

Soy Protein Adhesive Blends with Synthetic Latex on Wood Veneer

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Abstract Environmental pollution has prompted an interest in and a need for bio-based wood adhesives. Modified soy protein has shown adhesion properties similar to those of formaldehyde based adhesives. The objective of this research was to investigate the compatibility of a modified soy protein (MSP) with six commercial synthetic latex adhesives (SLAs). Four different blending ratios of MSP and SLAs were studied. Adhesion; structural change; and rheological, thermal, and morphological properties of the MSP/SLAs blends were characterized. Dry adhesion strength of MSP, SLAs and their blends were all similar with 100% wood cohesive failure. Water resistance of all six SLAs was improved by blending with MSP in terms of the wet adhesion strength. The wet adhesion strength of MSP/PBG (40/60) blends was 6.416 MPa, as compared to 4.66 MPa of pure PBG (press bond glue, urea formaldehyde based resin). Viscosity of MSP/SLAs blends was reduced significantly and reached the lowest value at 40–60% MSP. Infrared spectra, thermal properties, and morphological images indicated that chemical reactions occurred between soy protein and PBG molecules. The MSP provided some functional groups, such as carboxylic (–COOH), hydroxyl (–OH) and amino groups (–NH₂), that cross-linked with hydroxymethyl groups (–CH₂–OH) of PBG, and also acted as an acidic catalyst for the self-polymerization of urea formaldehyde based resin.

Keywords Sodium bisulfite · Soy protein adhesive · Urea formaldehyde resin · FTIR · Thermal properties · Rheological properties · Water resistance

Introduction

Most of the currently available commercial adhesives for wood composites are petroleum based; these include thermosetting resins such as phenol–formaldehyde (PF), urea–formaldehyde (UF), and melamine–formaldehyde (MF) and isocyanates. Polyvinyl acetate adhesive (PVA) is a thermoplastic resin used mainly in furniture assembling [1]. A few bio based adhesives such as soybean adhesive, phenolic-containing lignins and tannins adhesives, animal glue, casein-based adhesive, and blood based adhesive are also currently used as wood adhesives. Bio based adhesives are inferior to petroleum based adhesives in terms of water resistance and cost. However, in recent years, limited petroleum resources and the pollution caused by formaldehyde-based adhesives have spurred many efforts to develop bio-based adhesives with good adhesion properties that can compete with synthetic petroleum based adhesives.

Soy-protein-based adhesives have shown great potential as bio-based adhesives since the 1930s; they are abundant, inexpensive, renewable, and easy to handle. Efforts to improve adhesion properties of these adhesives have included using denaturants, reducing agents, and cross-linking agents as well as enzyme hydrolysis [2–7]. However, the low water resistance of soy protein based adhesives still limits their extensive application.

Blending soy protein with synthetic resins is a short-term solution for reducing dependence on petrochemicals and lowering emissions of volatile organic compounds. Blends of soy based protein with blood, casein, polyvinyl

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alcohol, polyvinyl acetate resin, or PF showed improved water resistance for wood applications [8]. Steele et al. [9] developed blends of soy protein and phenolic resins used for finger jointing of green lumber that cured rapidly at room temperature and had excellent water resistance and reduced formaldehyde emissions. As much as 70% of PF can be replaced by soy protein based adhesive with comparable physical properties for oriented and random strandboard [10, 11]. In a study by Zhong and Sun [12], blends adhesives (soy protein isolate/PF = 100/20) had the same level of adhesion strength as commercial PF adhesive alone, reduced formaldehyde usage, and had economic advantages. Polyamide-epichlorohydrin (PAE) is an excellent curing agent for soy protein; Zhong and Sun [13] also showed that the complexation interaction for PAE–soy protein blends greatly enhanced their adhesion properties.

To promote reaction with synthetic polymers, soy protein must be unfolded to expose its functional groups. Various hydrolysis methods have been used to unfold soy proteins [14, 15], but these methods have not been able to overcome the hurdles of high viscosity, low concentration of soy protein, low water resistance, and short pot life. Sun et al. [16] previously showed that a partially unfolded soy protein with 38% solids content had dry and wet adhesion strength comparable to formaldehyde-based adhesives. We hypothesized that unfolded soy protein may act as a copolymer, reacting with various synthetic resins to enhance adhesion performance and reduce emissions of volatile organic compounds. Therefore, the objectives of this study were to investigate the compatibility of modified soy protein (MSP) with commercial synthetic latex adhesives (SLAs) and characterize the adhesion; structural change; and rheological, thermal, and morphological properties of MSP/SLAs blends.

Materials and Methods

Materials

Defatted soy flour (Cargill, Cedar Rapids, IA, USA) was used as the starting material. The soy flour contained about 50% protein and 10% moisture with a dispersion index of 90. Sodium bisulfite (NaHSO_3) was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Cherry wood veneers with dimensions of $50 \times 127 \times 3$ mm (width \times length \times thickness) were provided by Veneer One (Oceanside, NY, USA). Six different commercial SLAs were used. Press bond glue (PBG, UF based resin) and Veneer Glue (VG, dichloromethane and toluene based resin) were purchased from Constantine's Wood Center (Fort Lauderdale, FL, USA). Heat Lock Iron Veneer Glue (HLIG, PVA based resin) and

Cold Press Veneer Glue (CPG) were purchased from Highland Woodworking Company (Atlanta, GA, USA). Cold Press Light Veneer Glue (CPLG) and Flex-Pro Veneer Adhesive (FPV) were purchased from Veneer Supplies Company (Louisville, KY, USA). The detailed MSDS sheet of each product is available online from the website of each company. For example, PBG is described online as “easy to use, very water resistant, does not creep minimize bleed-through on veneers. Suggested hot pressing pressure is 100–200 psi, pressing temperature is 250 °F, and pressing time is 1 to 3.5 min.”

Adhesive Preparation

The MSP was prepared according to the method described by Sun et al. [16]. Soy flour was dispersed in water at 6.25% solids content at pH 9.5, NaHSO_3 was added to the slurry at 6 g/L on the basis of water volume, and the slurry was stirred for 2 h at room temperature. The pH of the slurry was adjusted to 5.4 with 2 N HCl to remove carbohydrates and some glycinin proteins by centrifuging at $12,000 \times g$. The pH of the supernatant was then adjusted to 4.8 with 2 N HCl, and the slurry was centrifuged at $8,000 \times g$ to obtain MSP with a solids content of 38%. MSP and SLAs were mixed manually until it become uniform; the ratios of MSP/PBG blends were: 20/80, 40/60, 60/40, and 80/20 (total weight basis). Following initial analyses, the MSP/PBG (40/60) blends was prepared for further analysis and characterized in detail.

Apparent Viscosity

Apparent viscosity measurements of fresh MSP/SLAs blends were performed using a Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA, USA) with a CP 4/40 cone and plate fixture (4 cone angle, 40 mm cone diameter). The distance between cone and plate was set as 150 μm for all measurements. Experiments were conducted under steady shear flow at 23 °C. Shear rate was set at 50 s^{-1} .

Spread Rates

Cherry wood was oven dried at 130 °C for 1 h, weighed, and then conditioned at 23 °C and 50% relative humidity for 2 days. The conditioned cherry veneer was coated with fresh MSP/SLAs (40/60) blends on one side uniformly, and was allowed to rest at room temperature for 10 min. The coated cherry veneer was then oven dried at 130 °C for 1 h and weighed. Spread rate of the adhesive was calculated as the dry adhesive weight per square meter of single glue line. Reported values are the average of three replications.

Wood Specimen Preparation

Cherry wood veneers were preconditioned in a chamber (Electro-Tech Systems, Inc., Glenside, PA, USA) for 7 days at 23 °C and 50% relative humidity. The MSP/SLAs adhesives were brushed onto one end of a piece of cherry wood with dimensions of 127 × 20 mm (length × width) until the entire area was completely wet. The amount of adhesive on each piece was controlled with a balance. Two brushed wood pieces were left at room conditions for 5 min then assembled and pressed with a hot press (Model 3890 Auto M; Carver, Inc., Wabash, IN, USA) at 2 MPa and 170 °C for 10 min (lab procedure). In the preliminary test, we compared the adhesion strength of each SLAs under its suggested bonding procedure with the one under the soy protein adhesive curing procedure in our lab, and the data showed that latter condition exhibited a much better adhesion performance (results were not shown). Therefore, in order to coincide with the curing condition, the lab curing procedure was chosen in this study.

Shear Adhesion Strength

The wood assemblies glued with MSP/SLAs blends were cooled, conditioned at 23 °C and 50% relative humidity for 2 days, and cut into five pieces with dimensions of 80 × 20 mm (glued area of 20 × 20 mm). The cut wood specimens were conditioned for another 4 days before measurements were taken. Wood specimens were tested with an Instron Tester (Model 4465, Canton, MA, USA) according to ASTM Standard Method D2339-98 [17] at a crosshead speed of 1.6 mm/min. Shear adhesion strength at maximum load was recorded; reported values are the average of five specimen measurements.

Water Resistance

Water resistance of the wood assemblies was measured following ASTM Standard Methods D1183-96 and D1151-00 [18, 19]. The preconditioned specimens were soaked in tap water at 23 °C for 48 h, and wet strength was tested immediately after soaking.

Infrared Spectroscopy

On the basis of the shear adhesion results, the MSP/PBG (40/60) blends was selected for further characterization. The MSP/HLIG (40/60) blends was used for comparison purposes as needed.

Fourier transform infrared (FTIR) spectroscopic data were collected in the region of 800–4,000 cm^{-1} with a Perkin-Elmer Spotlight 300 spectrometer (Shelton, CT,

USA). Fresh adhesive blends were dried for 24 h in a vacuum oven at 50 °C and then ground into powder. A very thin layer of adhesive samples (i.e., easy for light to penetrate) was put on low-e microscope slides for the test. The transmission spectra of 64 scans of each disk were collected at a resolution of 2 cm^{-1} .

Transmission Electron Microscopy

A Philips CM 100 (FEI Company, Hillsboro, OR, USA) TEM was used to observe the microstructure of selected blends at the 40/60 ratio. Fresh adhesive blends were diluted to 1% with deionized water for imaging and sonicated for 5 min in an L&R320 ultrasonic stirrer (L&R Manufacturing Company, Keary, NJ, USA). Diluted samples were absorbed onto Formvar/carbon-coated 200-mesh copper grids (Electron Microscopy Science, Fort Washington, PA, USA) and stained with 2% (w/v) uranyl acetate (Ladd Research Industries, Inc., Burlington, VT, USA) for 60 s at room temperature.

Dynamic Viscoelastic Measurement

Dynamic oscillatory shear testing of the fresh MSP/PBG blends was performed with a Bohlin CVOR 150 rheometer to characterize the gelling process. A parallel plate head with an 8-mm plate diameter and a 500- μm gap was used. The measurements were performed at 50 °C with a small strain (5%) at frequency value of 1 Hz. The elastic modulus (G') and viscous modulus (G'') were continuously registered.

Scanning Electron Microscopy

A Hitachi S-3500 N (Hitachi Science System, Ibaraki, Japan) SEM was used to observe the microstructure of cured MSP/PBG blends. The cured MSP/PBG blends grounded powder were affixed to an aluminum stub with two-sided adhesive tape, and coated with an alloy of 60% gold and 40% palladium with a sputter coater (Desk II Sputter/Etch Unit, Moorestown, NJ, USA). The SEM images of the blends were performed with operation conditions at an accelerating voltage of 5 kV.

Differential Scanning Calorimetry

Thermal denaturation properties of the MSP/PBG blends were studied using a DSC (DSC7, Perkin-Elmer, Norwalk, CT, USA) calibrated with indium and zinc. Fresh MSP/PBG blends (5 mg) were hermetically sealed in the large-volume stainless steel pan. All samples were held at 20 °C for 1 min and then scanned from 20 to 180 °C at a heating rate of 10 °C/min. Peak temperatures and denaturation enthalpies were calculated from thermograms.

Thermogravimetric Analysis

Thermal degradation patterns of the cured MSP/PBG blends were studied using a TGA (TGA 7, Perkin-Elmer, Norwalk, CT, USA) in a nitrogen atmosphere. Fresh MSP/PBG blends were vacuum dried at 50 °C for 24 h and ground. Then 15 mg of the ground powder was weighed into a platinum cup and scanned from 20 to 700 °C at a heating rate of 10 °C/min. Maximum degradation rate was calculated as mass (%) at peak temperature divided by peak temperature.

Results and Discussion

Apparent Viscosity

Viscosity is an important physical property that governs the adhesive behavior of wood adhesives. Low viscosity allows easy handling and good flowability on the wood surface. The apparent viscosity of HLIg and FPV decreased significantly when blended with 20–60% MSP, whereas adhesive blends with 80% MSP had apparent viscosity similar to that of pure MSP (Fig. 1). The other three synthetic adhesives (CPLG, CPG, and VG) exhibited similar trends (results not shown). For PBG (Fig. 1), apparent viscosity was reduced extensively in the range of 20–40% MSP (4.5 and 3.1 Pa s, respectively, compared with 12.7 Pa s for pure PBG). However, viscosity of the PBG/MSP blends started to increase dramatically at 60% MSP and increased to 14.53 Pa.s at 80% MSP. For all MSP/SLAs blends, viscosity was lowest at a MSP/SLAs ratio of 40/60. In addition, all MSP/PBG blends gradually

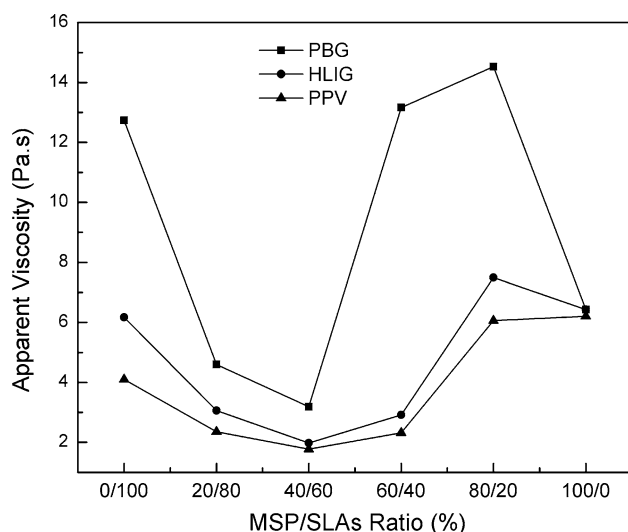


Fig. 1 Effects of MSP concentration on apparent viscosity of MSP and MSP/SLAs blends

became a gel and finally a complete solid. The gelling process was from 3 to 48 h depending on MSP concentration; the higher the MSP concentration, the faster the gelling process.

Spread Rates

Spread rate is a characterization of the amount of adhesive usage per unit area. The spread rates of SLAs, MSP, and MSP/SLAs (40/60) blends are shown in Fig. 2. Except for PBG, there were no obvious differences in spread rates between MSP/SLAs blends and pure SLAs. As mentioned in “Apparent viscosity”, the MSP/PBG (40/60) blends had the lowest apparent viscosity compared with pure PBG which led to good flow ability and easy spread ability, and subsequently having the largest spread rate reduction of all blends.

Shear Adhesion Strength

Dry shear adhesion strength of the MSP, SLAs (except for VG), and their blends was similar; all exhibited 100% wood cohesive failure (Table 1). The dry shear adhesion strength of VG was low but significantly increased when VG was blended with MSP. The blends had 100% wood cohesive failure at 60–80% MSP.

Wet shear adhesion strength of all SLAs except PBG was low (0.7–1.8 MPa; Table 2) but improved to different levels when the SLAs were blended with MSP and increased as the percentage of MSP increased. For example, wet shear adhesion strength was 3.29 MPa for MSP/VG (60/40) and 1.8 MPa for pure VG. It was assumed that VG is a viscoelastic polymer with good cohesiveness

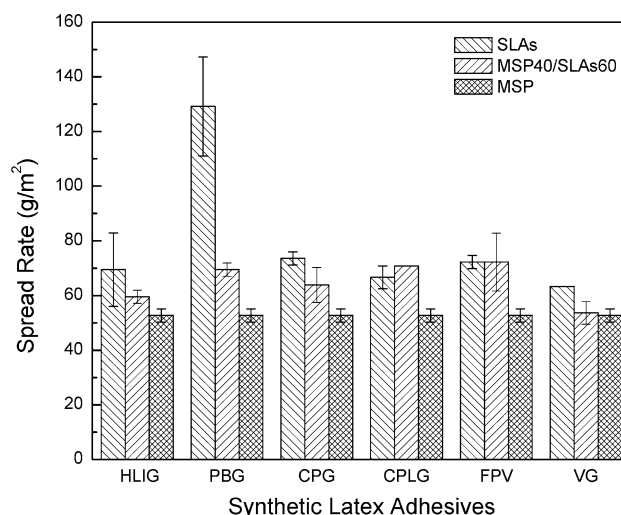


Fig. 2 Effects of MSP concentration on spread rate of MSP and MSP/SLAs blends

Table 1 Dry shear adhesion strength of MSP and MSP/SLAs blends

Adhesive	Dry shear strength (MPa)					
	PBG	HLIG	CPLG	CPG	FPV	VG
0% MSP	5.60 ± 0.31 cwf	7.51 ± 0.21 cwf	7.79 ± 1.17 cwf	5.61 ± 0.51 cwf	5.73 ± 0.91 cwf	3.50 ± 0.40
20% MSP	5.41 ± 0.68 cwf	7.51 ± 0.52 cwf	6.10 ± 0.49 cwf	5.85 ± 1.01 cwf	6.53 ± 1.38 cwf	4.25 ± 0.59
40% MSP	6.13 ± 0.28 cwf	7.26 ± 0.32 cwf	6.72 ± 0.26 cwf	5.75 ± 0.50 cwf	6.72 ± 0.51 cwf	4.45 ± 0.23
60% MSP	5.37 ± 0.29 cwf	5.72 ± 0.24 cwf	5.92 ± 0.89 cwf	6.72 ± 0.49 cwf	5.94 ± 0.76 cwf	4.28 ± 0.28 cwf
80% MSP	5.53 ± 0.44 cwf	4.49 ± 0.48 cwf	5.74 ± 0.24 cwf	4.72 ± 0.63 cwf	6.21 ± 0.47 cwf	5.46 ± 1.53 cwf
100% MSP	5.58 ± 0.41 cwf	5.58 ± 0.41 cwf	5.58 ± 0.41 cwf	5.58 ± 0.41 cwf	5.58 ± 0.41 cwf	5.58 ± 0.41 cwf

cwf 100% Cohesive wood failure

Table 2 Wet shear strength of MSP and MSP/SLAs blends

Adhesive	Wet shear strength (MPa)					
	PBG	HLIG	CPLG	CPG	FPV	VG
0% MSP	4.66 ± 0.09 cwf	1.43 ± 0.30	0.74 ± 0.40	1.61 ± 0.12	1.18 ± 0.18	1.81 ± 0.21
20% MSP	5.91 ± 0.52 cwf	1.65 ± 0.23	0.83 ± 0.29	1.36 ± 0.31	0.90 ± 0.37	1.81 ± 0.09
40% MSP	6.42 ± 0.49 cwf	2.01 ± 0.39	1.11 ± 0.16	1.55 ± 0.22	1.20 ± 0.17	2.93 ± 0.18
60% MSP	4.37 ± 0.58 cwf	1.90 ± 0.20	1.23 ± 0.22	2.12 ± 0.28	1.51 ± 0.34	3.29 ± 0.44
80% MSP	4.08 ± 0.24 cwf	2.35 ± 0.45	2.32 ± 0.46	1.86 ± 0.18	2.82 ± 0.47	3.74 ± 0.04
100% MSP	3.60 ± 0.42	3.60 ± 0.42	3.60 ± 0.42	3.60 ± 0.42	3.60 ± 0.42	3.60 ± 0.42

cwf 100% Cohesive wood failure

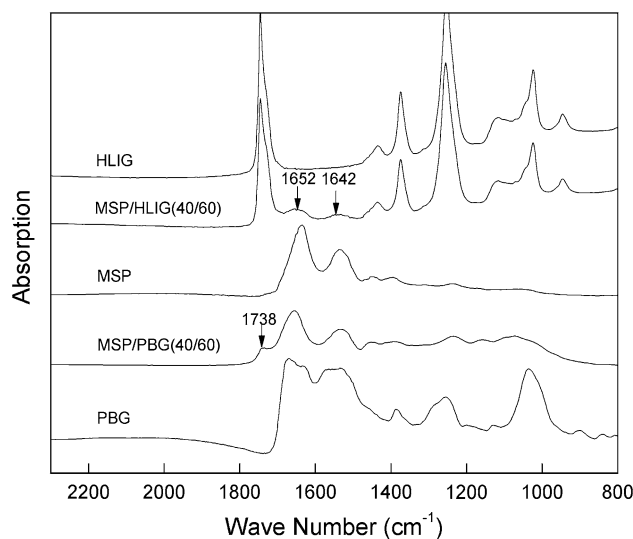
properties and water resistance; while blending with MSP, VG could entrap the soy protein molecules more efficiently than others, thus leading to an obvious improved adhesion strength (no chemical reaction occurred between them, preliminary data not shown). The PBG was more hydrophobic, with wet shear adhesion strength of 4.66 MPa. Wet shear adhesion strength of PBG progressively improved from 20 to 40% MSP, reaching 6.42 MPa with 100% wood cohesive failure at 40% MSP, and then decreased at 60% and 80% MSP. Similar to other SLAs, PBG exhibited a significant reduction in apparent viscosity in the range of 20–40% MSP. As discussed in “Dynamic viscoelasticity”, blends of PBG with 60 and 80% MSP had high viscosity because of the fast curing process which led to a poor diffusion ability and lower adhesion strength. Besides the physical synergistic effects, the interaction between soy protein and selected synthetic adhesives was further characterized in the following sections.

FTIR Spectra

On the basis of the initial analysis, PBG and HLIG were selected for further study of chemical interactions between SLAs and MSP. Two typical characteristic absorption bands of protein (amide I and II) normally appear at about 1,653 and 1,567 cm^{-1} , respectively [20], which are related

to C=O stretching and N–H bending. As shown in Fig. 3, amide I and II bands appeared at 1,667 and 1,543 cm^{-1} in MSP. The bands related to COO⁻, amide III (–N–H in plane and C–N stretch), and –C–NH₂ bending were located at 1,398, 1,234, and 1,079 cm^{-1} , respectively.

Because PBG is a type of amino resin, the main characteristic absorption bands that appeared in PBG at 1,668

**Fig. 3** FTIR spectra of MSP, MSP/PBG, and MSP/HLIG blends

and $1,534\text{ cm}^{-1}$ were identified as amide I and II, respectively. The band at $1,255\text{ cm}^{-1}$ represents C–N and N–H stretching of tertiary amides. The bands at $1,130$ and $1,035\text{ cm}^{-1}$ are due to C–O stretching of aliphatic ether and C–N or N–C–N stretching of methylene linkage. All of the basic structural absorption peaks of amino resins still appeared in the spectra of MSP/PBG (40/60) blends, and the band intensities seemed to occupy an intermediate position between those of MSP and PBG. The amide I peak shifted to $1,655\text{ cm}^{-1}$, indicating that possible intra-hydrogen bonding was involved between two polymers, resulting in the C=O stretching frequency change. Soy protein contains many functional groups including carboxylic (–COOH), hydroxyl (–OH) and amino groups (–NH₂), which have potential to react with hydroxymethyl groups (–CH₂–OH) of PBG to form ester bonds (C–(C=O)–O–C), ether linkages (–CH₂–O–CH₂–), and amide linkages (–NH–CO–), respectively. The new small peak observed at $1,738\text{ cm}^{-1}$ in MSP/PBG blends is likely the C=O absorption from the new ester bond. The other absorption bands arising from C–O stretching vibration of esters consisted of C(C=O)–O and O–C–C and normally occurred in the region of $1,300$ – $1,000\text{ cm}^{-1}$ [21]. We believed these bands overlapped with amide III and –C–NH₂ bending in amide resin (Fig. 3). The ether and amide linkages of MSP/PBG blends could also be formed and were overlapped with the large number of amide linkages in the amide resin. In addition, although MSP is a partially unfolded soy protein modified by reducing agent NaHSO₃, many functional groups available for the chemical reaction were still buried inside; therefore, the absorption peaks for the new bonds were not strong enough to be observed in the infrared spectra.

Figure 3 shows that HLIG, a PVA based adhesive, had two characteristic absorption bands at $1,745$ and $1,253\text{ cm}^{-1}$ corresponding to C=O and C–O stretching [22]. In the MSP/HLIG blends, specific absorption peaks from HLIG occurred in the same positions as those in pure HLIG. Characteristic bands related to soy protein (amide I and II) were present, and no new absorption bands were observed; these results indicated there were no chemical interactions between MSP and HLIG.

Transmission Electron Microscopy

Morphological properties of the MSP/PBG (40/60) and MSP/HLIG (40/60) blends are shown in Fig. 4. Pure MSP existed mainly in the form of globular aggregates with different sizes and a chain-like network (Fig. 4a). PBG is a chain-like network (Fig. 4b) connected by methylene and methylene ether bridges [23]. In the MSP/PBG (40/60) blends, some globular aggregates formed into the larger ones, accompanied with the many small ones (Fig. 4d),

uniformly embedded in a much denser networks. This arrangement improves water resistance; the small aggregates facilitate the penetration of adhesive into the wood surface, and the dense structure reduces the penetration of water into the interfacial layer between wood and adhesives.

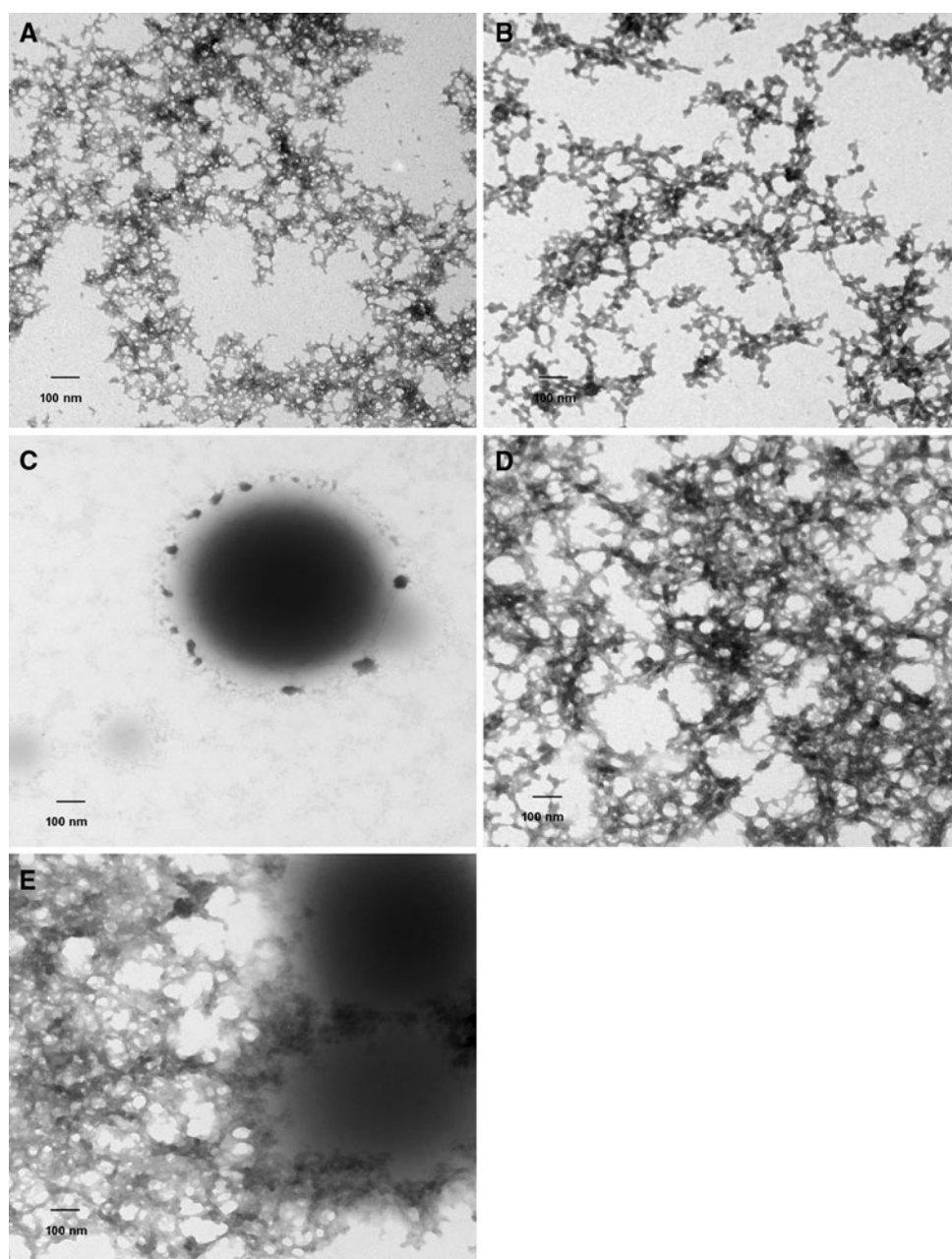
The HLIG mainly formed small, irregular aggregates (Fig. 4c); these aggregates surrounded a big, black, globular chunk. Similar to the MSP/PBG (40/60) blends, larger globular aggregates of protein formed and were embedded in a much denser structure in the MSP/HLIG (40/60) blends (Fig. 4e). The big, black, globular chunk was still retained in the blends. Soy protein aggregates and much denser structures were formed in MSP/PBG blends with chemical reaction and in MSP/HLIG blends without chemical reaction; this denser structure is beneficial for adhesive performance. The larger aggregates in the blends also could be one of the reasons for the reduced viscosity of adhesive blends. These aggregates reduce water-imbibing capacity, resulting in more free water in the adhesive blends system [24]. Consequently, friction between protein molecules is reduced and a less viscous system is formed.

Dynamic Viscoelasticity

The gelling process of wood adhesives is important in terms of adhesion strength [25]. During the curing process, high molecular weight, three-dimensional networks formed and resulted in a strong, tight bond. The MSP/PBG blends gradually became gel and finally became solid. The gelling time of blends decreased as the amount of MSP increased. Dynamic rheological properties of the MSP/PBG blends in the initial 30 min of the curing process are summarized in Fig. 5. The elastic modulus (G') of MSP/PBG blends with 60 and 80% MSP increased rapidly, indicating the formation of a viscoelastic soy protein–UF network. When PBG was blended with 80% MSP, G' increased from 300 Pa to 20,000 Pa at the end of the oscillatory shear performance. At low MSP concentration (i.e., 20%), gelling time increased significantly and the final G' was only approximately 400 Pa. However, pure PBG and MSP were still in a liquid state after 30 min of oscillation, and G' remained almost the same as well.

Urea–formaldehyde resins are obtained from the reaction of urea and formaldehyde through a two-step process consisting of alkaline methylation followed by acid condensation. It is well known that the condensation polymerization reaction of UF occurs under acidic conditions; however, the initial pH of PBG resin is always adjusted to 7.0–8.0 for storage reasons [26]. Pure MSP and PBG had pH 4.8 and 7.8, respectively, whereas the pH of MSP/PBG blends was in the range of 4.9–5.5 (Fig. 6). Addition of MSP to PBG resin provides an acidic environment for the

Fig. 4 TEM image of MSP/SLAs blends: soy protein modified by sodium bisulfite, MSP (a), PBG resin (b), HLIg resin (c), MSP/PBG (40/60) (d), and MSP/HLIG (40/60) (e)



UF curing process that facilitates chain length growth and formation of cross links between chains. A higher MSP concentration in blends led to a more acidic environment, which made UF resin cure faster. And as mentioned in the “FTIR spectra” section, there were chemical reactions between MSP and PBG. At the higher levels of MSP, more functional groups ($-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$) were available for the cross-linking reaction with PBG. Therefore, MSP/PBG blends with high MSP content cured faster than blends with low MSP content. This fast curing might also explain why MSP/PBG blends with 60 and 80% MSP had higher viscosity. Overall, results indicated that MSP

provided functional groups for the chemical reactions with PBG and also acted as an acidic catalyst.

Scanning Electron Microscopy

The microstructures of cured MSP/PBG blends are presented in Fig. 7. Both MSP and PBG showed irregular particles with different sizes and smooth surfaces. Some small particles were stuck to the surfaces of the larger particles (Fig. 7a, f). At 80% MSP, many small, rough particles with porous morphology were attached to large individual particles (Fig. 7b). At MSP loading levels lower

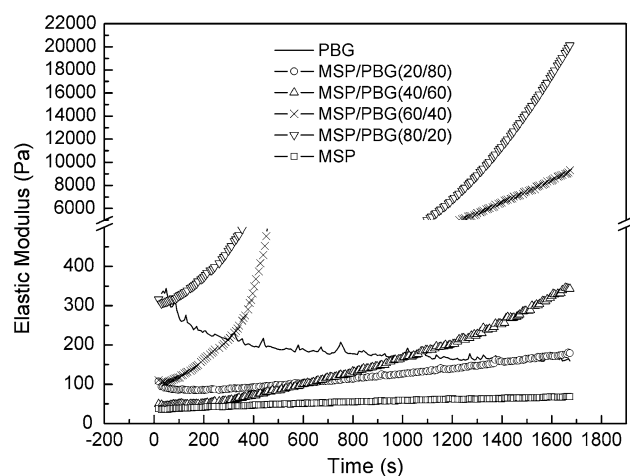


Fig. 5 Effects of MSP concentration on elastic modulus (G') of MSP/PBG blends

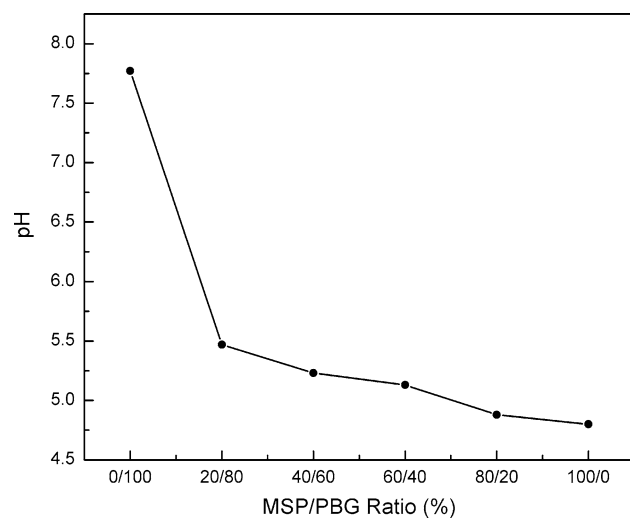


Fig. 6 Effects of MSP concentration on pH values of MSP/PBG blends

than 80% (Fig. 7c–e), these small particles became more compacted and tightly coated the surface of reacted soy protein and UF polymers. In addition, the amount of these coatings decreased as MSP content decreased. As described in “Dynamic viscoelasticity”, a higher MSP content would lead to more cross-linking reactions with PBG and, subsequently, more reacted rough coatings. Soy proteins are highly complex ordered macromolecules with many functional groups buried inside; this structure limits the degree of cross-linking with PBG. As the reaction proceeded, more compact particles were produced and attached to PBG and the soy protein surface, preventing further interaction between these two polymers. Also, because MSP is a partially unfolded protein, there are not enough functional groups available for a complete reaction with PBG; this results in a limited coating substance on the surface of these two polymers.

Denaturation Properties

The typical DSC thermogram of MSP showed two endothermic transitions (T_d) at about 79.5 and 96.6 °C caused by conglycinin (7S) and glycinin (11S) denaturation and had a total denaturation enthalpy (ΔH_d) of 8.12 J/g (Table 3). In this study, the MSP modified with the reducing agent NaHSO_3 was more thermally stable than the 10% soy protein isolate suspension with T_d values of 74.9 and 88.8 °C for 7S and 11S reported by Huang and Sun [5]. The salt's screening effects of NaHSO_3 on the protein's electrostatic forces resulted in greater hydrophobic interactions, which could compensate for the negative destabilization effect of NaHSO_3 as a reducing agent.

The two endothermic transitions caused by 7S and 11S denaturation were also observed in all MSP/PBG blends (Fig. 8). In terms of overall denaturation trends of subunits in MSP, both T_d and ΔH_d increased with PBG concentration (Table 3). The denaturation temperature increased to approximately 90 °C from 80 °C for 7S and to 100 °C from 96 °C for 11S, which could be a result of their different native structures. Chemical reactions and interhydrogen bonding between the two polymers could form macro complexes with more compact structures, which would make soy protein chains less mobile and resulted in higher thermal stability. However, the limited reactions between MSP and PBG observed in SEM images indicated there might be a threshold for the cross-linking reaction at a certain PBG concentration (possibly, lower than 20% PBG). It is well known that 7S globulin exists as trimeric complexes through non-covalent bonds such as hydrogen and electrostatic force, whereas 11S has a hexameric form connected by disulfide bonds [27]. Although MSP was modified by reducing agent NaHSO_3 , complete reduction of disulfide bonds could not be achieved in glycinin [28]. The disulfide bonds make 11S more thermally stable than 7S [29]. The total enthalpy of soy protein decreased to 5.12 from 8.12 J/g when the soy protein was blended with 20% PBG (Table 3). Protein aggregates formed when soy protein was mixed with PBG (Fig. 2d); this is an exothermal process and could compensate for the energy absorbed by the cross-linking reaction, resulting in lower ΔH . Furthermore, PBG resin is a mixture of polymer and mono free formaldehyde. More PBG resin would provide more hydroxymethyl groups and free formaldehyde cross-linked with soy protein, resulting in increasing total denaturation enthalpy with increasing amount of PBG.

Thermogravimetric Analysis

The TGA and differential TGA (dTG) curves of cured MSP/PBG blends (ground powder in an N_2 atmosphere) are shown in Fig. 9. The MSP degraded in three weight

Fig. 7 SEM image of MSP/PBG blends: MSP (**A, a**), MSP/PBG (80/20) (**B, b**), MSP/PBG (60/40) (**C, c**), MSP/PBG (40/60) (**D, d**), MSP/PBG (20/80) (**E, e**), and PBG (**F, f**)

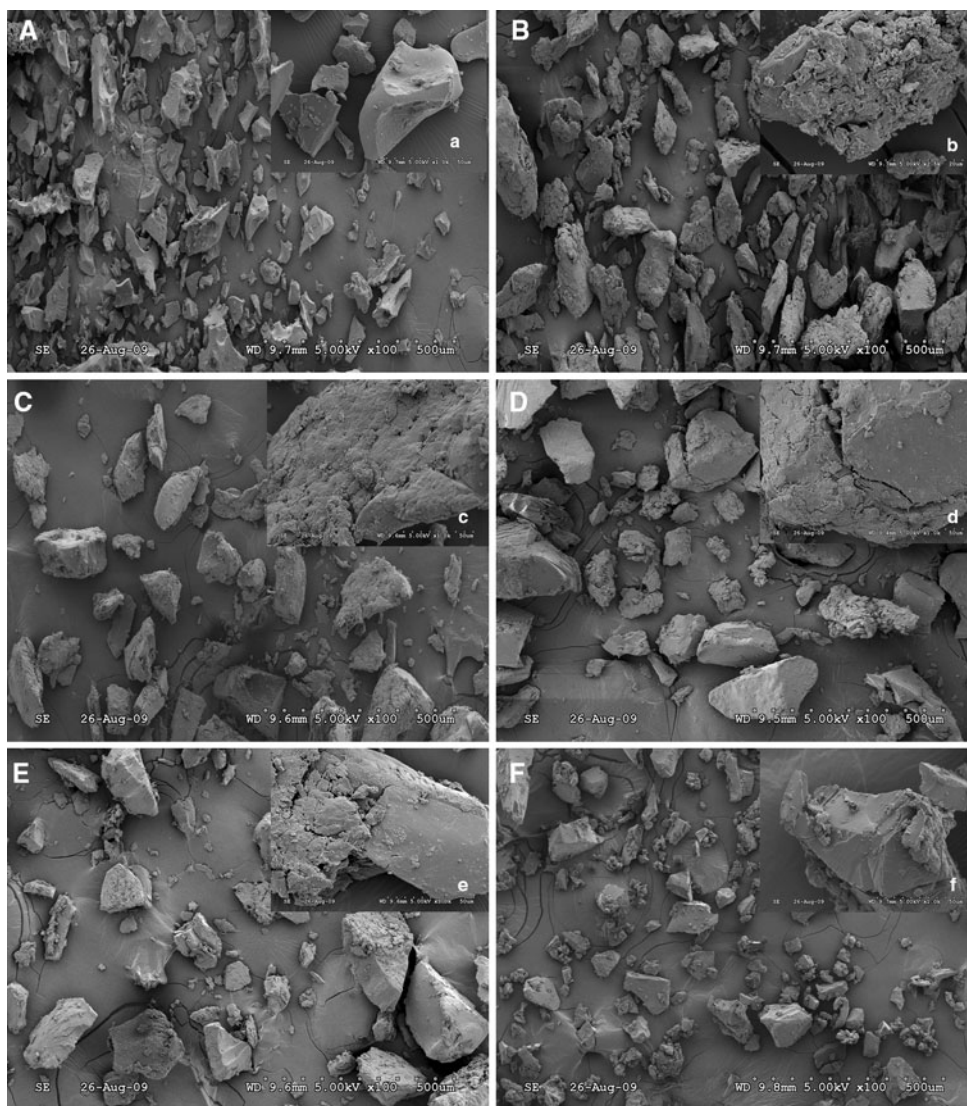


Table 3 Denaturation temperature (T_d) and enthalpy of denaturation (ΔH) of MSP in MSP/PBG blends

MSP/PBG Blends	T_d (°C)		Total (ΔH_d) (J/g)
	7S	11S	
MSP	79.49	96.75	8.12
MSP/PBG (80/20)	89.83	101.18	5.85
MSP/PBG (60/40)	89.15	99.22	10.57
MSP/PBG (40/60)	90.43	98.55	9.84
MSP/PBG (20/80)	90.30	99.19	13.80

loss stages (Fig. 9b). In the first stage, from 25 to 160 °C, 10% weight loss for MSP was due to evaporation of residual moisture. Weight loss in the second stage, between 208 and 400 °C, was due to the degradation of soy protein involving broken intermolecular and intramolecular hydrogen bonds, electrostatic bonds, and cleavage of the

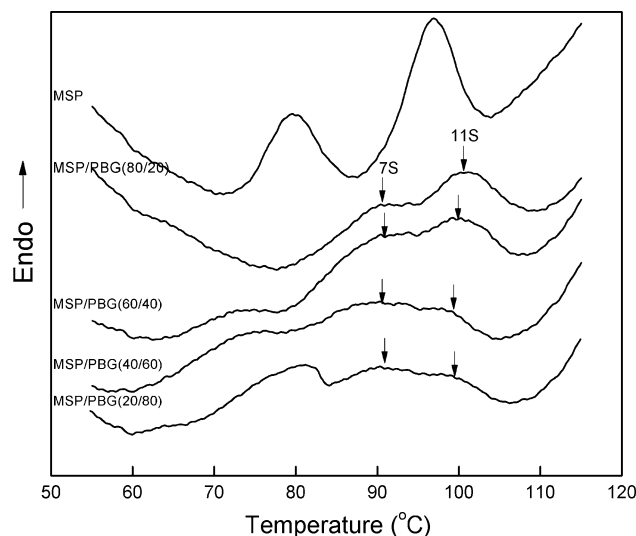


Fig. 8 DSC thermogram of MSP and MSP/PBG blends

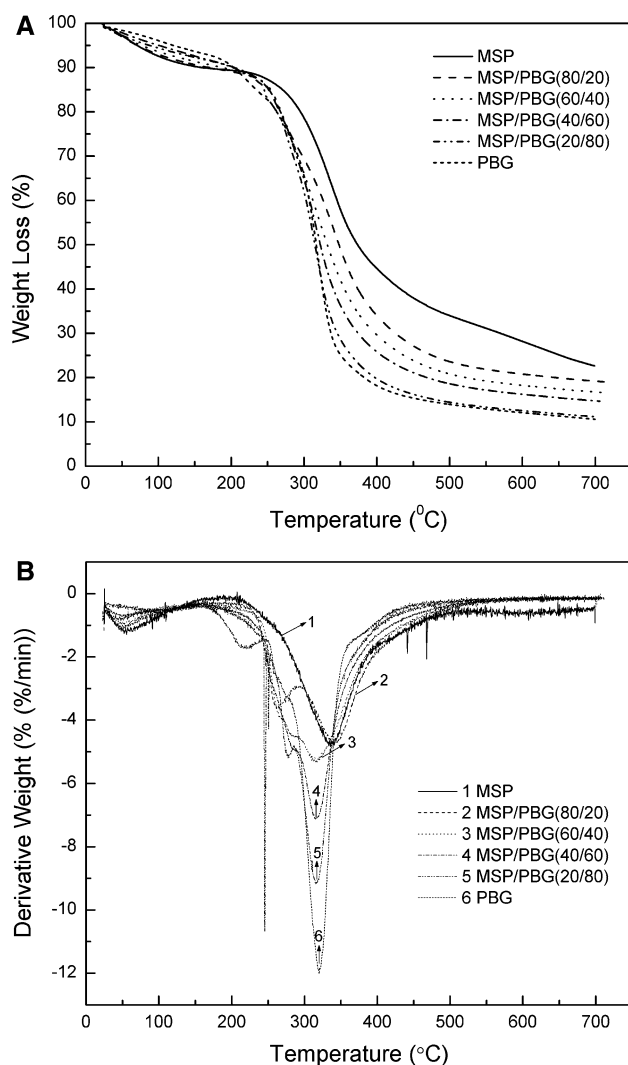


Fig. 9 Thermogravimetric (a) and derivative thermogravimetric (b) curves for MSP/PBG blends

covalent bonding between the peptide bonds of amino acid residues [30]. Further heating caused breakage of S–S, O–N, and O–O linkages, and finally protein backbone peptide bonds were decomposed, producing various gases such as CO, CO₂, NH₃, and H₂S. The first weight loss stage (5%) of PBG, from 50 to 170 °C, was due to the residue water and the water that resulted from the condensation reaction. The exothermic peak due to PBG curing overlapped with the endothermic effects of water evaporation [31]. Almost 60% weight loss occurred in the second stage with a peak temperature of 320 °C; it was caused by decomposition of the most stable unit in the PBG resin-methylenediurea [32]. The small peak that appeared in the temperature of 201–228 °C was the formaldehyde emitted from the PBG resin.

During the heating process, the decomposition rate varied from 90 to 20% (Fig. 9a). As MSP content increased in MSP/PBG blends, the weight-temperature slopes

became smaller. Similar trends were observed for the final residues weights corresponding to the temperature. Variations in weight loss of different blends were not observed until approximately 245 °C (Fig. 9b), which is probably due to the cross-linking reaction between soy protein and formaldehyde emissions from pure PBG (small peak between 201 and 228 °C). New peaks appeared in dTG curves of MSP/PBG blends in the range of 270–281 °C, which is further evidence that chemical bonds formed between these two polymers. The main decomposition temperature of blends with different ratios decreased slightly, compared with either of the neat polymers. Soy protein powder is granular and has long protein chains compactly arranged in α -helix and β -sheet structures; this formation leads to a high initial decomposition temperature [33]. As shown in the SEM image, part of the PBG resin reacted with soy protein molecules. We assumed that the branched PBG structure could interrupt the regularity of soy protein macromolecule chains to a certain extent, leading to decreased thermal stability. Simultaneously, unreacted MSP dispersed in the PBG matrix, which could reduce such interaction.

Conclusions

Soy protein can be modified into functional copolymers that interact and react with commercial synthetic adhesives to enhance adhesion performance. Apparent viscosity of MSP/SLAs blends was reduced significantly at 20–60% MSP, which improved flowability and spread rate. The modified MSP reacted with UF based resin to form a gel within 3–48 h depending on soy protein concentration. The blends of MSP with 60% UF based resin (PBG) had the wet adhesion strength of 6.4 MPa with 100% wood cohesive failure; pure PBG had the wet adhesion strength of 4.7 MPa. Results indicated that MSP acts as an acidic catalyst for UF based resins such as PBG.

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