Colour Stability of Thermally Modified Wood during Short-Term Photodegradation

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Dry thermal treatments of wood samples were carried out at 160 and 200 °C. After each treatment, the samples were irradiated using a strong UV emitter mercury lamp, and the colour change was then evaluated. For control, untreated samples were also irradiated using the same mercury lamp. 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 due to 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 light degradation of lignin. The applied treatments slightly stabilized the wood against the degrading effect of light. The wood treated at lower temperature (160 °C) had less colour change induced by the light source.

Keywords: Thermal modification; Photodegradation; Colour change; Extractives

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INTRODUCTION

Thermal treatment of wood has been known for a long time to modify the physical properties (Kollman and Fengel 1965). The main advantages of thermal treatment include reduced hygroscopicity, improved dimensional stability, and better resistance to degradation due to insects and micro-organisms. The improvement of these properties makes it possible to use thermally modified wood for outdoor applications, such as for claddings, facade elements, garden furniture, and playground facilities (Brischke *et al.* 2007; Yildiz and Gümüşkaya 2007).

The colour of wood has become one of the most important parameters of wood products during the last two decades. As computer-supported colorimeters were introduced, colour measurement became a fast and sensitive research method. Objective colour measurement helped researchers to investigate the exact colour modification effects of different treatments (Tolvaj *et al.* 2010; Cao *et al.* 2012; Tolvaj *et al.* 2012). Thermal treatments of wood create dark and attractive brown colour, which is highly determined by the applied temperature. This colour alteration 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.

It is well known that natural wood is susceptible to environmental degradation induced by weathering. The main degradative factors are sunshine and rain. This phenomenon of photodegradation has been well studied for natural wood (Pandey 2005; Sharratt *et al.* 2009; Chang *et al.* 2010; Popescu *et al.* 2011; Persze and Tolvaj 2012; Agresti *et al.* 2013; Denes and Lang 2013; Teaca *et al.* 2013; Zivkovic *et al.* 2013).

Some research has been done on photodegradation of thermally treated wood during the last decade. For example, Ayadi *et al.* (2003) tested the colour stability of heat-treated wood samples. The heat treatment was done at 240 °C for 2 h, under nitrogen atmosphere. Heat-treated samples of ash (*Fraxinus* sp.), beech (*Fagus sylvatica* L.), maritime pine (*Pinus pinaster*), and poplar (*Populus* sp.) heartwood were exposed to UV light for 835 h. The total colour change was determined as a complex parameter representing the changes.

The experiments showed that the colour stability of the heat-treated wood was better during the 835 h of exposure when compared to untreated wood. The photodegradation difference between treated and thermally untreated wood increased rapidly during the first 36 h of UV light exposure. After this period, the trend lines of total colour change were close to parallel. Unfortunately, the total colour change did not give as detailed information about the colour change as the change of the individual colour coordinates L^*, a^*, b^* can provide.

Yildiz *et al.* (2011) investigated the outdoor weathering properties of heat-treated alder (*Alnus glutinosa* L.) wood. The treatment parameters were: 150 °C, 180 °C, and 200 °C, for periods of 2, 6, and 10 h. The samples were outside for 3 years in Turkey. It was found that heat treatments delayed and decreased the rate of colour change caused by the weathering factors but did not completely prevent it. The most advantageous treatment condition was at 200 °C for 10 h.

Huang *et al.* (2012) studied the photodegradation properties of heat-treated jack pine (*Pinus banksiana*) under artificial sunlight irradiation. The light source was a xenon lamp and the total irradiation time was 1500 h. There was no difference in the a^* and b^* values between thermally treated and the untreated wood after 400 h light irradiation. There were slight differences at shorter irradiation time, but the shortest period was 72 h.

The photodegradation behaviour of thermally treated rubber wood (*Hevea brasiliensis*) was investigated by Srinivas and Pandey (2012). Oven-dried samples were kept in a glass tray and were heat treated in a pre-heated vacuum oven at 225 °C for 2, 4, and 6 h under 400 mm (Hg) of vacuum to obtain three different levels of thermally modified wood specimens. The Fourier transform infrared (FTIR) spectra showed significant lignin degradation in 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.

A CO_2 laser was used by Kubovsky and Kacik (2013) to modify the surface colour of lime wood to brown, and the light stability of this modified surface was tested. A xenon lamp was used for light irradiation, and the irradiation time was 100 h. The durability of colour achieved by laser treatment was not too high. The xenon light irradiation caused significant colour changes.

The behaviour of thermally modified wood during UV light exposure is still not clearly understood. There is not much literature data found relating to the colour change for short term photodegradation of thermally treated wood. For this purpose the samples were irradiated using a strong UV emitter mercury lamp and colour measurements were made at chosen hour intervals of light irradiation.

MATERIALS AND METHODS

Materials

Samples of two hardwood and two softwood species were used for this study. The hardwood species were black locust heartwood (*Robinia pseudoacacia* L.) and poplar (*P. x euramericana Pannonia*). The softwood species were larch heartwood (*Larix decidua* L.) and spruce (*Picea abies* Mill.). The black locust and the larch were chosen because of their high extractive content and, for comparison, spruce and poplar were chosen as low extractive content species. All species were represented by 2 samples for each type of thermal treatment. The colours of 10 randomly chosen point were measured on each sample. The sample dimensions were 100x20x10 mm. The radially cut in-plane (*i.e.* 100x20 mm) surfaces contained earlywood and latewood regions as well, and this surface was used for colour measurement. The initial moisture content of the samples before thermal treatment was between 8 to 10%.

Methods

The dry thermal treatment was carried out in a laboratory scale drying chamber at 160 °C and 200 °C in presence of air and ventilation (open system). The heating up time was 30 min. The duration of the effective treatment time was 2, 4, and 6 h. The 2-h treatment time at 160 °C produced only very little colour change, so these samples were not used for further investigation.

The thermally treated samples underwent photodegradation together with the thermally not treated 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 lamp 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. Colour measurements were carried out with a colorimeter (Konica-Minolta 2600 d). 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. Measurements on thermally treated samples served as control values for comparison purposes for the photodegradation.

RESULTS AND DISCUSSION

The samples underwent considerable colour change during thermal treatments, as shown in Figs. 1, 2, and 3. The redness increased for all species with heating, and the order of change followed the intensity of the thermal treatment. The higher temperature and the longer treatment time produced greater redness increase. The spruce wood was highly sensitive to both thermal treatment temperature and duration of exposure. The poplar was also highly sensitive to the temperature of the thermal treatment, but not sensitive to the thermal treatment time. The yellow colour of larch, poplar, and spruce increased following the tendency of red colour change. The only exception was the black locust. Its originally high yellow colour decreased due to the thermal treatment following the same tendency as the lightness change produced. The lightness decreased for all species. The magnitude of change followed the intensity of the thermal treatment. In other words, higher temperature and longer treatment time produced greater lightness decrease. The selected thermal treatment parameters resulted in a large variety of lightness.

The colour of a material is created by the conjugated double bond (chromophore) chemical systems. Such chromophores consist of the lignin and certain extractive species in the natural wood. Thermally modified wood has additional chromophores produced by the degradation of the hemicelluloses. The natural colour of the wood is mostly determined by the extractives.

The photodegradation caused the most detailed differences in the redness change. The red colour changes are represented in Fig. 1. For proper comparison, all graphs have the same vertical scale magnitude. The redness change trend lines were convergent for the low extractive content species (poplar and spruce), but they were first rapidly convergent and later divergent for the high extractive content species (black locust and larch). The black locust and the larch samples produced rapid increase in redness during the first 3 hours of exposure.

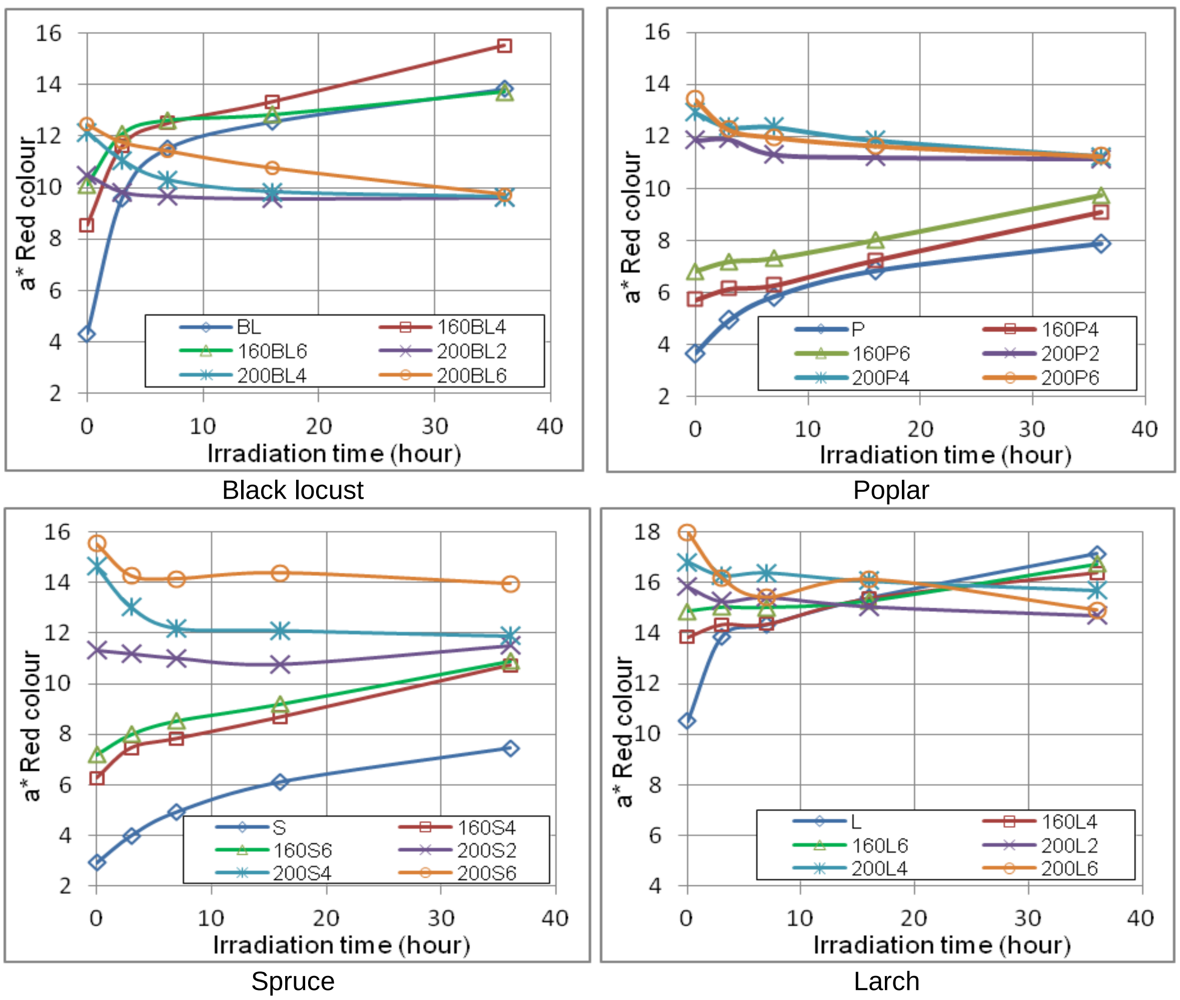
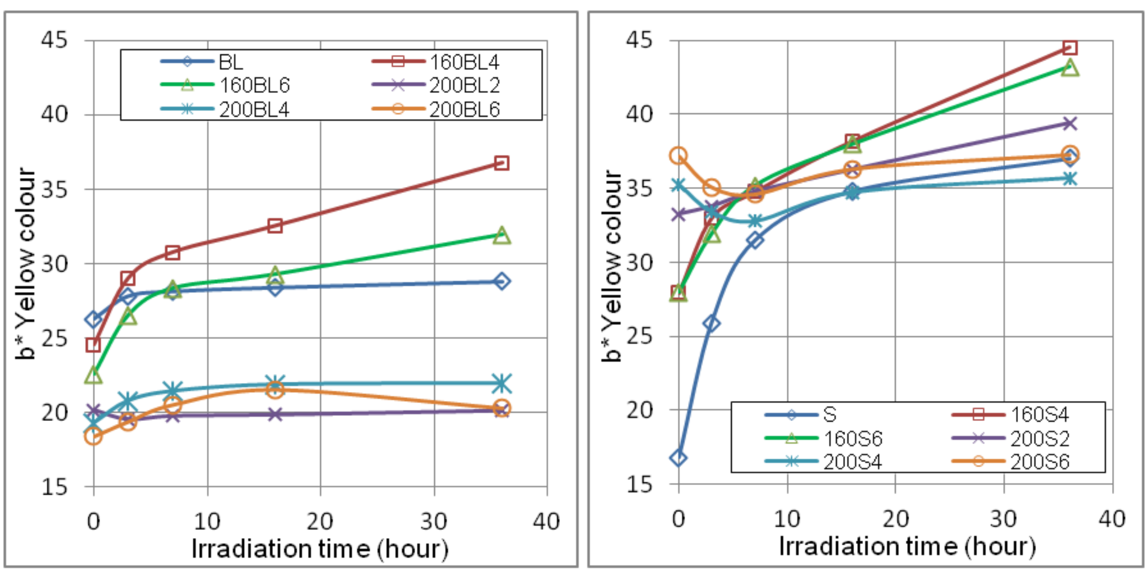


Fig. 1. The redness change in the four sample species caused by light irradiation (abbreviation: thermal treatment temperature/sample name/ thermal treatment time in hour)

In comparison, the other two species showed moderate redness increase during this period. (The trend lines of larch showed fluctuation. This was because the latewood of larch is much redder than the earlywood. The proportion of these two types of tissues within the measured area might be changed during the individual measurements.) After 7 h of treatment, the trend lines became straight, showing a slow increase. The thermally treated samples showed different changing behaviour depending on the treatment temperature. The samples treated at 160 °C followed the changing tendency of the natural wood (thermally untreated) samples in all cases. This means that the thermal treatment at 160 °C did not affect the redness change behaviour of wood.

The samples thermally treated at 200 °C changed their redness in a different way than untreated wood. After moderate decrease in redness during the first 7 h of light irradiation, these treated samples kept closely constant redness value during the examined time period. The samples treated at 200 °C for 2 h showed the most stable redness values during photodegradation. The redness change is mainly determined by the chemical changes of extractives and by the chromophore products of the thermally degraded hemicelluloses. It can be concluded that at 200 °C thermally modified extractives and the chromophore products of hemicelluloses are fairly stable during light irradiation.

The yellow colour changes of the examined species are presented in Fig. 2. Two graphs are presented here because the changing tendencies and values of poplar were the same as spruce and similar to larch. The larch samples showed similar behaviour as the spruce samples; only the intensity of the changes was a little higher for larch during the first 3 h of light exposure. The yellow colour of black locust is naturally different compared to the other European species. This deviation is caused by its high robinetin content. A previous study demonstrated that the high extractive content of black locust partly protects its lignin content during light irradiation (Tolvaj and Varga 2012).

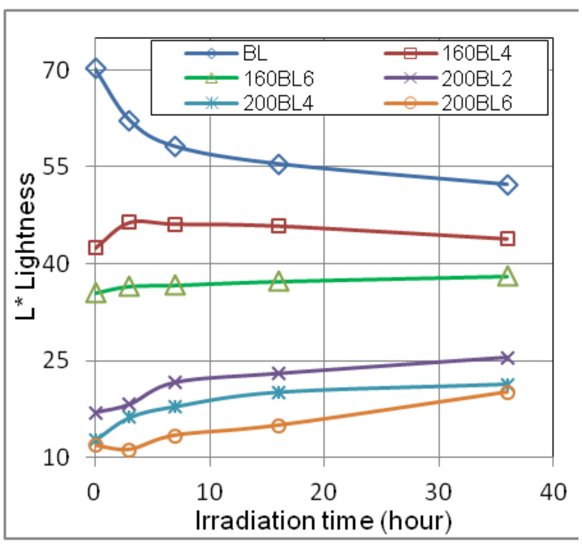


Black locust Spruce

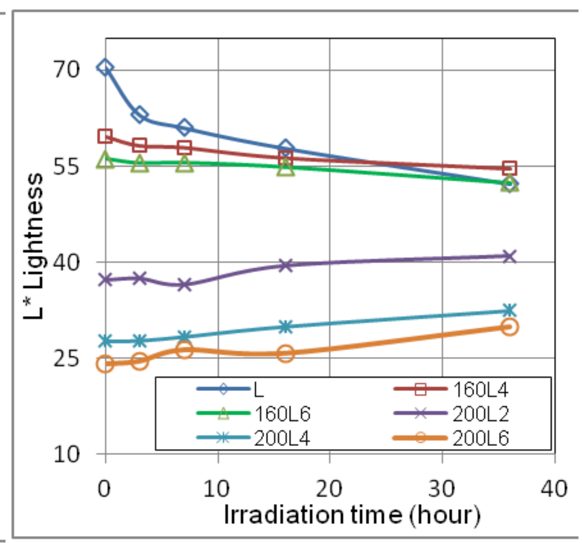
Fig. 2. The yellowing in the black locust and spruce samples caused by light irradiation (abbreviation: thermal treatment temperature/sample name/ thermal treatment time in hour)

The same finding is partly demonstrated here as well. The natural wood of black locust produced the least yellowing compared to the other examined natural samples. Some of the extractives for black locust underwent thermal degradation, represented by the increasing values of *a** and *b** coordinates. The extractives modified at 160 °C thermal treatment were not able to protect the lignin of black locust, as is visible in Fig. 2. The yellow colour increase in the black locust samples was much greater than the yellowing of the natural black locust samples. The degradation behaviour of thermally modified black locust at 160 °C was similar to the degradation of the other species that do not contain protective extractives. The thermally treated black locust samples at 200 °C did not produce remarkable yellowness changes. The other samples showed a slight yellow colour decline during the first 7 hours of light irradiation. After this time period the yellowing of the samples treated at 200 °C followed the slow increase in the yellowness of the natural samples. The yellow colour change in the samples treated at 200 °C for 2 h seemed to be the most stable, as was found for red colour as well. The yellow colour changes of the investigated samples showed that the lignin of thermally modified wood undergoes a similar photodegradation as the untreated natural wood. It was found in a previous study as well (Srinivas and Pandey 2012).

The lightness of the investigated samples decreased a lot during the thermal treatment (Fig. 3). This decrease was 83, 66, 62, and 56% for black locust, larch, poplar, and spruce, respectively.



Black locust



Larch

Fig. 3. The lightness change of the samples caused by light irradiation (abbreviation: thermal treatment temperature/sample name/ thermal treatment time in hour)

There were only minor differences among the species during the light irradiation. Poplar and spruce showed the same changing behaviours, and this pattern of change was also similar to that of the larch samples. That is why we present the data only of black locust and larch. The natural wood samples suffered rapid lightness decrease during the first 10 h of light irradiation, followed by moderate decrease. The originally dark thermally treated samples exhibited slow but continuous changes. The values of these changes were considerably less than those of the untreated samples. The direction of change was determined by the initial lightness value. Samples having initial lightness values greater than 40 units showed decreasing lightness; those that have initial lightness values less than 40 units showed lightening during irradiation. These results suggest that thermal treatment slightly reduced the lightness change effect of photodegradation. The samples thermally treated at 160 °C were more stable than the others treated at 200 °C from the point of view of lightness change.

CONCLUSIONS

Thermally treated (at 160 °C and 200 °C) wood samples were irradiated by a strong UV emitter mercury lamp, and the colour change was evaluated. Results showed that the extractive content of the wood plays an important role in the colour change not only during thermal treatment but also during light irradiation as well. It was found that thermal treatment at 200 °C reduces the red colour change caused by the photodegradation. The yellow colour change of photodegradation was hardly affected by the applied thermal treatments, showing that thermal treatments are not able to reduce the light-induced degradation of lignin. The applied treatments slightly reduced the lightness change effect of light irradiation. In that case the thermal treatment at 160 °C was more effective than the treatment at 200 °C.

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