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Invited feature article

## Temperature dependence of wood photodegradation monitored by infrared spectroscopy

Denes Varga<sup>a</sup>, Laszlo Tolvaj<sup>a,\*</sup>, Satoru Tsuchikawa<sup>b</sup>, Laszlo Bejo<sup>c</sup>, Edina Preklet<sup>a</sup><sup>a</sup> Institute of Physics and Electrotechnics, University of Sopron, HU-9400 Sopron, Bajcsy u. 4., Hungary<sup>b</sup> Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan<sup>c</sup> Institute of Wood Based Products and Technologies, University of Sopron, HU-9400 Sopron, Hungary

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## ABSTRACT

The temperature dependence of the photodegradation of hardwoods (beech, *Fagus sylvatica* L. and poplar, *Populus x euramericana* cv. *Pannonia*) and softwoods (Scots pine, *Pinus sylvestris* L. and spruce, *Picea abies* Karst.) was investigated. Samples were irradiated by a strong UV emitter mercury lamp at 30 °C, 80 °C, 120 °C and 160 °C. A series of samples was treated in the same chamber set to 30 °C, 80 °C, 120 °C and 160 °C but without light irradiation (pure thermal treatment). The chemical changes were detected by infrared spectroscopy. The same light irradiation generated much greater absorption change at 160 °C than at 30 °C. The simultaneous thermal and UV treatment generated much greater absorption increase in the whole investigated infrared region than the sum of absorption increases generated by the individual thermal treatment and UV radiation, separately. Softwoods were more sensitive to the light irradiation at elevated temperatures than hardwoods. Results revealed that four bands around 1770, 1750, 1720 and 1690 cm<sup>-1</sup> emerged in the unconjugated carbonyl region as a result of the UV irradiation at elevated temperatures. The intensity change of these bands is highly dependent on the wood species. Absorption increase was found at 1066 and 1035 cm<sup>-1</sup>.

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### 1. Introduction

Wood is a unique material that combines light weight with excellent physical and mechanical characteristics. Its colour ranges from red to yellow, and grants a feeling of warmth. The cellular components of wood combine to form a cylindrically layered composite, which, when cut tangentially, exhibits a unique pattern of the alternating colours of earlywood and latewood. This unique coloured surface texture is sensitive to light and heat. The most sensitive molecules are the lignin macromolecules and most types of extractives. The extractives are the basic colorant molecules determining the natural colour of wood. The extractives and the hemicelluloses are sensitive to heat treatment [1,2]. The presence of moisture amplifies this sensitivity [3–5].

The photodegradation of wood is a widely investigated phenomenon. During outdoor exposure, sunlight proved to be the main factor inducing the most significant alteration in the colour of wood [6]. The surface starts yellowing and eventually turns grey [7]. Chemical analyses show that the deterioration is

related primarily to the decomposition of lignin. The chromophoric groups of lignin are strong UV light absorbers [8–12]. The energy of absorbed UV photons is large enough to create free phenoxyl radicals. These free radicals react with oxygen to generate carbonyl chromophoric groups. These chromophore groups are partly responsible for the colour change of wood [8–14]. The degradation products of lignin are responsible for the yellowing of the surface [15,16].

Infrared (IR) studies reflect the chemical changes more clearly than the colour measurements do. After UV light irradiation, the usual changes include the carbonyl band increase between 1680 and 1900 cm<sup>-1</sup>, the decreases of the aromatic skeletal vibration arising from lignin (1510 cm<sup>-1</sup>) together with the guaiacyl vibration at 1275 cm<sup>-1</sup>. The band for the skeletal vibration of syringyl lignin at 1600 cm<sup>-1</sup> also decreases in the case of hardwoods [17–20].

The combined effect of two or more parameters has been rarely examined during wood degradation. Matsuo et al. [21,22] investigated the time-temperature superposition during thermal degradation of wood in the temperature range 90–180 °C. Xu et al. [23] investigated the hygrothermal discoloration of coloured high-density polypropylene-wood composites. A single horizontal shift was found to be adequate for the superposition of colour

\* Corresponding author.

E-mail address: [tolvaj.laszlo@uni-sopron.hu](mailto:tolvaj.laszlo@uni-sopron.hu) (L. Tolvaj).

parameter master curves, indicating that the temperature can be used as accelerating factor to the discoloration of the studied wood plastic composites.

The effect of elevated temperature during photo-irradiation (the superposition of light irradiation and thermal treatment) is not investigated frequently, either even though the surface temperature of wood is rising considerably during light irradiation. Persze and Tolvaj [24] irradiated wood samples using a mercury vapour lamp at 80 °C and at 30 °C to screen out the discoloration effect of thermal decomposition during photodegradation. Results demonstrated that the same light irradiation resulted in considerably greater redness increase at 80 °C than at 30 °C. The extractive content was found to have an important role in thermal decomposition during photodegradation. Tolvaj et al. [25] investigated the photodegradation behaviour of conifers and deciduous species at elevated (80 °C) and ambient (30 °C) temperatures by IR spectroscopy. An intensive UV emitter mercury lamp was used for irradiation. The results show considerably larger degree of degradation at 80 °C than at 30 °C. The difference spectrum method revealed the absorption increase of tree different types of carbonyl groups caused by the photodegradation and oxidation at 80 °C. Remarkable differences were found between the photodegradation behaviour of softwoods and hardwoods. Anatomically poplar belongs to the hardwood group's but its photodegradation properties were between those of hardwoods and softwoods.

Mitsui and Tsuchikawa [26] irradiated wood samples that were kept in a conditioning chamber set to -40 °C. They concluded that the measured degradation was much smaller at -40 °C than at usual laboratory conditions.

Conifers and deciduous wood species were irradiated by strong UV emitter mercury lamp at elevated temperatures up to 160 °C and the colour change was monitored [27]. Results showed that UV light irradiation produced more intense discoloration at elevated temperatures above 80 °C than at ambient temperature. The combined light irradiation and thermal treatment at 160 °C generated much larger discoloration than the sum of the discoloration data produced by UV light irradiation at 30 °C and by pure thermal treatment at 160 °C. The simultaneous impact of heat and light did not only cause a simple superposition of the two effects, but the elevated temperature intensified the effect of photodegradation. Red hue shift showed the greatest difference.

The aim of this study was to investigate the chemical changes in wood due to photo-irradiation at elevated temperatures using diffuse reflectance IR spectroscopy. To assess the influence of heat during photodegradation, samples were irradiated by UV light at 30 °C, 80 °C, 120 °C and 160 °C. The thermal treatment and the light irradiation were simultaneous in our study, the same way it happens in nature. The elevated temperature generates higher vibration energy, thus the photons are able to split chemical bonds more easily than at ambient temperature. A surface temperature of 80 °C, however, may actually occur during the summer, provided that the wood sample is dark enough. Higher temperatures are only important from a theoretical point of view when investigating wood photodegradation.

## 2. Materials and methods

Both hardwood and softwood species were chosen for the test. The investigated hardwoods samples were beech (*Fagus sylvatica* L.) and poplar (*Populus x euramericana* cv. *Pannonia*). Softwoods included Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst.). The samples of different series were prepared from the same board with dimensions of 30 mm × 10 mm × 5 mm (long × tang × rad.). All species were represented by 2 samples, and 2 points of fixed locations were measured on each sample. A double mercury vapour lamp as a strong UV light emitter, provided

the irradiation. The total electric power of the applied double mercury lamps was 800 W, and the distance between the samples and the lamps was 64 cm. The UV radiation was 80% of the total emission (31% UV-A, 24% UV-B and 25% UV-C). The irradiation chamber was set to 30 °C, 80 °C, 120 °C and 160 °C, respectively, for testing at various temperature conditions. The effectiveness of irradiation was tested on spruce samples. The irradiation was interrupted after 1; 2; 7 and 16 h to measure the IR spectra. The results demonstrated that 16 h light irradiation is enough to generate measurable changes. Another series of samples were treated in the same chamber set to 30 °C, 80 °C, 120 °C and 160 °C but without light irradiation. The effect of thermal degradation was determined based on this latter experiment. The total light irradiation/heat treatment time was 16 h in all cases.

All the IR measurements were performed on the tangential surfaces of the specimens. The surface of spruce and Scots pine samples contained only earlywood. The diffuse reflectance infrared Fourier transform (DRIFT) spectrum of the samples was measured before and after irradiation. Before all IR measurements, samples were stored for 3 days in the same laboratory in total darkness, to ensure equal moisture content for all measurements. Measurements were carried out using an IR spectrophotometer (JASCO FT/IR 6300). The resolution was 4 cm<sup>-1</sup> and 64 scans were obtained and averaged. The background spectrum was obtained against an aluminium plate. The spectral intensities were calculated in Kubelka-Munk (K-M) units. Two-point baseline correction at 3800 cm<sup>-1</sup> and at 1900 cm<sup>-1</sup> was carried out. The intensity of spectra were normalised to the band maximum at around 1375 cm<sup>-1</sup>. The intensity of spectra was adjusted to 1.0 by this normalisation at maximum around 1375 cm<sup>-1</sup>. This C—H band of cellulose is often used as internal standard because of its high intensity, central position and strong stability. The difference spectrum was calculated by subtracting the initial IR data from the data of irradiated sample. In this case the absorption increase is represented by a positive band while a negative band represents the absorption decrease. Details are in Ref. [3].

## 3. Results and discussion

Infrared spectroscopy is a useful method for studying chemical changes. It is extensively used to highlight alterations in the surface chemistry of photodegraded and thermally degraded wood [8–12,26]. It provides information related to the surface layer affected by the light irradiation. The fingerprint area (900–1900 cm<sup>-1</sup>) of all investigated species is presented in this work because the main differences were found in this region. The other IR area (2600–3800 cm<sup>-1</sup>) is presented only for Scots pine and beech. The fingerprint region consists of the highly overlapped absorption bands of lignin, cellulose and hemicelluloses. The band assignment can be found in Table 1.

The effects of photodegradation are represented in this work by the difference spectra. Fig. 1 represents the difference IR spectra of spruce caused by mercury lamp irradiation at 160 °C as function of irradiation time. For comparison, Fig. 1 shows the difference IR spectrum of spruce generated by the same light source at 30 °C during 16-h treatment as well. The effect of shorter exposure at 30 °C is not presented because the changes were minor.

Most of absorption changes increased rapidly by increasing irradiation time, at 160 °C. The absorption at 1510 cm<sup>-1</sup> decreased representing the degradation of guaiacyl lignin. This negative peak is evident together with the absorption decrease of the aromatic C—H deformation at 1469 and 1428 cm<sup>-1</sup> and with the absorption decrease of the guaiacyl ring breathing at 1267 cm<sup>-1</sup>. As a consequence, the unconjugated carbonyl band increased between 1680 and 1820 cm<sup>-1</sup>. This band consists of two visible bands and a shoulder at 1740, 1724 and 1690 cm<sup>-1</sup>, respectively. These bands

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