



Photostabilization of wood using low molecular weight phenol formaldehyde resin and hindered amine light stabilizer

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ABSTRACT

Phenol formaldehyde (PF) resin containing low molecular weight hydroxymethyl phenol species and a water soluble hindered amine light stabilizer (HALS) was synthesized and used to treat wood veneers. Treated veneers were exposed to natural weathering for 25, 35 and 50 days and the effectiveness of the modified PF resins as photoprotective treatments for wood was assessed. We hypothesized that the photostability of veneers would be positively correlated with concentration of PF resin (10, 20 and 30% w/v) and HALS (1 or 2% w/w) in solutions used to treat veneers. There was an inverse relationship between resin concentration in treatment solutions and tensile strength losses of treated veneers exposed to natural weathering. Mass losses of veneers treated with solutions containing 20 or 30% PF resin were lower than those of veneers treated with 10% PF resin. The addition of 2% HALS to solutions containing 30% PF resin had a significant ($p < 0.05$) effect at restricting mass and tensile strength losses of treated veneers exposed to the weather for 50 days. A PF resin treatment containing 30% resin and 2% HALS was as effective as chromic acid (a noted photostabilizer for wood) at restricting mass and tensile strength losses of veneers during natural weathering. Treated veneer in a plywood-type composite became darker and redder when exposed outdoors, but the addition of HALS to the resin restricted color changes of veneer treated with 10% PF resin. A 30% PF resin treatment on its own or containing 2% HALS protected wood's cellular structure from destruction during accelerated weathering and restricted, but did not prevent, delignification of wood. We conclude that the effectiveness of low molecular weight PF resin as a photoprotective treatment for wood can be improved by increasing the concentration of PF resin and by combining it with a water soluble HALS.

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1. Introduction

The photostability of synthetic polymers can be improved by altering their molecular structure, but this fundamental approach is rarely employed because additives such as UV absorbers and hindered amine light stabilizers (HALS) can provide good levels of protection [1]. These additives are less effective at photostabilizing wood and therefore greater attention has been devoted to chemically modifying wood to improve its photostability. For example, chromic acid alters the molecular structure of lignin, and is remarkably effective at photostabilizing wood [2,3]. But chromic acid is toxic, corrosive and carcinogenic, and attempts to find other metal compounds that are less harmful and equally effective at

photostabilizing wood surfaces have been unsuccessful [4,5]. The photostability of wood surfaces esterified to high weight gain with benzoyl chloride or vinyl benzoate, however, is similar to that of wood modified with chromic acid [6,7]. Benzoyl chloride and vinyl benzoate react with wood to create covalently-bonded aromatic groups in wood cell walls, but the reactions require solvent, catalyst and heat, and they also generate toxic by-products [6–8]. Hence, there is little commercial interest in benzoyl chloride and vinyl benzoate as treatments for wood. Nevertheless, the finding that large quantities of simple aromatic compounds in wood cell walls photostabilizes wood provides a possible route to the development of more practical treatments for improving the photostability of wood.

An alternative route to depositing aromatic compounds in wood cell walls is to impregnate wood with low molecular weight phenol formaldehyde (PF) resin. Low molecular weight PF resin can penetrate wood cell walls and the resin can then be cross-linked by

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heating the treated wood [9]. Treatment of wood with PF resin increases the hardness, dimensional stability and decay and acid resistance of wood [10,11]. The resistance of the treated wood to weathering is also increased, although it is not known whether PF resin treatment photostabilizes lignin [12–15]. PF resins 'are excellent absorbers of UV light' and this property of the resin, according to Tarkow and co-workers, explained why they improved the performance clear coatings on treated pine wood exposed to accelerated weathering [16].

The performance of UV absorbers as photostabilizers for polymers (including wood) can be improved by increasing the concentration of UV absorber (UVA) in the polymer or by combining the UVA with a HALS [17,18]. Accordingly, we hypothesize here that there will be a positive correlation between concentrations of PF resin and HALS in solutions used to treat wood veneers and the photostability of the treated veneers. We test this hypothesis and compare the effectiveness of the PF resin treatments with that of two other treatments, including chromic acid, that are effective at photostabilizing wood.

2. Experimental

2.1. Experimental design and statistical analyses

Factorial principles were used to design two experiments: (1) the effects of PF resin and HALS on mass and tensile strength losses of treated yellow cedar wood veneers exposed to natural weathering. This experiment also compared the effectiveness of PF/HALS treatments at photostabilizing yellow cedar veneers with that of chromic acid or a water-repellent containing UVA/HALS additives; (2) the effects of PF resin and HALS treatments on the color of a plywood-type composite exposed to natural weathering.

Radiata pine veneers for plywood-type composites were cut from eight different parent wood blocks. Replicate composites within each 'block' were randomly allocated to different chemical treatments. This approach provided replication at the higher level (8 blocks) and made it possible to statistically analyze data using analysis of variance (ANOVA) for a randomized block design. All statistical computation including model checking to ensure that data met the assumptions of ANOVA (normality and constant variance) was performed using Genstat. As a result of such checks, tensile strength data for treated yellow cedar veneers exposed to natural weathering was analyzed as natural logarithms. Statistically significant results are presented in graphs and error bars on graphs (\pm standard error of difference or least significant difference (LSD), $p < 0.05$) can be used to compare differences between individual means.

2.2. Synthesis and properties of low molecular weight PF resins

Technical grade 90% aqueous phenol (P) or industrial grade 99.7% phenol (stored at 60–70 °C), industrial grade 52% aqueous formaldehyde (F) (stored at 60–70 °C), industrial grade 50% NaOH (aqueous), and tap water were used for the synthesis of low molecular weight PF resin. The resins were formulated at an F/P molar ratio of 1.5–2.0; with a NaOH to P molar ratio of 0.10–0.15, and contained 40–45% total water. The phenol solution and water were added to a 4 L glass vessel equipped with agitation, cooling coils, heating jacket, and automatic temperature control. NaOH solution was added to the reactor over a period of 5 min while the temperature of the resulting clear sodium phenoxide solution was adjusted to 40–50 °C. Formaldehyde solution was then added to the reactor at a rate of 34–40 g/min and for the first 5–15 min the contents of the reactor were allowed to exotherm to 55–65 °C. Then the temperature of the reactor was held at 55–

65 °C. Once all formaldehyde was added to the reactor, the temperature of the solution was allowed to rise to 75–85 °C at a rate of 1.0–1.5 °C per min. The contents of the reactor were then cooled to 55–65 °C and held at a constant temperature for 2 h. The resulting PF resin was then cooled to 25 °C.

Viscosity of the PF resin was measured using the Gardner–Holdt (G–H) method at 25 °C and was converted to and reported in Centistokes [19]. The gel time of the resin was evaluated with 10 g of resin in a glass test tube at 100 °C until gelation occurred. The content of free F was determined by the hydroxylamine–HCl titration method [20]. The content of free P was determined by GC [21]. The non-quantitative phenolic speciation was conducted on a Waters Alliance 2690 HPLC solvent delivery system with Waters 2487 variable UV detector and a Waters C18 column. This analysis indicated that the resin contained significant amounts of substituted phenols in addition to phenol as follows: 2,4,6-trihydroxymethylphenol and 2,4-dihydroxymethylphenol = 41.55%; total dimers = 16.46%; 2-hydroxymethylphenol = 13.39%; 4-hydroxymethylphenol = 8.82%; tetra-dimer = 7.38%; and 2,6-dihydroxymethylphenol = 5.26%. The properties of the PF resin including the phenol content (7.51%) are shown in Table 1.

PF resins were stored in plastic containers and frozen. They were thawed, diluted with distilled water and used and/or modified by adding a water soluble HALS as required.

2.3. Wood specimens

Wood veneers, 50 μ m thick and 28 mg in weight on average, were cut from the radial faces of water-saturated yellow cedar (*Chamaecyparis nootkatensis* (D.Don) Spach) wood blocks [22]. Veneers were air-dried overnight, conditioned at 20 ± 1 °C and $65 \pm 5\%$ r.h. for 1 week and their thicknesses and oven dry weights were measured [5].

Three millimeter thick veneers were sawn from the tangential faces of 50 \times 50 mm square air-dry radiata pine (*Pinus radiata* D.Don) wood blocks. Four millimeter thick veneers were also sawn from the radial faces of air-dry western red cedar (*Thuja plicata* Donn ex. D.Don) wood blocks. Sawn radiata pine veneers were treated with PF resin, cured and conditioned (see below), and a thin film of phenol-resorcinol formaldehyde adhesive (Arclin 4001/5830) was applied to one side of each veneer. Two treated radiata pine veneers were placed on a sawn western red cedar veneer with their grain oriented perpendicular to that of the thicker western red cedar veneer. The resulting plywood-like composite was pressed together in a small press for 6 h at 20 °C using a clamping pressure of 861 kPa [23].

Small blocks measuring 5 mm (radial) \times 5 mm (tangential) \times 15 mm (longitudinal) were cut from yellow cedar heartwood and soaked in distilled water for 7 days until saturated. Sharp single-edged razor blades were then used to cut clean undamaged transverse surfaces for each small block, as described previously [24].

Table 1

Properties of the parent low molecular weight phenol formaldehyde resin that was diluted to create solutions used to treat wood veneers.

| Property of resin | Specification ranges |
|--|----------------------|
| Un-reacted phenol (%) ^a | 7.5–8.5 |
| Un-reacted formaldehyde (%) ^b | 0.7–0.9 |
| Non-volatile solids (%) | 46–48 |
| Gel time @100 °C (min.) | 70–80 |
| pH @ 25 °C | 9–10 |
| Viscosity @ 25 °C (Centistokes) ^c | 10–30 |

^a Gas chromatography.

^b (hydroxylamine HCl method).

^c Converted from G-H viscosity.

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