# Aging Resistance Properties of Poplar Plywood Bonded by Soy Protein-Based Adhesive

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The aging resistance properties of poplar plywood prepared with soy protein-based adhesives were investigated. The shear strength of soybean meal/bisphenol epoxy resin (SM/EP) adhesive increased by 197.5% (surface layer) to 1.19 MPa and 153.5% (core layer) to 1.09 MPa compared to soybean meal (SM) adhesive. Wet-dry cycles of 25 ± 3 °C, 63 ± 2 °C, and 95 ± 2 °C accelerated the aging of poplar plywood with soy protein-based adhesive. After eight 25 ± 3 °C wet-dry cycles, the shear strength of plywood bonded with SM/EP adhesive was reduced to 0.88 MPa (surface layer) and 0.71 MPa (core layer). Furthermore, the shear strength of SM adhesive gradually decreased to 0 (surface and core layer) after six and five 25 ± 3 °C wet-dry cycles. The shear strength of SM/EP adhesives was reduced to 0.96 MPa and 0.79 MPa (surface and core layer) after eight 63 ± 2 °C wet-dry cycles, and 0.53 MPa and 0.27 MPa (surface and core layer) after eight 95 ± 2 °C wet-dry cycles. Vertical density profiles indicated that the decrease of shear strength could be attributed to several factors: The small molecules were dissolved, the molecular chains of the adhesives were hydrolyzed by water, and the interior and thermal stress destroyed the bonding structure.

*Keywords:* Aging resistance; Soybean protein-based adhesive; Poplar plywood; Wet-dry cycle; Accelerated aging method

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## INTRODUCTION

Recently, soy protein-based adhesives have gained popularity as potential replacements for formaldehyde-based adhesives (Gao *et al.* 2011; Gao 2012; Mo and Sun 2013) because formaldehyde is a human carcinogen (Meyer *et al.* 1986). The disadvantages of soy protein-based adhesives, such as its low shear strength (Liu and Li 2004; Zhong and Sun 2007; Huang and Li 2008), low water resistance (Huang and Sun 2000; Zhong *et al.* 2003; Zhang and Hua 2007; Xiao *et al.* 2013; Lei *et al.* 2014; Zhang *et al.* 2014), and high viscosity (Amaral-Labat *et al.* 2008; Gao *et al.* 2011), have been addressed in various reports. In the plywood fabrication industry, melamine-urea-formaldehyde (MUF) resin with 3% melamine is used to bond indoor decorative-use plywood. Soy meal flour, sodium dodecyl sulfonate, and bisphenol epoxy resin (EP) can be combined into a soybean meal/bisphenol epoxy resin (SM/EP) adhesive (Luo and Luo 2014). The water resistance of the resultant adhesive was comparable to commercial MUF resin. The resultant durability of the bonded plywood is a crucial consideration in adhesive application and the aging resistance of plywood bonded by MUF has been evaluated in previous studies (Liu 2012); however, the properties of SM/EP have not been reported.

Commonly, aging resistance test methods are accelerated aging methods, including the ASTM D1037 (2006) and BS EN 321:2002 (2002) standards. However, these test

standards require strict, lengthy test conditions that hinder fast detection during production. Therefore, this study simulated indoor aging conditions with an accelerated wet-dry cycle and water temperatures of  $25 \pm 3$  °C,  $63 \pm 2$  °C, and  $95 \pm 2$  °C. These conditions were tested on plywood samples bonded with SM/EP, SM, and MUF adhesive, respectively. Aging experiments in natural conditions were also conducted. The vertical density profile of plywood bonded by soy protein-based adhesives was also evaluated.

## EXPERIMENTAL9

## Materials

Soybean meal (43% protein content) was provided by Xiangchi Grain and Oil Company (Shandong, China) and milled to 200 mesh size. MUF resin with a molar ratio of F: (M+U) = 1.01 and 3% melamine weight content was obtained from Jinyi Wood Products Corporation (Jiangsu, China). The polymer-bisphenol-A epoxy resin was synthesized from bisphenol-A, epichlorohydrin, and sodium hydroxide following a typical synthesis process where sodium hydroxide was added two times (Yang 2001). Guchuan Flour Mills (Beijing, China) provided flour for the MUF resin filler. Ammonium chloride (solid, analytically pure) was obtained from Beijing Chemical Industry Corporation (Beijing, China) and utilized as a curing agent for MUF resin. Poplar (*P. hopeiensis Hu et Chow*) veneer (8% to 10% moisture content) was obtained from Hebei Province, China.

## **Preparation of Adhesives**

To make the soybean meal (SM) adhesive, 28 g of soybean meal flour was added to 72 g of water and stirred for 20 min in a glass beaker at room temperature.

To make the soybean meal/epoxy resin (SM/EP) adhesive, 10 g of polymerbisphenol-A epoxy resin was added to SM and stirred for 20 min in a glass beaker at room temperature.

MUF adhesive was generated from MUF resin. MUF resin was synthesized with a F/(M+U) molar ratio of 1.01 and 3% melamine weight content. MUF resin synthesis was a typical three-step procedure (alkaline-acidic-alkaline), using a F/(M+U) molar ratio of 2.0 in the first stage and 1.4 in the second stage. MUF adhesive was produced by combining MUF resin, ammonium chloride, and flour at a weight ratio of 100: 0.6: 20. First, the ammonium chloride was added into the MUF resin and mixed for 5 min. The flour was added and further mixed for 15 min.

Process	Time (s)	Pressure (MPa)	
Booster	10	1.0	
Dwell	510	1.0	
Release	520	0.6	
Dwell	550	0.6	
Release	560	0.0	
Insulate	860	0.0	

## Table 1. Hot-Pressing Processes

## Preparation of the Samples

Adhesive was applied to one side of the poplar veneer ( $400 \times 400 \times 1.5$  mm) at a spread rate of 180 g/m<sup>2</sup>. Uncoated veneers were stacked between two adhesive-coated

veneers so that the grain direction of consecutive veneers perpendicular to one another. The assembled veneer stacks were pre-pressed at 1.0 MPa for approximately 10 min. Following the parameters shown in Table 1, the stacks were hot-pressed at 120 °C and stored in ambient conditions for 24 h before testing. Six samples of plywood were made for each formulation of the adhesive.

## Aging Methods

For each wet-dry cycle— $25 \pm 3 \,^{\circ}$ C (WD1),  $63 \pm 2 \,^{\circ}$ C (WD2), and  $95 \pm 2 \,^{\circ}$ C (WD3)—the specimens were soaked in water at the given temperature for 12 h, 3 h, and 3 h, respectively. They were then placed in a drying oven at 120  $^{\circ}$ C for several hours until a constant weight was obtained. After every treatment cycle, the shear strength of the specimens was determined as a measure aging resistance. For the natural aging process, the specimens were placed indoors and aged without any accelerated aging treatments. The shear strength of the specimens was tested every four months.

## Shear Strength Measurement

The shear strength of the plywood (type II) was determined using a wet shear strength test in accordance with GB/T 17657 (2013). Twelve plywood specimens (25 mm  $\times$  100 mm) were cut from two plywood panels, soaked in water at 63 ± 2 °C for 3 h, and dried at room temperature for 10 min before tension testing. The shear strength was calculated using Eq. 1.

Bonding strength (MPa) = 
$$\frac{\text{Tension Force (N)}}{\text{Gluing area}(\text{m}^2)}$$
 (1)

## **Vertical Density Profile Measurement**

Specimens of 50 mm  $\times$  50 mm were cut from the different plywood samples, and vertical density profile measurements were obtained using a section density meter (DA-X, GreCon Company, Alfeld, Germany).

Adhesive	SM/EP	SM	MUF
Surface Layer Shear Strength (MPa)	1.19±0.05	$0.40 \pm 0.05$	0.90±0.04
Core Layer Shear Strength (MPa)	1.09±0.06	0.43±0.04	0.98±0.11

Table 2. Plywood Shear Strength Before Aging

## **RESULTS AND DISCUSSION**

## Preparation of Plywood

In this study, SM/EP adhesive was developed to potentially replace the widely used MUF resin in indoor-use plywood. EP resin is a reactive cross-linker, with small resin molecules that react with themselves and with –NH2, –COOH, and other exposed groups of soy protein molecules. These cross-linking reactions increase the density of the adhesive and form a solid, interpenetrating network, which prevents moisture intrusion during hotpressing. As shown in Table 2, the shear strength of plywood bonded by SM/EP adhesive was increased by 197.5% (surface layer) to 1.19 MPa and 153.5% (core layer) to 1.09 MPa

compared with the SM adhesive; these values met the necessary requirements for interior plywood use ( $\geq 0.7$  MPa). The strength values were also 32% (surface layer) and 10% (core layer) higher than those of the MUF adhesive.

## WD1 Accelerated Aging

Figure 1 shows the effects of WD1 on plywood shear strength. The average shear strength (surface and core layer) values declined as the wet-dry cycles proceeded. Due to the low shear strength and water resistance associated with soy protein-based adhesives, the plywood bonded with SM showed poor aging resistance. After eight cycles the SM/EP plywood shear strength decreased by 26.05% (surface layer), from 1.19 MPa to 0.88 MPa, and 34.86% (core layer), from 1.09 MPa to 0.71 MPa. The shear strength of the MUF plywood decreased by 52.22% (surface layer), from 0.90 MPa to 0.43 MPa, and 68.37% (core layer), from 0.98 MPa to 0.31 MPa.

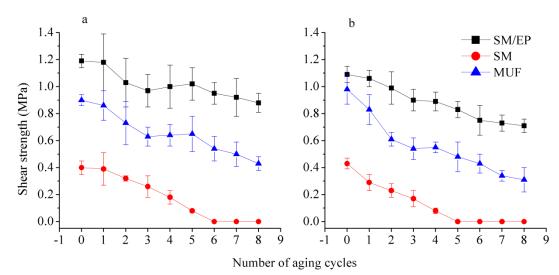


Fig. 1. The surface (a) and core layer (b) shear strength of plywood bonded with different adhesives after WD1 treatment

Water molecules are polar and small, and they destroy hydrogen bonds at the bonding interface, decreasing shear strength. Shear strength decreases further when bonded wood samples are submerged for a lengthier duration, due to polymer molecular chain hydrolysis. At the same time, the adhesive absorbs water and swells, creating interior forces at the bonding interface. When specimens were removed from the water and placed into the drying oven, the thermal stress quickly increased due to different thermal expansion coefficients between the wood and the adhesive, and the interior and thermal stress broke some polymer molecular chains. These factors combined to decrease the overall shear strength of the plywood.

These results demonstrated that the aging resistance of the SM/EP adhesive was better than that of the MUF adhesive. The SM/EP molecular chain had better tenacity than MUF, and the MUF resin hydrolyzed more. The core layer shear strength was lower than the surface layer for both SM/EP and MUF samples, likely because the water at the surface layer helped heat and re-cure some of the polymer molecules.

## WD2 Accelerating Aging

Figure 2 shows the effects of WD2 on plywood shear strength. Because hydrolysis is accelerated in higher temperatures, the soaking and drying times were reduced. The results differed considerably from those of WD1. In the SM/EP adhesive sample, the shear strength of the plywood increased by 21.85% (surface layer) to 1.45 MPa and 10.09% (core layer) to 1.20 MPa during the first two cycles. From the third cycle on, the shear strength continually decreased. After all eight cycles, the shear strength of the plywood had decreased by 19.33% (surface layer) to 0.96 MPa and 27.52% (core layer) to 0.79 MPa. Heating likely helped the epoxy resin interact with the soy protein-based adhesive and improved the degree of cross-linking in the cured adhesive. This enhancement mechanism was functionally stronger than interior/thermal stressor hydrolysis at the bonding interface during the first two cycles, increasing the overall shear strength. By the third cycle (and subsequently thereafter), the interior/thermal stress and hydrolysis became dominant and destroyed the bonding structure.

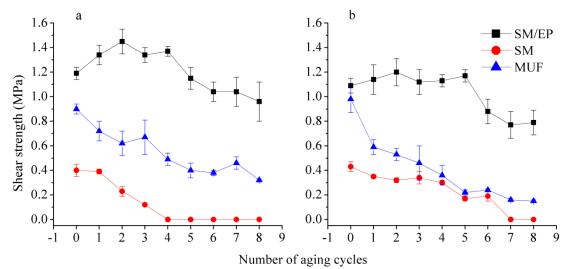


Fig. 2. The surface (a) and core layer (b) shear strength of plywood bonded with different adhesives after WD2 treatment

In the SM adhesive sample, the shear strength decreased compared to WD1 at a rate similar to what was expected. The SM sample likely re-cured during WD2 treatment to a greater extent than during WD1. In the MUF adhesive sample, interior/thermal stress and hydrolysis were consistently dominant in higher water temperatures, causing accelerated destruction of the molecular chain. The final shear strength was reduced by 64.44% (surface layer) to 0.32 MPa and 84.69% (core layer) to 0.15 MPa. WD2 test results also showed that the SM/EP adhesive had better aging resistance than the MUF adhesive and that SM/EP interacted more easily than MUF when heated.

## WD3 Wet-Dry Cycle Accelerating Aging

Figure 3 shows the effects of the WD3 treatment on plywood shear strength. Of all the treatments, WD3 was the harshest aging method. For all three adhesives, the majority of hydrolysis occurred within the first cycle and caused a rapid decline in the surface and core layer shear strength. MUF completely lost bond function, while the veneers in plywood were separated and the result also indicated that the 95 °C water had a strong destructive hydrolysis compared to 63 °C water. Moreover, the SM/EP surface and core

strength declined by 39.5% and 39.45%, respectively, and in SM, these values declined by 45% and 37%, respectively. The speed of hydrolysis then slowed and further destroyed the bonding structure under interior and thermal stress. The final shear strength of the SM/EP plywood was reduced by 55.46% (surface layer) to 0.53 MPa and 75.23% (core layer) to 0.27 MPa. Unexpectedly, the SM adhesive showed better resistance to boiling water than MUF. The soy protein molecular chain has certain tenacity while MUF molecular chain is brittle. This property helped SM resist separation from wood by water. Overall, WD3 testing showed that the SM/EP adhesive can have better aging resistance than MUF.

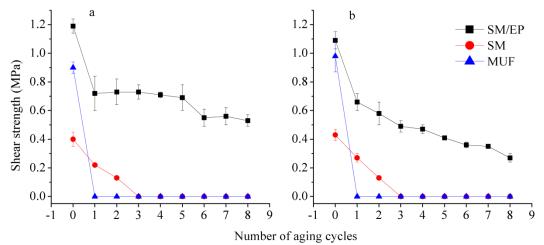


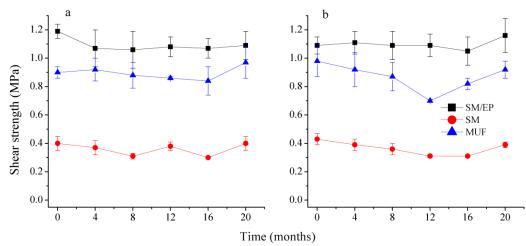
Fig. 3. The surface (a) and core layer (b) shear strength of plywood bonded with different adhesives after WD3 treatment

The results of tests with WD1, WD2, and WD3 all show that the SM/EP adhesive has the best aging resistance. The apparently different performance of MUF in each aging experiment shows its disadvantage of brittleness. The aging resistance of MUF under treatments of soaking the samples at temperatures of 63 °C and 95 °C for nearly 3 h has been evaluated the similar results in the study of Liu (2012). Compared with MUF, SM/EP molecular chain has a better tenacity to resist the destruction of water and stress.

## **Natural Aging**

When the specimens were placed indoors for 20 months without any treatment, the changes in plywood containing the different adhesives were irregular (Fig. 4). The testing time was not sufficient to distinguish the sample with the best aging resistance.

Humidity and temperature constantly change with the season and climate, causing a series of somewhat unpredictable chemical and physical changes at the bonding interface. Hydrogen bonds are recombined or destroyed, and the bonding structure loses or absorbs water and increases or reduces shear strength. Due to environmental variance during the natural aging test, changes in bond structure (which increased the shear strength) included the release of interior stress (which occurred during the hot press process), the re-curing of polymer molecules, and other relevant factors. These changes also may have occurred in inverse, reducing the shear strength. However, none of these changes existed independently. They varied according to the testing environment and worked together on the bonding structure, which generated irregular changes.



**Fig. 4.** The surface (a) and core layer (b) shear strength of plywood bonded with different adhesives after natural aging

Even though the changes were irregular, some values were consistent with the results of WD1. After one year of natural aging, the surface shear strength of SM and MUF plywood were 0.38 MPa and 0.86 MPa, respectively. The corresponding values of WD1 after one cycle of accelerated aging were 0.39 MPa and 0.86 MPa. Thus, the WD1 accelerated aging method approximated the natural aging results at some extent.

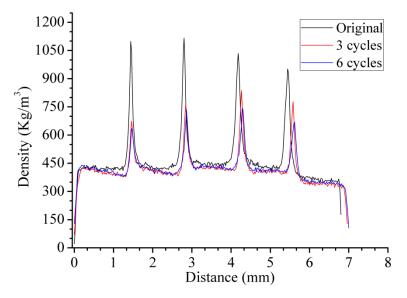


Fig. 5. Vertical density profile of plywood bonded with SM/EP adhesive

#### **Vertical Density Profile**

A vertical density profile shows the density distribution in composite panels, and it can detect adhesive layer variation during aging (Luo 2014). The  $25 \pm 3$  °C wet-dry cycle accelerating aging method was used to treat the sample for its steady and smooth decline of shear strength. The peaks in these figures represent the adhesive layers. During hot-pressing, the adhesive permeated into wood gaps, so that the density near the adhesive layer increased and showed penetration into the adhesive layer. After 3 cycles, the density of the three adhesive layers decreased sharply. Specifically, the penetration layer of SM/EP and

SM adhesives shrunk, which can be attributed to two events: the small adhesive molecule dissolved in water, and the adhesive molecular chain hydrolyzed. Results are shown in Figs. 5, 6, and 7.

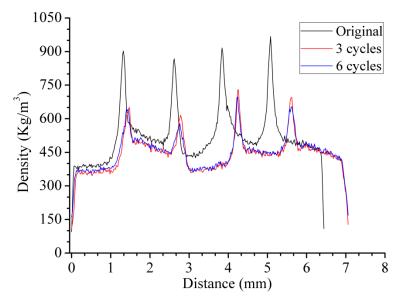


Fig. 6. Vertical density profile of plywood bonded with SM adhesive

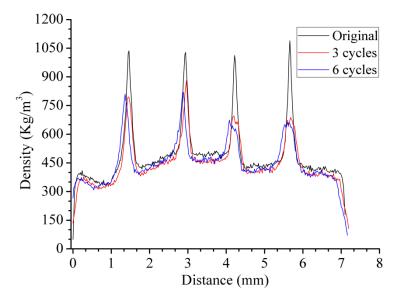


Fig. 7. Vertical density profile of plywood bonded with MUF adhesive

Both actions decreased the interlocking between wood and adhesive and greatly reduced the shear strength, which occurred within the 3-cycle treatment. The results were consistent with WD1 testing results, as the shear strength values declined. MUF adhesive had smaller polymer molecular chains, so the penetration layer did not shrink visibly. In the following 3 cycles, the density of the adhesive layers did not decrease obviously, but the shear strength declined steadily. Thus, the interior and thermal stress destroyed the bonding structure. Figure 6 shows that the plywood bonded by SM deviated significantly, and the bond structure was destroyed, which was consistent with the result showing that

SM had the poorest aging resistance in WD1. Compared with MUF resin, the SM/EP peaks were smoother, which indicated that the SM/EP molecular chain had a better tenacity than MUF. This observation was consistent with WD1 results showing that the SM/EP adhesive had the best aging resistance.

# CONCLUSIONS

- 1. SM/EP adhesive-bonded plywood had water resistance that was noticeably better than the SM adhesive and was better than MUF in the WD3 experiments. The SM adhesive benefited from the contributions of cross-linked network bonding structure and the resulting water resistance, tenacity, and re-curing.
- 2. Vertical density profiles showed that the shear strength decreased because the water dissolved small molecules and hydrolyzed the molecular chain of the adhesives, and the interior and thermal stress destroyed the bonding structure. The SM/EP molecular chain had a better tenacity than MUF.
- 3. SM/EP adhesive is a suitable replacement for the MUF adhesive, which is typically applied to decorative plywood because it has high shear strength and optimal aging resistance.
- 4. Of the accelerated aging methods tested, the  $25 \pm 3$  °C wet-dry cycle was the best aging method, as it best approximated the natural aging process.

## ACKNOWLEDGMENTS

The authors are grateful for financial support from the Beijing Natural Science Foundation (2151003) and the Special Fund for Forestry Research in the Public Interest (Project 201404501).

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Article submitted: October 23, 2015; Peer review completed: February 6, 2016; Revised version received: March 5, 2016; Accepted: March 19, 2016; Published: March 29, 2016. DOI: 10.15376/biores.11.2.4332-4341