Effect of p-Cumylyphenol on the Mold Resistance of Modified Soybean Flour Adhesive and Poplar Plywood

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Soy-based adhesive’s sensitivity to microbial attack is an aspect that restricts its future application. In an attempt to combat microbial attacks, several preservatives have been evaluated to determine their effects on mold resistance. In this paper, the inhibitory effect of p-cumylphenol was investigated by observing mold growth on modified soybean-flour adhesives and by evaluating the bonding strength and surface mold growth of bonded poplar plywood. Visual images, scanning electron microscopy, and tensile testing were used. The results showed that the initial microbial attack was delayed and the degree of attack was alleviated because of the preservatives. The bonding strength decreased in samples that contained p-cumylphenol after the samples were exposed to high humidity. Additionally, no correlation was observed between the degree of microbial growth on the surface of the plywood and amount of the preservatives. These results revealed that it was feasible to incorporate p-cumylphenol into soy-based adhesives as glue line treatment to improve the mold resistance. Finally, surface treatment of the veneer should be taken into consideration during the plywood manufacturing.

Keywords: Soybean-flour adhesive; P-cumylphenol; Mold resistance

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INTRODUCTION

The development of adhesives from renewable materials will allow for greater sustainability and continued success for the wood composite panel industry as alternatives to the finite reserves of natural gas and fossil oil (Schwarzkopf et al. 2009; Liu et al. 2014). As one of the most environmentally friendly wood adhesives, soy-based adhesive has numerous advantages, such as low cost, easy handling, and low pressing temperature (Huang and Li 2008).

However, further application of wood composites bonded with soy-based adhesives has been limited. This is partially due to the composite’s sensitivity to biological degradation with increased exposure to wetness and microorganisms (Rogers et al. 2004; Kirkpatrick and Barnes 2006). The damage to the plywood is identified as adhesive bond failure (Kartal and Green 2002), delamination, and the consequent weakening of plywood construction (Kaufert and Blew 1962). It also contributes to economic, health, and aesthetic problems (Johansson et al. 2012; Cheng et al. 2013). The costs associated with the renovation of the contaminated boards are substantial (Johansson et al. 2012). Furthermore, spores present in the air may cause asthma episodes, allergic reactions, infections, and other
respiratory diseases (Cheng et al. 2013). Aesthetic problems also should be taken into consideration when molds grow on boards. However, only limited numbers of studies have focused on this issue (Wang et al. 2008).

Experiments involving preservatives, soy-based adhesives, and glued plywood have been conducted at the Forest Products Laboratory from as early as 1940 (Forest Products Laboratory 1960; Kaufert 1961; Kaufert and Blew 1962). The primary objective of those studies was to determine the effectiveness of 20 chemicals and propose techniques for rapid and accurate evaluation for their efficiency. It was possible to greatly enhance the mold resistance of soybean glue joints with the addition of sufficient quantities of effective preservatives. Chlorophenols, sodium chlorophenates, orthophenylphenol, and sodium orthophenylphenate have been shown to be effective when used as preservatives for soy-based adhesives. *Rhizopus oryzae* and *Penicillium citrinum* were isolated from soy-based adhesive by Zhai et al. (2012). Sodium diacetate and sodium borate were believed to be the appropriate preservatives for inhibiting their growth.

As a material widely used for fungicide, preservative, and anti-termite agent (Nakazawa et al. 2009; Wantling 2010), *p*-cumylphenol has been reported in some patents as a wood preservative (Higaki 2003; Leach and Zhang 2013). Based on its known application in wood protection, it is possible to apply *p*-cumylphenol to the glue line as a preservative to alleviate mold growth on soy-based adhesives.

Uniform preservative distribution within the product provides much better protection than the typical “shell” treatments provided by post-treatment processes (Vidrine et al. 2008). Because the incorporation of preservatives, along with adhesives (also called glue line treatment), is one of the technological methods often adopted for use during in-process treatment (Kirkpatrick and Barnes 2006), it was used in this research. The objective of this research was to determine the effectiveness of *p*-cumylphenol for protecting modified soybean-flour adhesive from mold growth, as well as maintaining the durability of the bonded plywood.

**EXPERIMENTAL**

**Materials**

Soybean flour, with an average protein content of 45.2% and moisture content of 5.0%, was purchased from the Sanhe Hopefull Group Oil Grain Food Co. Ltd (Hebei, China). The poplar veneer was obtained from Wen’an (Hebei, China) and had a moisture content of 7% to 10%. Preservatives A (*p*-cumylphenol, white, purity > 99.7%) and B (*p*-cumylphenol, semi-finished product, red, purity of approximately 95%) were donated by the Beijing Xing Li Gong Mao Co., Ltd. All other chemicals used were analytical-grade reagents from Beijing Chemical Reagents Co., Ltd.

**Methods**

*Preparation of modified soybean-flour adhesives*

The modified soybean-flour (MSF) adhesive was prepared according to a previous study (Li et al. 2014). Soy flour, polyvinyl alcohol, glycerol polyglycidyl ether, and tap water were added to a three-neck flask and the mixture was stirred at room temperature. The solid content (30%) was determined according to China National Standard GB/T 14074-2006 (2006), and viscosity (10 mPa·s) was measured using a rheometer with a parallel plate fixture (20 mm diameter).
Preparation of preservative-treated MSF adhesives

Forty grams of preservatives A and B were dissolved, individually, in 20 g of ethanol solution and stirred for 20 min, until the preservatives were well dispersed, at room temperature. Various amounts of the resulting solutions were added to MSF adhesives (180 g) with sufficient stirring. Two replicates were prepared for each sample. Different formulations of the adhesives were as shown in Table 1.

Table 1. Formulations of Preservative-treated MSF Adhesives

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added MSF Adhesive (g)</th>
<th>Added Preservative Mixtures (g)</th>
<th>Contained Pure Preservatives (g)</th>
<th>wt% of Preservative</th>
<th>Preservative Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>180</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>1</td>
<td>180</td>
<td>1.35</td>
<td>0.90</td>
<td>0.50</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
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<td>1.80</td>
<td>1.00</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>4.05</td>
<td>2.70</td>
<td>1.50</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>5.40</td>
<td>3.60</td>
<td>2.00</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>1.35</td>
<td>0.90</td>
<td>0.50</td>
<td>B</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>2.70</td>
<td>1.80</td>
<td>1.00</td>
<td>B</td>
</tr>
<tr>
<td>7</td>
<td>180</td>
<td>4.05</td>
<td>2.70</td>
<td>1.50</td>
<td>B</td>
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<tr>
<td>8</td>
<td>180</td>
<td>5.40</td>
<td>3.60</td>
<td>2.00</td>
<td>B</td>
</tr>
</tbody>
</table>

- no preservative was used

Evaluation of mold resistance for preservative-treated MSF adhesives

Five grams of each fresh preservative-treated MSF adhesive were transferred into petri dishes and conditioned at 28 °C and 95% relative humidity (RH) in a conditioning chamber (JING HONG MJPS-150, China) for 12 weeks. Mold growth was graded visually and recorded by a digital camera (Nikon COOLPIX S3600, Japan).

After the high humidity exposure, samples No. 0, No. 4, and No. 8 were placed in an oven at 60 °C until a constant weight was obtained. Then, the morphology of the cross sections was observed using a scanning electron microscope (SEM, Hitachi S-3400N, Japan).

Preparation of plywood bonded by preservative-treated MSF adhesives

Poplar veneers with the dimensions of 400 mm × 400 mm × 1.6 mm were used. Then eight pieces of three-ply plywood with eight kinds of adhesive samples were prepared under the following hot-pressing parameters: 180 g/m² of glue spreading, 360 s of hot pressing time, 120 °C of hot pressing temperature, and 1.0 MPa of hot pressing pressure. After hot pressing, the plywood was stored at ambient conditions for a minimum of 24 h.

Evaluation of bonding strength for plywood specimens

Six replicated specimens, with dimensions of 100 mm × 25 mm, were cut from each piece of plywood, and then one small cut were made in each surface ply of the specimens to form an area of 25 mm × 25 mm. The bonding strength was determined after these specimens were stored at 28 °C and 95% RH for 2- and 4-week conditioning cycles.

The bonding strength of the plywood specimens was determined according to China National Standard GB/T 17657-1999 (1999). The specimens were soaked in a water bath at 63°C for 3 h and then cooled for 10 min at room temperature. The test was conducted on a tensile testing machine (Ke Hui WDW-50D, China) with a crosshead speed of 10.0
mm/min. The loading was applied until a break or separation occurred on the surface of the test specimens. Meanwhile, the observed maximum load ($F_{\text{max}}$, in kN), bonding surface ($A$, in mm$^2$), and bonding strength ($X$, in MPa) were calculated as follows. The average of six replicates was considered in the analysis.

$$X = \frac{F_{\text{max}}}{A} \quad (1)$$

**Evaluation of mold resistance for the plywood specimens**

In addition to the bonding strength, mold growth on the surface of the plywood specimens was recorded using a digital camera, after the specimens were conditioned at 28 °C and 95% RH for 4 weeks.

**RESULTS AND DISCUSSION**

**Evaluation of Mold Resistance for Preservative-treated MSF Adhesives**

*Visual observations of the adhesive surfaces*

All the adhesive samples successively showed mold growth during 12 weeks at 28 °C and 95% RH (Table 2). White colonies were first detected on the untreated MSF adhesive (Sample No. 0) rather than the preservative-treated ones, which suggested that the untreated adhesive is more vulnerable to microbial attack than the preserved ones.

**Table 2. Degree of Mold Growth on the Surface of Adhesive Samples at 28 °C and 95% RH for 12 Weeks**

<table>
<thead>
<tr>
<th>Time (week)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<td></td>
<td>+</td>
<td>++</td>
<td>+++</td>
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<td>+++</td>
<td>+++</td>
<td>+++</td>
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<tr>
<td>10</td>
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<td>+++</td>
<td>+</td>
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<tr>
<td>11</td>
<td>++++</td>
<td>+++</td>
<td>++</td>
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<td>+</td>
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<tr>
<td>12</td>
<td>++++</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Blank stands for absence of growth.  
+ infected area < 25%, ++ 25% < infected area < 50%, +++ 50% < infected area < 75%, ++++ 75% < infected area < 100%, +++++ 100% of adhesive surface was covered by microorganisms.  
+++++ Change in mycelium color.

On the 61$^{\text{st}}$ day, some visible white colonies appeared on Sample No. 1, which contained 0.5% preservative A. At the same time, Sample No. 0 contained the heaviest microorganism damage, and the color of some colonies had turned from white to yellow.

On the 65$^{\text{th}}$ day, some microbial growth was found on the surface edge of Sample No. 5, and the mold was more vigorous on Sample No. 1. Sample No. 4 (which contained the highest amount of preservative A) showed microbial growth earlier than Samples 2 and 3, which both contained lower amounts of preservative A. In sample No. 4, the high
Addition amount of preservative resulted in fully reaction between MSF adhesive and p-cumylphenol, causing the stretched structure of soy protein and expansion of the volume with scattered and thinner surface area. Additionally internal stress increased due to the active reaction and the difference with the surface tension produced more cracks in the sample No. 4. Therefore, the contact area between the adhesive and air, moisture, or microorganisms would be increased, subjecting the sample to increased microbial growth. However, successive mold growth was stabilized and inhibited because of the inhibitory effect caused by a greater amount of preservative A in the sample (Table 2 and Fig. 1a).

Microbial growth was found on all adhesive samples after 12 weeks at 28 °C and 95% RH (Fig. 1). Sample No. 0 suffered the heaviest microbial attack. The samples that contained a greater amount of preservatives suffered lighter microbial attack than those that contained less. A preservative content of 1.5% or 2% could be the appropriate formation if satisfactory mold resistance is desired. In addition, incorporating preservative A increased the inhibition effect on the surface of the samples compared to incorporation of preservative B.

A change in mycelium color from white to dark yellowish brown appeared on Sample No. 0; however, it was not observed among all preservative-treated MSF adhesives, suggesting that the physiological phases of the microorganism life cycle would be slowed down by incorporating preservatives A and B into the adhesives (Fig. 1). Similar color changes were detected by Zhai et al. (2012), which can be classified as one of the most prominent characteristic of Rhizopus oryzae. Therefore, identification of the fungal species, considering the micromorphology of the mycelium, should be conducted in follow-up research.

**Fig. 1.** All adhesive samples were conditioned at 28 °C and 95% RH for 12 weeks; a) control sample and samples that contained preservative A; b) control sample and samples that contained preservative B

**SEM analysis of the adhesive cross sections**

After being cultivated for 12 weeks, the whole area of the cross section in Sample No. 0 was densely full of microorganisms (Fig. 2a). However, no spores and mycelia were found in Samples No. 4 and No. 8 (Figs. 2b and 2c). The results indicated that the inhibitory effect of preservatives A and B did in fact exist in the internal portion of adhesive samples,
even if the microbial growth was solely found on the surfaces during visual observation (Fig. 1).

Phenolics are a major group of compounds that are considered to be toxic to microorganisms. They can potentially inactivate enzymes, intercalate into the cell wall or DNA, and disturb the function of bacterial cell membranes, which causes the retardation of both the growth and multiplication of bacteria (Sivarooban 2008). The p-cumylphenol compound has one phenolic hydroxyl group. The site and number of hydroxyl groups on the phenol group could possibly be responsible for the antimicrobial activities (Cowan 1999; Ultee et al. 2002).

**Fig. 2.** Cross sections of adhesive samples conditioned at 28 °C and 95% RH for 12 weeks; a) sample No.0, SEM picture at 100×; b) sample No.4, SEM picture at 100×; c) sample No.8, SEM picture at 100×

The spores and mycelia in Sample No. 0 are illustrated at a higher magnification in Fig. 3. Using a search software in the field of microbiology (Basic Local Alignment Search Tool), the internal transcribed spacer sequences of these microorganisms were highly homologous to those from *Aspergillus* sp., which suggested that the microorganisms which attacked the untreated MSF adhesive most likely belongs to *Aspergillus* sp. Other tests (such as phylogenetic analysis) are to be conducted to further identify the strains.

**Fig. 3.** Cross sections of sample No.0 conditioned at 28 °C and 95% RH for 12 weeks; a) SEM picture at 2.00 k×; b) SEM picture at 5.00 k×; c) SEM picture at 10.0 k×

**Evaluation of Mold Resistance for Plywood Specimens**

**Bonding strength**

Figure 4a shows the changes in the bonding strength of plywood specimens during high humidity exposure when different amounts of preservative A were incorporated. The bonding strength of Sample No. 0 was found to be decreased by 20.03% after exposure. The decreased bonding strength may result from the massive mold growth experienced by the sample (Fig. 2a). In addition, both Samples No. 1 and No. 2 showed a decrease of less than 8% after being conditioned for four weeks, while there was an increase in the bonding strengths of Samples No. 3 and No. 4, which contained higher dosages of preservative A.
Furthermore, there was a 26.75% increase in the bonding strength of Sample No. 4, which contained 2% preservative A. The increases in the bonding strength were attributed to the following aspects. Firstly, microbial attack was considerably avoided because of the excellent inhibitory effect brought by the high dosage of preservative. In this case, the bonding strength would not decrease due to the microbial attack. Otherwise, the presence of microorganisms will decompose soy protein, ruin the structure of its internal structure, and eventually degrade the bonding performance. Secondly, the adhesive continued to cure during the treating condition, permeating into wood gaps, forming an interlock between two veneers, and increasing the density of the adhesive layer. Additionally, the interior force was released and approached a balance during the conditioning, which also would improve the bonding strength (Luo et al. 2014). In addition, a dense and homogeneous phase of the blend also benefited from the increased bonding strength (Fig. 2b). A similar result was obtained by the Forest Product Laboratory, whereby in some cases the preservatives did not decrease but rather increased the joint strength after exposure for 4 weeks (Kaufert and Blew 1962).

Figure 4b shows the changes in the bonding strength after the addition of preservative B. The bonding strength for both samples No. 5 and No. 8 decreased to below 0.7 MPa, which is not acceptable according to the requirements of the China National Standard (GB/T 9846.3-2004 2004). Hydrogen bonds existed in amino and hydroxyl groups between MSF adhesive and P-cumylphenol. However, it was relatively weak because of the low purity of preservative B and the interference of some impurity components. In that case, a rough and heterogeneous surface was observed in Sample No. 8, which suggested that the compatibility between MSF adhesives and preservative B was not satisfactory (Fig. 2c). Additionally, lower bonding strength also resulted from the decreased water content due to the high solid content. Therefore these features resulted in the lower bonding strength.

Mold growth

The surfaces of all of the plywood segments, after being subjected to high humidity exposure for four weeks, were covered by black or yellow mycelia on the surfaces.
However, no distinguishable differences in the degree of mold growth were observed. One specimen of six replicates for eight kinds of plywood samples are shown in Fig. 5.

The veneers were not protected by preservatives and were still vulnerable to microorganisms during the storage. This phenomenon revealed that the preservation of the adhesive did not prevent the growth of molds on the surface of the panels, which (because no surface treatment was used) resulted in unprotected surfaces and edges. This finding was consistent with the results reported by the Forest Products Laboratory (Kaufert and Blew 1962). The study also highlights the necessity for the combination of the adhesive preservation and panel surface treatments.

Fig. 5. Surfaces of one specimen of six replicates conditioned at 28 °C and 95% RH for 4 weeks

CONCLUSIONS

1. The mold growth in the internal parts of treated MSF adhesives was restrained when preservative A and B were incorporated. Moreover, the mold resistance on the adhesive surfaces was better controlled when incorporating preservative A (higher purity) in a content range of 1.5 wt% to 2 wt%.

2. During high humidity exposure, the bonding strength of the plywood treated with preservative A declined minimally and even increased when a content of 2% was used while that of the plywood treated with preservative B was not satisfactory.

3. Both the mold resistance of MSF adhesives and poplar plywood were improved when p-cumylphenol was added in the glue line as a preservative. However, it did not successfully preserve the surfaces of the panels, which is considered a task for future work.

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