Formulation of a novel soybean protein-based wood adhesive with desired water resistance and technological applicability

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ABSTRACT: A novel soybean protein-based wood adhesive with good bond strength, excellent water resistance, and the desired technological applicability was formulated by combining thermal alkali degradation, thermal acid treatment, and crosslinking. The characterization results indicated that thermal alkali degradation could effectively improve the technological applicability, thermal acid treatment could positively improve the water resistance, and appropriate crosslinking modification could significantly enhance the bond strength and water resistance of the soybean protein adhesive. The crosslinker species, crosslinker level, and ratio of thermal alkali-degraded soybean protein (DSP) to thermal acid-treated soybean protein (TSP) had important effects on the primary properties of the soybean protein adhesives. The modified polyamide aqueous solution was the most preferable crosslinker because of its low viscosity, good crosslinking efficiency, and excellent miscibility with soybean protein solution. The optimal soybean protein adhesive that was formulated from 20 wt % modified polyamide as the crosslinker and a DSP/TSP ratio of 1:3 had a solid content of more than 35 wt %, suitable viscosity ($\sim$2180 mPa s), a long work life ($>$16 h), good dry bond strength (2.94 MPa), and 28 h of boiling–dry–boiling cycled wet strength (1.29 MPa) that met the required values for structural use according to JIS K6806-2003 commercial standards. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43586.

INTRODUCTION

Synthetic adhesives, such as urea-formaldehyde resin, phenol-formaldehyde resin, and melamine-urea-formaldehyde resin, have been widely applied in the wood industry since the 1930s because of their low costs and good bonding properties.[1,2] However, harmful releases from formaldehyde-based synthetic adhesives such as free formaldehyde and free phenol can harm the human body during their preparation, storage, transportation, and use.[3,4] In addition, these resins are dependent on non-renewable fossil resources. These facts have led to growing concerns about environmental protection and resource sustainability, and they have forced the development of biobased polymer materials from abundant renewable biomass resources.[5,6]

Soybean is one of the most widely grown vegetable crops in the world for its plant oil. As a byproduct of the soybean oil industry, soybean meals are primarily used as animal feeds and rarely as industrial raw materials. After further separation or appropriate modification, soybean meals can be used to prepare wood adhesives, which will increase their utilization value[7] and pro-

vide the wood processing industry with a sustainable and environmentally safe adhesive.[8] However, very few soybean protein adhesives are applied commercially within the wood industry except in some indoor plywood because of their disadvantages (such as moderate to low dry strength, moderate to low water resistance, high viscosity, and low solid content),which result from the particular molecular characteristics of soybean proteins,[9,10] It is well known that soybean protein is water-soluble and possesses complicated primary, secondary, tertiary, and quaternary structures that are primarily built by disulfide bonds and weak intermolecular interactions including hydrogen bonds, electrostatic bonds, Van der Waals forces, and hydrophobic interactions.[11] These weak intermolecular interactions are readily destroyed at room-temperature or in boiling water, leading to poor water resistance by traditional soybean protein adhesives that are less than that of urea-formaldehyde resins. The predominant fractions in soybean proteins, namely 11S and 7S (sedimentation constants), have molecular weights ranging from 150,000 to 360,000 g/mol,[7] and thus, soybean protein adhesives have high viscosity but low protein content solution/dispersion

because of severe molecular entanglements and frictions.[12] In other words, these soybean protein adhesives with high viscosity have poor technological applicability such as the difficulty of brushing the adhesives onto wood, poor wettability, and a long hot-press cycle or increased energy for removing water from the adhesive.[6,7]

Therefore, many attempts have been made to improve the water resistance and/or technological applicability of soybean protein adhesives, including thermal treatment,[13] thermal acid treatment,[14] the pretreatment of soybean protein in the presence of a reagent such as alkali, urea, guanidine, calcium chloride, and hydrochloride,[10,15,16] crosslinking modifications by blending with synthetic resins such as melamine-formaldehyde resin,[17] glyoxal,[18] epoxy latex,[19] polyisocyanate,[20] and modified polyamide,[21,22] and by nanomodification with a nanoscale filler such as MMT and SiO$_2$.[23] However, it is still highly challenging to improve the water resistance and technological applicability of soybean protein adhesive effectively for commercial applications.

It was reported that thermal-alkali degradation could turn the long polypeptide chains of soybean protein into low-molecular weight resultants via the hydrolysis of peptide bonds by NaOH.[24] This is thought to be an effective method to improve the technological applicability because the thermal-alkali degraded soybean protein (DSP) was a solution with low viscosity and high-protein content. Our previous study showed that thermal acid treatment could improve the water resistance of soybean proteins due to the formation of the water-resistant intermolecular network during treatment.[25] Literature review also indicated that crosslinking could significantly improve the water resistance of soybean protein adhesive due to the formation of chemical network between proteins.[17–25] Therefore, the current study attempts to develop a novel soybean protein adhesive with good water resistance and technological applicability through the combination of thermal alkali degradation, thermal acid treatment, and crosslinking modification. Because little information on this combination is available in the literature, the effects of the crosslinker species, the optimal crosslinker level, and the DSP/treated soybean protein (TSP) ratio on the water resistance of the soybean protein will be investigated to obtain a preferred soybean protein adhesive formulation for structural use.

EXPERIMENTAL

Materials

Soybean protein isolate (SPI) with a protein content of 93.4 wt % was provided by Harbin High Tech Soybean Food Co., Ltd., China. Birch veneers were provided by Harbin Plywood Factory, Harbin, at 420 mm × 420 mm × 1.6 mm sizes. The PMDI polyisocyanate (Millionate® MR-200) with an NCO content of 31.2 wt % or an NCO functionality of 2.8 was supplied by Nippon Polyurethane Industry Co., Ltd., Japan. The MU-618 epoxy latex was purchased from Asibo Co. Ltd., Shanghai, China, and it had an epoxide number of 212 g/mol. Modified polyamide (epichlorohydrin was used to modify the polyamide that was polymerized from diethylenetriamine and adipic acid) was supplied by the Xinquan Papermaking Additives Plant, Shandong,

China, and it had a solid content of 12.5%, a pH value of 4.9 and a viscosity of 68 mPa s (25 °C). Commercial urea-formaldehyde (UF) adhesive for plywood and its curing agent were provided by a local plywood plant, and this adhesive had a solid content of 52.8%, a pH value of 8.9 and a viscosity of 42 mPa s (25 °C). The other chemicals used in this study such as glyoxal and hydrochloric acid were reagent grade and purchased from local chemical companies.

Thermal Alkali Degradation of Soybean Protein

In the reaction kettle that was equipped with a mechanical stirrer, thermometer and condenser, 48 g of sodium hydroxide solution with a 50 wt % concentration and 352 g of water were charged and heated to 70 °C with stirring. A total of 245 g of SPI powder was then gradually charged and kept at 68–72 °C for 2 h. Finally, the degraded result was cooled to room temperature, and an appropriate amount of formic acid was added to adjust then pH value to 6.5–7.0, the mixture was then labeled as DSP.

Thermal Acid Treatment of Soybean Protein

In a high-speed mixer with a rotating speed of 800 rpm, 200 g of SPI was blended with 40 g of a 0.5 mol/L HCl solution. The mixture was wrapped with aluminum foil and kept at 120 °C in a preheated oven for 30 min. The foil was then removed, and the treated protein was kept at 50 °C in a blast oven for 24 h to dry the protein and remove the HCl. Finally, the thermal acid-treated protein was ground into powder that passed through a 100-mesh sieve before use, and then labeled as TSP.

Formulating Various Soybean Protein Adhesives

In every 100 g of DSP solution, 33, 66, 99, or 132 g of TSP powder was added and stirred at room temperature to form four soybean protein mixtures with DSP/TSP ratios of 1:1, 1:2, 1:3, and 1:4 (on the basis of solid protein), respectively.

To evaluate the effects of the crosslinker species on the properties of soybean protein-based adhesive, the protein mixture with a DSP/TSP = 1:2 was used. Each of the four crosslinkers (glyoxal, epoxy latex, polyisocyanate, and modified polyamide) and the appropriate amount of water was added to the protein mixture and blended well at room temperature to form a modified soybean protein adhesive with a crosslinker level of 20 wt % (on the basis of total solid protein). The protein mixture without crosslinker was used as one of the control adhesives (pure soybean protein adhesive), and the commercial UF adhesive was used as another control.

To evaluate the effects of the optimal crosslinker level on the properties of soybean protein-based adhesive, 0, 10, 20, 30, and 40% of the optimal crosslinker (modified polyamide) was added to the protein mixture at DSP/TSP = 1:2 at room temperature.

To investigate the effects of the protein mixture's DSP/TSP ratio on the properties of the soybean protein-based adhesive, the six soybean protein-based adhesives with various DSP/TSP ratios (1:0, 1:1, 1:2, 1:3, 1:4, and 0:1) were prepared by adding 20 wt % optimal crosslinkers (modified polyamide) and an appropriate amount of water to DSP, TSP, or DSP/TSP mixtures at room temperature, respectively.

All soybean protein adhesives in the current study had a solid content of 35 wt % that had been adjusted by adding an appropriate quantity of water before coated to veneers.

Characterization of Soybean Protein Adhesives

Viscosity. The viscosity of each soybean protein adhesive was tested by using a rotational viscometer at 25 °C (three replicates).

Work Life. The work life of the soybean protein adhesive was determined by observing the fluidity of the adhesive in a 25 °C chamber. The amount of time from the moment the soybean protein was blended with the crosslinker until the mixture could not be evenly spread onto the wood surface with a bristle brush by hand was defined as the work life (which was also called the pot life).

GPC Analysis. The DSP solution was diluted with deionized distilled water to a concentration of 0.5 wt % to determine the molecular weight by using an Agilent 1100 GPC equipped with two chromatographic columns in series, namely a 79911GF-083 (M_W range: 100–30,000) and a 79911GF-084 (M_W range: 10,000–200,000). The mobile phase was water, which was applied at a flow rate of 1 mL/min; the pressure on the columns was 78 psi, and a differential refractive index detector was employed.

SEM Analysis. Prior to SEM analysis, the appropriate soybean protein adhesives were placed inside Teflon pools. The pools were then placed in an oven at 120 ± 2 °C for 0.5 h to obtain a dry, cured adhesive film that was approximately 1-mm thick. Half the cured adhesive film was cut and placed into boiling water for 1 h, and then it was removed and dried at 63 °C for 24 h to obtain aged adhesive film. The adhesive films before and after boiling water aging were fractured at ambient condition, and the fractured surfaces were examined with a QUANTA-200 SEM (FEI Co., The United States) after being coated with approximately 10–20 nm of gold.

FTIR Analysis. Prior to Fourier transform infrared (FTIR) analysis with a Magna IR560 FTIR instrument (Nicolet Co., The United States), a piece of dry cured adhesive film without boiling water aging that was prepared in the SEM analysis 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 form a transparent FTIR disk before FTIR scanning from 4000 to 400 cm^{-1}.

Bond Strength and Water Resistance by Plywood Evaluation. Birch veneers with dimensions of 420 mm $\times$ 420 mm $\times$ 1.6 mm were used to prepare 3-ply plywood with a liquid adhesive loading of 140 g/m^2 (single bond line). The adhesive-coated veneers were first stacked and cold-pressed at 0.80 MPa for 5 min and then hot-pressed at 120 °C and 1.3 MPa for 4.5 min (for the soybean protein adhesives that were modified by crosslinkers). However, the DSP solution (which had a protein concentration of 35 wt % and an adhesive loading of 140 g/m^2) alone and SPI solution (with a protein concentration of 10 wt % and an adhesive loading of 350 g/m^2) alone without crosslinkers as adhesives had to be hot-pressed at 120°C for 8 and 9.5 min, respectively, to avoid delamination. Two rep-

licate panels were prepared. After the hot pressing, the panels were stored in an ambient environment for at least 24 h prior to evaluation. A total of 40 specimens with a bond area of 25 mm $\times$ 25 mm were cut from each panel according to the JIS K6806-2003 commercial standard to determine the bond strength and water resistance.

The bond strength and water resistance of all of the adhesives were determined in terms of the dry strength and cycled wet strength, respectively, by using a tensile testing machine with a crosshead speed of 5 mm/min. The specimens for cycled wet strength underwent a 28 h boiling–dry–boiling hygrothermal treatment (they were boiled for 4 h, oven-dried at 63 °C for 20 h, and boiled again for 4 h) before tensile determination under the wet state (they were cooled to room temperature).

Statistical Analysis

The data in the current study were statistically evaluated by using the Minitab version 15 statistical software package. The data are reported as the mean value ± standard deviation of the replicates. A single factor analysis of variance was conducted to differentiate significant differences among the mean values of the data according to the least significant difference criteria at a 95% confidence level ($P < 0.05$).

RESULTS AND DISCUSSION

Novel Formulation Design of a Soybean Protein Adhesive with Commercial Potential

Only soybean adhesives have levels of bond performance and technology applicability that are comparable to those of the two predominant wood adhesives (urea-formaldehyde resin and phenol formaldehyde), they are suitable for a wide variety of manufacturing options for various wood composites such as plywood, particleboard, MDF, and OSB. However, a literature review indicated that common soybean protein adhesives had the fatal disadvantages of low bond strength, poor water resistance, high viscosity, and low solid/protein content that highly restricted their broad applications in the wood industries.

Because of its larger molecular weight ranging from approximately 150,000 to 360,000 g/mol,[7] aqueous soybean protein solutions with only a 10 wt % protein concentration already had a very high viscosity of 58,000 mPa s (at 25 °C, Table I). A further increase in the protein level led to an almost gel-like solution with very poor fluidity that was difficult to spread evenly onto wood substrate. Our investigation in Table I indicated that the 3-ply plywood that was prepared with 10 wt % soybean protein solution only required one hot-press cycle for 9.5 min at 120 °C, which was much longer than the cycle used with commercial UF resin (for ~4 min).This difference is attributed to the low protein concentration of the adhesive to ensure that acceptable adhesive spreading resulted from its high viscosity. Therefore, it is necessary to increase the protein content or solid content of protein adhesive to shorten the hot-press cycle (or reduce energy consumption or increase plywood productivity).

The thermal alkali degradation of soybean protein, that is, the degradation of soybean protein at approximately 70 °C in the presence of 3–4 wt % NaOH, was expected to be a good approach to reduce the viscosity of protein solution because the

Table I. Primary Properties of Some Soybean Protein Adhesives with Various Formulation Designs

Adhesive formulation	Solid content (wt %)	Viscosity (mPa s, 25 °C)	Hot-press cycle (min)	Dry bond strength (MPa)	Cycled bond strength (MPa)
SPI solution only	10	58,000 A	9.5	1.19 ± 0.15C	NA[a]
DSP solution only	35	1162 B	8	1.28 ± 0.21BC	NA
DSP solution + crosslinker	35	1219 B	4.5	2.11 ± 0.28A	0.31 ± 0.09B
DSP/TSP mixture	35	1335 B	8	1.31 ± 0.24BC	NA
DSP/TSP mixture + crosslinker	35	1367 B	4.5	2.15 ± 0.30A	1.02 ± 0.19A
UF adhesive (control)	52.4	107.3 C	4.5	1.51 ± 0.12B	NA

[a] Not available because all specimens were delaminated after the first 4 h of boiling. The different letters (A, B, and C) after data are significantly different at $P < 0.05$.

long polypeptide chains could be degraded into a compound with lower molecular weights (which ranged from ∼3250 to 6300, as shown by the GPC in Figure 1) via the hydrolysis of peptide bonds by NaOH. The DSP solution was a transparent brown solution with a solid content of 37.7% and a viscosity of 1000–1700 mPa s (25 °C). Because of the increased protein content, the 3-ply plywood prepared with DSP solution alone as the adhesive (the protein content was adjusted to 35 wt % with water for comparison with other adhesives) required a shorter hot-press cycle (8 min at 120 °C) than the one with the 10 wt % SPI solution. However, this hot-press cycle was still undesired when compared with the one used with the commercial UF adhesive. As a result, the polyisocyanate crosslinker was added to the DSP solution to reduce the hot-press cycle further through the formation of a chemical network between soybean protein molecules. As expected, the combination adhesive of DSP and 20 wt % polyisocyanate could sufficiently shorten the hot-press cycle to 4–4.5min, which was comparable to that of the commercial UF adhesive.

Because the DSP had low viscosity, it was feasible to increase the protein content further so that the soybean protein adhesives might have sufficient solid contents for manufacturing particleboard or other wood composites (which are commonly more than 50 wt %). In current study, it found that the thermal acid-TSP could disperse well in DSP solution to form a stable DSP/TSP mixture with acceptable viscosity, likely attributing to the emulsifying ability of DSP solution. For instance, the protein mixture with a DSP/TSP ratio of 1:2 had viscosities of approximately 1335 and 3640 mPa s (at 25 °C) when its protein content was adjusted to 35 and 60 wt % with water, respectively. Without the polyisocyanate crosslinker, the 3-ply plywood prepared with the DSP/TSP mixture (which had a protein content of 35 wt %) used as adhesive still required a hot-press cycle of 7.5–8 min. However, when 20 wt % of polyisocyanate crosslinker was added to the DSP/TSP mixture (which had a protein content of 35 wt %), the hot-press cycle could be decreased to 4–4.5min. This finding indicated that the crosslinker played a significant role in reducing the hot-press cycle because crosslinking led to a great improvement in the bond strength (Table I) for the formation of three-dimensional networks that could withstand higher vapor pressure and, thus, prevent delamination during the hot pressing of the wood composite. The results

in Table I also indicated that after thermal acid treatment, the soybean protein could not only increase the protein content of the adhesive but also effectively improve the water resistance because the DSP/TSP/polyisocyanate adhesive had much better water resistance than DSP/polyisocyanate adhesive in terms of cycled bond strength after 28 h of boiling–dry–boiling hygrothermal aging. This finding apparently implied that the combination of thermal alkali degradation, thermal acid treatment and crosslinking may be an effective and novel approach for improving the bond strength, water resistance, and technological applicability of soybean protein adhesives. However, little information is available with regards to this novel adhesive formulation. Thus, the more preferable crosslinker species, crosslinker level and DSP/TSP ratio will be investigated intensively with the goal of optimizing the most preferable soybean protein adhesive formulation for commercial use; the end product should withstand 28 h of boiling–dry–boiling hygrothermal aging and still retain a cycled bond strength of greater than 0.98 MPa according to commercial standard JIS K6806-2003.

Effects of Crosslinker Species on the Primary Properties of Combination Soybean Protein Adhesives

Four crosslinkers (glyoxal, epoxy latex, polyisocyanate, and modified polyamide) were investigated because they were commonly used as the crosslinkers of soybean protein adhesives.[18–22,25] The test results in Table II indicated that the crosslinker species had important effects on the bond strength, water resistance, and technological applicability of DSP/TSP/crosslinker combination soybean protein adhesives according to their various crosslinking mechanisms.
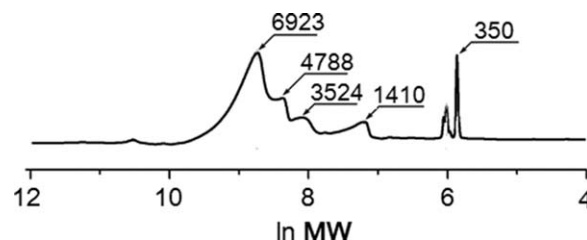

Figure 1. GPC spectrum of DSP solution (the values marked on the GPC peaks are peak molecular weights).

Table II. Primary Property of Soybean Protein Adhesives that were Modified with Various Crosslinkers

Adhesive formulation	Viscosity (mPa s, 25 °C)	Work life (h)	Hot-press cycle (min)	Dry bond strength (MPa)	Cycled bond strength (MPa)
DSP/TSP mixture only	1335 B	≫20 E	8	1.31 ± 0.24 C	NA
DSP/TSP/glyoxal	1255 B	>20 CD	4.5	1.25 ± 0.22 C	NA
DSP/TSP/epoxy	3470 A	>4 B	4.5	1.30 ± 0.20 C	NA
DSP/TSP/polyisocyanate	1367 B	0.5 A	4.5	2.15 ± 0.30 B	1.02 ± 0.19 AB
DSP/TSP/polyamide	1234 B	>16 C	4.5	2.71 ± 0.23 A	1.12 ± 0.13 A

Not available because all specimens were delaminated after the first 4 h of boiling. The different letters (A, B, C, D, and E) after data are significantly different at $P < 0.05$.

Every glyoxal molecule contains two reactive aldehyde groups that are able to crosslink soybean proteins through Maillard reactions, as illustrated by eq. (1) in Figure 2. The formation of a Schiff-base structure (—C═N—) in glyoxal-crosslinked soybean protein was confirmed by FTIR at approximately 1445 cm^{-1}, which is attributed to the C═N stretching modes, and at approximately 1306 cm^{-1}, which is attributed to the C—N bending deformation modes (Figure 3). Given the intermolecular crosslinking of soybean protein by glyoxal that intensified the adhesive bulk strength, the DSP/TSP/glyoxal adhesive
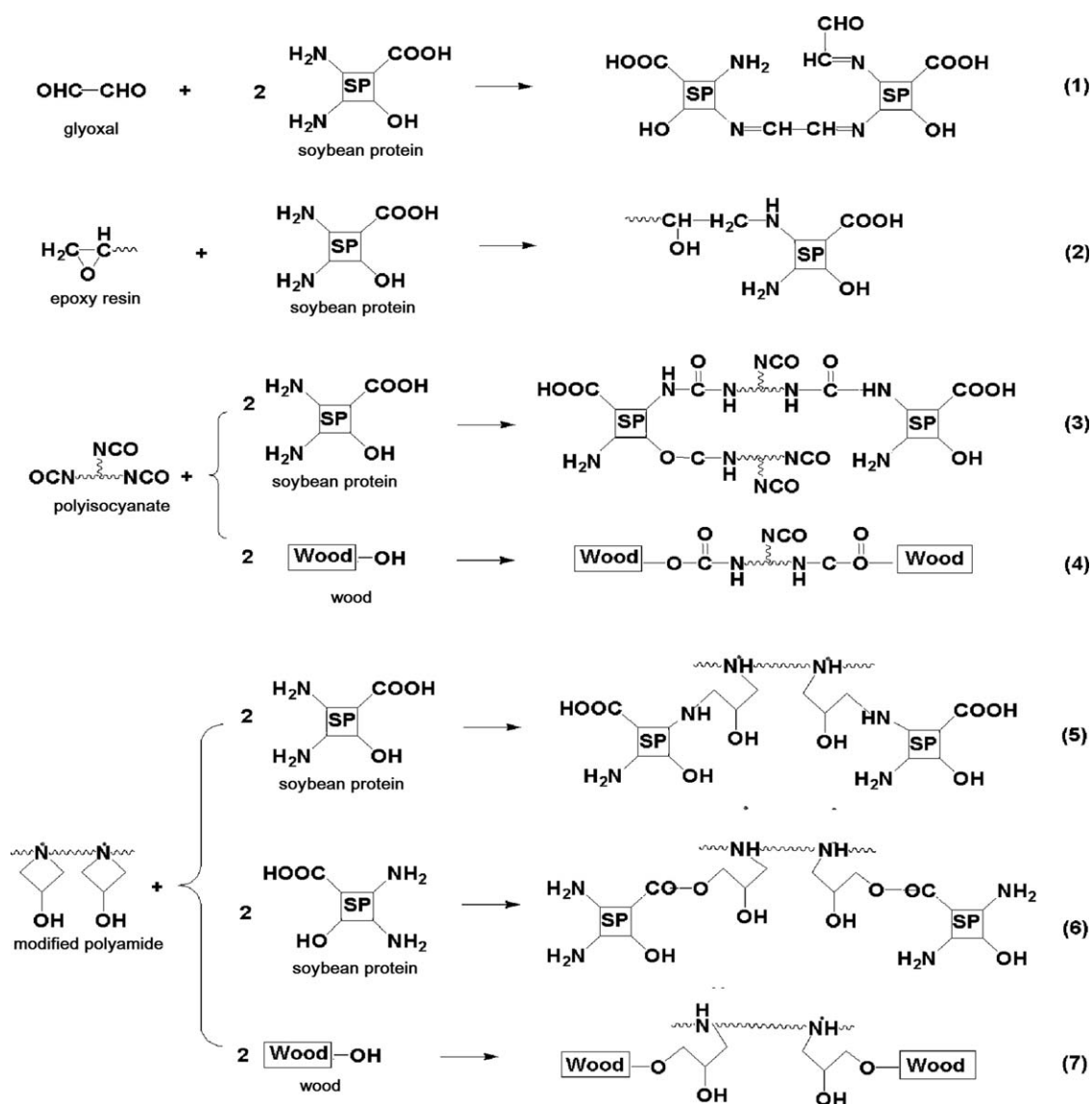
Figure 2. Schematic illustrations of the crosslinking mechanisms for the four crosslinkers.
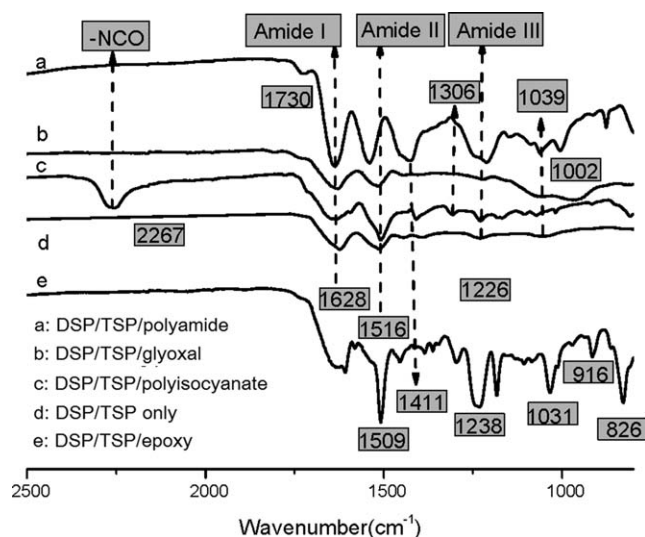
Figure 3. FTIR of the cured soybean protein adhesives with various crosslinkers.

could shorten its hot-press cycle to approximately 4.5 min. However, when one aldehyde group in the glyoxal reacted with the soybean protein adhesive, it was difficult for the other to react further because of the steric hindrance of two neighboring aldehyde groups.[18] This difficulty led to lower crosslinking reactivity (as evidenced by the long work life of DSP/TSP/glyoxal adhesive) and inadequate crosslinking density during the hot pressing of the plywood panel (as indicated by the similar bond strength and water resistance of DSP/TSP/glyoxal adhesive with DSP/TSP adhesive), which was further confirmed by SEM observation as shown in Figure 4. The cured DSP/TSP/glyoxal adhesive had many apparent etch pits after 1 h of water boiling in [Figure 4(E)], and it was relatively smooth before boiling

[Figure 4(A)], indicating that some proteins were eroded by water for insufficient crosslinking density and unstable chemical bonds resulting from the glyoxal crosslinking. Thus, although the glyoxal crosslinker could effectively shorten the hot-press cycle, it was not suitable for preparing the soybean protein adhesive for structural use because of its poor water resistance.

The epoxy crosslinker used here had many free epoxy groups (with an epoxide number of 212 g/mol) that could react with the residual amino groups of the soybean protein because the curing reaction of the epoxy resin often uses an amino catalyst,[19] as shown by eq. (2) in Figure 2. The IR absorption peak detected at 1238 cm^{-1} was assigned to the C—N—C stretching mode formed by the crosslinking reaction between the epoxy groups and the amino groups of the soybean protein (Figure 3). However, the epoxy latex showed poor miscibility with the soybean protein adhesive because the mixture was heterogeneous and assumed to have an obvious viscosity increase (up to 3470 mPa s). This increase led to the phase separation of the epoxy latex from the soybean protein adhesive and therefore an insufficient crosslinking density of the modified soybean protein. The SEM observation in Figure 4(F) indicated that the fractured surface of the cured soybean protein adhesive that was crosslinked by the epoxy latex showed the typical phase-separation microstructure of the many smooth balls and their matched pits after 1 h of water boiling, indicating that the epoxy resin was primarily self-polymerized rather than crosslinked with the soybean protein because of immiscibility. Therefore, the DSP/TSP/epoxy adhesive exhibited similar dry bond strength and poor water resistance to that of DSP/TSP adhesive and DSP/TSP/glyoxal adhesives, indicating that epoxy latex was not a good crosslinker for soybean protein adhesives.

The PMDI polyisocyanate crosslinker has an average of 2.8 highly active isocyano groups per molecule, and it can effectively crosslink soybean protein to form a network structure
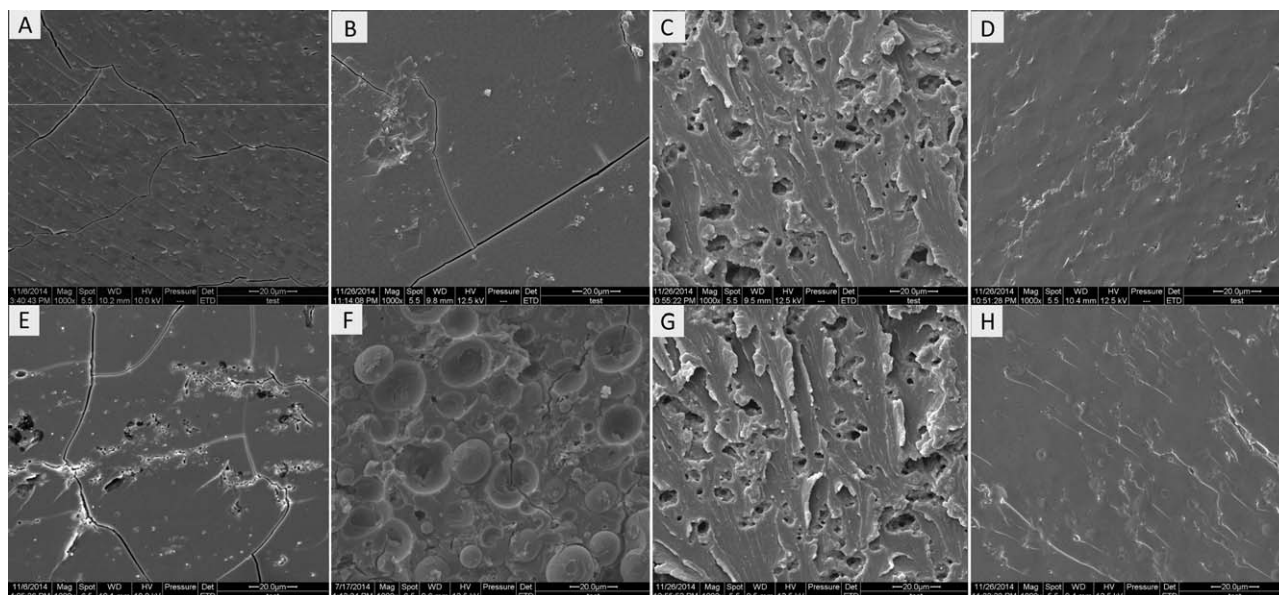

Figure 4. SEM micrographs of crosslinked soybean protein adhesive films before and after 1 h of boiling in water (A,E) crosslinked by glyoxal; (B,F) crosslinked by epoxy; (C,G) crosslinked by polyisocyanate; and D&H, crosslinked by polyamide. (A–D) were dry-state samples before boiling; (E–H) referred to the water-boiled samples).
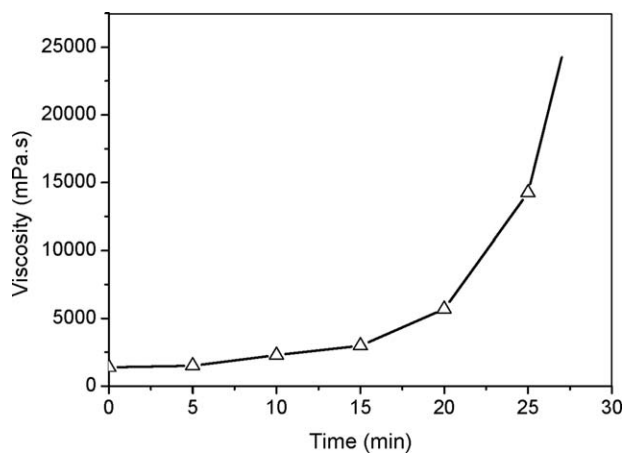
Figure 5. Viscosity increase of DSP/TSP/polyisocyanate adhesive as a function of time.

through the reaction of isocyano groups with the amino and hydroxyl groups of soybean protein as shown by eq. (3) in Figure 2. In comparison with the DSP/TSP system, the intensified FTIR absorptions of DSP/TSP/polyisocyanate adhesive in Figure 3 were detected at approximately 1590 cm^{-1} (attributed to the C—N stretching modes) and at approximately 1351 cm^{-1} (attributed to C—N bending deformation modes), confirming the formation of urea bridges and urethane bridges during the crosslinking reaction. Some unreacted isocyano groups that remained after polyisocyanate-protein crosslinking were also detected at 2267 cm^{-1}, which indicated that DSP/TSP/polyisocyanate adhesive could form a strong chemical adhesion between adhesive–wood interfaces through the reaction of active isocyano groups with the hydroxyl groups of wood during hot pressing, as illustrated by eq. (4) in Figure 3. As a result, DSP/TSP/polyisocyanate adhesive was not only able to shorten the hot-press cycle of 3-ply plywood to approximately 4 min but also resulted in a much higher dry bond strength (2.15 MPa) than that of DSP/TSP/glyoxal adhesive (1.25 MPa) and DSP/TSP/epoxy adhesive (1.30 MPa). The plywood that was bonded by DSP/TSP/polyisocyanate adhesive could withstand 28 h of boiling–dry–boiling hygrothermal aging, indicating that its excellent water resistance resulted from strong chemical adhesion between adhesive–wood interfaces. Because the active isocyano groups could also react with the water in the adhesive and generated CO_2 gas when polyisocyanate was mixed with the DSP/TSP mixture, it led to the formation of cellular microstructure in the cured adhesive, as shown in Figure 4(C,G). This cellular microstructure harmed the dry bond strength and cycled bond strength of the adhesive–wood bond line, for ease stress concentration when it was subjected to an external load. Therefore, the formation of cellular microstructure should be the key reason that the plywood bonded by DSP/TSP/polyisocyanate adhesive had a cycled bond strength (1.02 MPa) that was just marginally beyond the required value for structural use according to the JIS K6806-2003 commercial standard. However, polyisocyanate is very reactive to the amino groups of protein.[26] When polyisocyanate was introduced into the DSP/TSP mixture, the crosslinking reactions immediately occurred and formed urea bridges, leading to a rapid increase in adhesive vis-

cosity (as shown in Figure 5) or a short work life (~25–30 min). Therefore, polyisocyanate was not a desired crosslinker for the soybean protein adhesive because of its poor technological applicability resulting from its short work life.

The modified polyamide used here was an aqueous solution that contains abundant amide, hydroxyl, and azetidinium (a cationic four-membered ring structure) groups and is widely used as a wet-strength agent for papermaking.[21,22,27,28] Its azetidinium group could react with both the carboxyl and amino groups of the soybean protein, as illustrated by eqs. (5) and (6) in Figure 2, which could be evidenced by the obviously intensified and wide IR absorption peak at approximately 1226 cm^{-1} (as assigned to the C—N—C and C—O—C stretching mode) in Figure 3. The SEM observations in Figure 4(D,H) showed that the DSP/TSP/polyamide adhesive had relatively similar fractured surfaces before and after 1 h of water boiling, without apparent erosion and phase separation. These findings implied that the modified polyamide could effectively and sufficiently crosslink the soybean protein and therefore endow the DSP/TSP/polyamide adhesive with excellent water resistance. In addition, the azetidinium group of modified polyamide could also react with the hydroxyl and carboxyl groups of wood to form a chemical bridge between the protein–wood interface, as illustrated by eq. (7) in Figure 2, which further improved the bond strength and water resistance of DSP/TSP/polyamide adhesive.

As a result, this adhesive could not only shorten the hot-press cycle of 3-ply plywood to approximately 4 min but also resulted in the highest dry bond strength (2.71 MPa) and the best water resistance in terms of the highest cycled bond strength (1.12 MPa) after 28 h of boiling–dry–boiling hygrothermal aging. Additionally, the modified polyamide was a low-viscosity aqueous solution that could be miscible with the DSP/TSP mixture to form a stable and solution-like adhesive. The resulting DSP/TSP/polyamide adhesive showed good technological applicability for both the desired work life (for more than 16 h, which was attributed to the slow reaction rate of modified polyamide with soybean protein at ambient temperature) and low viscosity (~1230 mPa s when the solid content was 35 wt %) that could be easily spread onto the wood substitutes. Therefore, the modified polyamide was the preferred crosslinker, and it endowed the soybean protein adhesive with better bond strength, water resistance, and technological applicability in comparison with other crosslinkers such as glyoxal, epoxy latex, and polyisocyanate.

Effects of Crosslinker Levels on the Primary Properties of Combination Soybean Protein Adhesives

Theoretically, a higher crosslinker level will lead to better bond strength and water resistance because a higher crosslinking density and greater chemical interfacial adhesion can be obtained. However, the results in Figure 6 indicated that both the bond strength and water resistance of the plywood panels passed through a maximum value before decreasing when the level of the modified polyamide increased from 0 (control) to 40% on the solid basis of the soybean protein. This finding was attributed to the ever-decreasing viscosity of the final soybean protein adhesive with the higher level of crosslinker that was a low-viscosity aqueous solution, as shown in Figure 7, which led to
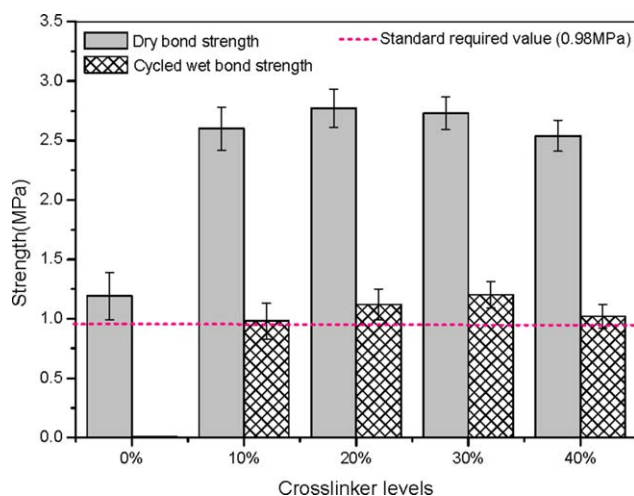
Figure 6. Dry bond strength and cycled bond strength of the DSP/TSP/polyamide adhesive with various crosslinker levels (DSP/TSP = 1:2 and solid content 35 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

insufficient adhesive content between the two veneers because the most liquid components of the adhesive (including the crosslinker) penetrated the veneers through the vessels and the wood pits. The results in Figure 6 also indicated that the maximum dry bond strength resulted from the adhesive that contained 20% added crosslinker, which was slightly higher than that of the 30% added crosslinker, and the maximum cycled bond strength (i.e., water resistance) was obtained from the adhesive with 30% added crosslinker. Therefore, the preferable crosslinker level was 20% on the solid basis of the soybean protein because it was the lowest crosslinker level that could prepare the plywood in terms of the bond strength and water resistance that met the requirement for structural use (i.e., more than 0.98 MPa) according to the JIS K6806-2003 commercial standard. This crosslinker usage was lower than some research results, such as the results for SPI-Kymene adhesives with a 1.33:1 SPI/Kymene weight ratio, to insure the shear strength.[22]
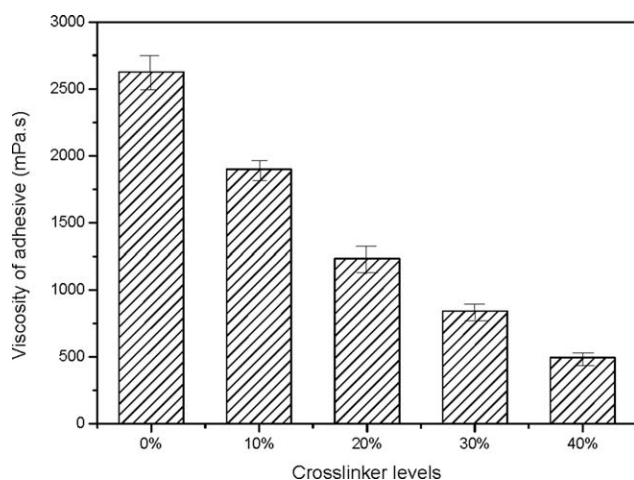

Figure 7. Viscosity of DSP/TSP/polyamide adhesive with various crosslinker levels.
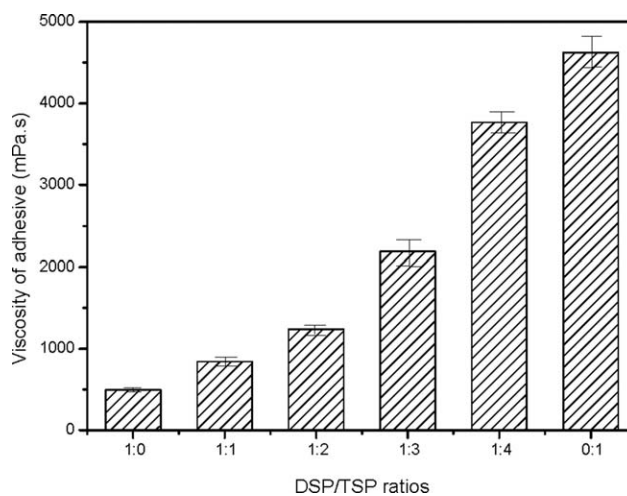

Figure 8. Viscosity of DSP/TSP/polyamide adhesive with various DSP/TSP ratios.

Effects of the DSP/TSP Ratio on the Primary Properties of Combination Soybean Protein Adhesives

After thermal acid treatment, the soybean protein was a fine powder that passed through a 100-mesh sieve. When the powder was added to the low-viscosity DSP solution, some advantages could be observed. Because of its larger surface area, this solution could effectively absorb the liquid component of the soybean protein adhesive and increase the viscosity of the final adhesive, as shown in Figure 8, which prevented the overpenetration of the liquid component into the wood. The addition of this powder could also conveniently and effectively increase the solid content of the soybean protein adhesive to 60 wt %, which was comparable to that of commercial UF adhesive (commonly 50–65 wt %). The test results in Table I confirmed that TSP could apparently improve the water resistance of crosslinker-modified soybean protein adhesive because the soybean protein post-thermal acid treatment had an increased boiling water-insoluble network structure.[25]
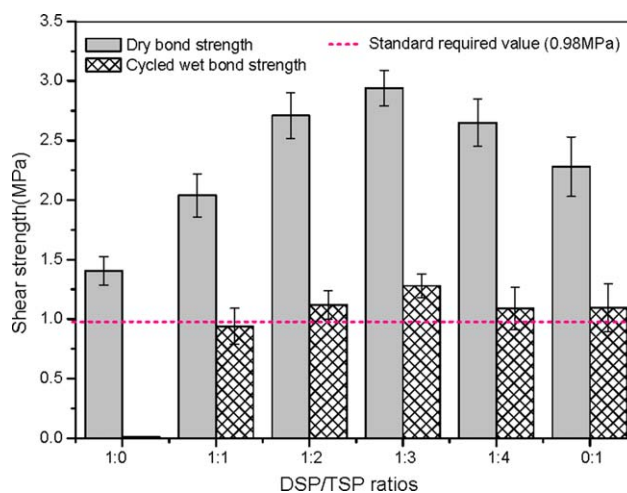

Figure 9. Dry bond strength and cycled bond strength of DSP/TSP/polyamide adhesive with various DSP/TSP ratios (crosslinker level 20% and solid content 35 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
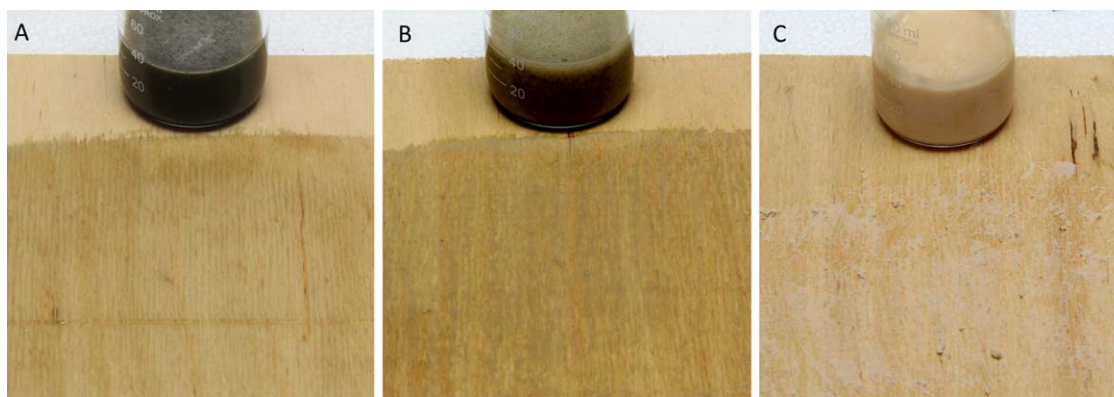
Figure 10. Apparent states of three DSP/TSP/polyamide adhesives after being spread on veneer for 10 min (the DSP/TSP ratios were (A) 1:0; (B) 1:3; and (C) 0:1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The results of the plywood evaluation in Figure 9 indicated that the appropriate addition of TSP powder could further increase the bond strength and water resistance of the DSP/TSP/polyamide adhesive. When the soybean protein adhesive was composed of only DSP and modified polyamide (DSP/TSP ratio of 1:0), its bonded plywood could only withstand 4 h of water boiling. All the plywood was delaminated in the second 4 h of water boiling, indicating the undesired water resistance of this adhesive because the lower viscosity resulted in the over-penetration of the adhesive into the wood [as shown by Figure 10(A)]. Other soybean protein adhesives that were made of TSP powder had good cycled bond strengths after 28 h of boiling–dry–boiling hygrothermal aging (ranging from 0.94 to 1.29 MPa), indicating the improved water resistance from TSP. Although the adhesive that was prepared with TSP alone and modified polyamide (DSP/TSP ratio of 0:1) had acceptable bond strength and water resistance, this adhesive became powdered soon after it was spread on veneer [as shown in Figure 10(C)] because the larger surface of the TSP powder absorbed more water from the adhesive, which hindered effective adhesion due to the poor wettability. Because soybean protein has both hydrophobic and hydrophilic chains, the DSP solution could act as a surfactant that made the TSP powder evenly and stably dispersed in the soybean protein adhesive. As a result, these DSP/TSP/polyamide adhesives appeared to be stable homogeneous solutions, as shown in Figure 10(B), which had a desirable work life (more than 16 h), a suitable viscosity for plywood production (ranging from 500 to 2000 mPa s at 25 °C), and non-obvious powdering after being spread on veneer.

The results in Figure 9 also indicated that the adhesive that was prepared with DSP/TSP ratio of 1:3 had the highest dry bond strength (2.94 MPa) and the best water resistance in terms of the highest and cycled bond strength (1.29 MPa). These values were all beyond the required values (0.98 MPa) for structural plywood according to the JIS K6806-2003 commercial standard, showing the high potential of this adhesive for applications to manufacturing structural plywood.

CONCLUSIONS

A novel soybean protein adhesive was developed through the combination of thermal alkali degradation, thermal acid treat-

ment, and crosslinking on the soybean protein, which resulted in the desired bond strength, water resistance, and good technological applicability and, therefore, showed good potential for commercial applications in structural wood composites. The crosslinker species had important effects on the primary properties of soybean protein adhesives, and the aqueous modified polyamide was the preferable crosslinker. In addition to having good technological applicability such as acceptable viscosity, a moderate solid content and a long work life, the optimal DSP/TSP/polyamide adhesive that was prepared with 20 wt % modified polyamide and a DSP/TSP ratio of 1:3 had a dry bond strength of 2.94 MPa and a cycled bond strength of 1.29 MPa, which were all above the required values (0.98 MPa) for structural plywood according to the JIS K6806-2003 commercial standard.

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