

## PHOTO-DEGRADATION OF WATER BORNE ACRYLIC COATED MODIFIED AND NON-MODIFIED WOOD DURING ARTIFICIAL LIGHT EXPOSURE

Manabendra Deka<sup>a\*</sup> and Marko Petrič<sup>b</sup>

A series of experiments were carried out to investigate photo-degradation of thermally modified (at 210°C and minus 0.9 bars for two hours) and non-modified spruce wood [*Picea abies* L (Karst)], coated with transparent and semitransparent (with 3% pigment content) acrylic coatings during artificial UV light irradiation for 200 hours. Photo-degradation was evaluated in terms of colour changes throughout the irradiation period at an interval of 50 hours, along with IR and EPR spectroscopic study. One set of modified and non-modified woods was painted with coatings, while the other set was covered with free films made of coatings, just to simulate coated wood. The colour changes for both modified and non-modified wood samples without paint-coat or free film cover were comparable to that of wood samples with paint-coat and free film cover for transparent coat type, which indicated its ineffectiveness to prevent photo-degradation of wood underneath. However, the colour changes for both modified and non-modified wood samples with paint-coat and free film cover were much lower than those of samples without paint-coat or free film cover for semitransparent coat type, which might be due to hindrance of transmission of light energy through pigment to reach the underlying wood surface. On the other hand, whole substrate-coating system showed better photo-stability, when thermally modified wood was used as substrate. However, the colour changes of paint-coated and free-film covered samples for both modified and non modified woods might be due to colour changes of wood specimen underneath, because free films of both the coat types showed negligible colour change during UV irradiation.

*Keywords:* Thermal modification; Acrylic coating; Color stability; EPR spectroscopy; IR spectroscopy

*Contact information:* a: Dept. of Forest Products & Wood Technology, College of Forestry, Allahabad Agricultural Institute-Deemed University, Allahabad-211007, India; b: Department of Wood Science & Technology, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia; \*Corresponding author: [mdeka33@yahoo.co.in](mailto:mdeka33@yahoo.co.in), [mdeka33@rediffmail.com](mailto:mdeka33@rediffmail.com)

### INTRODUCTION

Although wood is a versatile material for many applications such as building, construction or furniture, yet there are some inherent drawbacks, including dimensional instability with change in moisture content, low resistance against fungi and insect's attack, low durability of many species, noticeable photo-yellowing, and unsatisfying mechanical strength properties of wood, which are often perceived as negative factors by the end users. A promising way to overcome these limitations is controlled modification of wood, followed by appropriate coating on it, resulting in value-added materials for

different constructions that still possess all of the natural inherent properties of solid wood.

If natural wood is exposed to solar radiation, the exposure leads initially to a fast colour change due to absorption of all wavelengths of electromagnetic radiation, and in the further stages to large chemical changes and breakdown of the surface layer (Ayadi et al. 2003; Hayoz et al. 2003). This complex degradation process in combination with exposure to precipitation, often described as weathering (Feist 1982), plays an important role in using wood as constructional material when exposed to outdoor conditions (Jirous-Rajkovic et al. 2004; George et al. 2005; Hansmann et al. 2006). The colour stability of natural wood to light exposure is an important issue from an aesthetic point of view. On exposure to light, some woods become bleached or grey, others turn yellow, red-orange, or brown colour, depending on the influence of their extractive compositions (Sandermann and Schlumbom 1962; Hon 2001; Kamdem and Grelier 2002).

The UV spectrum of solar radiation is one of the most effective amongst environmental factors that contribute to the weathering process of wood (Kalnins 1966; Futo 1974; Feist and Hon 1984; Ayadi et al. 2003). Although the UV spectrum represents only 5% of the energy in sunlight, yet its strong effect on the wood degradation process is well documented (Feist and Hon 1984; Hon 2001). In the case of light-irradiated wood, out of the total UV absorption coefficient, lignin contributes 80% to 95%, carbohydrate 5% to 20%, and extractives 2% (Norrstrom 1969). Mostly, the UV spectrum absorbed by the light-irradiated wood initiates photochemical reactions that ultimately may lead to wood discolouration and photo-degradation (Hon 1981; Hon 2001; George et al. 2005). Apart from decrease in methoxyl and lignin content, and increase in carboxyl groups (Leary 1967, 1968), photo-degradation also results in increase in cellulose and decrease in lignin concentration on wood surface (Wang and Lin 1991; Evans et al. 1992; Hon 1994; Hon 2001; George et al. 2005) and it ultimately leads to deterioration of some physical, chemical, and biological properties of natural wood.

Absorption of light by lignin leads to the formation of free radical species (presumably, phenoxyl radicals) of long lifetime (Lin and Kringstad 1970; Hon 1981; Hon and Feist 1981; Evans et al. 2002; Petrič et al. 2004). These free radicals react with oxygen readily to produce carbonyl and carboxyl chromophoric groups (Hon 1991; Hon and Feist 1992), which are responsible for wood's colour changes (Dirckx et al. 1987; Ayadi et al. 2003). It is well established that apart from sunlight and temperature, oxygen plays an important role in photo-degradation process of wood (Dirckx et al. 1987). Water is also considered to be a critical element in wood's photo-degradability (Hon 1973; Feist et al. 1991; Hon 2001; Hansmann et al. 2006).

To limit photo-degradation of wood, attempts have been made with different water- and solvent-borne coatings (Feist 1988; Tomazic 2006). Recently, water-borne clear coatings have drawn attention in wood industries. Design for unpainted wood in exterior construction has created a demand for clear coatings that preserve the natural beauty of wood (Yalinkilic et al. 1999). However, clear transparent coatings such as urethane and marine varnishes are not generally recommended for exterior use on wood, because they allow transmission of sunlight, and surface degradation can take place to the underlying wood (Evans et al. 1992; Maclead et al. 1995; Williams et al. 1996). As a result, the coatings can only impart superficial protection to wood against some

deteriorative agents for limited time, often less than 2 years (Williams et al. 1996). In our present experiment, an investigation was carried out to study the effect of two water-borne acrylic coatings (transparent without any pigment and semitransparent with 3% pigment) that have been commonly used for coating wood in exterior applications (Tomazic 2006), on photodegradation of non-modified and thermally modified wood during artificial UV light irradiation for 200 hours.

## EXPERIMENTAL

### Materials and Methods

#### *Wood samples*

Thirty test samples of size 50 mm × 10 mm × 50 mm (radial × tangential × longitudinal) were prepared from a single air-dried block of spruce [*Picea abies* L (Karst)] wood to ensure homogeneity. The samples were then placed in a climate chamber (25°C and 50% RH) for one week to have constant weight prior to treatment.

#### *Modification of samples*

The test wood samples were divided into two sets of fifteen each. One set of the samples was thermally modified continuously for 2 hours at constant temperature (210°C) in vacuum (-0.90 bar), while the other set was used as the non-modified control. The average weight loss of thermally modified samples was 2.5% – 3.0% on an oven-dry basis. After modification, all the samples were conditioned in a climate chamber as mentioned above along with non-modified samples, before coating and free filming with two different water-borne acrylic coats.

#### *Preparation of free coat film*

The free films of water-borne acrylic polymer with 30% solid content were prepared with the help of a 4-Sided Stainless Steel Film Applicator (Erichsen GMBH & CO KG, D-5870 Hemer, W. Germany) on smooth plastic paper. The speed of pulling the film applicator with gap-depth of 480µm was approximately 25 mm/s. Then, the free films were placed in climate chamber as mentioned above for one week. The free films were then peeled out of the smooth plastic paper with appropriate dimension to cover the test wood samples completely. The characteristic properties of the free films are summarised in Table 1.

**Table 1.** Characteristic Properties of Free Coat Film

Sl. No.	Polymer	Solvent	Pigment	Average dry-film thickness [µm]
1	Acrylic	Water	3 %	143.4
2	Acrylic	Water	Nil	144.8

#### *Coating of wood samples*

The coating of wood samples was carried out thrice with a brush to have an average coat mass of 90g/m<sup>2</sup> and 80g/m<sup>2</sup> for pigmented and transparent coats (purchased from market), respectively. Then, the coated samples were conditioned in a climate

chamber as mentioned above for one week. The average thickness of the coating layer on wood after drying in climate chamber was 143.5 $\mu$ m and 144.7 $\mu$ m for coat types 1 and 2, respectively.

#### *Artificial UV light irradiation*

The first 3/15<sup>th</sup> of test samples from each non-modified and thermally modified set was without any paint coat or free film cover. The second and third 3/15<sup>th</sup> of test samples were painted with coat type 1 and 2, respectively, while the rest fourth and fifth 3/15<sup>th</sup> of test samples were covered with free film made from coat types 1 and 2, respectively. Then the wood samples were irradiated with OSRAM ULTRA-VITALUX 300W Sunlamp equipped with UVA (315 – 400 nm) and UVB (280 – 315 nm) radiation of 13.6W and 3W, respectively at a distance of 50 cm. The samples were irradiated for 200 hours intermittently with a one-week break after each 50 hours of exposure for evaluation of properties. Thus, the values of different properties, recorded in our present experiment were the averages of 3 parallel measurements.

#### *Colour measurement*

The colour of light irradiated surfaces of the test samples was measured with an X-Rite SP Series Spectrophotometer (X-Rite Incorporated, S.W. Grandville, Michigan, USA). The reflection spectrum was acquired from a measuring spot of 20 mm in 390 nm – 710 nm regions. Three measurements at precisely defined spots on the irradiated surface of each samples were carried out after an interval of 50 hours throughout the experimental period. The colour changes were monitored with the help of L\* a\* b\* colour spaces before and after exposure to light as per the CIE (Commission Internationale de l'Eclairage) L\*a\*b\* system. Then, overall colour differences  $\Delta E^*$  were computed using the following expression (Brock et al. 2000).

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (1)$$

where,  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  are changes between the initial and final value of L\*, a\* and b\* values, respectively.

#### *Electron paramagnetic resonance (EPR) measurement*

EPR spectra for wood samples without paint coat or free film cover, and with free film covers were recorded at room temperature using a Bruker ESP-300 X-band spectrometer (Microwave Frequency = 9.62 GHz, Microwave Power = 20 mV, Modulation Frequency = 100 KHz, Modulation Amplitude = 0.1 mT). Two matchstick-like samples (30 mm  $\times$  1 mm  $\times$  1 mm) were cut from the corner of each sample and inserted one at a time in to the resonator. Intensities of the free radical signals were measured using a Bruker spectrometer software based on the mass of the matchstick-like samples. In such a narrow signal, as found for a free radical, the intensity of the signal corresponded well with the amount of free radicals in the wood (Schmid et al. 2000).

*FTIR spectroscopic measurement*

FTIR spectra of irradiated surfaces of modified and non-modified wood samples with and/or without paint coat or free film cover were recorded between 4000  $\text{cm}^{-1}$  and 450  $\text{cm}^{-1}$  using Perkin Elmer FTIR 1720 X Spectrometer. The reflectance spectra obtained, were then transformed in to Kubelka-Munk (K-M) units as a function of wave number averaged over 16 scans.

**RESULTS AND DISCUSSION****Non-Modified Wood**

The colour changes of non-modified wood with and/or without paint coat or free film cover, resulting from artificial UV light irradiation for different time period are presented in Tables 2 & 3 and Figs. 1 & 2. The overall colour changes ( $\Delta E^*$ ) of non-modified wood without paint coat or free film cover were increased from 0 to +17.5 compared to wood samples painted with coat 1 and covered with free film of coat 1, for which these values changed from 0 to +0.5 and 0 to +3.4, respectively (Fig. 1). The colour changes of wood samples painted with coat 1 and covered with free film of coat 1 were negligible compared to those of wood samples without paint coat or free film cover, which indicated that paint coat 1 and free film cover of coat 1 caused decrease in light energy to reach wood surface underneath, or caused prevention of the presence of oxygen and some other air-borne species participating in colour change reactions, during 200 hours of exposure. As a result of this, wood samples with paint coat and free film cover of coat type 1 showed resistance to photo-degradation during 200 hours exposure to artificial UV light. This effectiveness of coat type 1 to prevent photo-degradation of underlying wood substrates might be due to presence of pigment in the coat system.

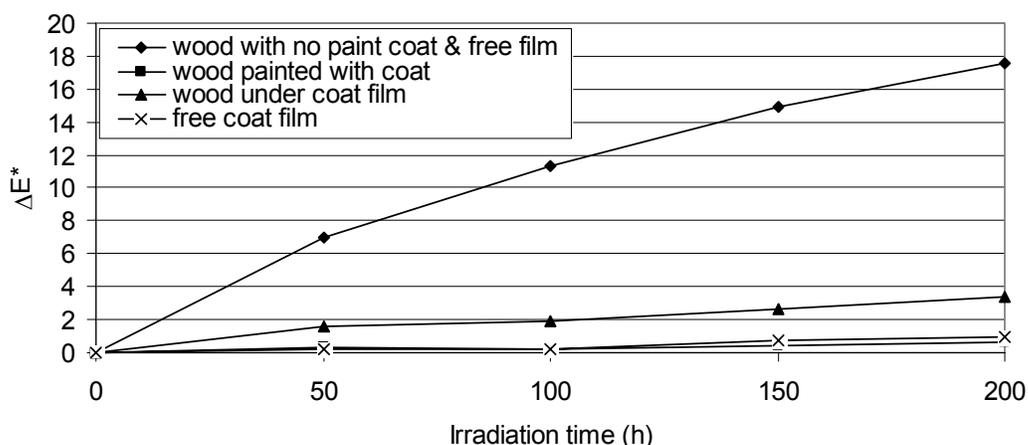
**Table 2.** Changes in Chromaticity of Non-modified Wood with and/or without Paint Coat and Free Film Cover for Semitransparent Coat Type (Coat 1) after 200 h of Irradiation

Samples	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
Free Film	-0.6	-0.1	-0.7
Wood without paint coat & free film	-8.2	5.5	14.5
Wood with paint coat	-0.04	0.2	0.5
Wood under free film	-0.7	-0.3	3.3

**Table 3.** Changes in Chromaticity of Non-modified Wood with and/or without Paint Coat and Free Film Cover for Transparent Coat Type (Coat 2) after 200 h of Irradiation

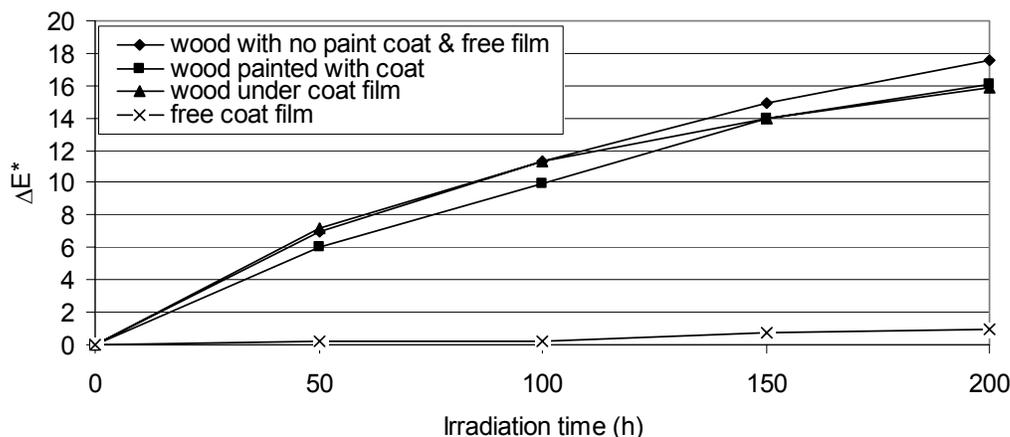
Samples	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
Free Film	-0.4	-0.3	0.8
Wood without paint coat & free film	-8.2	5.5	14.5
Wood with paint coat	-6.2	3.6	14.4
Wood under free film	-7.9	5.3	12.7

However, the colour changes of wood samples painted with coat 2 (from 0 to +16.1) and covered with free film of coat 2 (from 0 to +15.9) were comparable to the colour change of wood samples without paint coat or free film cover (Table 3 and Fig. 2). Like coat type 1, the colour changes of free film of coat type 2 were negligible compared to those of wood samples without paint coat or free film cover, and with paint coat and/or free film cover (Tables 2 & 3 and Figs. 1 & 2). This indicated that colour changes of wood samples painted with coat 2 and covered with free film of coat 2 were due to the wood substrate underneath, which are not protected by paint coat 2 or free film cover of coat 2 against photo-degradation. Therefore, we can come to conclusion that the transparent coat (coat 2) cannot prevent photo-degradation of wood underneath during exposure to UV light for 200 hours. The fact that a clear acrylic coating and free film made of it did not affect photo-degradation of wood underneath was also reported by Chang and Chou (1999), which support our present findings. The negative value of  $\Delta L^*$  for all the substrate types of non-modified wood indicates that UV light irradiation darkened (Hansmann et al. 2006; Deka et al. 2008) the wood surface (Table 2 & 3).



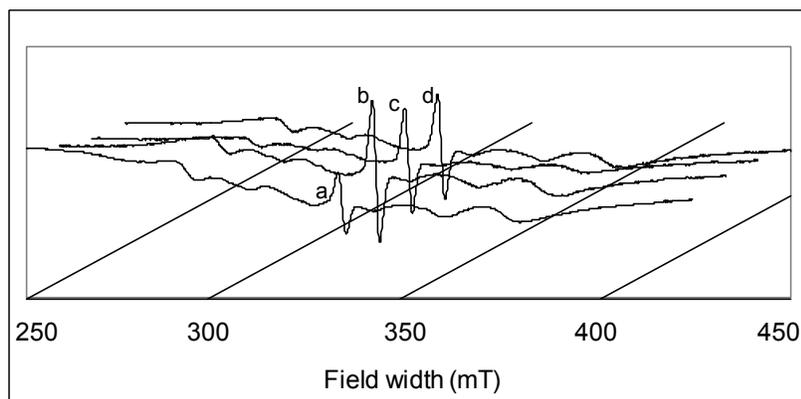
**Fig. 1.** Colour changes of non-modified wood with and/or without paint coat and free film cover of semitransparent coat type (Coat 1) during UV light irradiation for different time periods

The darkening of light-irradiated surfaces of all the non-modified wood substrate types, irrespective to coat type used, might be due to degradation of lignin and other non-cellulosic polysaccharides (Hon and Chang 1985; Grelier et al. 2000; Petrič et al. 2004). The significant increase in the chromaticity coordinates,  $\Delta a^*$  and  $\Delta b^*$  for all the wood substrate types with respect to coat type 2 indicated yellowing and reddishness of the same due to exposure to UV light (Table 3). This can be attributed to the formation of quinones and quinone-like structures due to depolymerisation and oxidation of lignin involving free radicals (presumably, phenoxyl radicals) in this process (Kamdern and Grelier 2002; Ayadi et al. 2003).



**Fig. 2.** Colour changes of non-modified wood with and/or without paint coat and free film cover of transparent coat type (Coat 2) during UV light irradiation for different time periods

The fact that the changes of colour of the exposed wood surfaces could be due to the involvement of free radical reactions was proved by the detection of free-radical signals in EPR spectra of non-modified wood (with or without free film cover of coat type 1 and 2) after exposure to light for 200 hours (Fig. 3). The intensity of the EPR free radical signal was greater for wood samples without paint coat and free film cover, followed by wood samples under free film cover of coat 2, and free film cover of coat 1 (Fig. 3).



**Fig. 3.** EPR spectra of non-modified wood before and after irradiation to UV light for 200 hours [a] wood before irradiation; b) wood after irradiation without paint coat or free film cover; c) wood after irradiation under free film of coat 2 and d) wood after irradiation under free film of coat 1].

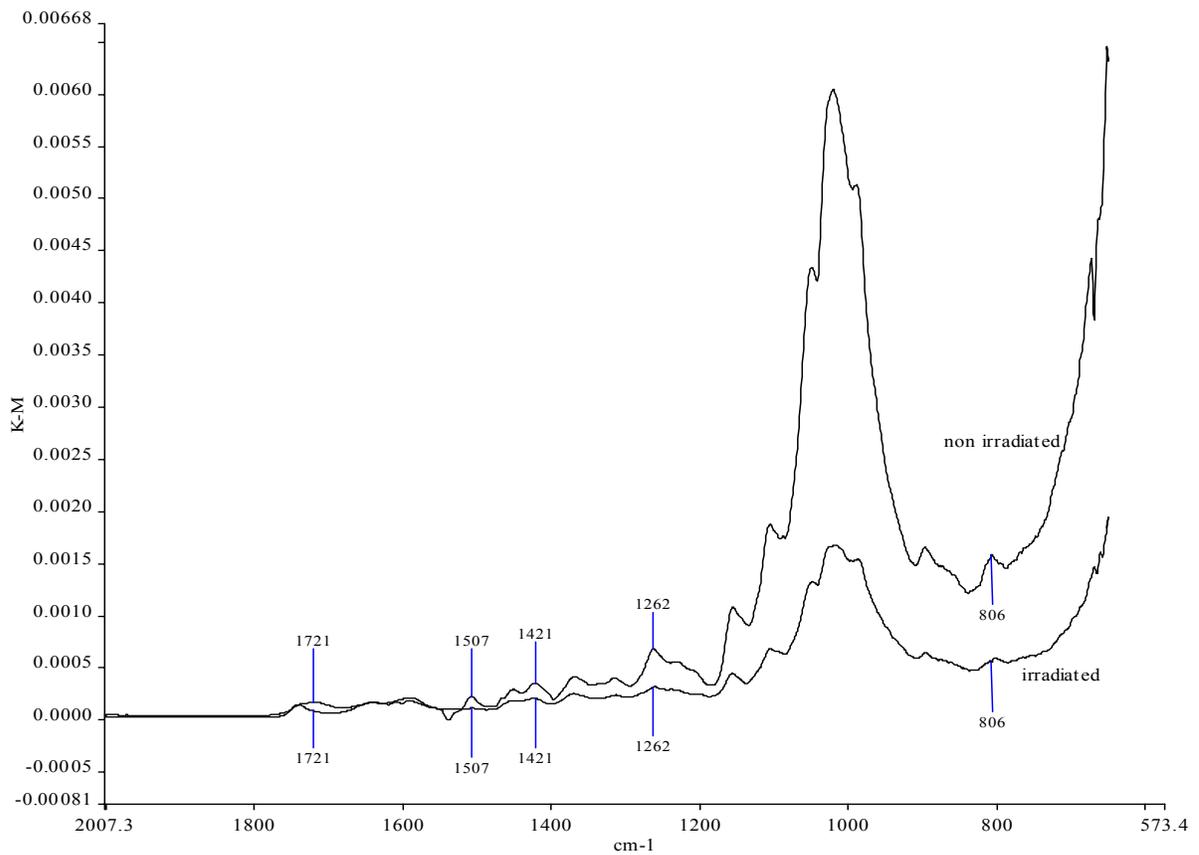
The chemical changes occurring in non-modified wood during light exposure, which ultimately resulted colour changes in our present study, can also be well explained with the help of IR spectroscopic study. Figure 4 shows the chemical changes of non-modified wood surfaces due to UV light irradiation. It is apparent from the IR spectra that light-irradiated wood surfaces showed decrease in absorption bands at around  $1507\text{ cm}^{-1}$ ,

1262  $\text{cm}^{-1}$ , and 1035  $\text{cm}^{-1}$ . The absorption bands at around 1507  $\text{cm}^{-1}$ , 262  $\text{cm}^{-1}$ , and 1035  $\text{cm}^{-1}$  are due to benzene ring stretching vibration in lignin,  $-\text{C}=\text{O}$  group stretching vibration in lignin, and  $-\text{C}=\text{O}$  group stretching vibration in cellulose, hemicellulose and lignin, respectively (Harrington et al. 1964). The decrease in absorption bands at these wavelengths reveals degradation (loss) of lignin, cellulose, and hemicellulose (Ohkoshi 2002; Petrič et al. 2004). Likewise, a weak band of light irradiated samples compared to non irradiated samples at 1421  $\text{cm}^{-1}$  was due to  $-\text{CH}_2$  deformation vibration in lignin and xylane, and benzene ring vibration in lignin. Again, strengthening of the band at 1721  $\text{cm}^{-1}$  for irradiated wood can be attributed to the formation of non-conjugated carbonyl groups and degradation of lignin (Ohkoshi 2002). The light-irradiated samples also showed reduction in intensity of absorption band at around 806  $\text{cm}^{-1}$ , which might be due to degradation of non-cellulosic polysaccharides, the hemicelluloses (Harrington et al. 1964).

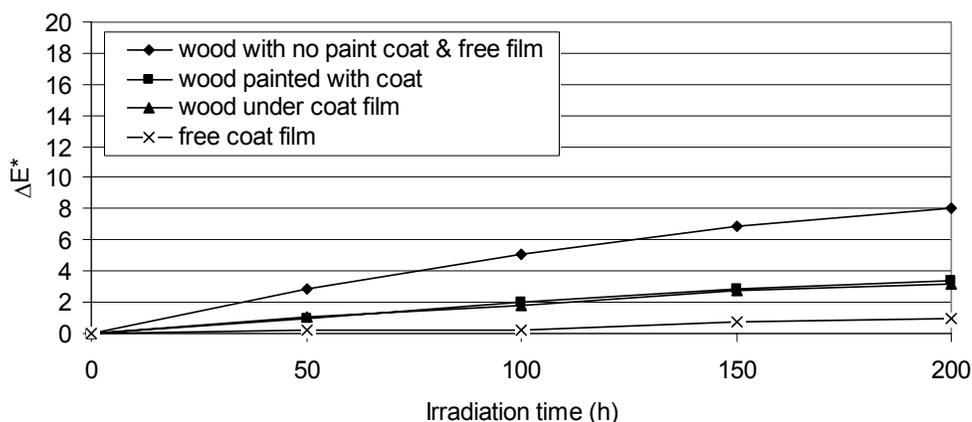
### Thermally Modified Wood

The colour changes of thermally modified wood with and/or without paint coat or free film cover along with free film resulting from UV light irradiation for different time periods are presented in Tables 4 & 5 and Figs. 5 & 6. The overall colour changes ( $\Delta E^*$ ) of thermally modified wood without paint coat and free film cover was increased from 0 to +8.0 compared to wood samples painted with coat 1 and covered with free film of coat 1, for which these values changed from 0 to +3.3 and 0 to +3.2, respectively (Table 4, Fig. 5). The colour changes of wood samples under paint coat 1 and free film of coat 1 were very low compared to those of wood samples without paint coat or free film cover, which indicated that paint coat 1 and free film cover of coat 1 caused decrease in light energy reaching the wood surface underneath, or caused prevention of the presence of oxygen and some other air-borne species participating in colour change reactions, during 200 hours of exposure. As a result of these, wood samples of paint coated and free film covered with coat type 1 showed resistance to photo-degradation during 200 hours of light exposure. This effectiveness of coat type 1 to prevent photo-degradation of wood samples underneath might be due to presence of pigment in the coat substrate.

However, the colour changes of wood samples painted with coat type 2 (from 0 to +11.1) and covered with free film of coat type 2 (from 0 to + 6.8) were comparable to the colour change of wood samples without paint coat or free film cover (Table 5 and Fig. 6). Like coat type 1, the colour changes of free film of coat type 2 were negligible compared to that of wood samples without paint coat or free film cover, and with paint coat and/or free film cover (Tables 4 & 5 and Figs. 5 and 6). This indicated that colour changes of wood samples under paint coat type 2 and free film of coat type 2 were due to the wood specimens underneath, which are not protected by paint coat 2 or free film cover of coat type 2 against photo-degradation. Therefore, we can come to conclusion that transparent coat type 2 cannot prevent photo-degradation of wood underneath during exposure to UV light in case of thermally modified wood also. However, the thermally modified wood showed better photo-stability than that of non-modified wood for the transparent coat type (Figs. 2 & 6).



**Fig. 4.** IR spectra of untreated wood samples before and after 200 hours of artificial UV light irradiation



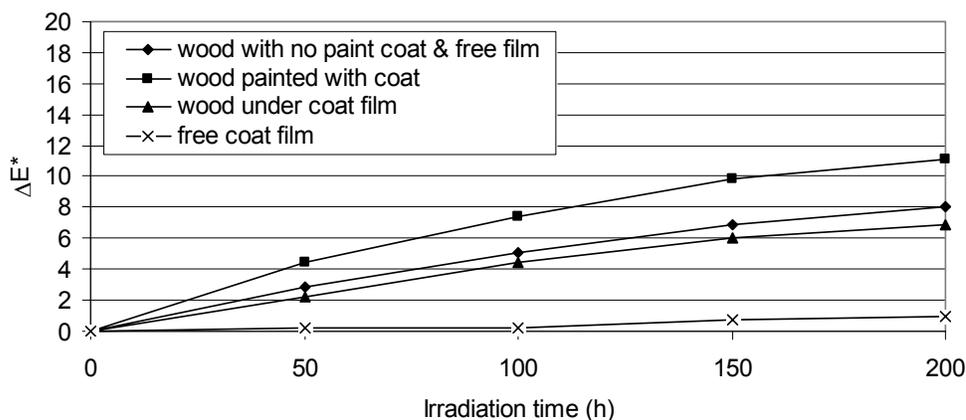
**Fig. 5.** Colour changes of modified wood with and/or without paint coat and free film cover of semitransparent coat type (Coat 1) during UV light irradiation for different time periods

**Table 4.** Changes in Chromaticity of Modified Wood with and/or without Paint Coat and Free Film Cover for Semitransparent Coat Type (Coat 1) after 200 h of Irradiation

Samples	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
Free Film	-0.6	-0.1	-0.7
Wood without paint coat & free film	6.2	-0.8	5.0
Wood with paint coat	1.9	-1.3	2.4
Wood under free film	2.3	-0.4	2.2

The better photo-stability of thermally modified wood compared to non-modified wood might be due to increase in lignin stability by condensation during the thermal modification process (Ayadi et al. 2003). They reported that thermal modification process of wood caused lignin condensation at 170°C, which even increased with increase in temperature up to 240°C.

That the clear acrylic coating and free film made of it did not affect photo-degradation of wood underneath was also reported by Chang and Chou (1999), which support our present findings. Unlike non-modified wood, the thermally modified wood showed much lower darkening during UV light exposure. The changes in chromaticity coordinates,  $\Delta a^*$  and  $\Delta b^*$  of modified wood substrate systems, irrespective to coat type, were much lower, which indicates better photo-stability of thermally modified wood compared to non-modified samples (Tables 2, 3, 4, & 5). But still, there was some degree of colour changes for modified wood during UV light exposure.

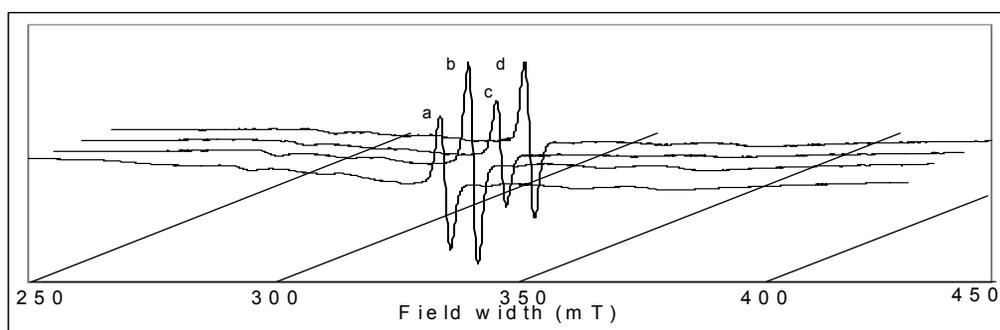


**Fig. 6.** Colour changes of modified wood with and/or without paint coat and free film cover of transparent coat type (Coat 2) during UV light irradiation for different time periods

**Table 5.** Changes in Chromaticity of Modified Wood with and/or without Paint Coat and Free Film Cover for Transparent Coat Type (Coat 2) after 200 h of Irradiation

Samples	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$
Free Film	-0.4	-0.3	0.8
Wood without paint coat & free film	6.2	-0.8	5.0
Wood with paint coat	9.1	-2.0	6.1
Wood under free film	5.1	-0.8	4.4

The fact that the colour changes of modified wood occurred as a result of irradiation is revealed from the involvement of free radical reactions, which was proved by the detection of free radical signals in EPR spectra (with or without free film covers of coat 1 and 2) after exposure to light for 200 hours (Fig. 7). The intensity of the EPR free radical signal was more for wood samples without coat paint and free film cover followed by wood samples under free film of coat 2 and free film of coat 1 (Fig. 7).

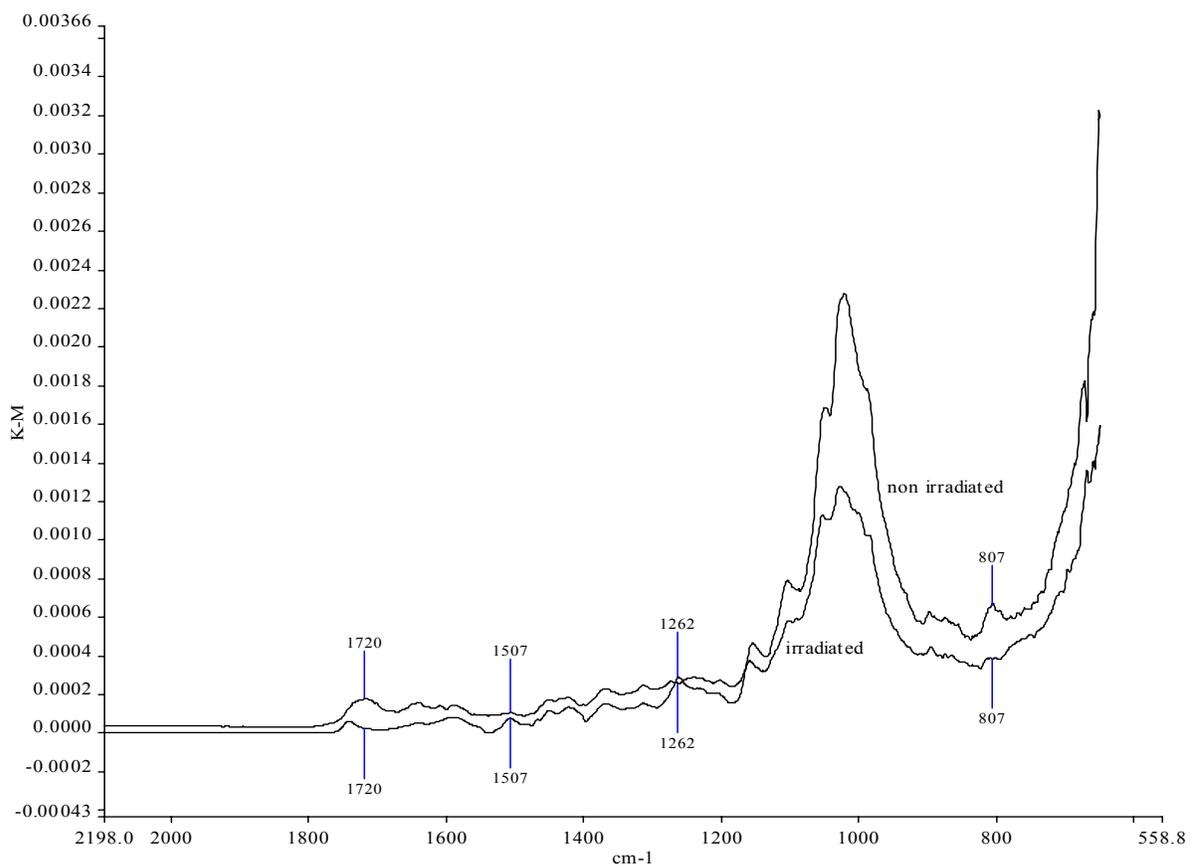


**Fig. 7.** EPR spectra of thermally treated spruce wood before and after irradiation to UV light for 200 hours [a) wood before irradiation; b) wood after irradiation without paint coat & free film cover; c) wood after irradiation under free film of semitransparent coat (coat type 1) and d) wood after irradiation under free film of transparent coat (coat type 2)].

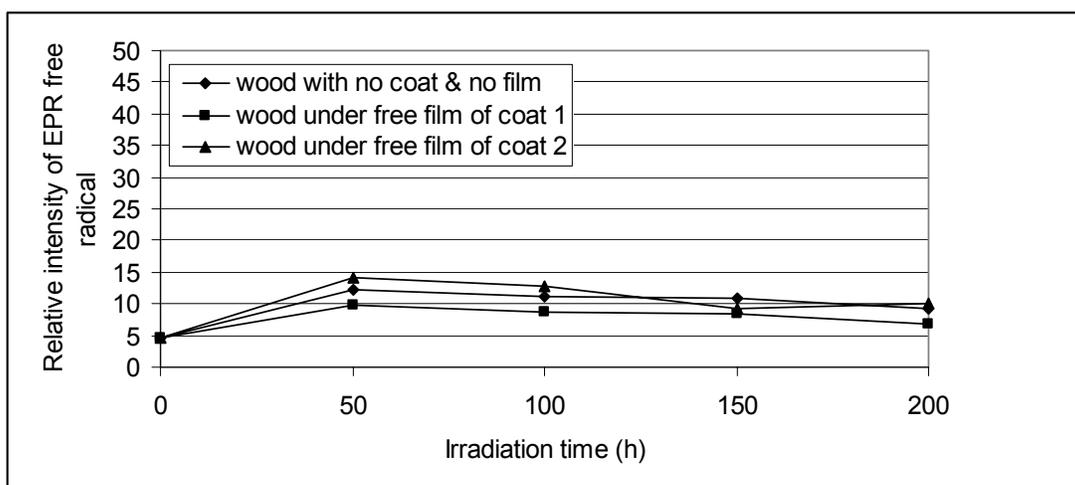
The chemical changes that occurred in thermally modified wood samples during light exposure could also be well explained with the help of IR spectroscopic data (Fig. 8). Although the colour change of thermally modified wood during UV light exposure was much lower than that of non-modified wood in our present study, yet some degree of colour change was still occurring. It is apparent from the IR spectra that light-irradiated wood surfaces of thermally modified wood showed similar changes as non-modified wood but less pronounced, indicating that there was still some degradation of lignin and non-cellulosic polysaccharides, and formation of non conjugated carbonyl groups, that ultimately resulted in some degree of colour changes to light irradiated wood. Also, an increase of free radical production was detected in modified wood after light irradiation, which might involve in the colour changes of wood surface exposed to UV light (Figs. 9 & 10). From Figs. 9 & 10 it is also evident that the intensity of the EPR signal in modified wood was higher than non-modified wood, which indicates formation of free radicals during thermal modification process of wood, which is in accordance with previous results (Petrič et al. 2004; Deka et al. 2008). These free radicals, which are generated during the thermal modification process, may also be expected to take part in colour changes, combined with the effects of subsequent free radicals generated during UV light exposure.

## CONCLUSIONS

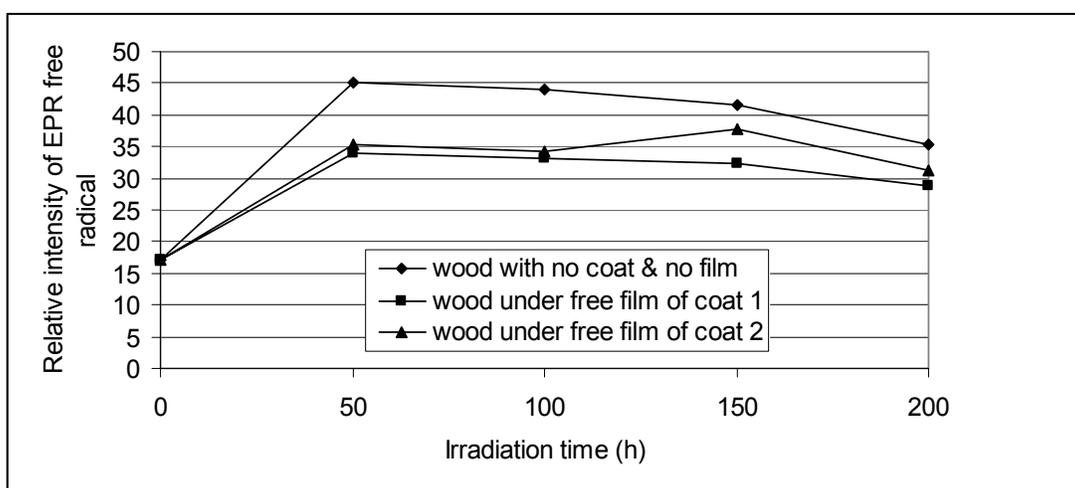
Coating wood with water-borne transparent acrylic coating is not effective against photo-discolouration. On the contrary, the semitransparent acrylic coating is found to be effective against photo-degradation, which might be due to pigment present in it, which restrict transmittance of UV light to wood surface, underneath. It is therefore important to reduce light energy reaching the wood surface with coating to prevent its photo-degradation. This experiment encourages the use of UV light absorber in the coat, which screens UV light without affecting natural colour of coating. In agreement with earlier research work, thermal modification of wood followed by appropriate coating system may be feasible industrially to protect wood against photo-degradation and thereby to increase its life time.



**Fig. 8.** IR spectra of thermally modified wood samples before and after 200 hours of artificial UV light irradiation



**Fig. 9.** Relative intensity of EPR free radical of non-modified wood after exposure to UV light for different time periods



**Fig. 10.** Relative intensity of EPR free radical of thermally modified wood after exposure to UV light for different time periods

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