesion [18, 33]. Fourth, lignin concentration at 20% of soy protein caused optimum penetration and left an adequate amount of a protein active group to form covalent bonds with the wood surface. Therefore, the adhesive layer remained intact after the wet adhesion test (Fig. 8a). In contrast, a higher amount of lignin (i.e. 50%) disturbed the network, enlarged the contact angle, and reduced the degree of penetration. The gradual decrease of the COO^- peak at 1391 cm^{-1} (Fig. 5c, d) referred to more soy protein and lignin interaction and left less active groups to adhere to the wood surface. Excess soy protein and lignin interaction contributed to deteriorated bonding to the wood surface and the breakage of the adhesive layer (Fig. 8b, c, d) resulted in relatively low adhesion strength.

4. Conclusions

The addition of lignin improved the wet shear strength of soy protein adhesives, and the wet shear strength increased with decreasing lignin particle size. The optimum soy protein and lignin ratio of 10:2 (w/w) led to a 53.3% increase in wet strength compared to 10% soy protein adhesive only. The addition of lignin increased the spreadability and thermal stability of soy protein adhesives. It is believed that lignin has a great potential to improve the water resistance of protein-based adhesives.

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357 **Table captions:**

358 Table 1. Denaturation temperature (T_d) and total enthalpy of protein denaturation (ΔH_d) of soy
359 protein adhesive with lignin.

Table 1

Denaturation temperature (T_d) and total enthalpy of protein denaturation (ΔH_d) of soy protein adhesive with lignin¹

Soy protein/lignin ratio at different lignin particle size	7S T_d °C	11S T_d °C	Total Heat Flow/g protein (ΔH_d)
SP	77.80 ^a	93.07 ^a	4.21 ^a
10:2 (SP:LL) ²	77.90 ^a	93.83 ^{ab}	4.74 ^{ab}
10:2 (SP:SL) ³	77.69 ^a	94.90 ^b	4.97 ^b
6:6 (SP:SL)	77.32 ^a	93.48 ^{ab}	4.90 ^b
10:2 (SP:SL)	77.69 ^a	94.90 ^b	4.97 ^b
10:5 (SP:SL)	77.22 ^a	93.73 ^{ab}	5.77 ^{cd}
12:2 (SP:SL)	77.41 ^a	93.75 ^{ab}	6.29 ^{de}
12:5 (SP:SL)	77.27 ^a	93.68 ^{ab}	6.72 ^{ef}

¹ Values in the same column followed by different letters are different at $P < 0.05$ level.

² SP: Soy protein; LL: large particle size lignin.

³ SL: Small particle size lignin.

Figure captions:

Fig. 1. A model of lignin-protein network.

Fig. 2. Particle size distribution of large size lignin (L), medium size lignin (M), and small size lignin (S).

Fig. 3. Shear rate dependence of apparent viscosity of soy protein with different lignin particle size (a), different ratios of soy protein and small size lignin (b), different ratios of soy protein and small size lignin at 10% soy protein (c), and different ratios of soy protein and small particle lignin at 12% soy protein (d).

Fig. 4. Contact angle of soy protein with different lignin particle size (a), different ratios of soy protein and small size lignin (b), different ratios of soy protein and small size lignin at 10% soy protein (c), and different ratios of soy protein and small particle lignin at 12% soy protein (d). Means followed by different letters are significantly different at $P < 0.05$

Fig. 5. FTIR spectra of large size and small size lignin (a), soy protein with different lignin particle size (b), different ratios of soy protein and small size lignin at 12% soy protein (c), and different ratios of soy protein and small particle lignin at 10% soy protein (d).

Fig. 6. Thermogravimetric (TG) and derivative thermogravimetric curves of soy protein with different lignin particle size (a), different ratios of soy protein and small size lignin (b), different ratios of soy protein and small size lignin at 10% soy protein (c), and different ratios of soy protein and small particle lignin at 12% soy protein (d).

Fig. 7. Wet and dry shear strength of soy protein with different lignin particle size (a), different ratios of soy protein and small size lignin (b), different ratios of soy protein and small size lignin at 10% soy protein (c), and different ratios of soy protein and small particle lignin at

389 12% soy protein (d). Means followed by different letters are significantly different at $P <$
390 0.05

391 **Fig. 8.** Stereomicroscope images of wood surface of cured adhesives after shear strength test
392 with small size lignin at 4x magnifications: (a) at soy protein to lignin ratio of 10:2, (b) at
393 soy protein to lignin ratio of 6:6, (c) at soy protein to lignin ration of 10:5, and (d) at soy
394 protein to lignin ratio of 12:5.

Fig. 1. A model of lignin-protein network.

Fig. 2. Particle size distribution of large size lignin, medium size lignin, and small size lignin.

Fig. 3. Shear rate dependence of apparent viscosity of soy protein with (a) different lignin particle size, (b) different ratios of soy protein and small size lignin, (c) different ratios of soy protein and small size lignin at 10% soy protein, and (d) different ratios of soy protein and small particle lignin at 12% soy protein. SP: soy protein; LL: large particle size lignin; ML: medium particle size lignin; SL: small particle size lignin.

Fig. 4. Contact angle of soy protein with (a) different lignin particle size, (b) different ratios of soy protein and small size lignin, (c) different ratios of soy protein and small size lignin at 10% soy protein, and (d) different ratios of soy protein and small particle lignin at 12% soy protein. Means followed by different letters are significantly different at $P < 0.05$. SP: soy protein; LL: large particle size lignin; SL: small particle size lignin.

Fig. 5. FTIR spectra of (a) large size and small size lignin, (b) soy protein with different lignin particle size, (c) different ratios of soy protein and small size lignin at 12% soy protein, and (d) different ratios of soy protein and small particle lignin at 10% soy protein. SP: soy protein; LL: large particle size lignin; SL: small particle size lignin.

Fig. 6. Thermogravimetric (TG) and derivative thermogravimetric curves of (a) soy protein with different lignin particle size, (b) different ratios of soy protein and small size lignin, (c) different ratios of soy protein and small size lignin at 10% soy protein, and (d) different ratios of soy protein and small particle lignin at 12% soy protein. SP: soy protein; LL: large particle size lignin; SL: small particle size lignin.

Fig. 7. Wet and dry shear strength of (a) soy protein with different lignin particle size, (b) different ratios of soy protein and small size lignin, (c) different ratios of soy protein and small size lignin at 10% soy protein, and (d) different ratios of soy protein and small particle lignin at 12% soy protein. Means followed by different letters are significantly different at $P < 0.05$. SP: soy protein; LL: large particle size lignin; ML: medium particle size lignin; SL: small particle size lignin.

438

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