

Water-Resistant Soybean Adhesive for Wood Binder Employing Combinations of Caustic Degradation, Nano-Modification, and Chemical Crosslinking

Yuehong Zhang,^a Wuquan Zhu,^a Ying Lu, Zhenhua Gao,^{a,b,*} and Jiyou Gu^{a,b}

In an attempt to develop a soybean-protein wood adhesive with improved water resistance and good technical applicability, soybean protein was first degraded under strong alkali conditions and then subjected to chemical crosslinking combined with nano-modification. Results of plywood evaluation, GPC analysis, and XRD determination indicated that a soybean-protein adhesive that could bear 28 h boiling-dry cycled treatment according to standard JIS K6806-2003. The water-resistance improvement was attributed to both the chemical crosslinking of the degraded soybean protein (DSP) by MDI and the nano-modification of DSP by intercalated or exfoliated montmorillonite (MMT). Caustic degradation improved the technical applicability of the DSP adhesive by sharply reducing the viscosity of high-content protein solution. MMT nano-modification can obviously prolong the pot lives of MDI-modified DSP adhesives but slightly decrease their dry bond strength.

Keywords: Wood adhesive; Soybean protein; Caustic degradation; MMT nano-modification; Chemical crosslinking; Water resistance

Contact information: a: College of Material Science and Engineering, Northeast Forestry University, Harbin, China 150040; b: Key Lab of Bio-Based Material Science and Technology (Ministry of Education), Northeast Forestry University, Harbin, China 150040;

* Corresponding author: gao_zhenhua@yahoo.com

INTRODUCTION

Synthetic resins, such as urea-formaldehyde (UF), phenol-formaldehyde (PF), polyvinyl acetate (PVAc), and polyurethane (PU), are dominant in wood adhesion applications because of their excellent performance and technical availability; however, bio-based adhesives prepared from renewable bio-resources such as bark, starch, lignin, and protein have attracted more and more interest due to environmental concerns in terms of limiting the use of finite non-renewable fossil resources.

Soybean is an important crop cultivated widely throughout the world. Not only is it an oil seed crop, feed for livestock and aquaculture, and a good source of protein for the human diet, but it is also a biofuel feedstock (Masuda and Goldsmith 2009). In the 2011-2012 crop year the world soybean production was expected to be 260.7 million tons according to FAO estimates. Many attempts in recent years have been carried out to utilize this abundant plant protein for manufacturing wood adhesives with improved strength and/or water resistance; however, very few soybean adhesives are applied commercially in the wood industry due to their disadvantages (moderate to low dry strength, moderate to low resistance to water and damp atmospheres, and moderate

resistance to intermediate temperatures, high viscosity, low solid content, *etc.*) that highly limit the use of soy-based adhesives to interior applications, mainly as plywood (Chen *et al.* 2012; Gao *et al.* 2012; Lin *et al.* 2012). However, only commercial soybean adhesives have such a good performance and applicability compared with those of the two predominant wood adhesives (urea-formaldehyde resin and phenol formaldehyde), being suitable for a broad range of manufacturing wood composites such as plywood, particle-board, MDF, and OSB.

It is well known that soybean proteins consist of two major fractions according to their sedimentation constants, 11S and 7s, with molecular weights ranging from 15,000 to 36,000 (Kumar *et al.* 2002; van der Leeden *et al.* 2000). The large molecular weight can lead to severe molecular entanglements and friction, such that soybean-protein adhesives commonly are provided in high-viscosity solution/dispersion form (Frihart and Wescott 2004). Alternatively, the soybean-protein adhesives generally require that much lower protein concentrations (about 10 wt% soybean protein) be used in order to effectively reduce the viscosity enough so that the adhesive could be spread onto the wood. This has led to not only great energy consumption during hot pressing of the wood composites in order to remove most of the water in the adhesive, but also to the limiting of the soybean adhesive applications in plywood due to the difficulty in spreading the viscous adhesive evenly onto the wood particles or fibers.

Meanwhile, the macroscopic soybean proteins are composed of large-molecular-weight linear polypeptides via weak intermolecular interactions including hydrogen bonds, electrostatics bonds, Van der Waals forces, disulfide bonds, and hydrophobic interactions; these polypeptides are composed of many hydrophilic polar groups such as amides, hydroxyls, and residual aminos and carboxyls (Branden and Tooze 1999). This results in the poor water/moisture resistance of soybean adhesives due to the hydrophilicity of soybean protein and easy damage of weak intermolecular interactions.

Any good adhesive must consist of relatively large, flexible, and interwoven polymer chains, firmly attached to the solid surface by adsorption. Gelatin and casein are examples of adhesives that have been used for centuries. Soybean proteins have globular structures in their native form and, therefore, they mostly adsorb as compact layers or sometimes even as rigid particles when attached as an adhesive to a solid substrate, resulting in poor stress transfer from the interface to the bulk or poor bond strength (van der Leeden *et al.* 2000).

As a result, it is necessary to boldly and resolutely modify the chemical structure of soybean protein in order to overcome the critical disadvantages mentioned above in order to develop a water-resistant wood adhesive employing soybean protein. A novel scheme for developing a water resistant soybean-protein wood adhesive is proposed in the current study. The first step is to degrade soybean protein under strong alkaline conditions in order to reduce the molecular weight of the protein and to eliminate the weak intermolecular interactions. The next step is to rebuild the larger molecular weight and crosslinking density of the degraded soybean proteins with the combination of nano-modification with MMT in order to tailor the bond strength and bond durability. This novel soybean adhesive improved water resistance, lowered viscosity, and was suitable to be used at a relatively high protein concentration, showing good potential for widespread commercial applications.

EXPERIMENTAL

Materials and Preparations

Soybean protein isolate (SPI) with a protein content of 93.1 wt% was provided by Harbin High Tech Soybean Food Co. Ltd, China. Polymeric MDI, Millionate[®] MR-200 and with a NCO content of 31.2 wt%, supplied by Nippon Polyurethane Industry Co. Ltd, Japan. MMT G-105 without organic modification is a hydrophilic nano-clay, which was obtained from Nanocor Inc., Chicago.

The other chemicals employed in this study (sodium hydroxide, glyoxal, glutaraldehyde, and formic acid) were reagent grade and purchased from local chemical companies.

Birch veneers with dimensions of 420 mm × 420 mm × 1.5 mm were obtained from a local plywood plant. The veneers were dried to moisture contents ranging from 2.0 to 3.5%.

Caustic Degradation of Soybean Protein and Characterizations

In a reaction kettle equipped with a mechanical stirrer, condenser, and thermometer, 246 g of water and 54 g of 50 wt% NaOH solution were added and then heated to between 75 and 80°C. After 180 g of SPI had been gradually introduced, the mixtures were heated to 90 to 92°C and kept for various times (1.5 h, 2 h, and 2.5 h, labeled as DSP-I, DSP-II, and DSP-III, respectively) for caustic degradation. Finally the resultant mixtures were cooled to room temperature, and the pH was adjusted to between 6.5 and 7.0, obtaining a homogenous, transparent, and middle-brown DSP solution.

The DSP solutions were kept in a 25°C water bath for 1 h before testing viscosity, and then kept in a 103°C oven for 5 h before determining the solid content. The DSP solutions were diluted into thinner solutions with concentrations of 0.5wt% for determining molecular weight by Agilent 1100 GPC equipped with two chromatographic columns in series, namely a 79911GF-083 (MW range: 100 to 30,000) and a 79911GF-084 (MW range: 10,000 to 200,000). Each GPC sample was diluted with water to a concentration of 0.5% by weight. The mobile phase was water with a flow rate of 1 mL/min. The pressure on the columns was 78 psi. A differential refractive index detector was employed.

Nano-Modification of DSP by MMT and Characterizations

In a 250 mL beaker containing a magnetic stirrer and 150 g of DSP, 3 wt% of MMT was added on the basis of solid DSP and then stirred at ambient temperature until the MMT was evenly dispersed in the DSP. The mixture was then heated gradually to 90°C and kept at 90°C for 1 h to obtain a stable MMT-modified DSP. Otherwise, the MMT would quickly precipitate from the obtained MMT-intercalated DSP.

The MMT-modified DSP was freeze-dried at -50°C and 15 kPa for a week before X-ray diffraction (XRD) analysis to determine the MMT nano-modification on DSP. Also, the solid MMT alone and the blend of 10g of freeze-dried DSP briefly mixed with 0.3g of MMT were selected as controls. Our XRD spectra were collected on a D/max-2200 diffractometer (Rigaku, Tokyo, Japan) at room temperature. The radiation of XRD was generated from a Cu-K α ($\lambda = 0.154$ nm) source and the diffraction data was collected from 2 θ values of 2.5° to 12° with a step size of 0.02°, accelerating voltage of 40 kV, and current of 30 mA.

Formulation of DSP-Based Adhesive and Characterizations

A stoichiometric crosslinker (MDI or glyoxal, 15 wt% on the basis of liquid DSP) was introduced into the MMT-modified DSP or non-modified DSP, respectively, in order to obtain a water-resistant wood adhesive by crosslinking DSP. The crosslinker (18.0 g) was blended by hand with DSP (120.0 g) for about 90 to 120 s in a 250 mL beaker using a glass rod in order to obtain an even DSP adhesive modified by MDI or glyoxal.

The bond strength and bond durability of the DSP-based adhesives, in terms of dry strength and cycled wet strength, respectively, were determined via plywood evaluation. Birch veneers with dimensions of 420 mm × 420 mm × 1.6 mm were used to prepare 3-ply plywood panels at an adhesive spread rate of 150 g·m⁻². The adhesive-coated veneers were then stacked and hot-pressed at 125°C and 1.4 MPa for 4.5 min or 7 min to form plywood panels. Two replicate panels were prepared with each adhesive. A total of 40 specimens were cut from each panel for evaluating bond strength (20 specimens; dry state) and bond durability (20 specimens; wet state after undergoing 4 h boiling, 20 h oven-drying at 60°C, and another 4 h boiling treatment) according to the JIS K6806-2003 standard.

The pot life of the DSP-based adhesive was the duration determined by observing the viscosity increase of the adhesive in a 25°C chamber, since the DSP was mixed with MDI until the adhesive could not be spread onto the wood surface.

RESULTS AND DISCUSSION

In the current study, the caustic degradation of soybean protein was carried out in 2.25 M NaOH at a temperature of 90 to 95°C, which differed from the reported caustic treatment/denaturation under moderate to weak alkaline conditions (pH ranging from 8 to 12) at a temperature between 30 and 70°C (Hettiarachchy *et al.* 1995; Kumar *et al.* 2002). Under such conditions, soybean proteins not only unfolded their globular structures via destroying all the weak intermolecular interactions between the polypeptides, but also degraded to form smaller polypeptide fragments via the hydrolysis of the peptide groups. The molecular weight of degraded protein was sharply reduced from hundreds of thousands to thousands and was dependent upon the caustic content, as shown by the GPC analysis in Fig. 1. As a result, the DSP had much lower viscosity, ranging from 872 mPa·s to 325 mPa·s with a higher solid content of 36.7 to 38.2%, as shown in Table 1.

Table 1. Main Properties of DSP with Various Degrading Times

DSP ID	Degrading times (h)	Solid content (%)	Viscosity(mPa·s@25°C)	pH value
DSP-I	1.5	38.2	872	6.82
DSP-II	2	37.6	564	6.64
DSP-III	2.5	36.7	325	6.69

The solid contents of DSP were acceptable for wood adhesives and the viscosities were comparable to those of the UF resin and PF resin, which can be easily spread onto wood units in forms of fiber, particle, veneer, and timber. Therefore, caustic degradation was found to improve the technical applicability of soybean protein adhesives. In addition, it may also improve the water resistance of DSP-based adhesives because the degradation eliminates all the weak intermolecular interactions between the polypeptides

that lead to adhesion failure when the adhesive layer and/or adhesion interface are corroded and destroyed by water or moisture.

The DSP without further modification, on the other hand, had poor bond strength because the smaller molecular weights of DSP resulted in lower cohesive strength of the adhesive. For instance, for the regular hot-press cycle (4.5 min) at 125°C, three-ply plywood bonded by DSP alone was partly delaminated during degassing because the adhesion strength was not strong enough to withstand the internal gas pressure. As a remedy, the hot-press cycle should be prolonged to 7 min or more for safe degassing. These plywood panels had acceptable dry strength, ranging from 1.19 MPa to 1.28 MPa, as shown in Table 2, but their water resistances were very poor because all specimens for water-resistant evaluation completely delaminated when soaked in 63°C for only about 1h. As can be expected, the boiling-dry cycled treatment also caused failure. The DSP should therefore be rebuilt via chemical crosslinking to increase the molecular weight and chemical crosslinking density for improving the bond strength and water resistance.

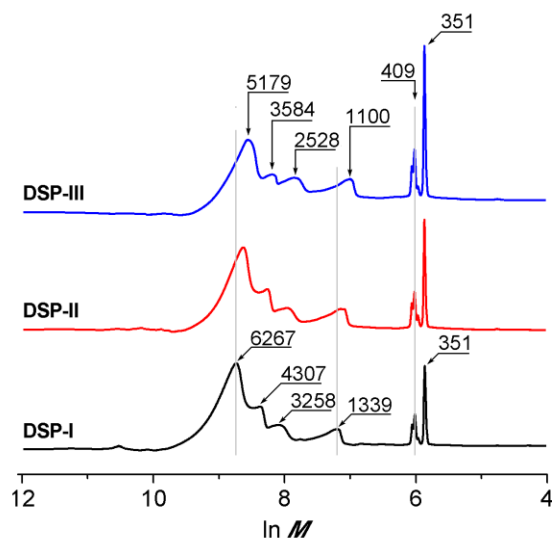


Fig. 1. GPC spectra of DSP with various degrading times

*The values marked on the GPC peaks are peak molecular weights

Three crosslinkers, MDI, glyoxal, and glutaraldehyde, were used to crosslink DSP because they contain two or more active groups (either isocyanato or aldehyde) that can react with the amino groups of DSP. When glutaraldehyde (15 wt% based on liquid DSP) was added into the DSP solution, the mixtures gelled quickly due to the highly active aldehyde groups of the glutaraldehyde, which immediately reacted with the amino groups of the DSP. The mixture of 15 wt% glyoxal with the DSP solution had a pot life of about 48 h due to the steric hindrance of the two adjoining aldehyde groups, and this effectively retarded the crosslinking reaction. The mixture of 15 wt% MDI with the DSP solution had a pot life between 20 and 30 min, revealing that the obtained adhesive should be quickly spread onto veneers and hot pressed in 20 min. As a result, glyoxal and MDI rather than glutaraldehyde might be used as the crosslinker. The formulations and the main properties of the DSP-based adhesives crosslinked by glyoxal and MDI are summarized in Table 2.

Test results in Table 2 indicate that the DSP-based adhesives prepared with longer degradation times had higher dry strength. This is attributed to the increase of polar groups of DSP with the longer degradation time. When a long-chain polypeptide is degraded into two smaller fragments via amide group hydrolysis, as indicated by the obvious decreases in viscosity (Table 1) and molecular weight (Fig. 1), one amino group and one carboxyl group are formed. Release of polar groups increases the absorption between the DSP and solid substrate surface and, therefore, improves the dry bond strength. Compared with controlled DSP adhesives without crosslinker (from Control 1 to Control 3), DSP-based adhesive modified with glyoxal (from A1 to A3) only slightly increased dry strength but there was no apparent improvement in water resistance. This is attributed to the obvious steric hindrance from the two adjoining aldehyde groups that could not effectively crosslink the DSP molecules, as evidenced by the much longer pot life of glyoxal-DSP mixture. However, the glyoxal modification improved the adhesion strength and the cohesive strength of DSP-based adhesive to some extent so that their hot-pressing cycles could be shortened from 7 min to 4.5 min without delamination.

Further compared with the DSP-based adhesive modified with glyoxal (from A1 to A3), the adhesive modified with MDI (from B1 to B3) had significantly higher dry strength and better wet strength. This indicates that MDI can crosslink DSP more effectively than glyoxal due to the high reactivity of its isocyanate groups and the absence of obvious steric hindrance. The plywood specimen bonded with MDI-modified DSP adhesive could bear 28 h of the boiling-dry cycle (boiling in water for 4 h then dried at 63°C for 20 h followed by another 4 h of boiling) and yielded a cycled wet strength up to 0.33 MPa, suggesting an improved water resistance. The cycled wet strength showed a decreasing tendency upon increasing degradation time, which can be attributed to the decreased molecular weight of DSP as shown by GPC spectra in Fig. 1. The molecular weight is correlated to the cohesive strength of polymer according to modern knowledge on polymer physics. The MDI-modified DSP adhesives, however, had too low of a pot life, only 20 to 30 min, for commercial application.

Table 2. Main Properties of DSP-Based Adhesives

Adhesive ID	Degradation time (h)	Crosslinker	MMT intercalation	Pot life (h)	Hot-press cycle (min)	Dry strength (MPa)	Wet strength (MPa)
Control 1	1.5	No	No	Very long	7	1.19(0.22)	NA ^a
Control 2	2	No	No	Very long	7	1.21(0.20)	NA ^a
Control 3	2.5	No	No	Very long	7	1.28(0.10)	NA ^a
A1	1.5	Glyoxal	No	About 48	4.5	1.32(0.19)	NA ^a
A2	2	Glyoxal	No	About 48	4.5	1.56(0.21)	NA ^a
A3	2.5	Glyoxal	No	About 48	4.5	1.69(0.25)	NA ^a
B1	1.5	MDI	No	0.33	4.5	2.11(0.31)	0.33(0.09)
B2	2	MDI	No	0.50	4.5	2.12(0.29)	0.18 ^b (0.06)
B3	2.5	MDI	No	0.50	4.5	2.34(0.27)	0 ^c
C1	1.5	MDI	Yes	2.17	4.5	1.87(0.31)	0.79(0.14)
C2	2	MDI	Yes	2.25	4.5	1.97(0.15)	0.51(0.09)
C3	2.5	MDI	Yes	2.67	4.5	2.05(0.28)	0.45(0.12)

^a Not available because all specimens delaminated after the first 4 h of boiling;

^b Because 13 out of 20 specimens delaminated after the second 4 h of boiling, the average of the remaining 7 specimens was reported;

^c All specimens almost delaminated after the second boiling.

The value in the parentheses refers to the standard deviation.

In a previous unpublished study, MDI was taken as the PF resin and added into MMT-modified soybean protein. It was observed that the mixture gelled in about 3 hours. This accident provided the insight that MMT-modified DSP may be able to prolong the pot life of MDI-modified DSP adhesives. As expected, test results in Table 2 indicate that the MMT-modified DSP adhesives (from C1 to C3) had not only much longer pot lives but also better wet strength than those without MMT modification (from B1 to B3). XRD analysis in Fig. 2 indicates that MMT were intercalated by DSP after modification and converted into a nano-platelet filler. The peak of XRD at about 7.08 to 7.13° is attributed to interlayer spacing or d-spacing (d_{001}), which represents the distance between two platelets of the MMT primary particle (Avérous and Pollet 2011). According to Bragg's law, it was calculated that the d_{001} of the MMT used in the current study was about 1.25 nm. The MMT sample or the simple blend of MMT with solid soybean protein (MP blend) had this XRD peak, indicating that the MMT still kept its original platelet structure; however, this peak disappeared in the MMT-modified DSP (MP intercalation), confirming that the MMT was intercalated and even exfoliated by DSP to form a nano-composite during the adhesive preparation.

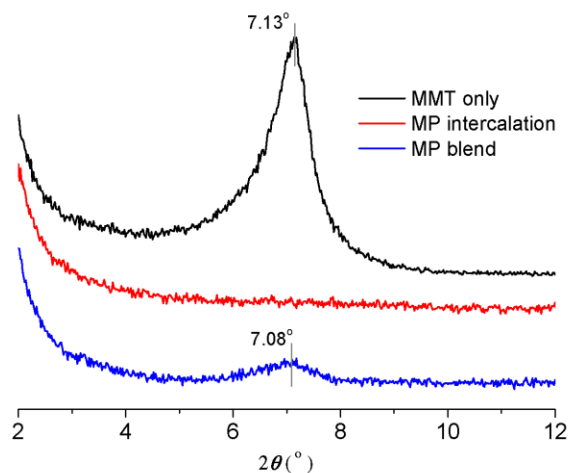


Fig. 2. XRD curves of MMT, MMT-DSP (MP) blend, and MP intercalation

After the MMT nano-modification, the pot lives of the DSP-MDI mixtures increased to 160 min (C3), which is 5.33 times as great as that without MMT modification (B3). The wet strengths also improved; however, the dry strength declined to some extent. Although the modifying mechanism was not well-understood, it is certain that the improvement of pot life and wet strength correlates with the MMT nano-modification on DSP solution. The nano-scale MMT platelets most likely blocked some active groups of the DSP via intercalation and/or exfoliation, which effectively retarded the crosslinking reactions between the MDI and DSP and led to a longer pot life. This might be evidenced by the obvious viscosity increase of DSP solution before and after MMT modification. For instance, DSP-II increased from about 560 cP up to 1025 cP. The blocking of active groups may have reduced the adsorption between the DSP and wood substrate and led to the decrease of dry strength. The improvement of wet strength may be attributed to the more sufficient and even crosslinking of DSP with MDI with less structural defects at the retarded crosslinking reaction rate. All these are to be confirmed in subsequent studies; however, the improvements in DSP-based adhesives have given an

instructive enlightenment that MMT nano-modification may become an effective approach in improving some important properties of soybean-protein adhesives.

CONCLUSIONS

1. A novel scheme that can contribute to the development of water-resistant soybean-protein wood adhesives was proposed, including caustic degradation of soybean protein, MMT nano-modification, and chemical crosslinking of DSP.
2. Caustic degradation can improve the technical applicability of DSP adhesives.
3. DSP adhesive chemically crosslinked with MDI exhibited improved bond strength and water resistance but very short pot life.
4. After MMT nano-modification, the MDI-modified DSP adhesives had much longer pot lives, improved water resistances, but slightly lower bond strengths.
5. MMT nano-modification may become an effective technique in improving some important properties of soybean-protein adhesives, but its modifying mechanism has yet to be uncovered.

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