FUNGAL RESISTANCE OF LOBLOLLY PINE REACTED WITH PARA-TOLUENE SULFONYL CHLORIDE OR ISOCYANATE

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ABSTRACT

Loblolly pine sapwood reacted with para-toluene sulfonyl chloride or isocyanate to form bonded toluene sulfonate or toluene sulfonyl carbamate in situ resisted attack by the brown-rot fungus Gloeoephyllum trabeum. Wood reacted with para-toluene sulfonyl chloride to 9.1% chemical weight gain (59 mmol/100 g wood) and para-toluene sulfonyl isocyanate to 7.5% chemical weight gain (56 mmol/100 g wood) had 3.8 and 2.7% weight losses, respectively, in a standard 12-week soil-block fungal decay test. The tosylated wood lost 23% of the tosyl group in the decay test, whereas the wood modified with tosyl carbamate lost 8.4% of the tosyl carbamoyl group. The greater leach resistance of wood reacted with para-toluene sulfonyl isocyanate may indicate that the stability of the bond between fungicidal groups and wood plays a more important role than the hydrophobicity of fungicidal groups in the permanence of the fungicidal groups in modified wood.

Keywords: Para-toluene sulfonyl chloride, para-toluene sulfonyl isocyanate, modified wood, fungal resistance, Gloeoephyllum trabeum, loblolly pine.

INTRODUCTION

The Forest Products Laboratory has been investigating unconventional wood protection methods for many years (Rowell 1975, 1977, 1982, 1983a). Two methods are currently under investigation: the controlled release of biocides and the bonding of nonbiocidal reactive compounds to wood.

Protecting wood against biodegradation through the controlled release of biocides has two advantages: this method minimizes leaching of excess biocides into the environment, and it extends the period of decay control. The biocides are released in the treated wood at a specified rate. They can be introduced in the wood in three ways. The first way is direct impregnation of biocidal polymers into the cell lumen of wood. Organotin polymers have been impregnated directly into the cell lumen of wood (Anderson 1979). Biocidal polymers in the form of films (Pittman et al. 1978; Pittman and Lawyer 1982) or biocides encapsulated in the polymeric matrixes (Noren et al. 1986) have also been investigated for protection of the wood surface. The second way is in situ polymerization of the biocide-bonded monomers in the cell lumen of wood. Acrylates or methacrylates of pentachlorophenol, pentabromophenol, and tri-n-butyltin have been polymerized in the cell lumen of wood (Rowell 1983b; Subramanian et al. 1978). The third way is direct bonding of biocidal compounds to the cell-wall polymers of wood (Rowell 1984; Chen et al. 1990). In bonding biocides to wood, we found that reacting wood with fluorophenyl isocyanates was effective in preventing attack by wood decay fungi (Chen et al. 1990). The mechanism of efficacy against fungal degradation is due primarily to the release of fungicidal fluorophenyl compounds from the modified wood. However, the hydrophobicity
of the fungicidal groups also plays an important role in the permanence of these groups in wood.

The other unconventional wood protection method, the bonding of wood to compounds containing reactive functional groups, is being investigated to a greater extent than is the controlled release of biocides. Isocyanates, epoxides, and anhydrides have been bonded to wood; the resultant modified woods have been resistant to attack by fungi (Ellis and Rowell 1984; Rowell and Gutzmer 1975; Phil and Olsson 1968; Goldstein et al. 1961; Tarkow et al. 1950), termites (Rowell et al. 1979; Imamura and Nishimoto 1986), and marine organisms (Rowell 1982; Johnson and Rowell 1989). The mechanism by which these modified woods resist attack by fungi is mainly an increase in the hydrophobicity of the wood as a result of wood-substrate modifications. Hydrophobicity prevents water diffusion into the cell-wall polymers of wood, thereby preventing enzymatic hydrolysis of the wood (Stamm and Baechler 1960).

In our continuing investigation of bonding biocidal compounds to wood, we are searching for potential fungicides with reactive functional groups that can react with hydroxyl groups of the cell-wall polymers of wood. Para-toluene sulfonyl isocyanate and para-toluene sulfonyl chloride are reactive organic compounds that react with active hydrogen compounds, including hydroxyl groups of wood cell-wall polymers. Popov et al. (1980) showed that sulfones of benzene sulfonyl chloride as well as benzene sulfonamide possess fungicidal activity. Sulfones of 2,3,5,6-tetrachloro-4-methylsulfonyl pyridine (Noren et al. 1986) and diiodomethyl-p-tolyl sulfone (Cassens and Eslyn 1981) are known fungicides. The purpose of our study was to bond para-toluene sulfonyl chloride or para-toluene sulfonyl isocyanate to wood and to determine the fungal decay resistance of these modified woods.

**MATERIALS AND METHODS**

*Reaction of wood with para-toluene sulfonyl chloride*

Twenty-eight loblolly pine sapwood blocks (95.1 g, calculated as anhydrous glucose pyranose equivalent, 517 mmol) (1.9-cm cubes) were dried at 60 C for 1 day and weighed. The blocks were placed in a desiccator under vacuum at 2.0 to 3.3 kPa for 2 h. The blocks were impregnated with pyridine (500 ml, dried over a 4-Å molecular sieve for more than 1 day). Para-toluene sulfonyl chloride (98.52 g, 517 mmol) was then added to the blocks and reacted at 75 C for 6 h. During reaction, seven blocks were withdrawn at intervals of 1, 2, 4, and 6 h. The seven blocks from each treatment group were soaked in acetone (350 ml) for 1 day and then extracted with acetone for 12 h in a Soxhlet extractor. The blocks were air-dried under a hood for 1 day and then heated in an oven at 60 C for 1 day. The average weight gain of chemical in the wood was 1.2, 3.2, 6.2, and 8.7% for the blocks reacted for 1, 2, 4, and 6 h, respectively. Chemical weight gain in the wood was based on weight of oven-dried wood at 60 C for 1 day before and after reaction. Five blocks from each treatment group were conditioned at 27 C and 30% relative humidity (RH) for 3 weeks prior to the soil-block decay test.

Blocks with an average weight gain of 9.1% chemical were obtained as follows. Twelve loblolly pine sapwood blocks (45.5 g, calculated as anhydrous glucose pyranose equivalent, 247 mmol) were dried at 60 C for 1 day and then placed in a desiccator under vacuum at 2.1 to 3.3 kPa for 40 min. The blocks were impregnated with pyridine (200 ml, dried over a 4-Å molecular sieve for more than 1 day). Para-toluene sulfonyl chloride (47.15 g, 247 mmol) was then added to the blocks and reacted at 75 C for 10 or 12 h. Six blocks were withdrawn at each time point. Procedures to purify and to condition the blocks were the

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2 This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed have been registered. All uses of pesticides must be registered by appropriate state and/or federal agencies before they can be recommended.
same as described for the set of 28 blocks. The average chemical weight gain in the wood was 7.8 and 9.1% for 10 and 12 h of reaction, respectively.

Reaction of wood with para-toluene sulfonyl isocyanate

Twelve loblolly pine sapwood blocks (45.2 g, calculated as anhydrous glucose pyranose equivalent, 246 mmol) were dried at 60 C for 1 day and weighed. The blocks were placed in a desiccator under vacuum at 2.1 to 3.3 kPa for 40 min and then impregnated with pyridine (190 ml, dried over a 4-A molecular sieve for more than 1 day). Para-toluene sulfonyl isocyanate (14.52 ml, 113 mmol) was then added to the blocks and reacted at 80 C for 6 h. During reaction, six blocks were withdrawn after 3 h, and the remaining 6 blocks were withdrawn after 6 h. The six blocks from each treatment group were soaked in acetone (300 ml) for 1 day and then extracted with acetone in a Soxhlet extractor for 12 h. The blocks were air-dried for 1 day and then heated in an oven at 60 C for 1 day. The average chemical weight gain in the wood was 1.5 and 2.8% for 3 and 6 h of reaction, respectively. Chemical weight gain in the wood was based on weight of oven-dried wood at 60 C for 1 day before and after reaction. Five blocks from each treatment were conditioned at 27 C and 30% RH for 3 weeks prior to the soil-block decay test.

Blocks with average chemical weight gain of 5.7 and 7.5% were obtained as follows. Twelve loblolly pine sapwood blocks (44 g, calculated as anhydrous glucose pyranose equivalent, 239 mmol) were dried at 60 C for 1 day and weighed. The blocks were placed in a desiccator under vacuum at 2.1 to 3.3 kPa for 40 min and then impregnated with pyridine (200 ml, dried over a 4-A molecular sieve for more than 1 day). Para-toluene sulfonyl isocyanate (18.94 ml, 147 mmoles) was then added to the blocks and reacted at 90 C for 10 or 14 h. Six blocks were withdrawn at each time point. The procedures to purify and condition the blocks were the same as described for the other treatment groups. The average chemical weight gain in the wood was 5.7 and 7.5% for the blocks reacted for 10 and 14 h, respectively.

Analysis

Infrared spectra of wood reacted with para-toluene sulfonyl chloride or isocyanate were recorded on an infrared instrument using KBr pellets.

Decay test

Fungal decay tests were performed for 12 weeks according to the ASTM standard (ASTM 1990) using the brown-rot fungus Gloeophyllum trabeum (Pers. ex Fr.) Murr. (Madison 617). Five replicate blocks were used in the fungal decay test. The extent of fungal attack was determined by weight loss of the blocks.

RESULTS AND DISCUSSION

Proof of bonding

Bond formation between para-toluene sulfonyl chloride and wood was evidenced by the characteristic sulfonate and phenyl infrared absorptions of the modified wood. The absorptions at 1,365 and 1,165 cm⁻¹ are attributed to asymmetric and symmetric stretching vibrations of the SO₂ group, and those at 1,235 and 1,035 cm⁻¹ to stretching vibration of the S=O group (Socrates 1980; Conley 1970). The absorption at 2,850 cm⁻¹ is attributed to aromatic C-H stretching vibration; those at 1,600, 1,510, and 1,450 cm⁻¹ to aromatic ring vibration; and those at 8 15 and 660 cm⁻¹ to out-of-plane aromatic C-H bending vibration (Socrates 1980; Conley 1970) (Fig. 1 B).

For wood reacted with para-toluene sulfonyl isocyanate, bond formation between para-toluene sulfonyl isocyanate and wood was evidenced by the characteristic carbamate and sulfonamide infrared absorptions. The spectrum for unmodified wood, which absorbs strongly at 1,730 cm⁻¹, is attributed to aromatic C-H stretching vibration; those at 1,600, 1,510, and 1,450 cm⁻¹ to aromatic ring vibration; and those at 815 and 660 cm⁻¹ to out-of-plane aromatic C-H bending vibration (Socrates 1980; Conley 1970) (Fig. 1B).
Wavenumber (cm\(^{-1}\))

Fig. 1. Infrared spectra of control wood and wood reacted with para-toluene sulfonyl chloride: (A) control; (B) 8.1% sulfonylate.

The carbamoyl group in modified wood absorbs strongly at 1,740 cm\(^{-1}\), which is attributed to carbonyl stretching vibration. The spectrum of sulfonamide, which absorbs at 1,360 and 1,160 cm\(^{-1}\), is attributed to asymmetric and symmetric stretching vibrations of the SO\(_2\) group. The absorptions at 1,230 and 1,035 cm\(^{-1}\) are attributed to stretching vibration of the S=O group (Socrates 1980; Conley 1970). The spectrum of the phenyl group of wood modified with para-toluene sulfonyl carbamate, which absorbs at 2,890 cm\(^{-1}\), is attributed to aromatic C-H stretching vibration, the absorption at 1,450 cm\(^{-1}\) to aromatic ring vibration, and the absorptions at 815 and 660 cm\(^{-1}\) to out-of-plane aromatic C-H bending vibration (Socrates 1980; Conley 1970). The intensity of these absorptions became stronger as weight gain of the para-toluene sulfonyl carbamoyl group in the modified wood increased from 6.1 to 12.4% (Fig. 2B, C).

Wood decay and loss of chemicals

Gloeophyllum trabeum caused weight losses of 5.1 and 3.8% in wood reacted with para-toluene sulfonyl chloride to weight gain of 8.7% (56 mmol/100 g wood) and 9.1% (59 mmol/100 g wood), respectively. Wood reacted with para-toluene sulfonyl isocyanate to a weight gain of 7.5% (56 mmol/100 g wood) also had a small weight loss (2.7%) (Table 1). This indicates that wood modified with para-toluene sulfonyl isocyanate was more effective in resisting fungal attack than was wood modified with para-toluene sulfonyl chloride.

We compared the stability of the sulfonyl ester bond with that of sulfonyl carbamate of the modified woods under the decay conditions. We analyzed the sulfur content of the decayed and undecayed blocks in both treatment groups. Wood reacted with para-toluene sulfonyl chloride to 8.8% chemical weight gain lost 23% sulfur in the 12-week-decay test, whereas wood reacted with para-toluene sulfonyl isocyanate to 7.7% chemical weight gain lost 8.4% sulfur (Table 2). This indicates that the reaction of wood with para-toluene sulfonyl chloride caused the formation of a labile sulfonate ester bond with the wood cell-wall polymers, and the wood was thus subject to greater weight loss during the decay test. In contrast, the reaction of wood with para-toluene sulfonyl isocyanate caused the formation of a much more stable sulfonamide bond with the wood, and thus the wood resisted leaching during the decay test. The tosylated wood released 13.6 mmol of tosyl group per 100 g wood in the decay test, and modification caused 3.8% weight loss of wood; the wood modified with tosyl carbamate released only 5 mmol of tosyl carbamoyl group per 100 g wood and caused 2.7% weight loss of wood in the same test.
TABLE 1. Effect of Gloeophyllum trabeum on pine blocks reacted with para-toluene sulfonyl chloride or isocyanate.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight gain of chemical(^a) (percent, w/w)</th>
<th>Weight loss by decay(^b) (percent, w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Para-toluene sulfonyl chloride</td>
<td>1.2 (8)</td>
<td>33.4</td>
</tr>
<tr>
<td></td>
<td>3.2 (21)</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>6.2 (40)</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>8.7 (56)</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>9.1 (59)</td>
<td>3.8</td>
</tr>
<tr>
<td>Para-toluene sulfonyl isocyanate</td>
<td>1.5 (11)</td>
<td>52.6</td>
</tr>
<tr>
<td></td>
<td>2.8 (21)</td>
<td>37.4</td>
</tr>
<tr>
<td></td>
<td>5.7 (43)</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>7.5 (56)</td>
<td>2.7</td>
</tr>
<tr>
<td>Solvent only (pyridine)</td>
<td>-</td>
<td>47.7</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>51.2</td>
</tr>
</tbody>
</table>

\(^a\) Mean of five replicates.  
\(^b\) Values in parentheses are millimoles/100 g wood.

decay test period. Therefore, wood reacted with para-toluene sulfonyl isocyanate requires 2.7 times less chemical to resist fungal attack than wood reacted with para-toluene sulfonyl chloride.

These results suggest that the stability of the bond between the fungicidal groups tested and the cell-wall polymers in wood may play a more important role than the hydrophobicity of the fungicidal groups in the permanence of the fungicidal groups in wood. This is because woods modified with tosyl or tosyl carbamoyl group have the same tolyl group; consequently, the contribution of hydrophobicity to the bond stability in both modified woods is similar.

This finding is in contrast to results from our previous investigations (Chen et al. 1990; Chen submitted). We found that the hydrophobicity of the fungicidal groups in the modified wood plays an important role in extending the period of decay control. For example, wood reacted with pentafluorophenyl isocyanate lost only 6% fluorine in a 12-week decay test whereas wood reacted with monofluorophenyl isocyanate lost 27% fluorine. The more stable bond of the wood modified with pentafluorophenyl carbamate compared with that of the wood modified with monofluorophenyl carbamate is attributed to the more hydrophobic nature of the pentafluorophenyl group. During enzymatic hydrolysis, water diffuses less readily in wood reacted with pentafluorophenyl isocyanate than in wood reacted with monofluorophenyl isocyanate.

Wood bonded to fungicidal compounds is more stable than wood impregnated with the same fungicidal compounds. For example, wood reacted with pentafluorophenyl isocyanate lost 6% of the fungicidal group, whereas wood impregnated with methyl pentafluorophenyl carbamate lost 79% of the fungicidal group (Chen et al. 1990). Wood modified with para-toluene sulfonyl isocyanate also lost only 8.4% of the fungicidal group. Therefore, bonding of wood with fungicidal groups can prolong the period of decay control.

Our results show that both the stability of

TABLE 2. Sulfur content of pine blocks reacted with para-toluene sulfonyl chloride or isocyanate before and after 12-week soil-block decay test.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight gain of chemical in wood (percent)</th>
<th>Sulfur content (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Content based on weight gain of chemical in wood(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Undecayed blocks(^e)</td>
</tr>
<tr>
<td>Para-toluene sulfonyl chloride</td>
<td>8.83</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>8.12</td>
<td>1.64</td>
</tr>
<tr>
<td>Para-toluene sulfonyl isocyanate</td>
<td>7.73</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>5.91</td>
<td>0.92</td>
</tr>
<tr>
<td>Solvent only (pyridine)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Correction for sulfur (0.04%) in reacted wood as a result of solvent (pyridine).  
\(^b\) Chemically analyzed.  
\(^c\) Values of undecayed blocks are higher than values based on chemical weight gain as a result of loss of extractives by acetone extraction.  
\(^d\) 12-week soil-block decay test.
the bond between fungicidal groups and wood and the hydrophobicity of fungicidal groups play an important role in prolonging the period of decay control.

CONCLUSIONS

Wood reacted with para-toluene sulfonyle chloride or para-toluene sulfonyle isocyanate resisted attack by the brown-rot fungus *Gloeophyllum trabeum*. Wood reacted with para-toluene sulfonyle isocyanate was more effective in resisting both fungal attack and leaching than was wood reacted with para-toluene sulfonyle chloride. The results suggest that the stability of the bond between fungicidal groups and wood plays a more important role than the hydrophobicity of the tolyl group in the permanence of fungicidal groups in wood. Our results show that bonding fungicidal compounds to wood can extend the period of decay control by increasing the stability of the bond between fungicidal groups and wood or by increasing the hydrophobicity of the fungicidal groups.

REFERENCES


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