Improved Plywood Strength and Lowered Emissions from Soybean Meal/Melamine Urea-Formaldehyde Adhesives

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Abstract

The objective of this study was to improve the wet shear strength and reduce the formaldehyde emissions for the soybean meal/melamine urea-formaldehyde (MUF) adhesive–bonded plywood by optimizing the hot pressing parameters in plywood manufacturing. An $L(4^4)$ experimental design was used. A dynamic mechanical analyzer (DMA) was used to study the curing process of the adhesive during hot pressing. The DMA results showed that the storage modulus (E') first decreased to a minimum at 72.9°C and then increased as the temperature increased to a maximum at 157.2°C. At temperatures higher than 157.2°C, the storage modulus decreased as the temperature increased. The hot press temperature had a significant effect on both the wet shear strength and the formaldehyde emissions from 120°C to 150°C, while no significant effect was found by varying the hot press time from 50 to 80 s/mm and changing the pressure from 0.8 to 1.2 MPa. The adhesive spread rate had a significant effect on the formaldehyde emissions. No significant effect was found on the wet shear strength of plywood by varying the adhesive spread rate from 145 to 205 g/m^2. The optimum hot pressing parameters were found: 150°C hot press temperature, 70 s/mm in hot press time, 1.2 MPa in hot press pressure, and 165 g/m^2 in adhesive spread rate. Under such optimum processing conditions, the wet shear strength of the plywood was improved by 24.2 percent from 0.95 to 1.18 MPa, while the formaldehyde emissions was reduced by 21.4 percent from 0.28 to 0.22 mg/liter, which met the type II plywood requirement for wet shear strength and the level E_0 requirement for formaldehyde emissions described in the China National Standard GB/T 9846.3-2004.

Formaldehyde-based adhesives, such as urea-formaldehyde (UF) resin, phenol-formaldehyde (PF) resin, and melamine-modified urea-formaldehyde (MUF) resin, are currently the most popular adhesives in the wood composites industry. However, the formaldehyde-based adhesives and resulting products may present an environmental concern because of the formaldehyde emissions issue. The World Health Organization has concluded that formaldehyde is a human carcinogen (Meyer et al. 1986). Strict requirements (≤0.05 ppm of plywood) on plywood's formaldehyde emissions have been included in Airborne Toxic Control Measure §93120 (California Code of Regulations 2008) of California and have limited the applications of formaldehyde-based adhesives. Therefore, the wood composites industry is currently looking for more environmentally friendly adhesives and wood products.

Soy-based adhesives were first developed in 1923 (Jhonson et al. 1984). They had been widely used in plywood from the 1930s to the 1960s (Liu 1997). The soy-based adhesives are renewable and environmentally friendly. However, some issues, such as low bonding strength and low water resistance, have restricted their applications. In recent years, most researchers have modified soy-based adhesives to improve their bonding strength and develop environmentally friendly products (Liu and Li 2002, 2004; Stoll et al. 2006; Zhong and Sun 2007; Amaral-Labat et al. 2008; Huang and Li 2008).

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In our preliminary experiments (Gao et al., in press), a soybean meal/MUF adhesive was developed by mixing the soybean meal adhesive and a MUF resin. The hot pressing parameters used were 140°C hot press temperature, 65 s/mm in hot press time, 1.0 MPa in hot press pressure, and 160 g/m^2 adhesive spread rate. The wet shear strength and the formaldehyde emissions of the plywood bonded by the adhesive were 0.95 MPa and 0.28 mg/liter, respectively.

The objectives of this study were to optimize the hot pressing parameters in plywood manufacturing to improve the wet shear strength and reduce the formaldehyde emissions for soybean/MUF adhesive–bonded plywood. A dynamic mechanical analyzer was used to study the dynamic thermal behavior of the adhesive. Three-ply plywood panels were fabricated, and their wet shear strength and formaldehyde emissions were tested.

Materials and Methods

Materials

Soybean meal (43% soy protein content) was provided by Shandong Xiangchi Grain and Oil Company (Shandong, China). The soybean meal was milled to 200 meshes by a laboratory grinder. Polyethylene glycol-400 (PEG) and sodium hydroxide (NaOH) were obtained from Tianjin Chemical Reagent Company, Ltd. (Tianjin, China). The 1.5-mm-thick poplar veneers were obtained from Wen'an of Hebei province, China (8% moisture content).

Preparation of the soybean meal/MUF adhesive

Soybean meal adhesive preparation was based on the procedure described in Gao et al. (in press). The MUF resin was added into soybean meal adhesive and stirred for 20 minutes to form the soybean meal/MUF adhesive. The weight rates of the components were 70:30 (soybean meal adhesive:MUF resin). The total solids content of the resulting adhesive was 36 percent.

Experimental design

An $L(4^4)$ experimental design was used to analyze the effects of the process parameters (hot press temperature, hot press time, hot press pressure, and adhesive spread rate) on the wet shear strength and the formaldehyde emissions of the plywood at a reduced number of experiments. A total of 16 experiments were conducted under the designed hot press parameters. The details of the $L(4^4)$ experimental design are shown in Table 1.

Three-layer plywood fabrication

Six pieces of three-layer plywood (400 by 400 by 4.5 mm) were pressed with a laboratory hot press under the designed conditions as specified in Table 1. After hot pressing, the plywood was stored in the ambient environment (20°C and 12% relative humidity) for 48 hours before it was tested. Three panels of plywood were made for each adhesive formulation.

Wet shear strength measurement

The wet shear strength of the plywood was determined in accordance with the procedure described in China National Standard GB/T 17657-1999 (Standardization Administration of The People's Republic of China 1999) for Type II plywood. Twelve plywood specimens (Fig. 1) per panel were soaked in water at 63°C ± 2°C for 3 hours and were then dried at room temperature for 10 minutes before the shear testing. The values of the wet shear strength were calculated by the following equation. The average strength was calculated for 36 test specimens from three panels:

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

Formaldehyde emissions measurement

The formaldehyde emissions of the plywood were determined by the desiccator method in accordance with the procedure described in China National Standard GB/T 17657-1999. After storing in a ventilated environment (20°C and 12% relative humidity) for 20 days, plywood specimens were prepared with dimensions of 50 by 150 mm. Ten specimens per panel were put into a 9- to 11-liter sealed desiccator at 20°C ± 2°C for 24 hours. The emitted formaldehyde was absorbed by 300 mL of deionized water in a container. The formaldehyde content in the water was measured using a visible light spectrophotometer to obtain

Table 1.—The $L(4^4)$ experimental design and results.

ID	Hot pressing temp (°C)	Hot pressing time (s/mm)	Hot pressing pressure (MPa)	Adhesive spread rate (g/m^2)	Wet shear strength (SD) (MPa)	Formaldehyde emissions (SD) (mg/liter)
1	120	50	0.6	145	0.72 (0.06)	0.72 (0.01)
2	120	60	0.8	165	0.82 (0.08)	0.77 (0.02)
3	120	70	1.0	185	0.78 (0.05)	0.83 (0.01)
4	120	80	1.2	205	0.91 (0.07)	0.86 (0.01)
5	130	50	0.8	185	0.91 (0.09)	0.74 (0.01)
6	130	60	0.6	205	0.88 (0.05)	0.83 (0.00)
7	130	70	1.2	145	0.95 (0.03)	0.48 (0.01)
8	130	80	1.0	165	0.94 (0.07)	0.51 (0.02)
9	140	50	1.0	205	1.07 (0.07)	0.43 (0.00)
10	140	60	1.2	185	0.99 (0.05)	0.26 (0.02)
11	140	70	0.6	165	1.07 (0.06)	0.27 (0.01)
12	140	80	0.8	145	1.05 (0.00)	0.24 (0.01)
13	150	50	1.2	165	1.21 (0.05)	0.23 (0.02)
14	150	60	1.0	145	1.10 (0.04)	0.20 (0.01)
15	150	70	0.8	205	1.21 (0.03)	0.25 (0.01)
16	150	80	0.6	185	1.32 (0.05)	0.21 (0.01)

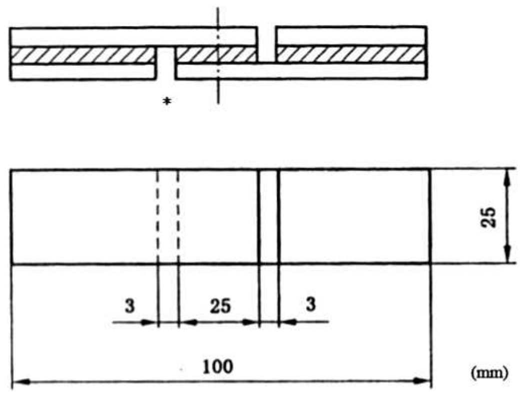

Figure 1.—Sizes of specimen for water resistance test (grooves cut only two-thirds of the way into the core veneer).*

the value of the formaldehyde emissions. The average value of formaldehyde emissions was calculated from three panels.

Dynamic mechanical analysis test

The dynamic mechanical analysis (DMA) test was conducted through an oscillating force applied to a sample and the material's response to the force was analyzed. The DMA test provides mechanical responses of the sample such as the storage modulus (E′), loss modulus (E″), and tan δ (the ratio of E″ to E′); E′ is a measure of the stored energy of a material depending on the polymer type, temperature, and frequency of oscillation, whereas loss modulus measures the dissipated energy of a sample due to the molecular friction occurring in viscous flow. For a thermoset material, DMA can be used to follow the curing process by tracking modulus changes (Menard 1999). It has been used to investigate the curing process of phenol-formaldehyde resin (Wang et al. 2009b) and urea-formaldehyde resin (Park and Kim 2008). In our research, the DMA test was used to characterize the modulus changes of the sample by simulating the hot pressing process in plywood manufacture.

The adhesive was symmetrically applied to one side of a poplar veneer (5 by 5 by 0.05 cm; moisture content, 8%). The spread rate of the adhesive was 160 g/m^2. The coated veneer was covered by an uncoated veneer of the same size with the same grain direction. The stacked veneers were cold pressed at 1.0 MPa and 20°C for 15 minutes. After cold pressing, the panel was cut into several small samples (0.5 by 5 cm) to be evaluated by DMA (NETZSCH DMA 242). All the specimens were evaluated in a three-point bending mode. A fixed displacement mode with 15-μm amplitude and a 1-Hz oscillation frequency was used. For a dynamic DMA scan, the temperature was increased from 25°C to 300°C at a heating rate of 10°C/min.

Results and Discussion

The storage modulus (E′) curve of the sample bonded by the soybean meal/MUF adhesive is shown in Figure 2. As the temperature increased, the storage modulus decreased to a minimum at 72.9°C and then increased to a maximum at 157.2°C. The initial decrease of the storage modulus from 30°C to 72.9°C was attributed to the softening of the adhesive as the temperature increased. After the temperature passed 72.9°C, the increase of storage modulus was attributed to the change of the network from a liquid state to a glassy state. The adhesive was turning to a cross-linked polymer via the hot pressing curing process. At a temperature higher than 157.2°C, the storage modulus went down because of the devitrification of the adhesive. Therefore, the hot pressing temperature should be in the range of 72.9°C to 157.2°C.

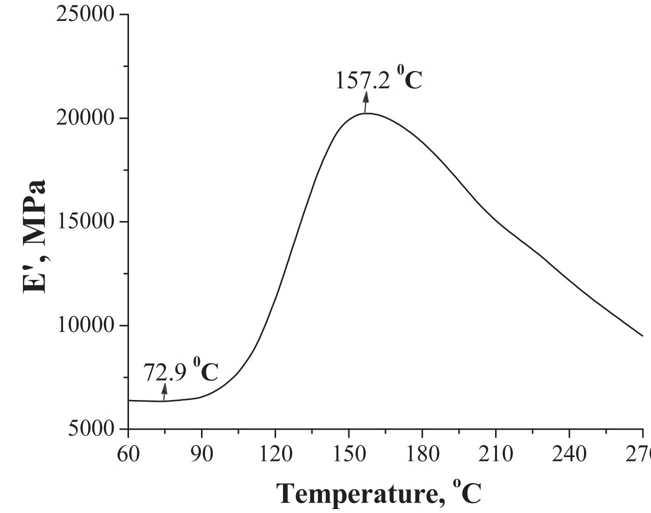

Figure 2.—The storage modulus (E′) curve of the sample.

Figure 3 shows the dE′/dT curve of the sample bonded by the soybean meal/MUF adhesive. A peak observed at 127.2°C indicates that the fastest growth of storage modulus occurred at that temperature.

The tan δ curve of the sample bonded by the soybean/MUF adhesive is shown in Figure 4. The peak observed at 107.3°C was the initial temperature of the vitrification for the adhesive. At a temperature lower than 107.3°C, the evaporation of water and the curing of the adhesive greatly increased viscosity and decreased the flowability of the adhesive. The adhesive changed from an aqueous solution state to a rubbery elastic state. At a temperature higher than 107.3°C, the adhesive was turning to the glassy state from the rubbery elastic state as the curing proceeded further. A

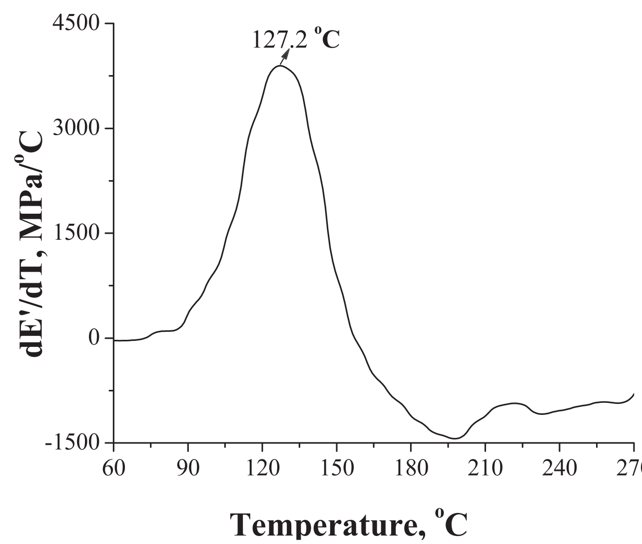

Figure 3.—The dE′/dT curve of the sample.

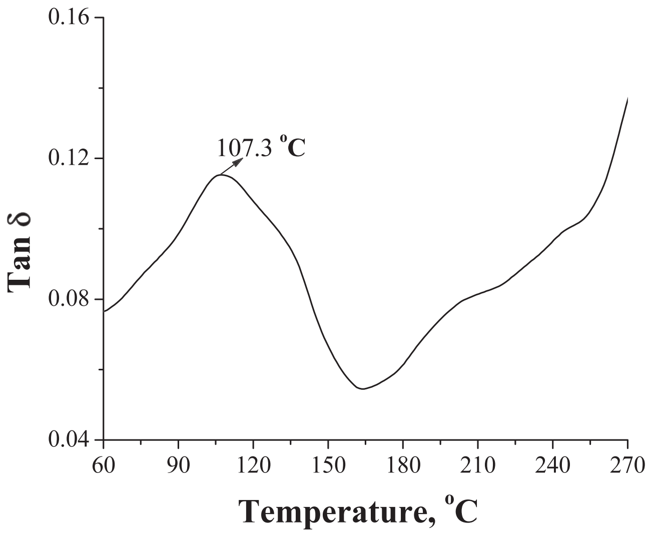

Figure 4.—The tan δ curve of the sample.

similar process was reported in dynamical mechanical analysis of PF resins (Kim et al. 1991, Wang et al. 2009a).

According to the results of the DMA test, the range of temperature from 120°C to 150°C was selected to test the effect of hot press temperature on the wet shear strength and formaldehyde emissions. The other parameters were based on the practices of using UF resin. The results of the $L(4^4)$ experimental design are shown in Table 1.

Figure 5 shows the effect of process parameters on the wet shear strength of the plywood bonded by the soybean meal/MUF adhesive. The wet shear strength increased as the hot press temperature increased from 120°C to 150°C, which was in accordance with the results of the DMA test. An elevated temperature made the adhesive cure more completely by increasing the core temperature of the composites. Generally, long hot press times improved the wet shear strength. The hot press time curve showed that the values of wet shear strength at 70 and 80 s/mm were higher than those at 50 and 60 s/mm. The hot press pressure curve showed that the effect of pressure on wet shear strength was not strong. But at an elevated hot press pressure, more adhesive molecules could be pushed into the pore structure of the wood veneers to form a mechanical interlock in the hot press process to enhance the adhesion. According to the adhesive spread rate curve, the wet shear strength increased with the adhesive spread rate and remained constant when the adhesive spread rate was greater than 165 g/m^2. Increased adhesive spread rates enlarged the interlocked area between wood and the adhesive and distributed the adhesive more uniformly to enhance the adhesion. According to the variance analysis at $\alpha = 0.05$, the hot press temperature presented the highest effect on the wet shear strength, then the hot press time, then the adhesive spread rate, and then the hot pressing pressure. At temperatures from 120°C to 150°C, the hot press temperature had a significant effect on the wet shear strength. No significant effect was observed when the hot press time was varied from 50 to 80 s/mm, by altering the hot press pressure from

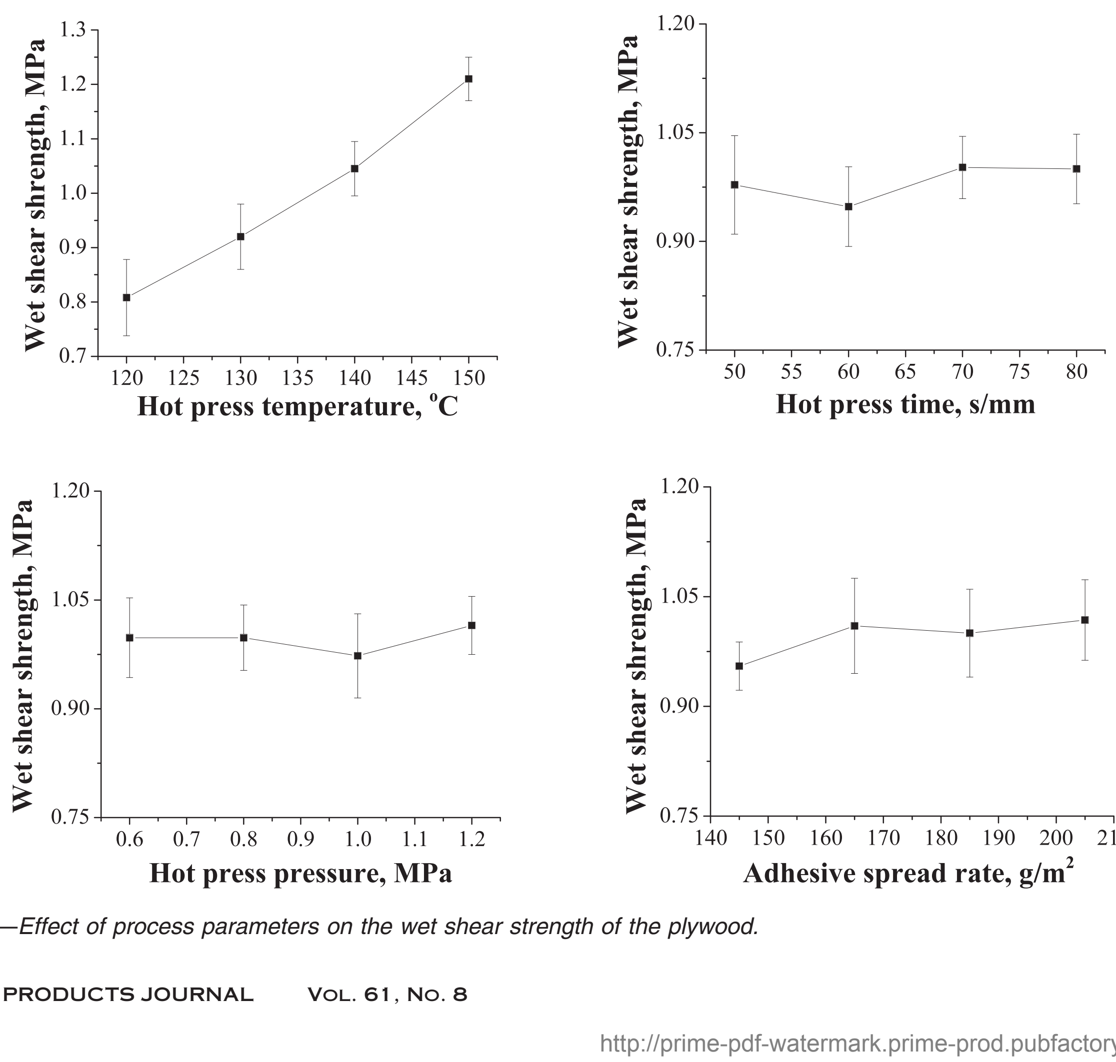

Figure 5.—Effect of process parameters on the wet shear strength of the plywood.

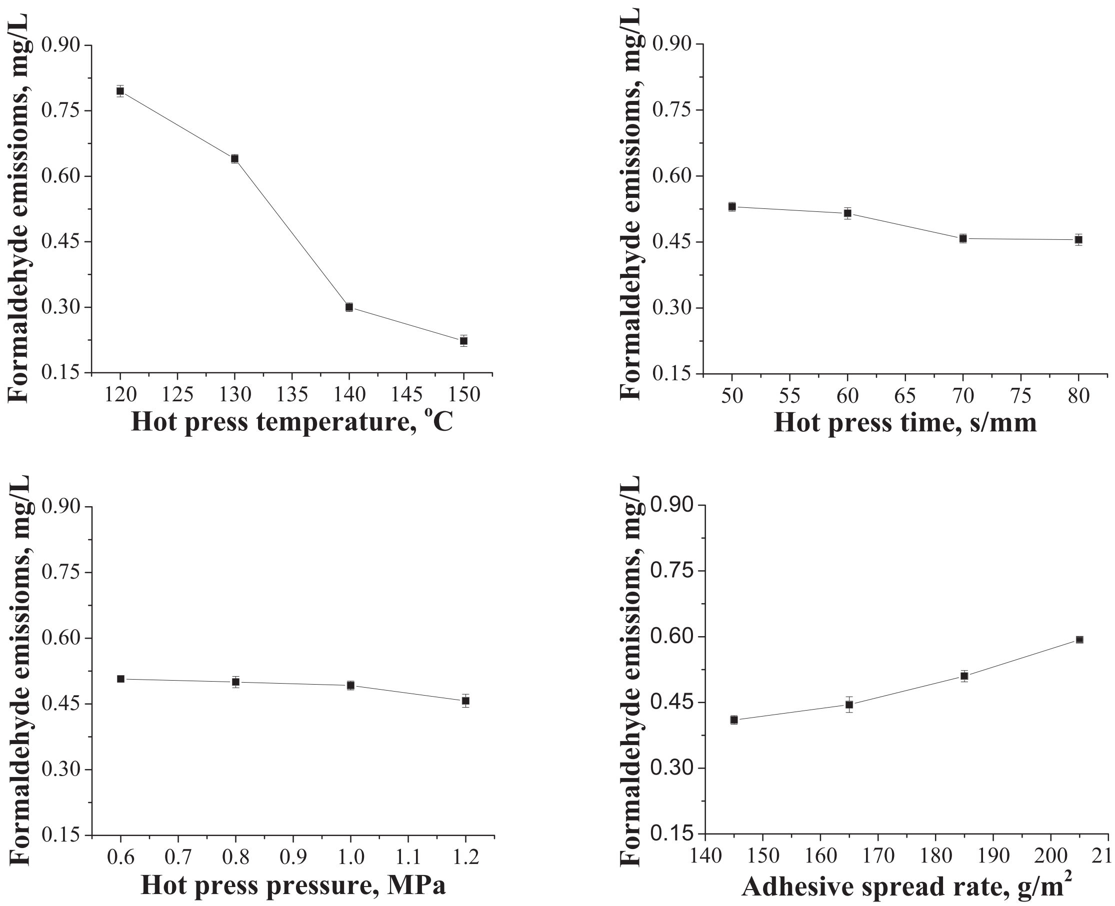

Figure 6.—Effect of process parameters on the formaldehyde emissions of the plywood.

0.6 to 1.2 MPa, or by changing the adhesive spread rate from 145 to 205 g/m^2.

Figure 6 shows the effect of processing parameters on the formaldehyde emissions of plywood panels bonded with the soybean meal/MUF adhesive. The formaldehyde emissions decreased as the hot press temperature increased from 120°C to 150°C. An elevated hot press temperature improved the extent of cure of the adhesive and reduced the residual free formaldehyde in the cured adhesive. The hot press time and pressure curves showed that the effects of hot press time (from 50 to 80 s/mm) and pressure (from 0.6 to 1.2 MPa) on formaldehyde emissions of plywood bonded by soybean meal/MUF adhesive were not strong. The adhesive spread rate curve showed that higher levels of adhesive spread rate increased the formaldehyde emissions of plywood. A higher level of adhesive spread rate brought more free formaldehyde into plywood to increase the formaldehyde emissions. According to the variance analysis at $\alpha = 0.05$, hot press temperature presented the highest effect on the formaldehyde emissions, then the adhesive spread rate, then the hot press time, and then the hot press pressure. No significant effect was observed when the hot press time varied from 50 to 80 s/mm and when the hot press pressure was changed from 0.6 to 1.2 MPa.

Based on balancing the wet shear strength and the formaldehyde emissions of the plywood bonded by the soybean meal/MUF adhesive and on energy saving, the optimum process parameters of the plywood were obtained and are shown in Table 2. The wet shear strength and the formaldehyde emissions of the plywood under the optimum hot pressing parameters are 1.18 MPa and 0.22 mg/liter, respectively, which met the Type II standard and E_0 level described in China National Standard GB/T 9846.3-2004 (Standardization Administration of The People's Republic of China 2004).

Conclusions

The DMA test showed that the storage modulus of the adhesive decreased to a minimum at the gelation temperature of 72.9°C and turned to increase to a maximum at 157.2°C. The vitrification temperature of the adhesive was obtained as 107.3°C. At a temperature higher than 157.2°C, the storage modulus began to decrease as the temperature increased because of the devitrification of the adhesive.

Table 2.—The wet shear strength and the formaldehyde emissions under the optimum hot pressing parameters.

Hot pressing temp (°C)	Hot pressing time (s/mm)	Hot pressing pressure (MPa)	Adhesive spreading (g/m)	Wet shear strength (SD) (MPa)	Formaldehyde emissions (SD) (mg/liter)
150	70	1.2	165	1.18 (0.03)	0.22 (0.01)

During hot pressing, the press temperature had a significant effect on both the wet shear strength and the formaldehyde emissions of plywood panels made with soybean meal/MUF adhesive. No significant effect was found on the wet shear strength and formaldehyde emissions of plywood by the hot press time from 50 to 80 s/mm and hot press pressure from 0.8 to 1.2 MPa. The adhesive spread rate had a significant effect on the formaldehyde emissions but not on wet shear strength from 145 to 205 g/m^2. The wet shear strength increased as the hot press temperature increased. The formaldehyde emissions decreased as the hot pressing temperature increased and increased as the adhesive spread rate increased. The optimum hot pressing parameters were 150°C hot press temperature, 70 s/mm hot press time, 1.2 MPa hot press pressure, and 165 g/m^2 adhesive spread rate. The values for the wet shear strength and the formaldehyde emissions under the optimum hot pressing parameters were 1.18 MPa and 0.22 mg/liter, respectively, which met the Type II plywood standard for bond strength and level E_0 for formaldehyde emissions described in China National Standard GB/T 9846.3-2004. Compared with the result of previous experiments (Gao et al., in press), the wet shear strength of the plywood was improved by 24.2 percent and the formaldehyde emissions of the plywood reduced by 21.4 percent when using the optimized hot press parameters.

Acknowledgments

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Literature Cited

Amaral-Labat, G. A., A. Pizzi, A. R. Goncalves, A. Celzard, S. Rigolet, and G. J. M. Rocha. 2008. Environment-friendly soy flour-based resins without formaldehyde. *J. Appl. Polym. Sci*. 108(1):624–632.

California Code of Regulations. 2008. Airborne Toxic Control Measure to reduce formaldehyde emissions from composite wood products. http://www.arb.ca.gov/regact/2007/compwood07/fro-final.pdf. Accessed December 12, 2011.

Gao, Q., S. Q. Shi, S. Zhang, and J. Li. Soybean meal based adhesive enhanced by MUF resin. *J. Appl. Polym. Sci*. (in press).

Huang, J. and K. C. Li. 2008. A new soy flour-based adhesive for making interior type II plywood. *J. Am. Oil Chem. Soc*. 85(1):63–70.

Jhonson, L. A., D. J. Myers, and D. J. Burden. 1984. Early uses of soy protein in Far East. *INFORM* 3:282–284.

Kim, M. G., W. L. S. Nieh, and R. M. Meacham. 1991. Study on the curing of phenol-formaldehyde resol resins by dynamic mechanical analysis. *Ind. Eng. Chem. Res*. 30(4):798–803.

Liu, K. S. 1997. Soybeans: Chemistry, Technology, and Utilization. Aspen Publication, New York.

Liu, Y. and K. C. Li. 2002. Chemical modification of soy protein for wood adhesives. *Macromol. Rapid Commun*. 23(13):739–742.

Liu, Y. and K. C. Li. 2004. Modification of soy protein for wood adhesives using mussel protein as a model: The influence of a mercapto group. *Macromol. Rapid Commun*. 25(21):1835–1838.

Menard, K. P. 1999. Dynamic Mechanical Analysis: A Practical Introduction. CRC Press, New York.

Meyer, B., B. A. K. Andrews, and R. M. Reinhardt. 1986. Formaldehyde Release from Wood Products. American Chemical Society, Washington, D.C.

Park, B. D. and J. W. Kim. 2008. Dynamic mechanical analysis of urea-formaldehyde resin adhesives with different formaldehyde-to-urea molar ratios. *J. Appl. Polym. Sci*. 108(3):2045–2051.

Standardization Administration of The People's Republic of China. 1999. Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels. GB/T 17657-1999. China Standard Press, Beijing.

Standardization Administration of The People's Republic of China. 2004. Plywood—Part 3: General specification for plywood for general use. GB/T 9846.3-2004. China Standard Press, Beijing.

Stoll, M. E., W. T. Schapaugh, M. S. Zutara, J. Hu, and X. S. Sun. 2006. Genotype and environment effects on adhesive shear strength in soybean-based adhesives. *Crop Sci*. 46(5):2008–2012.

Wang, D., X. S. Sun, G. Yang, and Y. Wang. 2009a. Improved water resistance of soy protein adhesive at isoelectric point. *Trans. ASABE* 52(1):173–177.

Wang, J. W., M. P. G. Laborie, and M. P. Wolcott. 2009b. Kinetic analysis of phenol-formaldehyde bonded wood joints with dynamical mechanical analysis. *Thermochim. Acta* 491(1–2):58–62.

Zhong, Z. and X. S. Sun. 2007. Plywood adhesives by blending soy protein polymer with phenol-formaldehyde resin. *J. Biobased Mater. Bioenergy* 1(3):380–387.