

## Photodegradation and thermal degradation of outdoor wood

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### **Abstract**

In this study, wood samples were exposed to thermal treatment in dry- and humid conditions and to light irradiation. The results showed that neither xenon lamp nor mercury lamp can simulate properly the effect of sunlight. Light irradiated samples put behind an aluminium plate also suffered considerable chemical changes, measured by infrared technique and colour measurement. Degradation of lignin was inconsiderable in the shadow. Carbonyl groups generated by sunlight were partly contrary to those generated in shadow. The latewood suffered considerably less photodegradation than earlywood. Thermal degradation was much greater in humid condition than in dry condition.

## INTRODUCTION

The main factor that causes the greatest changes in the surface properties of wood during outdoor exposure is sunlight. Resistance of degraded surface to water movement and fungi attack decreases by weathering. Careful investigation of such wood degradation is difficult using outdoor exposure, because weather conditions are not repeatable, and there are many other factors beside sunlight influencing the results. Therefore light-induced degradation of wood is usually investigated under artificial conditions. The most frequently used artificial light source is the xenon lamp. Because of the thinning of earth's ozone layer, nowadays more ultraviolet (UV) radiation reaches the earth's surface than before. Therefore the UV B wavelength region (280-315 nm) has to be taken into consideration as a strong degrader of biological molecules. Since xenon lamps have no emission in the UV B region, a new light source (or combination of light sources) should be introduced to simulate the sunlight.

Beside photodegradation, surface thermal degradation has to be taken into account, too. Surface temperature of sun-irradiated outdoor wood can reach 60°C, or even 90°C if it is dark enough. This local temperature is high enough to produce chemical degradation. In the scientific literature, similar investigation can hardly be found.

To protect our outdoor wooden cultural heritages, first of all the mechanism of photodegradation and thermal degradation of wood has to be clearly understood.

## EXPERIMENTAL

The following hardwood species were investigated: beech (*Fagus crenata*), black locust (*Robinia pseudoacacia*), poplar (*Populus caulescens*), and zelkova (*Zelkova serrata*), the softwood samples were: Japanese cedar (*Cryptomeria japonica* D. Don), Japanese cypress (*Chamaecyparis obtusa*), Scots pine (*Pinus sylvestris*), spruce (*Picea abies*) larch (*Larix decidua*) and as a unique wood bamboo (*Phyllostachys pubescens*) also was investigated. Planed surfaces with a tangential orientation were prepared. The sample size was 50x10x2 (mm). Samples of different series were prepared using the same board. All species were represented by a series of 2 samples, and 5 points of fixed location were measured. The data presented in this study are the average of 10 measurements. The natural sunlight irradiations were carried out between 5th of May and 19th of August, 2003 (air temp. varied 16-41 °C, max. RH 80%). In order to determine the effect of the sunlight alone, samples were exposed outside only on sunny days. The other series of specimens were irradiated with a xenon lamp, in a commercial chamber (SX-75: Suga Test Instruments Co. Ltd., Tokyo). A mercury lamp as a strong UV light emitter was also used to irradiate specimens (HAL 800NL, installed into a KBP.659 Nippon Denchi Co. Ltd. chamber.). Total irradiation time was 200 hours for sunlight and xenon light, and 20 hours for mercury light. One part of the samples was covered with an aluminium plate in all experiments. These surfaces were used to determine the thermal degradation caused by the applied irradiation.

Earlywood and latewood surfaces were investigated parallel in order to find the photodegradation differences. To determine the thermal degradation solely, samples were stored in total darkness at 90°C under both dry and humid conditions.

The colour and the infrared (IR) spectra of wood specimens were measured before and after irradiation. Exposures were interrupted after 5; 10; 20; 30; 60; 120 and 200 hours to obtain colour and IR data. Colour measurements were carried out with a colorimeter (SE-2000 Nippon Denshoku Industries Co. Ltd., Tokyo). L\*, a\*, and b\* colour co-ordinates were calculated based on D<sub>65</sub> light source. The IR spectra measurements were performed with a JASCO FTIR double beam spectrometer equipped with a diffuse reflectance unit (JASCO: DR-81). 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 1900 cm<sup>-1</sup> was carried out. Difference spectra were calculated by subtraction of non-irradiated from the irradiated.

## RESULTS AND DISCUSSION

Ultraviolet (UV) photodegradation of wood is a widely investigated phenomenon [1] [2] [3], however thermal degradation occurring during photodegradation is hardly investigated. It is usually thought to

be negligible by researchers. New results show, that the thermal degradation of wood is faster if the sample got UV irradiation previously [4] [5] [6]. This finding highlights that this problem needs further investigation. Therefore, this study discusses these two phenomena separately. One part of all samples was covered by an aluminium plate to filter the direct UV radiation. With this method, only the minimum of the thermal degradation could be determined. The real surface temperature is higher than behind the aluminium plate and the thermal degradation depends on the temperature exponentially. The colour changes of beech wood are presented in Fig. 1. The darkening caused by sunlight was fast in the first 10 hours. After 30 hours the lightness decrease was moderate but it decreased linearly.

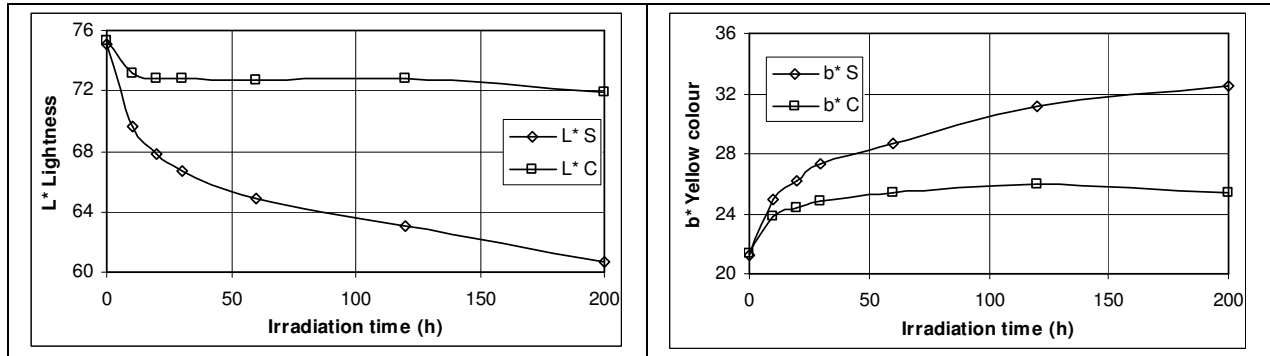


Figure 1 Colour change of beech wood caused by direct sunlight radiation (S) and behind an aluminium plate (C)

The covered area suffered considerable lightness decrease during the first 10 hours of exposure, and then the lightness remained constant. The yellowing (increase of  $b^*$  colour co-ordinate) showed similar changes but in the opposite direction. The rates of the changes were different. The lightness decrease of the exposed area was 2.6 times higher than that of the covered area after 10 hours exposure. The rate of the yellowing was only 1.5.

The colour change is a sensitive indicator of photo- and thermal degradation of wood but it does not show the chemical changes. The IR spectrum gives information about the chemical structure. The difference IR spectra of spruce earlywood are presented in Fig. 2. The positive peaks represent the absorption increase while the negative peaks represent the absorption decrease caused by the treatment. The band assignment can be found in a previous work [1]. After light irradiation, the carbonyl band between  $1680$  and  $1900\text{ cm}^{-1}$  increased and the peak of the aromatic skeletal vibration arising from lignin ( $1510\text{ cm}^{-1}$ ) decreased together with the guaiacyl vibrations at  $1275\text{ cm}^{-1}$ . There is an absorption decrease at  $1174\text{ cm}^{-1}$  because of the ether splitting.

Since there is no absorption change at  $1510\text{ cm}^{-1}$ , the lignin did not suffered degradation in the shadow. The aluminium plate protected it against light irradiation. The ether band was split although

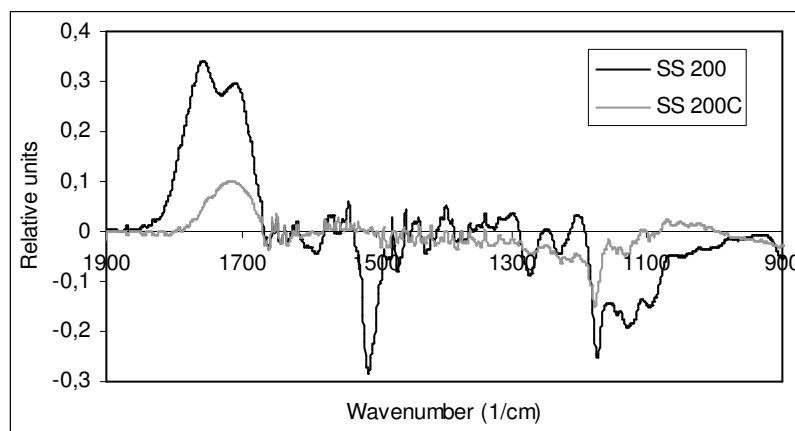


Figure 2 Difference IR spectra of spruce earlywood (S) after 200 hours sunlight (S) irradiation and behind an aluminium plate (C)

it is about half part compared to the effect of sunlight. The carbonyl groups generated in shadow are different to those generated by sunlight. The band at  $1764\text{ cm}^{-1}$  (unconjugated ketones, carboxyl groups and lactones) is completely missing. It means that the unconjugated ketones, carboxyl groups and lactones are generated after the splitting of the aromatic ring of lignin. The number of generated carbonyl groups absorbing around  $1720\text{ cm}^{-1}$  is much less in shadow than in the exposed area. It can be concluded, that the outdoor wood suffers degradation in shadow, too. This chemical change is different from that caused by the sunlight. Our results show the importance of thermal degradation during outdoor exposure.

Experiments in total darkness were carried out to determine the effect of thermal degradation. Samples were placed in two desiccators, both over  $\text{P}_2\text{O}_5$  (dry condition) and over water (wet condition). The desiccators were placed in a drying chamber at  $90^\circ\text{C}$ . The results of black locust wood are presented in Fig. 3. In dry condition, samples colour shifted towards red (increase of  $a^*$  co-ordinate). Under wet condition the colour change was more intensive. The red colour co-ordinate increased and the yellow ( $b^*$ ) decreased. After 120 hours treatment, the red component also decreased. (Here, the data are presented up to 200 hours, but this test was continued up to 36 days.) The saturated vapour removed the coloured degradation products from the samples. This removal is confirmed by the IR spectra as well. (These spectra are not presented here.) The decrease of  $b^*$  shows the removal of the water-soluble extractives. Black locust is rich in extractives creating its unique yellow colour. The decrease of  $b^*$  was less pronounced in case of the other samples. Real weather conditions are between the simulated dry and wet conditions. Air humidity plays an important role in thermal degradation.

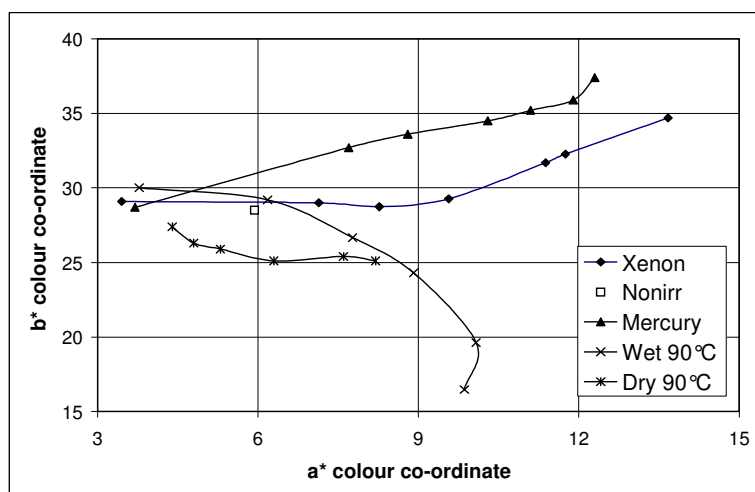


Figure 3 Colour change of black locust wood caused by different treatments (treatment duration was 200 hours)

The effect of UV photodegradation is usually investigated in artificial conditions. The most frequently used artificial light source is the xenon lamp. Because of the thinning of earth's ozone layer, nowadays more ultraviolet (UV) radiation reaches the earth's surface than before. Therefore the UV B wavelength region (280-315 nm) has to be taken into consideration. Xenon lamps have no emission in the UV B region while the emission spectrum of mercury lamp has wider range of UV light. To simulate the effect of this UV B radiation, a mercury lamp may be used. The disadvantage of the mercury lamp is that it emits in UV C region as well, however, the UV C radiation of sun does not reaches the surface of the earth. Both light sources were tested. It is difficult to compare the light sources because its light emission power and spectrum are individual. These data of light sources are usually partly presented by the suppliers. That is why the absolute intensities of the generated changes are not suitable for comparison. The tendency of changes has to be compared.

The colour changes caused by the artificial light sources are presented in Fig. 3. Both lamps had the same electric power (300 Watt). The mercury lamp produced continuous and parallel yellow and red colour changes. Colour shift occurred only after 30 hours of irradiation in case of xenon lamp. The control samples were stored in the laboratory on an open place. Their colour also shifted towards red a little (marked as "Nonirr" in Fig. 3.).

For comparison of light source, IR spectra give more detailed data. These difference spectra of poplar wood are presented in Fig. 4-5. The large positive peaks in Fig. 5 around  $1100\text{ cm}^{-1}$  do not represent absorption increase. This is a distortion caused by the applied Kubelka-Munk theory. In this experiment, the electric power consumption of mercury lamp was about 10 times higher than that of xenon lamp, therefore the irradiation times are different. The effect of the two irradiation types (*i. e.* sunlight and xenon light) differed on peaks in the  $1900$  and  $1680\text{ cm}^{-1}$  wavenumber region. Usually two peaks develop in this region during the exposure of wood to UV radiation. The xenon light causes a slightly greater increase in the peak at  $1716\text{ cm}^{-1}$  wavenumber than at  $1775\text{ cm}^{-1}$ . As a single measure of the deviation between these two peak intensities, their ratio was calculated on the basis of the higher wavenumber. The  $1716\text{ cm}^{-1} / 1775\text{ cm}^{-1}$  ratio after the exposure to xenon light was 1.05. On the other hand, exposure to sunlight for 200 hours created the opposite change in intensity, the  $1716\text{ cm}^{-1} / 1775\text{ cm}^{-1}$  ratio was 0.81. These ratios changed during exposure. In the first hours of exposure, deviation in the peak intensity ratio increased, mainly because of the rapid increase of the peak at  $1716\text{ cm}^{-1}$  in case of xenon light. After 60 hours, the deviation decreased. The increase of the band at  $1716\text{ cm}^{-1}$  was rapid at the beginning of xenon light irradiation and stayed the same after 60 hours of irradiation. In contrast this band increased continuously during the 200 hours sunlight irradiation. Our experiments suggest that the xenon light can simulate the effects of sunlight only after long-term irradiation.

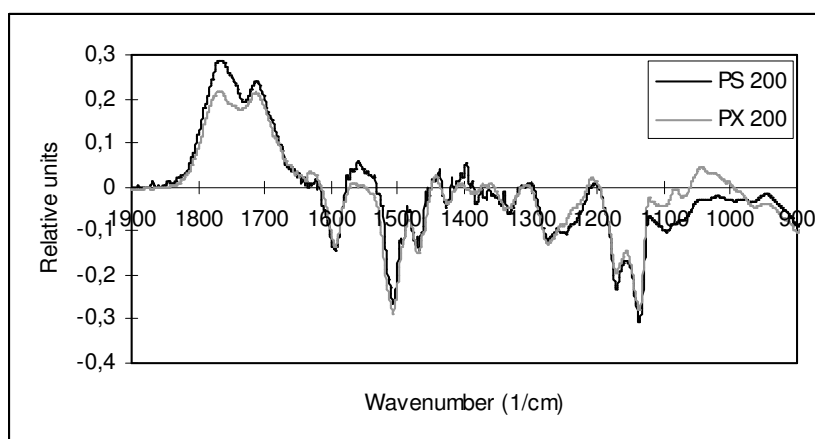


Figure 4 Difference IR spectra of poplar wood (P) after 200 hours sun (S) and xenon lamp (X) irradiation

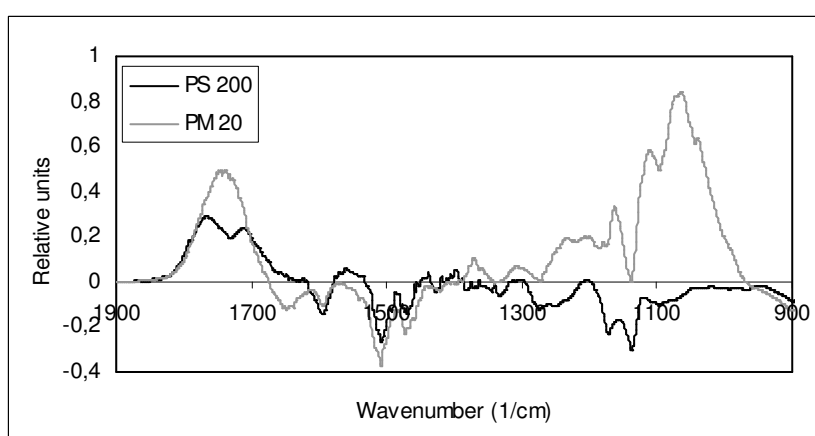


Figure 5 Difference IR spectra of poplar wood (P) after 200 hours sun (S) and 20 hours mercury lamp (M) irradiation

The differences between mercury lamp and sunlight irradiation can be seen mainly in the carbonyl groups region (Fig. 5). In the unconjugated carbonyl groups region, the mercury lamp created a large united peak with a maximum at  $1750\text{ cm}^{-1}$ . In contrast, the sunlight created two well separated peaks.

These two peaks were also visible in the case of mercury light irradiation up to 1 hour of irradiation. After 3 hours irradiation they were completely integrated within one peak. In the conjugated carbonyl groups region (1620-1690  $\text{cm}^{-1}$ ), absorption decrease was found only in the case of mercury light irradiation. Probably it is created by the UV C part of irradiation. It can be concluded that the mercury lamp is not able to simulate the degradation caused by sunlight. Further investigation is needed to clarify the effect of mercury lamp if the UV C part is filtered out.

The sensitivity of earlywood and latewood within the heartwood and sapwood was investigated, too. The results of 120 hours sunlight irradiation of Japanese cedar are presented in Fig. 6. The obvious changes are visible in the aromatic ring region around 1510  $\text{cm}^{-1}$  and in the carbonyl group region (1680-1850  $\text{cm}^{-1}$ ). The latewood suffered the same changes independently on its position within the wood. The smallest degradation was found in the case of larch latewood. The earlywood suffered much greater degradation than the latewood. Comparing the sensitivity of the two types of earlywood, it can be seen that within the sapwood the sensitivity of earlywood is a little greater than within heartwood. It means that the latewood surface gives protection for the other layers in the case of outdoor roundwood.

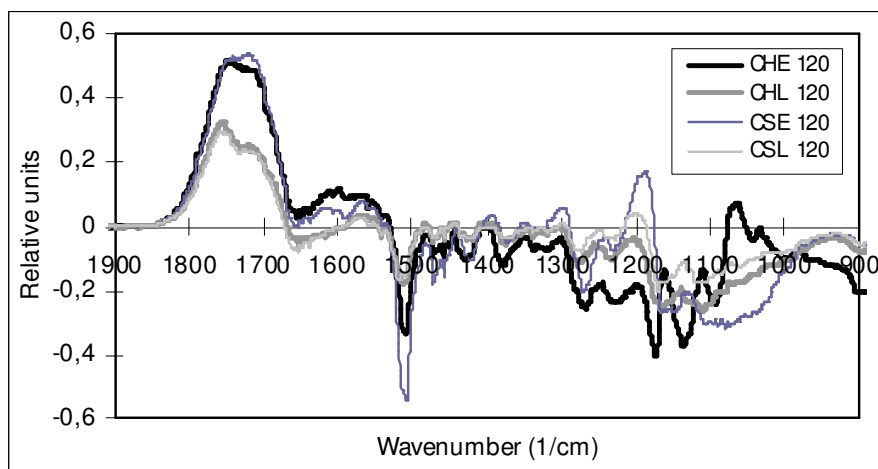


Figure 6 Difference IR spectra of Japanese cedar (C) heartwood (H), sapwood (S), earlywood (E) and latewood (L) after 120 hours sunlight irradiation

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