Fungal Decay Resistance of Wood Reacted with Chlorosulfonyl Isocyanate or Epichlorohydrin

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Keywords
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Cross-linked wood
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Summary
We are searching for chemical treatments that can cross-link with wood causing minimal damage to mechanical properties while also improving decay resistance. The objective of this study was to investigate the reactions between wood and chlorosulfonyl isocyanate or epichlorohydrin and to determine fungal resistance of the treated wood. Loblolly pine (Pinus taeda L.) reacted with chlorosulfonyl isocyanate to 6.1% weight gain of chemical and epichlorohydrin to 10.9% weight gain of chemical had 1.3% and 2.3% weight loss, respectively, by the fungus Gloeophyllum trabeum. Wood cross-linked with chlorosulfonyl isocyanate lost 50% of the sulfonyl carbamoyl groups in the decay test, whereas wood reacted with epichlorohydrin lost 17% of the alkoxy-bonded product; the loss from the cross-linked product was not determined. Cross-linking between wood and chlorosulfonyl isocyanate was evidenced by the characteristic sulfonate and carbamate infrared absorptions. For wood reacted with epichlorohydrin, chemical analyses showed that 50% of the bond between epichlorohydrin and wood was alkoxy-bonded wood and the remaining 50% was mainly cross-linked with wood.

Introduction
In studies on decay resistance of the modified wood, wood cross-linked with formaldehyde required only a small amount of reacted formaldehyde (2% to 5% weight gain of chemical) to resist decay (Stamm and Beachler 1960; Stevens et al. 1979). However, formaldehyde cross-linking adversely affected the mechanical properties of the wood (Stamm 1959). Therefore, we are searching for chemical treatments that can cross-link with wood causing minimal damage to mechanical properties and also improving decay resistance and dimensional stability. In a previous study, we found that diisocyanates showed good results. For example, wood cross-linked with 1,6 diisocyanatohexane to 26% weight gain of chemical had no weight loss by decay fungi and had improved dimensional stability by 64% (Chen 1992 a). Other reactive chemicals that have been used to cross-link with polysaccharides include chlorosulfonyl isocyanate (Rousseau et al. 1969) and epichlorohydrin (Kuniak 1974; Hollinger and Marchessault 1975; Weber et al. 1976). Moreover, epichlorohydrin alone or mixed with propylene oxide has been reacted with wood. These modified woods resisted fungal decay (Rowell and Gutzmer 1975; Enoki et al. 1990) and showed improved dimensional stability (Enoki et al. 1990). However, evidence of bonding between epichlorohydrin and wood has never been reported. The purpose of this study was to investigate the reactions between wood and chlorosulfonyl isocyanate or epichlorohydrin and to determine fungal resistance of these modified woods.

Methods and Materials
Chemical modification of wood

General methods of preparing wood blocks cross-linked with chlorosulfonyl isocyanate or epichlorohydrin are described in this section. Detailed descriptions of the individual chemical used in the cross-linking with wood blocks are described in the following two subsections. These reacted wood blocks (1.9cm³) were used in the decay tests.

Reactions between wood and chlorosulfonyl isocyanate or epichlorohydrin were carried out under different conditions. Wood blocks (1.9cm³) were reacted with chlorosulfonyl isocyanate in 1:1, 1:3, and 1:5 molar ratios of chlorosulfonyl isocyanate to anhydrous glucose pyranose equivalent of wood in pyridine (Chen 1992a, b) at 60°C for 1 to 24h. The level of chemical weight gain in wood was controlled by chemical concentration and reaction time. For wood reacted with epichlorohydrin, epichlorohydrin to catalyst (triethylamine) ratio was 95/5 (v/v) and wood to epichlorohydrin ratio was 25g wood/100ml epichlorohydrin (Rowell et al. 1976): no solvent was used in the reaction.
Reaction with chlorosulfonyl isocyanate

Blocks with an average chemical weight gain of 9.1%, 10.7%, and 14.7% were obtained as follows. Eighteen loblolly pine (Pinus taeda L.) sapwood blocks (61.5g, 334mmol, 1.9cm in radial, tangential, and longitudinal directions) were dried at 60°C for 1 day and weighed. The blocks were placed in a desiccator under vacuum at 4.4kPa for 1h. The blocks were impregnated with pyridine (300ml, dried over a 4A molecular sieve for more than 1 day: pyridine was used as a solvent as well as a catalyst to react chlorosulfonyl isocyanate with wood), and chlorosulfonyl isocyanate (29.1ml, 334mmol) was then added. The blocks containing solution were soaked for 1 day and then reacted at 60°C for 24h. During reaction, six blocks each were withdrawn at 3-, 5-, and 24-h intervals. The six blocks from each treatment were soaked in acetone (300ml, dried over a 4A molecular sieve for more than 1 day) for 1 day and then extracted with acetone for 12h in a Soxhlet extractor. The blocks were air-dried under a hood for 1 day and then (ovendried at 60°C for 1 day). The average chemical weight gain in the wood was 9.1%, 10.7%, and 14.7% for the blocks reacted for 3, 5, and 24h, 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 treated with 5- and 24-h reactions were used in the soil-block decay test.

Blocks with an average chemical weight gain of 4.1% and 6.1% were obtained by reacting wood (18 blocks, 62.7g, 341mmol, 1.9cm in radial, tangential, and longitudinal directions) with chlorosulfonyl isocyanate (9.9ml, 114mmol) at 60°C for 1, 3, and 6h in pyridine (300ml, dried over a 4A molecular sieve for more than 1 day). The blocks were reacted immediately without presoaking in the solution. The average chemical weight gain in the wood was 3.8%, 4.1%, and 6.1% for the blocks reacted for 1, 3, and 6h, respectively. The procedures to impregnate, purify, and condition the blocks were the same as described previously. Five blocks treated with 3- and 6-h reactions were used in the soil-block decay test.

Blocks with an average weight gain of 2.7% were obtained by reacting wood (12 blocks, 44.7g, 243mmol) with chlorosulfonyl isocyanate (4.3ml, 49mmol) in pyridine (300ml, dried over a 4A molecular sieve for more than 1 day) at 60°C for 1 and 2h. The blocks were reacted immediately without presoaking in the solution. The average chemical weight gain in the wood was 2.7% and 3.9% for the blocks reacted for 1 and 2h, respectively. Five blocks treated with the 1-h reaction were used in the soil-block decay test.

Reactions with epichlorohydrin

Eighteen loblolly pine sapwood blocks (63.1g, 19cm in radial, tangential, and longitudinal directions) were dried at 60°C for 1 day and weighed. The blocks were placed in a desiccator under vacuum at 2.4kPa for 1h. The blocks were impregnated with epichlorohydrin (250ml), and triethylamine (13.2ml) was added. The blocks were soaked for 1 day and were reacted at refluxed temperature for 7h. During reaction, six blocks each were withdrawn at 1-, 3-, and 7-h intervals. The six blocks from each treatment were soaked in acetone (300ml, dried over a 4A molecular sieve for more than 1 day) for 1 day and then extracted with acetone for 12h in a Soxhlet extractor. The blocks were air-dried under a hood for 1 day. The average chemical weight gain in the wood was 5%, 8%, and 10.9% for the reactions of 1, 3, and 7h, respectively. Chemical weight gain of wood was based on weight gain of oven-dried wood at 60°C for 1 day before and after the 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 2.3% and 2.8% were obtained as follows. Twelve loblolly pine sapwood blocks (42.4g, 1.9cm in radial, tangential, and longitudinal directions) were placed in a desiccator under vacuum at 2.2kPa for 40min. The blocks were then impregnated with epichlorohydrin (168ml), and triethylamine (8.8ml) was added. Without presoaking, the blocks were reacted at refluxed temperature for 4h. During reaction, six blocks each were withdrawn at 2- and 4-h intervals. The procedures to purify and condition the blocks were the same as described previously. The average chemical weight gain in the wood was 2.3% and 2.8% for the blocks reacted for 2 and 4h, respectively. Five blocks from each treatment group were used in the soil-block decay test.

Soil-block decay tests

Soil-block fungal decay tests were performed for 12 weeks according to ASTM Standard D1413-86 (ASTM 1990) using the brown rot fungus Gloeophyllum trabeum (Pers: Fr.) Murr. (Madison-617). Five blocks were used for each fungal decay test. The extent of fungal attack was determined by weight loss of the block.

Chlorine or sulfur content in wood with or without chemical treatments was determined by the Galbraith Laboratories, Inc. (Knoxville, TN). Infrared spectra of wood reacted with chlorosulfonyl isocyanate to a weight gain of 13.4% and epichlorohydrin to a weight gain of 11.2% were recorded using potassium bromide pellets.

Results and Discussion

In this study, pyridine or triethylamine was used as a solvent or a catalyst and also served as an acid scavenger in the reaction, minimizing damage to the mechanical properties of reacted wood. Loblolly pine was used in this study because it is one of the important commercial species.

Decay resistance

Wood cross-linked with chlorosulfonyl isocyanate to a weight gain of 10.7% (101 mmol/100g wood) had a weight loss of 1.3% by G. trabeum, whereas wood reacted with epichlorohydrin to a weight gain of 10.9% (190mmol/100g wood) had a weight loss of 2.3% (Table 1). Therefore, wood cross-linked with chlorosulfonyl isocyanate was about two times more effective than was wood reacted with epichlorohydrin. However, the loss of chemical from wood cross-linked with chlorosulfonyl isocyanate was high (around 50%). The loss of chemical from wood reacted with epichlorohydrin was 17% for the product containing alkoxy-bonded wood (Fig. 4, product 1), but loss of chemical was not determined for the product containing cross-linked wood (Fig. 4, product 2; Tables 2 and 3). Moreover, the two modified woods each responded differently to decay by G. trabeum. Wood cross-linked with chlorosulfonyl isocyanate to a weight gain of only 2.6% (24mmol/100g wood) had a smaller weight loss (14.9%) than that of wood reacted with epichlorohydrin (37.4% weight loss, 2.2% chemical weight gain, 23mmol/100g wood) based on a similar molar ratio of chemical in wood (Table 1). This difference in decay resistance suggests that chlorosulfonyl isocyanate can penetrate and react easily in the amorphous region of cellulose in wood, whereas epichlo-
rohydrin is less accessible in this region. Chlorosulfonyl isocyanate is more polar and more reactive than is epichlorohydrin toward cell wall polymers of wood. This difference in decay resistance also suggests that reaction of chemicals with cellulose in wood plays an important role in decay resistance.

**Bond stability**

Wood blocks reacted with chlorosulfonyl isocyanate or epichlorohydrin were compared for bond stability after the 12-week soil-block decay test. Wood cross-linked with chlorosulfonyl isocyanate to weight gains of 10.9% and 14.4% had sulfur losses of 47% and 52%, respectively, at the end of the decay test (Table 3). These large sulfur losses may indicate that the bonds between chlorosulfonyl isocyanate and cell wall polymers of wood are very unstable. This was attributed to the lability of the sulfonate ester bond, which was hydrolyzed readily during fungal degradation. A similar result from a previous study showed that wood reacted with tosyl chloride lost 23% of the sulfonate ester groups during the 12-week decay test (Chen 1992b). Less chemical was lost from wood reacted with epichlorohydrin than from wood cross-linked with chlorosulfonyl isocyanate during the same 12-week decay test. For example, wood reacted with epichlorohydrin to a weight gain of 11.1% lost 17% chlorine during the decay test (Table 2). These results indicate that the ether bond between epichlorohydrin and wood is more stable than the sulfonate bond in wood cross-linked with chlorosulfonyl isocyanate. Therefore, the stability of the bond between chemicals and cell wall polymers of wood plays an important role in the permanence of the chemical in wood and contributes to a long duration of wood protection. Previous studies showed that increased hydrophobicity of the chemicals being reacted with wood can stabilize the chemicals in wood (Chen et al. 1990; Chen 1992a, b, c).

Because wood reacted with epichlorohydrin required a large amount of bonded chemical (190mmol/100g wood) to resist fungal decay (Table 1), its protection mechanism probably resembles wood cross-linked with 1,6-diisocyanatohexane (153mmol/100g wood) (Chen 1992a) in which hydrophobicity played a more important role than did substrate modification. For wood cross-linked with chlorosulfonyl isocyanate, the mechanism of decay protection may involve toxicity (release of toxic compounds from the modified wood), substrate modification, or hydrophobicity. It is not clear which protection mechanisms play a more important role.

**Infared analysis**

Infrared (IR) absorptions of wood reacted with chlorosulfonyl isocyanate showed the characteristic sulfonate and carbamate absorptions. This indicates that cross-linking between chlorosulfonyl isocyanate and wood took place. The absorption at 1,640 cm\(^{-1}\) is attributed to the carbonyl stretching vibration of the carbamate group, and the absorptions at 1,024 cm\(^{-1}\) and 1,365 cm\(^{-1}\) are attributed to symmetric and asymmetric stretching vibrations of \(\text{SO}_2\) group (1B). At 1,025 cm\(^{-1}\), a small peak is observed, which is usually attributed to the stretching vibration of the sulfonate ester bond.

### Table 2. Percentage of chlorine in pine wood reacted with epichlorohydrin before and after 12-week soil-block decay test

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight gain of chemical (%)</th>
<th>Chlorine in wood (%: w/w)</th>
<th>Chlorine loss of decayed wood (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical(^b)</td>
<td>Undecayed wood</td>
<td>Decayed wood</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>11.01</td>
<td>4.23</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>11.09</td>
<td>4.25</td>
<td>-3</td>
</tr>
<tr>
<td>Solvent only (pyridine)</td>
<td>0.03</td>
<td>-4</td>
<td>1.83</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>0.02</td>
<td>17</td>
</tr>
</tbody>
</table>

*Chemically analyzed by Galbraith Laboratories, Inc. (Knoxville, TN). \(^b\) Based on chemical weight gain in wood in form of alkoxy-bonded wood. \(^c\) Compared with undecayed blocks. \(^d\) For blocks used in decay tests, no chlorine was analyzed before decay tests.
Table 3. Percentage of sulfur in pine wood reacted with chlorosulfonfyl isocyanate before an after 12-week soil-block decay test.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Weight gain of chemical (%)</th>
<th>Sulfur in wood (% w/w)</th>
<th>Sulfur loss of decayed wood (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical</td>
<td>Undecayed wood</td>
</tr>
<tr>
<td>Chlorosulfonfyl isocyanate</td>
<td>9.7</td>
<td>2.91</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td>3.27</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>3.96</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>14.4</td>
<td>4.31</td>
<td>0.65</td>
</tr>
<tr>
<td>Solvent only (pyridine)</td>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Chemically analyzed by Galbraith Laboratories, Inc. (Knoxville, TN). Based on chemical weight gain in wood. Compared with undecayed blocks. For blocks used in decay tests, no sulfur was analyzed before decay tests.

and 1,225 cm\(^{-1}\), absorptions are attributed to the symmetric and asymmetric stretching vibrations of the SO group (Fig. 1B) (Conley 1970; Socrates 1980). However, the frequency of carbonyl absorptions (1,640 cm\(^{-1}\)) of sulfonyl carbamate in modified wood (Fig. 1B) was lower than that of the carbonyl absorption (1,740 cm\(^{-1}\)) of normal carbamates. This is attributed to delocalization of electrons in the carba-

[Fig. 1. Infrared spectra of (A) untreated wood (control) and (B) wood reacted with chlorosulfonfyl isocyanate to 13.4% weight gain of chemical.]

[Fig. 2. Resonance effect causing delocalization of electrons in carbanate group.]

mate group because of the resonance effect as shown (Fig. 2). This resonance effect contributes to a much lower frequency of carbonyl absorption of carbamate (1,640 cm\(^{-1}\)) in wood cross-linked with chlorosulfonfyl isocyanate than that of the ordinary carbamates (1,740 cm\(^{-1}\)) (Colthup et al. 1964).

For wood reacted with epichlorohydrin, IR spectra showed the characteristic ether and carbon-chlorine absorptions. The absorptions at 810, 1,150, and 1,255 cm\(^{-1}\) are attributed to the C–O–C stretching vibration, and at 1,120 cm\(^{-1}\), the absorptions are attributed to aliphatic C–O stretching vibration (Fig. 3B). The absorption at 620 cm\(^{-1}\) is attributed to C–Cl stretching vibration (Conley 1970; Socrates 1980) (Fig. 3B). The absorptions at 810, 1,150, and 1,255 cm\(^{-1}\) are strong (Fig. 3B).

[Fig. 3B. Resonance effect causing delocalization of electrons in carbanate group.]

Reaction of epichlorohydrin with wood can lead to four products (Fig. 4). Chemical analysis of chlorine in the epichlorohydrin-reacted wood indicated that 50% of the bond between epichlorohydrin and wood was in the form of alkoxy-bonded wood (single ether-bonded wood) containing chlorine in the alkyl side chain (product 1). The remaining 50% of the bond was mainly in the form of cross-links with wood (product 2). The product containing epoxy groups in the alkyl side chain (product 3) did not appear in the IR spectra. Further reaction of the epoxy group with water formed dihydroxy groups in the side chain (product 4) which probably existed in very small amounts because the reaction was carried out in the absence of water. Cross-linking of epichlorohydrin with polysacharides including cellulose and starch has been reported (Kuniak 1974; Hollinger and Marchessault 1975; Weber et al. 1976). Because of less accessibility of cellulose to chemicals in wood, a greater extent of cross-linking of wood with epichlorohydrin may take place in lignin and hemicelluloses, and a lesser extent may take place in cellulose. This is because a large amount of epichlorohydrin (190 mmol/100 g wood) was required to protect wood from decay (Chen 1992a).
Concluding Remarks

Loblolly pine wood cross-linked with chlorosulfonyl isocyanate to 6.1% weight gain of chemical and epichlorohydrin to 10.9% weight gain of chemical had 1.3% and 2.3% weight losses, respectively, by the fungus *Gloeophyllum trabeum*. During the decay tests, the chlorosulfonyl isocyanate cross-linked wood lost 50% bonded chemical, whereas the epichlorohydrin-reacted wood lost 17% alkoxy-bonded chemical; the loss from cross-linked wood was not determined. The greater loss of chemical from wood cross-linked with chlorosulfonyl isocyanate is attributed to the labile sulfonate bond. The smaller loss of the alkoxy-bonded chemical from wood reacted with epichlorohydrin may indicate that the ether bond is more stable than the sulfonate bond. This study indicated that the stability of the bonded chemicals in wood plays an important role in the permanence of the chemicals in wood and contributes to a longer duration of decay control. Evidence of cross-linking between chlorosulfonyl isocyanate and wood was provided by the characteristic sulfonate and carbamate infrared absorptions. The epichlorohydrin-reacted wood showed the characteristic ether and carbon-chlorine infrared absorptions. Chemical analyses of chlorine in the epichlorohydrin-reacted wood indicated that 50% of the bond between epichlorohydrin and wood was in the form of alkoxy-bonded wood (single ether-bonded wood); the remaining 50% was mainly in the form of cross-links with wood. Future research in cross-linking chemicals with wood will use more polar and more stable cross-linking compounds that can react readily with the cellulose region in wood.

References


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