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Colour stability of oil-heat treated black locust and poplar wood during short-term UV radiation

Robert Nemeth[a], Laszlo Tolvaj[b,*], Miklos Bak[a], Tibor Alpar[c]

[a] Institute of Wood Science, University of West Hungary, HU-9400 Sopron, Hungary
[b] Institute of Physics and Electrotechnics, University of West Hungary, HU-9400 Sopron, Hungary
[c] Institute of Wood Based Products and Technologies, University of West Hungary, HU-9400 Sopron, Hungary

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ABSTRACT

Black locust (*Robinia pseudoacacia* L) samples with high extractive content and poplar (*Populus* × *euramericana cv.* Pannónia) samples with low extractive content were chosen for the test. The specimens were thermally treated at 160 and 200 °C in sunflower oil for 2, 4, and 6 h then irradiated by a strong UV emitter mercury lamp up to 36 h. The effects of thermal treatment and UV radiation were monitored by colour measurement. The results indicated that the extractives play an important role in the photodegradation of oil-heat treated wood. Thermal treatments reduced the lightness change effect of photodegradation. The oil-heat treated black locust samples showed similar photodegradation properties independently on the thermal pre-treatment time and temperature. The redness of oil-heat treated black locust samples hardly changed during UV radiation proving the photostability of the thermally modified extractives. The redness change of poplar samples caused by UV radiation was partly determined by the temperature of thermal treatment (darkening and lightening also happened). The yellow colour change of the investigated samples showed that the lignin of thermally modified wood undergoes similar photodegradation as that of the untreated natural wood.

1. Introduction

The thermal treatment of wood has a long history, and the different methods have been continuously modified and developed in European countries and worldwide as well. The main advantages of thermal treatment are: reduced hygroscopicity, improved dimensional stability, and better resistance to degradation due to insects and micro-organisms. The improvement of these properties gives the possibility to use thermally modified wood for outdoor applications.

During thermal treatments the hemicelluloses are the most affected compounds of wood. “The degradation starts by deacetylation, and the released acetic acid acts as depolymerisation catalyst, which further increases polysaccharide decomposition. Acid-catalysed degradation leads to the formation of formaldehyde, furfural and other aldehydes. Furfural and hydroxymethylfurfural are degradation products of pentoses and hexoses, respectively. At the same time hemicelluloses undergo dehydration reactions with a decrease of hydroxyl groups” [1]. Extractives also undergo degradation and new extractable compounds are created during thermal treatments. The oxidation of hydroxyl groups in flavonol molecules can be a reason of the formation for new colour substances during heat treatment [2].

The colour stability of thermally modified wood under outdoor conditions is also an important parameter for the costumers. Thermal treatments of wood create dark and attractive brown colour, which is highly determined by the applied temperature and treatment time [3–11]. The colour modification by thermal treatment is important for those species that have naturally unattractive light grey colour, such as poplar, or those that have highly inhomogeneous colour, such as black locust.

The colour change caused by the sunshine and the rain for natural wood is a well investigated phenomenon [12–19]. But the colour change caused by the photodegradation for thermally treated wood is not well researched, and the published results are sometimes contradictory. The real comparison is difficult because of the different conditions applied.

Ayadi et al. [20] tested the colour stability of heat-treated ash (*Fraxinus* sp.), beech (*Fagus sylvatica* L.), maritime pine (*Pinus pinaster*), and poplar (*Populus sp.*) wood samples. The heat treatment was done at 240 °C for 2 h, under nitrogen atmosphere. The heat-treated samples were exposed to UV light for 835 h. The

* Corresponding author.
E-mail addresses: tolvaj.laszlo@nyme.hu, laszlo.tolvaj@skk.nyme.hu (L. Tolvaj).

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total colour change was determined representing the changes. The results showed that the colour stability of the heat-treated wood was better than that of the untreated control samples.

Yildiz et al. [21] exposed outside heat-treated alder (*Alnus glutinosa* L.) wood in Turkey for 3 years. The treatment parameters were: 150 °C, 180 °C, and 200 °C, for periods of 2, 6, and 10 h. The results showed that heat treatments delayed and decreased the rate of colour change caused by the weathering but did not completely prevent it. The most advantageous treatment parameters were 200 °C for 10 h. Similar results were found during artificial weathering (UV + water spray) of Scots pine (*Pinus sylvestris* L.), spruce (*Picea orientalis* L.), iroko (*Chlorophora excelsa*) and ash (*Fraxinus excelsior* L.) as well [22].

The artificial photodegradation properties of heat-treated jack pine (*Pinus banksiana*) were studied using xenon lamp [9,10]. The total irradiation time was 1500 h. There was no difference in the a^* and b^* colour coordinate values between thermally treated and the untreated wood after 400 h light irradiation. There were slight differences at shorter irradiation time, but the authors did not measure the colour parameters before 72 h of treatment. The same authors stated in other paper: "The heat treatment increases the lignin and crystallised cellulose contents, which to some extent protects heat-treated birch against degradation due to weathering" [23].

Noupponen et al. [24] reported that heat treated wood was more resistant to natural weathering mainly because some of its lignin degradation products are less leachable than those of untreated wood.

Tolvaj et al. [25] monitored the short-therm photodegradation properties of black locust, poplar, spruce and larch samples pre-treated at 160 and 200 °C for 2, 4 and 6 h. The short term UV irradiation was carried out for up to 36 h. "Results showed that the extractive content of the wood played an important role in the colour change not only during thermal treatment but also during light irradiation. It was found that, compared to the thermally untreated samples; the thermal treatment at 200 °C reduced the red colour change caused by photodegradation. The yellow colour change of photodegradation was hardly affected by the applied thermal treatments, showing that thermal treatments were not able to reduce the degradation of lignin. The applied treatments slightly stabilized the wood against the degrading effect of light."

Similar results were found by Miklečić and his coworkers [26]. "In the first half of exposure to UV light, the surface of uncoated thermally modified (at 190 and 212 °C) ash, beech and hornbeam wood samples discolored slowly compared to uncoated unmodified wood samples. FTIR spectra of thermally modified ash, beech and hornbeam wood samples exposed to UV light showed similar chemical changes as unmodified wood samples exposed to UV light, but less pronounced." The duration of UV treatment was 32 days.

Srinivas and Pandey [27] investigated the photodegradation behaviour of thermally treated rubber wood (*Hevea brasiliensis*). The thermal treatment was carried out in vacuum atmosphere at 225 °C for 2, 4, and 6 h. The IR spectra showed significant lignin degradation in thermally modified wood within few hours of exposure. Results of colour changes and FTIR spectroscopy revealed that thermal modification of wood does not induce resistance against UV radiation.

The light wavelength dependence of photodegradation for thermally modified and unmodified aspen samples were also investigated [28,29]. The total irradiation time was 100 h. It was found, that wavelength longer than 600 nm did not generate degradation of wood. "Greater changes in IR spectra were observed for thermally modified wood compared to unmodified wood for all analysed wavebands and irradiation systems, which suggests that thermally modified wood was more chemically transformed by irradiation."

The literature review shows that the behaviour of thermally modified wood during UV light exposure is still not clearly understood. There are only a few papers dealing with the oil-heat treated wood [30,31].

The purpose of this study was to monitor the colour change of oil-heat treated black locust and poplar wood during short term UV radiation. Strong UV emitter mercury lamp was used. The colour change was compared to that of thermally treated samples in dry condition. The treatment parameters were identical in both cases for the correct comparison.

The main difference between the applied two types of pre-treatments is that oil excludes the oxidation of thermally degraded chemical components.

2. Materials and methods

2.1. Materials

Black locust (*Robinia pseudoacacia* L.) and Pannonia poplar (*Populus* × *euramericana cv.* Pannónia) wood were oil-heat treated (OHT) in sunflower oil. These species were chosen because black locust has high while poplar has low extractive content. The dimensions of the samples were $100 \times 20 \times 10\,mm^3$ (L;R;T directions).

2.2. Treatments

The thermal treatments were performed at two different temperatures: 160 °C and 200 °C, the applied durations were 2 h, 4 h and 6 h. In all 6 schedules 4 samples were treated with an initial moisture content of 13%. The samples were immersed directly into the hot oil bath without preheating. At the end of the oil-heat treatment the samples were taken out from the oil bath (without cooling schedule). Untreated samples with same dimensions served as control (4/species).

The thermally treated samples underwent photodegradation together with the untreated control samples. A strong UV light emitter, mercury vapour lamp provided the light irradiation. The UV radiation was 80% of the total emission (31% UV-A, 24% UV-B and 25% UV-C). The total electric power of the applied double mercury lamps was 800 W and the distance between the samples and the light source was 64 cm. An irradiation chamber set for 70 °C ensured ambient temperature conditions. The total irradiation time was 36 h. The irradiation was interrupted after 3, 7, 16, and 36 h for measuring the colour change, based on previous experiences.

2.3. Colour measurement

Colour measurements were carried out with a colorimeter (Konica-Minolta 2600d). The CIE L^*, a^*, b^* colour coordinates were calculated based on the D_{65} illuminant and 10° standard observer with a test-window diameter of 8 mm. The relatively large window was chosen to measure the average colour of earlywood and latewood regions combined. The radial surface of the sample was used for colour measurement. The colour of randomly chosen 10 points were measured on each sample. Measurements on thermally treated samples served as control values for comparison purposes for the photodegradation.

The colour stability of OHT samples was compared to the results of dry heat-treated samples published in Tolvaj et al. [25]. Some of these data are presented in this paper as well. For proper comparison, the related graphs have the same vertical scale magnitude.