

Structural Changes in Wood under Artificial UV Light Irradiation Determined by FTIR Spectroscopy and Color Measurements – A Brief Review

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UV weathering, a process initiated primarily by the ultraviolet portion of the solar spectrum, causes surface degradation of wood. Additionally, the wetting and drying of wood through precipitation, diurnal and seasonal changes in relative humidity, abrasion by air particulates, temperature changes, atmospheric pollution, oxygen, and human activities, all contribute to the degradation of wood surfaces. Photo-oxidation or photo-chemical degradation affects only the wood surface, starting immediately after exposure to sunlight. Understanding the chemistry of UV degradation of wood requires knowledge of the chemical nature of wood components, the UV spectrum, and the interactions of UV radiation with various chemical structures in wood. Chemical changes can be evidenced by FTIR spectroscopy. Previous study has shown that wood chemical modification with succinic anhydride makes it slightly more stable to the artificial light action than non-modified wood, which might be due to a slight increase in lignin stability to the polychromatic light action. Analysis of color changes on coated wood surfaces for modified wood treated with epoxidized soybean oil (ESO) has shown that lightness (ΔL^*) decreases, whereas a^* , b^* , and ΔE^* increase with increasing irradiation time.

Keywords: Wood; Chemical modification; Coating; UV irradiation; FT-IR spectroscopy; Color changes

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WOOD PHOTODEGRADATION PROCESS

Photo-degradation in wood caused by solar radiation is a complicated process. The intensity and wavelength of the solar radiation depends on a number of uncontrolled parameters. In addition, these parameters are changing not only throughout the year but even throughout the day. This is why artificial light sources are often used to clarify the mechanism of wood photo-degradation. Some of these light sources can imitate the contents of solar radiation, while others emit only a part (or some parts) of the spectra emitted by the sun. UV radiation represents only 4.6% of the solar spectrum, but it causes the most significant damage to polymeric materials. The complete solar UV spectrum ranges between 280 and 400 nm, but the most aggressive part is the UVB range with very short wavelengths between 280 and 315 nm (Fig. 1). Due to a need for more rapid evaluation of the resistance of materials to outdoor weathering, devices with artificial light sources are generally used to accelerate the degradation. These sources include filtered long arc xenon, fluorescent, metal halide lamps, and carbon arc lamps. Less commonly used sources include mercury vapor and tungsten lamps. These laboratory-accelerated weathering tests are more appropriately referred to as “artificial weathering”.

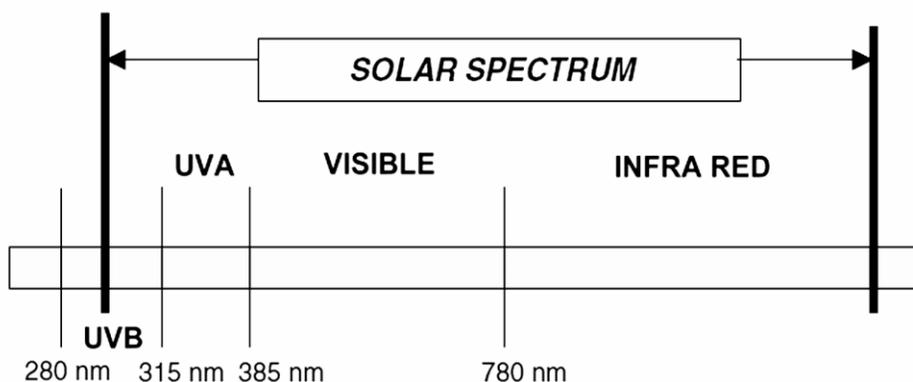


Fig. 1. Components of the solar spectrum

The study of UV photo-degradation of wood began some decades ago (Kalnins 1966; Hon and Chang 1984). Such investigation typically has two steps: first irradiation of the wood's surface by a UV-containing light beam and then detecting the changes caused by the radiation. Besides natural environmental weathering, several test methods have been developed using artificial light sources to provide accelerated test procedures. All methods are based on the regular observation of characteristics reflecting an ageing process such as mechanical properties and optical characteristics (crack formation, changes in color and gloss). Natural weathering tests provide the most accurate and reproducible data; however, their duration can be very long, which frequently instead favors the selection of an artificial weathering method.

Artificial weathering methods are useful tools for studying the durability of unfinished and finished wood products that will be used outdoors. Such weathering tests can accelerate the effects of natural weathering from 5 to 20 times depending on the exposure conditions chosen. The tests are valuable tools since the conditions can be controlled and reproduced. Because all the modes of natural weathering degradation cannot be simulated collectively (such as degradation by UV light, wetting by liquid water, and discoloration by mold and stain fungi), accelerated tests generally focus on the effects of UV light, moisture, and temperature.

Neither in a natural environment, nor with traditional UV lamp (xenon and mercury vapor lamps) experiments, is there a precise way to measure the energy of radiation on the wood sample's surface. In addition, UV photo-degradation is influenced by other factors (moisture, temperature, visible light, and infrared radiation) that are difficult to exclude. Using UV-laser instead of traditional lamps during irradiation could solve all of the above-mentioned problems. By using lasers as radiation sources (Barta *et al.* 2005; Papp *et al.* 2005) the duration of the treatment can be shortened, the wavelength of the radiation is known, the energy can be determined, and the intensity of the radiation at the surface also can be determined.

Weathering chambers have been developed to provide a QUV® (registered trademark of Q-Lab Corporation, USA) weathering testing environment (ASTM G154). The QUV® simulates the effect of sunlight with fluorescent ultraviolet (UV) lamps, while rain and dew are simulated by the condensation of humid air. QUV® equipment employs mainly two types of lamps: UVA-340 and UVB-313 (where 340 and 313, respectively, represent the peak emission expressed in "nm"). These lamps have different

light emission spectra, and are both characterized by maximum emission in the UV range.

Among all artificial UV sources, xenon lights provide the best simulation of natural sunlight. With an appropriate filter combination (usually a borosilicate type), the xenon light irradiance spectrum can be adapted to match closely to natural sunlight over a broad range of wavelengths.

Published studies have included in-air irradiation experiments of polymer materials, including wood samples with different chemical treatments, by means of a rotation device equipped with a middle pressure mercury lamp HQE-40 type, with 100W power, having a polychrome emission spectrum in the field of 240 to 570 nm (Fig. 2).

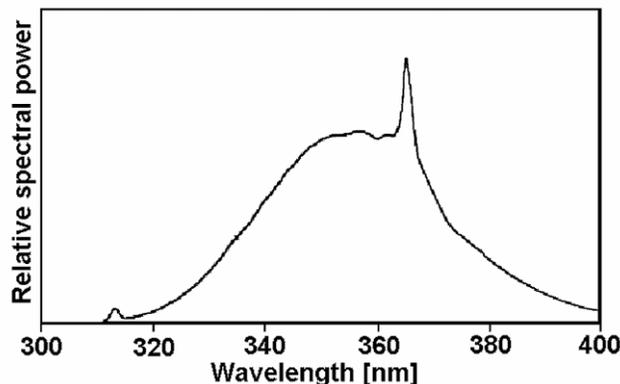


Fig. 2. Emission spectrum of the applied mercury lamp

The more energetic types of radiation, with $\lambda < 300$ nm, are not found in the natural light spectrum, but they can be eliminated using a 30 μm borosilicate glass filter. A water filter and a fan are used to prevent the thermal degradation of the polymer sample during the photochemical treatment. The samples are mounted on the device, which is positioned at a distance of 60 mm from the lamp. The irradiance value and average radiant exposure measured on the sample surface are 97 Wm^{-2} , and $350 \text{ kJm}^{-2}\text{h}^{-1}$, respectively. The temperature inside the irradiation chamber is kept at around 40 to 45°C. The samples are withdrawn from the device after different irradiation times and further investigated for structural and color changes.

WOOD WEATHERING UNDER UV RADIATION ACTION

Wood Behavior under Exposure to Solar UV Radiation

Since ancient times, wood has been continuously present in the human environment. Nowadays, in the context of the sustainability concept, the importance of wood as a renewable and ecological construction material is continuously increasing. Wood is used in many interior and exterior applications, for which an extended service life and conservation of both aesthetical appearance and mechanical properties are important. Under certain use conditions, however, wood is affected by biotic and non-biotic factors, causing degradation phenomena that will alter firstly the visual aspect and then the mechanical resistance of wood, hence limiting its service-life.

When wood is exposed outdoors above ground, a complex combination of chemical and mechanical factors contributes to what can be described as weathering, a

long-term process resulting in a color change to grey, a roughened texture, and cracks following the combined action of ultraviolet radiation from sunlight and rainwater (Williams 2005). The same factors that cause weathering can actually facilitate the biological degradation of wood and diminish in time the efficacy of the protective treatments applied, namely wood preservation and coatings. Weathering should not be confused with decay, which results from decay organisms (*e.g.*, fungi) acting in the presence of excess moisture and air for an extended period of time.

Not all fungi that attack wood cause degradation (Evans 2012). In fact, many are classified as wood-staining or mildew (mold) fungi because they discolor or stain wood rather than causing decay. These fungi typically develop because of poor drying practices or excessively wet conditions. Stain fungi do not cause strength loss but result in a lower grade and are considered unfavorable because of their appearance. Conditions that favor stain fungi are often ideal for wood-degrading organisms (Williams 2005).

Wood-staining fungi differ from the wood-destroying fungi in that wood-staining fungi do not noticeably affect wood strength or texture. Mold and stain are often considered together because of the similarity of action of the fungi on wood micro-structure. Mold and stain induce little injury to the structure of wood they infest. A number of wood-staining fungi produce a wide range of color effects or different stains. Control can be accomplished either by rapid drying of the wood to reduce moisture content or by dipping or spraying with fungicidal solutions. Dipping is usually fairly inexpensive. If the risk of stain is severe, both fungicidal protection and good drying practices are recommended for high-grade products.

In addition to discolorations produced by fungi, wood is also subject to certain other stains that result from chemical changes in wood cell walls. The nature and causes of these changes are not definitely known, although, in some cases at least, they involve enzymatic or non-enzymatic oxidation of certain organic compounds. Certain molds, similar to those that form on old bread, can form on the surface of wood and produce “cottony” growths that range from white and other light shades to black. These organisms differ from wood-staining fungi mainly in their habit of surface growth. The same conditions of moisture, air, and temperature that promote wood-destroying and wood-staining fungi will favor the growth of molds (Williams 2010).

Although molds (mildew) are more common with untreated wood, they can also be a problem in cases of preservative-treated wood. Annual treatment of the preservative-treated wood with a water-repellent preservative can reduce molds. Most unprotected wood will be discolored to a dull gray or black by mold. Preservative-treated wood that has not been treated with a water-repellent preservative will quickly turn to a dull gray or silver gray in some areas. Some molds are surprisingly tolerant of wood preservatives.

Because most molds need a surface moisture content of about 20 percent to begin growth, they can be controlled by controlling air moisture levels and minimizing condensation. If preventive measures fail, then other methods are available. The natural color of an outdoor wood structure can be partially maintained by scrubbing the wood surface annually with a bleach/water mixture or a commercial wood cleaner. The cleaned wood surface should be scrubbed with a stiff bristle brush and rinsed thoroughly with water. Always the wood surface needs to dry for several days before refinishing. However, aggressive cleaning methods to remove molds using strong chemicals and/or power-washing can greatly accelerate the loss of wood fiber from wood surfaces (Williams 2010).

The wood properties that vary greatly from species to species are: density, grain characteristics (presence of earlywood and latewood), texture (hardwood or softwood), extractives, resins, and oils content (Williams 2005). The wood density is one of the most important factors that affect weathering characteristics. This parameter varies to a large extent from species to species and it is important because hardwoods shrink and swell more than softwoods.

The amount of warping and checking that occurs as wood changes its dimensional stability under natural weathering process is directly related to wood density. High-density woods (generally hardwoods) tend to warp and check more than do the low-density woods (generally softwoods). Hardwoods are primarily composed of relatively short, small-diameter cells (fibers), and large-diameter pores (vessels); softwoods, in contrast, are composed of longer small-diameter cells (tracheids). The size and arrangement of the pores may enhance the effect of density and grain pattern on the weathering process. Hardwoods with large pores, such as oak and ash, may erode more quickly at the pores than the surrounding fibers.

Williams and co-authors reported on the effects of surface roughness, grain angle, exposure angle, and earlywood/latewood ratio on weathering rates of several softwood and hardwood species (Williams *et al.* 2001 a, b, and c). Erosion was slower for most hardwood species and faster for low-density softwood ones. For all wood species, the erosion rates for earlywood and latewood were greatly different during the first 7 years of weathering (outdoor experiments spanned 16 years). The erosion rates of all species were considerably higher at 45° exposure angle than at 90°.

Latewood is denser, harder, smoother, and darker than earlywood, and its cells have thicker walls and smaller cavities. The wider the latewood band, the denser will be the wood. Differences in morphology have been shown to affect weathering of the wood surface. Wood species with wide latewood bands weathers differently than do species with thin latewood bands. As wood weathers, the extractives are leached from the surface, which becomes less water-repellent. The loss of lignin also makes the surface more hydrophilic. Contact angle measurements on weathered western red cedar dropped from 77° to 55° after four weeks of outdoor weathering (Kalnins and Feist 1993).

In addition to the slow erosion of the wood surface under weathering conditions, the surface also can develop checks and raised grain. This type of degradation is often more severe than erosion. For example, wooden decks are often replaced long before their expected service life because of raised grain and splitting. This degradation is caused primarily by moisture. During outdoor weathering, water mechanically abrades the wood surface and removes degradation products. In addition, water hydrolyzes mainly hemicelluloses at the wood surface, noting that these become more susceptible to hydrolysis as lignin degrades.

Studies of wood-weathering phenomena are numerous, and principle breakdown processes during exposures are generally known; however, results obtained using different methods are incoherent and dependent on the particularities of the applied testing method. Weathering occurs through the combined effects of UV-light, water, oxygen, heat, and atmospheric pollutants such as SO₂, NO₂, and O₃. Wood surfaces become rough as the grain raises during the weathering process. The dimensional stability of the wood is also affected as checking and cracking become severe.

The roughened surface changes in color and becomes more susceptible to decay and may fragment (Feist and Hon 1984). Ultraviolet radiation from sunlight is the most

damaging component of the outdoor environment because it initiates a wide variety of chemical changes in wood surfaces, which lead to discoloration and deterioration. The surface of wood becomes grey, rough, and stringy. It loses not only its usual appearance, but also its mechanical properties, as the strength characteristics degrade. These damages caused from exposure are called degradation processes.

Wood is capable of absorbing several different wavelengths of electromagnetic radiation, initiating photo-chemical reactions leading to wood discoloration. Wood contains cellulose, hemicellulose, lignin, and extractives. Wood polymer components contain internal chemical labile entities such as carbonyl, carboxyl, aldehyde, phenolic hydroxyl, unsaturated double bonds, and external entities such as waxes, fats, and metal ions. All wood polymers are sensitive to ultraviolet radiation (Fig. 3). Solar radiation depolymerizes lignin and cellulose, and water leaches the resulting photo-degraded fragments from the wood (Derbyshire and Miller 1981; Evans *et al.* 1993).

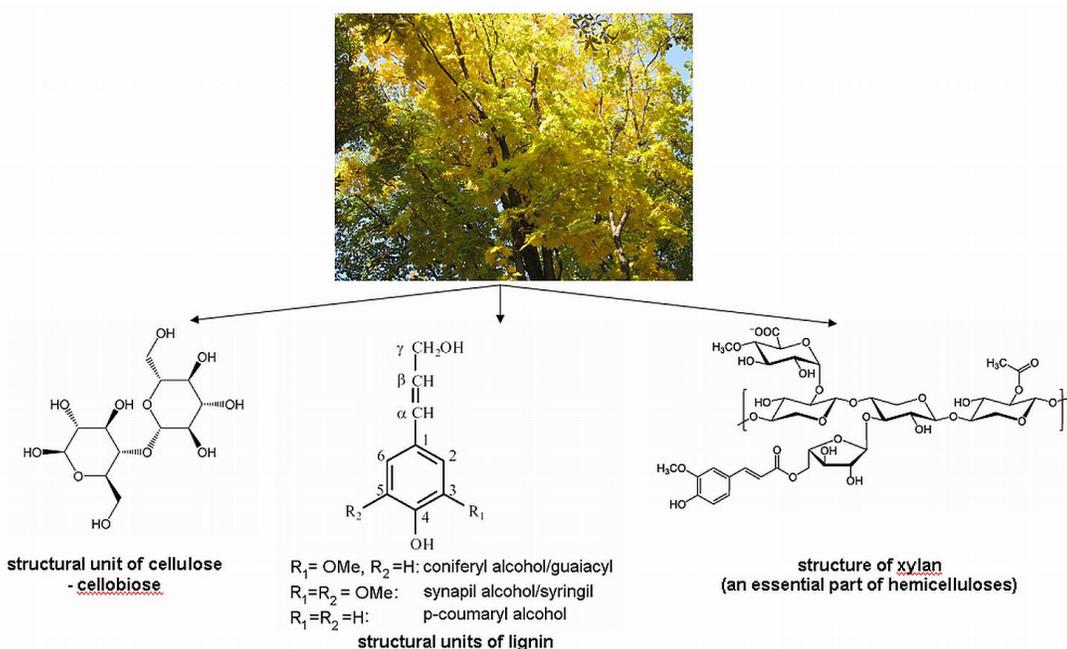


Fig. 3. Main chemical constituents of plant and wood biomass

Natural biopolymer materials undergo UV-induced discoloration, usually resulting in an increase in the yellowness on exposure. Lignocellulosic materials such as wood and paper readily undergo light-induced yellowing (Hon 1991).

A schematic representation of light action upon wood biomass is presented in Fig. 4. While both the cellulose and lignin constituents are sensitive to solar radiation, it is the latter that is mostly responsible for the phenomenon. Lignin, which makes up 29 to 33 wt% of softwood, contains numerous chromophores that efficiently absorb UV radiation. Lignin is responsible for absorbing 80 to 95% of the total UV light absorbed by wood, carbohydrates 5 to 20%, and extractives about 2% (Norrstrom 1969).

Although the weathering of wood materials depends on many environmental factors, only a relatively narrow band of the electromagnetic spectrum, the UV-light portion of sunlight, is responsible for the primary photo-oxidative degradation of wood. The first law of photochemistry, the Grotthus–Draper principle, states that for a photo-

chemical reaction to occur, some component of the system must first absorb light. The second law of photochemistry, the Stark–Einstein principle, states that a molecule can only absorb one quantum of radiation at a time (Rabek 1995). The absorbed energy can cause the dissociation of bonds in the molecules of the wood constituents. This homolytic process produces free radicals as the primary photochemical products. This event, with or without the participation of oxygen and water, can lead to depolymerization and to the formation of chromophoric groups such as carbonyls, carboxyls, quinones, peroxides, hydroperoxides, and conjugated double bonds (Feist and Hon 1984).

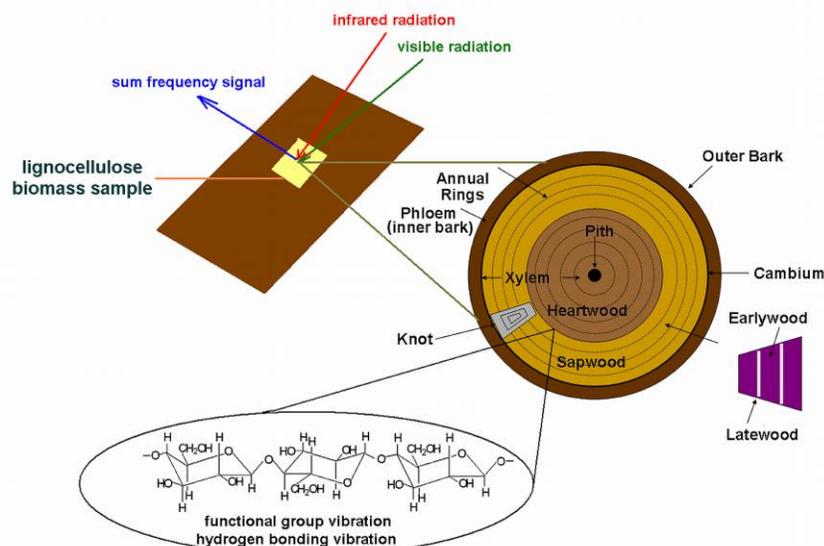


Fig. 4. Schematic representation of light action upon wood biomass

Most of the components in wood are obviously capable of absorbing enough visible and UV light to undergo photochemical reactions leading ultimately to discoloration and degradation. Because of the wide range of chromophoric groups associated with its surface components, wood cannot easily be penetrated by light. Essentially, discoloration of wood by light is a superficial surface phenomenon.

Apart from a decrease in the methoxyl and lignin contents, and an increase in the carboxyl content inside the wood (Leary 1967; Leary 1968), photo-degradation also results in an increase in cellulose content and a decrease in lignin content on the wood surface (Wang and Lin 1991; Evans *et al.* 1992; Hon 1994, 2001; George *et al.* 2005). This result ultimately leads to a reduction of some physical, chemical, and biological properties of natural wood.

The discoloration of wood is attributed to the modification of the chromophores, which are capable of absorbing UV light in the range of 300 to 400 nm. Another indication of chemical change on the wood surface is the decrease in lignin content relative to cellulose content on the weathered wood surfaces. There have been many studies attempted to clarify the mechanism of wood weathering (Hon 1983; Hon and Chang 1984; Pandey 2005a; George *et al.* 2005; Evans 2012). It has been shown that the degradation process is triggered by the formation of free radicals by UV irradiation (Moore and Owen 2001; Müller *et al.* 2003).

The wood constituent polymers show different capacities with respect to absorbing UV light to form radicals. Lignin is extremely susceptible to UV irradiation, leading to the formation of aromatic free radicals (phenoxyl radicals), which further react with oxygen to produce carbonyl and carboxyl groups (Pandey 2005), these being related to wood discoloration by the occurrence of unsaturated carbonyl compounds (quinones). The presence of lignin in the formulation of wood-plastic composites (WPCs) can accelerate the composites' photo-degradation under UV weathering (Chaochanchaikul *et al.* 2012).

Photo-degradation of WPCs involves several factors including the wood flour content, coupling agents, manufacturing methods, and weathering conditions, among others. Matuana and Kamdem (2002) investigated the influence of accelerated artificial weathering on the color changes and tensile properties of PVC/wood-flour composites with various wood flour contents. While the composites retained their original tensile properties, they experienced severe discoloration (darkening) after weathering for 2600 h. PVC/wood-flour composites containing 15% wood flour were darkened more than those containing 30% and 45% wood flour. Conversely, reports indicate the opposite trend for weathered HDPE/wood-flour composites; the composites containing 50% wood flour were lightened more than their counterparts with 25% wood flour (Stark and Mueller 2008). Ndiaye and coworkers (2008) studied the effects of wood flour content and compatibilizer on the durability of HDPE-based and PP-based WPCs. Their results indicated that the oxidation rate of the composites increases with wood content and decreases with the presence of compatibilizer due to better dispersion of wood flour in polymer matrix.

Some investigations have studied the effects of natural and accelerated artificial weathering on the appearance and chemical changes of HDPE-based and PP-based WPCs (Muasher and Sain 2006; Stark and Matuana 2004a; Stark and Matuana 2004b; Matuana and Kamdem 2002; Stark and Mueller 2008; Matuana *et al.* 2001; Stark and Matuana 2007; Stark 2006; Stark *et al.* 2004; Stark and Matuana 2006; Fabiyi *et al.* 2008). The lightness, total color change, and wood loss increased with exposure time. PP-based WPCs experienced quicker photo-degradation in terms of lightness and wood loss. Delignification and oxidation accounted for the increased lightness of weathered composites. Muasher and Sain (2006) also investigated the discoloration of HDPE-based WPCs exposed to natural weathering and reported that WPCs undergoes two competing redox reactions upon UV exposure: the formation of paraquinone chromophoric structures generated by the oxidation of lignin, resulting in yellowing, as well as the reduction of the paraquinone structures to hydroquinones, leading to photo-bleaching. The yellowing mechanism dominant during the first 250 hours of exposure precedes the photo-bleaching mechanism, which becomes dominant with increased exposure time.

Evidence of Chemical Changes in Wood after Exposure to Artificial UV Radiation

Wood is a good absorber of infrared (IR), visible, and ultraviolet (UV) light. UV light is fully absorbed by a 75 μm -thick layer of wood (Hon and Ifju 1978). The penetration depth profile of light into wood, which was found to be dependent on the wavelength of the light, was investigated by Kataoka *et al.* (2004; 2005; 2007). The effects of UV light irradiation can be detected at a depth of 400 to 500 μm for aromatic skeletal vibration (1510 cm^{-1}) and at a depth of 600 to 700 μm for carbonyl vibration (1730 cm^{-1})

under long-term treatment (Kataoka and Kiguchi 2001). This means that wood is not transparent for light, and the usual transmission method is not suitable for measuring the absorption properties of wood. For this purpose, powdered wood is mixed with a light-transparent material (usually and widely used potassium bromide). This mixture is pressed into pellets, and the pellets are used to measure the wood absorption using the transmission method. This method constitutes an excellent analytical tool to reveal evidence of the chemical composition of wood by IR spectroscopy. Since the change caused by irradiation appears in a thin surface layer, it is not easy to remove the proper thin layer for pellet preparation. In the case of wood, it is difficult to remove a layer thinner than 80 μm that has suffered change during the treatment. Concerning this difficulty, many investigators have used the pellet method without indicating the thickness of the wood layer (Hon and Feist 1986; Košíková and Tolvaj 1998; Müller *et al.* 2003; Pandey 2005; Umemura *et al.* 2008).

The Fourier transform IR technique can measure the diffusely reflected (DRIFT) intensity of a thin layer. This is a useful technique to investigate photo-degradation because the information is given for the same layer on which the photo-degradation process occurred. The absorption properties of the surface layer using the reflected light can be calculated by means of the Kubelka–Munk (K-M) theory (Kubelka and Munk 1931; Kubelka 1948). This theory was created for poorly absorbent materials. Since photo-degradation is a surface phenomenon and wood is a good light absorber, the K-M theory is widely applied to determine the light absorption of wood (Owen and Thomas 1989; Horn *et al.* 1994; Tolvaj and Faix 1995; Zanuttini *et al.* 1998; Košíková and Tolvaj 1998; Barta *et al.* 1998; Pandey and Theagarajan 1997; Pandey 1999; Moore and Owen 2001; Weiland and Guyonnet 2003; Mitsui *et al.* 2003; Cui *et al.* 2004; Papp *et al.* 2004; Kishino and Nakano 2004; Tolvaj and Mitsui 2004; Tolvaj and Mitsui 2005). In order to obtain reproducible FTIR spectra from wood surfaces, the roughness and the anatomical directions of the cut sections must be constant. It is difficult to compare the FTIR spectra of different solid wood surfaces because the natural roughness of the wood species varies widely. The validity of the Kubelka–Munk (K-M) theory was investigated to determine the IR absorption spectra of wood based on DRIFT measurements taken on photo-degraded samples (Tolvaj *et al.* 2011). It was evidenced that the measured K-M function can be used as an absorption spectrum if its values are below 14 K-M units. Above this limit, the K-M theory, which was created for poorly absorbing materials, does not give the absorption of wood properly. If a matt aluminium plate is used as a background material and the values are between 14 and 40, absorption changes can be calculated after normalization of the spectra. This manipulation is only successful if there is an absorption peak close to the examined one which does not change its absorption during the photo-degradation process.

Infrared studies revealed that, during UV irradiation of wood, absorption due to carbonyl groups at 1720 and 1735 cm^{-1} increased, whereas the absorption for lignin at 1265 and 1510 cm^{-1} gradually decreased. The increment of carbonyl groups was the result of oxidation of cellulose and lignin, and the reduction in the amount of lignin was due to its degradation by light (Feist and Hon 1984). A convenient measure of the change in carbonyl groups and lignin is given by the ratio of the IR absorbance bands of carbonyl groups and lignin to the absorption band at 895 cm^{-1} , an absorption band due to hydrogen located at the C1 position, which is normally unchanged during photo-irradiation.

The aesthetic appearance of wood is an important factor concerning wood quality, and color and has a significant impact on each individual's perception of this appearance. Unfortunately, wood surfaces undergo drastic color changes when exposed outdoors, and they mostly turn grey. In order to compare the quality of different wood products, it is necessary to determine the rate of discoloration that wood surfaces undergo when exposed outdoors. Color can be measured using a wide range of spectrophotometers according to the EN ISO 11664-4 (Colorimetry - Part 4: CIE 1976 $L^*a^*b^*$ Color space). The CIEL^{*} a^*b^* system is one of the systems used to quantify color. The color parameters of this system are as follows: the L^* axis is the lightness (ranging from 0 (black) to 100 (white)) and a^* and b^* axes represent the chromaticity coordinates (a positive a^* value refers to red and a negative a^* value to green while $+b^*$ and $-b^*$ denote yellow and blue, respectively). The color difference ΔE^* is the combined effect of the parameters and can be calculated according to Equation 1:

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

Generally, wood is colored by painting. Wood painting has mainly two objectives: one to change the color, and the other to protect the surface. The emission of volatile organic compounds such as toluene and xylene from paint, however, is a health concern. Coloring by irradiation and heat treatment emits no volatile organic compounds and is very simple (Mitsui *et al.* 2001). Furthermore, there is less damage, such as cracking and bending, because the wood is treated at a comparatively low temperature. The change in the lightness, ΔL^* , of light-irradiated wood with heat treatment (both dry heating at 120°C, 140°C, and 160°C in air and humid heating at 50°C, 70°C, and 90°C, at a high relative humidity 90% RH for up to 150 h) was much greater than that of un-irradiated wood. With low temperature treatment, the color of irradiated wood (Δa^* and Δb^* parameters) changed remarkably with high relative humidity; therefore, heat and the presence of water accelerated the change in the color of irradiated wood. It is thought that the amount of change in color is due to the light-irradiation time and heat treatment conditions (*i.e.*, heating temperature, time, and relative humidity). Moreover, it is reported that the ultraviolet region is effective in this method. This treatment can be a useful alternative as a new coloring method.

CHEMICAL TREATMENTS AGAINST WEATHERING PROCESS

Wood Coating Treatments

Wood is a material sensitive to humidity because of the hydrophilic nature of its cell wall constituent polymers cellulose, hemicelluloses, and lignin. Moist wood is vulnerable to attack by fungi and termites, these affecting its dimensional stability. The polar surface associated to the hydroxyl nature enables the establishment of strong hydrogen bonding between wood fibers, as a three-dimensional network.

To obtain long-term service life, wood must have proper protection. There are several approaches to improve water-repellency and dimensional stability of wood, including immersion-diffusion or vacuum-impregnation with preservatives, heating, brushing paint, and surface coating (Forsthuber and Gröll 2010; George *et al.* 2005; Mitsui *et al.* 2003; Mitsui *et al.* 2001). One emerging technique is chemical modification,

where chemicals such as anhydrides, isocyanates, alkyl chlorides, *etc.*, react with hydroxyl groups, *i.e.*, with the most reactive groups of cell wall polymers (Rowell 2005).

For economic reasons and for simplicity, surface coating has long been preferred to modifications by chemical immersion. The primary function of any coating is to prevent moisture penetration, improve resistance to weathering, and maintain the natural appearance of wood. A common method to achieve coating and wood extensive protection is the addition of pigment particles to a coating. These particles absorb, reflect, or scatter the incoming UV radiation and hinder it from reaching the wood substrate. The most effective UV absorber known is carbon black, but also other pigments such as TiO₂ are in common use today. Another effective treatment that protects against photochemical degradation and is water repellent is treatment of wood with chromic acid. This compound alters the molecular structure of lignin, and is remarkably effective at photo-stabilizing wood (Schmalzl *et al.* 2003). Due to the molecular structure of this chemical it is classified as especially hazardous, being toxic, corrosive, and carcinogenic. Attempts to find less harmful metal compounds to contribute at photo-stabilizing wood surfaces have been undertaken without effective results (Schmalzl and Evans 2003).

However, in many cases other types of photo-stabilizers are required to protect the wood, without coloring the surface. One of the most common ways of achieving this is to add low molecular weight substances that have the ability to absorb some of the incoming radiation from the sun and then dissipate it as heat. Such substances are called UV absorbers (UVA) and can be used to protect both the substrate and the coating itself. Examples of such substances are benzotriazole, triazine (Hayoz *et al.* 2003), and also substituted 2-hydroxybenzophenones which, due to their structure, can convert UV energy into thermal energy by intramolecular hydrogen transfer or *cis-trans* isomerization (Evans and Chowdhury 2010).

Other types of substances that are commonly used for UV protection in coatings are the hindered amine light stabilizers (HALS). These are amines with two methyl groups; such compounds undergo photo-oxidative conversion, thus hindering degradation of the coating and the substrate (George *et al.* 2005). Use of UV absorbers (UVA) and hindered amine light stabilizers (HALS) both in the coating system and also in a direct wood impregnation step can improve the light stability considerably (Schaller and Rogez 2007; Forsthuber and Gröll 2010). Usually, an efficient protection strategy is to impregnate the wood surface with a solution of HALS, which will inhibit or at least reduce the lignin sensitivity to photo-oxidation, before applying the transparent top coat containing the UV absorber.

An alternative route to increase the hardness, dimensional stability, decay and acid resistance of wood is to impregnate wood with low molecular weight phenol formaldehyde (PF) resin, which penetrates the wood cell walls and can be cross-linked by heating (Furuno *et al.* 2004). PF resins are good absorbers of UV light. The resistance of wood treated with low molecular weight PF resin to weathering can be improved by increasing the concentration of PF resin and by combining it with a water-soluble hindered amine light stabilizer HALS (Evans *et al.* 2012). This approach may be justified in some higher value exterior applications of wood.

In recent years, the development of inorganic coatings on polymer surfaces has been fostered because of their excellent mechanical and thermal performance, optical properties, and bacterial resistance. On the other hand, the presence of the hydroxyl groups can promote the nucleation and growth of inorganic phases such as TiO₂ and SiO₂

(Schmalzl and Evans 2003; Tshabalala and Gangstad 2003; Barata *et al.* 2005; Kim *et al.* 2006; Tshabalala and Sung 2007; Mahltig *et al.* 2008; Kuroda *et al.* 2008; Chen *et al.* 2009; Li *et al.* 2010; Sun *et al.* 2011) on the wood surface, thus producing organic–inorganic hybrid materials. These inorganic particles are usually generated from their monomer precursors containing reactive organic groups to build up chemical bonds to the hydroxyl groups of wood. Encountering the hydroxyl groups of wood, the monomer precursors would be hydrolyzed, generating inorganic particles and reactive organic groups with the continuous condensation reactions to form a solid inorganic coating on the wood surface. These inorganic particles have great potential as photo-protective agents for wood because of their high chemical stability, nontoxic nature, and ability to absorb or scatter UV irradiation (Hon 2001; Ncube and Meincken 2010).

The aesthetic value of wood can quickly be lost if left unprotected from weathering. The absorption of UV radiation in the coating and the underlying wood substrate can cause a series of complex chemical reactions that amongst other effects, resulting in the loss of adhesion between the coating and the substrate. Degradation can occur either in the coating, on the wood surface, or in both materials (Chang and Chou 1999). Wood materials with significantly improved UV resistance were successfully fabricated by growing highly ordered ZnO nanorod arrays on wood surfaces using a facile one-pot hydrothermal method (Sun *et al.* 2012).

Inorganic nanoparticles, for example CeO₂ and ZnO, have the same function as pigment particles, although they are much smaller in size and are hence transparent in the visible light spectrum. CeO₂ and ZnO have significant absorption in the UV region of the light spectrum, indicating that these substances could be interesting for use as UV absorbers in coatings (Blanchard and Blanchet 2011). The efficiency of adding these types of particles to a coating varies depending on the particle size and a synergetic effect is possible when inorganic and organic particles are combined.

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. 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). Despite the advantage of vegetable and fish oils being a renewable resource, the use of drying oils as pure binders has decreased over the years. However, they still play a large role as raw materials for other binders such as alkyds and epoxy esters. Natural oils are triglycerides, consisting of glycerol and different fatty acids, such as stearic acid and oleic acid. The composition is different for each type of oil, 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 components depends on the composition of different fatty acids and their unsaturation level, or more specifically, the number of diallylic methylene groups in the chain. These natural oils can be modified by introducing new groups to the fatty acid chains in order to increase the compatibility with a potential top coating system or even to get the oils to react with the substrate. One example of this is to introduce epoxy groups to the fatty acid chains by, for example, lipase catalyzed *in situ* epoxidation (Vlcek and Petrovic 2006), in order to get other types of reactive groups on the fatty acids. These epoxy groups can then react covalently with the substrate, in order to create a better coating system due to less leaching (Kiguchi and Evans 1998; Olsson *et al.* 2012).

Wood Coating with Epoxidized Vegetable Oils

Coatings present a physical barrier that protects the wood substrate from the adverse effect of environmental factors, such as solar irradiation, moisture, as well as staining and decay fungi. Clear coatings with high transparency, however, require additional UV absorbers and a radical scavenger, such as hindered amine light stabilizers to protect the coating itself and the wood surface underneath (Ahola 1991). Accordingly, it is assumed that certain pre-treatments of the wood substrate can improve the performance of exterior wood coatings providing dimensional stabilization, a reduction in capillarity, and a greater fungal resistance.

Epoxidized vegetable oils and their derivatives have been used for many commercial applications, e.g., as plasticisers and stabilisers in chlorine-containing resins, as additives in lubricants, as components in thermosetting plastics, in cosmetics and pharmaceutical formulations, in urethane foams, and as wood impregnants (Wu *et al.* 2000). Epoxy fatty acid compounds are obtained on an industrial scale mainly by the peracid process (Rangarajan *et al.* 1995; Sinadinovic-Fiseret *et al.* 2001; Hill 2000). Soybean oil is a triglyceride that typically contains 14% stearic, 23% oleic, 55% linoleic, and 8% linolenic acid. Chemical modification of commercially available soybean oil, such as epoxidation, can enhance its properties (reactivity) for certain industrial applications. The epoxidized soybean oil (ESO), an epoxidized glycerol fatty ester with the structure given in Fig. 5, is extensively used in the plastic industry as a plasticizer to increase flexibility in poly (vinyl chloride) (PVC) products and as a stabilizer to minimize decomposition.

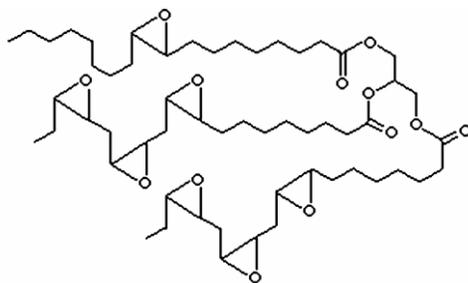


Fig. 5. Chemical structure of epoxidized soybean oil (ESO)

Wood originating from a softwood species has been chemically modified by reaction with succinic anhydride in dimethylformamide (DMF) (Matsuda 1996). Modified wood samples were further coated with epoxidized soybean oil (ESO) in the presence of triethylamine (TEA). Synthesis of ESO was presented in a previous work (Mustață *et al.* 2011). The photostability of modified wood and ESO-coated modified wood during artificial light irradiation was investigated (Teacă *et al.* 2010; Teacă *et al.* 2012). Analysis of the color changes in the wood surfaces was carried out by measuring CIELAB parameters. Structural changes were analyzed by Fourier transform infrared spectroscopy. The color difference, yellowing index, and weight loss were also evaluated. The FTIR spectrum of the non-modified wood sample (A) presented characteristic bands of wood (Fig. 6). In the spectrum of the modified wood sample with succinic anhydride (spectrum B) the absorbance intensity at 3330 cm^{-1} decreased and enlarged to the lower wavelength and the band at 1736 cm^{-1} significantly increased in intensity. The spectral changes confirmed the wood esterification with succinic anhydride. In the FTIR spectrum

C, the signals at 2918, 2890, and 1736 cm^{-1} increased due to the reaction between the succinic monoester with ESO.

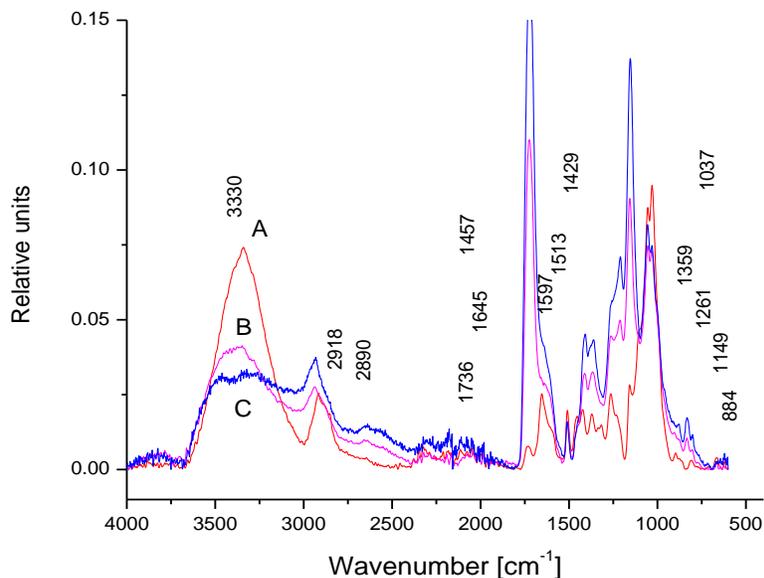


Fig. 6. FTIR spectra recorded for the non-modified wood sample (A), wood modified with succinic anhydride (B), and wood sample modified with succinic anhydride and coated with ESO (C)

The FTIR spectra recorded for wood modified with SA before and after irradiation (exposure times of 200h and 400h, respectively) are shown in Fig. 7.

Wood samples modified with SA and coated with ESO were also investigated by FTIR spectroscopy for evidence of chemical changes after UV light exposure for different time values (Fig. 8).

As can be observed in Fig. 8, absorption bands at 2925 cm^{-1} and 2855 cm^{-1} increase as intensity with irradiation time exposure, while the band at 1509 cm^{-1} specific to aromatic skeletal vibration decreases during irradiation time, which can be attributed to the lignin degradation process (Hon 2001). Nevertheless, this evolution can be also due to the increasing roughness of wood surface. The absorption band at 1509 cm^{-1} is also noticed for wood samples modified with SA and coated with ESO in comparison with non-irradiated sample.

Absorption bands at 3419 cm^{-1} and 1732 cm^{-1} , as well as those at 2925 cm^{-1} and 2855 cm^{-1} , significantly increase in intensity as irradiation time exposure increases. Analysis of color changes at coated wood surfaces shows that lightness (ΔL^*) decreases whereas a^* , b^* , and ΔE^* increases with increasing irradiation time. The rate of color change is very high during initial period of exposure. Total color change (ΔE^*) is related with rate of formation of carbonyl groups and degradation of lignin (Hon 2001). Changes in wood color reflect chemical changes in its structure during irradiation. Yellowing of wood surfaces indicate modification of lignin and hemicelluloses with occurrence of unstable products. These chromophores are different, as color depends on the irradiation time and coating modified wood with ESO.

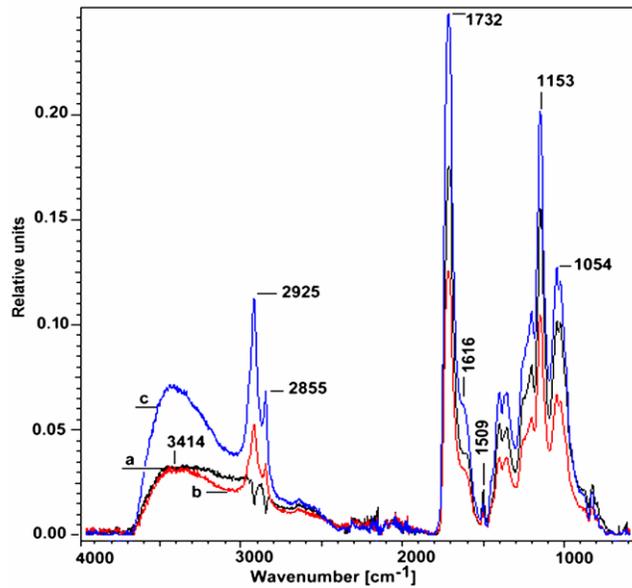


Fig. 7. FTIR spectra recorded for wood treated with SA 80%: a- non-irradiated; b- irradiation 200 h; c- irradiation 400 h

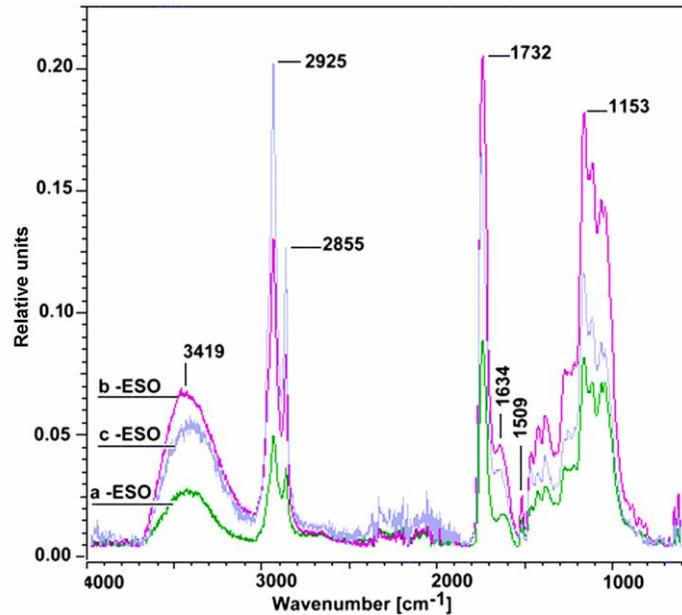


Fig. 8. FTIR spectra recorded for wood treated with SA 80% and further coated with ESO: a- non-irradiated; b- irradiation 200 h; c- irradiation 400 h

From Fig. 9, it is apparent that the increase of ΔE_{ab} values with irradiation time. There is a high rate of increase of ΔE_{ab} that is characteristic of the non-modified wood sample compared with the samples representing modified wood coated with ESO. The ΔL^*_{ab} index of the samples significantly decreases as a result of photochemical aging (Pandey 2005b).

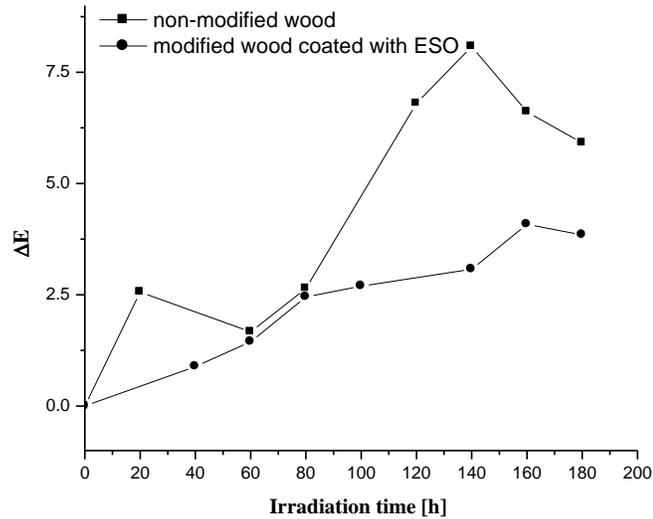


Fig. 9. Total color difference of modified wood coated with ESO as a function of irradiation time (Teacă *et al.* 2012)

Figure 10 presents the variation of ΔL^* with irradiation time. From Fig. 10, one can observe the blackening of the wood samples after irradiation. The ΔL^* values decrease during irradiation. The wood samples, modified with SA and coated with ESO, exhibited greater stability to blackening.

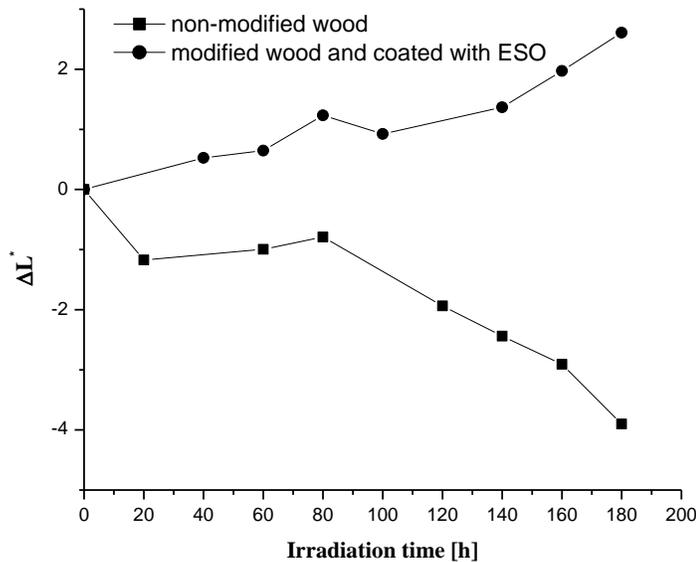


Fig. 10. Lightness factor of modified wood coated with ESO as a function of irradiation time (Teacă *et al.* 2012)

The positive values of Δa^* (Fig. 11) show a progressive accumulation of red chromophores on the surface of the samples during irradiation. At irradiation times longer than 100 hours, the accumulation of red chromophores is less evidenced on the surface of coated softwood samples compared with the surface of reference sample. Less colored is the modified wood sample after coating with ESO. The increase in the chromaticity coordinates, Δa^* and Δb^* can be attributed to the formation of quinones and quinoide-like structures due to depolymerisation and oxidation of lignin involving free radicals (presumably phenoxyl radicals) in this process (Hon 2001).

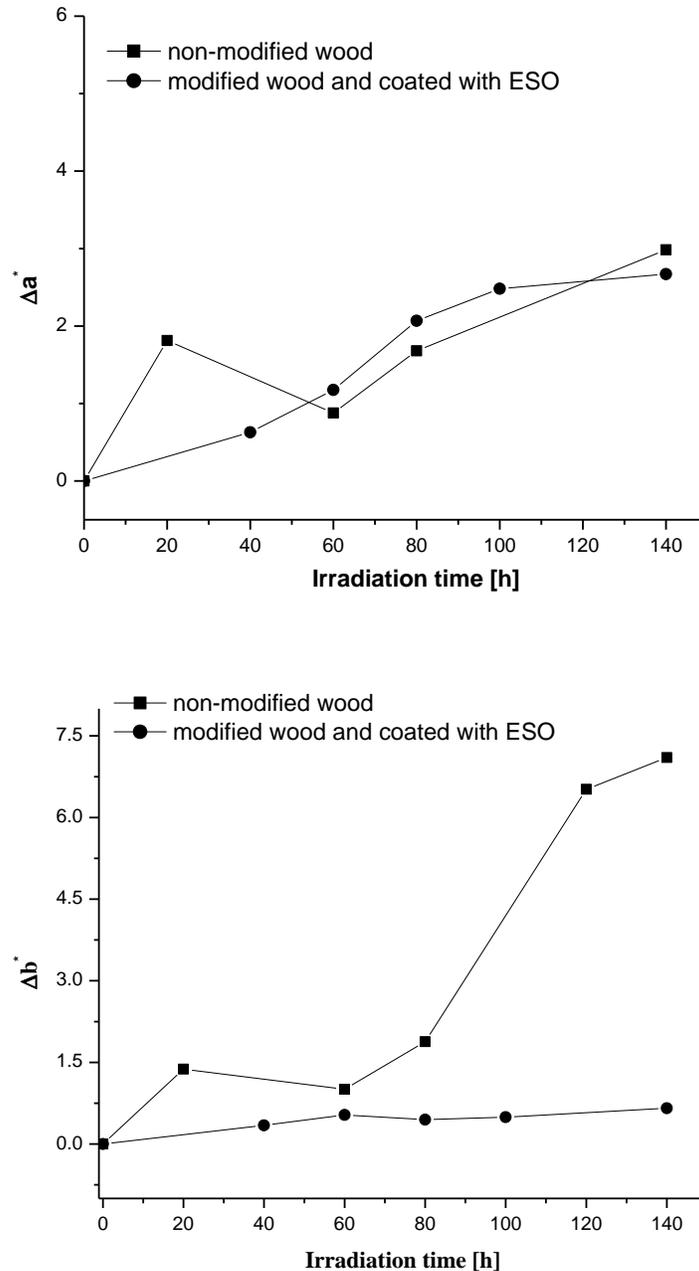


Fig. 11. Redness factor (a^*) and yellowness factor (b^*) variation of modified wood coated with ESO with the irradiation time (Teacă *et al.* 2012)

In the first 50 hours of irradiation, some blue chromophores were accumulated in all studied samples. By extension of irradiation time to 200 hours the blue chromophores are destroyed and yellowness shows systematic trends with increasing of the irradiation time. There is a slow increase of Δb^* values for modified wood samples coated with ESO.

Wood Chemical Modification

In order to obtain a wood-based material with a long service life it is necessary to interfere with the natural degradation process of wood as much as possible. One way of achieving this is to modify the wood surface chemically by different treatments. Thus, the wood polymers (cellulose, hemicelluloses, and lignin) are modified, which leads to a change in the wood properties. To increase water repellency, for example, one way would be to reduce the hydrophilic character of the wood cell wall by introducing hydrophobic groups. Other types of chemical modifications are acetylation, furfurylation, *etc.* (Rowell 2012). The basis of these modifications is OH-substitution of the wood components, in which the aliphatic and aromatic hydroxyl groups of the lignin are substituted by new groups. Apart from acetylation and furfurylation, another method is to graft UV protective additives onto the wood surface by covalently bonding the epoxy- or isocyanate functionalized additives to the hydroxyl groups of the wood. In these types of grafting reactions it is of course desirable to get the grafting on the OH groups of the lignin, since these are the most susceptible to UV degradation. All of these modification methods can prevent the formation of phenoxy radicals, and thus the susceptibility to photo-degradation is decreased (George *et al.* 2005).

Greater wettability of weathered wood was suggested as a contributing factor to the deterioration of wood structures (Kalnins and Feist 1993). Previous researchers have demonstrated that lignocellulosic material properties (such as dimensional instability due to moisture and low durability due to biodegradation) can be improved by chemical modification using esterification (Efanov 2001; Hon and Xing 1992; Sereshiti and Rovshandeh 2003), etherification (Hon and Ou 1989; Norimoto *et al.* 1983), and cyanoethylation (Hon and San Luis 1989; Liga *et al.* 1995) reactions. Lignocellulosic materials are favored as a new generation reinforcing materials in thermoplastics since they represent renewable natural resources. Considering the increasing environmental concerns and the urge to promote recyclable raw materials and products, an emphasizing demand for lignocellulosic-thermoplastic composite materials (Mahlberg *et al.* 2001) is obvious. Chemical modification of wood is defined as chemical reactions involving functional groups of wood polymers and a simple single chemical reagent that form covalent bonds (Rowell 1991; Kumar 1994). Dicarboxylic acid anhydrides such as phthalic (PA), maleic (MA), and succinic (SA) anhydrides have been used to esterify the lignocellulosic materials to obtain thermoformable products (Hassan *et al.* 2000).

Lignocellulosic materials may be used as filler for polymer materials, which are characterized through increased water and fire resistance in comparison with wood (Rowell 1991; Lee *et al.* 2000). An attractive option for outdoor wood use is to prevent its photo-degradation through chemical modification by esterification or etherification (Matsuda 1996; Chang and Chang 2002; Chang and Chang 2006). Wood esterification has primarily focused on the use of anhydrides (Chang and Chang 2001), or fatty acids and acid chlorides (Prakash and Mahadevan 2008), to improve dimensional stability, preservation, wood thermoplastic-matrix compatibility, and photo-stability. Although this

subject has been investigated extensively (Evans 2009), relevant studies on photo-discoloration of modified wood surfaces are of great importance to protect products against weathering.

The esterification reaction applied to lignocellulosic materials may use different linear and cyclic anhydrides. The reaction between wood and linear anhydrides is a single site reaction yielding the corresponding carboxylic acid as a by-product of its reaction with wood. Figure 12 presents the reaction between wood and organic anhydrides (maleic and phthalic).

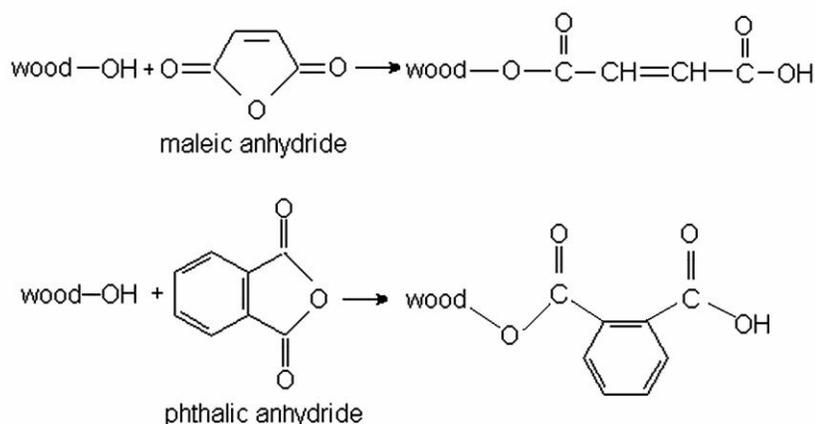


Fig. 12. Wood chemical modification by reaction with organic anhydrides

Roşu *et al.* (2010) demonstrated that succinic anhydride (SA)-modified softwood can be slightly more stable to the artificial light action than non-modified wood. The light with $\lambda > 300$ nm leads to significant changes in the structure of softwood samples.

Structural changes in softwood after chemical modification evidenced by FTIR spectroscopy are shown in Fig. 13.

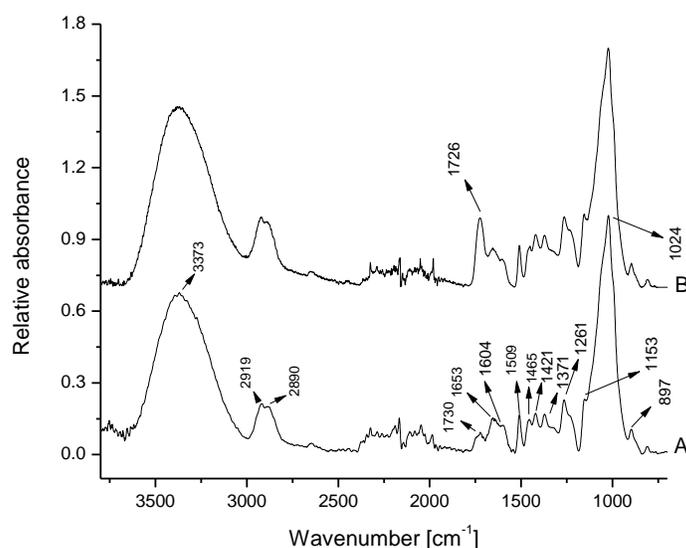


Fig. 13. FT-IR spectra: (A) etalon sample (*Abies alba* wood); (B) *Abies alba* wood sample esterified with succinic anhydride – adapted (Roşu *et al.* 2010)

The FTIR spectrum of non-modified wood samples (A) presents characteristic bands of wood. In the spectrum of the modified wood sample with succinic anhydride (spectrum B) the absorbance intensity at 1726 cm^{-1} significantly increases, evidencing wood reaction with succinic anhydride.

Figure 14 shows the difference between the absorbances of the non-irradiated softwood sample and the absorbances recorded after 200 h of irradiation from the FTIR spectra. The difference spectrum shows a positive signal at 1509 cm^{-1} , which can be assigned to the partial decomposition of lignin. The decomposition of lignin is also indicated by the reduction of the signals in the range $2300\text{ to }1900\text{ cm}^{-1}$.

The intensity of bands characteristic to the carbonyl groups with aliphatic structures at 1726 cm^{-1} and with aromatic conjugated ketones such as quinones at 1630 cm^{-1} were enhanced significantly with increasing irradiation time. UV light results in the decrease of the lignin content. Some chromophores with carbonyl groups are formed through lignin degradation.

In Fig. 14 the negative absorbance values correspond to the new structures that were formed during irradiation. The peaks from 3300 cm^{-1} to 3000 cm^{-1} and also at 1729 cm^{-1} , 1627 cm^{-1} , 1595 cm^{-1} , 1431 cm^{-1} , 1313 cm^{-1} , 1238 cm^{-1} , 1107 cm^{-1} , and 1056 cm^{-1} are signals corresponding to the oxidized lignin.

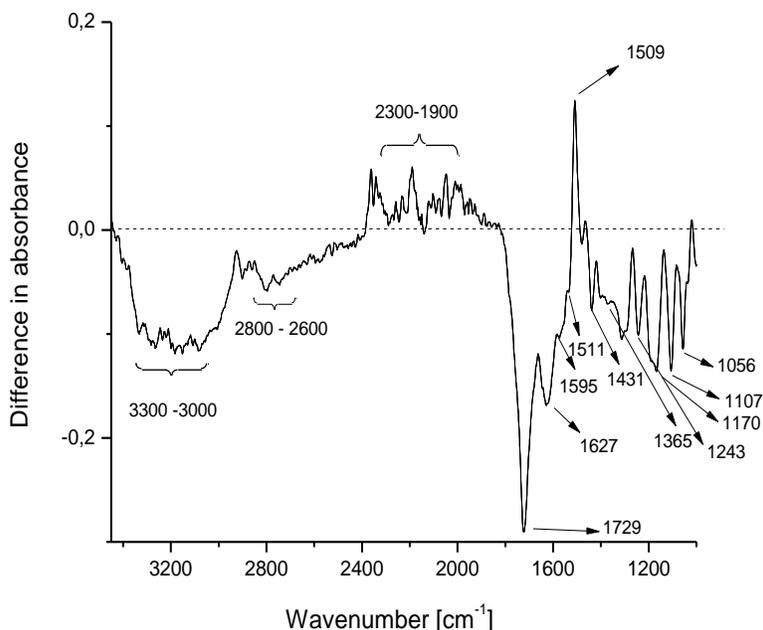


Fig. 14. FT-IR difference spectrum between the absorbance of non-irradiated, non-modified wood and the absorbance of wood recorded after 200 h of irradiation time – adapted (Roşu *et al.* 2010)

Changes in the lignin content during irradiation were monitored from the FTIR signals area ratio $[(A_{1509}/A_{897})_t]/[(A_{1509}/A_{897})_0]$ where “t” corresponds to the irradiated sample at different irradiation times and “0” corresponds to the non-irradiated sample. The photo-chemical decomposition of lignin in the non-modified and modified wood sample decreases as a function of irradiation time after an exponential law as shown in Fig. 15.

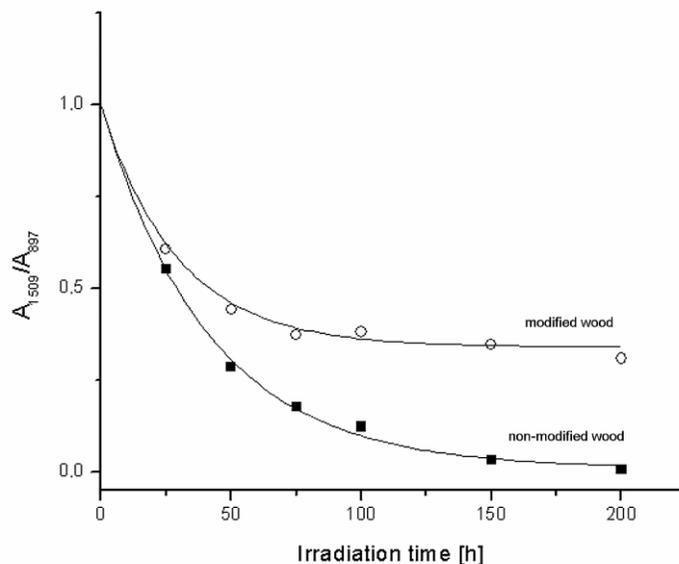


Fig. 15. Variation of lignin content as a function of irradiation time measured by the ratio between the absorbance values at 1509 cm^{-1} (A_{1509}) and 897 cm^{-1} (A_{897}) for non-modified and modified wood samples – adapted (Roşu *et al.* 2010)

Photo-chemical stability of the modified wood slightly increases with the increase in concentration of the succinic anhydride solution used in the esterification reaction. The decrease in photo-degradation in terms of reduced color changes on the surface of modified wood might be due to a slight increase in lignin stability to the polychromatic light action, induced by the esterification of wood with succinic anhydride (Roşu *et al.* 2010). Color changes and the lightness factor variation during irradiation are presented in Fig. 16 and Fig. 17, respectively.

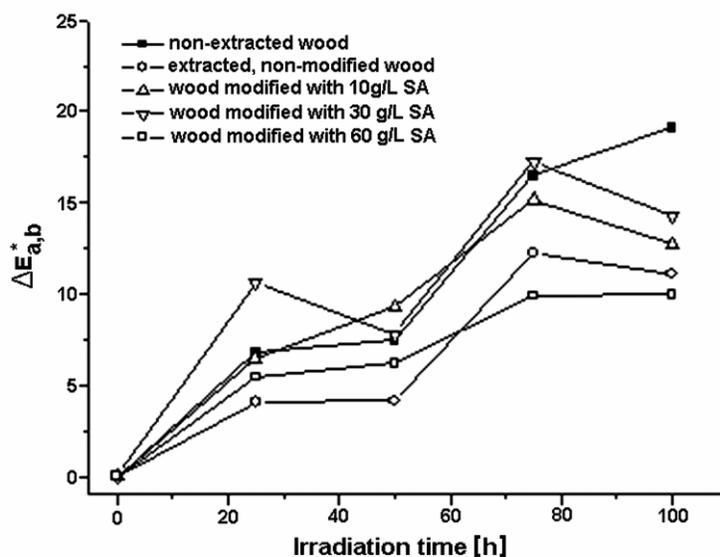


Fig. 16. Color change as a function of irradiation time: (■) non-extracted wood; (○) extracted, non-modified wood; (△) wood modified with 10 g/L SA; (▽) wood modified with 30 g/L SA; (□) wood modified with 60 g/L SA (Teacă *et al.* 2010)

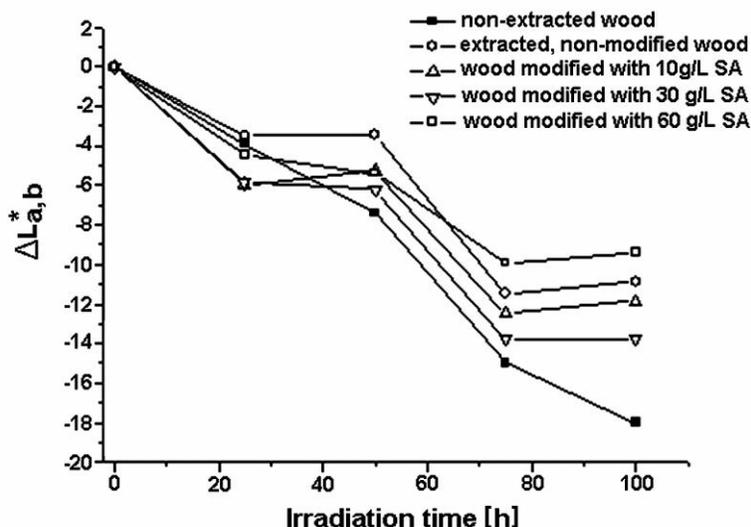


Fig. 17. Dependence of lightness factor on the irradiation time: (■) non-extracted wood; (○) extracted, non-modified wood; (△) wood modified with 10 g/L SA; (▽) wood modified with 30 g/L SA; (□) wood modified with 60 g/L SA (Teacă *et al.* 2010)

The negative value of ΔL^* for non-modified wood indicates that wood surface becomes darkened due to the UV light irradiation. The darkening of light irradiated surfaces of the non-modified wood might be due to degradation of lignin and other non-cellulosic polysaccharides (Hon and Chang 1984). The lignin decomposition during irradiation was delayed for esterified wood samples. The increase in esterification degree provided a better protection of wood exposed to artificial light.

CONCLUSIONS

1. Wood, a naturally occurring polymer composite, is the most versatile and widely used structural engineering material for indoor and outdoor applications. Due to its biological nature and aesthetic features, unprotected wood is susceptible to weathering and photo-oxidative degradation.
2. Deterioration of wood materials upon weathering involves a very complex process. Wood surface reactions initiated or accelerated by light can be manifested as discoloration, loss of brightness, and change in surface texture after artificial UV light irradiation or long-term solar irradiation.
3. The rate of discoloration depends upon light intensity and wavelength, and wood species. Changes in wood color reflect chemical changes during UV light irradiation. All wood polymers (cellulose, lignin, hemicelluloses) are capable of absorbing enough UV and VIS light to initiate wood photo-degradation, leading ultimately to changes in aesthetic, physical, chemical, and mechanical properties.
4. In order to prevent wood photo-induced discoloration, one or a combination of the following methods may be efficient as follows: cutting off UV light (by using UV absorbers), modification of wood light absorbing structures (by chemical treatments), destroying the structures involved in discoloration (*e.g.* acetylation

- combined with oxidative bleaching and treatment with NaBH₄), cutting off oxygen and capturing the singlet oxygen (*e.g.* by using wood in wood-plastic composites, or using various quenchers), scavenging free radicals (by using compounds with active hydrogen such as phenolic derivatives and phenolic amines), and use of solvents to extract and remove precursors to discoloration.
5. Our previous work has provided evidence that succinic anhydride modified wood becomes more stable to the artificial light action than non-modified wood. Modified wood samples have been further investigated after coating with epoxy functionalized soybean oil (ESO). Yellowing of wood surfaces indicates that lignin and hemicelluloses are modified, with occurrence of unstable products. The resulting chromophores vary in color, depending on the irradiation time and with the modification of the wood by coating with ESO.

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