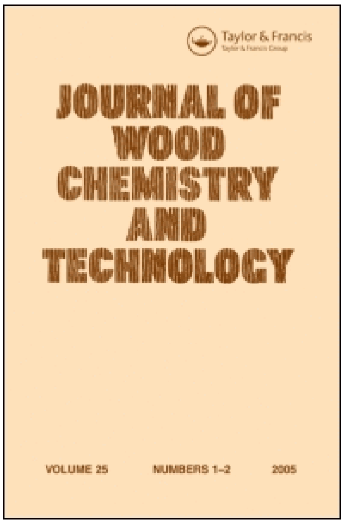

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Photoprotection of Wood Using Polyester-Type UV-Absorbers Derived from the Reaction of 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone with Dicarboxylic Acid Anhydrides

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Abstract: Polyester-type UV absorbers were created by reacting the epoxy-functionalized UV absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) with maleic, phthalic, or succinic anhydride. The ability of the UV absorbers to photostabilize wood was then examined. Fourier transform infra-red (FTIR) spectroscopy confirmed that HEPBP reacted with phthalic anhydride to create a polyester that preserved the UV-absorbing benzophenone group. There was less evidence that the polyester was formed when HEPBP was reacted with maleic or succinic anhydride. HEPBP-phthalic anhydride was the most effective UV absorber at photostabilising wood. This UV absorber showed increased UV absorption around 270 nm, formed a leach-resistant film at wood surfaces and was able to restrict both weight and tensile strength losses of thin wood veneers during accelerated weathering, unlike chromium trioxide and a UV absorber-hindered amine light stabilizer. We conclude that polymeric polyester-type UV absorbers show promise as a way of photostabilizing wood and briefly discuss how more effective systems could be developed in future.

Keywords: Accelerated weathering, dicarboxylic acid anhydrides, epoxy, FTIR-spectroscopy, photoprotection, polyester, polymeric UV absorbers, SEM, tensile strength, weight loss, wood veneers

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INTRODUCTION

Wood is very susceptible to photodegradation because lignin strongly absorbs UV radiation, which leads to the photolysis of lignin and the formation of aromatic and other radicals that further degrade lignin and depolymerize cellulose and hemicelluloses.[1] Wood can be protected from photodegradation by modifying its molecular structure using chromium trioxide, benzoyl chloride, or vinyl benzoate.[2–5] Previous research has demonstrated the practical benefits of chromium trioxide treatment on the performance of wood exposed outdoors.[6–7] Chromium trioxide, however, cannot be used to protect wood in most countries, and attempts to find other inorganic compounds that are as effective have been unsuccessful.[8] Hence, there is a strong need to develop alternative cost-effective photoprotective treatments for wood.

An effective way of protecting polymers from photodegradation is to use additives that absorb UV radiation and dissipate the energy as heat.[9] A range of different UV absorbers, including derivatives of phenyl salicylate, hydroxybenzophenones, hydroxyphenyl benzotriazoles, and triazines have been commercialized and are commonly used to photostabilize polymers.[9] These UV absorbers can also protect wood from photodegradation.[10] The effectiveness of UV absorbers at preventing photodegradation of polymers can be increased by chemically bonding or grafting them to the polymer,[11] and a number of studies have demonstrated the effectiveness of this approach at protecting wood from photodegradation.[12–15] An alternative approach to increasing the effectiveness of UV absorbers in materials is to increase their molecular weight, which can be done by reacting the parent UV absorber with other compounds.[16] For example, reaction of the epoxy-functionalized UV absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) with dicarboxylic acid anhydrides can create higher molecular weight (MW) polyester-type UV absorbers without destroying the UV-absorbing 2-hydroxybenzophenone unit ($MW < 1600$).[17–19] HEPBP is effective at protecting wood from photodegradation.[12,14] Furthermore, wood that has been chemically modified with the dicarboxylic acid anhydride, phthalic anhydride, followed by oligomerization with the epoxide, 1-chloro-2,3-epoxypropane (epichlorohydrin), is also resistant to weathering.[20] Therefore, we hypothesize that polymeric polyester-type UV absorbers created from HEPBP and dicarboxylic acid anhydrides will be effective at protecting wood from photodegradation.

In this study we reacted wood with HEPBP and 3 different dicarboxylic acid anhydrides and examined the ability of the treatments to protect the wood from photodegradation. The best treatment was then compared with the recognized photoprotective treatments for wood, chromium trioxide, HEPBP (alone) and another effective photostabilizer consisting of a UV absorber and hindered amine light stabilizer. The aim was to test the hypothesis that polymeric polyester-type UV absorbers derived from HEPBP and dicarboxylic acid anhydrides will be effective photoprotective treatments for wood.

EXPERIMENTAL

Preparation of Wood Veneers

Wood veneers, 85 mm (length) × 20 mm (width) and 80–85 μm thick with oven-dry weights of ~52–55 mg each were cut using a sledge microtome (Spencer Lens Buffalo, New York, USA) from the radial faces of water-saturated yellow cedar (*Chamaecyparis nootkatensis* (D. Don) Spach) blocks, as described previously.[21] Wet veneers were placed under restraint on glass plates and air-dried for 4 hours. Veneers were conditioned at 20 ± 1°C and 65 ± 5% relative humidity (r.h.) for two weeks. The thickness of each veneer was measured using a digital micrometer (Lorentzen & Wettre type 222, Kista, Sweden). Each veneer was then weighed, oven dried at 105 ± 5°C for 45 minutes, reweighed and re-conditioned, as above. Five randomly selected veneers were assigned to each of the 13 different treatments assessed in the first experiment (Table 1). Ten veneers were assigned to each of the treatments that were assessed in the

Table 1. Chemicals, solution concentrations and weight gains of treated veneers in each experiment

Experiment	Chemicals*	Soln Concentration†	Treatment ID	Weight gain gain (%)
1	Acetone (untreated)	—	Acetone	—
1	Maleic anhydride	30	Ma	6.9
1	Phthalic anhydride	30	Pa	4.2
1	Succinic anhydride	30	Sa	9.1
1	HEPBP and Ma	10	HE/Ma1	10.5
1	HEPBP and Ma	20	HE/Ma2	16.2
1	HEPBP and Ma	30	HE/Ma3	22.3
1	HEPBP and Pa	10	HE/Pa1	10.8
1	HEPBP and Pa	20	HE/Pa2	18.2
1	HEPBP and Pa	30	HE/Pa3	24.7
1	HEPBP and Sa	10	HE/Sa1	10.8
1	HEPBP and Sa	20	HE/Sa2	16.7
1	HEPBP and Sa	30	HE/Sa3	27.9
2	Water (untreated)	—	Water	—
2	Chromium trioxide	30	CrO3	20.9
2	HEPBP	30	HEPBP	18.7
2	HEPBP and Pa	30	HEPBP/Pa	20.2
2	UVA/HALS (1:1)	30	UVA/HALS	28.8

*All chemicals were dissolved in acetone except for chromium trioxide (water) and UVA/HALS (mineral spirits); Acetone treatment solutions contained tri-n-hexylamine as a catalyst (2.5 mol.%); †Solution concentrations calculated as a percentage of veneer weight.

second experiment. Separate batches of ten veneers were stored in a conditioning room (as above) for the duration of the exposure trials. These veneers (untreated and unexposed) provided a means of estimating the initial tensile strength of veneers.

Chemical Treatments

The dicarboxylic acid anhydrides used in this work were maleic, phthalic, and succinic anhydride obtained from Sigma-Aldrich (Oakville, Canada). HEPBP was synthesized by reacting 2,4-dihydroxy-benzophenone (Sigma D-9400) with 1-chloro-2,3-epoxypropane (epichlorohydrin:BDH-27706) as described by Mañásek et al.[22] (Figure 1a). The synthesis of polymeric UV absorbers from HEPBP and dicarboxlic acid anhydrides followed the methods developed by Lustoň et al.[17–19] They showed that an alternating copolymer of HEPBP and anhydride is formed when an equimolar ratio of HEPBP and anhydride is reacted together using a tertiary amine as a catalyst.[17–19] Therefore, in this study an equimolar ratio of HEPBP and individual dicarboxylic acid anhydrides were dissolved together with 2.5 mol% of tri-n-hexylamine in a minimum amount of acetone. Three solutions were prepared for each HEPBP/anhydride combination (9 solutions in total). These solutions contained 10%, 20%, or 30% of HEPBP and anhydride calculated as a percentage of the weight of veneers. The chemical solutions were painted onto pre-weighed and conditioned veneers with an art brush. Treated veneers were heated in an oven for 4 hours at 120°C to polymerize HEPBP and the dicarboxylic acid anhydride. The weight gains of veneers after treatment are shown in Table 1. Figure 1b shows a scheme for the tri-n-hexylamine catalyzed copolymerization of HEPBP and phthalic anhydride, which accords with steps outlined by Rocks et al.[23] for the tertiary amine catalyzed alternating copolymerization of epoxides and anhydrides. The UV absorber, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid octyl ester and the hindered amine light stabilizer 1,10-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) decanedioic acid ester were donated by Ciba-Geigy (Sydney, Australia) and dissolved in mineral spirits. Chromium trioxide was purchased from Sigma-Aldrich and dissolved in water. In both cases the concentrations of chemicals in solution were 30%, based on veneer weight (Table 1). After chemical treatment, veneers were oven dried at 105°C for 2 h and reweighed. The veneers were then reconditioned for two weeks and reweighed.

Assessment of Weight and Tensile Strength Losses of Treated Veneers during Accelerated Weathering

Treated veneers and untreated controls were attached to glass plates using small plastic clips, and the plates were placed randomly in the upper rack of a Weather-o-Meter (Model 65-W, Atlas Electric Devices Co., Chicago, USA,

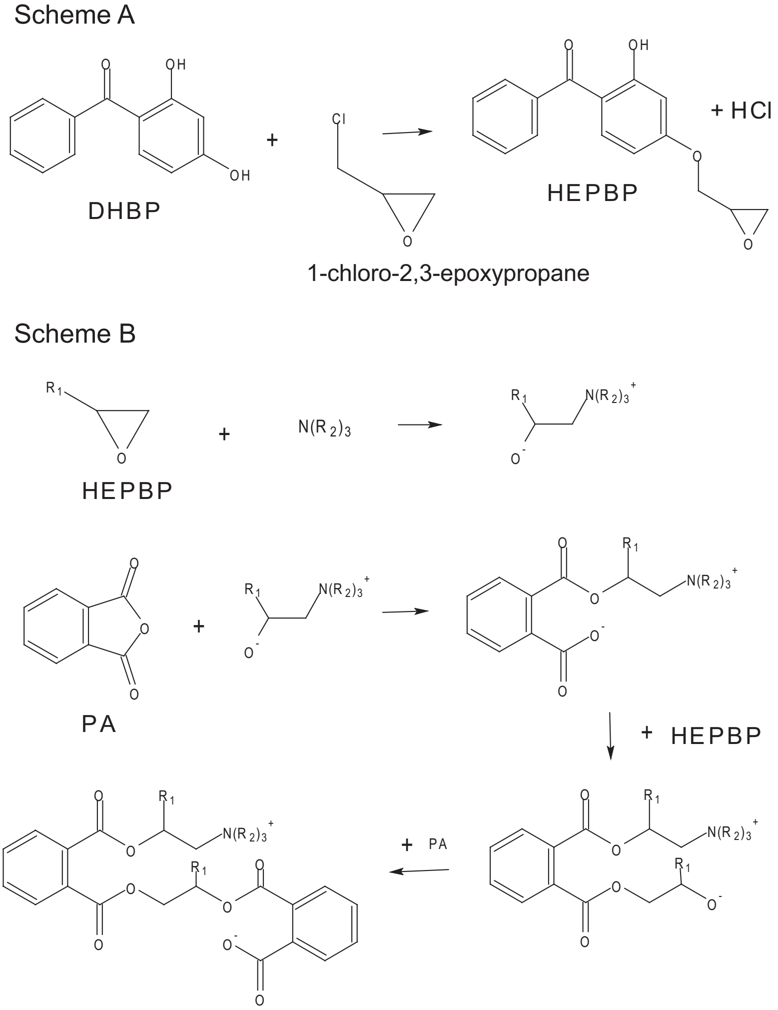

Figure 1. Scheme A, Reaction between 2,4-dihydroxy-benzophenone (DHBP) and 1-chloro-2,3-epoxypropane to form 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP); Scheme B, The tri-n-hexylamine catalysed alternating copolymerization of phthalic anhydride (Pa) and 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP). R1 = methyleneoxy hydroxybenzophenone. R2 = n-hexyl (scheme based on the steps outlined by Rocks et al. 2004.[23])

Xenon Arc., 6500 Watt bulb, temperature 40°C, r.h. 25–30%). Treated veneers were subjected to either 150 h (Experiment 1) or 200 h (Experiment 2) of accelerated weathering, involving continuous exposure to UV radiation and 1 h of water spray every 24 h. At the end of each experiment, veneers were removed from the Weather-o-Meter, oven dried for 2 h and their dry weights were measured to calculate weight losses. The veneers were reconditioned for a week and their zero-span tensile strength was measured using a paper tester (Pulmac, Montreal, Canada).[24] Results were subjected to analysis of variance to determine the effects of treatment on weight loss and tensile strength of veneers after artificial weathering. Statistical computation was performed using Genstat (version 10).[25] Significant results are plotted and significance (p) values for the effect of treatment on weight losses and tensile strength of veneers after weathering are included on graphs. Error bars on graphs (± standard error of difference) can be used to compare differences between the means for individual treatments.

Scanning Electron Microscopy

Scanning electron microscopy was used to examine the surfaces of unexposed veneers and those exposed to artificial accelerated weathering in experiment 2. Small samples measuring 10 × 10 mm were cut from veneers and attached to separate aluminum stubs using double-sided self-adhesive tabs. The stubs were coated with a 10 nm layer of gold using a sputter coater (SEM Prep II, Nano-tech Thin Films, Manchester, UK) and they were then examined using a field emission scanning electron microscope (Hitachi S-4700, Tokyo, Japan) at an accelerating voltage of 1 kV. Digital secondary electron images of samples were obtained and saved as TIFF files.

Infra-Red and UV Spectroscopy

Fourier transform infra-red (FTIR) spectroscopy was used to examine the products of the reactions between HEPBP and maleic, phthalic, or succinic anhydride. Equimolar ratios of HEPBP and individual dicarboxylic acid anhydrides were dissolved in a minimum amount of acetone with 2.5 mol% of tri-n-hexylamine as a catalyst (as above). The chemical solutions were painted onto quartz slides with art brushes and the slides were heated at 120°C for 4 h to polymerize HEPBP and the dicarboxylic acid anhydride. FTIR spectra of the co-polymers and the parent materials, cyclic anhydrides and HEPBP, were obtained using a single bounce attenuated total reflectance accessory (Pike MIRacle, PIKE Technologies, Madison, USA) attached to a spectrometer (Perkin Elmer Spectrum One, Waltham, Massachusetts, USA). Each spectrum represents 16 accumulations at 8 cm^{-1} resolution. The same method was used to obtain FTIR spectra of untreated wood veneers and veneers treated with HEPBP and phthalic anhydride before and after accelerated weathering.

A spectrophotometer was used to examine the absorbance of the polyester-type UV absorbers in the UV/Vis range. Two coated quartz slides for each treatment (as above) were placed in a UV/Vis scanning spectrophotometer

(Shimadzu 2101, Kyoto, Japan) with an integrating sphere attachment. Absorbance spectra were obtained from 200 to 500 nm at two points on the polymer films using a clean quartz slide as a reference. A fast scan speed with a 2 nm slit width was used to obtain all spectra. Six scans were averaged for each spectrum.

RESULTS

Weight and Tensile Strength Losses of Treated Veneers during Accelerated Weathering

There were statistically significant ($p < .001$) effects of the different treatments on the weight losses and tensile strength of veneers during the first accelerated weathering experiment. Figure 2a shows the weight losses of treated veneers and the acetone-treated control exposed to artificial accelerated weathering for 150 h. Treatment of veneers with HEPBP in combination with dicarboxylic acid anhydrides significantly reduced weight losses of veneers compared to the control, whereas treatment of veneers with maleic, phthalic, and succinic

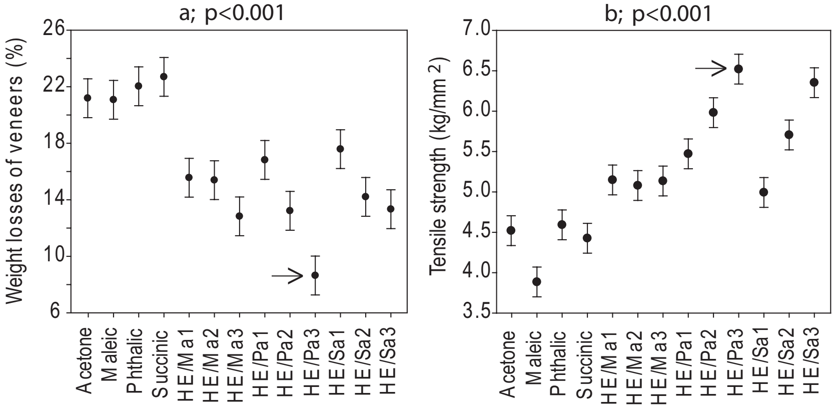

Figure 2. Photostability of wood veneers modified with maleic, phthalic and succinic anhydride alone or in combination with HEPBP, after 150 hours of accelerated weathering; 2a, = weight losses of wood veneers; 2b, = tensile strength of weathered veneers; the tensile strength of a batch of 20 untreated unweathered veneers was 9.48 kg/mm^2. X axis labels are the same as those in Table 1. Error bars represent ± standard error of difference (from analysis of variance) and non-overlap of these bars indicates that means are significantly different at 5% ($p < 0.05$) level. The probability value at the top of each graph is the statistical significance of the effect of treatment on weight losses or tensile strength of veneers.

anhydride on their own was ineffective (Figure 2a). There were inverse relationships between weight gains of veneers due to treatment with HEPBP and different anhydrides and weight losses of veneers during artificial accelerated weathering (Figure 2a). Veneers treated with the combination of HEPBP and phthalic anhydride at the highest weight gain of 24.7% (HE/Pa3, arrowed in Figure 2a) lost significantly ($p < .05$) less weight than veneers treated with HEPBP and the other dicarboxylic acid anhydrides. Figure 2b shows the tensile strength of treated veneers following 150 h of accelerated weathering. The effects of the different treatments on tensile strength of veneers after weathering are similar to their effects on weight losses, except that the tensile strength losses of veneers treated with maleic anhydride were greater than those of veneers treated with phthalic or succinic anhydride, and also the combination of HEPBP and succinic anhydride at the highest weight gain of 27.9% (HE/Sa3) was more effective at restricting losses in tensile strength of veneers than losses in weight (Figure 2b). The lower tensile strength of maleic anhydride treated veneers after weathering may be due to the effects of this treatment on the initial strength of veneers, as we have observed that esterification of veneers with maleic anhydride causes greater strength losses than esterification with either phthalic or succinic anhydride. The combination of HEPBP and phthalic anhydride at the highest weight gain was the most effective treatment at preventing losses in tensile strength of veneers (arrowed in Figure 2b). Hence, the ability of this treatment to restrict weight and tensile strength losses of thin wood veneers during accelerated weathering was compared with those of chromium trioxide, HEPBP alone, and a UV absorber and hindered amine light stabilizer (UVA/HALS). Results from this second experiment showed that the combination of HEPBP and phthalic anhydride (HEPBP/Pa) was more effective than HEPBP alone at restricting weight losses of veneers during accelerated weathering, but it was less effective than chromium trioxide (CrO3) (Figure 3a). Veneers treated with UVA/HALS lost more weight during accelerated weathering than the untreated (exposed) controls (Figure 3a). The UVA/HALS treatment, however, was the most effective treatment at restricting losses in tensile strength of veneers during accelerated weathering followed by the combination of HEPBP and phthalic anhydride (Figure 3b). The HEPBP and phthalic anhydride treatment was more effective than HEPBP on its own. Veneers treated with all of these chemicals and exposed to accelerated weathering were significantly stronger than similarly exposed water-treated controls and chromium trioxide-treated veneers (Figure 3b).

Scanning Electron Microscopy

Scanning electron microscopy of veneers revealed changes to the surface structure of wood as a result of treatment and accelerated weathering. Figure 4a shows the surface of an untreated veneer before weathering. Bordered pits (arrowed left and center) are prominent on the radial walls of tracheids. These pits

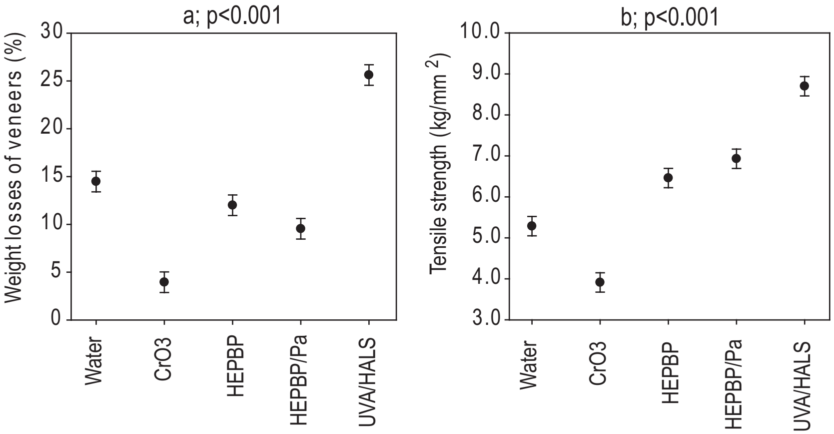

Figure 3. Comparison of the ability of the co-polymer of HEPBP and phthalic anhydride (HEPBP-Pa) and three other photostabilizing systems to restrict weight and tensile strength losses of treated wood veneers after 200 hours of accelerated weathering; 3a, = weight losses of wood veneers; 3b, = tensile strength of veneers. Water = control veneers; CrO3 = veneers treated with chromium trioxide; HEPBP = veneers grafted with 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone; HEPBP-Pa = veneers treated with HEPBP and phthalic anhydride; UVA/HALS = veneers treated with a combination of a benzotriazole UV absorber and hindered amine light stabilizer.

developed micro-checks (arrowed top left and right in Figure 4b) and tracheids separated at the middle lamella (arrowed bottom left in Figure 4b) during accelerated weathering. The HEPBP-Pa, HEPBP, and UVA/HALS treatments coated the surface of veneers and obscured surface anatomical features, for example, bordered pits (arrowed in Figure 4c, 4e and 4g, respectively). Following weathering, some micro-checking of bordered pits in these treated veneers occurred (arrowed in Figure 4d, 4f, and 4h), but such micro-checking, particularly for veneers treated with HEPBP-Pa (Figure 4d), was less pronounced compared to untreated weathered wood veneers (Figure 4b). HEPBP-Pa and HEPBP (to a lesser extent) still appeared to coat parts of veneer surfaces after weathering (Figure 4d and 4f). This was not the case, however, for weathered samples that had been treated with UVA/HALS, whose surface anatomical features, including checking of pit apertures and separation of tracheids (arrowed right in Figure 4h), can be more clearly seen than those in weathered HEPBP-Pa and HEPBP treated veneers. Treatment of veneers with chromium trioxide (before weathering) caused checks to develop in cell walls (arrowed left in Figure 4i). Checks in bordered pit apertures were also present in chromium trioxide treated samples after weathering (arrowed left in Figure 4j), but there was little separation of tracheids at the middle lamella (Figure 4j).

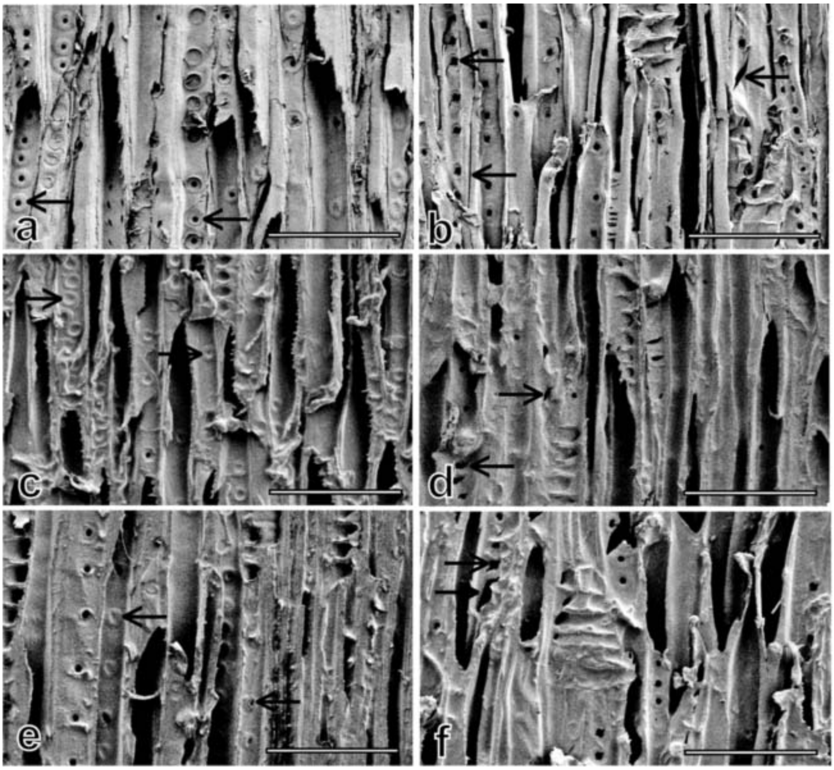

Figure 4. Scanning electron photomicrographs of the surfaces of untreated and treated veneers before and after exposure to 200 hours of accelerated weathering. Scale bars = 100 μm; Fig. 4a = Unexposed control, note bordered pits (arrowed); Fig. 4b = Untreated exposed control, note micro-checking of bordered pits (arrowed top left and right) and separation of tracheids (arrowed bottom left); Fig. 4c = Unexposed veneer treated with HEPBP-Pa, note film obscuring bordered pits (arrowed); Fig 4d = Veneer treated with HEPBP-Pa after accelerated weathering, note slight micro-checking of bordered pits (arrowed); Fig. 4e = Unexposed veneer treated with HEPBP, note film obscuring bordered pits (arrowed); 4f = Veneer treated with HEPBP after accelerated weathering, note slight micro-checking of bordered pits (arrowed); Fig 4g = Unexposed veneer treated with UVA/HALS, note film obscuring bordered pits (arrowed); Fig 4h = Veneer treated with UVA/HALS after accelerated weathering, note micro-checking of bordered pits (arrowed top right) and separation of tracheids (arrowed bottom); Fig. 4i = Unexposed chromium trioxide treated veneer, note cell wall checking (arrowed left); Fig. 4j = Chromium trioxide treated veneer exposed to accelerated weathering, note micro-checking of bordered pits (arrowed left). (*Continued*)

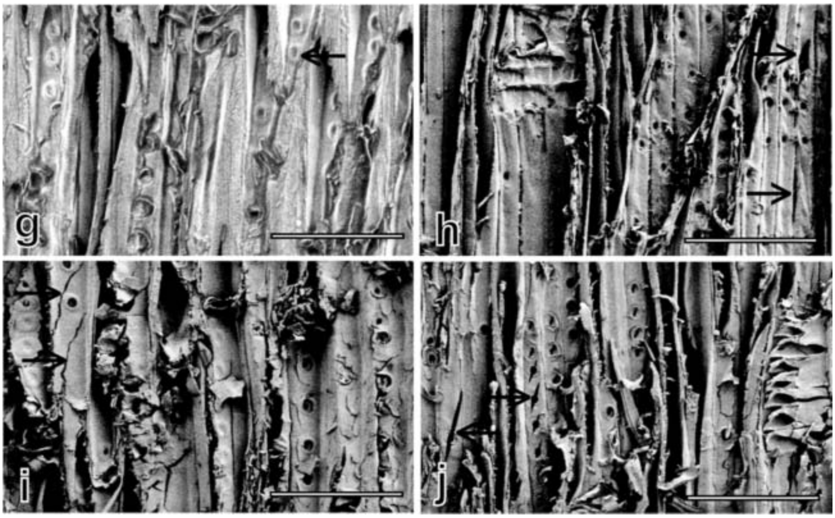

Figure 4. (*Continued*).

Infra-Red and UV Spectroscopy

Infra-red spectra from 750 to 2000 cm^{-1} for phthalic anhydride (Pa), HEPBP and the reaction product of HEPBP and phthalic anhydride (HEPBP-Pa) on a glass slide are shown in Figure 5a. The spectrum for phthalic anhydride (Pa) at the bottom of Figure 5a shows prominent absorption peaks at 1851 and 1762 (C=O stretching vibrations), 1599 (C—C, and/or C=C stretching vibrations in aromatic rings), 1471 cm^{-1} (C=C stretching vibration in aromatic rings), 1258 cm^{-1} and 906 cm^{-1} (C—O stretching), 1109 and 1072 cm^{-1} (C—H in-plane bending), and 800 (C—H bonds of aromatic rings).[26] In contrast to phthalic anhydride, the peaks in the spectrum of HEPBP have not been well defined by previous studies, but the spectrum for HEPBP at the very top of Figure 5a shows prominent absorption peaks for the carbonyl group at 1625 cm^{-1}, which is a distinctive band for benzophenone according to Lustoň et al.[17], peaks at 1600, 1581, 1501 cm^{-1} (C=C stretching in aromatic rings), 1380 cm^{-1} (CH_2), 1113 cm^{-1} (C—H aromatic in-plane bending), and 860 cm^{-1} (epoxy ring deformation).[27–28] The reaction of phthalic anhydride and HEPBP *in vitro* results in the loss of anhydride C=O absorption peaks at 1851 and 1762, and the appearance of a strong peak at 1729 cm^{-1} (C=O stretching in ester group) indicating that phthalic anhydride is bonding to HEPBP via an ester bond.[17] The characteristic absorption peak corresponding to the vibrations of the carbonyl group of *o*-hydroxybenzophenone at 1625 cm^{-1} remains preserved in the spectrum for HEPBP-Pa.[17] The decrease in the peak at 860 cm^{-1} in HEPBP-Pa is indicative of reduction of epoxy groups. Another notable change

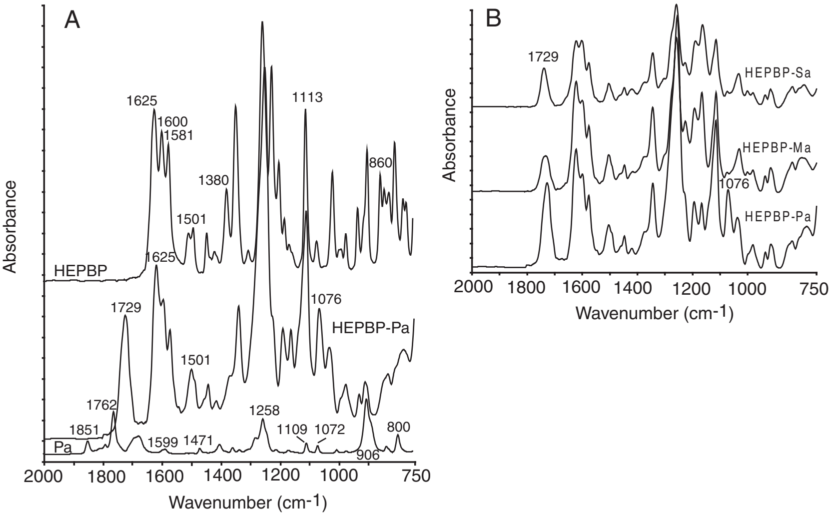

Figure 5. (a) FTIR spectra of phthalic anhydride (Pa), 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP), and the co-polymer of HEPBP and phthalic anhydride (HEPBP-Pa) on a glass slide; (b) FTIR spectra of HEPBP-Pa, HEPBP and maleic anhydride (HEPBP-Ma) and HEPBP and succinic anhydride (HEPBP-Sa) at the same level of attenuation.

that occurs when HEPBP is reacted with phthalic anhydride is the strengthening of the peak at 1076 cm^{-1} (C—O—C stretching), which is characteristic of the formation of ether bonds in cured epoxy polymers.[29] Figure 5b compares the infra-red spectra of the reaction products of HEPBP and maleic, phthalic, and succinic anhydride at the same level of attenuation. The main differences between the spectra are the much stronger peaks due to the polymerization of HEPBP and anhydride at 1729 and 1076 cm^{-1} in the spectrum for HEPBP and phthalic anhydride (HEPBP-Pa), compared to the spectra for HEPBP and maleic (HEPBP-Ma) and succinic anhydride (HEPBP-Sa).

Figure 6 shows FTIR spectra of untreated veneers and veneers treated with HEPBP-Pa, both before and after accelerated weathering. Accelerated weathering of untreated veneers resulted in significant decreases in absorption peaks associated with lignin, at 1505 cm^{-1} (benzene ring stretching in lignin), 1460 cm^{-1} (CH_3 deformation in lignin), and 1275 cm^{-1} (guaiacyl nuclei in lignin), whereas there was little change in absorption peaks assigned to cellulose and hemicelluloses at 1425 cm^{-1} (CH_2 scissor vibration in cellulose), 1370 cm^{-1} (CH_2 bending vibration in cellulose and hemicellulose), and 1050 cm^{-1} (C—O stretching in cellulose and hemicellulose). Changes in the "lignin peaks" at 1505, 1460, and 1275 cm^{-1} are accompanied by an increase in the absorption at 1729 cm^{-1} (arrowed at the top of Figure 6) probably due to the formation

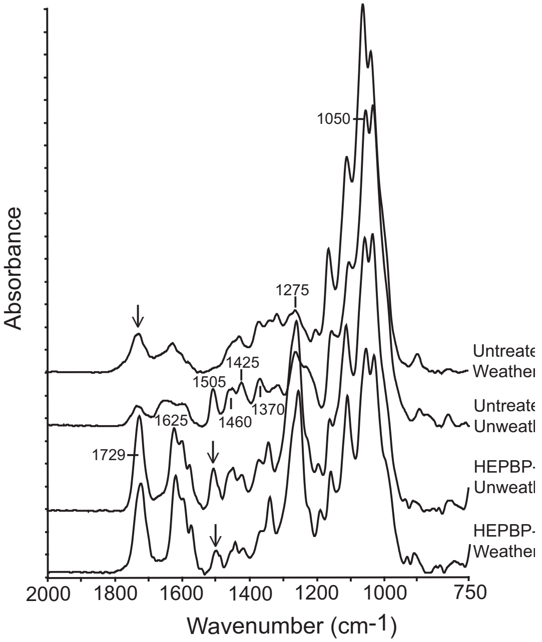

Figure 6. FTIR spectra of untreated and HEPBP-Pa treated wood veneers before and after 200 h of artificial accelerated weathering.

of unsaturated aromatic (quinone) compounds as a result of photodegradation of lignin[30] or carbonylic/carboxylic ring opening degradation products of aromatic lignin moieties. The spectrum for wood veneers modified with HEPBP-Pa shows similarities to the spectrum of HEPBP-Pa in Figure 5 as there are prominent absorption peaks at 1729 cm^{-1} and 1625 cm^{-1} in addition to peaks associated with lignin, cellulose, and hemicellulose. After weathering the absorption peak at 1505 cm^{-1} decreased suggesting some photodegradation of lignin or loss of the HEPBP-Pa polymer (arrowed in Figure 6), but the overall changes in the spectrum are less pronounced compared to those observed in the spectrum of the unmodified (weathered) control.

The UV absorption spectra of films of HEPBP alone and in combination with different dicarboxylic acid anhydrides are shown in Figure 7. HEPBP absorbs UV radiation quite broadly, and has a slight shoulder extending into the visible region. The reaction of HEPBP with dicarboxylic acid anhydrides increased UV absorption around 270 nm (arrowed in Figure 7), and further extends absorption into the visible spectrum. The overall absorption of UV and visible light was greatest for HEPBP in combination with phthalic anhydride (HEPBP + Pa).

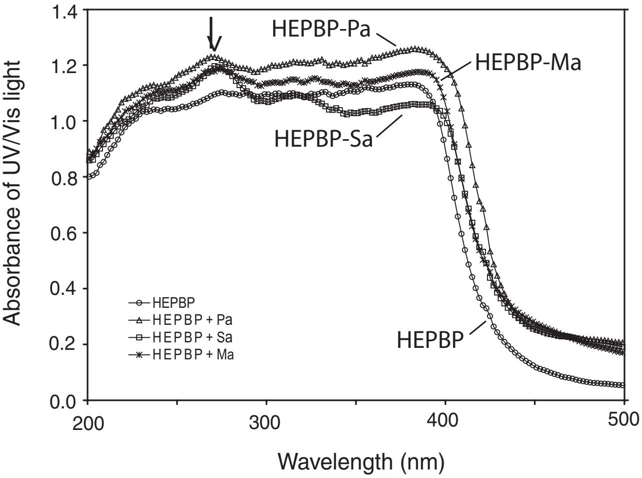

Figure 7. Absorbance of UV and visible radiation in the region from 200 to 500 nm by 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) and the co-polymers of HEPBP and maleic (HEPBP + Ma), phthalic (HEPBP + Pa) and succinic anhydride (HEPBP + Sa)

DISCUSSION

In the introduction to this article we hypothesized that higher molecular weight polyester-type UV absorbers derived from 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) and dicarboxylic acid anhydrides would be effective photoprotective treatments for wood. This hypothesis is partially supported by our results. The different polymeric UV absorbers created from HEPBP and dicarboxylic acid anhydrides were able to protect wood from photodegradation, but their effectiveness depended on the type of anhydride used and the weight gain of veneers due to treatment. The combination of HEPBP and phthalic anhydride (HEPBP-Pa) at a weight gain of 24.7% was the most effective treatment at preventing the photodegradation of wood possibly because phthalic anhydride reacted more completely with HEPBP to form the polyester-type UV absorber than maleic or succinic anhydride. HEPBP-Pa formed a film that coated the wood surface. This would reduce the transmission of UV radiation and the photochemically active region of the visible spectrum (380 to 405 nm)[31] through to the underlying wood in accord with Lambert-Beer's law, thus protecting the wood from photodegradation. This coating was still present in some areas of veneer surfaces after weathering and would have prevented the photodegradation and loss of lignin during weathering. The retention of HEPBP-Pa at wood surfaces may explain why weight losses of veneers treated with HEPBP-Pa during weathering were the lowest apart from those treated with chromium trioxide, which is known to bond very strongly to lignin to create wood surfaces that are photo-resistant and hydrolytically stable.[2] In contrast, the coating of UVA/HALS was leached from wood surfaces during weathering, which probably accounts for the high weight losses of veneers treated with this photostabilizer. The UVA/HALS combination, however, was the most effective treatment at restricting losses in tensile strength of veneers during weathering, but it is possible that leaching of the UVA and HALS from wood surfaces might reduce its effectiveness in the long term (although generally these photoprotective additives are used in combination with a coating to reduce leaching). The increased leaching resistance of HEPBP-Pa may explain in part why it was effective at photostabilizing wood veneers. Similar, leaching resistance can be obtained by grafting UV absorbers to wood surfaces, and our results have confirmed that HEPBP is effective at photostabilizing wood veneers, possibly because it is grafted or homopolymerized within wood, as suggested by an earlier study.[14]

FTIR spectroscopy was used to examine the reaction of HEPBP with dicarboxylic acid anhydrides. The reaction mechanisms between epoxy monomers and these anhydrides have been the subject of controversy, and various reactions leading to the formation of the polyester have been proposed.[23,32] Our findings shed no light on this subject, rather they simply confirm the findings of Lustoň and co-workers that the reaction of HEPBP and phthalic anhydride *in vitro* and in the presence of an amine catalyst at high temperature (120°C) leads to the formation of a polyester in which the benzophenone group of HEPBP is preserved.[17–19] Our results suggest, however, that the same reaction conditions are not as effective at creating polyesters of HEPBP and maleic or succinic anhydride. When wood was reacted with HEPBP and phthalic anhydride a polymer film was formed at the wood surface, as mentioned earlier, which obscured the wood's anatomical features. FTIR spectroscopy suggested that this polymer was the polyester of phthalic anhydride and HEPBP because features of the spectrum of the treated wood surface resembled that of the co-polymer formed *in-vitro*. The direct reaction of phthalic anhydride and HEPBP with hydroxyl groups in wood, however, could account, in part, for the increased absorption at 1729 cm^{-1} and loss of the peak at 860 cm^{-1}, which provide evidence for the formation of the polyester-type UV absorber. Therefore it is possible that wood veneers treated with HEPBP and dicarboxylic acid anhydrides are modified in a complex way involving coating of the wood with the polyester-type UV absorber and possibly grafting of HEPBP and the anhydride to wood.

HEPBP-Pa was slightly more effective than HEPBP at photostabilizing wood, but the major advantage of using HEPBP-Pa compared to HEPBP on its own is the lower cost of the former system. Phthalic anhydride is an inexpensive bulk chemical whereas a simple UV absorber such as 2,4-dihydroxybenzophenone costs three times as much, and functionalized UV absorbers such as HEPBP are even more expensive (figures from www.sciencelab.com).

Our results show that HEPBP can be substituted with phthalic anhydride to create a photostabilizing system that is as effective as HEPBP at similar weight gains.

The formation of polymeric UV absorbers at wood surfaces shows promise as a means of photostabilizing wood. This study built on previous research that grafted HEPBP to wood.[12,14] Therefore, we chose to use a UV absorber with an epoxide group as the polymerizable group to create polymeric UV absorbers. Other types of UV absorbers with different functional groups for example, benzophenones or benzotriazoles containing acrylic or vinyl groups, can be homopolymerized with radical initiators or copolymerized with other compounds to increase their molecular weight.[16,33–35] The rationale for using such UV absorbers to protect polymers from photodegradation lies mainly in their increased permanence in the polymer.[16] The increased permanence of one of the polymeric UV absorbers examined here (HEPBP-Pa) does appear to enhance its effectiveness at protecting wood from photodegradation. Hence, our results suggest that copolymerization of functionalized UV absorbers with other compounds to increase the molecular weight of the UV absorber is an effective strategy for photostabilizing wood. Higher levels of UV absorbers than those used here may be required, however, to completely protect wood from photodegradation.

CONCLUSIONS

In conclusion we have shown that a polymeric polyester-type UV absorber created from the reaction of the epoxy-functionalized UV absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone with phthalic anhydride (HEPBP-Pa) is an effective photo-protective treatment for wood. HEPBP-Pa is effective because it strongly absorbs UV radiation with an absorption peak that coincides with that of lignin, the photolabile constituent of wood, and it forms a thin leach-resistant film at wood surfaces. HEPBP-Pa is more effective at restricting the weight and tensile strength losses of thin wood veneers exposed to accelerated weathering than treatments involving UV absorbers formed from HEPBP and maleic or succinic anhydride possibly because phthalic anhydride reacts more readily than maleic or succinic anhydride with HEPBP to form the polyester UV absorber. HEPBP-Pa was slightly more effective than HEPBP at photostabilizing wood and we conclude that partial substitution of the benzophenone in polymeric UV absorbers with an inexpensive compound such as phthalic anhydride can increase the cost-effectiveness of the treatment. HEPBP-Pa was not as effective as chromium trioxide and a UVA/HALS combination at restricting weight and tensile strength losses, respectively, of veneers exposed to accelerated weathering. However, HEPBP did not degrade the wood surface like chromium trioxide and it was not leached from the surface to the same extent as a UVA/HALS combination. In addition it may be possible to further improve the effectiveness of polymeric UV absorbers by changing the reactive UV absorber and the copolymer or by increasing weight gain of veneers. We plan to extend our work in these directions to develop more effective photoprotective treatments for wood and test their ability to improve the performance of clear coatings on wood exposed outdoors.

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