

Preparation of a High-Temperature Soybean Meal-Based Adhesive with Desired Properties via Recombination of Protein Molecules

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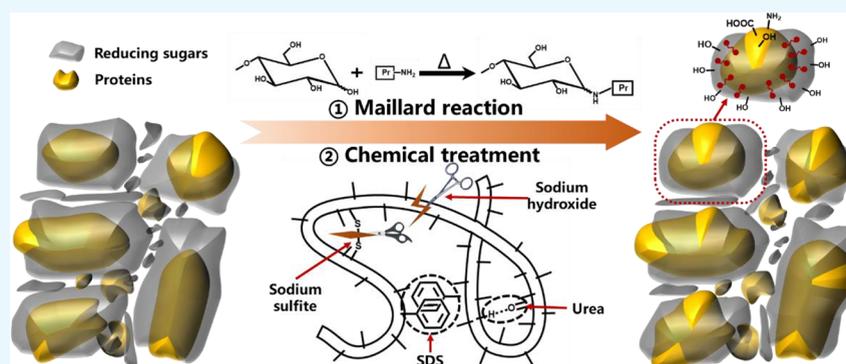
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ABSTRACT: A soybean protein-based adhesive with desired adhesion properties and low processing cost is prepared by a simple and practical method, which is of great significance to the sustainable utilization of resources and human health. Nevertheless, the protein of high-temperature soybean meal (HSM) has a high degree of denaturation and low solubility, endowing the resultant soybean-based adhesive with a high viscosity and unstable bonding performance. Herein, we propose the strategy of protein molecular recombination to improve the bonding properties of the adhesive. First, chemical denaturation was carried out under the combined action of sodium sulfite, sodium dodecyl sulfate, sodium hydroxide, urea, or sodium dodecyl sulfate/sodium hydroxide to reshape the structure of the protein to release active groups. Then, thermal treatment was employed to facilitate the protein repolymerization and protein–carbohydrate Maillard reaction. Meanwhile, the epichlorohydrin-modified polyamide (PAE) as a crosslinking agent was introduced to recombine unfolded protein and the products from Maillard reaction to develop an eco-friendly soy protein-based adhesive with an excellent and stable bonding performance. As expected, the highest cycle wet bond strength of the adhesive sample of 1.20 MPa was attained by adding a combination of 2% SDS and 0.5% sodium hydroxide, exceeding the value required for structural use (0.98 MPa) of 22.44% according to the JIS K6806-2003 commercial standard. Moreover, the adhesive possessed the preferable viscosity and viscosity stability accompanied by good wettability. Noteworthy, the adhesive had a short time of dry glue, which could be solved by combining it with soybean meal (SM) at the ratio of 30:10.

1. INTRODUCTION

With the boom in the petrochemical industry in the 20th century, synthetic adhesives and their modified products gradually replace most biobased adhesives into people's daily life. However, those adhesives are derived from unsustainable petroleum resources and release carcinogenic formaldehyde and other harmful substances into the environment, resulting in pollution problem and endangering human health.¹ Therefore, there is a tremendous demand for the development of sustainable adhesives preferably using natural and renewable resources, such as soybean meal (SM), starch, lignin, and tannin that are eco-friendly and renewable.^{2,3}

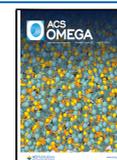
An SM-based adhesive is one of the more potential candidates for replacing petroleum-based adhesives in the future.⁴ However, its poor water resistance, high viscosity, low

solid content, low bonding strength, and high cost are still urgent problems.^{5–7} Many attempts have been made to improve the properties of SM-based adhesives, mainly including physical treatment,^{8,9} chemical denaturation,^{10,11} crosslinking with crosslinkers or synthetic resins,¹² biomimetic structure construction,¹³ biological treatment,¹⁴ organic–inorganic hybridization,^{15–17} carbohydrate modification,¹⁸ and the combination of some of the above-mentioned

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methods.^{19,20} The methods mentioned above were the effective ways to prepare high-performance SM-based adhesives, especially crosslinking with crosslinkers. Many studies demonstrated that the use of polyamidoamine-epichlorohydrin (PAE) resin as a crosslinking agent could be effective in increasing the wet bond strength of SM-based adhesives and lead to an increase in the use of soybean meal-based adhesives.^{21,22} PAE is a stable low-viscosity aqueous solution, and it can effectively dissolve and disperse SM to form a uniform glue with a solid content of 30–41.3% and a viscosity of 2200–50,000 mPa·s (25 °C). The *N*-heterocycle in PAE can react with the amino and carboxyl groups in the protein molecule to form a three-dimensional network structure to increase the performance of the adhesive.²³ Nowadays, the bond strength and water resistance of SM-based adhesives have significantly improved and can withstand hydrothermal testing (soaking in water at 63 °C and in boiling water).²⁴ However, there is no superiority compared to formaldehyde synthetic resin adhesives in terms of price or water resistance. Therefore, effectively reducing the production costs and improving the adhesion properties of SM-based adhesives are the key issues that need to be resolved in the current research.

SM is a by-product of soybean oil processing, which can be divided into low-temperature soybean meal (LSM) and high-temperature soybean meal (HSM) according to the desolvation temperature and processing technology by which it was generated. LSM is obtained by low-temperature desolventizing treatment and has a low degree of protein denaturation, high nitrogen solubility index, and high protein dispersion index. HSM is obtained by high-temperature desolventizing treatment, leading to a high extent of protein component denaturation and a decrease in the solubility of the protein, but the price of HSM is about 250 to 320 USD/ton cheaper than that of LSM, which has a great advantage in industrialization.²⁵ In our previous research, we discussed the possibility of preparing an adhesive with HSM and found that the content of active groups such as amino and carboxyl groups in HSM is lower than that in LSM. The adhesive prepared by LSM and a crosslinking agent has a higher crosslinking density to effectively prevent the damage of moisture to the cured adhesives, making the adhesive have a higher bonding performance and better stability.²⁵ Therefore, releasing the active groups of HSM to improve its reactivity is the key step in preparing HSM-based adhesives.

In the daily process of cooking and baking food, we often find that brown dough is difficult to dissolve in hot water, which is mainly due to the polymerization reaction between carbonyl compounds (reducing sugars) and amino compounds (amino acids and proteins). This reaction is called Maillard reaction.⁴ Inspired by this cooking phenomenon (Maillard reaction), the molecular recombination strategy was used to guide soy protein adhesive modification by thermochemical treatment. Thermochemical treatment makes use of the synergistic effect of thermal activation and chemical reagent denaturation to realize the reorganization of the protein structure, promote the repolymerization of protein, and make the Maillard reaction between the protein and soybean carbohydrates.^{20,26}

In this work, the different kinds of denaturing reagents (sodium sulfite, SDS, sodium hydroxide, and/or urea) were used to unfold the structure of protein in HSM to release active groups since sodium sulfite, SDS, sodium hydroxide, and

urea caused different degrees of damage or fracture to the inter- and intradisulfide bonds,²⁷ the hydrophobic moieties,²⁸ the primary structure,²⁹ and the hydrogen bond,³⁰ respectively. Then, these polypeptide chains were recombined by thermal treatment at 140 °C, facilitating the reorganization of protein and the Maillard reaction between the protein and soybean carbohydrates. After that, using PAE as a crosslinking agent further improved the performance and bond stability of the adhesive. This work makes it possible to prepare low-cost, high-performance soybean adhesives from high-temperature soybean meal and will guide the further development of soybean meal-based adhesives.

2. EXPERIMENTAL SECTION

2.1. Materials. HSM (average protein content, 50.4%; water content, 6.7%; –160 mesh) were obtained from Laihe Oil Pressing Factory, Shandong, China. PAE was synthesized in our lab using diethylenetriamine, adipic acid, and epichlorohydrin and had a solid content of 13.4%, a pH value of 3.2, and a viscosity of 96.4 mPa·s (25 °C).³¹ Birch veneers (420 mm × 420 mm × 1.6 mm, 8–10% moisture content) were provided by Weihe Fulin Plywood Plant, Heilongjiang, China. Other chemicals, such as sodium sulfite, SDS, sodium hydroxide, and urea, were of reagent grade and were purchased from local chemical companies.

2.2. Thermochemical Treatment of HSM. About 100 g of HSM was blended with 35 g of a solution containing 2.5 g of modifier in a high-speed mixer at 800 rpm. After uniform mixing, the mixture was placed on a polytetrafluoroethylene film to form a thin layer and then placed in an oven at 140 °C for 30 min. After cooling to room temperature, the product was ground to a fine powder, passed through a 120-mesh sieve, and marked as shown in Table 1. Native HSM and HSM that were thermally treated without using modifiers were selected as the controls and labeled HSM and TSM, respectively.

Table 1. Components in Each Thermochemical Treatment Formulation of HSM

sample ID	HSM/g	sodium sulfite/g	SDS/g	sodium hydroxide/g	urea/g
TSM-S	100	2.5	0	0	0
TSM-D	100	0	2.5	0	0
TSM-H	100	0	0	2.5	0
TSM-U	100	0	0	0	2.5
TSM-SH-1	100	0	2	0.5	0
TSM-SH-2	100	0	1.5	1	0
TSM-SH-3	100	0	1	1.5	0
TSM-SH-4	100	0	0.5	2	0

2.3. Preparation of the HSM-Based Adhesives and Cured Samples. The various adhesives, which were composed of HSM/modified HSM and PAE solution at a mass ratio of 1:4, were formed by mixing in a beaker at room temperature until no particle clusters were observed. These samples were labeled as “HSM-based adhesive”, “TSM-based adhesive”, “TSM-X-based adhesive”, and “TSM-SH-Y-based adhesive”, respectively, where X was represented as S, D, H, or U, and Y was represented as 1, 2, 3, or 4. About 5 g of the above-prepared HSM-based adhesives was then placed in a polytetrafluoroethylene container and cured at 120–125 °C for 2 h to produce the cured HSM-based adhesive samples with curing reactions (Figure 1). After cooling to room

temperature, these samples were ground to a fine powder and passed through a 160-mesh sieve prior to characterization.

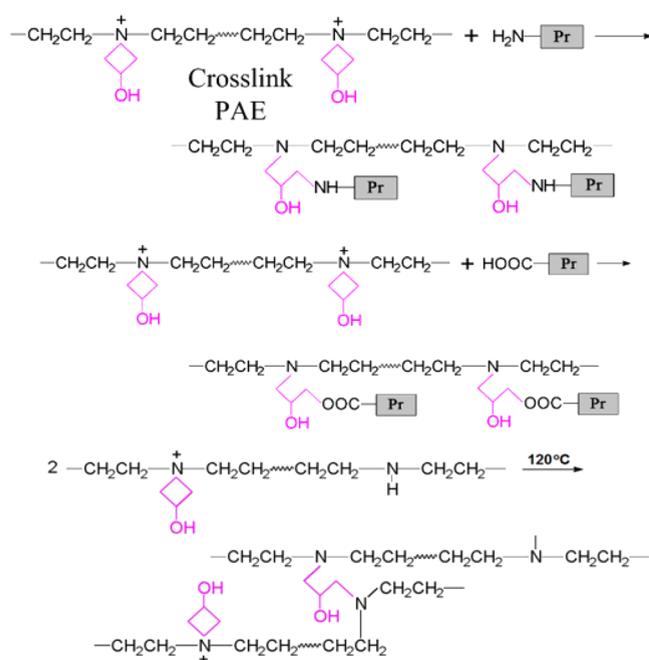


Figure 1. Schematic illustration of the crosslinking reaction between the protein and PAE.

2.4. Preparation of the Three-Plywood Sample. A three-plywood sample was fabricated from a liquid adhesive loading of 180 g/m² for a single glue line by coating the adhesive onto both surfaces of the core veneer (1.6 mm thick). This core veneer was sandwiched between two uncoated face veneers (1.6 mm thick) by hand, with the grains of adjacent veneers vertical to each other. Then, the sample was cold-pressed at 1.1 MPa at room temperature for 45 min, followed by hot pressing at 120 °C and 1.3 MPa for 4 min. After hot pressing, the panels were stored openly under an ambient environment for ≥ 24 h before testing.

From each prepared panel, 30 specimens with a bond area of 25 mm \times 25 mm were cut out to determine the bond strength and water resistance. Specifically, 10 specimens were used to determine each of the three properties: dry bond strength, soaked wet bond strength, and cycled wet bond strength. The tests were conducted according to the commercial standard JIS K6806-2003 using a tensile testing machine with a crosshead speed of 5 mm/min. For the soaked wet bond strength test, the specimen was soaked in 63 \pm 2 °C water for 3 h and then cooled at room temperature for 10 min before measuring the shear tensile strength. For the cycled wet bond strength test, the specimen was subjected to boiling–dry–boiling hygro-thermal treatment (4 h of boiling, 20 h of oven-drying at 63 \pm 2 °C, and then another 4 h of boiling) before the measurement of the shear tensile strength in the wet state at room temperature.

2.5. Determination of the Boiling Water-Insoluble Content. To a 250 mL flask equipped with mechanical stirring and refluxing, approximately 2.0 g of the sample was passed through a 120-mesh sieve (W_0 , accurate to 0.0001 g) and 200.0 g of distilled water was added, and the mixture was stirred and boiled for 4 h. The solution or dispersion was then allowed to cool to room temperature and filtered, and the residue was

rinsed twice with 50 mL of distilled water. The residue on glass-filter paper (W_1 , accurate to 0.0001 g) was oven-dried at 120 °C to a constant weight (W_2 , accurate to 0.0001 g). The boiling water-insoluble content was defined as the mass percentage of soybean protein insoluble in boiling water, $[(W_2 - W_1)/W_0] \times 100\%$.

2.6. Determination of the Acetaldehyde Value. A 100 mL reaction flask equipped with a mechanical stirrer, thermostat, and condenser (Lichen, Shanghai, China) for reflux was charged with approximately 1.5 g of the sample, 50.0 mL of water, and 5.00 mL of 40.0 wt % acetaldehyde. The pH of the mixture was then adjusted to 8.5–8.7 using a 20 wt % sodium hydroxide solution. The mixture was then maintained at 50 \pm 2 °C for 120 min. The reaction mixture was allowed to cool to room temperature and then diluted to 1000 mL in a volumetric flask. The unreacted acetaldehyde content in the diluted filtrate (F_1 , mmol/L) was tested according to the method described in the technical bulletin “Test method for free formaldehyde” issued in April 1994 by the Structure Board Association of Canada. Three blank tests were conducted under the same conditions without samples to determine the total free acetaldehyde content (F_0 , mmol/L) prior to the reaction. The acetaldehyde value (mg/g) of the sample was defined as the equivalent mass of acetaldehyde (mg) that can react with 1 g of the sample and calculated according to $(F_0 - F_1) \times 44/m_1$.

2.7. Gel Permeation Chromatography (GPC) Analysis of HSM. A reaction kettle equipped with a mechanical stirrer and refluxing equipment was charged with 5 g of HSM and 100 g of urea solution (8 mol/L). The mixture was maintained at 50 \pm 2 °C for 2.5 h with stirring to dissolve the HSM completely, during which partial urea might convert to ammonia by the urease in HSM without de-enzyming or thermal treatment, however, the urea concentration (8 mol/L) was sufficient for complete dissolution of the HSM sample. After that, the resultant product was cooled to room temperature and then filtered with a glass fiber filter. The filtered solution was then diluted to 0.1 wt % with deionized distilled water before the determination of the molecular weight (MW) using an Agilent 1100 GPC equipped with a differential refraction detector and two chromatographic columns in series (namely, 79911GF-083, with an MW ranging from 100 to 30k, and 79911GF-084, with an MW ranging from 10k to 200k). The mobile phase was 4.8 wt % (0.8 mol/L) urea solution with a flow rate of 1 mL/min, and the pressure on the columns was 78 psi. GPC was calibrated with four standard polysaccharides produced by Polymer Laboratories, USA. These polysaccharides have MWs of 12,000, 50,000, 150,000, and 410,000, and their distribution indexes ranged from 1.0 to 1.05.³²

2.8. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis. The samples were taken to freeze-dry at –50 °C and 15 kPa for 1 week and then ground in a mortar. Each powder sample of pure freeze-dried products was mixed with potassium bromide crystals at a weight ratio of approximately 1:150 and then thoroughly ground. The mixture was then pressed into a special mold to obtain a sample for FT-IR analysis. The spectra were recorded from 450 to 4000 cm^{–1} using a Spectrum One FT-IR spectrophotometer (Nicolet Co., USA). Each sample was scanned 32 times with a resolution of 4 cm^{–1}.

The internal standard method was applied to determine the accurate group concentrations of various HSM-based adhesive,

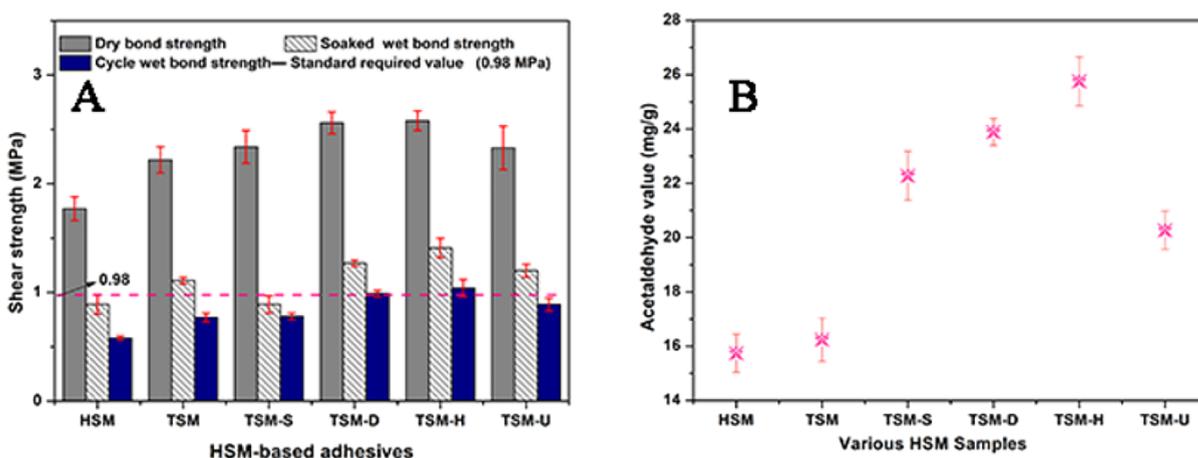


Figure 2. Bond strength of various HSM-based adhesives (A) and acetaldehyde values of various HSM samples (B).

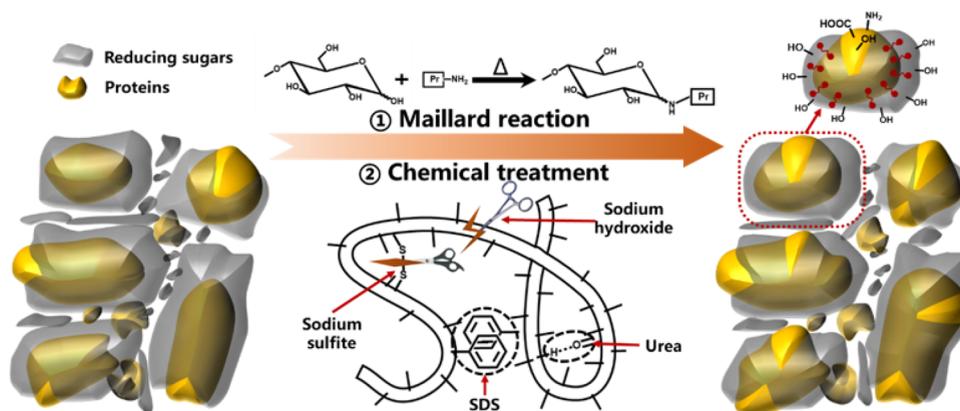


Figure 3. Schematic of the thermochemical treatment of HSM.

attributed to the fact that the sample thickness and potassium bromide/protein ratio might vary from each other. The IR peak at approximately 2941 cm^{-1} , which represents the stretching mode of the inert C–H group, was selected as an internal standard. The spectrum was subjected to baseline correction and concentration correction using the software OMNIC E.S.P. (Nicolet Co., USA).³³

2.9. X-ray Diffraction Spectroscopy (XRD) Analysis.

The changes in the crystalline structure of native HSM, thermally treated HSM, and thermochemically treated HSM were recorded on a D/MAX-2200 diffractometer (Rigaku, Tokyo, Japan) using a Cu-K α source. Diffraction data were collected from 5° to 50° with a step interval of 0.02° , an accelerating voltage of 40 kV, and a current of 30 mA.

2.10. Contact Angle of HSM-Based Adhesives. The contact angle was measured using a Theta optical contact angle meter (Biolin Scientific, Sweden). Thirty seconds after a liquid adhesive drop was placed onto a birch veneer surface at room temperature ($23\text{--}25^\circ\text{C}$) and a relative humidity of 50–60%, the shape of the sample was recorded by a CCD video camera. The contact angle was determined by fitting the Young–Laplace equation to the drop profile. The data presented in this study are an average of seven replicated tests.

2.11. Amount of Load of HSM-Based Adhesives. The preweighed veneers (denoted as M_1) were rolled by a rubber roller covered with an equal weight of adhesives, and then the glued veneers were weighed immediately, denoted as M_2 . The area of the veneer is $75\text{ mm} \times 165\text{ mm}$, and the width of the

rubber roller is smaller than the width of the veneer. The amount of load is calculated according to $M_2 - M_1$. The data presented in this study are an average of three replicated tests.

2.12. Time of Dry Glue of HSM-Based Adhesives. The veneer was coated with a liquid adhesive with a loading of 180 g/m^2 ; after gluing, the veneer should be aired at $20\text{--}25^\circ\text{C}$ and 40–60 RH%, and the time of dry glue was recorded. The data presented in this study are an average of three replicated tests.

2.13. Density of HSM-Based Adhesives. The preweighed weight cup (denoted as M_1) with a capacity of 37 mL was filled with a sample of evenly stirred adhesive at 25°C , keeping the lid close and the overflow opening open. Then, the spill was wiped up with a volatile solvent. After that, the weight cup was placed in a constant temperature chamber ($23 \pm 1^\circ\text{C}$). Next, the weight cup was weighed and denoted as M_2 . The density of the HSM-based adhesive was calculated according to $(M_2 - M_1)/37$. The data presented in this study are an average of three replicated tests.

2.14. Statistical Analysis. The data in the current study were evaluated using the statistical software package Minitab version 15 and reported as the mean value \pm standard deviation of the replicates. A single-factor analysis of variance was conducted to identify significant differences among mean values according to least significant difference criteria with a 95% confidence level ($p < 0.05$).

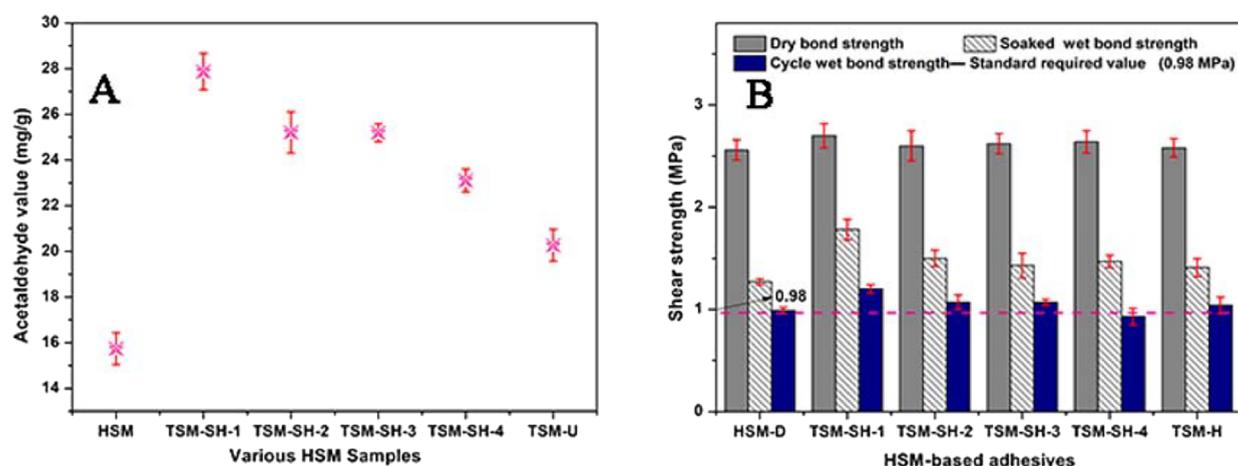


Figure 4. Acetaldehyde values of various HSM samples (A) and bond strength of various HSM-based adhesives (B).

3. RESULTS AND DISCUSSION

3.1. Adhesive Formulation and Testing. Soybean proteins consist of two major fractions according to their sedimentation constants, 11S and 7S, with molecular weights ranging from 150,000 to 360,000.³⁴ HSM would inevitably undergo thermal treatment during the production process, resulting in the occurrence of Maillard reaction and other polycondensation reactions and further increasing the molecular weight of the protein to 434,500, as shown in Figure S1. This process would consume a large number of the exposed reactive groups ($-\text{NH}_2$, $-\text{OH}$, and $-\text{COOH}$) of soybean protein and hindered the deep crosslinking reaction between the active azetidinium groups in PAE and the amino/carboxyl groups of soybean protein (Figure 1),²⁰ thereby affecting the preparation of high-performance adhesives. As expected, the plywood bonded with HSM-based adhesives, which were prepared by uniform mixing of HSM and crosslinker (PAE solution), showed a soaking wet bond strength of 0.89 ± 0.06 MPa and a cycle wet bond strength of 0.58 ± 0.02 MPa (Figure 2A), exhibiting the insufficient water or weather resistance to either indoor or outdoor products. To conquer the deficiency of the poor bond strength of HSM-based adhesives, the design strategy concentrated on releasing the reactive groups in HSM for further crosslinking with the PAE solution.

As shown in Figure 3, thermal treatment at appropriate temperature can expand the spherical structure of soybean protein (Figure S2),³⁵ expose some functional groups (such as $-\text{SH}$ and $\text{S}-\text{S}$), promote the intermolecular repolymerization of soybean protein and the Maillard reaction between proteins and reducing sugars, and realize the molecular reconstruction of each component in HSM. Figure S1 shows that there are two different molecular weight distribution characteristics of HSM after thermal treatment, one of which is significantly higher than that without thermal treatment, which further infers that the reducing sugar in HSM was grafted to the surface of spherical soybean protein by Maillard reaction under the thermal environment. The plywood bonded with the TSM-based adhesive had a soaked wet bond strength of 1.11 MPa and a cycle wet bond strength of 0.77 MPa (Figure 2A). However, the cycle wet bond strength was still lower than the required value for structural use (0.98 MPa) according to the commercial standard JIS K6806-2003. This is due to the fact that the protein structure of HSM does not expand deeply after

thermal treatment, and the aggregation of unfolded protein molecules limits the reaction between amino groups on the protein chain and crosslinking agents, which can be proved by the less increase in acetaldehyde values of TSM compared with that of HSM as shown in Figure 2B. If the structure of the protein is expanded deeply, then more active groups including amino groups will be released, which can be manifested as an increase in acetaldehyde values. Because the consumption of acetaldehyde was attributed to the reaction between acetaldehyde and the amino groups of soybean protein, the acetaldehyde value represented the quantity of active amino groups in the protein.

To further improve the water resistance of the soybean protein-based adhesive, it is necessary to further unfold the tight structure of soybean protein and expose the active groups (amino groups) for crosslinking with PAE. As shown in Figure 3, we propose a strategy of thermal and chemical denaturation synergistic treatment of soybean protein, which can not only graft the reducing sugars onto the surface of soybean protein by Maillard reaction but also expose the active groups to increase the crosslinking density of the adhesive layer. Accordingly, thermochemical treatment in the presence of sodium sulfite, SDS, sodium hydroxide, or urea was introduced to reorganize the protein structure to release more reactive groups. The results presented in Figure 2B revealed that the acetaldehyde values of HSM modified by various thermochemical treatment significantly increased, especially TSM-D and TSM-H, suggesting that more reactive groups were released in TSM-D and TSM-H. This is due to the ability of SDS that can unfold the globular structure of soybean proteins by destroying the hydrophobic moieties and exposing the buried reactive groups,²⁸ while sodium hydroxide can degrade protein macromolecules and expose more active groups. Correspondingly, the cycle wet bond strengths of the TSM-D-based adhesive and TSM-H-based adhesive were further improved and were higher than the required value (0.98 MPa) for structural use.

To further explore the greater possibility that the plywood prepared with the HSM-based adhesive can be used in outdoor or structural products, combinations with different ratios of SDS and sodium hydroxide were introduced to modify HSM. The results presented in Figure 4A showed that HSM-SH-1 displayed a higher acetaldehyde value (27.8 mg/g) than that of solely HSM (15.74 mg/g), which confirmed that more active

amino groups were released after thermochemical treatment. This benefits from the tailoring of the molecular structure under the synergy of SDS, sodium hydroxide, and heat. Additionally, the presence of SDS could effectively inhibit macromolecular aggregation during thermal treatment, and this ensured that a large number of reactive groups would be left after the repolymerization of protein and the Maillard reaction between the protein and the soy carbohydrate during the thermochemical treatment, which could be confirmed by the decrease in the molecular weight of about 334,700 as shown in Figure S1. A high acetaldehyde value suggested the presence of more crosslinking reactions between the HSM sample and the post-added PAE crosslinker, resulting in the formation of a dense and crosslinked network structure that prevents the invasion of water. Therefore, the adhesive composed of HSM-SH-1 displayed a higher water resistance. Its bonded plywood had a soaked wet bond strength of 1.11 MPa and a cycle wet bond strength of 1.20 MPa (Figure 4B).

3.2. Adhesive Characterization. To further investigate the structure changes of HSM, XRD measurements were conducted as shown in Figure 5. The broad characteristic

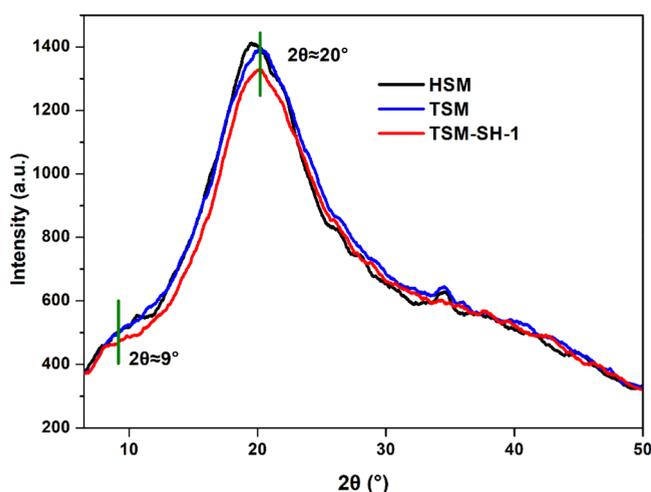


Figure 5. X-ray diffraction spectroscopy (XRD) patterns of various samples.

peaks at $2\theta \approx 9^\circ$ and 20° correspond to the α -helix and β -sheet structures of the HSM soybean protein component, respectively.³⁶ Compared to the values observed for HSM

and TSM, the peak of TSM-SH-1 at $2\theta \approx 9^\circ$ and 20° decreased. The α -helix and β -sheet structure is an important form of the protein secondary structure, and a decreased content means that the maintained protein molecular space conformation was destroyed and was beneficial to the release of reactive groups, which are consistent with the test results of acetaldehyde reactivity.

The molecular interaction in the adhesive system composed of HSM, TSM, or TSM-SH-1 was investigated via FT-IR and TGA tests. As shown in Figure 6A, all samples had typical infrared absorption characteristics of proteins for amide I (1624 cm^{-1} , C=O stretching), amide II (1514 cm^{-1} , N-H bending), and amide III (1401 and 1242 cm^{-1} , C-N stretching and N-H deformation) and no new absorption peak was detected,³⁷ indicating no apparent change in the chemical composition after thermal or thermochemical treatment of HSM. However, compared with native HSM without modification, the peak intensities at 3274 cm^{-1} (N-H and O-H stretching), 1624 cm^{-1} (amide I, C=O stretching), and 1514 cm^{-1} (amide II, N-H bending) of the TSM-based adhesive and TSM-SH-1-based adhesive decreased, especially the TSM-SH-1-based adhesive. Meanwhile, the cured HSM-based adhesive composed of TSM-SH-1 displayed a higher boiling water-insoluble content (78.07%) than the adhesive composed of HSM (72.39%) or TSM (73.55%) as shown in Table 2. These indicated an increase in crosslink density in adhesives; thus, the factor led to the formation of a more compact network structure. Furthermore, the TGA data in Figure 6B revealed that there are no significant differences in the main decomposition temperatures of the various cured adhesives. However, the "TSM-SH-1-based adhesive" displayed a slower and lower weight loss, indicating its improved thermal stability. This was also attributed to the improved crosslinking density and more compact network structure of the cured adhesive.

The contact angle test result is illustrated in Table 2. Compared with the HSM-based adhesive (57.4°), the contact angles of the TSM-based adhesive and TSM-SH-1-based adhesive had significantly decreased, which were 44.7° and 32.7° , respectively. This indicated that thermal and thermochemical treatment could improve the wettability of adhesives on a plywood substrate, especially thermochemical treatment. Meanwhile, the viscosity of the TSM-based adhesive and TSM-SH-1-based adhesive decreased obviously, which was beneficial to the improvement of wettability. According to the modern

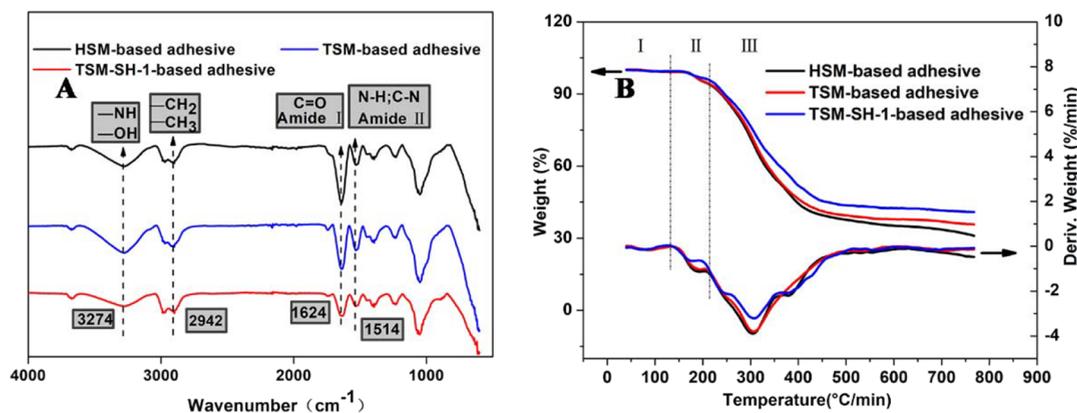


Figure 6. FT-IR analyses of various HSM-based adhesives (A) and TGA analyses of various HSM-based adhesives (B).

Table 2. Main Physicochemical Properties of Various HSM-Based Adhesives^a

Sample-ID	Droplet image	Contact angle (°)	Viscosity (mPa·s)	Boiling-water- insoluble content (%)
HSM-based adhesive		57.4 ± 0.5	87400 ± 220 a	72.39 ± 1.2 b
TSM-based adhesive		44.7 ± 0.7	76300 ± 160 b	73.55 ± 1.5 b
TSM-SH-1-based adhesive		32.7 ± 0.9	63000 ± 110 c	78.07 ± 0.8 a

^aNote: Data in the table are means ± standard deviation of their replicates. The different letters (a, b, and c) indicate data that are significantly different at $p < 0.05$.

bonding mechanism, the improvement of wettability and the decrease in viscosity are beneficial to the improvement of the bonding property of the adhesive.³⁸

3.3. Practicability of the Adhesive. To further verify the practicability of the adhesive, the rheological properties of the soybean protein-based adhesive were investigated. Figure 7

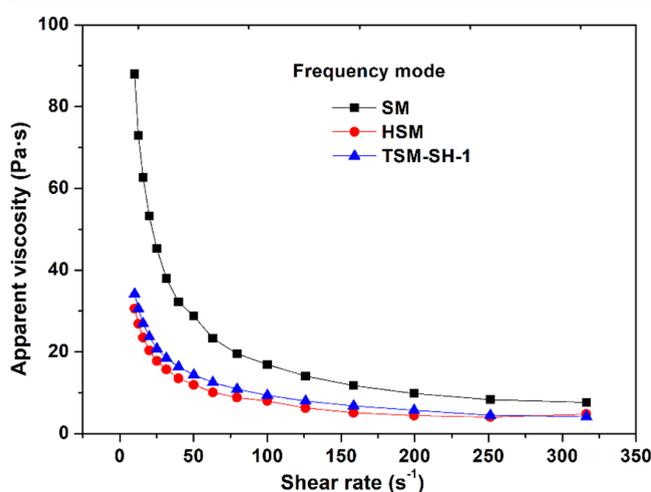


Figure 7. Apparent viscosity of various adhesives at different shear rates.

shows the apparent viscosity of the soybean protein-based adhesives at different shear rates, which indicates that the shear thinning behavior of all adhesives is similar to that of other reported soybean-based adhesives.⁹ The initial apparent viscosity of the SM-based soybean protein adhesive is significantly higher than that of the HSM-based adhesive and TSM-SH-1-based adhesive, which indicates that SM can be well and easily dispersed in PAE aqueous solution. Because Maillard reaction occurred in the processing and later modification of soybean meal, reducing sugars are grafted onto the surface of soybean protein, resulting in poor water solubility and lower apparent viscosity at different shear rates. However, in the process of mixing SM and PAE aqueous solution, reducing sugars can quickly dissolve and disperse in the solution, and the interaction between naked soybean protein and PAE significantly increased the apparent viscosity. Additionally, the amount of load, time of dry glue, and density of various HSM-based adhesives were further statistically

characterized, and these are shown in Table 3. After thermal or thermochemical treatment, the change in the molecular

Table 3. Amount of Load, Time of Dry Glue, and Density of Various HSM-Based Adhesives^a

sample ID	amount of load (g)	time of dry glue (min)	density (mPa·s)
SM-based adhesive	0.31 ± 0.02a,b	45 ± 0.5a	0.92 ± 0.08c
HSM-based adhesive	0.26 ± 0.03c	42 ± 0.8a	0.90 ± 0.09c
TSM-based adhesive	0.30 ± 0.02b	38 ± 1.0b	1.10 ± 0.05b
TSM-SH-1-based adhesive	0.33 ± 0.01a	30 ± 0.5c	1.17 ± 0.08a

^aNote: Data in the table are means ± standard deviation of their replicates. The different letters (a, b, and c) indicate data that are significantly different at $p < 0.05$.

structure of HSM improved the compatibility with PAE, thereby increasing the amount of load and density, which was beneficial to the bonding property. However, higher density meant lower water content, and this would have a negative impact on the time of dry glue. It was found that the plywood coated with the TSM-SH-1-based adhesive would result in the phenomenon of desertification after 30 min, which seriously affected its large-scale promotion and application.

Considering the bond strength and technological practicability of the soybean protein-based adhesive, it was proposed that SM and TSM-SH-1 were compounded by the problem of the short time of dry glue of the TSM-SH-1-based adhesive (the complex of SM and TSM-SH-1 is referred to as MSF). As shown in Figure 8, with the increase in the amount of SM in the soybean protein-based adhesive, the bonding strength of the plywood bonded by the adhesive decreases gradually, but the dry adhesive time is significantly prolonged. When the mass ratio of TSM-SH-1 to SM is 30:10 or 25:15, the bonding strengths of the plywood bonded by the MSF-based adhesive reach 1.20 and 1.10 MPa, respectively, which meet the requirements of commercial plywood according to the commercial standard JIS K6806-2003. Meanwhile, the time of dry glue of the MSF-based adhesive is longer than 40 min, which is beneficial to the processing technology of plywood.

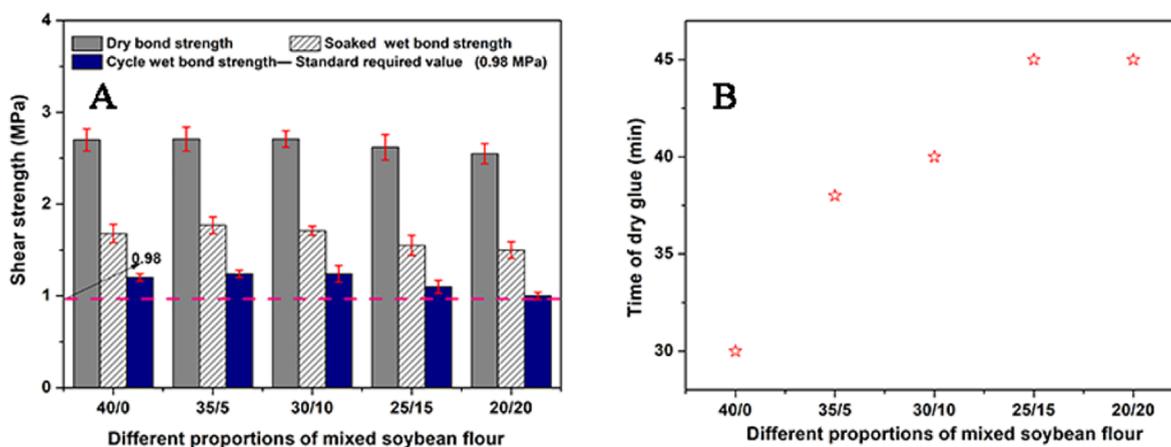


Figure 8. Bonding properties of the MSF-based adhesive (A) and the time of dry glue of the MSF-based adhesive (B).

4. CONCLUSIONS

In this study, thermal and chemical denaturation synergistic treatment was employed to reconstruct the aggregated structure of HSM. Under the induction of thermal treatment, reducing sugars were grafted on the surface of soybean protein by Maillard reaction. Meanwhile, SDS and sodium hydroxide were used to destroy the hydrophobic interaction between polypeptide chains and the amide bonds on polypeptide chains to expose more active groups to increase the crosslinking density of the adhesive layer. The plywood prepared with the TSM-SH-1-based adhesive is able to withstand a 28 h boiling–dry–boiling aging test and exhibits an aged bond strength of 1.20 MPa, which exceeds the required value for structural use (0.98 MPa). However, the drying time of the adhesive is too short, which is not conducive to large-scale industrial production and application. Based on the principle of simplicity and convenience, making MSF by compounding TSM-SH-1 and SM according to the mass ratio of 30:10 was proposed to solve the problem of the short time of dry glue of the TSM-SH-1-based adhesive. The adhesive prepared with MSF and PAE possessed stable water resistance that met the requirements of the commercial standard.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c00833>.

Figure S1: GPC analysis of various HSM samples;
Figure S2: SEM images of HSM, TSM-SH-1, and SPI
(PDF)

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Notes

The authors declare no competing financial interest.

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