Weathering and photostability of benzoylated wood

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1. Introduction

Wood surfaces exposed outdoors are rapidly degraded because lignin strongly absorbs UV light, which leads to radical-induced depolymerisation of lignin and cellulose, the major structural constituents of wood [1,2]. Photodegradation of wood also occurs beneath clear finishes and this greatly reduces the durability of transparent film-forming varnishes used outdoors [3,4]. It is possible to improve the performance of clear finishes on wood by photostabilising the wood before application of the finish [5]. Williams [6] showed that grafting of the modified benzophenone UV absorber (UVA), 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPB) to wood reduced the erosion of unfinished western red cedar (Thuja plicata Donn ex D. Don) and, as a pretreatment, improved the performance of clear finishes during artificial accelerated weathering (xenon-arc UV light and water spray). Recently it was shown that grafting of HEPBP to wood increased the performance of clear silicone-urethane and polybutadiene varnishes on Japanese cedar (Cryptomeria japonica D. Don) [7]. Grafting of an isocyanate functionalised UVA to wood has also been shown to be effective in retarding the photo-induced discolouration of wood [8]. Despite the promise of UVA grafting as a means of photostabilising wood, the current systems have a number of limitations in that they require the synthesis of a functionalised UVA and the use of high temperatures or microwave irradiation to bond the UVA to wood. From a practical point of view it would therefore be desirable to develop less costly UVAs that can be more easily bonded to wood.

Large numbers of chemicals including anhydrides, acid chlorides, carboxylic acids, isocyanates, aldehydes, alkyl chlorides, lactones, nitriles and epoxides have been used to chemically modify wood [9]. These chemicals are capable of forming covalent linkages with hydroxyl groups on lignin and cellulose and, in certain cases, also bulking the wood cell wall with reacted chemical. Chemical modification of wood dramatically reduces the potential of water to interact with the polymeric constituents of wood, which is why it has been widely used to improve the durability of wood products. Chemical modification of wood is also a potential means of improving the durability of wood by photostabilising the wood before application of clear finishes [5].
studied, and in certain cases used commercially, as a means of enhancing the dimensional stability and decay resistance of wood [9]. Relatively few chemical modification techniques, however, have been assessed for their ability to photostabilise wood and previous studies have generally tested those systems that have shown promise in protecting wood from decay rather than selecting ones for their potential to protect wood from photodegradation. Furthermore, in most previous studies of the photostability of chemically modified wood, solid wood was modified to weight gains (WGs) of 10–20%.

At such levels of modification, acetylation has been shown to reduce the photoyellowing and checking of wood exposed to natural or artificial accelerated weathering [10,11]. Cellulose is also protected to some degree but acetylation is unable to photostabilise lignin [12–14]. Similar findings have been obtained for other systems including modification of wood with simple epoxides [15], isocyanates [15,16] and carboxylic acid anhydrides [17]. Recently we observed a positive correlation between weight gain, in the range of 5–20%, of thin wood veneers due to acetylation and the photostability of the modified wood, suggesting that further beneficial effects of chemical modification on the photostability of wood could be obtained by increasing WGs beyond 20% [18].

In this study, thin Scots pine (Pinus sylvestris L.) veneers and small Scots pine wood blocks were chemically modified (esterified) to high weight gains with the aromatic acid chloride, benzoyl chloride, and the photostability of the chemically modified wood was assessed. Benzoyl chloride reacts with hydroxyl groups in wood (Scheme 1) and preliminary experimentation had shown that it reacted very rapidly with wood veneers producing very high WGs. Furthermore, it was reasoned that the introduction of large quantities of benzoyl groups into the wood cell wall might act as a UV screen protecting lignin and cellulose from photodegradation. The photostability of wood modified with simple aromatic chemicals such as benzoyl chloride has received little attention and, if effective in protecting wood, they offer advantages over epoxide or isocyanate functionalised UV absorbers in that they are relatively inexpensive and can be more easily bonded to wood.

2. Experimental

2.1. Wood veneers and chemical modification

Wood veneers approximately 85 μm thick were cut from the radial face of Scots pine sapwood blocks measuring 80 mm (longitudinal) × 50 mm (tangential) × 20 mm (radial) as described previously [19]. Veneers were conditioned at 20 ± 1 °C and 65 ± 5% relative humidity (r.h.) for 2 weeks and the thickness of individual veneers was measured using a digital micrometer (Lorentzen and Wettre). Veneers were extracted with a mixture of acetone (4): ethanol (1): toluene (1) (all industrial grade) for 4 h in a soxhlet apparatus. Veneers were then grouped in batches of 5, oven dried at 105 ± 5 °C overnight, cooled in a desiccator over silica gel for 10 min and weighed. Batches of veneers were placed separately in groups of five in 100 mL boiling tubes. A solution of benzoyl chloride (50 mL, BDH reagent grade): pyridine (500 mL, Aldrich reagent grade) was added to each tube to completely immerse the veneers (approximately 75 mL). Each tube was covered with a rubber septum and then placed in an oil bath at 50 or 65 °C for various periods of time to achieve different weight gains. Pyridine was chosen as the solvent for the reaction because it is a good catalyst for esterification of wood and it neutralises the hydrochloric acid that is a by-product of the reaction of benzoyl chloride with wood (Scheme 1).

After reaction, veneers were placed in acetone (800 mL, industrial grade) for 10 min and then refluxed in fresh acetone (500 mL) for 30 min to remove any unreacted chemical. Veneers were oven dried and reweighed as above and weight gains due to chemical modification were calculated and expressed as a percentage of the initial, unreacted, oven dry weight. The chemically modified veneers and controls were placed in a conditioning room at 20 ± 1 °C and 65 ± 5% r.h. for 2 weeks.

2.2. Weathering assessments

The photostability of benzoylated wood specimens was assessed using both natural and artificial accelerated weathering. Chemically modified veneers and untreated controls were placed against glass backing plates and clamped lightly at their ends. These plates were exposed outdoors facing equatorially and at an angle of 45° to the horizontal in Canberra, Australia during the summer of 1999 for 25, 50 and 75 days. In the case of artificial accelerated weathering, glass plates containing veneers were placed in a weatherometer (Atlas model 600/XW-WR) and exposed continuously to UV light, generated by a xenon-arc lamp, and 4 h of water spray every 24 h. Batches of modified veneers and unmodified controls were removed from the weatherometer after 50, 100, 150 and 200 h. After weathering, veneers were oven dried as above and the mass of each individual veneer recorded. Mass losses during weathering are expressed simply in percentage terms or as mass losses (mg). Tensile strength tests were carried out on conditioned veneers at zero-span using a Pulmac paper tester as described previously [19].
2.3. Scanning electron microscopy

Specimens measuring 5 mm (radial) \times 5 mm (tangential) \times 15 mm (longitudinal) were cut from Scots pine sapwood and soaked in distilled water for 4 days until saturated. Blocks were then clamped in a small vice, viewed under a stereo-microscope at a magnification of \times 20, and single edged razor blades (Magnuson Injector blades 500/1 890018) were used to prepare clean transverse (TS) surfaces. Blocks were then dried over silica gel for 2 weeks. One half of each block was reacted in a 10\% solution of benzoyl chloride in pyridine for 1 h (as above) to achieve weight gain of \sim 30\% while the other half was reacted in pyridine for a similar length of time. After reaction, specimens were soaked in acetone for 24 h, refluxed in acetone for 3 h and dried over silica gel for 2 weeks. Half of the benzoylated specimens and pyridine treated controls were attached to wooden backing plates using alligator clips with the transverse surface uppermost and exposed (as above) to the weather for 30, 100 or 365 days starting in the summer of 1999. The remaining blocks were kept in a conditioning room for the duration of the exposure periods. After weathering, dust was removed from exposed blocks using a stream of nitrogen gas and all blocks, including unexposed controls, were dried at atmospheric pressure over silica gel at 20 °C for 2 weeks and then attached to aluminium stubs using nylon fingernail varnish as an adhesive. They were then sputter coated with a 10 nm layer of gold and the transverse surface of each block was examined using a scanning electron microscope (SEM) (Cambridge 360) operating at 10 kV. Selected images of unweathered and weathered wood surfaces were recorded on Ilford FP4 film.

2.4. Analytical techniques

Infrared spectra of weathered veneers and controls were obtained using a Mattson Sirius 100 spectrometer operating at 4 cm\(^{-1}\) resolution and incorporating a Spectra Tech diffuse reflectance (collector) accessory unit [20]. A Bruker ER 200D continuous wave X-band spectrometer with a TE102 cavity was used to obtain electron spin resonance (ESR) spectra of benzoylated veneers (74\% WG) and unmodified controls before, during and after exposure to UV light. The modulation frequency was set at 50 KHz, microwave power at 2.0 mW and the modulation amplitude at 2.0 Gauss. The samples were placed inside 3 mm (id) silica tubes and exposed to light generated by an Osram 500W mercury lamp connected to an Oriel Optics power supply. The mercury arc lamp has intense emissions in the ultra-violet (253.7, 365–366 nm) and visible (405, 436, 546 and 577 nm) regions. In situ ESR-photolysis experiments were conducted at ambient temperatures, similar to those encountered during the weathering trials (see Section 2.2). The effect of benzoylation on the UV absorption characteristics of veneers was assessed using UV spectroscopy. Thin wood veneers approximately 25 \mu m thick were cut (as above) from the radial face of a water saturated Scots pine block measuring 20 \times 50 \times 20 mm. Veneers were conditioned for 1 week and the UV absorption of 5 veneers was measured using a Varian Cary 5E UV-VIS-NIR spectrophotometer. Veneers were then benzoylated to high weight gain (as above), reconditioned, and their UV absorption characteristics remeasured.

3. Results

3.1. Weight and tensile strength losses of veneers

Losses in the mass and tensile strength of thin wood veneers during natural and artificial weathering have been widely used to assess the resistance of wood to weathering [1,19,21–24]. Mass losses of wood veneers during weathering occur due to photodegradation of lignin and leaching of the degraded lignin fragments from exposed wood surfaces [2]. Losses in tensile strength occur due to photo-induced depolymerisation of cellulose [1]. By combining measures of the losses in mass and tensile strength of treated wood veneers during exposure to natural or artificial weathering it is therefore possible to obtain information on the ability of a chemical treatment to photostabilise lignin and cellulose [19], the main structural constituents of wood. Accordingly, the main technique used in this study to assess whether benzoylation was effective in photostabilising wood involved measurement of the losses in mass and tensile strength of treated veneers on exposure to natural or artificial weathering. A preliminary exposure trial of veneers reacted to different weight gains with benzoyl chloride and then exposed to natural weathering for 50 days showed that at WGs in excess of 20\% there was an inverse relationship between WG and mass losses of veneers during exterior exposure (Fig. 1). Below 20\% WG benzoylation had little photoprotective effect or increased the mass losses of veneers during weathering (Fig. 1).

Because benzoylation of wood veneers to high WGs was highly effective in restricting losses in mass of veneers during natural weathering (Fig. 1) subsequent exposure trials involved veneers modified to high WGs. The mass losses of batches of veneers reacted with benzoyl chloride to 72.4\% WG and exposed to the weather for 25, 50 and 75 days are shown in Fig. 2. The mass losses of untreated veneers are shown for comparison. Both untreated and benzoylated veneers showed increased mass losses with exposure to the weather, but at each exposure period the mass losses of benzoylated veneers were approximately half those of the untreated controls. Losses in tensile strength of benzoylated veneers and controls during natural weathering are shown in Fig. 3.
As expected the untreated controls showed large losses in tensile strength during exposure to weathering. The benzoylation treatment alone caused large losses in the tensile strength of veneers, but thereafter, during exposure to weathering, losses in tensile strength were less pronounced (Fig. 3).

The effectiveness of benzoylation in restricting mass losses of veneers during weathering was confirmed by an artificial accelerated weathering trial of batches of veneers modified to 71.4% WG. Fig. 4 shows the mass losses of benzoylated veneers and untreated controls exposed to artificial accelerated weathering in a xenon-arc weatherometer for 50, 100, 150 and 200 h. The mass losses of the benzoylated veneers were approximately half those of the control after 50 h. Thereafter the rate of increase in mass losses of benzoylated veneers with exposure decreased and after 200 h exposure the mass losses of benzoylated veneers were one third of those of

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Fig. 1. Effect of weight gain due to benzoylation on % weight losses of veneers after 50 days natural weathering.

Fig. 2. Effect of benzoylation to high WG on the mass loss of Scots pine veneers during natural weathering, confidence intervals (± standard deviation) show sample variability around means.

Fig. 3. Effect of benzoylation to high WG on the tensile strength of Scots pine veneers during natural weathering, confidence intervals (± standard deviation) show sample variability around means.

Fig. 4. Effect of benzoylation to high WG on the mass loss of Scots pine veneers during artificial accelerated weathering, confidence intervals (± standard deviation) show sample variability around means.
the untreated control. In accord with the findings of the natural weathering trial (Fig. 3) the benzoylation treatment caused large losses in the tensile strength of veneers, but protected veneers from further large decreases in strength during weathering (Fig. 5).

3.2. Chemical changes

The chemical changes occurring in untreated and benzoylated wood veneers (72% WG) during natural weathering were examined by FTIR spectroscopy. Only the fingerprint region between 500 and 2000 cm\(^{-1}\) is shown in Figs. 6 and 7 since this is where significant spectral changes may be observed. The infrared spectra of unmodified wood, before and after weathering, are shown in Fig. 6, and it can be seen that weathering has a pronounced effect on the spectra of unmodified wood. The most obvious differences between spectra of the

![Fig. 5](image5) Effect of benzoylation to high WG on the tensile strength of Scots pine veneers during artificial accelerated weathering, confidence intervals (±standard deviation) show sample variability around means.

![Fig. 6](image6) Infra-red spectra of unmodified veneers before and after 25, 50 and 75 days natural weathering.

![Fig. 7](image7) Infra-red spectra of benzoylated veneers before and after 25, 50 and 75 days natural weathering.
unweathered veneers (0d) and the spectra of those subjected to weathering for 25, 50 and 75 days include the weakening of absorptions at 1602, 1508 and 1265 cm\(^{-1}\) indicating delignification of the weathered samples. Some reduction in the intensity of the 1728 and 808 cm\(^{-1}\) peaks was also observed, consistent with degradation of non-cellulosic polysaccharides (hemicelluloses) [25].

The spectra of benzoylated veneers before and after weathering are shown in Fig. 7. The introduction of benzoyl groups results in large increases in the carbonyl stretching absorption (now centered at about 1760 cm\(^{-1}\)) and in bands characteristic of mono-substituted aromatic rings (e.g. 1600, 1500, 1450, and 700 cm\(^{-1}\)). Another strong absorption observed at about 1265 cm\(^{-1}\) is probably caused by the introduction of the C(=O)O groups. This is consistent with the IR-spectrum of the closely related ester, methyl benzoate, which shows a strong absorption at \(\sim 1280\) cm\(^{-1}\) (Fig. 8). An increase in the intensity of other peaks at 1312, 1160, 1100, 1030, 805, and 617 cm\(^{-1}\) is also consistent with the presence of benzoyl groups in the wood. The most important feature of the spectra shown in Fig. 7 is the fact that the weathered samples (25, 50 and 75 days) show relatively little of the delignification effects seen so prominently in the spectra of the unmodified samples. For example, the aromatic ring breathing mode at 1508 cm\(^{-1}\) and other “lignin” peaks at 1450 (CH\(_3\) deformation) and 1600 cm\(^{-1}\) (C=C stretching), although slightly decreased in intensity, are still prominent after 75 days of weathering. Another notable feature is the absence of an intense band at 870 cm\(^{-1}\) which is present in the IR-spectrum of benzoyl chloride (Fig. 8). This indicates that the esterification reaction (Scheme 1) has gone to a high degree of completion and there is little or no benzoyl chloride remaining in the benzoylated wood.

Fig. 9(a) show ESR spectra of untreated Scots pine veneer before and after exposure to UV light from a mercury arc lamp (see Section 2.4). Wood does not possess inherent free radicals [26,27], therefore, the presence of a residual ESR signal at 3477 G with a line width of ca. 10 G before exposure to light from the lamp [Fig. 9(a), Initial] is thought to be due to the effects of ambient light on the wood prior to recording the spectrum. After the mercury light was turned on there was an immediate increase in the intensity of the ESR signal (Fig. 9, 1 min) and a continual increase over time (Fig. 9, 3–60 min), with a levelling off in intensity at longer times. When the light was extinguished after 60 min the ESR signal gradually decayed to the intensity of the initial scan after a period of ca. 24 h, indicating that the free radicals formed by photolysis were only moderately stable.

Fig. 9(b) show ESR spectra of benzoylated Scots pine veneer before and after exposure to UV light. The spectra were obtained with identical instrumental parameters and with a sample of identical wood mass to the untreated sample, which was placed in the same position within the EPR cavity as the untreated sample [Fig. 9(a)]. Therefore the signal intensity measurements allow a quantitative measure of the difference in amount...
of free radicals produced during photolysis between the two samples. Prior to the photolysis experiments [Fig. 9(b), Initial] the benzoylated sample showed at least 10 times less free radicals than the untreated sample. Similarly, during exposure to strong light the benzoylated sample showed an increase in the amount of free radicals produced, but the ESR signal intensity and hence the amount of free radicals generated were approximately 10 fold less than in the untreated sample. Overall the ESR data suggest that the benzoylation modification inhibits the generation of free radicals in wood during exposure to light, which may account for

![Graphs showing ESR spectra](image)

Fig. 9. X-band ESR spectra obtained prior to and during the in situ photolysis of (a) untreated and (b) treated Scots pine veneers. Microwave frequency = 9.78 GHz. $T = 25\pm 5$ °C.
the improved photostability of the chemically treated wood. Turning off the light source and allowing the sample to recover overnight [Fig. 9(b), 12 h] showed the radical signal decreasing in a similar fashion to that observed in the untreated sample. The sharp signal present in Fig. 9(b) at ca. 3485 G is also present in Fig. 9(a) but is masked by the much stronger signal at 3477 G, and is presumably due to the presence of a small amount of another free radical (whose intensity is less affected by the strong light conditions).

The UV spectra of unmodified and treated veneers are shown in Fig. 10. Unmodified veneers show a strong peak at around 280 nm due to the absorption of UV light by lignin. This peak becomes less pronounced as a result of benzoylation, possibly because chemical modification of the veneer alters the absorption characteristics of lignin. The benzoylated sample does not show the strong band at 250 nm present in pure benzoyl chloride (Fig. 10), which is further evidence in addition to the IR data presented above that there is no residual unbound benzoyl chloride in modified veneers.

3.3. Scanning electron microscopy

The appearance of thin walled earlywood tracheids and thicker walled latewood tracheids in Scots pine wood before benzoylation are shown in Fig. 11a and b, respectively. Reaction of small wood blocks with benzoyl chloride had significant effects on the morphology of these cell types (Fig. 11c–d). Benzoylation caused swelling of wood cell walls, which was particularly apparent in latewood tracheids (Fig. 11d) and closure of cell lumens in latetwood (Fig. 11d). Swelling of the wood cell wall was pronounced in the S1 layer of the secondary wall probably because it is found adjacent to cell lumens and would therefore be readily accessible to benzoyl chloride. Swelling of the middle lamella layer that bonds tracheids together was also conspicuous (Fig. 11d, arrowed), perhaps also because at the surface of tracheids this layer was accessible to benzoyl chloride. The middle lamella also has a high concentration of lignin, which has been shown to react more readily with chemicals used to modify wood than cellulose [9]. This may also partially explain the pronounced swelling of the middle lamella observed here (Fig. 11d). After wood blocks were reacted with benzoyl chloride they were washed and refluxed with acetone to remove any unreacted chemicals. If this step was omitted prior to SEM, small nodules were present on the surface of benzoylated latewood tracheids (Fig. 11e–f). The chemical composition of these nodules is not known, but they were found mainly on the middle lamella (Fig. 11f) suggesting that they might be a product arising from the reaction of lignin and benzoyl chloride.

The surface appearance of benzoylated tracheids and unmodified controls after 30 days natural weathering is shown in Fig. 12a–f. The unmodified controls showed loss of the middle lamella, distortion of cell lumens and delamination of the S1 layer of the secondary wall (Fig. 12a–c). The cell walls of unmodified, weathered, earlywood tracheids appeared to be much thinner than those of unweathered tracheids (compare Fig. 12a with Fig. 11a), suggesting erosion of the cell wall. Loss of the middle lamella layer appeared to be complete at the surface of unmodified, weathered, earlywood and latewood tracheids (Fig. 12a–c). In contrast the middle lamella could still be clearly discerned in benzoylated earlywood tracheids after 30 days weathering (Fig. 12d). Some erosion of the middle lamella and delamination of the cell wall was apparent in benzoylated latewood tracheids after 30 days weathering (Fig. 12e–f), but overall the changes were less pronounced than in unmodified, weathered, samples.

After 100 days weathering, distortion of tracheids and erosion of cell walls became more pronounced in the unmodified controls (Fig. 13a and b), particularly in earlywood (Fig. 13a). Changes in the morphology of benzoylated specimens were also apparent after 100 days weathering (Fig. 13c and d). In both earlywood and latewood tracheids, erosion of the middle lamella occurred and splits developed in cell walls (Fig. 13c and d). In latewood tracheids cell lumens opened up suggesting loss of esterified cell wall material (Fig. 13d). After 1 year exposure to the weather, the cellular structure of unmodified specimens was largely destroyed (Fig. 13e and f) whereas that of benzoylated specimens was preserved, albeit with further erosion of the cell walls and opening up of cell lumens (Fig. 13g and h).
4. Discussion

The mass loss results from the natural and artificial weathering trials both suggested that benzoylation of wood veneers to high WGs ($\sim 72\%$) was effective at protecting wood from photodegradation. The photoprotective effect of benzoylation appeared to be less pronounced in the natural weathering trial compared to the artificial accelerated weathering test possibly because in the former, veneers were more susceptible to mass losses arising from physical damage to veneers such as erosion and loss of thin slivers of wood. The results from the artificial weathering test may therefore be a better guide to the ability of benzoylation to photostabilise the chemical constituents of wood, a suggestion that runs contrary to the perceived wisdom of the reliability of data from artificial as opposed to natural weathering trials.

FTIR spectroscopy and scanning electron microscopy of modified and weathered wood samples suggested that benzoylation of wood to high WGs reduced the rate at which lignin was removed from wood surfaces as a result of the weathering process. Weight losses of wood veneers during weathering occur due to photodegradation and leaching of lignin from exposed wood surfaces [2]. Accordingly, the ability of benzoylation to protect

![Fig. 11. Effect of benzoylation on the morphology of Scots pine tracheids: (a), unmodified earlywood $\times 1.1k$, (b) unmodified latewood $\times 1.52k$, (c) benzoylated earlywood $\times 1.1k$, (d) benzoylated latewood $\times 1.05k$, (e) benzoylated latewood (not refluxed in acetone) $\times 914$, (f) benzoylated late-wood (not refluxed in acetone) $\times 2.73k$. Scale bar $= 20 \, \mu m$.](image-url)
lignin from photodegradation may explain why weight losses of benzoylated veneers during natural and artificial weathering were significantly lower than those of unmodified controls. Previous studies of the weathering of chemically modified wood in which samples were modified to low WGs have shown little if any photoprotective effect of chemical modification on the lignin component of wood. For example both acetylation [12–14,18] and alkylation (at low WGs) [14] have been shown to be ineffective in photostabilising lignin in wood. Therefore the finding here that chemical modification of wood to high WGs with benzoyl chloride can photostabilise lignin is noteworthy.

The precise mechanisms and pathways involved in the photodegradation of lignin and cellulose in wood have yet to be elucidated. However, it is clear that the key step is absorption of UV light by lignin and photolysis and fragmentation of lignin resulting in the formation of aromatic and other radicals [27]. These free radicals may then cause further degradation of lignin and photooxidation of cellulose and hemicellulose. Free radical reactions may be terminated by reaction of radicals with photodegraded lignin fragments forming coloured, unsaturated, carbonyl compounds, which explains why wood yellows when exposed to light. Benzoyl groups in wood absorbed UV light in the same part of the

Fig. 12. Effect of 30 days weathering on the morphology of benzoylated Scots pine tracheids and unmodified controls: (a) unmodified earlywood ×1.2k, (b) unmodified latewood ×1.2k, (c) unmodified latewood ×2.27k, (d) benzoylated earlywood ×844, (e) benzoylated latewood ×1.1k, (f) benzoylated latewood ×2.1k. Scale bar = 20 μm.
Fig. 13. Effect of prolonged weathering [100 days (a–d) and 1 year (e–h) on the morphology of benzoylated Scots pine tracheids and unmodified controls: (a) unmodified earlywood ×726, (b) unmodified latewood ×1.0k, (c) benzoylated earlywood ×600, (d) benzoylated latewood ×1.0k, (e) unmodified earlywood ×500, (f) unmodified latewood ×816, (g) benzoylated earlywood ×1.0k, (h) benzoylated latewood ×1.02k. Scale bar = 20 μm.
spectrum that is strongly absorbed by lignin and ESR spectra of benzoylated and untreated veneers clearly showed that benzoylation retarded the formation of free radicals. Therefore the photoprotective effects of benzoylation could result from the introduction of benzoyl groups into wood that absorb UV light and retard the formation of aromatic (lignin) radicals that initiate photo-oxidation. Alternatively it is possible that benzoyl groups in wood scavenged free radicals preventing them from attacking lignin and cellulose. Such a suggestion is consistent with observations of the ability of hindered phenolic antioxidants to terminate free radicals and photostabilise polymers [28].

The tensile strength of wood depends on the properties of cellulose, specifically its degree of polymerisation and the extent to which it is cross-linked at the molecular level. Benzoylation of wood veneers to high WGs was associated with large losses in the tensile strength of veneers possibly because the introduction of bulky benzoyl groups into the cell wall disrupted intermolecular bonding of cellulose. Further losses in tensile strength of benzoylated veneers during weathering, however, were small suggesting that benzoylation was able to protect cellulose from photodegradation. Acetylated cellulose derivatives such as cellulose acetate and triacetate are reported to be less susceptible to photodegradation than cellulose [29,30]. Benzoates show similar properties to acetates [31]. Therefore the finding that benzoylation of wood to high WG provided some photoprotection to the cellulose component of wood accords with the known properties of esterified celluloses.

The finding that at low weight gains benzoylation increased the photodegradation of wood is similar to our previous observations of the effect of acetylation to 5 or 10% WG on the susceptibility of wood to photodegradation [18]. An explanation for this effect is that substitution of phenolic hydroxyl groups, which occurs preferentially at low WGs, prevents the formation of unsaturated carbonyl compounds that terminate the phenoxy and peroxy radicals involved in photodegradation. Thus the blocking of such a reaction pathway may increase the susceptibility of the chemically modified wood to photodegradation by reducing the ability of lignin to act as a natural phenolic antioxidant. Results here, which indicated that wood veneers benzoylated to low weight gains showed greater losses in weight than unmodified wood, are consistent with such a suggestion.

It was relatively easy to modify thin wood veneers to high WGs using benzoyl chloride and therefore benzoylation might be a suitable treatment for wood veneer, which could then be used as a photoprotective overlay for solid timber or composites. An envelope treatment that produced a high surface WG might be sufficient to protect solid wood from photodegradation, but further research is needed to obtain a more complete understanding of the ability of benzoylation to protect solid timber from photodegradation.

5. Conclusions

Interest in photostabilising wood arises, in part, from the desire to improve the performance of clear coatings on wood. Pretreatment of wood with chromium trioxide, or commercially available UV absorbers and hindered amine light stabilisers can significantly improve the longevity of clear coatings applied to wood. Grafting of UV absorbers to wood can also improve the performance of clear coatings on wood, but the systems developed to date have their limitations in that they require the synthesis of a functionalised UVA and the use of high temperatures or microwave irradiation to bond the UVA to wood. Chemical modification offers an alternative to grafting, but previous attempts to photostabilise wood using esterification have met with limited success, possibly because the systems were selected on the basis of their ability to reduce the hygroscopicity of wood rather than for their potential to prevent photodegradation. This study showed that esterification of wood to high weight gains with the aromatic acid chloride, benzoyl chloride, was effective at photostabilising lignin, the component of wood that is most susceptible to photodegradation. Benzoylation appears to reduce the quantity of free radicals formed in wood when it is exposed to UV light, possibly because the benzoyl groups in wood absorb UV light or scavenge free radicals. Our findings suggest that there is merit in examining the ability of other chemical modification systems involving aromatic chemicals to photostabilise wood. As a commercial pre-treatment method intended to improve the performance of clear finishes on wood, benzoylation is clearly unsuitable for the DIY market, but it could conceivably be used as an industrial pre-treatment method for wood veneer which could then be used as a photoprotective overlay for solid timber.

References


