

Abstract

Plasma treatment is a novel and promising technology in the field of wood surface modification. Deposition of micro-particles on wood surfaces by means of plasma is an interesting approach to enhance wood properties and thus, to extend the service life of wood products. On the other hand, several silicone formulations have been already shown to cause excellent water repellence and interaction with cell wall components, besides to impart high chemical and weathering stability as well as biological resistance in treated wood. Based on that, this study focussed on both treatments separately in an initial stage of the research; followed by the combination, in a two-step treatment, of vacuum-pressure impregnation of solid wood with siloxanes and additional copper deposition on wood surface using atmospheric pressure plasma.

At the first phase of the study, amino-functional siloxane emulsions with different chain lengths were vacuum-pressure impregnated into Scots pine (*Pinus sylvestris* L.) sapwood and subsequently cured to assess their potential in protecting wood from termite attack. Half of the number of the wood specimens was subjected to a leaching procedure according to EN 84 (1997). Although in a no-choice test none of the formulations imparted resistance in wood according to EN 117 (2012) and 350 (2013), it was found a significant reduction in mass loss compared to untreated wood. In a choice test situation, however, termites exhibited significant avoidance towards siloxane-treated wood and revealed effectiveness of the treatment under this feeding situation. The mode of action might be associated with the presence of the amino groups.

In the second part of the study, thin layer of copper micro-particles were deposited on wood micro-veneers via atmospheric air plasma. Micro-veneers were exposed to artificial weathering in a QUV weathering tester following the standard EN 927-6 (2006). Tensile strength was determined at zero-span (z-strength) and finite-span (f-strength) under dry conditions (20°C, 65% RH). Enhanced z-strength of treated micro-veneers during artificial weathering in a QUV indicated a photo-protective effect of the treatment. F-span strength was also improved by the



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treatment, but to a lesser extent. FT-IR spectra, however, revealed that copper-plasma treatment did not protect lignin in wood from photo-degradation. Therefore, these findings indicated that copper-plasma treatment only caused photo-stabilisation of polysaccharides. Further investigations were also implemented with aluminium deposition on solid wood via plasma treatment. Additional wood boards were topcoated with an acrylic binder. Copper- and aluminium-plasma treated boards were exposed to natural weathering for 18 months following the standard EN 927-3 (2012). Copper-plasma at highest loading was found to improve the general appearance of wood surfaces. When wood was additionally topcoated with acrylic binder, the treatment was also found to prevent fungal discolouration. Although infrared spectroscopy confirmed lignin and hemicelluloses breakdown and thus, degradation products available as nutrients for fungal growth, copper coating reduced fungal infestation and blue stain hyphae could not penetrate through the treated surface at highest loading of copper. In contrast, none of the aluminium-plasma treated wood boards without topcoating could resist the weathering conditions.

In the third part of the study, siloxane treatment was combined with copper-plasma deposition on wood surface in a two-step treatment. Short-chain siloxane-treatment alone did not impart resistance to blue stain, while copper-plasma was found to reduce fungal growth compared to untreated wood. The two-step treatment resulted in high blue stain resistance and, moreover, the hyphae were unable to penetrate the wood. Although all the specimens were severely attacked by termites in a no-choice test, differences in termite mortalities were found between treated and untreated wood. In contrast, at choice of feeding, the two-step treated-wood resulted in high resistance to termite attack. The improved resistance to termites when there is a choice of feeding and to blue stain might be attributable to the combination of short-chain siloxane and amino groups, and the additional deposition of copper that resulted in the formation of copper-amino complexes to promote fixation in wood.

Zusammenfassung

Die Plasmabehandlung ist eine neue und vielversprechende Technologie im Bereich der Modifikation von Holzoberflächen. Ein Auftragen von Mikropartikeln auf Holzoberflächen durch Plasma ist ein interessanter Ansatz, um Holzeigenschaften so zu verbessern, dass die Lebensdauer von Holzprodukten verlängert wird. Darüber hinaus haben bereits einige Silikonrezepturen eine ausgezeichnete wasserabweisende Wirkung und Interaktion mit Zellwandbestandteilen gezeigt und dem behandelten Holz sowohl eine hohe chemische- und Witterungsbeständigkeit, als auch eine biologische Resistenz verliehen. Darauf basierend richtete sich diese Studie anfänglich auf die Untersuchungen beider Verfahren getrennt voneinander. Anschließend wurden beide Verfahren kombiniert: in einer 2-stufigen Behandlung wird Massivholz zunächst unter Vakuum mit Siloxanen imprägniert und dann die Holzoberfläche unter Verwendung von Atmosphärendruckplasma mit Kupferpartikeln beaufschlagt.

Im ersten Teil der Studie wurde Kiefern-Splintholz (*Pinus sylvestris* L.) mit Aminofunktionellen Siloxanemulsionen mit unterschiedlichen Kettenlängen vakuum-imprägniert und anschließend getrocknet, um dessen Potential zum Schutz von Holz gegen Termitenbefall zu bewerten. Die Hälfte der Holzproben wurden einer Auswaschung gemäß EN 84 (1997) unterzogen. Obwohl in einer Versuchsanordnung „ohne Auswahl des Substrats“ keines der Präparate dem Holz eine Dauerhaftigkeit gemäß EN 117 (2012) und 350 (2013) verlieh, konnte eine signifikante Reduzierung des Masseverlusts im Vergleich zum unbehandelten Holz beobachtet werden. In einer Versuchssituation „mit Auswahl des Substrats“ zeigten Termiten dagegen eine signifikante Vermeidung des mit Siloxanen behandelten Holzes, welches die Effektivität der Behandlung in dieser „Auswahlsituation“ verdeutlichte. Diese Wirkungsweise könnte mit der Anwesenheit von Aminogruppen zusammenhängen.

Im zweiten Teil der Studie wurde eine dünne Schicht von Kupfer-Mikropartikeln durch atmosphärisches Luftplasma auf Mikrofurnierholz aufgetragen. Das

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Mikrofurnier wurde einer künstlichen Bewitterung in einem QUV Bewitterungssimulator gemäß dem Standard EN 927-6 (2006) ausgesetzt. Die Zugfestigkeit wurde bei Zero-Span (z-Festigkeit) und Finite-Span (f-Festigkeit) unter trockenen Bedingungen (20°C, 65% relative Luftfeuchtigkeit) bestimmt. Die verbesserte z-Festigkeit von behandeltem Mikrofurnier während der künstlichen Bewitterung in einem QUV deutete auf einen Lichtschutzeffekt der Behandlung hin. Die f-Festigkeit wurde ebenfalls verbessert, allerdings in einem geringeren Maße. FT-IR-Spektren zeigten jedoch, dass eine Kupfer-Plasmabehandlung das Lignin im Holz nicht vor einer Photodegradation schützt. Diese Ergebnisse wiesen daher darauf hin, dass eine Kupfer-Plasmabehandlung nur eine Photostabilisierung von Polysacchariden bewirkt. Weitere Untersuchungen wurden auch mit einer Aluminiumbeaufschlagung auf Massivholz durch Plasmabehandlung durchgeführt. Weitere Holzproben wurden mit einer Acrylbeschichtung gestrichen. Die mit Kupfer- und Aluminiumplasma behandelten Proben wurden für 18 Monate einer natürlichen Bewitterung gemäß dem Standard EN 927-3 (2012) ausgesetzt. Es wurde beobachtet, dass Kupferplasma, bei der höchsten Konzentration und wenn mit einer Acrylbeschichtung gestrichen, nicht nur das Aussehen der Holzoberfläche verbesserte, sondern auch Pilzverfärbungen verhinderte. Obwohl die Infrarotspektroskopie den Abbau von Lignin und Hemicellulosen, und damit Abbauprodukte, die für das Pilzwachstum als Nährstoffe zur Verfügung stehen, bestätigte, reduzierte die Kupferschicht den Pilzbefall. Dabei können die Hyphen von Bläuepilzen die behandelte Oberfläche bei der höchsten Konzentration von Kupfer nicht durchdringen. Im Gegensatz dazu konnte keine der mit Aluminiumplasma behandelten Holzproben ohne Beschichtung den Witterungsbedingungen standhalten.

Im dritten Teil der Studie wurde eine Siloxanbehandlung mit einer Plasmabeaufschlagung mit Kupferpartikeln auf der Holzoberfläche in einer zweistufigen Behandlung kombiniert. Eine Behandlung mit kurzkettigen Siloxanen allein bewirkte keine Beständigkeit gegen Bläue, während Kupferplasma das Pilzwachstum im Vergleich zu unbehandelten Holz reduzierte. Die zweistufige Behandlung führte zu einer hohen Beständigkeit gegen Bläuebefall und darüber



hinaus waren die Hyphen nicht in der Lage, in das Holz einzudringen. Obwohl in einem Test „ohne Auswahl des Substrats“ alle Proben stark von Termiten angegriffen wurden, konnten Unterschiede in der Mortalität der Termiten zwischen behandeltem und unbehandeltem Holz gefunden werden. Im Gegensatz dazu wies in einer Versuchsanordnung „mit Auswahl des Substrats“ das zweistufig behandelte Holz eine hohe Resistenz gegen Termitenbefall auf. Die erhöhte Widerstandsfähigkeit gegen Termiten („mit Auswahl des Substrats“) und Bläue könnte auf die Kombination von kurzkettigen Siloxan- und Aminogruppen, sowie der Beaufschlagung von Kupfer zurückzuführen sein, was zu einer Bildung von Kupfer-Amino-Komplexen zur Erhöhung der Fixierung im Holz führte.





1. Introduction

Wood has been widely used by mankind since before recorded history. Wood is by far the principal forest product, but not all the forests are focussed on wood production. Approximately two thirds of annual EU wood growth is used in wood, energy and paper industries (Eurostat, 2011). Nevertheless, global production of all major wood products has been gradually recovering in the last five years, and nowadays is showing its largest growth since the global economic downturn of 2008-2009. The total apparent consumption of industrial roundwood (which does not include woodfuel) in the UNECE region reached 1.06 billion m³ in 2014 (UNECE/FAO, 2015). Overall, the consumption of timber continues to rise, and new forecasts predict continued demands for wood products. Due to concerns that the supply of timber for industry may not be able to match demand, the price of raw material is predicted to increase. Consequently this requires the implementation of technologies to promote the more efficient use of the resource by, for instance, extending the life of wood products.

Naturally grown wood has some excellent properties such as high strength with low weight, warm appearance and colour. However, there are certain drawbacks that restrict its use as high performance material. For instance, wood is an anisotropic material that shrinks and swells depending on the moisture content (Glass and Zelinka, 2010). When wood is exposed to outdoor conditions, it undergoes photodegradation caused by UV-radiation (Feist and Hon, 1984). Furthermore, because of its biodegradability, wood is susceptible (under certain conditions) to damage by biological organisms like fungi, insects, bacteria and marine borers (Clausen, 2010). The degradation of wood by any biological or physical agent modifies some of its organic components, which are primarily polysaccharides and polyphenolics: cellulose, hemicelluloses, and lignin (Feist and Hon, 1984).

1.1. Chemical composition of wood

Wood is a very complex material and its structure can be examined at different levels (Fig. 1). In chemical terms, wood is defined as a three-dimensional

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biopolymer composite comprising an interconnected network of cellulose, hemicelluloses, and lignin with minor amounts of extractives and inorganics (Rowell et al., 2012).

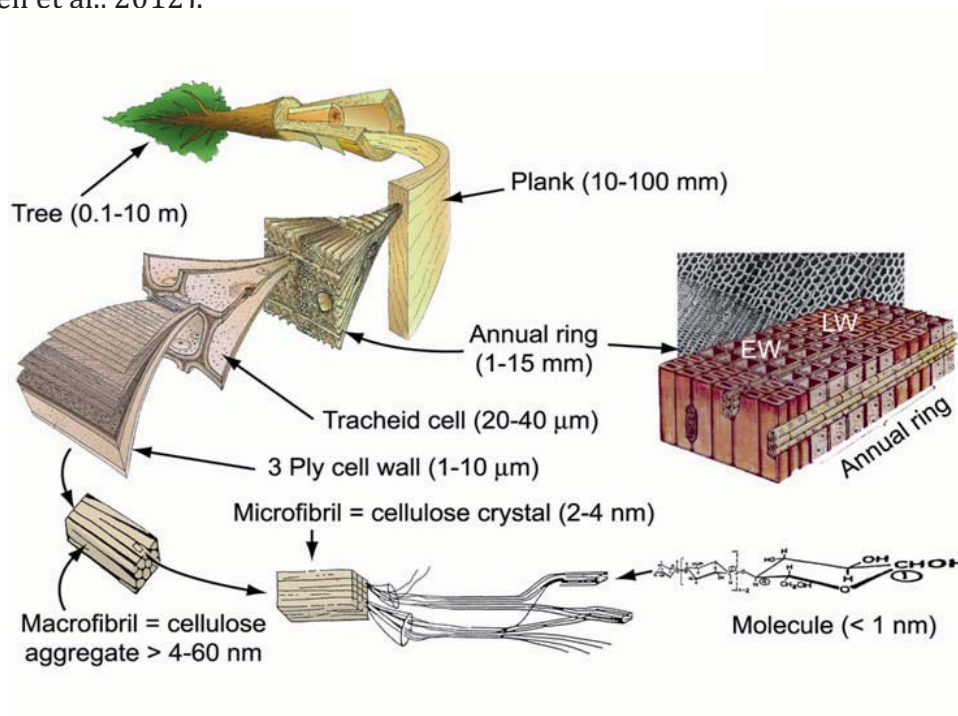


Fig. 1. Complexity of softwood structure (adapted from Harrington, 2002; Militz and Lande, 2009).

1.1.1. Cellulose

Cellulose is the most abundant organic polymer on Earth (Klemm et al., 2005). In wood, the cellulose content ranges from 40% to 50% (Fengel and Wegener, 1989). Cellulose is a linear polymer of $\beta(1\rightarrow4)$ linked D-glucose units (Crawford, 1981). The degree of polymerisation (DP) is usually defined as the number of glucose units in a cellulose molecule. Goring and Timell (1962) reported that wood cellulose has an average DP of at least 9,000–10,000 and possibly as high as 15,000. There are different kinds of cellulose in wood: crystalline and non-crystalline, and accessible and non-accessible. The crystalline regions are formed when the cellulose chains that comprise the microfibril are close enough to form aggregated bundles via hydrogen bonds, creating a regularly patterned structure (O'Sullivan, 1997). These crystalline regions give important mechanical properties to the cellulose fibers (Börjesson and Westman, 2015), and are the primary reinforcing elements in the cell wall (Fengel and Wegener, 1989). Most of cellulose



in wood is crystalline (60-70%), while amorphous cellulose is found to a lesser extent (30-40%) (Salmen and Olsson, 1998; Neagu et al., 2006). Accessible and non-accessible refer to the availability of the cellulose to water, microorganisms, etc. The surfaces of crystalline cellulose are accessible but the rest of the crystalline cellulose is non-accessible. Most of the non-crystalline cellulose is accessible but part of the non-crystalline cellulose, which is surrounded by both hemicelluloses and lignin, becomes non-accessible (Rowell et al., 2012).

1.1.2. Hemicelluloses

Like cellulose, hemicelluloses are polysaccharides, but contain many different sugar monomers: D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, D-glucopyranosyluronic acid, and D-galactopyranosyluronic acid with minor amounts of other sugars (Rowell et al., 2012). The DP of hemicelluloses vary from 200 to 300, and they are usually less ordered than cellulose, although some can form crystalline units (Savage, 2003). Due to the generally amorphous nature of the hemicelluloses, they contain the greatest proportion of the accessible OH content of the cell wall, react more readily, and are less thermally stable than cellulose or lignin (Hill, 2006). Koshijima and Watanabe (2003) reported that the hemicelluloses form hydrogen bonds with the surface of the microfibrils and covalent linkages with the lignin matrix.

1.1.3. Lignin

Lignin is a highly amorphous aromatic polymer composed of phenylpropane units. It constitutes approximately 30% of the wood weight. The three-dimensional polymer is made up of C-O-C and C-C linkages (Rowell et al., 2012). Lignins are usually classified according to their structural elements (Sjöström 1981). Wood lignins consist mainly of three basic building blocks of guaiacyl, syringyl, and *p*-hydroxyphenyl moieties, but other aromatic units also exist in many different types of wood species. Since it is based on aromatic rings, lignin limits the penetration of water into the wood cells (Alder, 1977; Fengel and Wegener, 1989;



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Sjöström, 1981). Lignin provides stiffness to the cell wall and acts as bond in the middle lamella region (Zabel and Morrell, 1992).

1.1.4. Extractives

As the term implies, extractives are mostly low-molecular weight compounds that are readily extracted from the wood using solvents. These compounds are found in parenchyma cells and in the lumen in amounts ranging from 1 to 5% of the total weight. Depending on the wood species, and in exceptional cases, extractives may represent 10-40% of the wood weight (Zabel and Morrell, 1992). The extractives are a group of cell wall chemicals mainly comprising fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and many other minor organic compounds (Rowell et al., 2012). Secondary extractives are mainly located in heartwood, and are responsible for the colour, smell, and durability of the wood (Kai, 1991).

1.1.5. Inorganics

Generally, the inorganic or mineral content of the wood refers to its ash content. Although some tropical hardwoods contain high levels of silica, which may improve the resistance to marine borers, in temperate zones species the inorganic content of wood is low and rarely exceeds 0.5% (Browning, 1967). The inorganic material is composed of a wide variety of elements that are essential for wood growth. The elements present are calcium, potassium, magnesium, manganese, sodium, phosphorus, and chlorine, among trace of other elements in low concentrations (Young and Guinn, 1966). Several minerals play significant direct or indirect roles in the development of decay and wood defects (Zabel and Morrell, 1992).

1.2. Distribution of the chemical components in the cell wall

Cell walls in wood impart the majority of the wood properties (Wiedenhoef, 2012). While the lumen is void, the cell wall is multilayered and consists of three main regions: the middle lamella, the primary wall, and the secondary wall (divided in outer S_1 , middle S_2 , and inner S_3). In each region, the cell wall has three

major components: cellulose microfibrils (with characteristic distributions and organisation), hemicelluloses, and a matrix or encrusting material, typically pectin in primary walls and lignin in secondary walls (Panshin and de Zeeuw, 1980).

The chemical components across the cell wall are depicted in Figure 2. The content of cell wall components depends principally on the tree species and the part of the tree from which the sample is taken. Saka (2000) reported on the contents of the cell wall components of Scots pine. The middle lamella and primary wall consist mainly of lignin (80%) with lesser amounts of hemicelluloses (13%) and even less cellulose (6.7%). The S_1 layer is composed of 51.7% lignin, 30.0% cellulose, and 18.3% hemicelluloses. The S_2 layer is composed of 15.1% lignin, 54.3% cellulose, and 30.6% hemicelluloses. The S_3 layer has little or no lignin, 13% cellulose, and 87% hemicelluloses. Although the main component in the middle lamella is lignin, this region can contain at most 40% of the total of the lignin in wood due to its small volumen fraction of wood (Berlyn and Mark, 1965). In addition to this, several studies reported that the secondary wall lignin of softwoods contains twice as many phenolic groups as the middle lamella (Yang and Goring, 1978; Yang and Goring, 1980; Whiting and Goring, 1982). This can be explained because the S_2 is much thicker layer as compared to the middle lamella and primary wall (Rowell et al., 2012).

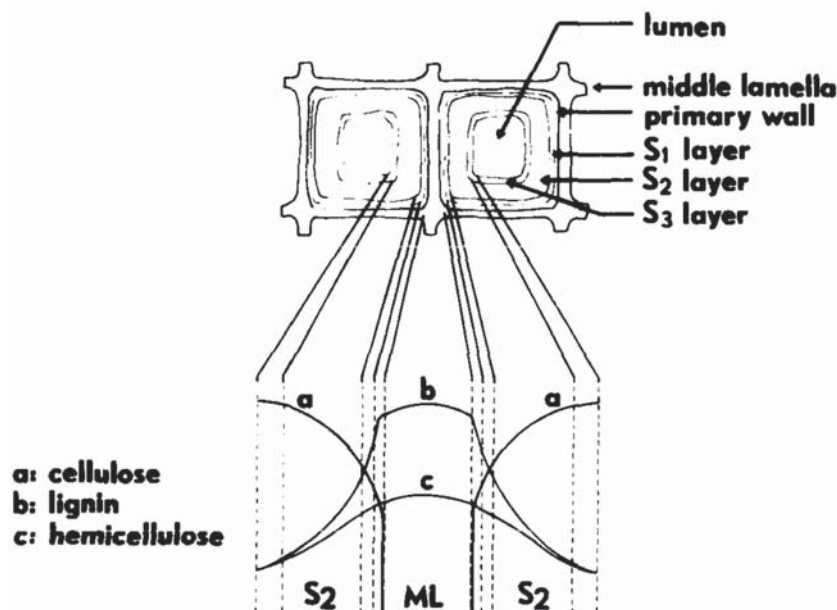


Fig. 2. Chemical components across the cell wall (Feist and Hon, 1984).



1.3. Weathering properties

The increasing trend towards the use of wood for exterior applications has been accompanied by the growth of the wood products industry. Unfortunately, the difficult outdoor conditions are adverse to wood stability (Feist, 1982). When wood is exposed outdoors without any protection, it is susceptible to a relatively fast environmental deterioration (Evans et al., 1996). This has focussed the attention to the importance of weathering and light-induced chemical reactions, which define the usefulness of wood products (Hon, 2001). In this way, by enhancing the resistance of wood to weathering deterioration and increase its durability, it is possible to extend the service life of wood products.

The term weathering involves the degradation of wood exposed above ground that is initiated by ultraviolet (UV) radiation in sunlight (Williams, 2001). The rate of degradation is increased due to the leaching of products by rain water, but other factors such as moisture, heat, abrasion by windblown particulates, atmospheric pollution, oxygen and human activities also contribute to degradation of wood surfaces (Williams, 2005). The effect of acids (acid rain) on wood weathering has also been studied (Williams, 1987; Williams, 1988). The wood surface exposed outdoors undergoes complex physico-chemical changes which will mainly result in a loss of original colour, defibration and greying (Derbyshire and Miller, 1981). Weathering is primarily a surface phenomenon that results in the slow erosion of wood fibers from the surface (Williams, 2001). Although the erosion rate is a variable that depends on the anatomy of wood, grain angle, density, and angle of exposure, it ranges generally between 3 to 12 mm/century (Browne, 1960; Feist and Mraz, 1978; Williams, 2005).

As previously mentioned, the weathering process affects only the wood surface because the penetration of UV light is not deeper than 200 μm (Kataoka and Kiguchi, 2001). Hon and Ifju (1978) reported that UV light cannot penetrate deeper than 75 μm , whereas visible light, on the other hand, penetrates up to 200 μm into wood surfaces. They concluded that chromophor formation in wood exposed to light is due to the direct light effects only to a depth of 200 μm . Many studies differ in the depth of degradation, but they can be reconciled by



considering some other factors that affect the penetration of UV radiation into wood, like wood density and wavelength distribution of the UV radiation and visible light. The wood density would be different depending on the species and the amount of earlywood and latewood. For instance, denser wood is penetrated less by UV radiation, and shorter wavelengths also penetrate less (Williams, 2005).

Terrestrial UV radiation (at wavelengths between 295 and 400 nm) has enough energy to cause bond dissociation of lignin moieties having α -carbonyl, biphenyl, or ring-conjugated double bond structures. The UV-degradation process is initiated by the absorption of a UV photon resulting in the formation of a free radical (Feist and Hon, 1984; Hon and Chang, 1984). After free radical formation, and through the action of water and oxygen, hydroperoxides can be formed (Hon and Feist, 1992). Additional reactions result in the formation of carbonyl groups (Hon, 1981). This initiates a series of chain scission reactions to degrade the polymeric constituents of wood (Feist and Hon, 1984; Williams, 2005). The reactive groups available in lignin (ethers of various types, primary and secondary hydroxyl groups, carbonyl groups, and carboxyl groups) make it an excellent light absorber (Feist and Hon, 1984). That is why lignin appears to be photo-degraded more rapidly than the other wood components (Kalnins, 1984). Lignin absorbs 80-90% of the UV radiation, followed by holocellulose (5-20%) and extractives (2%) (Norrström, 1969). Besides lignin degradation, depolymerisation of cellulose and degradation of hemicelluloses take place as well (Evans et al., 1996). Later on, the rainwater washes out the photo-degraded fragments from wood surfaces (Hon, 2001). After leaching of fragments, subjacent cell layers are exposed and further eroded (Feist, 1982).

Exposure to artificial UV light causes wood bleaching, because of remaining cellulose at the surface. In contrast, natural weathered wood surfaces display a final grey hue due to growth of staining fungi on the wood surface (Feist, 1990). These fungi are able to metabolise photo-degraded products (Eaton and Hale, 1993; Schoeman and Dickinson, 1997). The most frequently observed species on weathered wood is *Aureobasidium pullulans* (Feist, 1983; Feist, 1990).