

Soybean Meal-Based Adhesive Enhanced by MUF Resin

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ABSTRACT: Soybean meal flour, polyethylene glycol (PEG), sodium hydroxide (NaOH), and a melamine-urea-formaldehyde (MUF) resin were used to formulate soybean meal/MUF resin adhesive. Effects of the adhesive components on the water resistance and formaldehyde emission were measured on three-ply plywood. The viscosity and solid content of the different adhesive formulations were measured. The functional groups of the cured adhesives were evaluated. The results showed that the wet shear strength of plywood bonded by soybean meal/NaOH adhesive increased by 33% to 0.61 MPa after adding NaOH into the adhesive formulation. Addition of PEG reduced the viscosity of the soybean meal/NaOH/PEG adhesive by 91% to 34,489 cP. By using the MUF resin, the solid content

of the soybean meal/MUF resin adhesive was improved to 39.2%, the viscosity of the adhesive was further reduced by 37% to 21,727 cP, and the wet shear strength of plywood bonded by the adhesive was increased to 0.95 MPa, which met the interior plywood requirements (≥ 0.7 MPa). The formaldehyde emission of plywood bonded by the soybean meal/MUF resin adhesive was obtained at 0.28 mg/L, which met the strictest requirement of the China National Standard (≤ 0.5 mg/L). FTIR showed using the MUF resin formed more $-\text{CH}_2-$ group in the cured adhesive. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: soybean adhesive; MUF; wet shear strength; viscosity; FTIR

INTRODUCTION

Currently, the formaldehyde-based adhesives, such as urea-formaldehyde (UF) resin and phenol formaldehyde (PF) resin, play a dominant role in the wood composite industry thanks to their high bonding strength and stability. However, the formaldehyde emission issue of these adhesives and the resulted panel products has raised a great concern because of the formaldehyde being considered as a human carcinogen.¹ In addition, most of the formaldehyde-based adhesives are derived from nonrenewable petrochemicals and natural gas. Limited petroleum resources and health considerations draw an urgent need on the development of environmentally friendly adhesives from renewable resources.

As one of the most popular crops in the world, soybean can be a good raw material for wood adhesives, because it is abundant, renewable, and envi-

ronmentally friendly. The two major products from soybean are soybean oil and soybean meal. The main portions of soybean meal are soy protein (44–55%), carbohydrate (27–34%), ash (5–6%), and moisture (6–10%).² It can be a feasible way to make adhesive with soybean meal because of the high soy protein content.

Researches on the soybean-based adhesives started in 1923. Between 1930s and 1960s, the soybean-based adhesives were widely used in the commercial production of plywood.³ The soybean-based adhesives had many advantages such as low cost and easy handling. However, they also had many inferior properties such as low water resistance, high viscosity, and instability, which restricted their applications. In recent years, most of researchers have focused on the investigation of the soy protein isolate (SPI)-based adhesives. The water resistance of SPI-based adhesive was improved by modifying SPI with chemical methods, such as alkali,⁴ urea,⁵ guanidine hydrochloride,⁶ sodium bisulfate,⁷ maleic anhydride,⁸ DOPA,⁹ sodium dodecyl sulfate (SDS),¹⁰ and glutaraldehyde,¹¹ and so on. However, the SPI-based adhesives might not be practical for commercialization in the wood composite panel industry because of the high price. Soybean-based adhesive was also investigated by mixing with synthetic resin, such as PF resin,¹² pMDI,¹³ (polymeric 4,4'-methylenediphenyl isocyanate), and Kymene¹⁴ (a commercial

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wet-strength agent for paper). The water resistance of the developed adhesive was greatly improved and comparable with the commercial formaldehyde-based adhesive. However, the high cost of the synthetic resin itself and the 40–50% of the synthetic resin addition limited their application.

Melamine-urea-formaldehyde (MUF) is widely used in wood composites industry because of the high water resistance compared with UF resin and the low cost compared with the PF resin. It also can be an effective cross linker for soy protein because of the multifunctional groups. However, the researches of using MUF resin to enhance the soybean-based adhesive and reduce the cost of the adhesive were barely addressed.

In this study, a MUF resin (0.9 : 1 of formaldehyde/(urea and melamine)) was used to enhance soybean meal-based adhesive and develop the soybean meal/MUF resin adhesive. Effects of the adhesive components on the wet shear strength and formaldehyde emission of the plywood bonded by the different adhesive formulations were measured and tested in accordance with the China National Standards (GB/T 17657-1999). Fourier transform infrared (FTIR) spectra of the cured adhesive were evaluated.

EXPERIMENTAL

Materials

Soybean meal (43% soy protein content) was provided by Shandong Xiangchi Grain and Oil Company in Shangdong, China. Polyethylene glycol-400 (PEG), sodium hydroxide (NaOH), formaldehyde solution (37%), urea, and melamine were obtained from Tianjin Chemical Reagent. Poplar veneer was obtained from Wen'an, Hebei province, China.

Preparation of MUF resin

The MUF resin was synthesized using formaldehyde, melamine, and urea at a molar ratio of 1 : 0.3 : 0.8 in the laboratory. Melamine and urea were mixed and added into formaldehyde solution for four times at the weight rates of 5 : 2 : 2 : 3. Formalin was placed in the reactor then adjusted to pH = 8 with aqueous NaOH and then the first amount of urea and melamine was added. Then the mixture was heated to 90°C under reflux for 1 h. The acidic reaction was brought by adding formic acid (30 wt % solution) to obtain a pH of about 5.0, and the condensation reactions were carried out until it reached a target viscosity. Then the mixture was adjusted to pH = 8 by the NaOH and the second amount of urea and melamine was added. After 0.5 h at 80°C, the third amount of urea and melamine was added and further stirred at 70°C for 0.5 h. Final mole

ratios of MUF resins were adjusted by adding the fourth amount of urea and melamine. Then, the UF resin was cooled to room temperature, later followed by adjusting the pH to 9.0.

Preparation of the different adhesives

1. Adhesive A: soybean meal flour (30 g) was added into water (70 g) and mixed for 30 min at 20°C to form soybean meal adhesive.
2. Adhesive B: NaOH solution was added into Adhesive A and adjusted to pH = 9 to form the soybean meal/NaOH adhesive.
3. Adhesive C: PEG (10 g) was added into Adhesive B to form the soybean meal/NaOH/PEG adhesive.
4. Adhesive D: the MUF resin (43 g) was incorporated into Adhesive C to develop the soybean meal/NaOH/PEG/MUF resin adhesive (Soybean meal/MUF resin Adhesive).
5. Adhesive E: the MUF resin (900 cP of viscosity, 56% of solid content).

Preparation of three-ply plywood

The adhesive was applied to two sides of a poplar veneer (40 cm × 40 cm × 1.5 mm; moisture content, 8%) with 320 g/m² of the adhesive spread rate. The coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. The stacked veneers were put on a table at ambient environment for 5 min and hot-pressed at following hot press parameters: 5 min of hot pressing time; 145°C of hot pressing temperature; 1.0 MPa of hot press pressure. After hot-pressing, the panel was stored at ambient environment for at least 24 h before it was evaluated for its wet shear strength test. Three panels of plywood were made for each formulation of the adhesive.

The water resistance measurement

The water resistance of the plywood was determined in accordance with the procedure described in China National Standard (GB/T 17657-1999) for interior plywood. Twelve plywood specimens (Fig. 1) per panel were soaked into water at 63 ± 2°C for 3 h, and then dried at room temperature for 10 min before the shear strength testing. The wet shear strength was calculated by the following equation. The average strength was calculated from 36 test specimens of three panels.

$$\text{Wet shear strength (MPa)} = \frac{\text{Tension force (N)}}{\text{Gluing area (m}^2\text{)}}$$

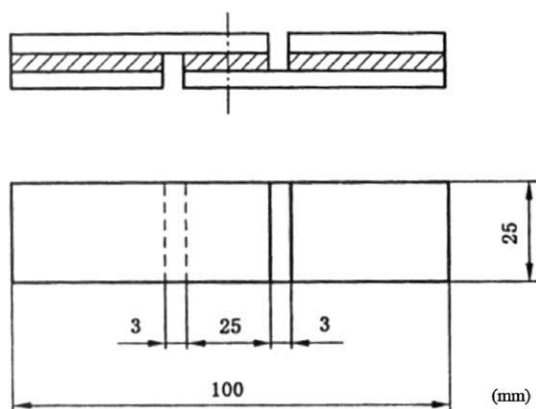


Figure 1 Sizes of specimen for water resistant measurement.

Formaldehyde emission measurement

The formaldehyde emission of plywood was determined using the desiccator method in accordance with the procedure described in China National Standard (GB/T 17657-1999). After storing at a ventilation environment for 20 days, the plywood was prepared with a dimension of 50 mm × 150 mm. Ten specimens per panel were put into a 9-11L sealed desiccator at 20 ± 2°C for 24 h. The emitted formaldehyde was absorbed by 300 mL deionized water in a container. The water was measured by a visible spectrophotometer to obtain the formaldehyde emission value. The average value of formaldehyde emission was calculated from three panels.

Solid content measurement

The solid content of the adhesive was measured based on the weight method according to the China National Standard (GB/T 14074-2006). About 3 g (weight α) adhesive was placed into an oven with the temperature was set at 105 ± 2°C for drying until a constant weight (weight β) was obtained. The value of the solid content was calculated by the following equation. The average value of solid content was calculated from three parallel samples.

$$\text{Solid content (\%)} = \frac{\beta \text{ (g)}}{\alpha \text{ (g)}} \times 100\%$$

Viscosity measurement

The viscosity of the adhesive was measured using Brookfield DV-II Pro with a spinning rate of 1 rpm. Data were collected 150 times in 5 min at 20°C and took an average value.

Fourier transform infrared (FTIR) spectroscopy test

The adhesive was placed in an oven at 140 ± 2°C to constant weight before scanning. The FTIR spectra of the cured adhesive sample was recorded by a Nicolet 6700 spectrometer over the range of 400–4,000 cm⁻¹ with a 4 cm⁻¹ resolution and 50 scans.

RESULTS AND DISCUSSION

Properties of Adhesive A

Figures 2–4 showed water resistance, apparent viscosity, and solid content of the different adhesive formulations. The wet shear strength of the plywood bonded by the soybean meal adhesive (Adhesive A) was measured at 0.49 MPa, which was much lower than the interior plywood requirement (≥0.7 MPa) of China National Standard (GB/T 9846.3-2004). For the Adhesive A, the high viscosity (40,122 cP, Fig. 3) caused the adhesive flow issue, which made it difficult to be applied on the veneer surface. Furthermore, the high viscosity also caused the distribution issue, which was difficult to form mechanical interlocking between wood and the adhesive during hot pressing and led to the low water resistance of the adhesive. In addition, Adhesive A required a long curing time during hot pressing because of the low solid content (27.5%, Fig. 4), which also caused the low water resistance of the adhesive.

Properties of Adhesive B

The soybean meal/NaOH adhesive (Adhesive B) was processed by adding NaOH to Adhesive A and mixing for 20 min. By testing the plywood specimens, the wet shear strength of Adhesive B was measured at 0.61 MPa, which was improved 25%

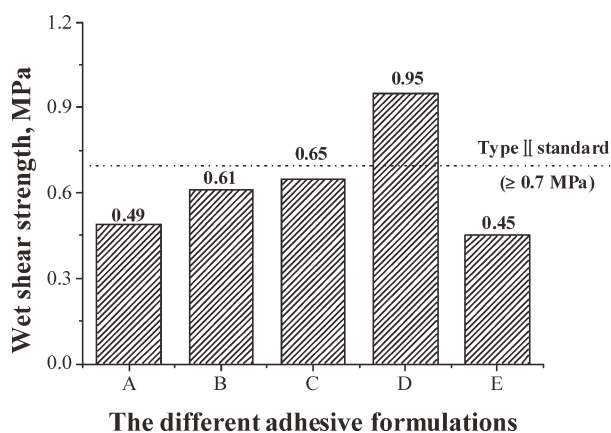


Figure 2 The wet shear strength of plywood specimens bonded by: (A) Soybean meal adhesive, (B) Soybean meal/NaOH adhesive, (C) Soybean meal/NaOH/PEG adhesive, (D) Soybean meal/NaOH/PEG/MUF resin adhesive, and (E) the MUF resin.

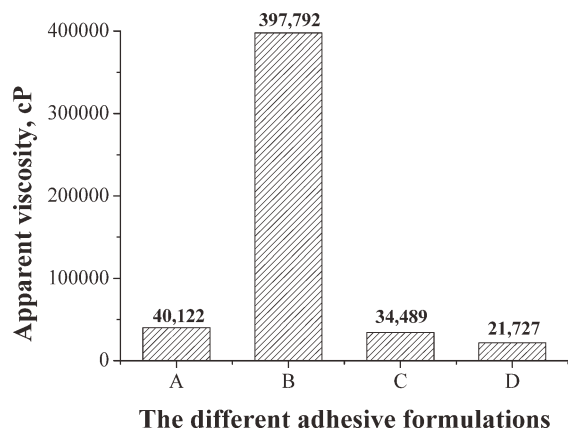


Figure 3 Apparent viscosity of the different adhesive formulations: (A) soybean meal adhesive, (B) soybean meal/NaOH adhesive, (C) Soybean meal/NaOH/PEG adhesive, (D) soybean meal/NaOH/PEG/MUF resin adhesive.

comparing to that of Adhesive A. The NaOH broke internal hydrogen bonds in coiled protein molecules and unfolded protein molecules. The available non-polar groups were exposed so that a stronger adhesion could be obtained.¹⁵ In addition, the soy protein molecules hydrolyzed in alkaline condition produced peptide chains with suitable molecular weight, which could further enhance the adhesion.¹⁶ However, it was also noticed that the viscosity of Adhesive B increased about 10 times higher than that of Adhesive A. It was because the spread molecule chain of protein could dramatically increase the force among the protein molecules, which made those protein molecules difficult to move.⁴

Properties of Adhesive C

High viscosity adhesive was not accepted in the wood composites industry. One of the most effective methods for reducing the viscosity of the soybean based adhesive was to decrease the intermolecular forces in the soy protein. PEG-400 was used in the adhesive formulation as a lubricant. The soybean meal/NaOH/PEG adhesive (Adhesive C) was processed by adding PEG to Adhesive B and mixing for 20 min. As expected, the viscosity of Adhesive C was decreased from 397,792 cP (Adhesive B) to 34,489 cP (about 11.5 times lower). When compared with Adhesive A, Adhesive C had 15% reduction in viscosity. As shown in Figure 2, the wet shear strength of the plywood bonded by the Adhesive C was measured at 0.65 MPa, which was 6.7% improved compared with Adhesive B. Because of the reduced viscosity, the Adhesive C distributed more uniformly than that of Adhesive B during hot pressing, which could improve the water resistance of the adhesive by forming more mechanical inter-

locks and increasing the intermolecular force at the wood/adhesive interface.

Properties of Adhesive D

For the Adhesive D formulation, the MUF resin (Adhesive E) was mixed into the adhesive C to further improve the water resistance, reduce the viscosity, and increase the solid content of the adhesive. The solid content of Adhesive D was increased to 39.2% compared with 34.4% for Adhesive C. Because of adding the low viscosity Adhesive E (900 cP), the overall viscosity of Adhesive D was obtained at 21,727 cP, which was 37% reduction compared to Adhesive C. The wet shear strength of plywood bonded by Adhesive D was improved to 0.95 MPa. As shown in Figure 2, the wet shear strength of plywood bonded by Adhesive E (0.45 MPa) was lower than that of other adhesive formulations used in this study. However, by adding Adhesive E, the wet shear strength of plywood bonded by Adhesive D was greatly improved exceeding interior plywood requirement (≥ 0.7 MPa) of China National Standard (GB/T 9846.3-2004). For the Adhesive E, insufficient crosslinking and unstable chemical bond were formed during the hot pressing because of the low molar ratio of Adhesive E, which led to the low water resistance of the adhesive. After mixing the Adhesives E and C, the Adhesive E acted as a cross linker with multifunctional groups reacting with the soybean protein molecules to improve the water resistance of the adhesive. In addition, since the molecule of Adhesive E was much smaller than that of the soybean protein, using Adhesive E could form more mechanical interlocks to improve the water resistance of the adhesive. The addition of Adhesive E also increased the flow ability of the adhesive to

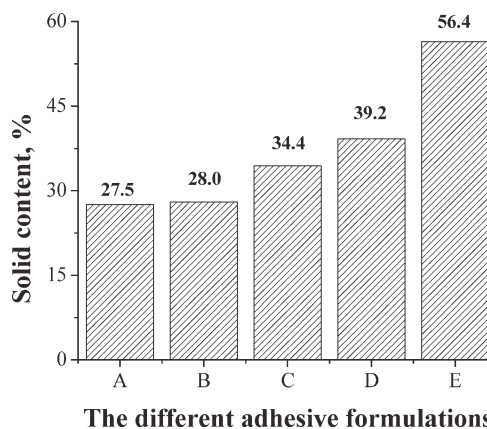


Figure 4 The solid content of the different adhesive formulations: (A) soybean meal adhesive, (B) soybean meal/NaOH adhesive, (C) soybean meal/NaOH/PEG adhesive, (D) soybean meal/NaOH/PEG/MUF resin adhesive, and (E) The MUF resin.

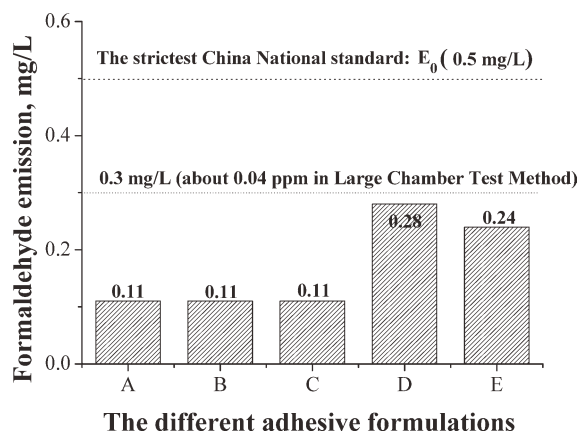


Figure 5 The formaldehyde emission of the plywood bonded by: (A) soybean meal adhesive, (B) soybean meal/NaOH adhesive, (C) soybean meal/NaOH/PEG adhesive, (D) soybean meal/NaOH/PEG/MUF resin adhesive, and (E) the MUF resin.

improve the interfacial bonding at the wood/adhesive interface, which could further improve the water resistance of the adhesive.

Effects of formulations on formaldehyde emission

Figure 5 showed the formaldehyde emission of the plywood bonded with different adhesive formulations. The formaldehyde emission of the plywood bonded with Adhesives A, B, and C was measured as 0.11 mg/L, which was produced by thermal decomposition of wood during hot pressing. The formaldehyde emission for the Adhesive E was measured as 0.24 mg/L, which was lower than the strictest standard requirement for the E₀ level (=0.5 mg/L) in the China National Standard (GB/T 9846.3-2004). After mixing C with E, the formaldehyde emission of plywood bonded by adhesive D was measured as 0.28 mg/L which increased about 16% compared to the Adhesive E, but it was also much lower than the strictest requirement (E₀ level, = 0.5 mg/L) of the China National Standard and met the requirement of the California Air Resources Board formaldehyde emission limitation of USA (= 0.05 ppm). Theoretically, Adhesive D supposed to have a lower formaldehyde emission than that of Adhesive E because the free formaldehyde in Adhesive E could react with the hydroxyl and amino groups of soybean protein molecule during hot pressing. The explanation was that Adhesive D formed a resin layer with more voids after curing because of the big molecular weight of soy protein, so that the free formaldehyde was much easier to release compared to the pure MUF resin. In addition, more unstable formaldehyde-generating products, such as dimethylolurea, monomethylolurea, and hexamine, formed in cured Adhesive D compared

with that the Adhesive E². At an elevated temperature with water, these products decomposed into formaldehyde and the other components, which could further release the free formaldehyde.

FTIR analysis

Figure 6 showed the FTIR spectrum for Adhesives A, C, and D. The broad band observed in the 3500–3000 cm⁻¹ range attributed to the free and bound O–H and N–H groups, which could form hydrogen bonding with the carbonyl group of the peptide linkage in the protein.¹⁷ The main absorption bands of peptide linkage were related to C=O stretching at 1628.9 cm⁻¹ (amide I), N–H bending at 1513.7 cm⁻¹ (amide II). The absorption band at 1231.8 cm⁻¹ contributed to the C–N stretching and N–H bending (amide III).^{17,18} Amide I shifted from 1628.9 to 1630.8 cm⁻¹, amide II shifted from 1513.7 cm⁻¹ to 1533.1 cm⁻¹, and amide III shifted from 1231.8 to 1247.1 cm⁻¹ (red shift) in the spectrum of Adhesives C and D, indicating that there were much more unfolded state to more random loose ones as compare with Adhesive A. The characteristic band of thiazine heterocyclic ring of melamine at 813.5 cm⁻¹ was observed in the spectrum of Adhesive D¹⁹; the band at 1533.5 cm⁻¹ (amide II) of Adhesive D became higher than the one at 1632.8 cm⁻¹ (amide I) compared with that of Adhesive A and C; the characteristic C–H stretching of CH₂ and CH₃ groups of saturated structures was observed in the range 2980–2850 cm⁻¹ (2920.1 cm⁻¹)²⁰ suggesting that using MUF resin formed more –CH₂– group in the cured adhesive, which could increase the crosslinking density and improve the water resistance of the adhesive.

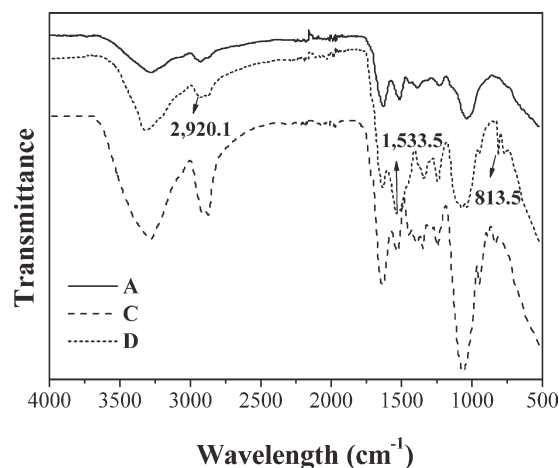


Figure 6 FTIR spectrums of the different adhesive formulations: (A) soybean meal adhesive, (C) soybean meal/NaOH/PEG adhesive, and (D) soybean meal/NaOH/PEG/MUF resin adhesive.

CONCLUSIONS

After using NaOH to modify soybean meal adhesive, the wet shear strength of plywood bonded by soybean meal/NaOH adhesive was improved by 33% to 0.65 MPa. Addition of PEG reduced the viscosity of soybean meal/NaOH/PEG adhesive by 91% to 34,489 cP. By using the MUF resin, the solid content of the soybean meal/MUF resin adhesive was improved to 39.2%, the viscosity of the adhesive was further reduced by 37% to 21,727 cP, and the wet shear strength of plywood bonded by the adhesive was increased to 0.95 MPa which met the interior plywood requirements of China national standard (GB/T 9846.3-2004). The formaldehyde emission of plywood bonded by the soybean meal/MUF resin adhesive was measured at 0.28 mg/L, which met the strictest requirement (E₀ level, =0.5 mg/L) of China National Standard. FTIR results showed using the MUF resin formed more —CH₂— group in the cured adhesive to improve the water resistance of the adhesive.

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