Monitoring of photodegradation for wood by infrared spectroscopy

Laszlo Tolvaj
Institute of Physics, University of West Hungary, Hungary

Abstract

The infrared (IR) spectroscopy is a good analytical tool to determine the chemical changes of photodegradation caused by sunlight exposure. Wood is an excellent light absorber material, so the diffuse reflectance technique can only be applied. This technique gives information from the same surface layer which is affected by photodegradation. The IR spectroscopy is a nondestructive method. This paper presents the main chemical changes caused by light irradiation. The time dependence of these changes is displayed as well. Well presented that the rain leaches out the photodegradation products from the surface of outdoor wooden construction giving place for further degradations. The earlywood and latewood have different sensitivity to photodegradation; the earlywood suffers much more degradation than latewood. Lasers are special light sources emitting only one wavelength. The wavelength dependence of photodegradation is investigated applying lasers.

INTRODUCTION

Infrared (IR) spectroscopy is a good analytical tool to determine the changes of chemical components in wood caused by different treatments. The wood is not transparent for light, so the DRIFT (diffuse reflectance infrared Fourier-transform) technique can be applied. The powerful Fourier-transform IR technique gives the possibility to measure the diffusely reflected intensity of a thin layer. This is a perfect technique to investigate the photodegradation because the information is given from the same layer which suffered photodegradation. The Kubelka-Munk (K-M) theory [1] was created to calculate the absorption properties of the surface layer using the reflected light.

The K-M theory is widely applied to determine the light absorption properties of wood and the effect of photodegradation [2-15]. The effect of light sources [15-16], surface roughness [17-18], wood species [19-21] and the protective effect of surface treatments [22-23] are widely investigated by IR spectroscopy. The penetration of light into wood and its degradation effect can also be monitored by IR spectroscopy [24-25].

Using lasers as radiation sources [26-27] the duration of the treatment can be shortened, the wavelength of the radiation can be known exactly, and the energy can be determined as well as the intensity of radiation at the surface. By laser irradiation more accurate information can be given than using traditional light sources.

In this study patterns are given demonstrating the usefulness of the IR spectroscopy monitoring the photodegradation of wood.

EXPERIMENTAL

Japanese cedar (*Cryptomeria japonica* D. Don), Scots pine (*Pinus sylvestris* L.), spruce (*Picea abies* Karst.) and beech (*Fagus crenata* Carr.) samples were 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. Earlywood and latewood surfaces were investigated parallel in order to find the photodegradation differences. 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% and the daily average of total solar power density were between 436-459 W/m^2). In order to determine the effect of the sunlight alone, samples were exposed outside only on sunny days. 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 20 hours for mercury light. One part of the samples was covered with a 2 mm thick aluminium plate in all experiments. These surfaces were used to determine the thermal degradation caused by the applied irradiation.

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^{-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. Two-point baseline correction at 3800 cm^{-1} and 1900 cm^{-1} was carried out. Difference spectra were calculated by subtraction of no irradiated from the irradiated.

Five types of impulse laser emitting different wavelengths were used to produce the photodegradation of the samples. The data of the applied lasers are presented in Table 1.

Table 1. Physical parameters of the applied lasers

Laser type	Wavelength (nm)	Impulse energy (m Joule)	Impulse time (ns)	Impulse frequency (Hz)	∑Energy (Joule)	Power density (W/m^2)
ArF	193	10	20	10	15	4.4 10^9
KrF	248,5	20	15	10	100	1.2 10^{10}
XeCl	308	20	20	10	100	8.8 10^9
Nitrogen	337	2,8	15	30	100	1.6 10^9
Rodamin	581	4	15	10	100	2.4 10^9

RESULTS AND DISCUSSION

Infrared spectroscopy is a useful method for studying the chemical changes in wood caused by light irradiation. The IR spectrum of wood has around twenty major bands. Fig. 1 represents the DRIFT spectrum of beech wood. The positions of the IR bands are listed in Table 2 together with their assignment. The latter can be given only in general terms since wood spectra are the results of heavily overlapping bands of lignin, hemicelluloses and cellulose.
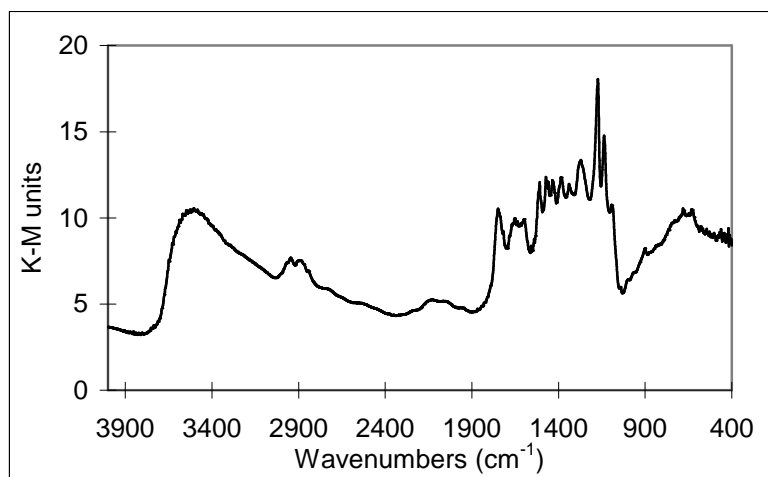

Figure 1 DRIFT spectrum of beech wood

Table 2 Position of the bands of DRIFT spectra at 4 cm^{-1} resolution and the band assignments

Conifers (cm^{-1})	Beech (cm^{-1})	Assignment
2472	3520	OH stretching
2930	2957	CH and CH_2 stretching (asymm.)
2904	2915	CH and CH_2 stretching (symm.)
1740	1750	CO stretch. in unconj. ketone, acetyl, carboxyl groups
1662	1655	H_2O; CO stretching in conj. systems
1599	1603	aromatic skeletal breathing with CO stretching
1510	1510	aromatic skeletal
1457	1465	C-H deformation (asymm.)
1427	1436	C-H deformation (asymm.)
1373	1387	C-H deformation (symm.)
-	1342	C-H deform., C-OH stretch., syringyl ring
1319	-	CH_2 wagging, C_H deformation
1275	1277	C_{aryl}-O, guaiacyl ring breathing with CO stretching
1238	-	C_{aryl}-O stretching, OH i.p. bending, acetyl in sylans
1170	1174	C-O-C stretching (asymm.)
1132	1138	C-O-C stretch. (symm.), arim. C-H i.p. deformation, glucose ring vibration
1047	1096	C_{aryl}-O
1003	1006	C_{aryl}-O
898	906	C-H deformation of cellulose

The difference spectrum shows only that peaks which changed by photodegradation. Positive peaks represent the increase and the negatives the decrease of the absorption. Fig. 2-3 represent the difference IR spectrum of beech caused by 200 hour sunlight irradiation. The most important region (fingerprint region) is zoomed in Fig. 3. Several spectral changes can be observed on the difference spectra in Fig. 2-3. The OH bans decreased around 3698 cm^{-1} and increased around 3496 cm^{-1}. The CH_n valence vibrations are presented between 2830 cm^{-1} and 3000 cm^{-1}. After irradiation the carbonyl band between 1680 and 1900 cm^{-1} increased and the peak of the aromatic skeletal vibration arising from lignin (1510 cm^{-1}) decreased together with the guaiacyl vibrations at 1282 cm^{-1}. The band for the aromatic skeletal vibration at 1603 cm^{-1} also decreased in the case of beech. The intensity decrease in the range of 1100 to 1200 cm^{-1} (C–O–C and C–O–H) is the expression of ether splitting and OH group consumption followed by dehydration during UV irradiation.
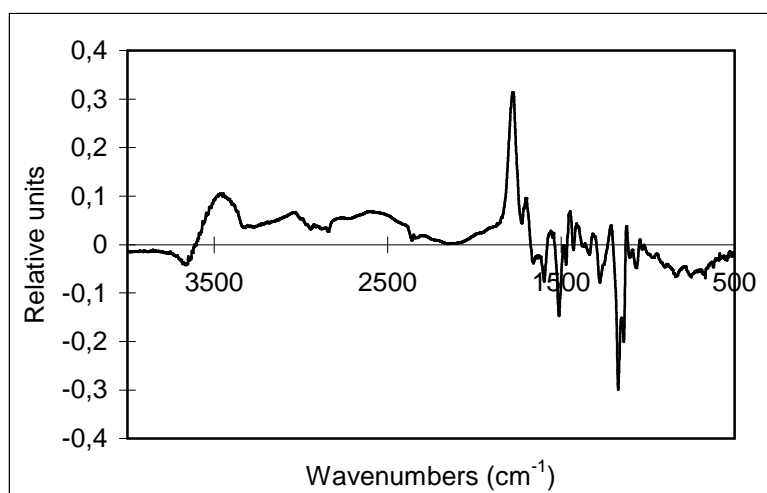

Figure 2 Difference IR spectrum of beech wood after 200 hours of sunlight irradiation
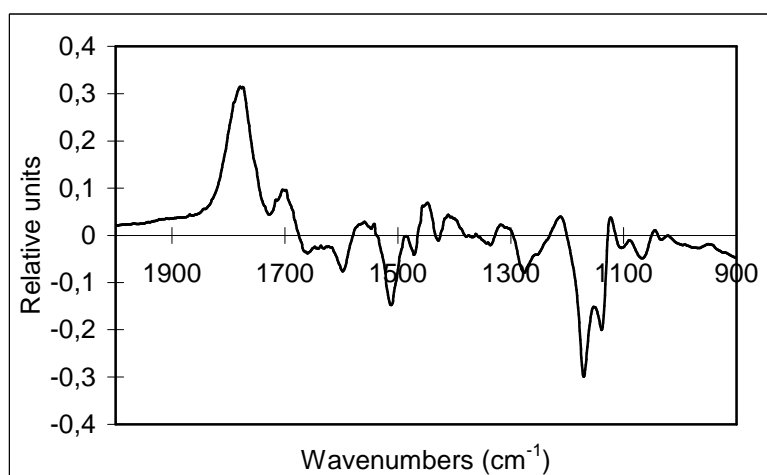

Figure 3 Difference IR spectrum of beech wood after 200 hours of sunlight irradiation (fingerprint region)

The enlarged segments of the difference spectra in Fig. 3 reveal an intensity increment in the carbonyl region in two distinct wavenumber ranges: at 1783 cm^{-1} (CO stretching in unconjugated ketones, carboxyl groups and lactones) and at 1710 cm^{-1} (CO stretching of various functional groups). The intensive band appears at 1764 cm^{-1} in case of conifers.

The IR spectroscopy is suitable to monitor the time dependence of photodegradation. This is well demonstrated in Fig. 4; where the changes of difference IR spectra are visible after 5; 10; 17; 25; 35; 50; 70 and 100 hours of mercury lamp irradiation. Usually two peaks develop in the 1900 and 1680 cm^{-1} region during the exposure of wood to UV radiation. In softwoods these peaks are close to each other. These highly overlapped bands are sometimes visible as one broad band if the irradiation is strong enough or prolonged. At the beginning of irradiation the peak at 1710 cm^{-1} is growing faster than the peak at 1764 cm^{-1}. The trend changes after 50 hours of treatment. The decrease of aromatic skeletal vibration at 1510 cm^{-1} and the decrease of the guaiacyl vibrations at 1282 cm^{-1} are also well demonstrated in Fig. 4.
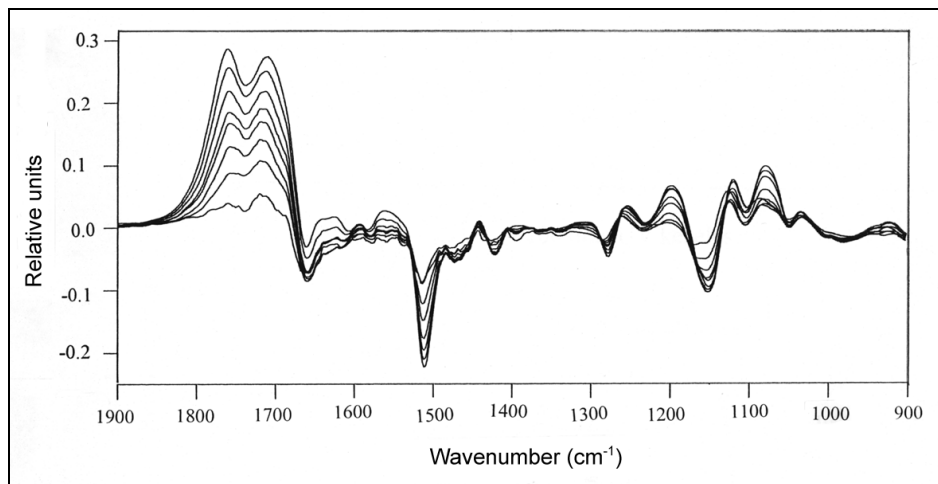

Figure 4 Difference IR spectrum of Scots pine (earlywood part of sapwood) caused by 5; 10; 17; 25; 35; 50; 70 and 100 hours mercury lamp irradiation

The rain can leach out the photodegradation products from the surface of wood. It can be detected by IR spectroscopy. Fig. 5 represents the effect of 200 hours mercury lamp irradiation and the leaching by distilled water during one day. Leaching removed remarkable part of carbonyl groups. The two main peaks decreased differently. Most part of carbonyls absorbing at 1764 cm^{-1} was leached out, but the others absorbing at 1710 cm^{-1} were only partly removed.
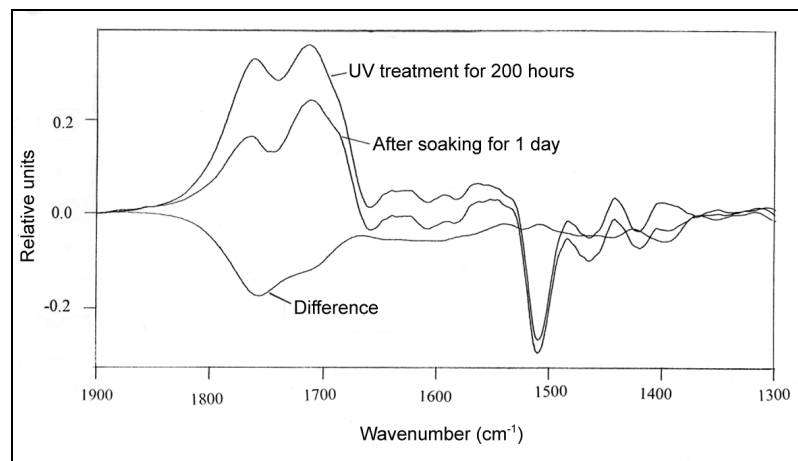

Figure 5 Difference IR spectra of spruce sapwood caused by 200 hours mercury lamp irradiation followed by one day leaching in distilled water

The lasers are suitable to determine the wavelength dependence of photodegradation. Here is presented only one new result. Further results can be found in other publications [16, 26, 27]. The decrease of CH_n groups during photodegradation is questionable. Some papers report this change but

the others not. Mostly mercury lamp irradiation creates this decrease. Figure 6 shows clearly that only short wavelengths produce the degradation of CH groups. The mostly used xenon lamps do not emit as short wavelengths as splitting of CH groups need. That is why most of papers report that CH groups are intact by photodegradation.
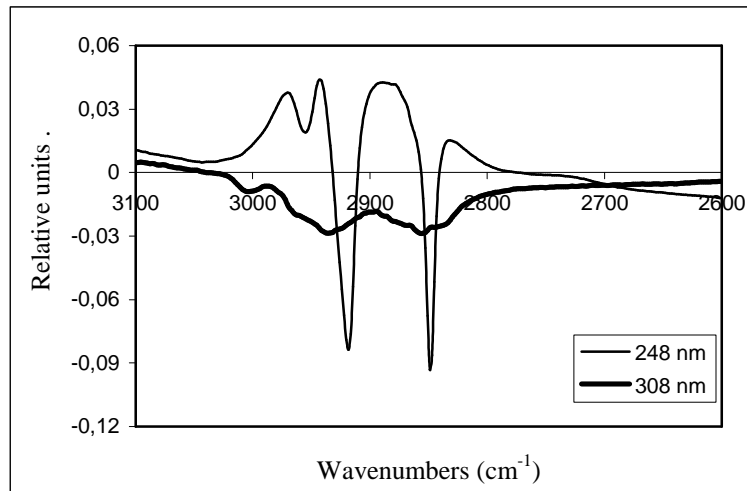
Figure 6 Difference IR spectra of Scots pine (earlywood part of sapwood) caused by lasers emitting at 248 and 308 nm. The total irradiation energy was 100 Joule in both cases.

The surface of wooden elements becomes rough during long term outdoor exposure. The sensitivity difference to photodegradation between earlywood and latewood is well demonstrated in Fig. 7. The degradation of lignin in latewood (presented at 1510 cm^{-1}) is much less intensive than in earlywood. More carbonyl groups are created in earlywood than in latewood. The changes caused by photodegradation are greater on the whole examined region in the case of earlywood.
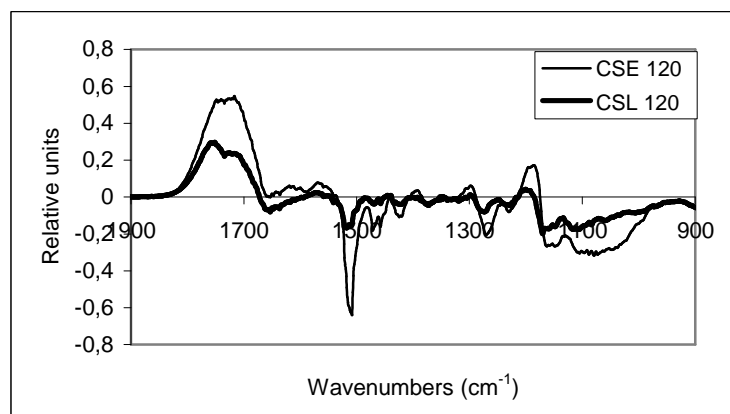
Figure 7 Difference IR spectra of Japanese cedar (C) earlywood (E) and latewood (L) caused by 120 hours sunlight (S) irradiation

References
1. Kubelka, P.J., Munk, F. (1931): Ein Beitrag zur Optik der Farbanstriche. Zeitschrift für Technische Physik 11a: 593-601.
2. Owen, N.L., Thomas, D.W. (1989): Infrared Studies of "Hard" and "Soft" Woods. Appl Spectrosc 43**:** 451-455.
3. Horn, B.A., Qiu, J., Owen. N.L. and Feist, W.C. (1994): FT-IR Studies of Weathering Effects in Western Redcedar and Southern Pine. Appl Spectrosc 48: 662-668.

4. Tolvaj, L., Faix, O. (1995): Artifical Ageing of Wood Monitored by DRIFT Spectroscopy and CIE L*a*b* Color Measurements. I. Effect of UV Light. Holzforschung 49: 397-404.

5. Craciun, R., Kamdem, P.D. (1997): XPS and FTIR applied to the study of waterborne copper naphthenate wood preservatives. Holzforschung 51: 207-213.

6. Takei, T., Hamajima, M., Kamba, N. (1997) Fourier Transform Infrared Spectroscopic Analysis of the Degradation of Structural Lumber in Horyi-ji Temple. Mokuzai Gakkaishi 43: 285-294.

7. Zanuttini, M., Citroni, M., Martinez, M.J. (1998): Application of diffuse reflectance infrared Fourier transform spectroscopy to the quantitative determination of acetyl groups in wood. Holzforschung 52**:** 263-267.

8. Pandey, K.K. (1999): A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. J Appl Polyme Sci 71**:** 1969-1975.

9. Moore, A.K., Owen, N.L. (2001): Infrared spectroscopic studies of solid wood. Appl Spectrosc Rev 36**:** 65-86.

10. Freer, J., Ruiz, J., Peredo, M.A., Rodriguez, J., Baeza, J. (2003): Estimating the density and pulping yield of E-globulus wood by DRIFT-MIR spectroscopy and principal components regression (PCR). J Chilean Chem Soc 48**:** 19-22.

11. Weiland, J.J., Guyonnet, R. (2003): Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy Holz Roh Werkst 61**:** 216-220.

12. Mitsui, K., Murata, A., Tolvaj, L. (2003): Investigation of the change in the DRIFT spectra of light-irradiated wood with heat treatment. Holz Roh Werkst 61: 82.

13. Cui, W., Kamdem, D., Rypstra, T. (2004): Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) and color changes of artificial weathered wood. Wood and Fiber Sci 36**:**291-301.

14. Kishino, M., Nakano, T. (2004): Artificial weathering of tropical woods. Part 1: Changes in wettability. Holzforschung 58**:** 552-557.

15. Tolvaj, L., Mitsui, K. (2005): Light Source Dependence of the Photodegradation of Wood. J Wood Sci 51: 468-473.

16. Papp, G., Preklet, E., Košiková, B., Barta, E., Tolvaj, L., Bohus, J., Szatmári, S., Berkesi O. (2004): Effect of UV laser radiation with different wavelengths on the spectrum of lignin extracted from hard wood materials. Journal of Photochemistry & Photobiology, A: Chemistry, 163: 187-192.

17. Chang, S.T., Wu, C.L., Wang, S.Y., Chang, H.T. (1998): Influence of Concentration and Particle Size on the DRIFT Spectroscopy of Wood. Taiwan Journal of Forest Science 13**:** 1-18.

18. Faix, O., Böttcher, J.H. (1992): The Influence of Particle Size and Concentration in Transmission and Diffuse Reflectance Spectroscopy of Wood. Holz Roh Werkst 50**:** 221-226.

19.Sudiyani, Y., Imamura, Y., Doi, S., Yamauchi, S. (2003) Infrared spectroscopic investigations of weathering effects on the surface of tropical wood. J. Wood Sci. 49: 86-92.

20. Wang, X.Q., Ren, H.Q. (2009):Surface deterioration of moso bamboo (Phyllostachys pubescens) induced by exposure to artificial sunlight. Journal of Wood Science 55 (1)**:** 47-52.

21. Ferraz, A., Baeza, J., Rodriguez, J., Freer, J. (2000): Estimating the chemical composition of biodegraded pine and eucalyptus wood by DRIFT spectroscopy and multivariate analysis. Bioresource Technol 74**:** 201-212.

22. Pandey, K.K., Khali, D.P. (1998): Accelerated Weathering of Wood Surfaces Modified by Chromium Trioxide. Holzforschung 52 (5): 467-471.

23. Umemura, K. Yamauchi, H., Ito, T., Shibata, M. and Kawai, S. (2008): Durability of isocyanate resin adhesives for wood V: Changes of color and chemical structure in photodegradation. J.Wood Sci 54: 289-293.

24. Kataoka, Y., Kiguchi, M. (2001): Depth profiling of photo-induced degradation in wood by FT-IR microspectroscopy. J Wood Sci 47: 325-327.

25.Kataoka, Y., Kiguchi, M., Williams, R.S., Evans, P.D. (2007): Violet light causes photodegradation of wood beyond the zone affected by ultraviolet radiation. Holzforschung 61 (1): 23-27.

26. Papp, G., Barta, E., Tolvaj, L., Berkesi, O., Nagy, T., Szatmári S. (2005): Changes in DRIFT spectra of wood irradiated by UV laser as a function of energy. Journal of Photochemistry & Photobiology, A: Chemistry, 173 (2): 137-142.

27. Pandey, K.K., Vuorinen, T. (2008): UV resonance Raman spectroscopic study of photodegradation of hardwood and softwood lignins by UV laser. Holzforschung 62 (2): 183-188