University of West Hungary

Ph.D. Theses

Infrared Spectroscopic Study of Wood Degradation Caused by Ultraviolet Laser

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1. Antecedents, importance and objects of the study

Because of its aesthetic and mechanical properties the wood has been a popular industrial raw material for ages. In our time it is more and more used on the one hand as interior and exterior decorative and functional units of buildings, as fence and as furniture. On the other hand the wood exposed to elements is sensitive to the environmental effects. One of the most important meteorological factors is the sun's ultrviolet radiation which damages mostly the wood surface. The study of the photodegradation of wood is important in terms of the wood protection. The improvement of protective chemicals becomes only possible having got aqquainted with the degradation processes.

The effects of UV-light for the wood degradation has begun to study some decades ago. The first step to induce photodegradation is irradiation of wood by UV-light. This is possible by two way: in natural environment using sunlight or in artificial conditions using UV-lamps. In the nature the photodegradation's processes proceed very slowly, for this reason their study requires long time (5-12 months). Moreover effects of other environmental factors (temperature changes, precipitation, fungi and insects, air pollution) superimpose on that of UV-light. In order to study the effects exclusively of certain components of sunlight, it is required to use filters. In spite of this fact the light reaching the wood surface contains the largest part of the wavelength over 320 nm and it contains only a small quantity of UV-light. So an opportunity only presents itself to study the effect of visible and infrared light. The energy of the light reaching the wood surface is not exactly measurable, so photodegradation as a function of irradiated energy cannot be studied.

Irradiation by artificial UV-lamps accelerates the processes of photodegradation and the specific effects can be separately studied. But experiments with the commonly used UV-lamps (xenon and mercury vapour lamps) require relatively long time (20-2400 hours) and the light reaching wood surface contains not only ultraviolet components but others, too. The use of light filters is needed, the irradiation time significantly increases due to the decrease of the energy reaching the sample however through the filter. The increase of the temperature of the experimental chamber caused by visible and infrared rays of UV-lamps results in the fact that a significant thermal degradation superimposes on the photodegradation. In order to avoid this situation it is necessary to cool the chamber.

The energy reaching the wood sample cannot be measured as exactly as required, therefore the degradation as a function of time is studied instead of that as a function of energy because of the proportionality of energy with the irradiation time.

The appearance of the high-powered lasers make possible another kind of irradiation procedure which enable us to carry out more exact and speedy experiments than those of the foregoing ones.

Accordingto the above the following research objects were drafted:

1. Working out a method being different from the foregoing to study the photodegradation based on the application of impulse-laser to irradiate wood samples instead of traditional UV-lamps.
2. Investigation of the changes of absorption in infrared spectra of wood samples irradiated by UV-laser, their comparison with those of wood samples irradiated by traditional UV-lamps.
3. Investigation of the changes in absorption as a function of solely energy, by changing only the energy reaching the wood surface, and by leaving unchanged every other experimental parameter.
4. Comparison of the changes in infrared spectra of the different hard- and softwood species, in order to determine which species are the most resistant against the UV photodegradation.

Using impulse-laser the energy reaches the wood surface in a few nanoseconds, whereas using natural sunlight or traditional UV-light sources it reaches the samples in a few minutes or in hours. Therefore numerous effects may appear that did not appear during the traditional experiments. For this reason my method for the irradiation is not simply a quicker and more exact version of the experiment using traditional UV-lamps, but it is an alternative possibility to study the UV photodegradation.

2. Materials and methods

2.1. Samples

Samples were prepared from four softwwod and four hardwood species. They were 1.5-2 mm thick wooden disks 10 nm in diametre. The surface contained only one type of tissue. Two sample series were made. One serie was treated neither thermally nor chemically before the irradiation while the other one was artificially dried during 2-3 days at a temperature of 70-75 °C.

2.2. Irradiation of samples by UV-light

Irradiation by UV-light was performed using a Krypton-Fluoride excimer laser. The figure shows the experimental arrangement.

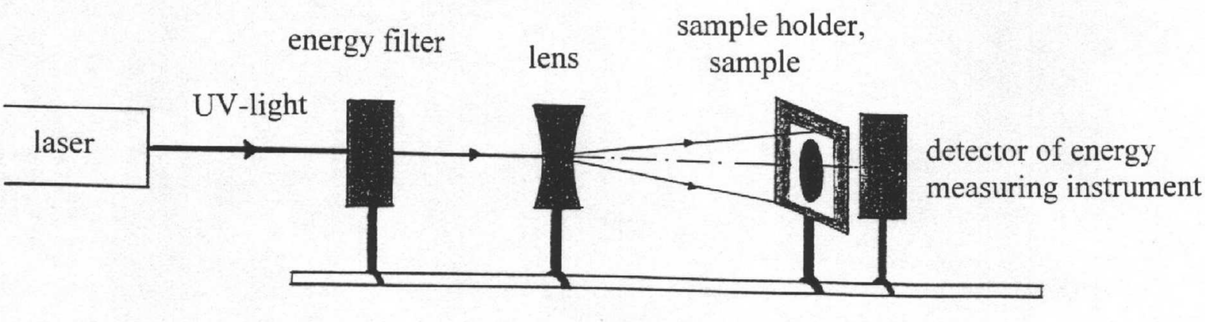

Figure. Experimental arrangement for the irradiation of samples by UV-laser.

The sample holder was made of cardboard, the hole in its centre was 10 mm in diametre. Samples were placed into the hole at right angle to the beam. The beam was made divergent using a quartz lens with a focal length of –10 cm, so the light reached the sample surface homogeneously.

The laser emitted light impulses with a wavelength of 248.5 nm and with a duration of 15 ns/impulse. The high energy of the impulses was diminished using an energy filter. The detector of the energy measuring instrument was placed immediately behind the sample holder so exclusively the energy was measured that passed through the hole of the holder. The energy reaching the sample can be diminished by further increasing the distance between the lens and the sample holder. This distance and the energy filter was set so as one sample should receive 20 mJ energy /impulse.

Two experimental series were performed. In the first all of the samples were irradiated once by 5000 pulses at 10 Hz repetition rate. So one sample received 100±10 J energy. This means an areal energy density of 1273 kJ/m^2. The aim of this experiment was the investigation of change in absorption in IR spectra of wood in controlled circumstances. No thermal or chemical treatment was used on these samples before the irradiation.

During the other experimental series each sample was repeatedly irradiated, their IR spectra were recorded after every irradiation act. The aim of this experiment was the investigation of the changes in absorption in the IR spectra as a function of irradiated energy. Each sample was irradiated by 2000 pulses per act at 10 Hz repetition rate. So one sample received 40 J energy in one irradiation act, that means an areal energy density of 510 kJ/m^2. These samples were dried artificially before the irradiation

The irradiation was carried out at atmospheric pressure and in open space. No cooling was used on the sample surface.

2.3. Infrared spectroscopic analysis

The Diffusely Reflected Infrared Spectrophotometry is the most suitable method to study surface properties by IR spectroscopy. DRIFT spectra of samples were recorded using a Bio-Rad Digilab FTS-65A/896 FTIR spectrometre. The samples were arranged in the spectrometre so that the longitudinal fibres of the wood should be parallel with the illuminating infrared beam and their surface should lie at the same level as that of the sample holder. Spectra of each sample were recorded before and after irradiation in the range of wavenumbers 400-4000 cm^{-1} with a resolution of

4 cm^{-1}, (scans: 256). The baseline correction was done with the help of three points: 3800, 1900 és 850 cm^{-1}.

Both simple comparison and difference spectra were used to study the changes in absorption. The spectrum of the irradiated sample was normalized to that of the non-irradiated one at the band of 1373 cm^{-1}: the spectrum of irradiated sample was multiplied with the ratio of spectrum intensities at 1373 cm^{-1} before and after irradiation. Difference spectra were obtained by substracting normalised spectra of irradiated samples from that of non-irradiated ones.

3. Theses

3.1.

A method different from the foregoing was worked out to study the UV photodegradation of wood ([1], [3]) and its components ([4], [6]). The method is based on the application of an impulse-laser to irradiate wood samples instead traditional UV-lamps.

3.1.1. The impulse-laser used radiates the energy with much higher energy and performance density than the natural sunlight or traditional UV-lamps.

3.1.2. Irradiation of samples is carried out so fast and simply. The treatment of one sample takes less than 10 minutes with the used experimental settings.

3.1.3. The laser radiates a well-determined wavelength of the beam, thus it is possible to study photodegradation only caused by UV-light separated from the effects of visible and infrared light.

3.1.4. The energy reaching the sample is exactly measurable thus it is possible to study the photodegradation as a function of irradiated energy.

3.1.5. The total energy reaching the sample, the energy of one laser pulse, the repetition rate of pulses and the wavelength of light can be changed thus it is possible to study separate and joint effects of this factors.

3.2.

The following was proved by the investigation of the changes in absorption in the IR spectra of samples irradiated by UV-laser ([2], [3], [5]):

3.2.1. The intensity of the wide band of OH-groups (3700-3050 cm^{-1}) increased significantly in all spectra of all samples. In this range of wavenumber decrease was exclusively observed in all previous publications. A slight decrease appeared in my experiments on the left side of the OH band in some cases, but its value was much smaller than that of the intensity increase of the centre of OH band. The decrease in intensity can be attributed to the rupture of OH···O bonds, and the increase may arise from the adsorption of the moisture from the air by the surface becoming rough as a consequence of the irradiation.

3.2.2. The two main peaks of the CH_n-region around 2910 and 2845 cm^{-1} decreased in intensity in most cases with the exception of some hardwood samples while the two most significant shoulders around 2947 and 2895 cm^{-1} increased in intensity. It is an important observation that the same processes take place in the CH_n band region during the photodegradation in all samples independently of the wood species. This is supported by the identity of the shape of the difference spectra of all samples. Previous publications described that the intensity did not change in this region.

3.2.3. A part of my observations in the range of 1850-850 cm^{-1} wavenumbers corresponds to changes in absorption of this range caused by traditional UV-lamps. These are the following:

- The intensity increased in the range of non-conjugated carbonyl-groups (1780-1700 cm^{-1}).
- The intensity decreased at the characteristic band of the aromatic rings of lignin at 1510 cm^{-1}.
- The intensity also decreased significantly at the characteristic band (1273 cm^{-1}) of the guaiacyl rings being present in large quantities in the lignin of softwoods.

- The changes were not uniform around the 1650 cm^{-1} band in case of different wood species, but the decrease caused by the loss of water adsorbed in wood can be detected.
- The changes in intensity were not uniform in the range below the 1170 cm^{-1} bands.

The fact that these observations correspond to changes described in previous publications indicates that there are some effects which are the same in spite of the different methods of irradiation. In this respect the treatment with impulse-laser is comparable with that by the classical methods.

3.2.4. In addition to the well-known changes some previously unknown changes also appeared being not mentioned in the literature. These are the following:

- The intensity decreased significantly around 1537, 1460, 1398 and 1170 cm^{-1} bands in case of all samples, and around 1425 and 1234 cm^{-1} in case of the hardwood species. The decrease in intensity of the 1456, 1425 and 1170 cm^{-1} bands shows that not only the lignin was damaged by the UV-laser light but the cellulose was also significantly damaged. An Unambiguous conclusion cannot be deducted from the decrease of the 1398 cm^{-1} band. The decrease of the 1234 cm^{-1} band shows the damage of the aromatic structure of lignin. The observations related to the 1537 cm^{-1} band require further investigations.
- The intensity increased around the 1320 and 1209 cm^{-1} bands in case of hardwoods. The increase of 1320 cm^{-1} is caused by changes of concentration of several components while the increase at 1209 cm^{-1} may be caused by increase in concentration of free phenolyc hidroxyl-groups of lignin.
- The peak around 1132 cm^{-1} shifted towards lower wavenumbers. This phenomenon can arise from the fact that the sample surface became rougher so the usually appearing anomalies in this region of the DRIFT spectra being dependent on surface properties changed.

These new observations show that the UV-light emitted by the laser damages chemiceal bonds being stable against the effects of traditional UV-laps.

3.3.

The following was proved by the investigation of the changes in absorption of the IR spectra of samples as a function of the energy [under publication]:

3.3.1. In the OH and CH_n band regions the same changes were observed as the changes desribed in the literature, due to irradiation with low energy: decrease in the OH band region and no change in the CH_n band region. Significant increase in the hydroxyl band region was only observed after irradiation with a high amount of energy. The reason for this phenomenon is that the weak OH···O bond split at first. At the same time the sample surface irradiated by a high performance density becomes more and more rough, so it is capable to adsorb more and more moisture from the surrounding air. This adsorbed moisture content appears as an increase in the OH band region.

3.3.2. Bands resulting from only one chemical component (1510 cm^{-1}: aromatic rings, 1273 cm^{-1}: guaiacyl units, 1170 cm^{-1}: C–O–C bonds in the cellulose), and containing no other absorption maxima around them, uniformly decreased. This decrease was continuous but damped down with absorbed energy, and after a certain amount of energy it can also come to a stop.

3.3.3. The regions where the band of a chemical component lies next to another one (for example 1650 cm^{-1}: conjugated carbonyl groups and adsorbed water in wood capillaries, 1620-1560 cm^{-1}: syringyl units and carboxylates in lignin, besides 1460, 1425, 1130 cm^{-1} bonds), showed no uniform changes during the irradiation. An increase followed the initial decrease. It depended on the wood species whether the increase ensued after a certain amount of energy, and whether it was beyond the decrease.

3.3.4. The same processes take place during the irradiation with UV-laser light at the surface of sample independently of the wood species and of wood issue. The characteristics of wood species are observable only after absorption of a small amount of energy while these characteristics disappear after a large amout of energy, changes in the IR spectra become uniform. The recorded spectra of treated samples show the momentary state of photodegradation. The differences in changes in absorption of different samples may arise from the difference of the initial spectra (features of wood species, surface properties), but it also can be caused by the fact that the samples are in different phases of the photodgradation at the moment. The value of changes in absorption becomes slower with the increase of energy.

3.4.

The following was proved by the comparison of wood species and tissues [3]:

3.4.1. The differences in changes in IR spectra of softwoods and hardwoods can be explained by the differences in their chemical structure. Softwood lignin contains significantly larger amounts of guaiacyl units than syringyl units while hardwood lignin contains around the same amount of both of them. This difference also appears in the spectra and it causes different changes in absorption around the bands of these two components: at 1620-1560, at 1340-1315 and at 1280-1230 cm^{-1} regions.

3.4.2. In case of the same softwood species the latewood of the heart-wood changed the least while the earlywood of sap-wood changed most. This unambiguous difference cannot be observed between the early- and latewood of hardwoods. Among hardwoods the bands of locust and beech changed the least.

3.4.3. The heart-wood of latewood of larch was far the most resistent against the ultraviolet photodegradation.

Those wood species and issues were most resistent against the photodegradation which contain higher amounts of extracts. Extracts protect wood against photodegradation by absorbing a part of energy reaching the wood surface and they compose stable radicals.

4. Proposals for utilization of the results and for further investigation

The irradiation method worked out is a big leap forward with respect to the investigation of wood degradation. It is possible to carry out fast, exact and reproducible experiment series using laser. Each parametre of the irradiation can be varied (energy and repetition rate of pulses, total energy reaching wood surface, wavelength). It is adviseable to study separate and joint effects of these factors. It is necessary to perform more exact measurements to reveal how the duration of irradiation time influences the degradation of wood in case of same amount of energy. It is also important to reveal how the degradation depends on the wavelength of absorbed light, since the ozone layer protecting the Earth grows thinner and thinner so we must reckon with the damaging effects of the UV-light with shorter wavelengths. It is necessary to perform more exact observations to identify the unidentified bands appearing in the recorded IR spectra (1537 and 1209 cm^{-1}) and to interprete their changes in intensity. As soon as the dependence of photodegradation on several factors will become known, research can start to develop protective chemicals for woods against the photodegradation. Observation of the effects of irradiation with UV-laser is also useful to test the effectivity of protectives.

5. Publications

[1] Barta, E., L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi, G. Papp (1998): *Wood degradation caused by UV-laser of 248 nm wavelength* Holz als Roh- und Werkstoff (Germany) 56. p. 318.

[2] Barta, E., L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi, G. Papp (1999): *Photodegradation of Leaf-woods Caused by 248.5 nm Laser* Drevársky Vyskum (Slovakia) 44 (1) pp. 13-19.

[3] Papp, G., E. Barta, L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi (2001): *Wood degradation caused by KrF UV-laser* Technology Letters 5 (1) pp. 1-6.

[4] Tolvaj, L., E. Barta, B. Kosikova, O. Berkesi, T. Nagy, S. Szatmári, G. Papp (1998): *UV-laser inducted photodegradation of lignin impregnated into cellulose plate*
Acta Facultatis Ligniensis (Sopron) pp. 51-54.

[5] Barta, E., L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi, G. Papp (1998): *Hardwood degradation caused by 248.5 nm UV laser*
Proceedings of the 3rd International Symposium „Wood Structure and Properties '98". Arbora Publishers, Zvolen, Slovakia, pp. 59-60. Zvolen, Slovakia, August 24-27.

[6] G. Papp, L. Tolvaj and E. Barta (1999): *Changes in DRIFT Spectra of Silver Maple and Lignin Extracted From the Same Wood Caused by 248.5 nm Laser.* Proceedings of The Fourth International Conference on The Developement of Wood Science, Wood Technology and Forestry. Missenden Abbey 14th-16th July 1999. Fair Print Ltd., High Wycombe, Buckinghamshire

6. Presentations

Papp, G., L. Tolvaj, E. Barta (1998):
Photodegradation in lignin and wood caused by UV-laser
Environment and Wood Science Jubilee Conf. Sopron, Sept. 1st-3rd.

Barta, E., L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi, G. Papp (1998):
Hardwood degradation caused by 248.5 nm UV laser
The 3rd International Symposium „Wood Structure and Properties '98".
Zvolen, Slovakia, August 24th-27th. (Poster)

Tolvaj, L., E. Preklet, E. Barta, G. Papp (2001):
Dependence on light sources of the artificial photodegradation of wood
Workshop within COST action E-18, High Performance Wood Coatings
Paris, France, June 18th-19th.

Tolvaj, L., E. Preklet, E. Barta, G. Papp (2001):
Photodegradation of wood caused by UV lasers
Workshop on photodegradation of wood within COST action E-18
(23rd November) BRE Watford England