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A SEM study on the use of epoxy functional vegetable oil and reactive UV-absorber as UV-protecting pretreatment for wood

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Abstract

The present study investigates the ageing performance of a UV protective system for wood, comprising the reactive UV absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) and epoxy functional vegetable oils (linseed and soybean oil). Scots pine samples of radial or cross-sectional surfaces were treated using a combination of the two components, or using only one of the oils. The treated samples were then aged in a Weather-Ometer for 2 x 60 h and analyzed using VPSEM to follow the degradation of the wood substrate in the exact same spot before, during and after ageing. The results of the radial surfaces show slightly less degradation of samples treated with a combination of HEPBP and oil, and for the cross-sectional surfaces an even stronger protective effect is visible. For samples treated with only one of the two oils, no improvement was detectable. The radial surfaces were also analyzed using FTIR where the results indicate presence of the protective treatment even after 120 h of exposure. Overall the combined pretreatment of HEPBP and epoxy functional linseed oil was concluded to have a photostabilising effect of the wood substrate.

Keywords: UV-absorber; epoxy functional vegetable oil; linseed oil; 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP)

1 Introduction

Wood is an aesthetically appreciated material but to achieve its full potential in outdoor applications it needs surface protection against several effects that cause degradation (e.g. biological attack, moisture effects and ultra violet radiation (UV radiation)). These issues are commonly addressed by coating the wood and adding appropriate additives that prevent the different degrading effects from occurring. Among the oldest wood coatings used, are vegetable or fish oils which react with oxygen to form solid films on the surface of the substrate (Wicks et al. 2007). However, their use as binders has decreased and today wood is commonly protected by using other binders such as acrylics and polyurethanes, although a primer treatment with drying oils is often still employed. To protect wood
from UV-initiated degradation coatings are today preferably pigmented, since the pigment particles absorb incoming UV radiation and dissipate it as heat before the radiation reaches the wood surface (Vollmer 2011) and hence protects the wood substrate from degradation. Clear coating systems, on the other hand, lack pigment particles but contain UV-absorbers (UVA) and hindered amine light stabilizers (HALS) that work simultaneously to protect the wood without altering the color. During UV and visible light exposure (especially violet light at 380-430 nm; Evans et al. 2008 and Kataoka et al. 2007), lignin structures start to oxidize to a penetration depth in the micrometer to millimeter scale, depending on the amount of light transmitted (Browne and Simonsen 1957, Hon and Ifju 1978, Hon 1981, Horn 1994, Park et al.1996, Kataoka and Kiguchi 2001 and Kataoka et al. 2007). The two UV absorbers then work differently to protect the product both at the lower parts of the system (eg. at the wood surface) and at the top surface of the coating (Kataoka et al. 2007). The former reduces the generation of radicals that cause this oxidation (UV absorber) and the latter one reduces the rate of the oxidation that to some extent will still occur (HALS; Wicks et al. 2007a). The drawback with both of these type of UV protectors is that they have a tendency to leach out of the coating as the product is used, which leads to increased maintenance costs and unnecessary impact on the environment. As the photodegradation of wood is greater when the cell wall contains water (Andersson et al. 1991, I and II), one option is to use hydrophobes in UV protection of wood (e.g. as a pretreatment), since they are shown to restrict both the photodegradation of wood and also the leaching of chemicals from the wood surface (Lesar et al. 2011 and Tomak et al 2011). Hence, both the oil and the UV absorber serve to protect the wood from photodegradation, but in different manners. Protection against leaching could also be achieved by attaching the UV-absorber to the coating polymer in order to prevent migration of the UV absorber through the protecting film (Kotlík et al. 2014). This, on the other hand, restricts to UV protection in the coating film whereas the interface between the wood and the coating remains unprotected. To achieve such protection an option is to attach the UV-absorber on the wood substrate and then add a coating film (Olsson et al. 2014), which would restrict the UV absorber to the interface instead of leaching out. This has been studied earlier (Kiguchi et al. 1998, Westin 2002, Olsson et al. 2012, Olsson et al. 2014), however, a drawback in those studies has been to visually show the effect of the treatment. The degradation has then been shown by measuring the color change of the samples since this is one of the first visible effects of degradation. In interesting studies performed by Hatae et al. 2012a, b the authors showed a method in which the exact same area in the wood sample could be studied before and after ageing using variable pressure scanning electron microscopy (VPSEM). The study also showed that attaching the UV absorber to the wood substrate slowed down the degradation of the wood surface and that VPSEM was a valuable tool to follow time dependent changes at wood surfaces.

The present paper hence comprises the results of a study using the valuable tool VPSEM in order to follow the changes of wood surfaces treated with epoxy functional vegetable oils and the reactive UV absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP). The study aims to show the effect of the combined treatment of HEPBP and epoxy functional vegetable oils attached on the wood surface, and also to illustrate the usefulness of VPSEM in evaluating the surface changes of wood during ageing.

2 Material and method

2.1 Materials

The chemicals used were: Ethanol (99.5%, Kemetyl and 99.5 %, denaturated by isopropanol, Kemetyl), 2,4-dihydroxy-benzophenone (DHBP, 99 %, Aldrich), 4-(dimethylamino)pyridine (DMAP, 99 %, Aldrich), epichlorohydrine (99 %, Aldrich), 3-pentanone (ReagentPlus >99 %, Sigma Aldrich),
potassium hydroxide (KOH, 85-87 %, Eka Nobel), epoxy functional soybean oil (ca. 4 epoxy groups/triglyceride, Lankroflex E2307, Akcros Chemicals) and epoxy functional linseed oil (ca. 5 epoxy groups/triglyceride, Lankroflex L, Akcros Chemicals). All chemicals were used as received.

2.2 HEPBP synthesis
The procedure for synthesizing 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) was according to description in previous literature (Manasek et al. 1976). In brief, the reactive UV-absorber HEPBP was synthesized by reacting DHBP and epichlorohydrin in 2M KOH at 80°C for 2 h with constant stirring and reflux. A yellow substance was produced which was washed 6 times with deionized water and the excess solvent was evaporated using a rotary evaporator. The product was recrystallized 3 times using ethanol resulting in a yellow crystalline powder. A schematic reaction path is illustrated in Scheme 1.

![Scheme 1 Schematic reaction path of the HEPBP synthesis](image)

2.3 Preparation of wood samples
Two types of samples were prepared, one where the radial surface is to be exposed and one where the cross-sectional surface is to be exposed. In both cases samples of Scots pine (Pinus sylvestris L.) sapwood were sawn into pieces measuring 15 (L) x 15 (R) mm and a thickness of 10 (T) mm for the radial surfaces and 15 (R) x 15 (T) mm and a thickness of 10 (L) mm for the cross-sectional surfaces. The radial samples were wet before cut using a microtome to even the surface before reaction, analysis and exposure.

To facilitate analysis using Scanning Electron Microscopy (SEM) the cross-sectional samples were cut using a pulsing UV excimer laser from Lumonics with a wavelength of 248 nm (krypton- and fluorine gas mixture in nitrogen). Helium was used as a protection gas. The irradiation energy was 270 mJ and the frequency was 6 Hz (i.e. 6 irradiations per second). An illustration of how the samples were cut is given in Figure 1. For more information regarding the UV excimer laser see Wålinder et al. (2009).

![Cross-section of sample](image)

Figure 1 Illustration describing the preparation procedure for the laser ablation of the cross sectional samples.

2.4 Grafting procedure
A total of 24 samples were prepared and divided into four sets of six samples. Each set contained 4 samples to be exposed and analyzed on the radial side (untreated, linseed oil treated, soybean oil treated and HEPBP/linseed oil treated) and 2 samples to be exposed on the cross-sectional side
Table 1 Description of performed reactions

<table>
<thead>
<tr>
<th>Batch name:</th>
<th>Reactant</th>
<th>Amount of each reactant (g)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1</td>
<td>Epox. soybean oil</td>
<td>5</td>
<td>4 (radial)</td>
</tr>
<tr>
<td>Reaction 2</td>
<td>Epox. linseed oil</td>
<td>5</td>
<td>4 (radial)</td>
</tr>
<tr>
<td>Reaction 3</td>
<td>Epox. linseed oil + HEPBP</td>
<td>2.5 + 2.5</td>
<td>8 (radial + cross-sectional)</td>
</tr>
<tr>
<td>No reaction</td>
<td>-</td>
<td>-</td>
<td>8 (radial + cross-sectional)</td>
</tr>
</tbody>
</table>

2.5 Scanning electron microscopy

The scanning electron microscopy imaging was performed on a JEOL JSM-5600 variable pressure scanning electron microscope (VP-SEM) using the backscattered electron mode. The conditions used were 15 kV voltage, 10-20 Pa pressure and 12-13 mm working distance. During the last 60 h of exposure samples were analysed using a Hitachi TM-1000 VP-SEM at 15 kV accelerating voltage in the backscattered mode. Samples were in all cases analysed without sputtering.

2.6 Infrared Spectroscopy

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to analyze the chemical composition of the wood surfaces before and after the treatments. All measurements were performed in air at room temperature using two measuring point for each sample, an average of the two was then used as result. The equipment used was a Perkin-Elmer Spectrum 2000 FT-IR equipped with a MKII Golden Gate, Single Reflection ATR System from Specac Ltd., London, U.K. The ATR crystal was a MKII heated Diamond 45° ATR Top Plate. The measurement range was 4000-650 cm⁻¹ and the curves are not normalized due to lack of stable reference wavelengths.

2.7 Accelerated ageing

Untreated and grafted samples were exposed to artificial weathering in two rounds of 60 h. The first round used an Atlas Ci4000 Xenon Weather-Ometer according to JIS K5600-7-7:2008 (Japanese standard identical to ISO 11341:2004) and the second using an Atlas Ci5000 Xenon Weather-Ometer according to a European standard EN ISO 11341:2004. The weathering regime for the first 60 h involved continuous exposure to xenon arc UV radiation (0.51 W/m² at 340 nm) and 18 minutes of deionized water spray every 120 minutes with a black standard temperature of 65° ± 2°C and a chamber temperature of 40° ± 2°C. The last 60 h used similar conditions except water spray was applied every 102 minutes.

3 Results and discussion

Figure 2 illustrates micrographs of the radial surfaces of the untreated control, the sample treated with epoxy functional linseed oil and the sample treated using epoxy functional linseed oil together with HEPBP. Studying these micrographs it is apparent that all samples show indications of
degradation already after 30 h of accelerated ageing, resulting in cracks. In some cases, especially for the untreated samples, destruction of the cells is also noticed, which indicates further degradation. When studying the sample treated with the epoxy functional linseed oil the degradation is less compared to the untreated sample, which indicates an improvement. The sample treated with epoxy functional soybean oil (supplementary information) show slightly more degradation than the sample treated with epoxy functional linseed oil, however, the difference was fairly small and is hence not considered significant. The sample treated with both HEPBP and epoxy functional linseed oil also show better result compared to the untreated sample, with fewer cracks and less destruction of the wood cells, indicating that using a combination of the two reactants is beneficial. This is in coherence both with the study performed by Hatae et al. (2012), where samples were treated using only HEPBP, and with the study performed by Olsson et al. (2012), in which epoxy functional soybean oil was used together with HEPBP. Results from the first study show an improvement of the photoprotection of wood when grafting with HEPBP, and the second study showed that the addition of the epoxy functional oil to the HEPBP pretreatment system further increased the performance. This is also described in earlier studies (Lesar et al. 2011 and Tomak et al 2011) where the use of hydrophobes was shown to restrict the leaching of and also decrease the degradation of wood during ageing. After 120 h of accelerated ageing the combined use of HEPBP and epoxy functional linseed oil show improved performance, with less degradation than the totally degraded untreated control. The sample treated with epoxy functional linseed oil also show improved result compared to the untreated sample, and the sample treated with the epoxy functional soybean oil performed slightly worse than the epoxy functional linseed oil. This indicates that the suggested pretreatment provides protection towards photo induced degradation, and that using a combination of the two reactants (HEPBP + epoxy functional linseed oil) has a positive effect on the system. To understand the system fully, it is suggested that a similar study is performed using different oils in combination with the UV absorber to further study the effect of the oil in a pretreatment system similar to the one described in this study.
Figure 2 VPSEM micrographs of radial surfaces of treated and untreated samples before and after ageing.

Figure 3 shows micrographs of the cross sectional surfaces of the untreated control and the sample treated using both HEPBP and epoxy functional linseed oil. These images show larger differences between the untreated and the pretreated sample than did the radial surfaces. After 30 h of accelerated ageing the two samples show slight indications of degradation, which is shown as loss of lignin in the middle lamella, and already at this stage the untreated sample show more degradation than the pretreated sample. In both cases cracks have also formed to a relatively equal extent. After 60 h of accelerated ageing the untreated sample show even more degradation in the middle lamella whereas the pretreated sample look more or less the same as after 30 h of ageing. In both cases the existing cracks have grown but no new have been formed. After 120 h of accelerated ageing the difference between the untreated and the treated sample is even more evident. After this exposure time the untreated sample shows severe, almost complete, degradation of the middle lamella whereas the sample treated with HEPBP and epoxy functional linseed oil only show much smaller indications of degradation in these areas. The difference in photo induced degradation between the pretreated and untreated sample is believed to be due to the grafting of the HEPBP, which is then attached to the surface and can hence protect the wood surface against degradation for a longer period of time. As mentioned above, the addition of epoxy functional oil also helps in protecting against degradation due to less leaching, increased hydrophobicity and increased flexibility of the system. The results described in this paragraph strengthen this hypothesis and shows that the treatment, to some extent, protects the wood towards photo initiated degradation.

An additional observation is that some of the cells of the pretreated samples appear to be covered. This pattern is not seen for the untreated samples and hence it is likely to be an effect of the pretreatment. This hypothesis is also strengthened by the indication that the effect seems to fade over time, which would be the case if the pretreatment was washed away during the accelerated ageing. In an earlier study, performed by Hatae et al. 2012b, untreated and HEPBP-treated cross sectional surfaces of sugi sapwood were analyzed using VP-SEM. In this study this covering of cells is not evident, and an explanation is thus that it is due to the presence of oil. It also appears as if theses covered cells do not show destruction of the middle lamella to the same extent as uncovered cells,
which further supports the hypothesis. After 120 h of ageing the pretreated sample still has several covered cells which show that the treatment is still present on the surface.
Figure 3 VPSEM micrographs of radial surfaces of treated and untreated samples before and after ageing.

The samples with the radial surface were also analyzed using FTIR microscopy before and after exposure in order to determine if the pretreatment is still on the surface even after exposure. This was not possible for the cross-sectional surfaces since parts of these surfaces have been laser ablated, and hence it is not possible to achieve a good connection with the ATR crystal. The results for the radial surfaces are shown in Figure 4 and indicate some differences between the systems. Starting with the presence of oil it is evident that after 60 h of ageing all the pretreated systems still have a large double peak around 2800-3000 cm$^{-1}$, representing the hydrocarbons of the oil, and one at 1750 cm$^{-1}$, representing the carbonyl of the fatty acids in the oil (Lazzari and Chiantore 1999). After 120 h of exposure these peaks are of similar size as after 60 h of exposure. This shows that there are still large amounts of oil on the surfaces and that the amounts do not significantly wash away during ageing. Either the oil is covalently attached to the wood substrate, or its hydrophobic nature enables it to stay on the surface even after ageing. Studying the carbonyl triple peak, at approximately 1600 cm$^{-1}$, of the system containing HEPBP it appears to have decreased after 60 h of exposure but is still present. After 120 h of exposure the peak is still approximately the same size and it is therefore believed that this amount is actually covalently attached to the wood substrate. The initial decrease after 60 h of accelerated ageing is likely a consequence of the lack of extraction of the samples after the reaction. This causes the unreacted reactants to wash away during the initial stages of exposure, whereas the reacted substances are still left on the surface. Another peak of interest is the singlet at 1505 cm$^{-1}$, which corresponds to the benzene ring stretching in lignin (Evans et al. 2010). Both the untreated and the treated samples show a decrease of this peak after exposure, which is likely due to photodegradation of the lignin, or possibly the HEPBP. In the case of a combined treatment of HEPBP and epoxy functional linseed oil, the decrease is, however, slightly smaller than for the untreated and oil treated samples, indicating less degradation of the lignin and hence a sign of improved photoprotection of wood.

Figure 4 FTIR spectra before and after ageing of untreated samples and samples treated with either linseed oil, or a combination of linseed oil and HEPBP. The arrows indicate the peaks originating from the hydrocarbons of the oil (a), the carbonyls from wood and HEPBP (b), and the benzene rings in lignin (c).

4 Conclusion
Radial and cross-sectional surfaces of Scots pine were treated with a UV protective treatment consisting of the reactive UV absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) and epoxy functional vegetable oil (linseed and soybean oil). Analysis using FTIR indicate presence of the pretreatment even after 120 h of exposure, indicating that the actual treatment is able to withstand a certain amount of UV exposure before degrading. Analysis using VPSEM before, during and after
Accelerated ageing in a Weather-Ometer shows that untreated samples show signs of wood degradation already after 30 h, which is also the case for samples treated with epoxy functional soybean oil. A combination of the HEPBP and the linseed oil does, on the other hand, show improvement in the UV protection of the samples already after 60 h, and even more after 120 h. This effect is even more visible for the cross-sectional surfaces, where after 120 h of exposure the untreated samples show severe degradation of the middle lamella and the samples treated with the combined pretreatment show only small indications of degradation. This shows that the treatment, to some extent, protects the wood towards photo initiated degradation.

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6 References


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Westin M. Utvärdering av en ny metod för UV-skydd av utomhusexponerat trä. L-Rapport 2002;0203008.


Figure S1 VPSEM micrographs of radial surfaces of soybean oil treated samples before and after ageing.
2,4-dihydroxy-benzophenone (DHBP) + Epichlorohydrin → 2-hydroxy-4-(2,3-epoxypropoxy)-benzophenone (HEPBP)
Soybean oil

0 h

30 h

60 h

120 h