ENHANCING UV PROTECTION OF CLEAR COATED EXTERIOR WOOD BY REACTIVE UV ABSORBER AND EPOXY FUNCTIONAL VEGETABLE OIL

Sara Olsson
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AKADEMISK AVHANDLING

To the people I love

“The greatest glory in living lies not in never falling, but in rising every time you fall”

Nelson Mandela
ABSTRACT

Since ancient times wood has played a large role in human activities, both in terms of fuel and for construction purposes. A drawback with wood in exterior applications is, however, its susceptibility to photo-initiated degradation, caused by radiation from the sun. Hence, wood needs to be protected against ageing by means of different surface treatments. The work presented in this thesis describes a possible method for protecting wood against photo-initiated degradation. The system comprises the UV absorber, 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP), which has a primary epoxy group with the ability to react covalently with hydroxyl groups, enabling reaction with hydroxyl groups of the wood (preferably phenolic hydroxyls in lignin). The epoxy functional vegetable oils (soybean and linseed oil) contain secondary epoxy groups which theoretically also enables reaction with the hydroxyl groups of the wood. This ability and a possible reaction with wood could result in a more long term protection since it prevents leaching of the protective substances. The study includes evaluation of several reaction parameters of the pretreatment, such as temperature, time, the influence of the oil, and also the photo protective ability of the sole pretreatment. The results show that a reaction temperature of 102 °C or higher results in presence of the reactants on the surface even after extraction, indicating grafting. Two different reaction procedures imply that reaction for 16 h results in slightly better results compared to a 1 h dipping procedure with 2 h subsequent drying in an oven. However, in terms of time and energy consumption the difference is considered too small to defend using the longer reaction procedure. Colour measurements of samples before, during and after ageing indicate a better performance of the pretreated samples compared to the untreated, and an effect of the oil is also noticed, giving the colour change a more stable increase that levels off instead of continuing to increase. The study also takes into account the use of a clear coating together with the pretreatment to study the performance of a complete coating system, in terms of photo protection. Coating of the pretreated samples is shown to work, with uncompromised adhesion as a result. Evaluations of natural and accelerated weathering of the full systems indicate only minor degradation after 1400 h of accelerated ageing or 14 months of natural exposure. After 4000 h of accelerated ageing, visible signs of degradation are detected, but the pretreated samples perform slightly better than the untreated. After 26 months of natural exposure the samples had too much mould in order to perform a reliable evaluation of the photo induced degradation. Overall the pretreatment is concluded to have a photostabilising effect of the wood.
SAMMANFATTNING

LIST OF PAPERS

This thesis is a summary of the following papers:


Author’s contribution to the appended papers:

I. Principal author. Took part in outlining the experiments and performed all experimental work at SP Wood Technology and KTH, also performed most of the preparation of the manuscript.

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IV. Principal author. Took part in outlining the experiments and performed all experimental work at SP Wood Technology and FFPRI/Kyushu University, also performed most of the preparation of the manuscript.

This thesis also contains unpublished results.

Other related materials:


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1. INTRODUCTION

1.1 BACKGROUND

In 2013 one third of the world’s total land area was covered with forest (Skogsstyrelsen 2013), and half of this was represented by the five most forested countries in the world, namely Russia, Brazil, Canada, The United States and China (in numerical order) (The Global Forest Resources Assessment 2010). Sweden has just over 28 million hectares of forest land, to compare with Russia’s 809 million hectares, but despite this Sweden is the third largest exporter of paper, pulp and sawn timber in the world (The Global Forest Resources Assessment 2010 and Skogsindustrierna 2013). Sweden is also one of the world’s leading producers and exporter of sawn and planed soft wood (FAO 2012), which is used for example in construction and for industrial production of e.g. furniture, doors, windows, flooring etc. (Skogsindustrierna 2013). The reason for this vast production of forest based products is of course the wood itself and its useful properties. One of the drawbacks of wood used in exterior applications is, however, its sensitivity towards photo-initiated degradation, including both ultraviolet light (UV light) and some wavelengths of visible light (Kataoka et al. 2007 and Evans et al. 2008). This is one of the reasons why exterior wood products are coated, using varying coating systems depending on their field of application and desired appearance. For many applications the use of pigmented coatings is appropriate and desirable, whereas in others a completely transparent coating, clear coating, is more suitable. While pigmented coating systems are
protecting the wood surface mainly through the pigment particles themselves together with a small addition of ultraviolet absorbers (UV absorbers, UVAs) and free-radical scavengers, the clear coated systems must rely solely on UVAs and other low molecular weight substances to avoid discolouration and further degradation of the wood surfaces. A drawback with the UVAs and the free-radical scavengers is that they have a tendency to leach out of the coating as the product is in use, and hence recoating is necessary fairly often in order to avoid degradation of the wood (Wicks et al. 2007a). To avoid this, the performance of these low molecular weight substances needs to be improved, and one example is to covalently attach the UV absorber to the wood itself (Kiguchi et al. 1998) and in that manner prevent leaching. Another alternative is to add the UV absorbing groups directly to the coating polymer in order to prevent migration of the UV absorber through the protecting film (Kotlík et al. 2014). This in turn leads to less leaching and decreases the need for recoating, which is a prerequisite when it comes to increasing the use of clear coated exterior products.

1.2 WOOD AND WOOD COMPOSITION

- **Structure and classification of trees**

Trees are types of woody plants that have evolved over millions of years. The trunk of the tree, which is the part mostly used for wood products, is composed of six circular layers: outer bark (ob), inner bark (ib), vascular cambium (vc), sapwood, heartwood and pith (p) (Figure 1). The outer bark provides mechanical support to the inner bark, which serves as a transport medium for sugars produced by photosynthesis. The vascular cambium is located between the inner bark and
the wood, and is responsible for producing both bark and wood. The sapwood is the “living” part of the tree that transports water from the roots to the leaves and it usually has a lighter colour than the nonconductive heartwood (Wiedenhoeft et al. 2005, Bergman 2011a). Heartwood is older growth rings that no longer participate in the life process of the tree but provide mechanical support (Tsoumis 1991a). Finally, the pith is found at the very centre of the trunk and is the remainder of the early growth of the trunk, before the wood was formed (Wiedenhoeft et al. 2005, Bergman 2011a).

![Cross-section of a tree trunk](image)

Figure 1. Cross-section of a tree trunk, illustrating the six circular layers present in a trunk. Image reproduced with the permission of Wiedenhoeft et al. 2005.

Different wood species are further divided into softwoods or hardwoods depending on their origin and components. In the northern hemisphere, softwoods are usually needle-leaved evergreen trees such as pine and spruce (generally conifers), whereas hardwoods are characterised by their broad leaves and deciduous nature, e.g. maple and birch (Wiedenhoeft et al. 2005). Hardwood species are angiosperms, having a characteristic cell type called the vessel
element, whereas softwood species are gymnosperms and lack this special kind of cell (Bergman 2011a). Softwoods instead have a relatively simple cell structure with an axial (vertical) system and a radial (horizontal) system, comprising mostly axial tracheids and ray parenchyma cells, respectively. The major component of softwood cells (ca. 90 %) are the tracheid cells, which are very long cells that provide both conductive and mechanical functions to wood. In order to allow communication and transport of water between the cells, along the long tracheids there are circular bordered pits with the ability to pass through water for transport throughout the tree. Pits are also found between two parenchyma cells (simple pits) and as connections between the tracheids and the parenchyma cells (half-bordered pits) to connect the vertical and radial systems. The ray parenchyma cells are rather long brick-shaped cells in the radial direction, which function in the synthesis, storage and transport of biochemicals in softwoods. Some softwood species also have resin canals in the vertical or horizontal direction. These are not cells but voids which are surrounded by specialised parenchyma cells that function in the resin production (Tsoumis 1991b, Wiedenhoeft et al. 2005).

- Wood cell wall and the basics of tree growth

The cells of wood are in some ways different to the cells of a single plant cell, which in general consists of the cell wall and the protoplast (living content bounded by the cell wall). In wood the situation is slightly more complicated, as in many cases the full function of the cell is carried solely by the cell wall. For this reason, many wood cells do not have the protoplasm at all since it is not necessary for the cell function. For wood cells the open space within the cell wall is instead referred to as the cell lumen and is in many cases an important component when it comes to water transport (Wiedenhoeft et al. 2005).
The cell wall is a non-living and carbohydrate-rich matrix that can provide mechanical support to the entire plant (Wiedenhoeft et al. 2005). The cell wall, in contrast to the lumen, has a highly regular structure with three major regions: the middle lamella, the primary cell wall and the secondary cell wall. The outermost part of the cell wall is a lignin rich layer known as the middle lamella, which acts as an adhesive that connects the wood cells to each other (Wiedenhoeft et al. 2005, Haygreen et al. 1996). The next layer is the primary cell wall which is also the first layer to be formed during production of new wood cells (Hill 2006a). The primary cell wall consists of randomly oriented cellulose microfibrils (similar to thin threads) and is usually very thin. The third and last layer of the cell wall is the secondary cell wall, which is divided into three subsequent layers known as S₁, S₂ and S₃. They are all composed of differently oriented cellulose microfibrils (Wiedenhoeft et al. 2005, Haygreen et al. 1996) and contain decreasing amounts of lignin as they get closer to the lumen in order to facilitate water transport up the tree (transpiration) (Wiedenhoeft et al. 2005). The S₂ layer occupies the greatest volume of the wood cell, and is hence also the layer with the greatest influence on many of the properties of the cell, and thus also the wood material (Hill 2006a). This structure of the cell wall is illustrated in Figure 2.
As mentioned in the previous section, wood is produced by the vascular cambium, usually one layer of cell division at a time. However, in many wood species large collections of cells are produced at the same time and create circles in the cross section of the wood trunk. They are known as growth rings. The growth rings are distinguished from one another due to differences between earlywood and latewood, where earlywood cells are cells formed in the beginning of the cell growth period whereas cells formed during the later growing period are called latewood cells (Tsoumis 1991a, Wiedenhoeft et al. 2005, Bergman 2011a). They can differ in several properties, such as density, colour and other structural features that reflect their micro-morphological structure (Tsoumis 1991a). This type of growth occurs for both softwoods and hardwoods and represents the way trees grow in parts of the world that have distinct and regular seasonality. For many species in tropical areas, however, growth rings are not evident due to the lack of seasonal changes (Wiedenhoeft et al. 2005, Bergman 2011a).
· **Chemical composition of wood**

Wood is in chemical terms best defined as a biopolymer composite of cellulose, hemicellulose and lignin. However, in a living tree the major chemical component is actually water, although in dry condition it consists mainly of the three previously mentioned substances. The amount of each component varies between softwoods and hardwoods, and also between different wood species (Rowell *et al.* 2005). Generally, wood contains 30-65 % cellulose, 20-35 % hemicellulose and 15-35 % lignin (Henriksson *et al.* 2009, Teleman 2009, Henriksson 2009). Softwoods, however, tend to have higher cellulose and lignin content than the hardwoods (Rowell *et al.* 2005).

Cellulose and hemicellulose are both carbohydrate polymers with simple sugars as their main components (Rowell *et al.* 2005, Haygreen *et al.* 1996). Cellulose (Figure 3) is a polymer of D-glucopyranose units connected by β-(1→4)-glucosidic bonds, although the repeating unit of the polymer is a two-sugar unit known as cellulose (Rowell *et al.* 2005). A number of the cellulose molecules are closely associated through hydrogen bonds to form the reinforcing element in the cell wall known as microfibrils. Due to the high crystallinity of these microfibrils the cellulose is rather unreactive and stable (Hill 2006a). Since the ability or inability to modify or graft cellulose can be of interest in many cases this is an important factor. In such cases it is not only a question of whether or not the cellulose is crystalline, but also about the accessibility of the cellulose. The cellulose found on the crystal surface is generally accessible, while the rest of the crystalline cellulose is not. When it comes to the amorphous cellulose most is accessible but parts of it will be covered with hemicellulose and lignin which makes it non-accessible (Rowell *et al.* 2005).
Hemicellulose, as already mentioned, also consists of sugar units linked together. In contrast to the cellulose, the hemicellulose consists of combinations of different types of sugar units and is often branched. Hardwoods and softwoods usually have slightly different hemicelluloses, with different combinations of sugars in them. For example, one of the major hemicelluloses in hardwoods is glucuronoxylan (15-30 % in wood), whereas in softwoods one of the major hemicelluloses is galactoglucomannan (10-15 % in wood), which also accounts for approximately 20 % of all the hemicelluloses (Rowell et al. 2005). Despite the content, the hemicelluloses fill an important function together with cellulose in giving the plant a supportive structure. The hemicelluloses can be found in the cell wall matrix between the cellulose fibrils, as is illustrated in Figure 4 (Teleman 2009). In similarity, or contrast, to the cellulose the hemicellulose plays an important role in chemical modification and grafting of wood. In a study performed by Rowell et al. (1994) hemicellulose was shown to react with uncatalysed acetic anhydride to the second highest rate (after lignin), whereas cellulose did not react at all under the same conditions.
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Figure 4. Model for the distribution of lignin, hemicellulose and cellulose in the S2 layer. Hemicelluloses are in the form of Glucomannan and Xylan. Image reproduced with the permission of Henriksson 2006.

Lignins are amorphous and mainly aromatic polymers of phenylpropane units which, in contrast to cellulose, do not have one single repeating unit (Rowell et al. 2005). Instead, they consist of a complex arrangement of substituted phenolic units connected by ether (C-O-C) or carbon-carbon (C-C) bonds to form a threedimensional network (Figure 5). The lignins are polymerised from three main monomers (monolignols) called coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. These are propylphenol derivatives with a varying number of methoxy groups attached to the ring. Based on these precursors, three main types of lignin are formed: guaiacyl lignin (G), syringyl lignin (S) and p-hydroxyphenyl lignin (H). Softwood lignins consists mainly of G with small quantities of H. Hardwood lignins consists of a mixture of G and S with very little H, whereas grass lignins consists of all three types but with only small quantities of S. Both softwood and hardwood lignins also contain small amounts of incomplete or modified monolignols. (Henriksson 2009, Sjöström 1993, Sarkanen and Ludwig 1971).
Lignin has several functions in the wood structure. It gives stiffness to the cell wall, since it has the ability to fixate the cellulose and hemicelluloses to each other (Henriksson 2009). It acts as an adhesive that glues different cells together and hence, the highest concentration of lignin can be found in the middle lamella (Haygreen et al. 1996, Henriksson 2009). It also makes the cell wall less hydrophilic and can to some extent provide protection against microbial degradation due to its compact structure (Sjöström 1993, Henriksson 2009). Due to its structure lignin is also shown to be more reactive than cellulose (Rowell et al. 1994), which is an important factor in the modification and grafting of different substances to wood (Rowell et al. 1984). In the study by Rowel et al.
(1994), the lignin was shown to react the fastest with acetic anhydride. It also showed that at high weight gains higher degree of acetyl groups were found in the lignin rich middle lamella compared to lower weight gains where they were mostly found in the secondary cell wall. This indicates that initial distribution is controlled by the diffusion of chemicals into the cell wall rather than the rate of the chemical reaction.

### 1.3 WOOD DEGRADATION

Weathering of wood is an expression used to define the slow degradation of a material exposed to the weather. Weathering is a surface phenomenon, primarily initiated by solar radiation, with a penetration depth in the micro- to millimetre scale (Browne and Simonsen 1957, Hon and Ifju 1978, Hon 1981, Horn 1994, Park et al. 1996, Kataoka and Kiguchi 2001) and varies depending on the wood density and the wavelength of the incoming light. Denser wood and shorter wavelengths penetrate less, which is supported by studies performed by Hon and Ifju (1978) and Hon (1981), who reported that UV light penetrated the wood down to 75 µm in the wood whereas visible light penetrated down to 200 µm. The wavelength of the incoming light plays a major role in the degradation process of wood, although several other non-microbial factors are also of importance. These factors can for example be wetting and drying of wood, changes in relative humidity (RH), abrasion by windblown particles, temperature changes, pollution, oxygen, and human activities such as walking on decks, cleaning surfaces or sanding. Microbial degradation of wood, mainly by fungi and bacteria, also play an important role under exterior conditions – often in combination with the non-microbial factors. All of these factors affect the degradation process, but the main reason for weathering is still UV radiation from the sun, which in combination
with atmospheric oxygen starts photochemical degradation of the surface (Williams 2005).

The first step of UV initiated degradation is a colour change of the wood due to photochemical reactions as the lignin degrades. The mechanism for these reactions is believed to be a combination of three different pathways leading to yellowing of wood components (a graphical summary of the pathways are given in Scheme 1): (1) the free phenoxy radical pathway, (2) the phenacyl pathway and (3) the ketyl pathway. In the first pathway, (1), phenoxy radicals are formed by direct excitation or free radical scavenging of phenolic groups, and these phenoxy radicals then oxidise into yellow quinones. The second pathway, (2), includes excitation of carbonyl groups in the lignin to form ketones (ketyl radical as intermediate) and phenoxy radicals, which once again can be oxidised into yellow quinones. Lignin also gives rise to the third pathway, (3), since it, together with other radicals, has been shown to form ketyl radicals, which in turn can break down to form ketones and phenoxy radicals. The phenoxy radicals cause yellow quinones to form and the ketones may act as secondary chromophores for further photodegradation (Leary 1994).
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Scheme 1. Probable paths of yellow quinone production. Structured with inspiration from (Leary 1994).

It was shown by George et al. (2004) that lignin is the only component in wood which absorbs relatively strongly in the UV/visible region and hence it implies that lignin is the main cause of photo degradation. Kalnins (1984) indicated that lignin was considered the first point of attack in the mentioned process and showed that UV-irradiation of wood causes the lignin content to decrease significantly. Similar results were also presented by Evans et al. (1995) who showed a decrease in lignin content already after 4 h of natural exposure, and substantial surface delignification after only 3 days. Since the lignin content is highest in the middle lamella the photo-initiated degradation will primarily occur
in this part of the wood surface. This is evident when studying micrographs of southern pine cross-sections before and after weathering (Figure 6). These images illustrate the degradation of the lignin in the middle lamella before and after 1000 h of UV radiation (Williams 2005).

Figure 6. Micrographs of cross-section of southern pine before (a) and after (b) UV exposure (1000 h). Image reproduced with the permission of Williams 2005.

The destruction of the middle lamella also leads to other microscopic effects in the wood. Checks tend to form at the bordered pits due to degradation of the lignin binding between the fibrils, and separation between the cell walls is evident due to the lack of lignin (Williams 2005). After further weathering, severe checking is developed and fibrils, tracheids and eventually also macroscopic fibres loosen and become detached from the surface (Williams 2005, Bergman 2011b). Another effect of the weathering process of wood is that as the lignin degrades this hydrophobic component of the wood decreases and hence creates a more hydrophilic surface. During weathering the extractives are also leached from the wood, which further decreases its water-repellence, causing it to become more sensitive to further degradation (Williams 2005).
1.4 WOOD PROTECTION

It is evident from the previous section, that wood needs extensive protection in order to be used in exterior applications, both in terms of photodegradation and wood-destroying organisms such as fungi, bacteria and insects. As discussed in Section 1.3, photodegradation is a surface phenomenon and in order to prevent it the added protection should be at the surface of the wood, and not penetrated into the wood. This is achieved by adding protective coatings to the wood surface with the ability to protect the wood from weathering (Bentley and Turner 1998) and biological factors (Williams et al. 1996a). The choice of finish depends on the application, and is hence chosen with respect to existing requirements and the desired properties of the product (von Tell 1990). Finishes can be transparent, semi-transparent or opaque depending on the coating system and the amount of pigments or dyes added. Coating systems without pigments or dyes are transparent and as a consequence also sensitive to UV light since it penetrates the coating and degrades the wood (Williams et al. 1996b), hence they are not generally recommended in exterior applications. However, in some cases clear coated surfaces are still desired outdoors since they retain the natural appearance of wood, and hence other alternatives for UV protection are needed. There are several methods available to protect wood from photodegradation and this chapter comprises a brief summary of some of the more common methods used today.

- Fungicides and wood preservatives

Protection against wood-destroying fungi has traditionally been achieved by using fungicides in wood preservatives and protective coatings, or by using a combination of the two. Fungicides in coatings act both as surface protection against discolouring fungi on the coated wood surface and as protection against
rot and blue stain in the interphase between the wood substrate and the coating. These biocidal compounds do, however, have the drawback of leaching out of the coating as the product is in use. In that sense wood preservatives applied by pressure processes are more effective in protecting the wood substrate as these substances penetrate into the wood itself, and hence gives a more long term protection. At present the most abundantly used wood preservatives for industrial treatments, apart from creosote, are based on copper compounds as the active ingredient (The Swedish Chemicals Agency 2013b). Creosote has been used since the 1830s and is presently restricted for heavy-duty end-uses, such as utility poles, piles and railway sleepers. Protection against biological degradation is an important part in protecting exterior wood from degradation, but in this thesis focus will be on the photo induced degradation and how wood can be protected from it. Hence, for more information on biological degradation of wood the author recommends Eaton and Hale (1993).

· Pigments and reactive transition metal compounds

One of the most common methods of protecting wood against photodegradation is adding pigment particles to a coating. They are commonly small particle solids, more or less insoluble in the binder, that absorb the incoming UV radiation and hinder it from reaching the wood substrate. Pigments are divided into three groups depending on origin and composition (Paul 1985). Inorganic pigments are for example metal oxides and sulphides, and the most common one is the white TiO₂ pigment, mainly due to its incomparable outdoor exposure performance, excellent hiding power and extraordinary chemical resistance (Goldschmidt and Streitberger 2003). The second group are organic pigments, which includes products such as the azo pigments (The Swedish Chemicals Agency 2013a), which are fairly cheap and give bright colours with good performance (Paul
The third group of pigments are the dispersed pigments which are organic or inorganic pigments dispersed in a medium instead of using them in their standard powder form. The most effective UV absorber known, however, is carbon black (Wicks et al. 2007a), but due to the resulting colour its use is limited.

Another effective treatment that protects against photochemical degradation, and is water repellent is treatment of wood with chromic acid. This compound interacts with the wood to form a highly insoluble complex with wood, cellulose or lignin model compounds and hence becomes an integrated part of the wood (Williams 2005). The treatment is effective (Williams 1983) but due to the molecular structure of this chemical it is also classified as especially hazardous by the European Chemical Agency and the European Commission (The Swedish Chemicals Agency 2012). Studies have, however, also been performed using other types of reactive transition metal compounds, such as trivalent chromium (Williams and Feist 1988), ferric chloride (Chang et al. 1982), titanium, zirconium and manganese (Schmalzl and Evans 2003). The latter study showed that the oxidative manganese compounds, potassium permanganate and manganic acetate, restricted both weight and tensile strength loss during weathering. The results also indicated that lignin was retained at the surface of weathered veneers treated with the two manganese compounds. They were, however, not as effective as chromium trioxide, indicating that stable weather resistant complexes with lignin were not formed (Schmalzl and Evans 2003).

**UV absorbers and HALS**

As mentioned above, pigment particles have a positive effect on the photostabilisation of wood. However, in many applications a photostabilising
effect is desired without colouring the wood. One of the most common ways of achieving this is to add low molecular weight substances with the ability to absorb incoming UV radiation from the sun and convert it into heat (Vollmer 2011). Substances with this ability are called UV absorbers (UVA) and are used to protect the substrate by preventing UV light from reaching the wood substrate (Schaller and Rogez 2006). Common examples of UVAs are benzotriazole and triazine (Hayoz et al. 2009), where 2-(2-hydroxy-phenyl)-benzotriazole (BTZ) is considered important for clear coatings (Schaller and Rogez 2006). However, limitations of this type of UVAs have opened up for the 2-hydroxyphenyl-s-triazines (HPT) which can be fine-tuned by choosing the appropriate substituent, and hence create tailor made UVAs for different substrates and industries (Schaller and Rogez 2006). One interesting example for the wood industry is, for example, the use of substituted tris-resorcinol triazine which is synthesised in an encapsulated form for waterborne wood coatings and has exceptional photo performance (Rogez et al. 2006). Another example is substituted 2-hydroxybenzophenones which have photo-antioxidative abilities. The degree of this property is highly dependent on the substituent and its positioning in the chemical structure. A study performed on this subject concludes that introducing a substituent of electron-donating character to the para-position of the phenol in the structure improves this photo-antioxidant ability, even more than in the meta-position (Dobashi et al. 2005). However, this does not consider that in some cases one might want to react additional substance to this substituent and hence some oxidative ability could be advantageous. Nevertheless, these molecules are able to convert UV energy into thermal energy by intramolecular hydrogen transfer or cis-trans isomerisation (Wicks et al. 2007a) which enables its UV stabilising ability. This is illustrated for 2-hydroxybenzophenone in Figure 7 below.
Other types of substances, commonly used for UV protection in coatings, are the hindered amine light stabilizers (HALS). These are amines with two methyl groups on each of the two alpha carbons, as illustrated in Figure 8. HALS undergo photooxidative conversion into nitroxy radicals (R$_2$NO$^\cdot$) that can react with carbon centred radicals formed by photo-initiated oxidation (Wicks et al. 2007a). Hence, HALS hinders degradation of the coating by blocking radical reactions initiated by light (Schaller and Rogez 2006). A number of different HALS compounds are available and by varying the R and R$'$ groups of the molecule, properties such as volatility and long term stability can be altered (Wicks et al. 2007a). The most important HALS compounds are the bifunctional derivatives (Figure 8), where the properties are determined by the substituent on the nitrogen atom due to basicity. The non-basic aminoethers (N-OR) have increased in the paint industry since they are, for example, non-interactive with biocides and acidic media (Schaller and Rogez 2006).
Currently, the most common practice is to use a combination of UVA and HALS (Schaller and Rogez 2006), where the UVA absorbs harmful UV light and quickly transforms it into heat, and the HALS reduces the rate of the oxidative degradation due to quenching of the radicals that, to some extent, will still be formed (Valet 1997, Wicks et al. 2007a). A fairly recent study also shows that the use of HALS in a clear coating system leads to an inhibition of the photo-oxidation of the UVA, and hence the coatings retain their UV absorbance longer (Forsthuber and Grüll 2010). A drawback with both of these substances is, however, their tendency to leach out of the coating as the product is being used, and hence clear coated surfaces need to be recoated fairly often in order to maintain their appearance (Wicks et al. 2007a).

· Nano sized particles
Other types of particles that have gained interest in UV protective purposes are nanoparticles of different metal oxides. These inorganic nanoparticles, for example TiO$_2$, CeO$_2$ and ZnO, have the same function as pigment particles, although they are much smaller in size and are hence more or less transparent. Studies have shown that both ZnO and TiO$_2$ are effective in protecting the wood substrate from UV degradation (Allen et al. 2002, Salla et al. 2012 and Fufa et al. 2013). The TiO$_2$ is even shown to perform better than the organic UVAs HPT and BTZ (Forsthuber et al. 2013) and also show good results when used in combination with an organic UVA (Mahltig et al. 2005). A study performed by Blanchard and Blanchet (2011) also indicate that the efficiency of adding these types of particles to a coating varies depending on the particle size and that a synergistic effect is possible when inorganic and organic particles are combined. Another study, comparing different pretreatments and clear coatings, concluded
that in terms of colour change after exposure, CeO$_2$ showed very little improvement compared to a standard acrylic coating (Vollmer 2011). Some general drawbacks of nanosized metal oxides are, however, their tendency to increase the T$_g$ of the coating during ageing, leading to cracks in the coating film (Aloui et al. 2007), and that they tend to slightly discolour the surface (Mahltig et al. 2005, Aloui et al. 2007, Forsthuber et al. 2013).

· **Oils**

Drying oils are among the oldest binders used for paints. They are liquid vegetable or fish oils that react with oxygen in the air to form solid films (Wicks et al. 2007b). Such oils, e.g. linseed oil, can also be used to impregnate wood in order to form a hydrophobic layer inside and outside the wood to retard the moisture uptake, and hence protect the wood substrate (Fredriksson et al. 2010). A recent study performed by Ozgenc et al. (2013) shows that treating wood with vegetable oils results in less colour change of the samples after weathering, hence indicating that the oils inhibit degradation of the lignin into yellow quinones. Despite the advantage of vegetable oils being a renewable resource, the use of drying oils as pure binders decreased markedly in the early 1930s due to the commercialisation of the oil based and more versatile alkyd resins (Hofland 2012). Development of new polymers and binders, such as acrylics and polyesters, did, however, damage the position of the alkyds considerably (Hofland 2012), but due to the growing interest of the environment and new developments an increase in linseed oil-based paints and functionalised fatty acids has been observed (Derksen et al. 1996).

Natural oils are triglycerides, consisting of glycerol and different fatty acids, such as stearic acid and oleic acid. Each oil has a different composition, and can also
be affected by the growth location of the plant. The ability of oils to act as drying, semi-drying or non-drying depends on the composition of different fatty acids and their degree of unsaturation, or more specifically, the number of diallylic methylene groups in the chain. As an example, soybean oil is a semi-drying oil with two diallylic groups on 9 % and one diallylic group on 51 % of the total amount of fatty acid chains respectively. Linseed oil, on the other hand, is a drying oil with two diallylic groups on 52 % and one diallylic group on 16 % of the fatty acid chains respectively. So the more diallylic groups on the fatty acids, the greater the drying capacity of the oil (Wicks et al. 2007b).

These natural oils can also be modified by introducing new groups to the fatty acid chains in order to increase the compatibility with a potential top coat system or even to get the oils to react with the substrate (Wicks et al. 2007a). One example of this is to introduce epoxy groups to the fatty acid chains, which can be performed by several different methods. The most common is by reaction of carboxylic acid and concentrated hydrogen peroxide, but other methods are also available, such as acid ion exchange resin, the use of metal catalysts (Saurabh 2011) or a lipase catalysed in situ epoxidation (Vlcek et al. 2006). Epoxy functional oils do, on the other hand, also occur naturally in nature. One example being suberin which can be found in the outer bark of birch trees where it acts as a hydrophobising barrier (Olsson 2009). This hydrophobising property is desirable when using within exterior wood products to provide protection from degradation due to moisture, and UV-light, since it is known that photodegradation of wood is greater when the cell wall contains water than when it is dry (Andersson et al. 1991a,b). Furthermore hydrophobes, such as vegetable oils, have been shown to restrict the leaching of chemicals from the wood surface (Lesar et al. 2011 and Tomak et al. 2011), which is beneficial when used in combination with easily leached UVA/HALS. To further prevent leaching the epoxy groups attached to
the fatty acid chains can then be covalently reacted to the wood substrate, in order to create a more long term coating system (Kiguchi et al. 1998, Westin 2002, Olsson et al. 2012).

**Chemical modification**

In order to create a wood based material with a long service life it is usually necessary to interfere with the natural degradation process of wood. One way of achieving this is to modify the wood surface chemically *via* a range of different methods. The basis of most chemical modifications is OH-substitution of the cell wall wood components (Hill 2006a), where aliphatic and/or aromatic hydroxyl groups of the wood components may be substituted by new functionalities in order to decrease degradation and improve the mechanical properties. Since the hydroxyl groups of lignin are the most susceptible to UV degradation it is of course desirable to get the grafting on the OH groups of the lignin (*i.e.* the aromatic hydroxyl groups), assuming preventing degradation is the aim of the treatment. One must, however, bear in mind that substituting the hydroxyl groups in wood does not by itself prevent photo oxidation reactions (Kalnins 1984), but relies on the added functionality to have some ability to prevent these reactions from occurring (*e.g.* by blocking the derivative pathways).

Depending on what property is to be changed, the modification will be different. To increase water repellence, for example, one way would be to reduce the hydrophilicity of the cell wall by introducing hydrophobic groups (Rowell 2005). If, on the other hand, the goal is to achieve dimensional stability then acetylation or a high degree of furfurylation could be the appropriate choice (Svenskt Trä 2014). The former conventionally uses acetic anhydride as reactant with the drawback of producing acetic acid in the process, which needs to be removed
from the wood before use. This has led to some interest in using other reactants for the acetylation of wood, *e.g.* vinyl acetate (VA) or ketene gas. The former reactant, VA, has been shown to successfully acetylate wood, creating acetaldehyde as a by-product instead of acetic acid, which is easier to remove due to its lower boiling point and non-acidic nature (Jebrane *et al.* 2007, Jebrane *et al.* 2011). Another alternative is ketene gas, which in absence of water produces no by-products during reaction with wood. Ketene gas does, however suffer from drawbacks such as toxicity, explosiveness and dimerisation (Hill 2006b), why the focus of acetylation still relies on the use of acetic anhydride. This process also improves the UV resistance to some extent (Svenskt Trä 2014), possibly due to a change in the chemical structure of the ketyl radical which retards the subsequent breakdown (Leary 1994), which makes it an interesting aspect for this thesis. The latter, furfurylation, is an impregnating treatment using the renewable furfuryl alcohol as a reactant, which is produced from biomass from corn and sugar canes. Using this type of modification also gives the wood increased fire stability and, in some aspects, aesthetically favourable darker colour similar to mahogony (Svenskt Trä 2014). Other types of chemical modifications include *e.g.* methylation or the use of isocyanates, carboxylic acids and epoxides (Rowell 2005).
2. AIM OF STUDY

The overall aim of this work is to develop a potential pretreatment for exterior clear coated wood with enhanced UV protection. The pretreatment comprises a reactive UV absorber together with two epoxy functional vegetable oils, all possessing the ability to react covalently with the wood substrate. The UV absorber is then believed to react covalently with the hydroxyl groups of the most UV sensitive wood components, and could in that sense decrease leaching of UV absorber from the coating. The vegetable oils are added in order to hydrophobise the surface, since this has been shown to decrease leaching and also prevent degradation. The combination of the two reactants (UV absorber and epoxy functional vegetable oil) is hence believed to give a more long term protection and increase the service life of clear coated wood products for exterior applications.
3. EXPERIMENTAL

For published material only brief descriptions of experimental methods are given, full details can be found in the related papers. Regarding unpublished material full descriptions are given in this thesis.

3.1 MATERIALS

Materials used for the published experiments can be found in the related papers. Materials used for unpublished experiments are given below.

2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPB, synthesised according to (Manasek et al. 1976)), 3-pentanone (ReagentPlus >99 %, Sigma Aldrich), 4-(dimethylamino)pyridine (DMAP, 99 %, Aldrich), epoxy functional soybean oil (ESBO, Lankroflex E2307, Akcros Chemicals), epoxy functional linseed oil (ELSO, Lankroflex L, Akcros Chemicals), 4,5-dichloro-2-octyl-4-isothiazolin-3-one (DCOIT, 20 %, Dow Chemical Company), marine epoxy adhesive (LePage), acrylic coating without biocide (Test product, Akzo Nobel Industrial Coatings), acrylic coating with standard amount UVA/HALS (0.6 % UVA/HALS of dry binder content, Test product, Akzo Nobel Industrial Coatings), acrylic coating with double amount UVA/HALS (1.2 % UVA/HALS of dry binder content, Test product, Akzo Nobel Industrial Coatings). All chemicals were used as received.
Wood veneers and samples were Scots pine obtained from JL Träproduktion in Bureå.

3.2 EXPERIMENTAL PROCEDURES

· Veneer and wood sample preparation

Defect free Scots pine veneers were prepared by first cutting the solid pieces of wood into rectangular blocks measuring 100 mm (longitudinal) x 50 mm (tangential) x 20 mm (radial), which were then soaked in water for approximately 24 h. Secondly, the wet wood blocks were fastened to a microtome and cut into approximately 85 µm thick veneers measuring 100 mm x 10 mm (Paper I) or 100 mm x 35 mm (Paper II, Paper III and unpublished study using fungicide), using disposable microtome blades in a blade holder. The wet veneers were then dried at room temperature prior to use. The growth ring density was 5 or 6.5 growth rings per cm for veneers used in Paper I and Paper II respectively.

Samples for Paper IV were made of sapwood Scots pine and sawn into smaller pieces with a radial surface size of 15 (L) x 15 (R) mm and a thickness of 10 (T) mm. The samples were then wet for 5 h before cut on the radial side using a microtome to even the surface before reaction, analysis and exposure.

· HEPBP synthesis

The procedure for synthesising HEPBP was according to previous literature (Manasek et al. 1976). In brief, the reactive UV-absorber HEPBP was synthesised
Experimental

by reacting DHBP and epichlorohydrine in 2 M KOH at 80 °C for 2 h with constant stirring and reflux. A yellow substance was produced which was washed 6 times with deionised water and the excess solvent was evaporated using a rotary evaporator. The product was recrystallised 3 times using ethanol, resulting in a yellow crystalline powder. A schematic reaction path is illustrated in Scheme 2.

![Scheme 2. Schematic reaction path of the synthesis of HEPBP.](image)

- **Reaction and grafting procedures**

The grafting procedure for the veneers and wood samples used in *Paper I, II, IV* and unpublished work in this thesis were divided into two different procedures, one where the veneers were boiled in a solution containing the reactants (boil, *Paper I and II*) and one where veneers were dipped in a solution with the same components (dip, *Paper II, III and IV*). For the second grafting procedure the veneers were transferred from the dipping solution onto glass plates and put in an oven at 105 °C for 1 or 2 h. Veneers were then left to cool down at room temperature for at least 2 h prior to use. Veneers used for *Paper I* were also extracted in an acetone- and ethanol solution (2:1) for 24 h using Soxhlet extraction. Veneers used for *Paper I* were treated using either HEPBP or a combination of HEPBP and epoxy functional soybean oil, *Paper II* used only a combination of the two reactants, and *Paper IV* used either of the two epoxy functional vegetable oils (linseed and soybean) or a combination of the epoxy
Experimental

functional linseed oil and HEPBP. Scheme 3 illustrates a possible reaction path for the reaction between HEPBP and wood.

In the reactions for the Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR) analysis in *Paper III* two different lignin model substances were used. After consolidating the literature (Nordstierna *et al.* 2008), 2-methoxy-4-methylphenol (creosol) was chosen to represent softwood and 4-methyl-2,6-dimethoxyphenol to represent hardwood, since their structures constitute the principal aromatic units of softwood and hardwood lignin respectively. The reaction procedure was as follows: HEPBP or epoxy functional vegetable oil and lignin model substance were added to a round bottom flask at a molar ratio 1:1. The content of HEPBP or epoxy functional oil was fixed at 1 g or 2 g, respectively, whereas the amount of lignin model substance varied depending on the molar weight of the model substance and HEPBP/epoxy functional oil to achieve the molar ratio 1:1. 3-pentanone (40 ml) and the catalyst DMAP (0.02 g) were added and the mixture was left to react for 8 h at 102 °C with constant stirring. Due to the restricted amount of HEPBP a smaller batch was produced, using only half the amounts. After reaction the solvent was evaporated using a rotary evaporator. Scheme 4 and Scheme 5 illustrates a proposed reaction path of the reaction between the model substance creosol and HEPBP, and between epoxy functional linseed oil and creosol.
A smaller study was also performed in *Paper III* to further show that the reaction of the HEPBP and the lignin model substance creosol occurs, and that exposure of the product to UV light causes the new bond between the two reactants to break. In this study creosol and HEPBP were added at a molar ratio 1:1 and 2:1 respectively as described in the preparation of the NMR and FTIR samples in the same study.

**Coating and gluing of samples**

After grafting, veneers used for *Paper II* and for an unpublished study were glued onto sanded (80 grit) western red cedar blocks using a marine-grade epoxy
Experimental

adhesive, and were cured for 2 h at ambient temperature and pressure. Samples for Paper II were then coated using two different commercial acrylic coatings, one with double amount of UVA/HALS (Ac-coating) and one with 1% nanoparticles of cerium oxide together with standard amount of UVA/HALS (Ce-coating). Six out of 12 veneers from each grafting process were coated with the Ac-coating, and the remaining 6 using the Ce-coating. None of the coatings contained any type of fungicide. Two layers were applied on each sample. After drying overnight, all samples were sealed on all sample sides except the veneer side using the same epoxy glue as previously mentioned. One sample of each pretreatment/coating combination for Paper II was kept in the conditioning room at 20 °C and 65% relative humidity for the entire trial.

For the unpublished study 12 samples were prepared as the above mentioned, only a thin layer of the fungicide 4,5-dichloro-2-octyl-4-isothiazolin-3-one, DCOIT, (ca. 0.1% of veneer weight) was added to the surface by brush and left to dry before coating. An acrylic coating with standard amount of UVA/HALS without fungicide was used to coat the samples in two layers. Samples were then exposed to five months of natural exposure (for more information see section Natural exposure).

Samples for Paper I, III and IV were not coated or glued but only pretreated.

· Preparation of samples for analysis

Samples exposed to accelerated ageing in Paper II and Paper IV were analysed using scanning electron microscopy and in order to achieve good imaging samples were cut using a pulsing UV excimer laser from Lumonics. A wavelength of 248 nm (krypton- and fluorine gas mixture in nitrogen), an
Experimental

irradiation energy of 270 mJ and a frequency of 6 Hz (*i.e.* 6 irradiations per second) were used. Helium was used as a protection gas. From each original sample in *Paper II* a slice was cut off and the upper parts of these slices (Figure 9), as well as part of the surface of selected samples for *Paper IV*, were then cut using a pulsing UV excimer laser in order to achieve visible cross-sectional surfaces. For more information regarding the UV excimer laser see Wålinder *et al.* 2009.

![Sawn Cross-section of sample Cut using the laser](image)

**Figure 9. Illustration of sawing and cutting procedure performed prior to VP-SEM analysis.**

3.3 INSTRUMENTATION

· *Thin Layer Chromatography (TLC)*

Thin Layer Chromatography (TLC) was used to determine the reaction between the lignin model substance creosol and the UV absorber HEPBP in the kinetic study in *Paper III*. Aluminium plates coated with silica were used as the stationary phase and a solvent solution comprising ethanol and hexane with a volume ratio 1:8 was used as the mobile phase. Several other solvents and combinations of solvents were tested and the one used was considered the most appropriate rate for the components analysed. The positioning of the substances on the plates were visualised using low wavelength (200-300 nm) UV-light.
**Experimental**

- *Fourier Transform Infrared (FTIR) spectroscopy*

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to analyse the chemical composition of the reactants and the product after reaction in *Paper I - IV*. All measurements were performed in air at room temperature. The equipment used was a Perkin-Elmer Frontier FT-IR equipped with a Frontier UATR ZnSe with Reflection Top-Plate and Pressure arm. The software used was Spectrum 10 software and 1-4 scans for each sample were used.

- *Fourier Transform Infrared (FTIR) microscopy*

Fourier Transform Infrared Microscopy (FTIR-microscopy) was used in *Paper III* to determine where in the surface structure of the wood the product is located after reaction. All measurements were performed at room temperature and the instrument used was a Spectrum Spotlight 400 FT-IR microscope connected to a Spectrum 100 FTIR spectrometer (Perkin-Elmer Inc.). Samples were analysed in image and ATR image mode (attenuated total reflectance, ATR) at two specific wavelength intervals and in 4 spots on each sample. The mentioned intervals were 2880-2844 cm\(^{-1}\) and 1690-1545 cm\(^{-1}\), representing the hydrocarbon peak from the oil and the carbonyl peak from the HEPBP respectively. The image mode measurements resulted in a photograph of the tested area (*ca.* 500 x 500 µm, pixel resolution *ca.* 5 µm) and an absorption image of that same area. In the ATR image mode only the absorption image of 100 x 100 µm with a pixel resolution of 1.56 x 1.56 µm was obtained. The software used was Spectrum Image.
Experimental

· **Scanning Electron Microscopy**

Samples used in *Paper II* and *IV* were studied using Scanning Electron Microscopy imaging (SEM). In *Paper II* the pretreated and coated samples in the accelerated ageing trial were studied using a Hitachi TM-1000 variable pressure SEM (VP-SEM) at 15 kV accelerating voltage in the backscatter mode. Samples were analysed without sputtering. Samples exposed to natural exposure were not analysed using SEM due to continued exposure, whereby the samples needed to remain intact.

In *Paper IV* all samples were analysed using SEM. During the first 60 h of exposure the samples were analysed using a JEOL JSM-5600 VP-SEM in the backscatter 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 the same Hitachi TM-1000 as mentioned in the previous paragraph.

· **Optical Microscopy**

Samples in the natural exposure trial in *Paper II*, as well as samples from the unpublished study using the fungicide DCOIT, were studied using optical microscopy to study the presence of mould on the samples. The instrument used was an Olympus BX51 equipped with polarised light and a CCD camera for image acquisition. All samples were wiped off with a moist cloth before analysis.

· **Nuclear Magnetic Resonance (NMR)**

Products from *Paper III* were analysed using Nuclear Magnetic Resonance (NMR). $^1$H-NMR spectra were recorded at 400 MHz on a Bruker Avance AM
400 using dimethyl sulfoxide (DMSO) as solvent. The solvent signal was used as internal standard. All peaks were determined using the centre proton on the triglyceride backbone as a reference.

**Accelerated ageing**

In *Paper I, II* and *III* samples were exposed to accelerated ageing in an accelerated weathering tester (QUV) at 340 nm (UVA radiation). An accelerated weathering tester with Solar Eye UV irradiance controller from the Q-Panel Company was used. In *Paper I* and *II* the veneers were exposed to 24 h cycles with 16 h of UV light at 60 °C followed by 8 h of condensation at 50 °C (Westin 2002). In *Paper I* samples were exposed to 272-368 h of UV light and in *Paper II* the veneers were evaluated after approximately 1400 h of UV light, and half of the veneers also after approximately 4000 h of UV light. Colour measurements were performed continuously during exposure. In *Paper III* filter papers soaked in reaction solution were exposed to 16 h or 140 h of accelerated ageing at approximately 40 °C without water condensation or spray.

In *Paper IV* untreated and grafted samples were exposed to artificial weathering in two rounds of 60 h. The first round used an Atlas Ci4000 Weather-Ometer according to JIS K5600-7-7 (Japanese standard) and the second using an Atlas Ci5000 Xenon Weather-Ometer according to 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 deionised water spray every 120 minutes with a black standard temperature of 65 °C ± 2 °C and a chamber temperature of 40 °C ± 2 °C. The last 60 h used similar conditions except water spray was applied every 102 minutes.
Experimental

· Natural exposure

One third of the samples for Paper II were exposed to natural weather conditions in Kioloa, Australia (35.55° S, 150.37° E) for 14 months (December 2011-February 2013) and subsequently in Stockholm, Sweden, (59° N, 18° E) for 12 months (Sep. 2013-Sep. 2014, unpublished results) to assess the performance of the pretreatments. Samples were placed on large holders using screws that were glued on to the back side of the samples using a marine epoxy adhesive. The sample holders were then mounted at a 10° angle for maximum exposure and effect.

Samples for unpublished results using the fungicide DCOIT were exposed to 5 months (May-September) natural weather conditions in Bogesund, Sweden (59° N, 18° E) on racks positioned at 10° angle to the horizontal, similar to Paper II.
4. RESULTS AND DISCUSSION

4.1 PERFORMANCE OF PRETREATMENT

This chapter comprises results from a selection of experiments performed within this work. For complete results the author refers to the corresponding papers.

- Grafting properties

During the HEPBP synthesis (Scheme 2) there are basically three possible reaction products; the epichlorohydrine can either react with the phenolic hydroxyl group in the *para* position, the *ortho* position or both. There is also the possibility that the epoxy group of the HEPBP reacts with the *para* hydroxyl of the DHBP. According to literature (Manasek *et al.* 1976) the main product will be 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone due to the pK values of the phenolic hydroxyl groups in the *para* and *ortho* position. However, in the TLC study presented in *Paper III* it is evident that there is more than one single compound in the sample, even if the melting point is according to literature (Manasek *et al.* 1976 and Kiguchi *et al.* 1998) and the product thus considered pure. This implies that instead of one product there are several, which is of great importance for the subsequent reactions. However, due to lack of further indications of more than one product (*eg.* NMR, FTIR) the amount of impurities is considered to be very small.
Another important point to be made is that during the reaction between HEPBP/epoxy functional vegetable oil and wood/lignin model substance one hydroxyl group is consumed while another one is formed. In theory this means that the next epoxy group can choose to react with such hydroxyl group instead of the hydroxyl group of the wood/lignin model substance and create an oligomer or polymer instead of a new wood/lignin bond. This would in practice mean fewer reactions with the wood/lignin model substance. However, since isolation of the UV absorber and epoxy functional oil between the wood and coating is the goal it is not necessary for all the reactants to be covalently attached to the surface. A similar point can be made from the TLC study performed for Paper III. In this paper results show that the proposed reaction does occur, but also that there is a small amount of what is believed to be polymer in the sample (Figure 18). This assumption is made since this spot on the TLC plate has not moved at all, indicating that this compound is not soluble in the mobile phase, which is likely the case if a polymer was formed.

*Paper III* also comprises a NMR study that further shows that the proposed reaction between HEPBP/epoxy functional oil and lignin model substance in Scheme 4 and 5 occurs. The choice to work with model substances was based on the experience that real lignin grades would be very difficult to interpret when analysed with NMR. The first analyses to be performed were between the reactive UV-absorber HEPBP and the two different lignin model substances. The resulting spectra from the $^1$H-NMR of HEPBP and creosol are given in Figure 10 and show that the proposed reaction, illustrated in Scheme 4, has actually occurred. The spectra clearly show that the hydrogen atoms on the oxirane ring (epoxy), at 2.75, 2.8 and 3.3 ppm, had decreased considerably due to a change in the chemical structure. The same effect can be seen for the peaks originating from the hydrogens on the carbon next to the epoxy group (3.9 and 4.45 ppm), which also
indicates reaction of the epoxy group. The peaks originating from the hydrogens closest to the ether bond on the phenol, at *ca.* 6.5 ppm, were difficult to determine if they have changed or not since they are located in the same area as some of the protons from the creosol. The peaks from the second benzene ring showed no change after reaction, indicating that this part of the HEPBP was unreacted, which is to be expected. It was also noticeable that the hydroxyl group of the creosol (8.7 ppm) had disappeared and that the peaks from the protons adjacent to the hydroxyl proton, at 6.5-6.8 ppm, had changed in position after reaction, all indicating the proposed reaction. The same trends were also seen for the reaction between HEPBP and 4-methyl-2,6-dimethoxyphenol, showing that also this lignin model substance reacts with HEPBP.

Figure 10. $^1$H-NMR spectra of HEPBP, creosol and the product of the two after 8 h reaction.
In the $^1$H-NMR spectra of the product solutions of the epoxy functional oils there are several indications of the proposed reactions, illustrated in Scheme 5. For both of the epoxy functional oils it is apparent that the hydroxyl proton from the lignin model substances, shown at approximately 8.7 or 8.0 ppm for creosol (Figure 11) and 4-methyl-2,6-dimethoxyphenol, respectively, decreased or disappeared after the reaction. This indicated consumption of the hydroxyl group. Methyl protons of creosol at 2.2 ppm and 3.7 ppm respectively both remained in the same position and had the same size after reaction (Figure 11), indicating that these protons have not reacted. It was also noticeable that the protons adjacent to the hydroxyl proton, at 6.5-6.8 ppm, had changed in position after reaction but not in size, which indicated chemical changes in the structure close to these protons. Since the methyl protons, as mentioned, had not changed it once again indicated that the hydroxyl group has reacted and that the proposed reaction had occurred. For 4-methyl-2,6-dimethoxyphenol the $^1$H-NMR showed that all protons in the structure, except for the hydroxyl proton, remained more or less in the same position after reaction. This indicated that the proposed reaction had occurred but to a lesser extent. This is likely due to the higher steric hindrance of the 4-methyl-2,6-dimethoxyphenol in comparison to the creosol.
Results and discussion

Figure 11. $^1$H-NMR spectra of epoxy functional linseed oil, creosol and the product of the two after 8 h reaction.

When studying the spectra in Figure 11 it can also be noticed that the peak from the epoxy group is still present even after reaction. This could be interpreted as a sign that the reaction had not occurred, but pointing out once again that the reactants have been added in a 1:1 molar ratio it becomes clear that the decrease in the epoxy groups of the oil was much less than the decrease of the hydroxyl group of the creosol, since the oil contains more epoxy groups than the creosol does hydroxyl groups. Considering that each soybean oil triglyceride contains four epoxy groups and each linseed oil triglyceride contains five epoxy groups, this would lead to a decrease of the peak by 1/4 or 1/5, respectively, which was difficult to detect.
The reactions in Paper III were also analysed using FTIR to investigate changes in the chemical structure. In the case of linseed oil and creosol a small decrease of the peak representing the epoxy group was actually noticed after the reaction, especially for the peak at 823 cm\(^{-1}\). This was not evident when studying the \(^1\)H-NMR spectra. It indicated a slight consumption of the epoxy group and hence that the proposed reaction had occurred (Figure 12). The same pattern was also seen for soybean oil and HEPBP, showing that creosol seemed to react with both oils and HEPBP as proposed. A change in the peak for the hydroxyl group was also seen but since the reaction both consumed and created a hydroxyl group it was difficult to use this peak as an indication of the reaction. When the more sterically hindered model substance, 4-methyl-2,6-dimethoxyphenol, was used the results indicated a slightly lower consumption of epoxy groups, which was likely a consequence of the lower accessibility of the hydroxyl group of this model substance due to steric hindrance.

![Figure 12. FTIR spectra of creosol, epoxy functional linseed oil and the product of the two, illustrating the decrease in the epoxy peak after reaction.](image)
To understand where in the wood cell structure this proposed reaction occurs, FTIR microscopy was used. The hope was to be able to see if the reaction occurred in the lignin rich areas of wood since lignin, as previously mentioned, reacts most of the three major components of wood (Rowell et al. 1994). Figure 13 shows images performed in the image mode of the carbonyl peak of the sample and the different colours represent the amount of light absorbed in the given wavelength interval (1690-1545 cm\(^{-1}\) for the carbonyl peak from HEPBP). Lighter colour means higher absorbance.

<table>
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<tr>
<th>Photograph</th>
<th>Absorption image</th>
<th>Absorption image - Extracted</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="untreated_extracted.png" alt="Absorption image - Extracted" /></td>
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Figure 13. Images and micrographs performed in the image mode of untreated wood veneers as well as veneers treated using epoxy functional linseed oil, epoxy functional soybean oil and a combination of epoxy functional linseed oil and HEPBP. Note that images for the extracted samples are not from the same sample as its un-extracted counterpart.
The results from analysis performed in image mode (Figure 13) shows very similar results for all samples and it was not possible to determine where in the cell structure the reaction occurs. Even after extraction, the samples still showed areas of fairly high absorption and no direct difference between the samples could be determined. It would appear that the absorption levels were too high in the selected wavelength intervals in order to get reliable results from the instrument. Analysis was hence also performed in the ATR image mode which only allows studies to a depth of a few micrometres instead of the entire thickness of the veneer. These measurements, on the other hand, do not provide the benefit of receiving photographs of the actual surface, to which the absorption image can be referred. Using this mode did, however, result in lower absorption levels, and a difference between treated and untreated samples was noticeable for the carbonyl peak (Figure 14). This suggested that there is an increased amount of carbonyls in the sample containing HEPBP and/or oil, which corresponded well with the hypothesis. Due to the lack of comparative photograph evidence it was difficult to determine where in the cell structure the concentration of HEPBP was the highest.
Results and discussion

Carbonyl peak

Oil peak

Untreated

HEPBP/ Linseed oil

Linseed oil

Figure 14. Micrographs performed in the ATR image mode for untreated wood veneers as well as veneers treated with epoxy functional oil and with a combination of HEPBP and epoxy functional linseed oil.

A possible reason why image mode did not show a difference between treated and untreated samples was that the wood itself contains so many carbonyl groups that when the whole veneer is studied these compete with and diminish the impact of the carbonyls from the HEPBP. If the sample is instead studied using FTIR spectroscopy or the ATR image mode of the FTIR microscopy instrument the depth is much smaller and hence the carbonyls from the HEPBP have greater impact on the results. A similar explanation can be given for the oil, although in this case the FTIR microscope did not manage to separate hydrocarbons from the wood and the oil in any of the two modes. This method is hence considered
Results and discussion

insufficiently detailed for this type of treatment, since it was not possible to determine where in the structure the reaction occurs.

- **Effect of reaction temperature**

Previous studies on the grafting of HEPBP on wood employed acetone as solvent and was performed in pressurised reaction vessels (Kiguchi *et al.* 1998, Westin 2002, Evans *et al.* 2010). These studies indicated that the reaction temperature was of great importance and that there was a strong relationship between the reaction temperature and the weight percent gain (WPG) of the veneers. Hence, by using a higher temperature of 120 °C a significant WPG was achieved (Evans *et al.* 2010). However, the use of acetone in these studies also implies that a high pressure is needed to avoid boiling and thus the temperature effect could also be due to other factors such as cell wall swelling.

For all experiments in this thesis, 3-pentanone was used as a solvent instead of acetone, since this solvent has a higher boiling point (102 °C) and hence allows grafting at ambient pressure at different temperatures. Studying the carbonyl triple peak in the FTIR spectra of reactions performed for *Paper II* and comparing with a non-treated veneer, it was evident that for reactions performed at up to 90 °C there was no change in this peak (Figure 15). However, when grafting at 120 °C is considered, it was possible to see an increase in the carbonyl peak in the FTIR spectra due to the HEPBP, indicating that the reaction did occur. It was hence assumed that at lower temperatures no reaction had occurred and it was thus concluded that a reaction temperature of up to 90 °C was insufficient to obtain any significant reaction. One concern is the homopolymerisation of HEPBP, which would also result in an increase in the carbonyl peak of the veneer, but is unlikely to bind to the wood and hence not provide the protection desired.
However, this homopolymerisation would result in a polymer partially soluble in acetone and would thus be washed away during extraction (Evans et al. 2010). Since the spectrum in Figure 15 showed results for veneers after extraction in an acetone/ethanol solution it indicated that there is HEPBP present on the wood surface.

![FTIR Spectra](image)

**Figure 15.** FTIR spectra of untreated and HEPBP treated veneers after reaction at 120 °C vs. a stepwise reaction at 50, 70 and 90 °C.

*Effect of oil as co-reactant*

When comparing the different reactions using HEPBP and oil, both as combinations and separately, it was possible to see some rather clear differences. Starting on the molecular scale, the FTIR spectra showed an interesting peak at 2900 cm\(^{-1}\) that was likely due to the presence of oil. It probably arose when the oil was attached to the wood surface, introducing new and longer chains of hydrocarbons (-CH-, -CH\(_2\)- and -CH\(_3\)) and hence slightly shifting part of the peak to higher wave numbers. This can be seen when comparing the FTIR spectrum of
the oil- and HEPBP-modified veneer to the untreated one, and also when studying
the analysis of the reaction where only HEPBP was used, as in Figure 16.

![FTIR spectra of untreated veneer as well as veneers treated using either only HEPBP or a combination of epoxy functional soybean oil and HEPBP.](image)

Figure 16. FTIR spectra of untreated veneer as well as veneers treated using either only HEPBP or a combination of epoxy functional soybean oil and HEPBP.

A general experience was also that adding the oil to the system greatly affected
the hydrophobicity of the samples. The veneers and samples treated with oil
seemed less susceptible to water and in combination with the HEPBP they
resulted in a more stable colour change with a fairly rapid increase which evens
out and remains stable (more information in Section Performance after accelerated ageing).

Effect of reaction procedure

The two different reaction procedures used for veneers and wood samples in this
study were described in Section 3.2 and differ only in the way the reactants were
introduced to the wood veneers. The first procedure, used in Paper I
predominantly, involved a considerably longer time of contact between the heated
substance and the veneers, which could allow for more grafting. The second procedure was, however, less time and energy consuming and was therefore more appropriate in any future industrial use.

The difference between the two procedures was analysed in *Paper II* by measuring the weight gains of the veneers before and after reaction. Weight gains were slightly larger for veneers treated with the boil process (average 26 %) in contrast to the dipping process (average 23 %), which was most likely due to the longer reaction time for the boil process and possibly also due to the longer temperature increase. It can also be mentioned that veneers grafted with the boil process had a brownish colour whereas veneers treated with the dip process had a colour similar to natural Scots pine. The brownish colour was probably due to the catalyst in combination with the solvent and the two reactants at the elevated temperature.

- *Performance after accelerated ageing*

In order to determine the actual light stabilising effect of the pretreatment, the veneers were exposed to accelerated ageing in a QUV. Since the first visible sign of wood degradation is colour change (Williams 2005), this was the method of study for following degradation. Hence, the colour changes of veneers in comparison to starting values were measured, giving an indication of the extent of degradation of the wood. Figure 17 shows the results from the colour measurements performed on samples in *Paper I*. The colour change of untreated veneers showed a rapid increase when exposed to UV-radiation. However, when HEPBP was introduced to the veneers the colour change becomes more gradual over the full exposure time and was consistently lower than for the untreated veneers. When both HEPBP and epoxy functional soybean oil were introduced,
clear improvements of the colour change were noted for the higher grafting temperatures (102 °C and 120 °C). Reactions performed at 102 °C showed better result than reactions performed at 120 °C, and as a result the lower of the two temperatures was used for subsequent experiments. As mentioned in earlier sections, reactions performed at 90 °C and lower showed no reaction. This was also reflected in the UV performance, illustrated by the colour change in Figure 17, where these veneers showed similar results as the untreated veneers.

Comparison of the HEPBP grafted veneers with the ESBO- and HEPBP grafted veneers indicated that when both reactants were used, the colour change increased rapidly initially but then stayed at a stable level, whereas when only HEPBP was used, a continuous increase was observed due to a yellow discolouration from the start. Some of the reactions using both ESBO and HEPBP also showed a brown discolouration which will be discussed further later on in this thesis.

Figure 17. Colour measurements of untreated and treated veneers performed for *Paper I* after ca. 270 or ca. 370 h of accelerated ageing.
The TLC study in *Paper III* also included results concerning the effect of UV radiation on the covalent bond produced in the reaction. These results, illustrated in Figure 18, showed that after ageing in a QUV for 16 h the product was still present as well as other substances in the reaction solution applied before ageing. There was, however, one new spot which was most likely a degradation product. After 140 h of UV light, there was considerably more evidence of reactions occurring with several substances observed in the reaction solution. These were believed to be degradation products of the HEPBP and creosol, and the results implied that after a sufficient amount of time the created bond between the wood and the HEPBP/epoxy functional oil broke and other compounds formed. Since the HEPBP and epoxy functional oils, in the scope of this study, will be isolated between the wood and the coating it is believed that the treatment will still have an effect. This is both due to the effect of the UV absorbers in the coating, which will hinder the initial radiation, and also due to the still fairly slow degradation at the interface which will act as another barrier before the radiation reaches the wood.
Figure 18. Images of TLC plates illuminated with UV light to visualise the change in and the movement of the different substances before and after ageing for 16 h or 140 h of accelerated ageing.

Samples presented in Paper IV were exposed to a total of 120 h of accelerated ageing in a Weather-Ometer and were analysed using VPSEM after 0, 30, 60 and
120 h of exposure. Figure 19 illustrates micrographs of the radial surfaces of the untreated control, the sample treated with epoxy functional linseed oil and one using epoxy functional linseed oil together with HEPBP. Studying these micrographs it was apparent that all samples showed indications of degradation already after 30 h of accelerated ageing, resulting in cracks and in some cases, destruction of the cells. When studying the sample treated with epoxy functional linseed oil the degradation was comparable to the untreated control, which was most likely due to the lack of UV absorber in this case. The sample treated with both HEPBP and epoxy functional linseed oil showed a slightly better result with fewer cracks and much less destruction of the cells, indicating less degradation and protection towards photodegradation. This is in coherences with previous studies (Olsson et al. 2012 and Hatae et al. 2012) which both showed improvements of the photo protection of wood using HEPBP as a grafted pretreatment on the surface. The study performed by Olsson et al. (2012) in addition, emphasised the improvement of the protection when using an epoxy functional vegetable oil in combination with the HEPBP. After 120 h of accelerated ageing this conclusion was still valid and the sample pretreated with a combination of HEPBP and epoxy functional linseed oil showed less degradation than the untreated control, which was completely degraded.
Figure 19. VPSEM micrographs of radial surfaces of untreated and HEPBP- and epoxy functional linseed oil treated wood samples before, during and after 120 h of accelerated ageing.

Figure 20 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 showed larger and more visible differences between the untreated and the pretreated sample than the radial surfaces. After 30 h of accelerated ageing the two samples showed slight indications of degradation,
which was shown as a loss of lignin in the middle lamella, and already at this stage the untreated sample showed more degradation than the pretreated sample. In both cases, cracks were formed to a relatively equal extent. After 60 h of accelerated ageing the untreated sample showed even more degradation in the middle lamella, whereas the pretreated sample looked more or less the same as after 30 h of ageing. After 120 h of accelerated ageing the difference between the untreated and the HEPBP/oil treated sample was even more pronounced with severe, almost complete, degradation of the middle lamella for the untreated sample, whereas the combined pretreated sample only showed small indications of degradation. The difference between the treated and untreated samples was believed to be due to actual grafting of the HEPBP, and to some extent perhaps also the epoxy functional oil, which enabled a more long term protection of the substrate. An additional observation was that some of the cells of the pretreated samples appear to be covered. This pattern was not seen for the untreated samples and not in the earlier study by Hatae et al. (2012), and hence it was likely to be an effect of the HEPBP/epoxy functional oil pretreatment. This hypothesis was also strengthened by the indication that the effect seemed to fade over time, which would be the case if the pretreatment was washed away during the accelerated ageing.
Figure 20. VPSEM micrographs of cross sectional surfaces of untreated and HEPBP- and epoxy functional linseed oil treated wood samples before, during and after 120 h of accelerated ageing.
The radial samples were also analysed using FTIR spectroscopy before and after exposure (after 60 h and 120 h) in order to determine if the pretreatment was present on the surface even after exposure. This analysis was not possible for the cross sectional surfaces since parts of these surfaces have been laser ablated, and hence a good connection with the ATR crystal is unattainable due to height differences in the sample. The results are shown in Figure 21, and starting with the presence of oil it was evident that after 60 h of ageing all the pretreated systems still had 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 the result was more or less unchanged, although the two peaks of interest had decreased slightly. This showed that there were still large amounts of oil on the surfaces and that the oils were not totally washed away after 60 or 120 h of accelerated ageing. Studying the carbonyl triple peak of the system containing HEPBP, at approximately 1600 cm\(^{-1}\), it had decreased after 60 h of exposure but was still present. After 120 h of exposure the peak was still approximately the same size and it was therefore believed that this amount was actually covalently attached to the wood substrate. The initial decrease could thus be explained by unreacted reactants on the surface due to absence of extraction after reaction. Combining these results with those from the TLC trial implies that the degradation of the two components occurred in such manner that the hydrocarbons of the oil and the carbonyl of the HEPBP remain uncompromised. This is in coherence with the TLC results, which implied that the degradation was mainly a consequence of the lignin model substance creosol (corresponding to lignin) and not the HEPBP. Another peak of interest is the singlet at 1705 cm\(^{-1}\), which corresponds to the benzene ring stretching in lignin (Evans et al. 2010). Both the untreated and the treated samples showed a decrease of this peak after exposure, which was likely due to photodegradation of the lignin, or possibly the
HEBP. In the case of a combined treatment of HEBP and epoxy functional linseed oil, the decrease was, 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 21. FTIR spectra before, during and after 120 h of accelerated ageing of untreated veneers, as well as veneers treated with epoxy functional linseed oil or a combination of HEBP and epoxy functional linseed oil.


4.2 PERFORMANCE OF PRETREATMENT IN COMBINATION WITH CLEAR COATING

· Performance after accelerated ageing

In Paper II, approximately half of the samples were exposed to accelerated ageing, and after ca. 1400 h of UV exposure, all samples still showed a good appearance and only a slight change in colour. After 4000 h of exposure a visual examination of the samples indicated further degradation. The initial colour changes were mostly evident for samples pretreated with the boil process, which seem to lose some of the brown discolouration as the exposure proceeded. The dip-pretreated samples still showed a light appearance after 1400 h of exposure, indicating little degradation; however, after 4000 h all samples were discoloured.

The reference sample of the coating containing ceria nano particles (Ce-coating) had two severe cracks along the veneer, which was most likely due to crack initiations prior to coating. The two samples showing the lowest total colour change and the least yellowing, and thus the best result as far as colour is concerned, were samples pretreated with the dip process and coated with the acrylic coating containing double amounts of UVA/HALS (Ac-coating) (Figure 22). One of these samples showed signs of moisture uptake in a few spots, however, it was not conclusive that these were due to photodegradation. Among the worst performing were the two non-pretreated references. In general, the samples pretreated using the dip process showed slightly better results. This was most likely due to the initial brown discolouration of the samples pretreated with the boil process. This discolouration was fading in the beginning of the exposure period, hence creating a larger colour change.
Results and discussion

Figure 22. Colour measurements for selected samples in Paper II during accelerated ageing. The figure depicts average colour changes for the two best (green) and the two worst (black/grey) performing samples.

An interesting observation was that apart from the reference sample of the Ce-coating, the adhesion between the samples and the coatings seemed very good. None of the coatings totally delaminated from the substrate even if there was a high degree of pretreatment on the surface and could have caused adhesion problems. The adhesion problems of the Ce-coating reference, was caused by moisture entering the two major cracks in the veneer and coating layers, which were already initiated before the ageing started. This meant that the pretreatment was compatible with the acrylate top coat.

SEM analysis was performed on the wood samples exposed to 1400 h and 4000 h of accelerated ageing and results were compared to samples kept in the conditioning room for the entire trial. Three representative images are given in Figure 23 below and show the cross section of three samples. The solid wood, the
adhesive, the veneer and the coating can all be seen in the image; however, the pretreatment was not possible to detect using these SEM images.

Figure 23. SEM micrographs of samples pretreated with the dip process and coated with the Ac-coating before and after 1400 or 4000 h of accelerated ageing.

Figure 23 showed slight differences between the conditioned sample and the sample exposed to 1400 h of accelerated ageing, but none that can be exclusively correlated to the degradation of the material. No cracks in the veneer or the coating, and no loss in adhesion were noticed; in fact, the adhesion appeared to be
very good. As the degradation of wood starts by discolouration and continues by breaking down the lignin in the middle lamella (Blanchard et al. 2011), an indication of wood degradation can be seen for samples exposed to 4000 h of artificial weathering, where the cells and the lignin in the middle lamella had started to break down. What is also visible in this micrograph is that the coating seems to have degraded, leading to a thin and uneven film. The vertical lines visible in the micrographs arose during the UV-laser preparation of the samples and thus were not due to degradation.

• Performance after natural weathering

Samples presented in Paper II were first exposed to natural weathering for 14 months in Kioloa, Australia (Dec 2011-Feb 2013) and then for 12 months in Stockholm, Sweden (Sep 2013-Sep 2014, unpublished). In general, all the samples showed good appearance after 14 months of exposure with only minor signs of photodegradation after the elapsed time. However, all samples showed certain degrees of surface mould as no fungicide was added to the coatings. After an additional 12 months of exposure further development of the mould growth was visible and the samples were more or less covered with mould (Figure 24). This is described further in a section below. The degradation caused by UV light was difficult to determine at this stage since the mould growth caused cracks and moisture uptake of the samples which obstructed the evaluation.
Results and discussion

Figure 24. Photographs of samples from Paper II or unpublished DCOIT study after natural exposure. The abbreviations LO and LOH stand for epoxy functional linseed oil and epoxy functional linseed oil plus HEPBP, respectively.

A visual assessment was performed after 14 and 26 months of exposure, whereby the general appearance, cracking, blistering and flaking were evaluated, and the results are illustrated in Figure 25. The evaluation of the general appearance showed that all samples had high values close to complete failure. All samples had fairly similar degrees of cracking, arising from the areas attacked by mould. Flaking and blistering results are not shown in the diagram since all samples, apart from one (pretreated with the dip process and coated with the Ce-coating), showed neither flaking nor blistering. Note that the effect of the mould is included in the visual assessment, and since all of the cracks arise from the mould growth the scores represent the mould factor rather than the photostabilisation. A general comment is also that due to this extensive amount of mould the visual assessment was very difficult to perform, and hence the results are not conclusive.
Results and discussion

Figure 25. Visual assessment for samples exposed to natural weathering for 14 and 26 months.

Gloss was also measured for the samples in Paper II. The gloss decreased for all systems after 14 and 26 months of outdoor exposure (Figure 26) and some systems showed greater decrease than others. Among them was the reference sample of the Ac-coating and the samples pretreated using the dip process and the Ac-coating. In general it seemed as if the dip process resulted in a larger decrease than the boil process and that the Ce-coating performed slightly better than the Ac-coating. This indicated that the slightly larger amount of pretreatment on the surface, or the brown discolouration of the surface, improved the gloss performance, and that the ceria nanoparticles had an effect in terms of gloss. It is also interesting that the gloss measurement was highly affected by the
pretreatment already at the initial measurement. The dip-pretreated samples in general showed higher gloss than the references and the boil-pretreated samples.

Figure 26. Gloss of samples for Paper II after 14 and 26 months natural exposure.

In terms of mould growth, all samples in Paper II showed some degree of moulding due to blue stain species. After 14 months of natural exposure, the references and the pretreated samples showed fairly different mould patterns on the macroscopic scale. The references (no presence of UVA or oil) showed mould with larger spots or areas of mould, whereas the pretreated samples showed a more evenly distributed amount, with very small spots of mould. The reason for this is not certain but a possible explanation is that the references contained a higher amount of moisture which enabled the mould to continue growing, hence leading to larger areas of mould. The spots of mould on the pretreated samples, on the other hand, were likely minimised due to the presence of hydrophobising oil in the interface between the veneer and the coating, hence the mould lacked enough moisture to continue growing. Figure 24 illustrates the mould of the panels after 26 months of natural exposure and show that this pattern is to some
Results and discussion

extent still valid. The two references still have larger spots of mould than the pretreated samples, and it also appears as if the samples treated with the Ce-coating have larger spots of mould than the Ac-coated samples. The amount of mould on the samples had increased considerably and noteworthy is that the worst performing sample was still the untreated sample with the Ac-coating, which was more or less completely destroyed.

By studying micrographs taken after 14 months of exposure it appeared as if all the samples were fairly similar. However, when studying the micrographs taken after 26 months (Figure 27) a general impression was that the samples pretreated with the boil process seemed to have higher mould density than the dip-pretreated samples. When looking at the samples in the microscope, the boil-pretreated samples had fewer areas in which no mould is visible compared to the dip-pretreated samples. The boil-pretreated samples also showed a different pattern of mould with larger spots than the dip treated samples. All samples showed a fair amount of mould after 26 months of exposure, which was also to be expected since the coating contained no fungicide. In terms of mould, the untreated sample with the Ac-coating seemed to perform the worst and the dip-pretreated samples appeared to perform the best.
Results and discussion

<table>
<thead>
<tr>
<th>Treatment</th>
<th>14 months exposure</th>
<th>26 months exposure</th>
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<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>Dip Ac.</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>Boil Ac.</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>Ref. Ce.</td>
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In a small unpublished study the same treatments were tested together with a thin layer of fungicide before the coating was applied. The hypothesis was that the addition of a fungicide, in this case DCOIT, as a pre-treatment would slow down the migration of the fungicide to the surface and hinder leaching, which in turn would result in a more long term protection against mould and UV light. In general it appeared as if the untreated samples all had cracks and moisture uptake under smaller areas of the coating and/or veneer, whereas only one of the pretreated samples showed a small crack in the veneer and coating (one sample with linseed oil without DCOIT). The pretreated samples hence appeared to be intact without any major indications of photo-initiated degradation. After visual inspection all samples showed a certain degree of mould and the sample pretreated with a combination of oil and HEPBP showed slightly less mould (Figure 24). However, visually the difference was not major and could be
Results and discussion

Circumstantial, but since this pattern was also seen in the micrographs of some typical areas in each sample (Figure 28) the difference is believed to be valid. The difference between the samples using DCOIT and the samples without was, on the other hand not that visible. A possible explanation of this was that keeping the fungicide in the interface between the wood and the coating was likely to result in a more long term protection where the substrate would first be protected by a fungicide incorporated in the coating and then by the fungicide in the interface. In this trial fungicide was only added to the interface in order to get faster results, but mostly to exclude any effects from a fungicide in the coating. The results thus imply that a longer exposure trial was needed in order to notice any major effects of using DCOIT as a fungicide in the interface between the wood and coating.
Figure 28. Micrographs taken using the optical microscope, illustrating the difference in mould growth between untreated and treated samples with and without the fungicide DCOIT.
5. CONCLUDING REMARKS

The hypothesis of this thesis was that using a combination of a reactive UV absorber and an epoxy functional vegetable oil on exterior wood products could improve the photostability of wood and hence prolong the service life of such products. Initial studies showed that using a pretreatment of HEPBP and epoxy functional soybean oil on wood veneers resulted in increased colour stability and hence improved photo protection of wood. Analysis using FTIR also indicated that the reactants are attached to the surface and that leaching could be decreased.

The effect of the pretreatment procedure, and the performance of the pretreatment in combination with a clear top coat were then illustrated. Using a dip process instead of a 16 h reaction shows lower weight gains, but the performance was not significantly lower and hence the dip process is considered a more feasible alternative. Accelerated ageing shows that after 4000 h degradation is visible but to a lesser extent for the pretreated samples. After natural weathering for 14 months all samples show mould growth due to lack of fungicide. Another 12 months of exposure results in further mould growth, which obstructs the evaluation. Hence, no conclusions of the photo induced degradation can be drawn at this stage.

A smaller study also incorporated a fungicide to the pretreatment system. After five months of natural exposure pretreated samples show better performance than
All samples show mould on the surface, although the sample pretreated with HEPBP and epoxy functional linseed oil show slightly less mould. No differences between samples with and without fungicide are evident. However, this treatment is rather believed to have a long term than short term effect and hence a longer exposure trial is needed in order to draw any conclusions.

The decrease in photo induced degradation for pretreated samples using VPSEM before and after accelerated ageing was also studied. The results show that samples pretreated with HEPBP and epoxy functional vegetable oil has less degradation after 120 h of ageing and that destruction of the middle lamella occurred to a considerably lower extent than for untreated samples.

Studying the ability of the epoxy functional vegetable oils and HEPBP to react with hydroxyl groups of lignin was then performed using lignin model compounds. Analysis using $^1$H-NMR, ATR-FTIR and TLC shows that the reaction occurs for the oils and the HEPBP with the soft wood imitating lignin model compound creosol, but to a lesser extent with the hardwood imitating model substance, 4-methyl-2,6-dimethoxyphenol. TLC further show that the resulting product is disintegrated upon UV exposure, and FTIR microscopy illustrates presence of HEPBP on the pretreated surface but was unable to show the location of the reaction in the wood cell structure.

Gathering all information from the papers incorporated in this thesis, this research has shown that pretreating the substrate with the reactive UV absorber HEPBP and epoxy functional vegetable oils results in an improved photo stabilising effect of wood, which in turn could result in a more long term protection against photo induced degradation.
6. FUTURE WORK

To achieve better knowledge of how this system works the author has some suggestions for future work. Firstly, to understand the true effect of the oil in this system it would be of interest to continue investigating how the oil behaves together with the wood, and also in combination with the UV absorber. An interesting aspect would be to broaden the research to look at other properties, apart from UV protection, that could influence the wood in an advantageous way. Since the system described in this thesis is developed for Swedish products, both production and utilisation, one aim is to use products from the Swedish agriculture in the production. A wish is hence to use the most commonly produced oil in Sweden, rapeseed oil, instead of linseed or soybean oil. The drawback of the rapeseed oil is, however, its few unsaturations in the fatty acid chains, which obstructs the epoxidation and also leads to fewer reaction sites for the proposed reaction with wood. Rapeseed oil is, however, versatile and can be refined to possess certain properties, by for example varying the composition of fatty acids in the triglyceride, which would enable more unsaturations. Hence, using rapeseed oil in the suggested pretreatment could be an alternative which would benefit both the Swedish agricultural industry and hopefully also the described treatment.

To gain more understanding of how the system is affected by the addition of a fungicide in the interface between the wood and the coating, a continuation of the
exposure test is recommended. Since the effect of a fungicide in the interface is believed to function after the fungicide incorporated in the coating is consumed or leached out, a longer exposure trial would be beneficial. It would also be of interest to test a system in which a fungicide is added both in the pretreatment and in the coating, and then perform natural exposure test to see the full potential of the system.
# 7. NOTATIONS

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
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<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>BP</td>
<td>Benzophenone</td>
</tr>
<tr>
<td>BTZ</td>
<td>2-(2-hydroxy-phenyl)-benzotriazole</td>
</tr>
<tr>
<td>CCA</td>
<td>Chromated Copper Arsenate</td>
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<tr>
<td>CeO₂</td>
<td>Cerium Dioxide</td>
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<td>4,5-dichloro-2-octyl-4-isothiazolin-3-one</td>
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<td>2,4-dihydroxy-benzophenone</td>
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<tr>
<td>ELSO</td>
<td>Epoxy Functional Linseed Oil</td>
</tr>
<tr>
<td>ESBO</td>
<td>Epoxy Functional Soybean Oil</td>
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<tr>
<td>FTIR</td>
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<td>HALS</td>
<td>Hindered Amine Light Stabiliser</td>
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<td>2-hydroxy-4(2,3-epoxypropoxy)-benzophenone</td>
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<td>ZnO</td>
<td>Zinc Oxide</td>
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