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Photostabilisation of wood using aromatic vinyl esters

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ABSTRACT

Thin wood veneers were esterified to different weight gains with vinyl benzoate, vinyl cinnamate or vinyl-4-T-butylbenzoate to graft aromatic groups to wood's molecular components. We hypothesised that such modification would increase the resistance of wood to photodegradation. There was a linear relationship between the level of esterification of wood with vinyl benzoate and the photostability of the modified veneers exposed to natural weathering. Vinyl benzoate protected lignin and cellulose in wood from photodegradation at high weight gains (>30%) whereas modification of wood with vinyl-4-T-butylbenzoate provided no such protection and vinyl cinnamate increased the photodegradation of wood. We provide an explanation for why these effects occurred and discuss the implications of our findings for the development of weather-resistant wood materials.

1. Introduction

Wood is very susceptible to photodegradation because one of its main chemical components, the aromatic polymer, lignin, strongly absorbs UV radiation [1]. Photolysis of lignin leads to the formation of aromatic and other radicals which further degrade lignin and depolymerise wood's other chemical components, cellulose and hemicelluloses [2]. The photodegradation and weathering of wood adversely affects its appearance and surface properties, and reduces the performance of coatings on wood, particularly those that are transparent to UV or visible light [3]. Hence, there is wide-spread interest in improving the resistance of wood to photodegradation, and a variety of different approaches have been tested [4]. The photodegradation of many polymers can be effectively controlled with additives such as UV absorbers and hindered amine light stabilisers [5]. These additives are less effective with wood, and higher concentrations are needed to provide adequate levels of protection [4]. Excellent photo-protection of wood can be achieved, however, with chromic acid, which chemically modifies the molecular structure of lignin to make it less photo-labile [6]. Chromic acid is toxic and attempts to find equally effective and safer alternatives have been unsuccessful [7,8]. Nevertheless, interest remains strong in the chemical modification of wood as a way of improving its photostability.

Wood can be easily modified using acid chlorides and anhydrides [9,10] and several studies have shown that these treatments improve the photostability and weathering resistance of wood [10]. The majority of these treatments are unable to protect lignin from photodegradation, unlike chromic acid. One exception, however, is esterification with benzoyl chloride, which can photostabilise lignin in wood, and provide levels of protection that match those of chromic acid [11,12]. Benzoyl chloride introduces large numbers of aromatic groups into wood, which may protect lignin and cellulose from photodegradation by absorbing UV radiation [11]. Modification of wood with benzoyl chloride, however, generates hydrochloric acid as a by-product, and this can depolymerise cellulose or cause corrosion of metal fasteners [9,10]. These undesirable side-effects are an obstacle to the use of benzoyl chloride for the photostabilisation of wood. Hence, it would be desirable to find a method of esterifying wood with aromatic compounds that can photostabilise wood and does not generate unwanted acidic by-products.

Recently, we showed that wood can be easily esterified using vinyl esters including aromatic vinyl esters [13,14]. The by-product of this reaction is acetaldehyde, which is not acidic and can be easily removed from wood after esterification because of its low boiling point (b.p. [760 mm Hg] = 21 °C). In this paper we esterified thin wood veneers to different weight gains with three different aromatic vinyl esters, vinyl benzoate, vinyl cinnamate and vinyl-4-ter-butylbenzoate and examined the photostability of the modified wood. We hypothesise that the introduction of aromatic groups into wood as a result of its modification with these vinyl esters will protect the wood from photodegradation. Furthermore, we anticipate that there will be a positive relationship between weight gain of chemically modified wood and its photostability.

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2. Experimental

2.1. Wood veneers and chemical modification

One hundred wood veneers approximately 85 µm thick were cut from the radial face of each of five different water-saturated yellow cedar (*Chamaecyparis nootkatensis* (D. Don) Spach) blocks, as described previously [15]. Yellow cedar was chosen because it is easy to microtome and is used for a range of different wood products (cladding, windows, exterior doors, boats, etc) exposed outdoors. Wet microtomed veneers were placed on glass plates, lightly clamped at their ends and air-dried for 4 h. Veneers were removed from the plates and placed in batches of 10 in paper envelopes and stored in a conditioning room at 20 ± 1 °C and 65 ± 5% relative humidity for two weeks. The thickness of each veneer was measured using a digital micrometer and each veneer was weighed, oven-dried at 105 ± 5 °C for 45 min and then re-weighed. All veneers, including untreated controls were Soxhlet extracted with toluene/ethanol (2:1 v:v) for 8 h and then with distilled water for an additional 8 h. Veneers were oven-dried and re-weighed, as above. For each treatment, 10 veneers were treated together in a solution containing the vinyl ester, 0.15 g of K_2CO_3 (catalyst) and 20 mL of dimethylformamide. The concentration of vinyl esters in solution was varied to obtain different weight gains and percentages of substituted OH groups in reacted veneers (Table 1). All reactions were performed at 90 °C for 3 h. The esterification reaction proceeds as follows, releasing acetaldehyde as a by-product (Scheme 1).

After reaction the esterified veneers were Soxhlet extracted with water for 2 h to remove the K_2CO_3 catalyst and then with toluene/ethanol/acetone (4:1:1 v:v:v) for an additional 8 h to remove non-bonded chemicals. The percentage weight gains (WPGs) of treated and extracted veneers were then calculated as: $WPG = 100(M_1 - M_0){:}M_0$, where M_0 and M_1 are the oven dry weights of the veneers before and after esterification, respectively.

2.2. Photostability of esterified veneers

The photostability of esterified and untreated veneers was assessed using natural weathering. Five veneers from each batch of 10 treated veneers for the ten different treatments (vinyl ester and weight gain combinations plus the untreated control) were selected at random, placed against glass backing plates and clamped lightly at their ends. The remaining five veneers for each treatment were placed in a conditioning room at 20 ± 1 °C and 65 ± 5% relative humidity for the duration of the exposure trial. These veneers acted as unexposed controls and were used to estimate the effects of the different treatments on the strength of veneers and the strength losses of veneers exposed to the weather. Ten glass plates each containing 25 esterified veneers and one batch of untreated veneers in groups of five were exposed outdoors for 25 days in Vancouver during the summer of 2007. The plates were oriented horizontally and facing south to maximise the total UV radiation received by veneers. After weathering, veneers were oven-dried as above and the mass of each individual veneer was recorded. Mass losses during weathering are expressed simply in percentage terms. Tensile strength tests were carried out on conditioned veneers at zero-span using a Pulmac paper tester as described previously [15].

2.3. Analytical techniques

Infrared spectra of weathered veneers and controls were obtained using an Omnic spectrometer. Weathered and unexposed veneers were placed under the silicon crystal of an attenuated total reflectance (ATR) accessory of the spectrometer. Spectra were collected over 4000–650 cm^{-1}, with a resolution of 8 (SSP 3.857 cm^{-1}) and 64 scans per veneer. Three spectra were collected for each veneer and averaged. The spectral data were imported into software (CAMO, v. 9.6), normalised and averaged.

The yellow colour of veneers and controls before and after weathering was measured using a Minolta CM-2600d spectrophotometer and is expressed using the CIELab colour coordinate b^* (+60 [yellow] to −60 [blue]). Using this system, increases in b^* represent yellowing of the wood.

The surfaces of unexposed veneers and those subjected to natural weathering were examined using scanning electron microscopy. Small samples measuring 10 × 10 mm were cut from veneers using a pair of scissors and attached to separate aluminium stubs using double-sided self-adhesive tabs. The stubs were coated with a 10 nm layer of gold using a sputter coater (Nanotech SEMPrep II) and they were then examined using a Hitachi S-4700 field emission scanning electron microscope at an accelerating voltage of 1 kV. Images of samples were obtained and saved as TIFF files.

Regression analysis was used to examine the relationship between weight gain of veneers as a result of esterification and the ability of the treatments to restrict losses in mass and tensile strength of veneers. Statistical computation was performed using Genstat [16].

3. Results

3.1. Weight and tensile strength losses

Modification of veneers to high weight gains with either vinyl benzoate or vinyl cinnamate was effective at reducing the weight losses of veneers when they were exposed to natural weathering (Fig. 1). Fig. 1 plots the average percentage weight losses of batches of five veneers during weathering against their average percentage weight gain due to esterification. There is an inverse linear relationship between weight gain of veneers due to esterification and weight losses of veneers during weathering (Fig. 1). Regression lines drawn through these data are parallel, but with different intercepts. Regression analysis was performed on weight gain of

Table 1
Solution concentrations, weight gains, degree of substitution and tensile strength gains of veneers modified with vinyl benzoate, vinyl cinnamate and vinyl-4-T-butylbenzoate.

Parameter	Vinyl ester and solution concentration (mol/L)								
	Vinyl benzoate			Vinyl cinnamate			Vinyl-4-T-butylbenzoate		
	0.12	0.78	1.52	0.07	0.18	0.9	0.32	0.88	1.13
Average WPG[a] (%)	14.8	24.1	29.8	10.1	17.6	29.1	11.4	16.1	15.9
Substitution[b] (mmol/g dry wood)	1.42	2.32	2.87	0.78	1.35	2.24	0.71	1.01	0.99
Strength gain (%)	7.2	8.1	4.5	5.0	5.8	2.8	2.8	4.1	9.6

[a] WPG = weight gain of veneers due to esterification.

[b] The number of OH groups substituted in wood after treatment was calculated from the WPG and the molecular weight of the adduct, assuming a 1:1 molar reaction between the vinyl esters and wood hydroxyl groups. The formula used accounts for the hydrogen atom transferred from wood to the vinyl alcohol (−1 in the formula): OH substituted (in mmol/g dry wood) = 0.01 × WPG/(molecular weight of adduct − 1) × 1000.