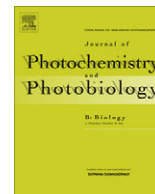




Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Photodegradation of wood at elevated temperature: Infrared spectroscopic study

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ARTICLE INFO

Article history:

Received 21 December 2012

Received in revised form 1 February 2013

Accepted 4 February 2013

Available online 16 February 2013

Keywords:

Wood

Photodegradation

Thermal degradation

Infrared spectrum

ABSTRACT

The purpose of this investigation was to evaluate the effect of elevated temperature on the photodegradation of solid wood. The work presented here, deals with the changes of infrared spectrum generated by the photodegradation process. Wood samples were irradiated with a mercury vapour lamp. The photodegradation behaviours of conifers and deciduous species were studied at elevated (80 °C) and at ambient (30 °C) temperatures. The infrared data were analysed using the difference spectrum method. The properly calculated difference spectrum gave much more information about the chemical changes than the visual comparison of the absorption spectra measured before and after the irradiation. The results showed considerably greater degradation at 80 °C than at 30 °C. The difference spectra revealed the absorption increase of tree different types of carbonyl groups. Remarkable differences were found between the photodegradation behaviours of softwoods and hardwoods. Poplar belongs anatomically to the hardwoods but its photodegradation properties were between that of hardwoods and softwoods.

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1. Introduction

The unique formations of the woody tissues offer their excellent mechanical and physical properties. The combination of cellulose biopolymer and lignin macromolecule naturally arranged into tubular structures and eventually forms a cylindrically layered composite; this is the solid wood. The colour hue of wood between red and yellow grant the feeling of warmness. Additionally, the machined surfaces of the different species include lots of micro mirrors aligned parallel to the grain. Gloss from these micro mirrors gives us more elegant, soft, natural and beautiful texture than that of plastics and metal [1]. This wonderful surface texture is rapidly degraded during weathering.

The chemical components of solid wood are sensitive to light and heat. The most sensitive molecule is the lignin macromolecule because it is good ultraviolet (UV) light absorber. Chemical analyses showed that the deterioration is primarily related to the decomposition of lignin [2–8]. The energy of the absorbed UV photons is large enough to create free phenoxyl radicals. These free radicals react with oxygen to produce carbonyl chromophoric groups [3–9]. The photodegradation causes absorption changes in the whole visible wavelength region creating the colour change [10–12]. These alterations are primarily attributable to the decomposition of lignin and the extractives. The degradation of lignin can be monitored by infrared (IR) spectroscopy. The chemical changes of extractives cannot be traced by IR spectroscopy because of their

low level quantity. Measuring the colour change can be followed the alterations of extractives.

The effect of elevated temperature during photo-irradiation is a hardly investigated phenomenon; however the surface temperature of wood rises considerably through the irradiation process. Mitsui et al. [13–16] found that the combination of light and heat treatment (light irradiation was followed by heat treatment) creates even more discolorations than the separate light or heat exposures do. The colour change caused by heat treatment was much greater after light irradiation than without it. The change of IR spectrum showed different alterations. The intensity of carbonyl groups (that increased with light irradiation) decreased with humid heat treatment. The increment of two carbonyl sub bands by light irradiation was similar, but the decrement of the carbonyl band at 1756 cm⁻¹ was greater than at 1716 cm⁻¹, with heat treatment after light irradiation. The effect of low temperature was also investigated. Mitsui and Tsuchikawa [17] irradiated wood samples that were kept in a conditioning chamber set for –40 °C. They concluded that the measured degradation was much smaller at –40 °C than at usual laboratory conditions. The first results of the investigation explaining the colour change were published recently [18]. Results demonstrated that the same light irradiation resulted in considerably greater redness increase at 80 °C than at 30 °C. The other finding was that the extractive content has an important role in thermal degradation during photodegradation.

The target of this study was to determine the artificial ageing of wood by IR spectral changes at normal and elevated temperatures. To determine the consequence of heat exposure during photodegradation, samples were irradiated at two different temperatures, i.e. 30 °C and 80 °C.

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The applied difference spectrum method gave the possibility to compare the degradation behaviours of softwood and hardwood species.

2. Materials and methods

The investigated hardwood samples were: ash (*Fraxinus excelsior* L.), beech (*Fagus sylvatica* L.) and poplar (*Populus x euramericana Pannonia*). Softwoods included: Scots pine (*Pinus sylvestris* L.) and spruce (*Picea abies* Karst.). The samples of different series were prepared from the same board with dimensions of 100 mm × 30 mm × 10 mm (long. × rad. × tan.). All species were represented by two samples, and two points of fixed locations were measured on each sample. Strong UV light emitter, mercury vapour lamp provided the irradiation. The total electric power of the applied double mercury lamps was 800 W and the samples were located 64 cm from the lamp. An irradiation chamber set for 30 °C and 80 °C ensured the ambient temperature conditions. The total irradiation time was 16 h in all cases. The moisture content of the samples was between 8% and 10% at the beginning of the treatment, and it decreased during the treatment at 80 °C.

All the IR measurements were performed on the tangential surfaces of the specimens. The surface of spruce, Scots pine and ash samples contained only earlywood. The diffuse reflectance infrared fourier transform (DRIFT) spectrum of the samples was measured before and after irradiation. Measurements were carried out with an IR spectrophotometer (JASCO FT/IR 6300). The resolution was 4 cm⁻¹ 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. The spectra were normalised to the band maximum around 1375 cm⁻¹. The intensity of spectra was adjusted to 1.0 by this normalisation. This C–H band of cellulose is often used as internal standard because of its high intensity and central position. Two-point baseline correction at 3800 cm⁻¹ and 1900 cm⁻¹ was carried out. The difference spectrum was calculated by subtracting the initial IR data from the data of irradiated sample.

3. Results and discussion

Infrared spectroscopy is a useful method for studying the chemical changes in wood caused by light irradiation and heat treatment. The fingerprint area (1000–1900 cm⁻¹) is presented in this work because the main differences were found in this region. The fingerprint region contains the highly overlapped absorption bands of cellulose, hemicelluloses and lignin. The band assignment can be found in a previous work [8]. Fig. 1 represents the absorption spectra (calculated by the K–M theory) of beech sample before and after 16-h irradiation by mercury lamp at 80 °C. The carbonyl band

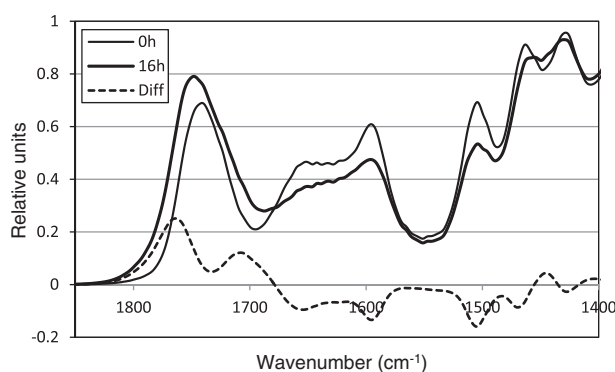


Fig. 1. IR spectra of beech sample irradiated with mercury lamp for 16 h at 80 °C.

between 1680 and 1820 cm⁻¹ increased and the peaks of the aromatic ring vibrations arising from lignin (at 1508, 1455 and 1430 cm⁻¹) decreased in the case of both (temperature) type of irradiations (Fig. 1), as it has been noted in previous studies [2,6–8]. The band for the aromatic skeletal vibration at 1596 cm⁻¹ also decreased but only in the case of hardwoods. Examining the width of the bands it was found that the bands at 1596; 1504; 1455 and 1430 cm⁻¹ have similar width but the carbonyl band with a maximum at 1741 cm⁻¹ is much wider than the others. It suggests that the carbonyl band is the superposition of some individual bands. Hence most publications treat the band of unconjugated carbonyls as one absorption band with a maximum around 1740 cm⁻¹. Moreover many publications report correlation between the height of this band and the total colour change in case of photodegradation. This correlation is highly questionable. The total colour change is an extremely complex parameter representing the colour change produced by the lignin degradation and mostly by the degradation of extractives. The chemical change of extractives cannot be followed by IR spectroscopy because of their low concentration. The change of unconjugated carbonyl band represents the increase of lignin derivatives having carbonyl bound. The high correlation (between total colour change and increase of carbonyl band at 1740 cm⁻¹) reported by many authors may be generated by the similar time dependence of this two parameters and not by the real correlation.

If we have a closer look at the change of the unconjugated carbonyl band (Fig. 1), the shift of the band towards higher wavenumbers is visible. The maximum moves to 1748 cm⁻¹. Moreover the greatest difference between the treated and the initial spectra appears not at the maximum but at the left side of the band. The difference at the maximum (1748 cm⁻¹) is 0.134 and at 1764 cm⁻¹ is 0.251 units, almost double. The initial spectrum has a minimum at 1695 cm⁻¹ and the absorption increases here by light irradiation. This increase represents a growing peak nearby. The above mentioned findings highlight the disadvantage of that comparison method where the initial and the treated spectra are presented on top of each other. The difference spectrum method solves this problem. Creating the difference spectrum (irradiated minus initial) only that absorption bands appear where change has happened. The absorption increase is represented by positive band while negative band represents the absorption decrease. The changes are clearly visible by calculating the difference spectrum of beech sample irradiated for 16 h (Fig. 1 dotted line). It is important to mention that the validity of small bands is questionable. In some cases the baseline may slightly differ from zero line. We did only two point baseline correction at 3800 and 1900 cm⁻¹ where the absorption of wood is zero. The difference spectrum of beech consists of two positive bands at 1765 and at 1705 cm⁻¹. This result is strengthened by 2D IR spectroscopy [19]. The band at 1765 cm⁻¹ represents the absorption of CO stretching for unconjugated ketones and γ lactones generated by the oxidation after the splitting of the aromatic ring. The band at 1705 cm⁻¹ represents the absorption aliphatic carboxyl groups.

The conjugated carbonyls in lignin and in phenolic molecules and quinone carbonyl groups absorb between 1600 and 1690 cm⁻¹ and the absorption of OH groups in water are also here. In this region beech presents a broad decrease with two minimums at 1655 and at 1596 cm⁻¹. The absorption decrease at 1596 cm⁻¹ presents the degradation of aromatic ring in lignin. This negative peak does not exist in the case of softwoods because it belongs to the so-called syringyl lignin found mostly in hardwood. The next typical negative peak at 1508 cm⁻¹ belongs to the aromatic skeletal vibration of guaiacyl lignin. This negative peak is visible together with the absorption decrease of the aromatic C–H deformation at 1469 and 1428 cm⁻¹ and with the absorption decrease of the guaiacyl ring breathing at 1265 cm⁻¹ (Fig. 2). These

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