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PhD thesis

Study of the photodegradation of wood due to irradiation by UV and visible laser light of different wavelengths

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The aim of the research was to study the photodegradation of wood due to ultraviolet and visible light. It is a prerequisite for the exploration of the damaging effect of solar radiation and for protection against it to get acquainted as exactly as possible with the processes playing a role in it. An important point is for this exploration to produce reproducible results in a short period. For the study of the damages due to irradiation, artificial sources of radiation are to be used. Parameters can be changed during the irradiation when impulsive lasers are used – in contrast to traditional (marcury vapour lamp, Xenon lamp) methods – such as the wavelength and intensity of the irradiation. If not only lasers radiating in the ultraviolet domain, but also those radiating in the visible domain are used, effects due to UV and visible light can be studied and compared in identical circumstances. Such irradiations, however, can not reproduce effect of the solar radiation. They offer only possibilities for the more detailed study of the photodegradation and for the research for its characteristics.

Aims of the research:

Study of the photodegradation of wood by infrared spectroscopy.

- Study of the wavelength dependence of the changes in the spectra of wood due to irradiation.
- Comparison of changes in the spectra of different wood arts and earlywood and latewood, respectively, due to irradiation at the same wavelengths.

Study of the photodegradation of lignin.

- Comparison of changes in spectra of lignin samples due to irradiation at different wavelengths.
- Comparison of changes in the spectra of samples due to changes in the number of impulses per unit surface.

Comparison of the photodegradation for white and red heartwood in beech.

Methods of the research:

Samples were taken from latewood and earlywood of heartwood of native Hungarian wood species.

The species are:

beech (*Fagus silvatica*)

Red heartwood of beech

common ash (*Fraxinus excelsior*)

Scots pine (*Pinus silvestris*) and

spruce (*Picea abies*)

Additional samples were made from other pine and deciduous woods also from lignin impregnated on cellulose plates in order to study in addition to changes in wood and changes in the chemical constituents of wood too. Lignin samples were taken from beech wood. Lignin was isolated and impregnated on cellulose plates by Professor Bozena Kosikova (Chemical Institute of the Slovak Academy of Sciences).

Irradiation was made by impulsive lasers. I tried to select lasers radiating in all radiation bands of solar radiation, the selection was, however, mainly determined by the availability of lasers.

The following lasers were used in the study (Table 1)

RADIATION DOMAIN	LASERS, WAVELENGTH OF THE IRRADIATION		NUMBER OF IMPULSES	ENERGY OF AN IMPULSE	ALL RADIATED ENERGY	SURFACE DENSITY OF ENERGY
190-210 nm atmospheric window UV	**ArF** **(argon fluoride)** **excimer laser**	**193 nm**	1500	10 mJ	**15 J**	$1.3\cdot10^5 J/m^2$
210-290 nm O_3 photodissociating UV	**KrF** **(crypton-fluoride)** **excimer laser**	**248.5 nm**	5000	20 mJ	**100 J**	$8.8\cdot10^5 J/m^2$
290-315 nm UV-B	**XeCl** **(xenon-cloride)** **excimer laser**	**308 nm**	5000	20 mJ	**100 J**	$8.8\cdot10^5 J/m^2$

315-380 nm UV-A	**N (nitrogene) excimer laser**	**337 nm**	35714	2.8 mJ	**100 J**	$8.8 \cdot 10^5$ J/m^2
380-720 nm visible radiation; (green, yellow)	**coumarine**	**500nm**	50000	2 mJ	**100 J**	$8.8 \cdot 10^5$ J/m^2
	rhodamin6G	**581 nm**	25000	4 mJ	**100 J**	$8.8 \cdot 10^5$ J/m^2

Table 1: Characteristics of the irradiation used for wood

In the case of lignin I only studied chemical changes due to irradiation at 193 nm, 248.5 nm, 308 nm at different number of impulses per unit surface.
In the case of irradiation of beech red heartwood, I used impulse numbers and radiated energy as given in Table 1 at wavelength 193 nm, 248.5 nm, 337 nm, 500 nm and 581nm.
An important condition was uniform irradiation on the surface of the samples. This aim was reached by lenses with made the beam divergent. The energy of the impulses radiated by the lasers proved to be to high in certain cases. The energy was diminished then by energy filters put into the path of the laser beam. The energy of the radiation arriving to the surface of the sample head to be controlled. As lasers do not ensure constant energy of the impulses, the energy reaching the sample have to be often measured by an energy measuring device behind the holder of the sample. If the energy of the impulses changes, I changed the arrangement of the experiment suitably by changing the distance of sample to lens. This ensured that the above given parameters were applied in the experiments.

Infrared spectra were determined by diffuse reflection infrared Fourier transform (DRIFT) technique. I obtained DRIFT spectra in the wave domain 3800-850 cm^{-1} with a resolution 4 cm^{-1}. The instrument used was a Fourier Transformation Infrared (FTIR) spectrometer (FTS-65A) developed by Bio-Rad Digilab Division, with an MCT detector. I corrected the baseline at three points (3800 cm^{-1} , 1900 cm^{-1}, 850 cm^{-1}) within the domain 3800-850 cm^{-1}. I fitted a straight line two point each to the obtained spectrum, then I subtracted the differences between the straight line and the 0 line from the spectrum intensities.

I used for the analyses – in addition to well-know methods (representation side by side, differential spectra) – new methods for comparative and detailed studies (band damage index, special application of the Fourier deconvolution).

Band damage index

I determined bands for the peaks in the infrared spectra of wood. I computed the definite integral of differential spectra and of the baseline-corrected spectra of virgin samples for this bands.

$$M\left[\bar{\nu}_1;\bar{\nu}_2\right]=\frac{\int_{\bar{\nu}_1}^{\bar{\nu}_2}\Delta I(\bar{\nu})d\bar{\nu}}{\int_{\bar{\nu}_1}^{\bar{\nu}_2}I(\bar{\nu})d\bar{\nu}}$$

where $I(\bar{\nu})$: is the intensity in Kubelka-Munk units vs.

where $\Delta I(\bar{\nu})$: is the differential spectrum vs wavenumber

By computing the quotients for corresponding pairs I obtained the parameter (band damage index, BDI). The absolute value of the index shows the magnitude of the change, i.e. how many times the original intensity is the change. The sign corresponds to the increase (positive) and decrease (negative) changes of the absorption. This method enabled me to compare spectral changes due to laser irradiation at different wavelengths.

When analysing spectra, methods are needed which give more detailed information then differential spectra offer.

Such a method is the Fourier-deconvolution.

In a first step, I deduced an average spectrum from the IR spectra of the lignin samples. I computed then Fourier components of the average spectrum, afterwards I determined the number and position of the bands in the spectra using Bessel functions. I fitted to these bands Gauss and Lorentz distributions and obtained the band with and the ratios Gauss-Lorentz. In a following steps, I fitted the spectra of the virgin samples to the average spectrum by allowing only the intensity to changes at the peaks. If certain parameters of the average spectrum proved to be in accurate then the position, with and Gauss-Lorentz ratio of the bands was slightly changed for a limited number of bands. I compared thereafter the spectra of samples before and after the irradiation by taking into account the changes of only the intensity. For this purpose the spectra had to be normalized to each other.

Two types of differential spectra were computed for each pair of virgin and irradiated samples by taking the different of the intensities of given bands and other parameters of the peaks respectively. The first types only contained pairs where the intensity increase, the second one contained pares where intensity decreased during the irradiation. Thus I got two synthesised spectra which split effect into those causing intensity increase and into those causing intensity decrease. Bonds and bond types belonging to these two groups can be then found from the database. Parameters of the fitted bands can be used for the quantitative determination of the spectral bands and for the discovery of hidden connections.

New scientific results

1. The method of irradiation applied in the investigation ensures broader possibilities for the study of photodegradation of wood ([2], [3], [4], [5], [6]).

- Lasers radiating at different wavelengths enable us to study the effects caused by irradiation at different wavelengths. Environmental influences could be excluded during the irradiation and parameters of the measurement could be kept constant, respectively.
- Lasers of discrete wavelengths worked in UV and visible domains. Using them comparison in a wavelength range being the widest up to now could be realized.

2. Especial application of the Furier-deconvolution enables us suggestive illustration and detailed analysis of spectral changes [4].

- This method necessitates a more circumstantial processing of data but such a processing significantly reduces the number of errors made in the interpretation of changes, and may lead to the discovery of hidden connections.

By introducing the band damage index based on traditional differential spectra, a uniform and quantitative analysis could be carried out ([4], [5]).

- Changes in the spectra in consequence of the irradiation were not only quantitatively compared but also enabled us an interpretation from different points of view of a great amount measurement results.

3. A comparison of the results with those in earlier publications has shown that domain UV-A is not present in the case of irradiation with traditional methods. Traditional investigations did not split irradiation according to wavelengths in detail, in an overwhelming part of the investigation the UV domain was considered as a single unit. Therefore the effect of irradiation in the near-visible, but still in the UV domain could not be detected.

4. Original spectra of the samples could be also compared as the number of samples was very high. It could be shown that the band 1537 cm^{-1} is only present in about 30 percent of pine samples, thus it deserves special attention in comparative analyses, and this facts explains why no corresponding band is mentioned in the literature.

5. Results obtained during general analyses

The domain 1825-1692 cm^{-1} of the spectra are characterized by an increase of the absorption due to short wavelengths irradiation while long wavelengths irradiation (with visible light) result in absorption decrease.

The same is not valid for other domains it is nevertheless it is valid in the domain 3024-2744 cm^{-1} in the case of beech earlywood and latewood.

6. Results obtained by the band damage index

It was found that by radiating an energy of 100 J on the surface samples – using irradiation by the same laser – the number of significant changes as defined in the thesis is higher at pines than at deciduous trees.

The highest number of significant changes due to photodegradation as defined in the thesis was obtained among all wavenumber domains in that belonging to the peak 1740 cm^{-1} i.e. in the domains 1825-1692 cm^{-1} .

7. Results from the study of the red heartwood

The photodegradation of the red heartwood for beech corresponds in most cases to that of the white beech. In the case of white beech it is characteristic that absorption increases due to UV irradiation in the domains 3024-2744 cm^{-1-} and 1825-1692 cm^{-1} in contrast it decreased due to irradiation while visible light. The same is valid for the changes of the red heartwood peak at 3450 cm^{-1} (band 3801-3024 cm^{-1}).

There is an unambiguous difference in the change of red heartwood and white beech samples when irradiated at 500 nm in the domains 1692-1630 cm^{-1} , 1630-1548 cm^{-1}. Absorption decreases in white beech and in creases in red heartwood.

I found for beech samples in certain selected domain of the range 1825-1300 cm^{-1} of the complete spectrum that the intensity of the photodegradation produced by lasers used in the present experiment does not characteristically depend on the type of the samples namely if it was taken from red heartwood from white beech, it is much more important whether it was taken from early- or from latewood. (By computing the average of the absolute values of all BDI-s obtain in certain domains for beech samples irradiated with all possible wavelengths.)

8. Results of study of lignin samples [4].

The opening of the glucopyranose ring is an important part of the process of photodegradation of lignin samples (lignin impregnated on cellulose plate). All subsequent steps depend on the energy and distribution of photons.

During the photodegradation of lignin, all possible chromophors (amid groups, benzoide rings and derivatives of organic acids) are affected what produces unsaturated compositions.

Proposals for future investigations:

Experimental methods and analyses presented in the theses can be used for wide-range investigations of the photodegradation of wood and of its main constituents. Using the proposed irradiation method, irradiations and wavelengths and with different energies can be realized. Energy and number of the impulses can be modified with in certain limits. Methods of analyses enable us not only to compare qualitatively results, but also quantitative comparisons are possible. Using BDI, great amounts of data can be compared and analyzed. UV tolerance of different wood species and of early- and latewood can also be studied. The special application of deconvolution ensures a more accurate analysis of the process of photodegradation and the interpretation of processes discovered, but not identified using differential spectra.

Publications connected with the thesis

[1] *Barta E., Preklet E., Tolvaj L., Papp Gy. 2002.* Energy dependence of the photodegradation of wood due to irradiation with UV light of certain wavelenghts. Day of Hungarian Science 2002, Scientific Conference at the occasion of the centenary of birth of Professor Nándor Pallay (Lecture)

[2] *Barta, E., G. Papp, E. Preklet, L. Tolvaj, O. Berkesi, T. Nagy, S. Szatmári 2005.* Changes of absorption in infrared spectra of softwood materials irradiated by UV-laser as a function of energy Acta Silvatica et Ligniensia Hungarica 1 (1) 83-91

[3] *Papp, G., E Barta, E. Preklet and L. Tolvaj 2004.* Using DRIFT technique to monitor the wood degradation caused by UV laser Workshop within COST action E-18, High Performance Wood Coatings (16-17 February) Copenhagen, Denmark

[4] *Papp, G., E. Preklet, B. Košiková, E. Barta, L. Tolvaj, J. Bohus, S. Szatmári, O. Berkesi 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

[5] *Preklet E., Papp Gy. 2001.* Changes of the infrared spectrum of wood VS. wavelengths of irradiations. Conference on the Day of Science.

[6] *Preklet Edina 2000.* Study of the photodegradation of wood due to irradiation by UV light of different wavelengths. Conference of Postgraduate Students of the Veszprém Region, Section Wood Science, University of Western Hungary, 94-97

[7] *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 (18-19 June), France

[8] *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 BRE Watford (23rd of November) England