

SOYBEAN MEAL-BASED WOOD ADHESIVES ENHANCED BY MODIFIED POLYACRYLIC ACID SOLUTION

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The effects of using sodium dodecyl sulfate (SDS) and a modified polyacrylic acid solution (MPA) on a soybean meal adhesive were investigated. Three-ply plywood specimens were fabricated to measure the water resistance of the adhesive (three-cycle soak test). The viscosity and solid content of the adhesive were measured. The cross-section and functional groups of the cured adhesive were evaluated using scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy, respectively. The results showed that using SDS improved the water resistance of the soybean meal adhesive by 30%. After incorporating MPA, the water resistance of the soybean meal/SDS/MPA adhesive was further improved by 60%, the viscosity of the adhesive was reduced by 81%, and the solid content of the adhesive increased by 15%. The plywood bonded by the soybean meal/SDS/MPA adhesive met the interior plywood requirements. SEM results showed no holes and cracks on the cross-section of the cured soybean meal/SDS/MPA adhesive. FTIR analysis indicated that more peptide linkages were formed in the cured adhesive as MPA was incorporated.

Keywords: Soybean meal; Plywood; Water resistance; Viscosity; SEM; FTIR

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INTRODUCTION

Soy protein-based adhesives were first used in the wood industry in 1923 (Liu 1997). Between the 1930s and the 1960s soy protein-based adhesives were widely used in the commercial production of plywood (Liu 1997) because of their ease of use and low cost. Soy protein-based adhesives also present disadvantages, however, such as low bond strength, low water resistance, and high viscosity. After 1960, the low price of most petrochemicals caused synthetic resin adhesives (formaldehyde-based adhesives) to take over the market (Pizzi 1989) because of their good water resistance and easy adaptability to a variety of curing conditions (Pizzi 1994).

Issues of formaldehyde emission and over-reliance on petrochemicals of the formaldehyde-based adhesive now present an urgent need for the development of environmentally friendly adhesives from renewable resources; therefore, a lot of researchers have turned their attention back to the investigation of soy protein-based adhesives, which are environmental friendly and renewable. Various new chemical

methods have been used for improving water resistance and reducing viscosity of soy protein-based adhesives.

The major chemical treatments could be classified into three categories, the first of which is protein denaturing agents. Researchers have used alkali (Hettiarachchy et al. 1995), urea (Zhang and Hua 2007), and sodium dodecyl sulfate (SDS) (Huang and Sun 2000) to denature proteins and improve the water resistance of the soy protein-based adhesive.

The second category is viscosity reducers. Sulfites (Kalapathy et al. 1996) and proteolytic enzyme (Kumar et al. 2004) have been used to reduce the viscosity of the soy protein-based adhesive; however, it also reduced the bond strength of the adhesive.

The third category is cross-linkers. Researchers have used guanidine hydrochloride (Zhong et al. 2003), maleic anhydride (Liu and Li 2007), and glutaraldehyde (Wang et al. 2007) as cross-linking agents to improve the water resistance of soy protein-based adhesives. The cross-linking agents react with the $-NH_2$, $-COOH$, and other exposed groups to increase the cross-linking density of the adhesive in the hot pressing process; however, the water resistance of the panel bonded by the modified soy protein-based adhesive hardly met the requirements for interior panels. Also, researchers have mixed soy protein products with synthetic resin to improve water resistance of soy protein-based adhesive, such as phenol formaldehyde resin (Zhong and Sun 2007), melamine urea formaldehyde resin (Gao et al. 2011), and polyamidoamine epichlorohydrin resin (Li et al. 2004). All of them were shown to be good curing agents for soybean protein.

Most researchers have used soy protein isolates (SPI) as the raw material to develop soy protein-based adhesive. The adhesives made with SPI have been relatively expensive and have had low solid content. As one of products of soy protein, soybean meal is abundant, is low in cost, and has a suitable protein content. The protein content of industrial grade soybean meal ranges from about 45% to 55% depending on the source (Pizzi 1989); therefore, it can be a feasible starting material for the manufacture of adhesives with soybean meal because of these advantages.

Acrodur DS 3530, an environmentally friendly binder from BASF Corporation, is used for wood fibers and bast fibers such as flax, sisal, and jute, etc. It becomes cross-linked to form a thermoset material. Because the major component is a modified polyacrylic acid solution, it could be an effective cross-linker and disperser for the soy protein-based adhesive. Therefore, using modified polyacrylic acid solution could be an ideal way to enhance soy protein-based adhesive, which was not addressed in the early papers.

In the present research, a modified polyacrylic acid solution was used to enhance soybean meal based adhesive. Three-ply plywood specimens were made by different adhesive formulations and tested in accordance with a three-cycle soak test described in the American National Standard (2000 (ANSI/HPVA HP-1)) to measure the water resistance. The functional groups and the cross-sections of the cured adhesives were evaluated to explain why the water resistance of the adhesive was enhanced. Viscosity and solid content of the adhesives were also measured.

EXPERIMENTAL

Materials

Soybean meal (43%-48% of soy protein, 30%-34% of carbohydrate, 8%-10% of moisture, 3%-5% of fiber, 5%-7% of ash, and 0.2%-0.8% of fat) was obtained from Ware Milling Incorporated Company (Mississippi, USA). Sodium dodecyl sulfate (SDS) was obtained from Fisher Scientific. Pine veneer (150 × 150 × 8 mm, 8% of moisture content) was provided from a local plywood mill. The modified polyacrylic acid solution (Acrodur DS3530, viscosity of 300 cP and a solid content of 49.1%) was obtained from BASF Corporation.

Preparation of Different Adhesives

For the soybean meal adhesive, soybean meal flour was added to water and mixed for 30 minutes at 20°C (weight ratio: soybean meal/water=30/70). For the soybean meal/SDS adhesive, SDS was added into soybean meal adhesive and further mixed for 30 minutes at 20°C (weight ratio: soybean meal/water/SDS=30/69/1). For the soybean meal/SDS/MPA adhesive, the modified polyacrylic acid solution (MPA, 20%) was mixed with the soybean meal/SDS adhesive system (80%), and the pH value was adjusted to 7 using NaOH. The weight ratio of the soybean meal/SDS/MPA adhesive components were: soybean meal, 24, water, 65.2, SDS, 0.8, MPA, 10.

Solid Content Measurement

The solid content of the adhesive was measured based on the oven dry method. About 5 g (weight α) of the adhesive was placed into an oven at a temperature of 100 ± 2°C until a constant weight (weight β) was obtained. The solid content was calculated using the following equation. An average of three replicates was used.

$$\text{Solid content (\%)} = \frac{\beta \text{ (g)}}{\alpha \text{ (g)}} \times 100\% \quad (1)$$

Viscosity Measurement

The viscosity of the adhesive was measured using a Brookfield viscometer with a spinning rate of 1 rpm and determined by averaging 5 measurements in 2 minutes at 20°C.

Water Resistance measurement

Three-ply plywood samples were made under the following conditions: 180 g/m² of glue spreading, 1 minutes/mm of hot pressing time, 160°C hot pressing temperature, and 1.0 MPa of hot pressing pressure. After hot pressing, the plywood samples were stored under ambient conditions for at least 24 h before testing. Five panels of plywood were made using each adhesive formulation.

The water resistance of the interior plywood panels (Type II plywood) was determined using a three-cycle soak test in accordance with the American National Standard for Hardwood and Decorative Plywood; Hardwood Plywood & Veneer Association; 2004 (ANSI/HPVA HP-1). Ten plywood specimens (2 inch × 5 inch) cut from five plywood

panels were submerged in water at $24 \pm 3^\circ\text{C}$ for 4 h, and then dried between 49°C and 52°C for 19 h with sufficient air circulation to lower the moisture content of specimens to within the range of 4 to 12 percent of the oven-dry weight. All specimens were inspected after the first cycle to determine whether delamination occurred and again after the third cycle, if applicable. This soaking/drying cycle was repeated until three cycles were completed. The criteria for interior application as described in the standard is that 95% of the specimens should not delaminate after the first soaking/drying cycle, and 85% of specimens should not delaminate after the third soaking/drying cycle. A specimen shall be considered as failing when any single delamination between two plies is greater than 2 inches in continuous length, over 0.25 inches in depth at any point, and 0.003 inches in width.

Fourier Transform Infrared (FTIR) Spectroscopy Test

The sample was placed in an oven at $120 \pm 2^\circ\text{C}$ until a constant weight was obtained. The FTIR spectra of the samples were recorded using a Thermo Nicolet 6700 FT-IR over the range of 400 to $4,000\text{ cm}^{-1}$ with a 4 cm^{-1} resolution and 50 scans.

Scanning Electron Microscope (SEM) Test

The samples were placed in an oven at $120 \pm 2^\circ\text{C}$ until a constant weight was obtained. Then all the samples were placed into a desiccator for 2 days before being examined. During testing, the samples were first placed on an aluminum stub. A coating of 10 nm Au/Pd film was applied to the samples using a Q150T S Turbo-Pumped Sputter Coater/Carbon Coater (Quorum Technologies Ltd., UK). The coated samples were then examined and imaged using a JSM-6500F field emission scanning electron microscope (FESEM) (JEOL USA Inc., Peabody, MA).

RESULTS AND DISCUSSION

The water resistance of an adhesive is an important property related to the bond durability. Table 1 shows the water resistance of plywood bonded by different adhesive formulations. All the specimens bonded with the soybean meal adhesives delaminated after the third cycle, which could be attributed to the low water resistance of the adhesive.

Table 1. Water Resistance of Plywood Specimens Bonded with the Different Adhesive Formulations

| | Adhesives | 1st cycle | 2nd cycle | 3rd cycle | Pass or Fail |
|-----|-------------------------------|-----------|-----------|-----------|--------------|
| (A) | Soybean meal adhesive | 4/10 * | 7/10 | 10/10 | F |
| (B) | Soybean meal/SDS adhesive | 1/10 | 4/10 | 7/10 | F |
| (C) | Soybean meal/SDS/MPA adhesive | 0/10 | 0/10 | 1/10 | P |
| (D) | Soybean meal/MPA adhesive | 0/10 | 2/10 | 6/10 | F |
| (E) | MPA | 10/10 | - | - | F |

* The first number was the number of delamination specimen and the second number was the total testing number of specimen.

SDS is a disperser and denaturation agent of protein. It can unfold the structure of soy protein and expose more hydrophobic side chains, of which could interact with the hydrophobic moieties of detergent molecules to form micelle-like regions so that the hydrophobicity of the adhesive is increased, thus improving the water resistance. As the soy protein molecules disperse and unfold in solution, the contact area increases and the interaction between the wood and the soy protein also increases during the curing process, so that a better bond strength is achieved (Huang and Sun 2000). After using SDS, three out of ten specimens bonded by the soybean meal/SDS adhesive didn't delaminate after the third cycle. All the specimens bonded by MPA delaminated in the first cycle of the water resistance test, indicating the lack of water resistance for MPA when used to bond plywood. After mixing MPA into the soybean meal/SDS adhesive, however, the water resistance of the soybean meal/SDS/MPA adhesive greatly increased. Only one out of ten specimen bonded by the soybean meal/SDS/MPA adhesive delaminated, which met the interior plywood requirements described in the American National Standard 2000 (ANSI/HPVA HP-1). Six out of ten specimens bonded by the soybean meal/MPA adhesive delaminated and failed to meet the standard requirements for interior plywood, indicating that the denaturation process was necessary in this experiment.

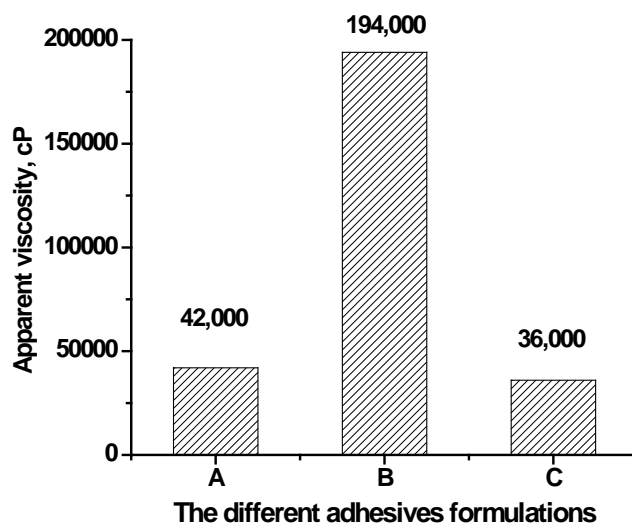


Fig. 1. Apparent viscosity of the adhesives: A (Soybean meal adhesive), B (Soybean meal/SDS adhesive), C (Soybean meal/SDS/MPA adhesive)

For a wood adhesive, viscosity is an important property, which largely governs the adhesive behavior. 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). A high viscosity of soy protein-based adhesives, especially after denaturing, not only causes difficulties in applying the adhesive on the veneer or particles, but also affects the adhesive distribution in the hot processing, which leads to the low bond strength. Figure 1 shows the apparent viscosity of the different adhesive formulations. After using SDS to denature the soybean meal adhesive, the viscosity of the soybean meal/SDS adhesive increased by 362% from

42,000 cP to 194,000 cP. The use of SDS resulted in a swelling and unfolding of the protein molecule and a decreasing of the distance between the protein molecules. The swelling and unfolding could increase the axial ratio or axis of rotation of the protein molecules, which would also increase the viscosity (Sherman 1979). The incorporation of MPA dramatically decreased the viscosity of the soybean meal/SDS/MPA adhesive by 81.4% from 194,000 cP to 36,000 cP, which was even lower than that of the soybean meal adhesive by 14.3%. This was because MPA presented a low viscosity and could be used as a disperser to reduce the viscosity.

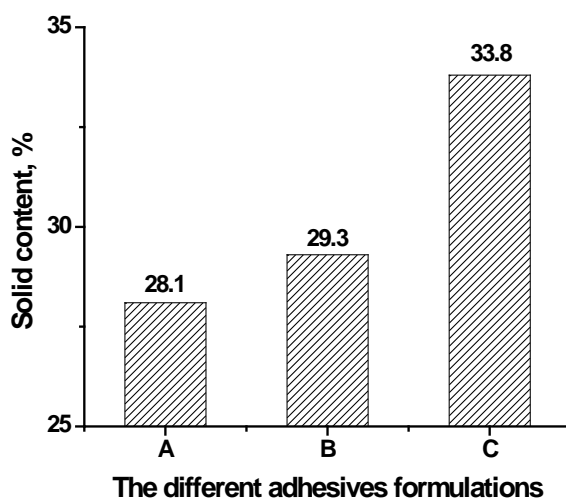


Fig. 2. Solid contents of the different adhesives: A (Soybean meal adhesive), B (Soybean meal/SDS adhesive), C (Soybean meal/SDS/MPA adhesive)

Solid content is another important property for the soy protein-based adhesive. Since soy protein-based adhesive is water-based, more water will be brought into composites with the low solid content adhesive and ejected out during hot pressing, which could reduce the bond strength of the composites. The solid content of soy protein-based adhesives ranges from 32% to 36% (Lorenz et al. 2007; Huang and Li 2008).

Figure 2 shows the solid contents of the different adhesive formulations. Results showed that the viscosity of the soybean meal adhesive would be greatly increased if the solid content was more than 30%, which made the adhesive difficult to stir. This could be a reason why the water resistance of the soybean meal adhesive was the lowest one (Table 1). The use of SDS increased the solid content of the soybean meal/SDS adhesive from 28.1% to 29.3%. After incorporating the MPA, the solid content of the adhesive was further increased by 15.4% from 29.3% to 33.8%, while the water resistance of the adhesive was greatly improved by 60%. The elevated solid content could promote the interlocking between wood and the adhesive and reduce evaporation of water to enhance the adhesion. Generally, the improved solid content of adhesive could increase adhesive viscosity. After incorporating the MPA, the solid content of the adhesive was increased, but the viscosity of the adhesive was reduced at the same time. This effect was attributed to the low viscosity of the MPA itself (300 cP) and the dispersion effect of the MPA.

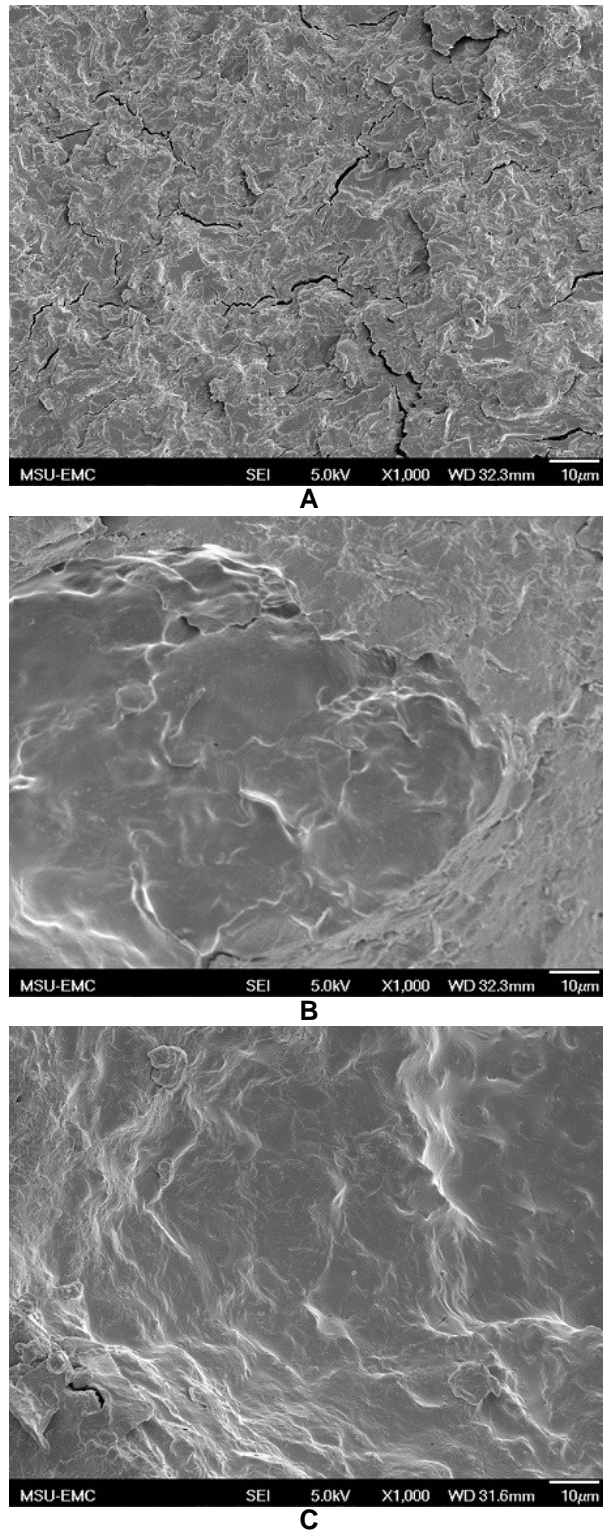


Fig. 3. Cross-sections of the cured different adhesive formulations: A (Soybean meal adhesive), B (Soybean meal/SDS adhesive), and C (Soybean meal/SDS/MPA adhesive)

Figure 3 shows the cross-sections of the cured different adhesive formulations. From the cross-sections of the cured soybean meal adhesive, holes and cracks were observed. These holes and cracks were caused by the evaporation of water in the adhesive during hot-pressing, which reduced the water resistance of the adhesive. Water or moisture were easily intruded into holes and cracks of the cured adhesive layer and broke the bond. When compared with the cross-section of the cured soybean meal adhesive, less holes and cracks were observed on the cross-section of cured soybean meal/SDS adhesive, indicating that the use of SDS reduced the water evaporation in the adhesive, which improved the water resistance of the adhesive. The incorporation of MPA could further reduce the water evaporation in the adhesive, because no holes and cracks were observed on the cross-section of the cured soybean meal/SDS/MPA adhesive; thus the adhesion was further reinforced.

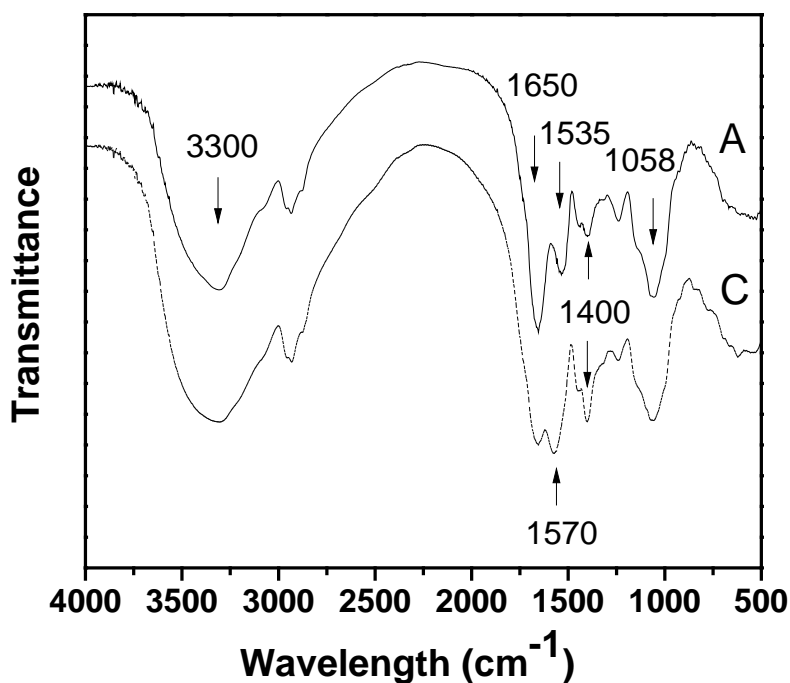
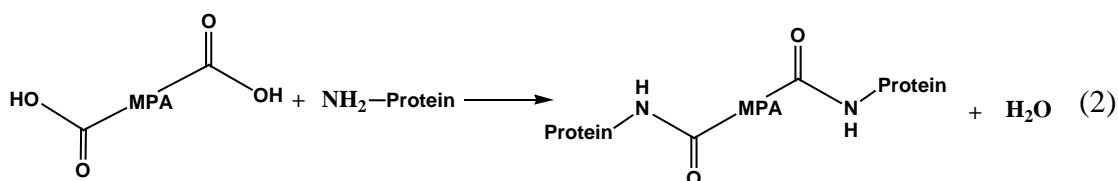


Fig. 4. FTIR spectrum of the different adhesive formulations: A (Soybean meal adhesive), and C (Soybean meal/SDS/MPA adhesive).

Figure 4 shows the FTIR spectra for adhesives A and C. For the spectrum of Adhesive A, the broad band observed in the 3,600 to 3,000 cm⁻¹ range was attributed to the free and bound O–H and N–H groups, which could form hydrogen bonds with the carbonyl group of the peptide linkage in the protein (Karnnet et al. 2005). The main absorption bands of the peptide linkage were related to C=O stretching at 1,650.5 cm⁻¹ (amide I), and N–H bending at 1,535.2 cm⁻¹ (amide II) (Schmidt et al. 2005). The absorption band at 1400.6 cm⁻¹ was attributed to C–N stretching. The amide II shifted from 1,535.2 cm⁻¹ to 1,572.2 cm⁻¹ (red shift) in the spectrum of Adhesive C, indicating that the soy protein molecule had more unfolded and random loose state in adhesive C

than that in Adhesive A. The band at $1,572.2\text{ cm}^{-1}$ (amide II) of Adhesive C became higher than the one at $1,650.5\text{ cm}^{-1}$ (amide I) compared to that of Adhesive A. The band at 1400.6 cm^{-1} (C-N stretching) of Adhesive C became as high as that at 1058 cm^{-1} compared with that of Adhesive A. Both of them indicated that the MPA had connected with the soy protein by forming peptide linkages during the curing process, which increased the cross-linking density and improved the water resistance of the adhesive. The following reaction might take place in that process.



CONCLUSIONS

1. The use of sodium dodecyl sulfate (SDS) improved the water resistance of a soybean meal adhesive. The delamination of specimens after the third cycle decreased from 10/10 to 7/10 pieces. However, adding SDS dramatically increased the viscosity of the soybean meal adhesive by 363%.
2. The incorporation of modified polyacrylic acid (MPA) greatly improved the water resistance of the adhesive from 7/10 pieces to 1/10 piece delamination, reduced the viscosity of the adhesive by 81.4% from 194,000 cP to 36,000 cP, and increased the solid content of the adhesive by 15.4% to 33.8%.
3. The plywood samples bonded by the soybean meal/SDS/MPA adhesive met the interior plywood requirements described in the American National Standard (2000 (ANSI/HPVA HP-1)).
4. SEM results showed no holes and cracks on the cross-section of the soybean meal/SDS/MPA adhesive, in contrast with what was observed with the soybean meal adhesive. The incorporation of the MPA reduced the evaporation of water in the adhesive during hot pressing, which enhanced the adhesion.
5. After mixing the MPA, FTIR analysis results indicated that more peptide linkages were formed in the cured soybean meal/SDS/MPA adhesive, which could increase the crosslinking density of the adhesive and improve the water resistance of the adhesive.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China (Project 30972310/C040302 & Project 31000268/C160302), and Special Fund for Forestry Research in the Public Interest (Project 201004006-2). The authors acknowledge the support from Mississippi State University and Beijing Forestry University for the research work described in the paper.

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Article submitted: September 8, 2011; Peer review completed: October 23, 2011;
Revised version received: December 28, 2011; Second revision received: January 8, 2012; Accepted: January 11, 2012; Published: January 15, 2012.