International Biodeterioration & Biodegradation 87 (2014) 26–33

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Fungal durability of polyaniline modified wood and the impact of a low pulsed electric field

Andreas Treu[a,*], Stig Bardage[b], Mats Johansson[c,e], Stacy Trey[b,d]

[a] Norwegian Forest and Landscape Institute, Section Wood Technology, PB. 115, 1431 Ås, Norway
[b] SP Wood Technology, SP Technical Research Institute of Sweden, Box 5609, Drottning Kristinas väg 67, SE-114 86 Stockholm, Sweden
[c] Wallenberg Wood Science Centre (WWSC), KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden
[d] Division of Surface and Corrosion Science, Chemistry Department, KTH Royal Institute of Technology, Drottning Kristinas väg 51, SE-10044 Stockholm, Sweden
[e] Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 30 September 2013
Received in revised form
30 October 2013
Accepted 3 November 2013
Available online 23 November 2013

Keywords:
Wood modification
Pulsed electric field
Polyaniline
Impregnation
Postia placenta

ABSTRACT

New wood protection technologies should be effective against biodeterioration and at the same time minimize environmental impact. The present study investigates the effect of polyaniline modification of wood and the effect of a pulsed electric field on fungal protection. The effect of fungi and a pulsed electric field on the conductivity of the modified wood was also measured.

It was found that it is possible to polymerize polyaniline particles in-situ homogeneously throughout the wood specimens. The polyaniline particles themselves were not found to be anti-fungal, however when in contact with water they affected the pH drastically and inhibited fungal growth. The wood treatment with polyaniline and the connection to a pulsed electric field were found to be effective in protecting the wood from deterioration when exposed to *Postia placenta*. The unmodified samples that were connected to a pulsed electric field lost under 10 wt% due to fungal degradation. The combination of polyaniline treatment with the connection to a pulsed electric field showed a slight synergistic effect which resulted in less weight loss due to fungal degradation. However, a more brittle wood structure was observed.

Leached and fungal exposed samples showed a significant drop in the conductivity, indicating that the network has broken down slightly.

1. Introduction

Most wood types used in outdoor applications must be treated to provide protection from environmental factors such as fungi, bacteria, insects, and marine-borers, sunlight, and rain. Increasingly stricter chemical regulations have resulted in the few copper-based and metal-free systems largely used today (Lebow, 2004; Obanda et al. 2008; Wormell, 2011). New technologies for wood protection are a priority in order to develop new systems that are effective and yet have a minimized environmental impact.

A potential new method for protection is the application of a direct current through a natural material, such as wood, which leads to the electrical transport of water and ions and has long been used for the application of removal of water from concrete and other building materials (Simons et al. 1998a). Electric fields have also been reported for use in wood protection against surface fungi (Bjurman, 1996) and wood destroying fungi (Hattori and Tamura, 1939) and in a reduction of microbial cells (MacGregor et al. 2000). When applied at specific pulsing patterns, a pulsed electric field (PEF) has been shown to protect Scots pine sapwood and beech wood samples from degradation by the brown rot fungus *Coniophora puteana*, the white rot fungus *Trametes versicolor*, molds, and termites (Treu and Larnøy, 2010; Treu et al. 2011). However, unpublished results regarding the protection of wood against the brown rot fungus *Postia placenta* by means of PEF, showed only a minor effect. This fungus is therefore an interesting species for further testing. PEF has a low frequency and is not harmful to humans, however, little is known in terms of the mechanism of protection, the effect on material moisture content, or the degree of protection provided when applied to larger samples.

Wood needs a certain amount of water in order to be electrically conductive (Zelinka et al. 2008). In order to test the effectiveness of an electric field against biological attack, the wood must have a moisture content higher than 20% in order to reach sufficient

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* Corresponding author. Tel.: +47 64949029.
E-mail address: andreas.treu@skogoglandskap.no (A. Treu).

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http://dx.doi.org/10.1016/j.ibiod.2013.11.001

electric conductivity and to create a suitable environment for the fungi (Lin, 1965). The dependence of a PEF system on water and the mobility of ions in wood can be a drawback in practical applications when isolated areas of otherwise dry wood constructions are exposed to fungal attack. Other issues include the conductive material that must be used to attach the electrodes to wood in order to subject wood to PEF, which can corrode over time. In order to circumvent these issues it is of interest to investigate wood that has been modified to a semi-conductive material, such as polyaniline modified wood that maintains conductivity and allows for PEF even in the dry state.

Interest in intrinsically conducting polymers (ICP) has been prolific in the past few decades (Heeger, 2001; Rimbu et al. 2006). Among the numerous conducting polymers, polyaniline is most often studied due to its lower cost, ease and control of synthesis, environmental stability, high electrical conductivity, and ease of blending with other polymers (Madani et al. 2010). These conductive polymers are insulators unless they are oxidized with protic acids allowing for tuning the degree of conductivity of the material to levels as high as 10^{-2}–100 S cm^{-1} (Wolszczak et al. 1995; Jafarzadeh et al. 2011). This tunability of the characteristics makes polyaniline of interest for many different applications including in electronic devices, batteries, solar cells, anti-static building materials, electric heaters, and even filtration of heavy metals (Park et al. 2004; Ansari, 2006).

Wood is an insulating material in the range of 10^{-16}–10^{-12} S cm^{-1}. Anti-static and static-dissipating materials are those with conductivities in the range of 10^{-11}–10^{-6} S cm^{-1} which allow movement of electrons from higher to lower charge densities, inhibiting the delivery of a spark or shock.

Adsorption of polyaniline (PA) particles throughout the structure of the wood is possible because the aqueous monomer solution is able to swell the wood, while the reaction proceeds slowly at low temperatures, with the polyaniline particles precipitating out of solution and filling in pores of the material (Cheung et al. 1997; Stockton and Rubner, 1997; Sapurina et al. 2005; Ansari and Fahim, 2007; Trey et al. 2012). The structure of wood provides a three dimensional template that is lightweight yet has mechanical strength even in the presence of water.

Polyaniline particles have been reported to be anti-bacterial and anti-fungal, protecting against *E. coli* and the fungi *A. solani* (Chauhan et al. 2010). Therefore, it is possible that polyaniline could provide wood protection or provide synergistic protection effects with PEF, while serving the main function of making wood a semi-conductive material.

The aim of this study was to evaluate the influence of polyaniline modification on the degradation of Scots pine sapwood by the brown rot fungus *Postia placenta*, both alone and in combination with a pulsed electric field (PEF). The specific objectives were 1) to study the efficacy of polyaniline in protecting wood, with and without the addition of a pulsed electric field, using rapid agar plate studies 2) to study the polymer uptake and location in wood, cell wall bulking and leaching of polyaniline 3) to investigate the change in electrical conductivity of polyaniline treated wood after exposure to fungi and a pulsed electric field. It was hypothesized that the pulsed electric field may have a synergistic role in combination with polyaniline in terms of providing fungal durability to wood.

2. Experimental sections

2.1. Materials

Scots pine (*Pinus sylvestris* L.) sapwood samples with dimensions of 10 mm × 5.0 mm × 30 mm (miniblock samples) were connected to a pulsed electric field (PEF) by inserting electrodes into holes (5 mm deep and 2.1 mm diameter) drilled in the center of each cross section of the wood specimen, which resulted in an electrode distance of 20 mm inside the wood. Two conductive polymer electrodes were inserted into either end of the wood specimens. The polymer electrodes (40 mm in length) were connected to Duraseal butt-splices, which were connected to Helutherm®145 cables (0.75 mm^2 cross section). Scots pine sapwood boards (further sawn to block size) (density of 528 ± 11 kg m^{-3} at 10.5 ± 0.3% wood moisture content (MC) and annual rings of avg. 1.2 mm periodicity) were supplied by Hallsjö Brädgård AB (Sweden). The aniline (≥99.5% purity), phosphoric acid (85 wt% in H_20, 99.9% trace metal basis), and peroxydisulfate (≥98.0%) were all used as received from Sigma Aldrich.

2.2. Method and procedures

2.2.1. Impregnation/polymerization procedure

The wood block specimens were placed under vacuum and then pressure impregnated for 24 h at 10 bars under inert atmosphere. The first hour of the impregnation process, the solutions were kept at 0 °C and then at room temperature for the remaining time, with solution of aniline in water at concentrations of 0.20 M phosphoric acid with (dopant)/aniline molar ratio of 1 and peroxydisulfate/aniline ratio of 1.25. These reactant ratios have been found to result in the emeraldine salt form of polyaniline with 50% of the emeraldine base protonated or oxidized (Fig. 1). Polyaniline particles formed not only within the wood blocks, but also in the solution containing the wood blocks. The wood samples were then dried in a vacuum oven at 50 °C for 48 h(Table 1).

2.2.2. Bulking of the wood structure, equilibrium water content, and leaching evaluation

The uptake of polyaniline was calculated by correcting for the 14% MC of the originally 65% RH conditioned wood samples and then gravimetrically calculating the weight gained in the samples removed from the oven after treatment. The dimensions of the samples were measured with a slide-caliper at midpoints of each sample in the dried state before and after modification. The water uptake of the samples was measured after 14 days in water gravimetrically by comparing the weight after being removed from the water to the oven dry weight. Leaching of modified wood samples was performed over a period of 14 days using a wood/water volume ratio of 1:5 in which the water was changed nine times according to the European standard EN-84 (ECS, 1997). All measurements are reported as the average of five sample measurements.

2.2.3. Electrical resistance measurements and conductivity determination

The mini-block specimens, both unmodified and modified by PA, leached and unleached, and those exposed to PEF, and/or *Postia placenta*, were cut in cross sections of 0.5 mm × 5 mm × 10 mm. Each cross-section was placed tightly between two gold plate

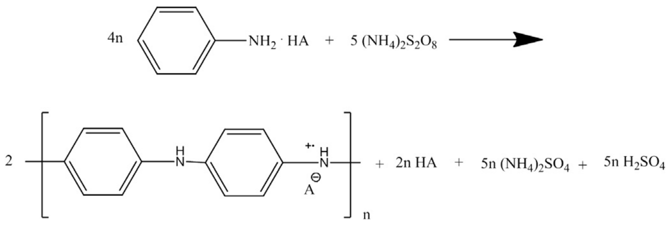

Fig. 1. Reaction scheme of 50% oxidized polyaniline.