**Soy-oil-based waterborne polyurethane improved wet strength of soy protein
adhesives on wood**

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Abstract

Soy-oil-based waterborne polyurethane (WPU) is used to improve wet strength in shear test of wood bonded with an adhesive of soy protein isolate (SPI) by dispersing WPU into SPI slurry. WPU's effects on the physiochemical properties of WPU-SPI adhesives are characterized through Fourier transform infrared spectrum, transmission electron microscopy, thermal analysis, contact angle, and mechanical strength. Wet strength of the WPU-SPI adhesives increases by 65% compared to SPI control. Moreover, the microstructure of WPU has effects on the interactions between WPU and SPI. In this study, smaller and more uniform distributed WPU0002 is easier to interact and form stronger crosslinking network with protein than WPU0500. The stronger interaction between WPU0002 and protein results in increased viscosity and bond strength. The WPU-SPI blended adhesives show significantly improved wet strength, demonstrating their potential as wood adhesives.

Keywords: Soy protein isolate (SPI); Waterborne polyurethane (WPU); Wood adhesive; Wet strength

Introduction

The necessity to develop greener materials to reduce the dependence on petroleum feedstock is growing. Not only is petroleum feedstock a limited resource, it also contributes to environmental pollution and human disease. Soy-protein-based adhesive has been commercially available as a replacement of urea formaldehyde. For example, Soyad from SolenisTM has been used in wood composites, which includes particleboard and medium-density fiberboard¹. Columbia Forest Products uses soy-based PureBond® for hardwood plywood manufacturing, which is formaldehyde-free and complies with the U.S. Green Building Council's Energy and Environment Design standards². Although soy flour is widely used as wood adhesives with excellent dry bond strength, the poor water resistance of soybean-protein-based adhesives has limited their application as high-performance wood adhesives compared with phenol-formaldehyde adhesives. There is a strong necessity to improve soy-protein-based adhesive to broaden its application.

The hydrophilic nature of amino acids results in the relative weak wet strength of SPI-based adhesives. It is hypothesized that blending SPI-based adhesives with functionalized hydrophobic soy oil through covalent and non-covalent interactions would increase SPI-based adhesive's water resistance.

Soy oil is naturally triglyceride with three fatty acid chains. The main fatty acids are unsaturated α -linolenic acid (C-18:3), linolenic acid (C-18:2), and oleic acid (C-18:1). It also contains the saturated fatty acids stearic acid (C-18:0) and palmitic acid (C-16:0). The native oil structure is not possible for polymerization reactions but can be functionalized through the reactive double bonds. Through the well-developed methods including hydroformylation, ozonolysis, and transesterification, hydroxyl groups can be successfully incorporated into the oil

structure to increase the future reactivity of soy oil ³⁻⁵. Cargill's BIOH with various hydroxyl functionalities is one of the commercial polyols from soy oil⁶. It has replaced ingredients derived from petroleum-based products in traditional foam, carpet backing, upholstered furniture, and so on. BIOH is one of the most important starting materials for polyurethane synthesis, which requires a di- or polyisocyanate with a polyol. Plant-oil-based waterborne polyurethanes (WPU) have been studied as coatings, adhesives, and foams since it is more environmental friendly than polyurethanes synthesized from petroleum based hydroxyl-bearing monomers and isocyanates. Because of the hydrophobic nature of the oil structure, polyurethanes derived from plant oil have enhanced hydrophobicity and thermal stability ^{7,8}. The storage stability of plant oil based WPU dispersions has been shown to be over six months, and the initial decomposition temperature of WPU-based film in excess of 250 °C ⁹.

WPU is highly reactive and interactive with other chemicals and compounds through covalent bonding, hydrogen bonding, hydrophobic interactions, and physical entanglement. Therefore, the physiochemical properties of the reacted compounds can be enhanced through crosslinking. Acrylic monomers were successfully grafted onto soy-oil-based WPU networks during emulsion polymerization. These WPU/acrylic hybrid latexes had a significant increase in Young's moduli and tensile strength compared with unmodified WPU⁸. Numerous previous studies found that soy protein isolate (SPI) had good miscibility and compatibility with WPU. For example, SPI plastics utilizing anionic WPU have tensile strengths up to 19 MPa and water resistance $\sigma_{b(wet)}/\sigma_{b(dry)}=0.4-0.5$, which was much better than those of pure SPI sheets. The SPI/WPU films made from poly (butylene adipate) also had higher contact angles with excellent water resistance. The water uptake of SPI/WPU blended films was dramatically reduced because of the incorporation of WPU into a protein matrix ¹¹⁻¹³.

In this study, we examined the interactions between a soy-oil-based WPU and SPI and how WPU would improve the wet strength of SPI based adhesives. Figure 1 presents the chemical pathway of soy-oil-based polyol derived WPU-SPI blended adhesives. The objectives of our study were to 1) Make soy-oil-based WPU with excellent stability and dispersibility; 2) Study the wood bonding strength, water resistance, thermal, and rheological properties of WPU-SPI blended adhesives.

Materials and methods

Materials

Defatted soy flour was purchased from Cargill (Cedar Rapids, IA). BIOH polyols (X-0002 and X-0500) were purchased from Cargill (Cedar Rapids, IA). The hydroxyl number of X-0002 is 117 mg KOH/g and that of X-0500 is 56 mg KOH/g. Isophorone diisocyanate (IPDI, 98%), trimethylamine (TEA, 99%), acetone (99%), and dime thylol propionic acid (DMPA, 98%) were purchased from Sigma-Aldrich (St. Louis, MO). Cherry wood veneers used for the wood test were provided by Veneer One (Oceanside, NY).

Preparation of SPI, WPU and WPU-SPI blend

SPI:

SPI was extracted from the defatted soy flour. The fiber was removed by dispersing soy flour at pH 8.5 and then centrifuging the soy flour dispersion. SPI was precipitated at pH 4.5 by 2mol/L hydrochloric acid, and redissolved at pH 7.6 by 2mol/L sodium hydroxide, and then freeze-dried (freeze dryer Model 6211-0459; The Virtis Company, Inc., Gardiner, NY). Dried SPI was milled into powder, and the powder was passed through a U.S. #100 mesh sieve.

WPU:

BIOH polyols X-0002 and IPDI were mixed into a three-neck flask equipped with a condenser tube (ratio of NCO/OH was 1.4.). The sample was placed in, and heated using a silicon oil bath for 1 h (Heidolph MR Hei-Standard Magnetic Stirrer with Temperature Sensor, Elk Grove Village, IL). The silicon oil temperature was 85°C. DMPA was added to the mixture after 1 h. The reaction conditions were maintained for 2 to 3 h, during which time acetone was added to reduce viscosity. The sample was cooled to 45°C, and TEA was used to neutralize the DMPA. Finally, water was added to make the water dispersion, and acetone was evaporated overnight in a fume hood. The solid content of WPU was adjusted to 10% by adding more water.

WPU-SPI:

2 g of SPI powder was suspended in 18 ml deionized water and stirred for one hour to make a uniform slurry with 10% solid content. The pH of the SPI slurry was adjusted to 9.0 ± 0.1 with 2 mol/L sodium hydroxide using a digital pH analyzer. Varying amounts of WPU (10%, 30%, 50%, and 60%/70% of SPI dry base) were then added drop by drop to the SPI slurry. The pH of the slurry was maintained at 9.0 by adding 2mol/L sodium hydroxide. The mixture was stirred for 2 h at room temperature (23 °C). A series of WPU-SPI blended adhesives were thus made and coded as WPU0002-SPI 10%, WPU0002-SPI 30%, WPU0002-SPI 50%, and WPU0002-SPI 60%. The same process was repeated with the BIOH polyol X-0500 to make a series of WPU0500-SPI adhesives, which were coded as WPU0500-SPI 10%, WPU0500-SPI 30%, WPU0500-SPI 50%, and WPU0500-SPI 70%.

Characterization

Fourier transform infrared spectroscopy (FTIR)

The control SPI and WPU-SPI slurries were freeze-dried and ground into fine powders for IR analysis. The blended WPU-SPI samples were first freeze-dried and then hot pressed at 170 °C for 10 min to mimic the adhesives' application condition. The IR spectra were recorded by a PerkinElmer Spectrum 100 FTIR spectrometer (Waltham, MA) in the MID-IR range (4000-600 cm⁻¹) with a universal attenuated total reflectance (ATR) sampling device. Each sample was scanned 32 times at a resolution of 2 cm⁻¹.

Contact angle

Measurements were made using a CAM 100 optical contact angle meter (KSV Instruments, CT). A sample was dropped onto a glass surface, and the shape of the sample was immediately recorded by a CCD video camera and the contact angle was determined by fitting the Young-Laplace equation to the drop profile. The data showed in this study was an average of eight replicated tests.

Water resistance of cured WPU-SPI samples

WPU-SPI samples were coated onto glass plates with an even thickness and cured at 115°C in an oven for 30 min. The cured samples were soaked in water for 30 min and then dried. The differences between dry sample weight before and after being soaked in water were calculated. Material lost resulting from the soaking process was expressed as the percentage of sample weight extracted by the water to the original sample dry weight.

Rheology properties

The apparent viscosities of the control SPI and WPU-SPI slurries were measured by a Bohlin CVOR150 rheometer (Malvern Instruments, Southborough, MA) with a parallel plate (PP20, 20-mm plate diameter). The distance between cone and plate was set at 500 nm for all samples. Shear rate was in the range of 0.1 to 50 s⁻¹, and the testing temperature was 23°C. To prevent

dehydration during testing, a thin layer of silicone oil was spread over the circumference of the samples.

Thermal analysis

Control SPI and WPU-SPI slurries were freeze-dried, and then the thermal hydrolysis curves of dry samples were determined using thermogravimetric analysis (TGA, PerkinElmer Pyris1 TGA, Norwalk, CT). For each sample, about 5 mg was loaded in the pan and heated from 50 to 700 °C at a rate of 10 °C/min. Onset (To) and peak temperatures (Tp) were calculated by TGA software.

Thermal denaturation of control SPI and WPU-SPI were measured via differential scanning calorimetry (DSC, Q200, TA instrument, Schaumburg, IL). Samples (about 10 mg) were hermetically sealed in T zero aluminum hermetic pans. The samples were heated from -50 to 300 °C and then cooled to -50 °C and heated again with a heating rate of 10 °C/min.

Particle size analysis

The 10% adhesive slurries were directly used for particle size analysis. A laser scattering particle size distribution analyzer (LA-910, HORIBA Company, Kyoto, Japan) was used to record and calculate particle size distribution.

Transmission electron microscopy (TEM)

TEM microstructure observation was carried out using a Philips CM 100 (FEI Company, Hillsboro, OR). Newly prepared WPU-SPI blended adhesives were diluted to 1% with deionized water and then sonicated for 5 min before imaging. Formvar/carbon-coated 200-mesh copper grids were used to absorb diluted samples and stained with 2% (w/v) uranyl acetate for 45-60s at room temperature.

Wood specimen preparation and shear strength measurements

Cherry wood pieces were preconditioned in a chamber (Electro Tech Systems, Inc., Glenside, PA) at 23 °C and 50% RH for at least one week before use. About 1 ml SPI adhesive was brushed onto the surface of cherry wood pieces; the dimensions of each piece were 50 mm × 127 mm × 5 mm (width × length × thickness). Wood pieces were allowed to rest at room temperature for 15 min and then layered and pressed with a hot press at 170 °C and 1.4 MPa for 10 min. Wood assemblies were removed and cooled at room temperature and then stored in a chamber at 23 °C and 50% RH for 1 day. Each wood assembly was cut into five pieces with dimensions of 50 mm × 20 mm (length × width) and then further conditioned for two days before the dry strength test. Two of the five pieces were used for dry strength test, and the other three were used for a wet strength test. Three duplicated wood assemblies were made for each adhesive sample.

For dry strength tests, wood specimens were tested with an Instron Tester (Model 4465, Canton, MA) according to ASTM Standard Method D2339-98 at a crosshead speed of 1.6 mm/min¹⁴. Bonding strength was recorded as stress at the maximum load. Wood failure was estimated in accordance with the standard method of determining the percentage of wood failure in adhesive-bonded joints¹⁵. For wet strength tests, the specimens were soaked in water at room temperature for 48 h. Wet strength was tested immediately after soaking, on the basis of ASTM Standard Methods D1183-96 and D1151-00¹⁶.

Results and discussion

FTIR spectra of SPI, WPU and their mixtures

FTIR spectra are shown in Figure 2. The characteristic peaks for SPI are as follows: amide I at 1634 cm⁻¹, which corresponds mainly to C=O stretching vibration (80%) with a minor

contribution from C-N stretching vibration; amide II at 1515 cm^{-1} , which arises from N-H bending (60%) and C-N stretching vibration (40%)^{17,18}. For WPU, the major peaks are from C=O, C-N, and N-H. The carbonyl group of WPU0500 was broad and seemed to be composed of two bonds at 1745 and 1715 cm^{-1} , which were from free C=O stretching and hydrogen bonded C=O, respectively¹⁹. The sharp peak at 1712 cm^{-1} with WPU0002 was assigned to the stretching of hydrogen bonded carboxyl groups and they were similar with that of WPU0500 containing both free and hydrogen bonding C=O. The N-H bending and C-N stretching of polyurethane contributed to peaks at 1536 and 1537 cm^{-1} . After blending with WPU, amide bonds of SPI (1634 cm^{-1} and 1515 cm^{-1}) shifted to higher frequency ($1645/1641\text{ cm}^{-1}$ and 1530 cm^{-1}) because strong intermolecular interactions between amide groups and polyurethane occurred and changed the chemical environment. The sharp carbonyl absorption turned into flat shoulder peaks besides amide I at a frequency of about 1736 cm^{-1} , which has less content of hydrogen bonding. The new shape and position of carbonyl absorption showed that C=O was in an entirely different chemical environment, for instance, it has less involving of N-H bonds from polyurethane as electron donor but more interaction with bonds from protein. FTIR spectra suggested that there were some intermolecular interactions between WPU and SPI.

Contact angle

Contact angle analysis was used to estimate the surface hydrophobic properties of the WPU-SPI blended adhesives. Contact angle changes with increasing WPU content are shown in Figure 3. For the pure SPI slurry, the contact angle was about $33 \pm 2^\circ$ (average of the two control tests), that was relatively hydrophilic and easier to wet the glass surface. The contact angles of WPU were difficult to measure because of the polarity effect between WPU and glass surface. But after WPU interacted with SPI, their contact angles increased up to $52 \pm 2^\circ$ and $50 \pm 2^\circ$ for WPU0002-SPI and WPU0500-SPI respectively. Interactions between SPI and WPU would change protein conformations and create a new and more hydrophobic surface with hydrophobic polyurethane segments. It is possible that this new hydrophobic surface is affected by the interactions between WPU and protein and that too much WPU would decrease the interactions.

Water resistance of WPU-SPI film curing on glass plate

WPU-SPI blended adhesives were cured at 115°C for 30 min on glass plates and then soaked in water for 30 min. The hydrophobic segments from the WPU are supposed to prevent water from breaking down and dissolving the cured SPI and thus reduce the solid lost in water. When blended with WPU, samples clearly exhibited much reduced levels of material extraction (Figure 4). The error within duplicated tests for SPI and 25%WPU-SPI were high because the cured samples were broken down into pieces, and the weights of some small pieces that became detached from the main body of the sample were impossible to measure. On the contrary, the 50%WPU-SPI sample maintained its shape very well with less material extracted and dispersed into the water. The above results demonstrated that with the incorporation of a certain amount of WPU, the SPI films had better water resistance than the control SPI film.

Viscosity analysis

Viscosity describes the resistance of adhesives to flow. It is an important factor determining products' handling properties and ability to wet a substrate surface. When intermolecular attractions become stronger, samples will show a higher viscosity²⁰. The apparent viscosity against shear rate was measured and plotted as indicated in Figures 5 and 6. The viscosity of the SPI slurry was very low and constant with increasing shear rate in this test range. All blended samples had a higher viscosity than SPI with viscosity increasing substantially as the WPU content was increased from 10% to 50%. The highest value occurred with the 50% WPU0002-SPI system, which was still flowable and easy to apply onto a substrate surface. For WPU-SPI samples the viscosity first increased with shear rate and then decreased presenting shear thinning characteristics at higher shear rates. The shear thinning behavior benefits adhesive application by making it easier to spread the adhesive onto a substrate surface. The increased viscosity demonstrates the growing interactions between WPU and SPI and the stronger cross-linking network between molecules. At pH 9.0, protein is partly unfolded with increased hydrodynamic volume and contact area²¹. The hydrophobic segments from WPU were likely to interact with the hydrophobic amino residues from SPI and thus formed bigger aggregates, which were more resistant to flow. Because of the hydroxyl, amine, and carboxyl groups in the mixed system, WPU and SPI could form hydrogen bonds and electrostatic interactions, which enhanced the crosslinking network as shown by the FTIR data in Figure 2. It was noticed that samples made with WPU0002 had significantly higher viscosities than WPU0500 (Figure 5 and 6). The possible reasons for this could be that WPU0002 has a larger contact surface due to its smaller molecular weight and thus more interacting groups, which benefit the interactions between WPU and SPI. Higher viscosity indicated stronger interaction between molecules or residues. The

contact angle of WPU0002-SPI was bigger than that for WPU0500-SPI (Figure 3) because with higher viscosity, WPU0002-SPI formed more hydrophobic liquid drops^{22, 23}.

Thermal properties analysis

DSC is a useful tool to characterize the thermal transitions of polymers. Differences in thermal transitions are related to composition and structural changes. Figure 7 shows that pure SPI had two endothermic peaks at temperatures of 186 and 217 °C in the first scan (Table 1), which were assigned to denaturation peaks of 7S and 11S subunits, respectively. Because 11S has a higher molecular weight and was the major compound of soy protein, it attains a higher denaturation temperature and enthalpy change. In the second scan, SPI had a very strong peak at 81°C and a weaker peak at 150 °C. These two peaks were believed to be melting peaks because during the cool down, protein could crystallize into different crystals, which melt when temperature increases. For WPU, there were two thermal transition peaks in the first scan. The first peak was 55 and 66 °C for WPU0002 and WPU0500 respectively. According to previous studies, this is the glass transition temperature and it varies with different polyurethane structure. The higher Tg of WPU0500 indicated that it had a higher molecular weight and crosslinking density than WPU0002^{24, 25}. The higher thermal transition peak of WPU0500 in comparison to WPU0002 corresponded to TEM images showing that the aggregate size of WPU0500 was much larger than that of WPU0002 (Figure 11). Another peak from the WPU thermogram in the first scan was exothermic at temperatures of 197 and 204°C for WPU0002 and WPU0500 respectively. This indicated a crosslinking reaction between free functional groups at the ends of the urethane prepolymer. The ΔH_d (-80.07J/g) change with WPU0002 was 3.5 times higher than that for WPU0500 (ΔH_d = -27.28 J/g, Table 1). The main reason for the difference is that WPU0002 was smaller in molecular weight and had more free functional groups available for further

crosslinking reactions ²⁶. In the second scan, the WPU curves were rather smooth with a small glass transition at 6 and 12 °C for WPU0002 and WPU0500 respectively.

The 50% WPU and SPI mixture had a slightly lower (about 5 °C) glass transition temperature and smaller ΔH_d than the pure WPU in the first scan, which indicated that interactions between protein and polyurethane molecules had changed the former crosslinking of WPU. Compared with pure WPU, crosslinking reactions within the WPU and SPI mixture occurred at a higher temperature, with ΔH_d reducing substantially. This suggested that crosslinking reactions between polyurethane molecules were weakened. A possible reason was that the interaction of WPU with protein had partly blocked the free functional groups of the WPU, which would otherwise participate in crosslinking reactions. The denaturation temperature of SPI also changed because protein conformation was disrupted due to its interaction with WPU. In the second scan, WPU0002-SPI had a much stronger melting peak than WPU0500-SPI. This melting peak was even stronger than that of pure SPI with a lower melting temperature. The new melting peak was from new crystal structure resulting from interactions between SPI and WPU0002. The differences between WPU0002-SPI and WPU0500-SPI in thermal behavior suggest they must have different interacting processes and different microstructures (Figure 7 and Table 1).

TGA

Thermogravimetric analysis gives information on thermal stability and decomposition as determined by weight loss. Figure 8 shows the derivative TGA curves of WPU, SPI, and their blends. SPI had only one decomposition peak from 304 °C to 358 °C. In the beginning of degradation, non-covalent bonds including hydrogen bonds, electrostatic interactions, and hydrophobic interactions were disrupted, and covalent bonds between C-N, C (O)-NH, C (O)-

NH₂ and –NH₂ on amino acid residues and peptide backbones decomposed as temperature increased. The complete decomposition of protein released various gases such as CO₂, CO, and NH₃^{27, 28}. WPU had two degradation peaks, which might be assigned to the two major segments with different thermal stability. The first one at 324 °C is similar for both WPU0002 and WPU0500, while the second peak with WPU0500 (415 °C) was much higher than that of WPU0002 (388 °C). The higher decomposition temperature of WPU0500 indicated that this had a more thermally stable segment which may result from more regular urea and urethane segments²⁹.

For WPU-SPI blends, the degradation peaks, although broadened, were still similar in shape, which meant that WPU and SPI had good compatibility. It was also noticed that there was a weak peak at a higher temperature, around 440 °C, for both blended samples, which suggests that SPI and WPU may combine into more stable and larger aggregates through interactions such as covalent linkages and electrostatic and hydrophobic interactions.

Particle size distribution and morphology of WPU-SPI adhesives

Particle size distribution

Because of the interactions between WPU and SPI molecules, the blended samples were expected to have different aggregate structures. For the WPU0500-SPI samples, including WPU0500 alone, had exhibited similar frequency v particle size curves (Figure 9) with the highest frequency around a particle size of 40 µm. Compared with SPI, the WPU0500-SPI blended samples had a slightly higher frequency when particle size <40 µm and a little lower frequency when particle size >40 µm. WPU0500 was smaller than SPI and their mixture should have a particle size between WPU0500 and SPI. While the WPU0002-SPI blends had a quite

different size distribution pattern (Figure 10), the size of WPU0002 was too small to be measured using the light scattering method and curves were moved to a larger size with multiple peaks after WPU0002 was blended with SPI (Figure 10). For example, 10% WPU0002-SPI had the highest frequency at 60 μm and another peak value around 400 μm . Therefore, there were two dominant sizes in the sample. The 50% WPU0002-SPI was relatively uniform with a major peak at 100 μm .

Since the particle size of WPU0002 was quite small, there was larger contact surface with SPI, which would facilitate interaction and result in more massive aggregates. The particle size data agreed well with the viscosity data. Stronger interactions between WPU0002 and SPI led to larger sizes and higher viscosity, while interactions between WPU0500 and SPI had a small influence on particle size and viscosity.

Morphology

Soy protein is globular in shape, and the protein aggregates formed exhibit a continuous linear chain network as shown in Figure 11 A. Proteins were connected to the surrounding molecules through hydrophobic interactions, hydrogen bonds, and electrostatic interactions. The darker color indicates that more layers of protein aggregates were stuck together. Figure 11 B and C are for WPU0002 and WPU0500, respectively. The WPUs were both round in shape with varied particle sizes, but WPU0500 was noticeably larger than WPU0002. As the measurement results show, for WPU0002, the larger particles were around 60 nm and the smaller ones were only around 16 nm, while for WPU0500, the larger ones were over 500 nm and even the smaller ones were 50 nm on average. WPU particles also had connections with each other, which resulted in larger aggregates. Multiple factors can affect the particle size of WPU, for example, the ratio between hydroxyl and isocyanate groups, carboxyl groups' content, and ionic, nonionic

hydrophilic segments^{30, 31}. The main reason for the different particle sizes in our WPU samples was the functionalities of BIOH 0002 and 0500.

With regard to microstructure, proteins were smaller and less folded in nature with WPU0002-SPI (Figure 11 D), whereas with WPU0500-SPI, a multiple layered linear chain network was observed (Figure 11 E). For WPU0002-SPI, proteins adhered to the surface of WPU particles, and the small particle size of WPU0002 made it easier to approach and interact with the protein crosslinking network and form new connections. For WPU0500, the particles were enclosed by a protein network. The WPU0002 had a more uniform distribution in the protein than WPU0500 because of its smaller size.

Dry and wet strength wood specimens

Both SPI and WPU-SPI blended adhesives exhibited good dry shear bond strength characteristics as shown in Table 2. However the bond strength for WPU was low and thus not shown in table 2 and figure 12. WPU0500 had a dry strength of 4.76 ± 0.42 MPa and wet strength of 1.85 ± 0.21 MPa; WPU0002 had a dry strength of $1.85 \text{ MPa} \pm 0.21$, and a wet strength of 0.09 ± 0.06 MPa For the dry tests, samples all exhibited 100% cohesive wood failure. All the samples of WPU0002-SPI had a higher value than WPU0500-SPI. It is possible that samples tested at different times were influenced by systematic error associated with both instrumentation and wood material variability However, it is possible that WPU0002 treated adhesives had a stronger adhesion property.

When WPU content reached 50%, both WPU0002-SPI and WPU0500-SPI experienced increased wet strength (Figure12). The wet strength was increased to 3.81 ± 0.34 MPa, i.e. about 66.7% more than that of pure SPI. The highest value occurred with 50% WPU samples. 30% and 50% WPU0002-SPI and 30% and 50% WPU0500-SPI samples had fiber pulled out of the wood

surface (Figure 13). Interactions between SPI and WPU could benefit adhesion performance. Their interactions can be due to covalent bonds between active functional groups such as amine and carbonyl as well as non-covalent linkages such as hydrophobic interaction and hydrogen bonds (Figure 2). Through these interactions, the protein might change to a more unfolded conformation so as to extend the contact area with WPU. Cavities between protein and wood resulting from the dissolution of hydrophilic amino acid residues into water are the main reason for poor wet strength. On the one hand, once the hydrophobic WPU adheres onto the protein surface, it would prevent water from penetrating into the interfacial surface between adhesive and wood. On the other hand because WPU was synthesized from hydrophobic soy oil, it is hard to dissolve in water so fewer cavities would form. However, when WPU content increased to 60% or 70%, the wet strength began to decrease. One possible reason for this is the decrease of adhesion groups from protein, which weakens the splice between adhesive and wood. The interaction between protein and WPU might also weaken if there was too much WPU. The WPU0002-SPI had a higher wet strength than WPU0500-SPI, which may relate to the differences in their physical properties such as aggregate sizes and viscosity. Particle size is related to mechanical properties^{32,33}. In the wet strength test, WPU0002-SPI blends had a higher strength than WPU0500-SPI on each blended level. A more uniform distribution of hydrophobic segments could better prevent water from penetrating into the interphasial region between adhesive and wood. On the other hand, the smaller and more open proteins would promote adhesive penetration into wood and thus increase bond strength.

Conclusions

Soy-oil-based waterborne polyurethanes (WPU) have been successfully merged with soy protein into homogeneous adhesives. These WPU-SPI blends showed improved wet strength up to 3.81 ± 0.34 MPa with fiber failure. The compatibility between WPU and SPI was the result of hydrogen bond and electrostatic and hydrophobic interactions. Based on FTIR and thermal behavior changes observed by DSC, it was inferred that a new crosslinking network may form between WPU and SPI. Microstructure and particle size information based on TEM images indicated that the smaller WPU0002 had more interactions with soy protein and that this contributed to improved mechanical properties. The WPU-SPI blended adhesives are safe, biodegradable, and renewable; therefore, they have great potential for the adhesive industries.

Acknowledgements

The authors thank the financial support from the USDA-NIFA Biomass Research and Development Initiative program (Grant No.2012-10006-20230). This contribution no. is 16-145-J of the Kansas Agricultural Experiment Station at Kansas State University.

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Figure and Table Legends

Figure 1 Proposed chemical scheme of possible interactions between WPU and SPI: covalent linkage; hydrogen bond; hydrophobic interaction; physical entanglement

Figure 2 FTIR spectra of SPI, WPU, and WPU-SPI

Figure 3 Contact angle of WPU-SPI blended adhesives as a function of WPU content

Note: Numbers in horizontal axis means dry base wt% of WPU in samples. The same applies to following figures

Figure 4 WPU-SPI blended samples' solid lost in water

Figure 5 Apparent viscosity of WPU0002-SPI blended adhesives as affected by shear rate

Figure 6 Apparent viscosity of WPU0500-SPI blended adhesives as affected by shear rate

Figure 7 DSC thermogram of SPI, WPU, and WPU-SPI blends. Graph on left is the first scan; graph on right is the second scan.

Figure 8 DTGA curves of WPU, SPI, and WPU-SPI blend

Figure 9 Particle size distribution of SPI, WPU0500, and WPU0500-SPI adhesives

Figure 10 Particle size distribution of SPI, WPU0002, and WPU0002-SPI adhesives

Figure 11 TEM images: A: SPI; B: WPU0002; C: WPU0500; D: WPU0002-SPI; E: WPU0500-SPI

Figure 12 Wet shear bond strength of WPU-SPI blended adhesives

Figure 13 Wood surface after dry and wet bond strength test

Table 1 Peak temperatures and enthalpy change for DSC thermogram

Notes: T_{d1} and T_{d2} means protein denaturation temperature; T_g means glass transition temperature; T_m means melting temperature; ΔH_d means enthalpy change.

Table 2 Dry shear bond strength of WPU-SPI blended adhesives

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506 Figure 2

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527 Figure 3

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Figure 7

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591 Table 1

Sample ID	First scan									
	Peak (°C)			ΔH_d		Peak (°C)			ΔH_d	
	T_{d1}	T_g	T_d (J/g)	T_g J/(g. °C)	T_{d2}	ΔH_d (J/g)	Peak (°C)	ΔH_d (J/g)	Peak (°C)	ΔH_d (J/g)
SPI	186		4		217	12				
WPU 0002		55		0.37	197	-80.07				
WPU0500		66		0.16	204	-27.28				
50% WPU 0002-SPI		49		0.11	181	0.50	207	-5.86	222	3.24
50% WPU 0500-SPI		62		0.08	202	1.98	212	-1.14	223	0.50
Sample ID	Second scan									
	Peak (°C)			ΔH_d		Peak (°C)			ΔH_d (J/g)	
	T_m	T_g		(J/g)	J/(g. °C)	T_m				
SPI	81			29.92		150			1.42	
WPU0002		6		0.75						
WPU0500		12		0.40						
50% WPU 0002-SPI		10		0.47		74			43.02	
50% WPU 0500-SPI		16		0.30		60			1.53	

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597 Table 2

Sample ID	Strength (MPa)	Cohesive Wood Failure	Sample ID	Strength (MPa)	Cohesive Wood Failure
SPI	5.78 ± 0.37	100%			
10% WPU0500-SPI	5.41 ± 0.62	100%	10% WPU0002-SPI	6.76 ± 0.56	100%
30% WPU0500-SPI	4.80 ± 0.42	100%	30% WPU0002-SPI	5.94 ± 0.38	100%
50% WPU0500-SPI	6.49 ± 0.55	100%	50% WPU0002-SPI	7.30 ± 0.61	100%
70% WPU0500-SPI	5.21 ± 0.25	100%	60% WPU0002-SPI	6.36 ± 0.74	100%

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