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Short communication

Fungal resistance of rubber wood modified by fatty acid chlorides

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ABSTRACT

Decay resistance of Rubber wood (*Hevea brasiliensis*) esterified with three fatty acid chlorides (hexanoyl chloride (C6), decanoyl chloride (C10) and tetra-decanoyl chloride (C14)) was evaluated. Unmodified and modified wood samples were exposed to a brown rot (*Polyporus meliae*) and a white rot (*Coriolus versicolor*) fungus for 12 weeks. Unmodified rubber wood was severely decayed by *P. meliae* and *C. versicolor*, which was indicated by significant weight loss. The rate of decay by brown rot was higher than white rot. Modified wood samples exhibited very good resistant to brown and white–rot fungi. The degree of protection increased with increase in degree of modification. *P. meliae*, a brown rot fungus, removed structural carbohydrate component in unmodified wood selectively whereas, *C. vesicolor* showed preference to lignin. The FTIR spectra of modified wood exposed to fungi show no significant changes in relative peak intensities of lignin/carbohydrates indicating effectiveness of chemically modified wood in restricting chemical degradation. Chemical modification occurred more efficiently at carbohydrate portion of the wood. Therefore, it is more effective in retarding decay due to *P. meliae*.

1. Introduction

Wood is an important sustainable, economical, renewable and biodegradable natural resource with diverse applications. The primary biotic decomposers of wood are basidiomycete decay fungi, which can attack and degrade both wood in the forest and wood in service. Wood provides a suitable substrate for fungus growth, and the cell walls components of the wood (cellulose, hemicelluloses, lignin) provide suitable food. Some species of wood are naturally more durable because they contain substances (extractives) toxic to fungi. It is possible to eliminate the food supply by treating it with certain toxic substances to fungi, called wood preservatives. Wood impregnation with biocides (containing e.g. creosote, arsenic, zinc, copper, and chromium) prevents biological degradation (Richardson 1978; Lebow 2010).

The decomposition of wood by fungi is of two main types, often referred to as brown rot and white rot. In brown rot the cellulose and hemicelluloses are attacked while the lignin is more or less unchanged. This causes wood to darken in color, In white rot, all the components of the wood, including the lignin, may be decomposed and used by the growing fungus. In some white rots, however, the cellulose may remain intact (Blanchette et al. 1985; Perez et al. 1993; Blanchette 1995; Worrall et al. 1997; Enoki et al. 1998).

The development of fungi on wood is largely controlled by the moisture content. All wood-decaying fungi require moderate amounts of water for growth. Wood cell wall is mainly composed of polymers with hydroxyl and other oxygen containing groups in cellulose, hemicellulose and lignin. Hydroxyl groups present in wood constituents attract moisture through hydrogen bonding. A treatment that reduces the tendency of wood to take up water may result in a reduction in shrinking and swelling. One of the effective methods is to remove the hydroxyl groups on the cell wall polymers and, thus, remove the sites for hydrogen bonding to water by chemical modification.

In the chemical modification process, timber is reacted with a chemical that produces changes within its cellular structure (Rowell 1983, 2006). The hydroxyl groups play the leading role in many chemical modification reactions. The chemical added into the wood undergoes a chemical reaction with a hydroxyl group within the wood structure and result is a strong covalent bond, which is hydrophobic and stable. This produces a new material within the wood structure, and alters the properties of the original material. The decrease in the number of accessible OH-groups result in a limited interaction with water restricts water absorption and hence helps in restricting growth of biological agents and thereby induce biological resistance.

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Typical modifications of wood are esterifications and etherification at hydroxyl groups of the cell wall. Wood esterified with different types of anhydrides exhibits good dimensional stability and biological resistance (Rowell et al. 1979; Kalinins 1982; Rowell 1983, 2006; Matsuda 1987; Chen 1992; Takahashi 1996; Ohkoshi et al. 1999). Etherified wood is also found to be dimensionally stable and resistant to attack by rot fungi (Rowell et al. 1979; Chang and Chang 2006). Chemical modification of wood with fatty acid chlorides induces hydrophobicity and thermoplasticity (Funakoshi et al. 1979; Shiraishi et al. 1979; Thiebaud et al. 1997).

In this work we have investigated the biological resistance of chemically modified rubberwood against fungus. Rubberwood was esterified with three fatty acid viz., hexanoyl chloride, decanoyl chloride and tetra-decanoyl chloride and exposed to a brown rot (*Polyporus meliae*) and a white rot (*Coriolus versicolor*) fungus under laboratory conditions. The level of decay was estimated by determining weight loss and chemical changes due to decay was monitored by FTIR spectroscopy. The objective of this work was to asses the efficacy of wood modified with fatty acid chlorides for inducing biological resistance.

2. Material and methods

2.1. Wood specimens

Specimens of rubber wood of size 20 mm × 20 mm × 10 mm (radial × tangential × longitudinal) were prepared from defect free wood. Rubber wood logs were procured from a saw mill and converted into specimens of desired size. Logs were visually inspected for any defects. Samples were extracted for 6 h in toluene, ethanol and acetone mixture (4:1:1) by Soxhlet extraction apparatus followed by washing with hot water. The extracted samples were then oven dried at 100–105 °C and the weight of oven dried samples were determined. Oven dried specimen were then chemically modified with three fatty acid chlorides.

2.2. Chemical modification of wood specimens

Oven dried specimens were modified with different acid chlorides (Hexnoyl, decanoyl and tetra-decanoyl chloride, procured from M/S Sigma Aldrich) in a mixture of pyridine and dimethyl formamide (DMF) at 80 °C. The wood specimens were immersed in DMF in a reaction vessel for 18–20 h at room temperature. Then the acid chloride (equivalent to total weight of the wood samples) was dissolved in DMF (acid chloride/DMF volume ratio was 1:1) and pyridine (acid chloride/pyridine, 1:2 molar volume ratio) was slowly added to the reaction flask and reaction was carried out at 80 °C for 3 h, 4 h and 6 h to get specimens having different weight gains. Specimens having three different levels of weight gains were obtained for each case. The samples were removed from reaction vessel and soaked in cold acetone to arrest the reaction. Modified wood blocks were subsequently extracted with acetone: toluene (1:1) to remove un-reacted reagent and then oven dried at 100 °C. The weight percent gain (WPG) was calculated using equation (1),

$$\mathrm{WPG} = [(W_m - W_0)/W_0] \times 100 \quad (1)$$

where W_0 and W_m are oven dried weight of unmodified and chemically modified wood, respectively.

2.3. Wood decay by fungi

Modified and unmodified rubberwood samples were exposed to a brown rot (*P. meliae*; FRI No. 836) and a white rot (*C. versicolor*; FRI No. 165) fungus under the laboratory conditions. The authentic fungal cultures were obtained from National Type Culture Collection, Dehradun, India and maintained on 2% malt agar medium. The test culture used for the experiment was actively growing one week old culture. Eight replicate blocks were used for each test. The samples were autoclaved and exposed to fungus on 2% malt extract agar (100 ml) in culture bottles. Culture bottles were inoculated with 1 cm^3 of actively cultured fungus one week prior to the test. The samples were supported on glass rod to avoid contact with agar and kept at room temperature (25 ± 5 °C) and 60–70% relative humidity for 12 weeks. The wood blocks were exposed to fungal attack by placing them aseptically in the culture bottles in which there are actively growing cultures of the test fungi. The blocks were placed in thing glass rods so that the test blocks come in contact with the aerial mycelium of the fungus and not the medium itself (Anon 2008). Samples were removed after 12 weeks, autoclaved, mycelium was removed and oven dried to constant weight. Weight loss was determined for individual sample using equation (2),

$$\%\,\mathrm{Weight\ loss} = \left[\left(W_0 - W_f\right)/W_0\right] \times 100 \quad (2)$$

where W_0 is oven dry weight of sample prior to exposure and W_f is the oven dry weight of samples after exposure to fungus.

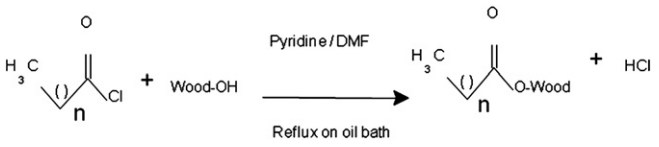
2.4. Measurement of FTIR and NMR spectra

The FTIR analysis of the decayed and undecayed wood blocks was performed using a FTIR Spectrometer (Bruker Germany, Tensor-27 model). The spectra were measured directly from modified/decayed wood surfaces using ATR method at a spectral resolution of 4 cm^{-1} at the rate of 64 scans/measurement and analyzed as per published literature (Harrington et al. 1964; Faix 1992; Pandey and Pitman 2003). NMR spectra were obtained using a Bruker DSX 300 MHz, CP/MAS ^{13}C NMR spectrometer at NMR Center, Indian Institute of Science, Bangalore.

3. Results and discussion

3.1. Chemical modification of wood and its characterization

Reaction scheme for wood-OH groups and different acid chlorides is given below:



where $n = 4$, 8, and 12 for hexanoyl, decanoyl and tetradecanoyl chloride, respectively.

Acid chloride reacts with –OH groups of wood to form an ester. The substitution of hydroxyl groups results in weight gain of wood specimen. The chemical modification of wood was characterized by FTIR and NMR spectroscopy.

The FTIR spectra of rubber wood modified with hexanoyl chloride is shown in Fig. 1. Most of the bands in FTIR spectrum of unmodified wood have contributions from both lignin and carbohydrates (cellulose and hemicellulose). Main peaks used in this study are assigned as (Harrington et al. 1964; Faix 1992; Pandey and Pitman 2003): 1738 cm^{-1} for unconjugated C=O in xylans (hemicellulose), 1505 cm^{-1} for aromatic skeletal vibration in lignin, 1454 cm^{-1} for aromatic C–H deformation, 1371 cm^{-1} for C–H deformation in cellulose and hemicelluloses, 1269 cm^{-1} for guaiacyl ring breathing plus C–O stretch in lignin, 1158 cm^{-1} for C–O–C vibration in cellulose and hemicelluloses and 898 cm^{-1} for C–H deformation in cellulose.