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Effect of accelerated weathering on surface chemistry of modified wood

Ali Temiz [a,*], Nasko Terziev [b], Morten Eikenes [c], Jonas Hafren [b]

[a] Department of Forest Industrial Engineering, Karadeniz Technical University, Faculty of Forestry, 61080 Trabzon, Turkey
[b] Swedish University of Agricultural Sciences, P.O. Box 7008, SE-750 07 Uppsala, Sweden
[c] Norwegian Forest Research Institute, Hogskoleveien 8, N-1432 Ås, Norway

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Abstract

In this study, the effects of UV-light irradiation and water spray on colour and surface chemistry of scots pine sapwood samples were investigated. The specimens were treated with chromated copper arsenate (CCA), a metal-free propiconazol-based formulation, chitosan, furfuryl alcohol and linseed and tall oils. The weathering experiment was performed by cycles of 2 h UV-light irradiation followed by water spray for 18 min. The changes at the surface of the weathered samples were characterised by Fourier transform infrared spectroscopy (FT-IR); colour characterizations were performed by measuring CIELab parameters.

The results show that all treatment methods except chitosan treatment provided lower colour changes than the control groups after 800 h exposure in weathering test cycle, but differences between chitosan and control were also small. The lowest colour changes were found on linseed oil (full cell process) and CCA treated wood. FT-IR results show that oil treatment (linseed and tall oil) decreased the intensities of a lignin specific peak (1500–1515 cm^{-1}). Absorption band changes at 1630–1660 cm^{-1} were reduced by all treatments.

Keywords: Chitosan; Colour changes; FT-IR; Furfurylation; Linseed oil; Tall oil; Weathering; Wood modification

1. Introduction

Chromated copper arsenate (CCA) is the most widely used waterborne wood preservative in the world. Standard CCA solutions contain Cr in the form of CrO_3, As in the form of As_2O_5 and Cu in the form of CuO. Inorganic arsenic and hexavalent chromium (Cr^{IV}) are known to be a hazard to the environment and humans. The increasing public concern about the use of arsenic has led to restrictions of chromium and arsenic containing wood preservatives in many countries and a total ban in the European Union [1–4].

The new trends in wood preservation focus on products and processes that utilise environmentally friendly technologies and sustainable resources using re-cycled material or by-products from other industries. Tall oil is a by-product from chemical pulping of resinous softwoods and can be obtained in vast amount at low cost. Crude tall oil is a complex mixture of 40–60% fatty acids, 40–55% resin acids and 5–10% neutral components. Linseed oil is commercially available and has been used for wood impregnation earlier, however, only for full cell impregnation process (to fill totally the cell lumen), thus resulting in a relatively pricy product. The use of furfuryl alcohol for wood modification has been known for decades [5]. Furfuryl alcohol is derived from corn cobs or sugar cane residues. Chitosan is another product obtained from chitin by hydrolysis of the amide C–N bond by strong alkali. The main chitin source is crustacean shells from crab and shrimp from fishing industry. Applications of chitosan in wood preservation are reported by several authors [6,7].

When wood is exposed outdoor, a variety of weathering factors degrades the main structural wood compounds [2,8–10]. The factors contributing most to the wood degradation by weathering are irradiation (UV) and water [2,11–13]. Weathering degradation is defined by colour changes of wood surface, followed by loss of gloss, roughening and checking. The change of wood colour is explained by the fact that the UV component of sunlight, changes in moisture and temperature as well as oxidative agents such as oxygen and/or ozone are able to depolymerise lignin and some polysaccharides in the wood cell wall [14,15]. Lignin is the compound that is most susceptible to

* Corresponding author. Tel.: +90 462 377 28 51; fax: +90 462 325 74 99.
E-mail address: alitemiz@gmail.com (A. Temiz).

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weathering. Deterioration of wood components by weathering causes reduction of, or influence negatively on, the wood's physical, mechanical, chemical and biological properties. Preservatives and modification of wood can significantly influence the behaviour of wood under weathering. Therefore, weathering aspects of treated wood with new wood preservatives and modification methods become of a practical importance.

The objective of the present study was to investigate the colour and changes in wood caused by weathering of CCA treated and modified wood. Chitosan treated, furfurylated, linseed and tall oil treated samples were exposed to accelerated weathering test cycles and the surface changes of wood were compared to those of CCA treated wood. Colour measurement and surface chemistry properties were used to characterise the changes of the wood's main structural compounds after weathering.

2. Material and methods

2.1. Samples and treatment processes

Scots pine (*Pinus sylvestris* L.) sapwood specimens (5 mm × 76 mm × 152 mm) were impregnated with 0.8% solution of CCA and 6% solution of a metal-free preservative. The metal-free preservative consisted of 30% solution of propyconazole mixtured with some additives. Specimens were also treated with linseed and tall oils, chitosan and furfuryl alcohol. The impregnation schedule for all treatments except for chitosan and furfurylation consisted of 30 min vacuum (90%) and 90 min pressure (11 bar). Full cell process, filling the wood cell lumens with chemicals and empty cell process, only treatment wood cell walls with chemicals, known as Lowry process were applied for linseed oil treatment in order to compare and reduce the oil uptake. All impregnation treatments were performed at room temperature.

Impregnations using tall oil with an organic acid catalyst (10 mol%), and pure crude tall oil were carried out by the Lowry process.

Chitosan was dissolved in water and its pH adjusted to 5.0 by acetic acid addition. The chitosan solution was mixed and when its dissolved completely, 4% aqueous solution of potassium nitrite was added and mixed continuously at 30 °C. The concentration of low molecular weight solution of chitosan was 5% for impregnation. The impregnation parameter consisted of 60 min vacuum of 40 mbar followed by 120 min of 12 bars pressure.

Samples treated with furfuryl alcohol had 40% weight percentage gain (WPG) relative to the wood dry weight before treatment. After treatments, reaction/curing step and final kiln drying were applied. Citric acid and cyclic carboxylic anhydrides are used for the catalysts. The 45 min vacuum was applied followed by 12 bar pressure for 120 min for impregnation.

2.2. Accelerated weathering test

The weathering experiment was performed by cycles of UV-light irradiation for 2 h followed by a water spray for 18 min in an accelerated weathering test cycle chamber. The average irradiance was carried out at a wavelength of 340 nm and the temperature in the chamber was 45 °C. Four replicates of each treatment were exposed for 0, 400 and 800 h. Each sample, 5 mm × 76 mm × 152 mm was analysed for colour changes according to ISO 7724, and for chemical degradation of the surface by Fourier transform infrared spectroscopy (FT-IR) spectroscopy.

2.3. Colour measurements

Colour evaluation was carried out according to ISO 7724 standard. The L^*a^*b colour space (according to the Commission International de l'Eclairage-CIE) was used for colour evaluation, in which L^* represents the lightness in the range from black (0) to white (100) and a^* and b^* are the chromaticity coordinates; $+a^*$ for red (+60), $-a^*$ for green (−60), $+b^*$ for yellow (+60) and $-b^*$ (−60) for blue. L^*, a^* and b^* colour coordinates for each sample were determined before and after exposure to accelerated weathering. These values were used to calculate the colour change ΔE^* as a function of the UV irradiation period according to the standard [16].

2.4. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained by a Perkin-Elmer Spectrum One FT-IR instrument with a Universal ATR

Table 1
Colour changes of weathered samples

	400 h				800 h			
	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE
Control	−18.29 (1.88)	3.59 (0.28)	−6.03 (1.07)	19.62 (1.44)	−14.33 (5.14)	0.55 (1.65)	−12.80 (2.04)	19.64 (2.69)
Metal-free 6%	−12.39 (3.87)	1.96 (1)	−9.39 (1.23)	15.88 (2.94)	−7.76 (1.22)	−0.13 (0.90)	−15.05 (0.75)	16.97 (1.01)
5% LMW Chitosan	−12.12 (3.21)	1.70 (1.68)	−12.57 (3.08)	18.01 (0.65)	−8.54 (1.17)	−1.23 (1.43)	−18.50 (0.94)	20.48 (0.73)
CCA	−11.83 (1.59)	7.09 (1.46)	−0.71 (1.70)	13.90 (2)	−5.64 (3.66)	5.03 (1.55)	−6.36 (2.60)	10.69 (0.56)
40% Furfurylated	12.12 (2.73)	−5.58 (0.63)	−4.86 (1.88)	14.25 (3.07)	13.10 (2.99)	−5.92 (1.31)	−7.90 (1.18)	16.58 (2.28)
Linseed oil empty cell	−9.67 (1.03)	3.45 (1.86)	−2.91 (4.36)	11.20 (0.33)	−10.37 (1.15)	4.92 (0.23)	−4.34 (0.98)	12.29 (1.22)
Linseed oil full cell					0.54 (4.20)	5.67 (0.11)	6.60 (4.19)	9.43 (3.11)
Tall oil	−14.69 (5.04)	1.52 (0.95)	−8.65 (2.63)	17.46 (3.02)	−13.42 (7.41)	0.73 (1.79)	−12.33 (1.29)	18.78 (4.52)
Esterified Tall oil	−15.47 (2.91)	5.85 (2.14)	−2.32 (2.25)	16.89 (3.07)	−11.32 (3.19)	3.83 (1.70)	−7.18 (1.79)	14.26 (2.13)

Standard deviations in parentheses.