Improved Water Resistance of Soybean Meal-based Adhesive with SDS and PAM

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In a previous study, a soybean meal-based adhesive was developed by mixing soybean meal flour with a self-made cross-linking agent. The objective of this study was to investigate the effects of retention agents on the properties of the adhesive. Soybean meal flour (together with a cross-linking agent) and two kinds of additives (SDS and cationic PAM) were used to develop the soybean meal-based adhesive. The water resistance of the adhesive was measured by testing the wet shear strength of the resulting three-ply plywood samples and the residual rate of the different adhesives themselves. The apparent viscosities of the adhesives were also measured. Cross sections of the cured adhesives were imaged with a scanning electron microscope (SEM). Results showed that adding 0.5% SDS to the adhesive formulation improved its wet shear strength by 38.6%, from 0.83 to 1.15 MPa, and increased the residual rate by 1.3%, from 76.5 to 77.5%. Adding 0.01% PAM improved the water resistance of the adhesive by 38.6%, from 0.83 to 1.15 MPa, and increased the residual rate by 2.2%, from 76.5 to 78.2%. Adding 0.2% SDS and 0.01% PAM together improved the water resistance of the adhesive by 55.4%, from 0.83 to 1.29 MPa. The plywood bonded with the soybean meal/SDS/PAM adhesive met interior plywood requirements. SEM results showed fewer holes and cracks on the cross section of the cured adhesive with the addition of SDS and PAM.

Keywords: Soybean meal adhesive; Plywood; Viscosity; Wet shear strength; SEM

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INTRODUCTION

The various uses of wood represent an extremely large and diverse market for adhesives (Lambuth 1994). Adhesives produced from petroleum typically have high bond strength and water resistance, but phenol and formaldehyde emissions have caused environmental and toxicity problems with adhesive manufacturing, distribution, and use (Henderson 1979; O'Brien and Olofsson 1980). The ever-expanding market for adhesives, increasingly limited world oil reserves, and increasing concern regarding pollution have forced the plywood industry to consider new types of wood adhesives produced from renewable sources.

Soy protein-based adhesives are attractive because they are environmentally friendly, renewable, and easy to use. They have the potential to replace synthetic, petroleum-based adhesives. Soy protein-based adhesives were first developed by the wood industry in 1923 when a patent was granted for a soy meal-based adhesive (Liu 1997). However, soy protein-based adhesives do have disadvantages, such as low bond strength, low water resistance, high cost, and high viscosity, which limit their use. For example, the wet shear strength of plywood bonded by the pure soy protein adhesive has been found to be under 0.5 MPa, which could not meet the requirement of plywood interior use ($\geqslant$0.7 MPa). And for commercial use a soy protein based adhesive would be preferred to exhibit $\geqslant$1.0MPa of plywood wet shear strength. Many researchers have focused their efforts on investigating the potential of soy protein-based adhesives. Various methods have been used to improve the water resistance, reduce the viscosity, and reduce the cost of soy protein-based adhesives.

Chemical treatment is one of the most effective methods of altering adhesives. It can be divided into three categories. The first is treatment with protein denaturing agents. Researchers have used alkali (Hettiarachchy *et al.* 1995), sodium dodecyl sulfate (SDS) (Huang and Sun 2000), polyacrylic acid (PAA) (Gao *et al.* 2012), and urea (Zhang and Hua 2007) to denature proteins and improve the water resistance of the adhesive. However, plywood bonded using the denatured adhesive did not meet interior usage requirements.

The second method is by reducing the viscosity of the adhesive. Researchers have used sulfites (Kalapathy *et al.* 1996) and proteolytic enzymes (Kumar *et al.* 2004) to reduce the viscosity of adhesive, but these treatments also reduced its bond strength.

The third is the use of cross-linkers. Guanidine hydrochloride (Zhong *et al.* 2003), maleic anhydride (Liu and Li 2007), and glutaraldehyde (Wang *et al.* 2007) have been used as cross-linking agents to improve the water resistance of soy protein-based adhesives. They react with $-NH_2$, -COOH, and other exposed groups to increase the cross-linking density of the adhesive during the hot pressing process. Unfortunately, the water resistance of the panel bonded with the modified soy protein-based adhesive only barely met the requirements for interior panels. Aside from these methods, researchers have also mixed soy protein products with synthetic resins such as phenol formaldehyde resin (Zhong and Sun 2007), melamine urea formaldehyde resin (Gao *et al.* 2012), and polyamidoamine epichlorohydrin resin (Li *et al.* 2004) to improve the water resistance of the adhesive. Each was shown to be a good curing agent for soy protein in that they greatly improved its water resistance.

Retention agents are widely used by the paper manufacturing industry. In the present application it is proposed that they can improve the strength of an adhesive formulation by binding to the cross-linking agent and keeping it well distributed in the mixture. In preliminary research, soybean meal flour and a self-made cross-linker were used to develop a soybean meal-based adhesive. The soybean meal flour contained fiber and protein so that the retention agents could increase the residual cross-linker present in the adhesive and improve its water resistance. Such research has not previously been conducted.

In this study, soybean meal flour and a self-made cross-linking agent were used to develop a soybean meal-based adhesive. Polyacrylamide (PAM) and SDS were used as retention agents to improve the water resistance of the adhesive. The effects of PAM and SDS on the wet shear strengths, viscosities, and residual rates of the adhesives were measured. Three-ply plywood specimens were made using different adhesive formulations in order to measure the water resistance of the adhesive. Cross sections of plywood specimens produced with adhesives of different formulations, with the cured resin within them, were examined by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Table 1 lists the main ingredients used in formulating the tested adhesives.

Table 1. Grades and Sources of Materials

Material	Grade	Manufacturer
Soybean meal flour	43 to 45% soy protein	Shandong Xiangchi Grain and Oil Co.
Cross-linking agent	Polymer-Bisphenol-A Epoxy Resin* (CA)	Made in laboratory
Poplar veneer	Level 1 (moisture content 8%)	Wen'an city of He Bei province
Sodium dodecyl sulfate (SDS)	analytically pure	Beijing chemical reagent Co.
Cationic polyacrylamide (PAM)	500-1200 molecular weight and 5-80 polydispersity	Beijing chemical reagent Co.

* The polymer-bisphenol-A epoxy resin was developed by bisphenol-A, epichlorohydrin, and sodium hydroxide, following a typical synthesis process. Sodium hydroxide was added two times.

Preparation of Adhesives

To create the soybean resin meal-based adhesives, soybean meal flour was added to water and mixed for 30 min at 20 °C before the cross-linking agent was added and mixed for another 10 min. The weight ratio of soybean meal-to-water-to-cross-linking agent was 28 to 72 to 10. SDS was added to the adhesive and mixed for 10 min at 20 °C (with adhesive-to-SDS ratios of 100:0.2, 100:0.5, 100:1, 100:1.5, and 100:2) to create SDS-fortified adhesives. To create the PAM-fortified adhesives, PAM was dissolved into water and mixed for 1 h before soybean meal flour and the cross-linking agent were added to the solution. Adhesive-to-PAM ratios of 100:0.005, 100:0.01, 100:0.03, 100:0.05, and 100:0.1 were employed. To create the adhesive with both PAM and SDS, PAM was dissolved into water and mixed for 10 min before the soybean meal flour and the cross-linking agent were added to the solution. Adhesive-to-PAM-to-SDS ratios of 100:0.005:0.2, 100:0.005:0.5, 100:0.01:0.2, and 100:0.1:0.5 were used.

Apparent Viscosity Measurement

Apparent viscosity measurements of the fresh adhesives were performed using Brookfield viscometer. Experiments were conducted under a steady spinning rate of 6 rpm at 23 °C. Data reported are average values of replicate experiments.

Wet Shear Strength Measurement

Three-ply plywood samples were made under the following conditions: 200 g/m^2 of glue spread (single side), 70 s/mm of hot-pressing time, 120 °C hot-press temperature, and 1.0 MPa of hot-press pressure (Gao 2004). After they were hot-pressed, the plywood samples were stored under ambient conditions for at least 24 h before testing. Seven panels of plywood were made with each adhesive formulation.

The wet shear strength of the plywood was determined in accordance with the procedure described in China National Standard (GB/T 17657-1999) for Type II plywood. Six plywood specimens per panel were soaked into water at 63 ± 2 ºC for 3 h, and then dried at room temperature for 10 min before the tension testing.

Residual Rate Test

The adhesives were placed in an oven at 120 ± 2 °C until a constant weight (*M*) was obtained. The cured adhesives were soaked in tap water for 10 h at ambient temperature, then oven-dried at 100 ± 2 °C for 5 h in an oven, until a constant weight was obtained (*m*). The residual rate is defined as *m* divided by *M*, as shown in Eq. (1),

$$\text{Residual Rate (\%)} = \frac{m(g)}{M(g)} \times 100\% \tag{1}$$

Scanning Electron Microscopy (SEM)

Samples were placed in an oven at 120 ± 2 °C until a constant weight was reached. To begin testing, the samples were placed on an aluminum stub. A 10-nm-thick coating of Au/Pd was applied to the samples using a Q 150T S Turbo-Pumped Sputter Coater/Carbon Coater (Quorum Technologies Ltd., UK). The coated samples were examined and images were generated using a JSM-6500F field emission scanning electron microscope (FESEM) (JEOL USA Inc., Peabody, MA) operating at an accelerating voltage of 5.0 kV.

RESULTS AND DISCUSSION

SDS Addition

Viscosity is an important physical property governing the behavior of wood adhesives. Low viscosity allows for easy handling and good flow across the wood surface. The operating viscosity limits of soy protein-based adhesives are very wide, ranging from 500 to 75,000 cP, depending upon the application and the nature of the materials to be glued (Kumar *et al.* 2002). Figure 1 shows the effect of SDS addition on the apparent viscosity of soybean meal-based adhesives.

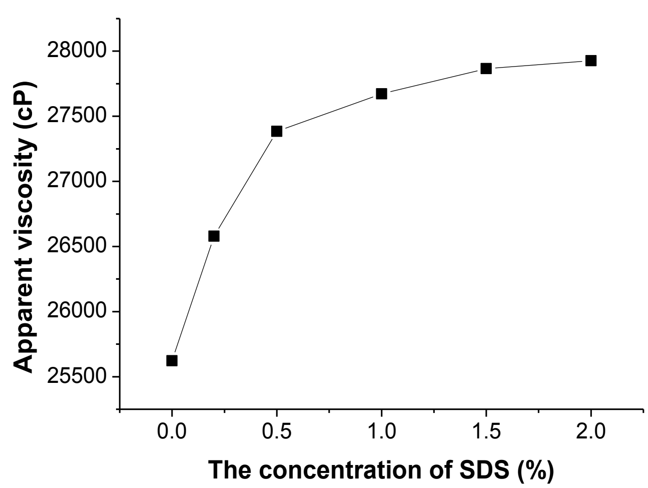
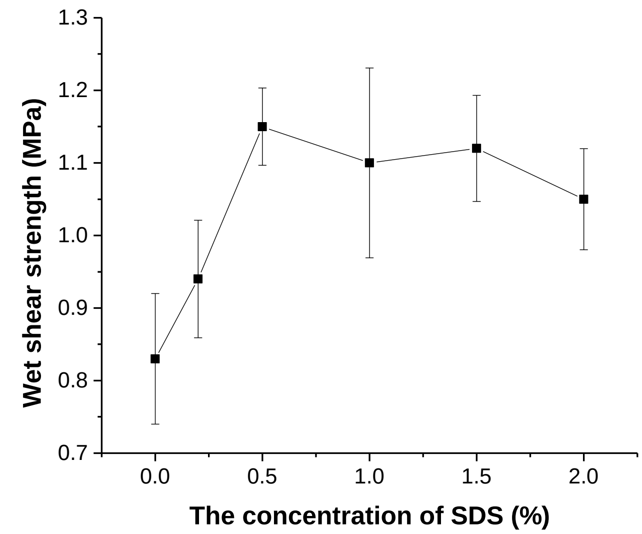
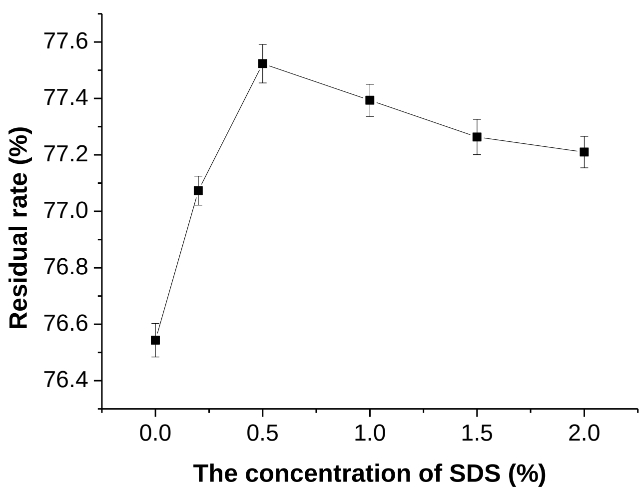


Fig. 1. Effect of SDS addition on apparent viscosity of soybean meal-based adhesives

The apparent viscosity of the adhesive increased significantly, by 6.9%, from 25,622 to 27,384 cP with an increase in SDS concentration from 0 to 0.5%. Above 0.5% SDS, the concentration increased more slowly, by a total of 2.0% (from 27,384 to 27,927 cP) with an increase in SDS concentration from 0.5 to 2.0%. SDS also acts as a denaturing agent for soy protein. In the presence of SDS, soy protein molecules unfold and the distance between the protein molecules decreases, which could increase the force acting between molecules, thus increasing the apparent viscosity of the soybean meal-based adhesive (Sherman 1979). One possible explanation for the slow increase in viscosity when the SDS concentration increased from 0.5 to 2.0% is that only a small fraction of the soy protein molecules can be further unfolded when the concentration of SDS exceeds 0.5%.



(a)



(b)

Fig. 2. Effects of SDS addition on the wet shear strength of plywood bonded by soybean meal-based adhesives and the residual rate of the adhesives

The wet shear strength of plywood bonded with modified soybean meal-based adhesive was 0.83 MPa, which meets the requirement of Ⅱtype plywood standard, but in terms of experimental error bar, 0.83 MPa is not high enough to make sure all plywood could meet the standard requirement. Therefore SDS is needed to improve the wet shear strength of this modified soy bean-meal based adhesive. Figure 2 shows the effect of SDS addition on the wet shear strength of plywood bonded with soybean meal-based adhesives and the residual rate of the adhesives. The wet shear strength of the plywood increased by 38.6%, from 0.83 to 1.15 MPa, and the residual rate increased by 1.3%, from 76.5 to 77.5%, as the SDS concentration increased from 0 to 0.5%. The wet shear strength of the plywood decreased by 8.7%, from 1.15 to 1.05 MPa (Fig. 2a), and the residual rate decreased by 0.3%, from 77.5 to 77.2%, as the SDS concentration increased from 0.5 to 2% (Fig. 2b). For soy protein, SDS is an effective dispersant and denaturing agent. The soy protein molecules were thoroughly unfolded and more hydrophobic side chains were exposed when SDS was added. Therefore, the contact area increased, strengthening the interaction between soy protein and wood during the curing process. Greater water resistance was also achieved (Huang and Sun 2000). In the presence of SDS, the structure of soy protein was destroyed and the hydrophobic groups within the soy protein molecule were exposed. The hydrophobic groups together with SDS formed the hydrophobic area of the adhesive. Further, SDS is an anionic surfactant whose negative charge can become electrostatically attracted to positively charged groups (*i.e.*, alanine, lysine, and tyrosine) on soy protein molecules, forming a complexed structure with the soy protein. This cross-linked structure is good for cross-linking agent molecules to attach to (Fig. 3). The cross-linking agents acted as a bridge between soy protein and timber to enhance the bonding strength of the adhesive.

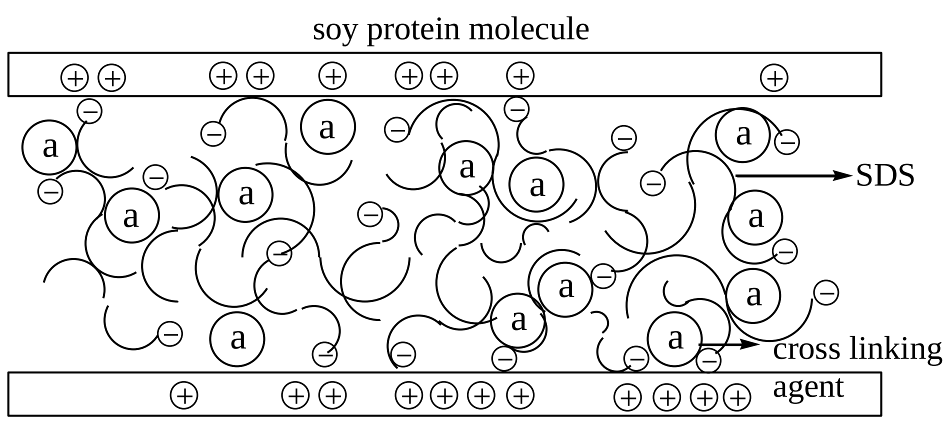


Fig. 3. SDS-enhanced, modified soybean meal-based adhesive illustration (a: cross-linking agent)

The concentration of Na^+ ions increased if the addition of SDS was increased. Na^+ ions diffusion in the internal and external polyanionic, and balanced part of the anion electrostatic field, resulting in decreased repulsion. The soy protein structure was originally stretched, but it curled and became compact with SDS doses under 0.5%. Accordingly, hydrophilic groups were exposed and hydrophobic groups were wrapped up inside the molecules, thereby decreasing the wet shear strength of soybean meal-based adhesive.

PAM Addition

In paper production, the use of polyacrylamide (PAM) can improve filler and fine retention, reduce drainage pollution, reduce production costs, and protect the environment. Figure 4 shows the effect of adding PAM on the apparent viscosity of soybean meal-based adhesives. The apparent viscosity of the adhesives decreased significantly, by 7.1%, from 25,622 to 23,812 cP when the concentration of PAM increased from 0 to 0.1%, which benefited adhesive flowing on the surface of wood. PAM is a water-soluble polymer that is insoluble in most organic solvents. It has strong flocculation capability and yields desirable flocculation, which can reduce frictional resistance within a liquid, thus decreasing its apparent viscosity. This phenomenon occurred in the case of the soybean meal-based adhesive.

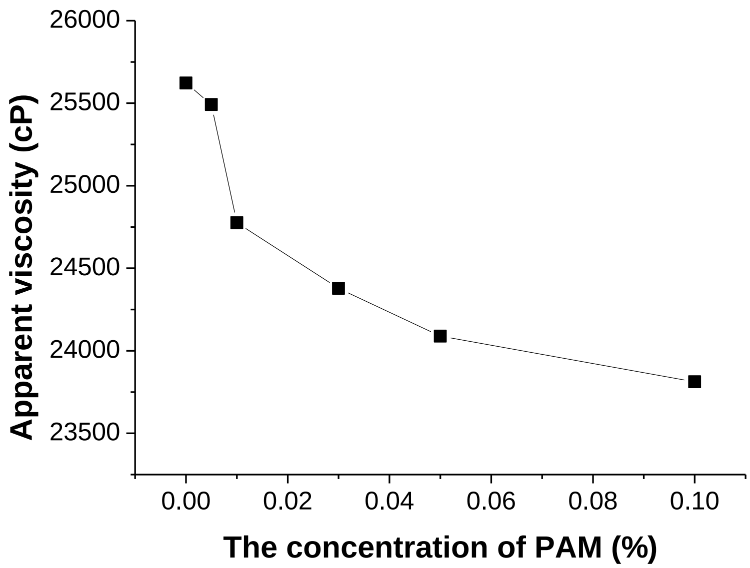
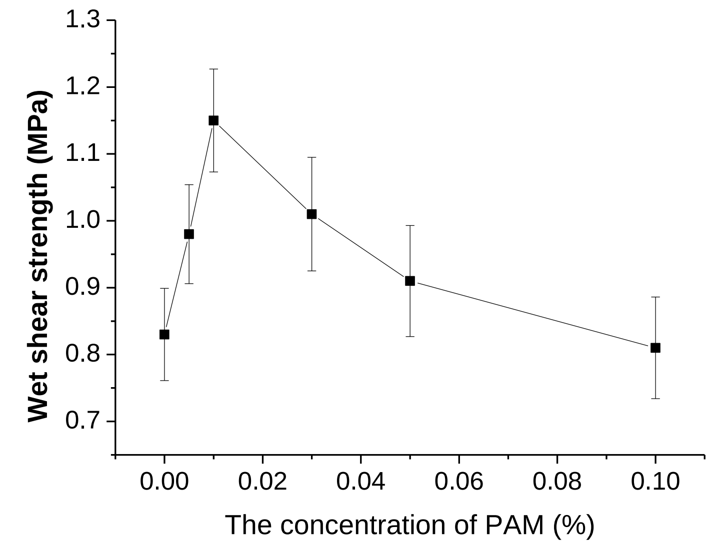


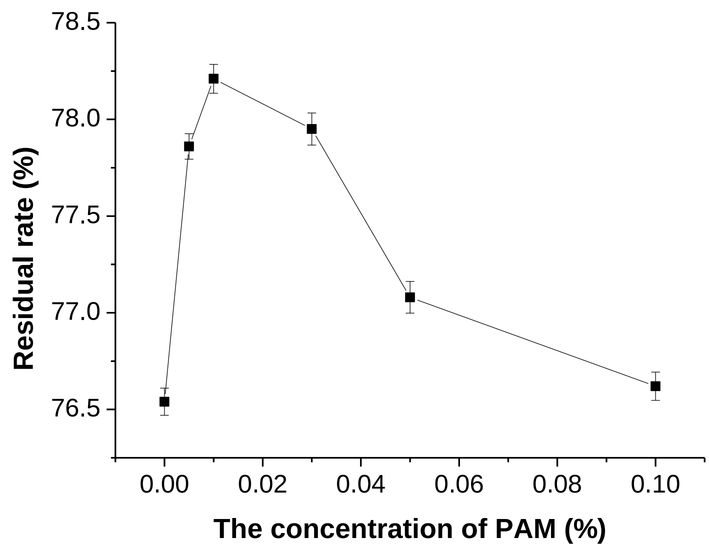
Fig. 4. Effect of PAM addition on the apparent viscosity of soybean meal-based adhesives

Figure 5 shows the effect of PAM addition on the wet shear strength of plywood bonded with soybean meal-based adhesives and the residual rate of the adhesives. The wet shear strength of the plywood increased by 38.6%, from 0.83 to 1.15 MPa (Fig. 5a), and the residual rate increased by 2.2%, from 76.5 to 78.2%, as the concentration of PAM increased from 0 to 0.01% (Fig. 5b). PAM is a cationic retention aid. Its positively charged groups can form a networked structure with negatively charged groups such as the aspartic acid and glutamic acid groups of soy protein molecules. This network is beneficial for the cross-linking agent molecules to attach to. And there are a large number of hydroxyl groups distributed on the cross-linking agent molecules, which can form hydrogen bonds with hydroxyl groups of wood fiber and soy protein molecules in the hot-pressing process (Fig. 6). Thus, better wet shear strength and residual rate were achieved when PAM was added. As the concentration of PAM was increased from 0.01 to 0.1%, the wet shear strength of the plywood decreased by 29.6%, from 1.15 to 0.81 MPa, and the residual rate decreased by 0.2%, from 78.2 to 76.6%. A possible cause for these decreases could be increasing numbers of hydrophilic amino groups in the adhesive.

PAM also likely consumed some cross-linking agent that was previously dissolved in the water. Accordingly, the water resistance and residual rate decreased.



(a)



(b)

Fig. 5. Effect of PAM addition on the wet shear strength of plywood bonded with soybean meal-based adhesives and the residual rate of the adhesives

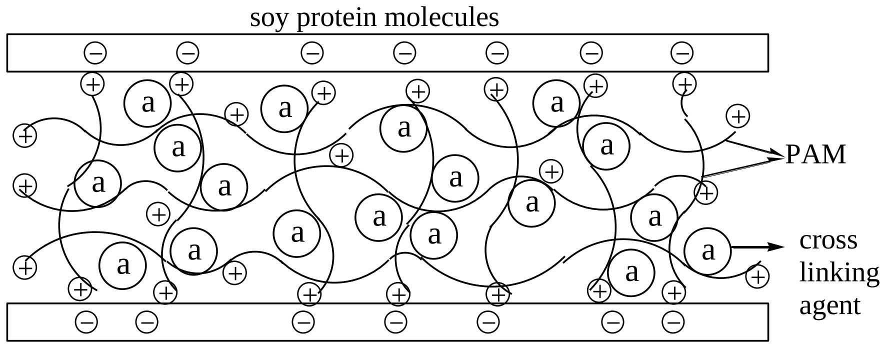


Fig. 6. PAM-enhanced, modified soybean meal-based adhesive schematic (a: cross-linking agent)

SDS/PAM Addition

Table 2. Wet Shear Strength and Apparent Viscosity of the Soybean Meal-based Adhesive with both SDS and PAM in the Formulation

Adhesive	Wet shear strength (MPa)	Viscosity (cP)
0.005%PAM+0.2% SDS	0.98	24921
0.005%PAM+0.5% SDS	0.80	25279
0.01%PAM+0.2% SDS	1.29	24875
0.01%PAM+0.5% SDS	1.09	24996

Table 2 shows the wet shear strength and apparent viscosity of the soybean meal-based adhesive with added SDS and PAM. The viscosity of the blends was similar to those of the blends with individual dosages of SDS and PAM. The wet shear strength increased by 55.4%, from 0.83 to 1.29 MPa, with the addition of 0.2% SDS and 0.1% PAM. This may be because SDS in the microemulsion interface did not compound with hydrolyzed polyacrylamide. It is also known that hydrolyzed polyacrylamide has no effect on the stability of microemulsions (Luan 1991) (Fig. 7). Because the SDS and the cationic PAM had opposite electrical charge, they could form chemical bonds with amino acids with opposite charges, respectively. The mesh structure became denser, then more cross-linking agent could cling, and acted with soy protein molecules, SDS, PAM and wood molecules, then enhancing the cross-linking effect of the cross-linking agent.

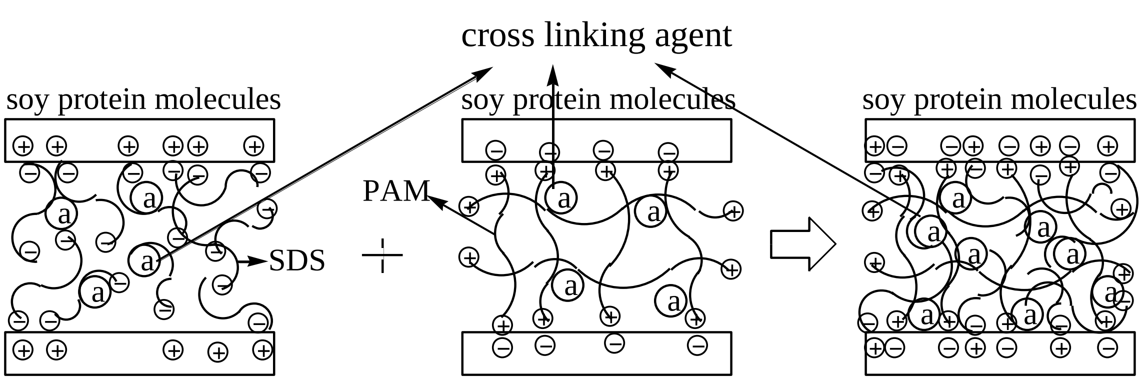


Fig. 7. SDS/PAM addition-enhanced, modified soybean meal-based adhesive schematic (a: cross-linking agent)

SEM Analysis

Figure 8 shows cross-sections of different cured adhesive formulations. Holes and cracks were observed in the cross-section of the cured soybean meal-based adhesive with only cross-linker added (Fig. 8a). Evaporation of water from the adhesive during hot-pressing caused these holes and cracks. Moisture was able to easily enter into the holes and cracks of the cured adhesive, decreasing the bonding strength of the plywood. Fewer holes and cracks were observed and a large flat area was formed between holes and cracks in the cross-sections of the adhesive with PAM and the adhesive with SDS. This structure may be been formed because the crosslink density increased, which could improve the wet shear strength of the adhesives with added cross-linker and SDS and cross-linker and PAM respectively. A mixture of SDS and PAM (with the cross-linker) could even further improve the wet shear strength of the adhesive probably because the curing cross-section became uniform and much fewer holes and cracks were observed in the board made with that formulation which reduce the moisture intrusion, thus improving the wet shear strength of the adhesive (Fig. 8d).

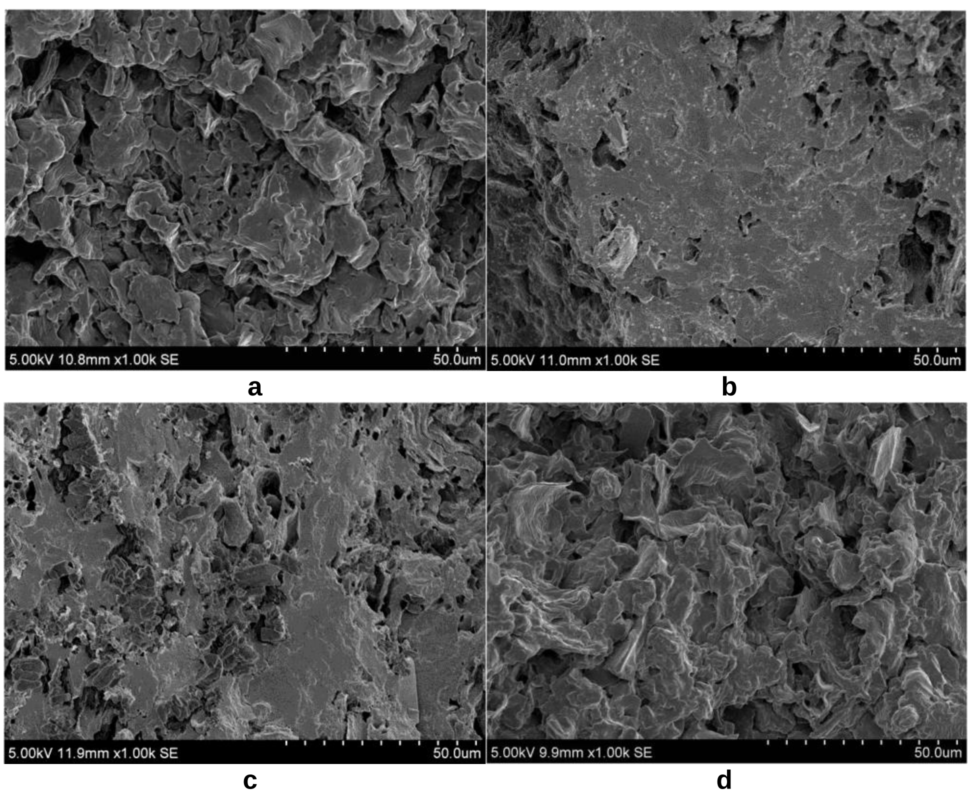


Fig. 8. Cross-sections of different cured adhesive formulations (a: soybean-meal adhesive with cross linking agent; b: adhesive with added cross linking agent and SDS; c: adhesive with added cross linking agent and PAM; d: adhesive with added cross linking agent, PAM, and SDS)

CONCLUSIONS

1. In the presence of a crosslinking agent, the addition of 0.5% sodium dodecyl sulfate (SDS) improved the wet shear strength of the soybean meal-based adhesive by 38.6%, from 0.83 to 1.15 MPa, which meets interior plywood requirements. SDS also increased the residual rate by 1.3% and increased the apparent viscosity of the adhesive by 6.9%.
2. Adding 0.01% cationic PAM improved the wet shear strength of the soybean meal-based adhesive by 38.6%, from 0.83 to 1.15 MPa, which meets interior plywood requirements. The cationic PAM also increased the residual rate by 2.2% and decreased the apparent viscosity by 3.3%.
3. The best adhesive formulation (with added cationic PAM and SDS) was found to be 0.2% SDS and 0.01% PAM. This formulation improved the wet shear strength of the adhesive by 55.4%, from 0.83 to 1.29 MPa, which meets interior plywood requirements.
4. SEM images revealed the fewest holes and cracks in the cross-section of the cured adhesive with added PAM and SDS.

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