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Changes in the DRIFT Spectra of Softwood Irradiated by UV-laser as a Function of Energy

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Abstract – We investigated energy dependence of the effect of UV-laser irradiation on the DRIFT spectra of softwood samples. Changes in the spectra of softwoods have been studied with 248.5 nm wavelength of UV-laser radiation. To monitor the energy dependence, different number of laser impulses were directed towards the sample's surface. The dependence on energy of different bands can be listed into four groups. Broad absorption bands, which belong to the same chemical groups located at various positions, do not show consistent changes due to the absorption of different energy dozes. The intensity of OH bands for the treated samples can be higher or lower depending on the amount of radiation energy. In the CH_n and in the band of non-conjugated carbonyl groups only absorption increase can be observed. Bands resulting from only one chemical component, and containing no other absorption maxima around them, uniformly decreased. The regions where the band of a chemical component lies next to another one, showed no consistent changes during the irradiation. The initial decrease was followed by increase.

softwood / UV laser / irradiation / energy dependence / degradation / DRIFT spectroscopy

Kivonat – **UV-lézerrel besugárzott fenyő faanyag DRIFT spektrumának változása az energia függvényében.** Fenyő faanyag DRIFT spektrumán vizsgáltuk UV-lézer besugárzással az energia függést. Az anyag spektrumának változását 248,5 nm hullámhosszú lézer sugárzásával idéztük elő. Az energiafüggés vizsgálatához változtattuk a minták felületére irányított lézerimpulzusok számát. Az energiafüggés szerint a különböző sávok négy csoportba sorolhatók. Azon széles sávok, amelyek az anyagot alkotó, különböző pozíciókban elhelyezkedő azonos kémiai csoportokhoz tartoznak, nem mutatnak egységes változást. A kezelt minták OH sávjainak intenzitása nőtt vagy csökkent, a sugárzás energiájának mennyiségétől függően. A CH_n és a nem konjugált karbonil csoportokhoz tartozó sávok abszorbciója nőtt. Azon sávok abszorbciója csökkent, amelyek egyetlen kémiai alkotótól származnak és környezetükben nem található más abszorbciós maximum. Azon tartományokban, ahol valamely kémiai komponens sávja mástól származó sáv közelében fekszik, alacsony energián csökkenés, magas energián növekedés következett be.

fenyő faanyag / UV-lézer / besugárzás / energiafüggés / degradáció / DRIFT spektroszkópia

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1 INTRODUCTION

The surface of wood exposed to elements becomes gray, rough and stringy. It looses not only the usual appearance, but also its mechanical properties, even the strength characteristics degrade. As a consequence its admissible load decreases and its functional characteristics are limited. The damages caused by exposure are called degradation processes. There are several factors determining degradation processes: sun radiation, rain, temperature fluctuation, air humidity, fungi and insects. Among them the ultraviolet (UV) radiation of the sun is the most important in the degradation of the wood's surface. The study of the UV-photodegradation of wood began some decades ago (Kalinins 1966; Hon – Chang 1984). The investigation has two steps: first irradiating the wood's surface by an UV beam and detecting the changes caused by the radiation. There are two ways of irradiation: in a natural environment using the sun as a source, or in artificial circumstances, with different kinds of UV lamps. Neither in a natural environment, nor with traditional UV lamp (Xenon and mercury vapor lamps) experiments, is there a precise way to measure the energy of radiation on the sample's surface. In addition, UV-photodegradation is influenced by other factors (moisture, temperature, visible light and infrared radiation) that are hard to exclude. Using UV-laser instead of traditional lamps during the irradiation could solve all of the above-mentioned problems. Using lasers as radiation sources (Barta et al. 1998; Papp et al. 2001) the duration of the treatment can be shortened, the wavelength of the radiation is known, and the energy can be determined, as well as the intensity of radiation at the surface. In order to investigate the UV photo degradation's dependence on radiation energy, we used UV laser working at definite wavelengths. The infrared (IR) spectrum of wood has already been studied in many respects (Hess 1952; Marton – Sparks 1967; Michell 1988). The diffuse reflection infrared Fourier transform (DRIFT) spectroscopy is a widely accepted method of analyzing the spectrum of wood, wood components and pulp, and of monitoring the changes occurring on the surface of the wood (Hon 1994; Schultz – Glasser 1986; Dirckx et al. 1987; Michell 1988; Owen – Thomas 1989; Zavarin et al. 1990; Backa – Brolin 1991; Tylli et al. 1993; Pandey – Theagarajan 1997; Koš´ıková – Tolvaj 1998; Barta et al. 1999; Papp et al. 1999; Papp et al. 2004). The energy dependence on changes in the absorption spectra of softwood materials will be discussed below.

2 MATERIAL AND METHODS

For the experiments the specimens were manufactured from softwood (larch, Scotch pine). Samples used were disks with 12 mm diameter and 1-2 mm thickness. Their surface contained only one type of tissue (early- or latewood of heartwood or sapwood). To attain uniform moisture content, the samples were dried at 70-75 ^{o}C during 3 days. Irradiation by UV-light was performed using a Krypton-Fluoride excimer laser. The schematic arrangement of experiments is shown in *Figure 1.*

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 reduced using an energy filter and the specimens were positioned with their surfaces perpendicular to the laser 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 detector of the energy-measuring instrument was placed immediately behind the sample holder, so exclusively the energy that passed through the hole of the holder was measured. Further increasing the distance between the lens and the sample holder can diminish the energy reaching the sample. This distance and the energy filter were set so that the sample should receive 20 mJ energy /impulse. Each sample was repeatedly irradiated; their IR spectra were recorded after every irradiation phase. Each sample was irradiated by 2000 pulses per phase, at 10 Hz repetition rate, so each sample received 40 J energy in each phase. This is equivalent to an area energy density of 510 kJ/m^2. The irradiation was carried out at atmospheric pressures and in an open space. No cooling was used on the sample surface.

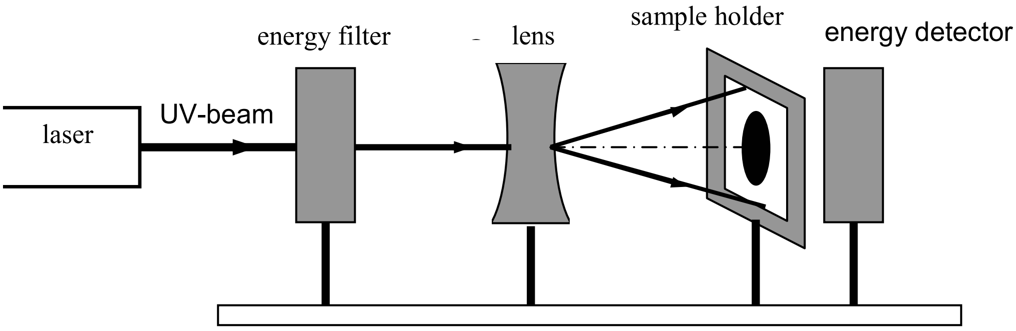


Figure 1. The schematic arrangement of irradiation setup

DRIFT spectra were recorded between 3800 and 850 cm^{-1} with 4 cm^{-1} resolution by using a Fourier-transform infrared (FTIR) spectrophotometer (Bio-Rad Digilab Division FTS-65A), modified according to our needs. Base-line correction was performed in two steps: between 3800 and 1900 cm^{-1} and 1900 and 850 cm^{-1}.

Changes caused by the UV irradiation in the chemical structure of wood samples were investigated by analyzing the difference spectra obtained by subtracting the appropriate spectrum (measured in Kubelka-Munk unit (Kubelka 1948; Kubelka 1954)) of untreated samples from the spectrum (measured in Kubelka-Munk unit) of treated samples. It is important that the absorbance be constant at wave number values where there is no change in the spectrum. On the basis of earlier studies (Barta et al. 1988) the absorbance maximum at around 1373 cm^{-1} was chosen as such a reference point. Each spectrum taken after UV treatment was multiplied by the factor obtained as the ratio of the absorbance at 1373 cm^{-1} measured before and after UV irradiation. Thus the intensity value on the difference spectra is also given in Kubelka-Munk unit. Positive and negative values refer to an increase and a decrease in absorbance, respectively.

3 RESULTS AND DISCUSSION

To reveal the qualitative features of the spectra and its changes, the spectra of the earlywood of larch's heartwood, for untreated samples and those treated with 8000 impulses, are shown in *Figure 2*. The relevant peak wave numbers are also indicated.

For the analysis of the change in spectra caused by the irradiation, the difference spectra were divided into two regions:

1) Spectra between 3800 and 1800 cm^{-1}, and

2) Spectra between 1800 and 850 cm^{-1}.

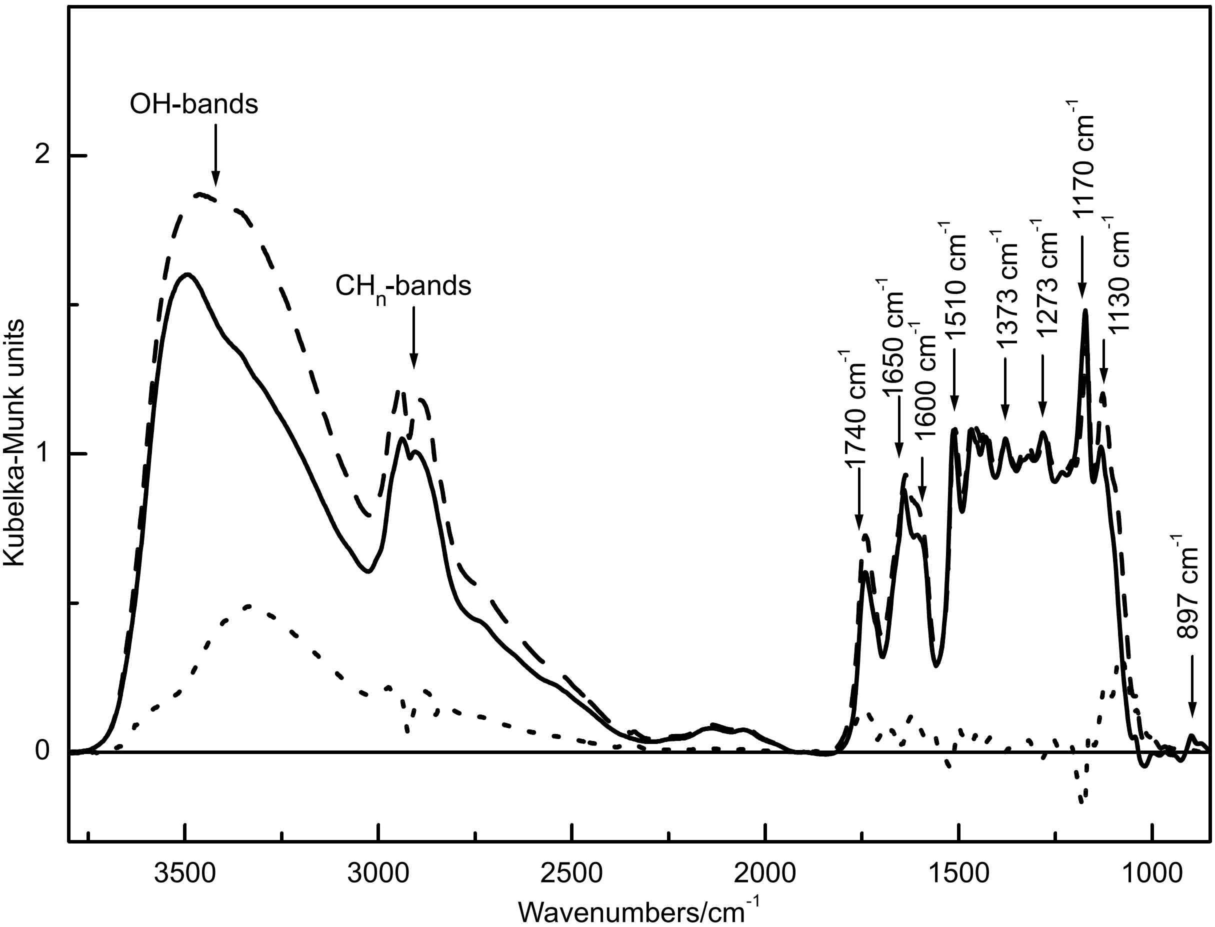


Figure 2. DRIFT spectra of larch between 3800 cm^{-1} and 850 cm^{-1} (earlywood of heartwood) without treatment (solid), irradiated with 160 J (dashed) and their difference (dotted)

3.1 Changes in the spectra between 3800 and 1800 cm^{-1} *(Figure 3)*

In the OH-band region (3700-3050 cm^{-1}) absorption may increase or decrease, depending on the energy. At low energy levels, the left side of the band and even the centre of the band decrease. In the case of 40 and 80 J this decrease is much more pronounced, than the nondescript increase in the absorption on the right side of the band. Around the maxima and the right side of the band the absorption increases with the rise of energy. In this range, the difference spectra are always positive for 120 and 160 J. At the same time the definite decrease at the left side of the band is followed by increase, and for 160 J the difference spectra became positive for all of the samples.

Investigation results indicate that there are several processes in the OH-band region during irradiation. At low energies, processes that cause decrease in absorption at the left side range of band are dominant. This is very likely due to the decomposition of H bridge bonds, which do not need large amount of energy. Concurrently, hydroxyl groups start to appear, but this process is slower. One of the reasons is that the surface of the specimen becomes rougher and rougher due to the high energy density laser impulses reaching the samples within a short time period, 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. In the CH$_n$ range (3000-2900 cm^{-1}) absorption always increases in softwood, regardless of energy.

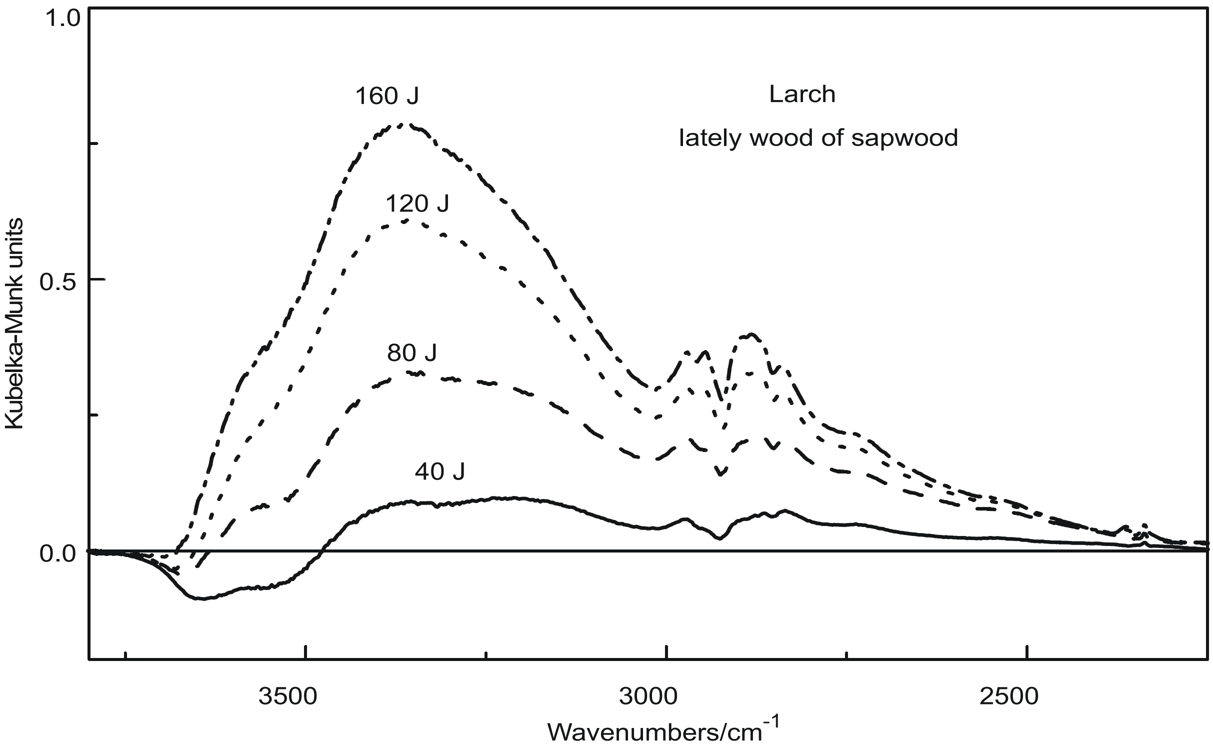
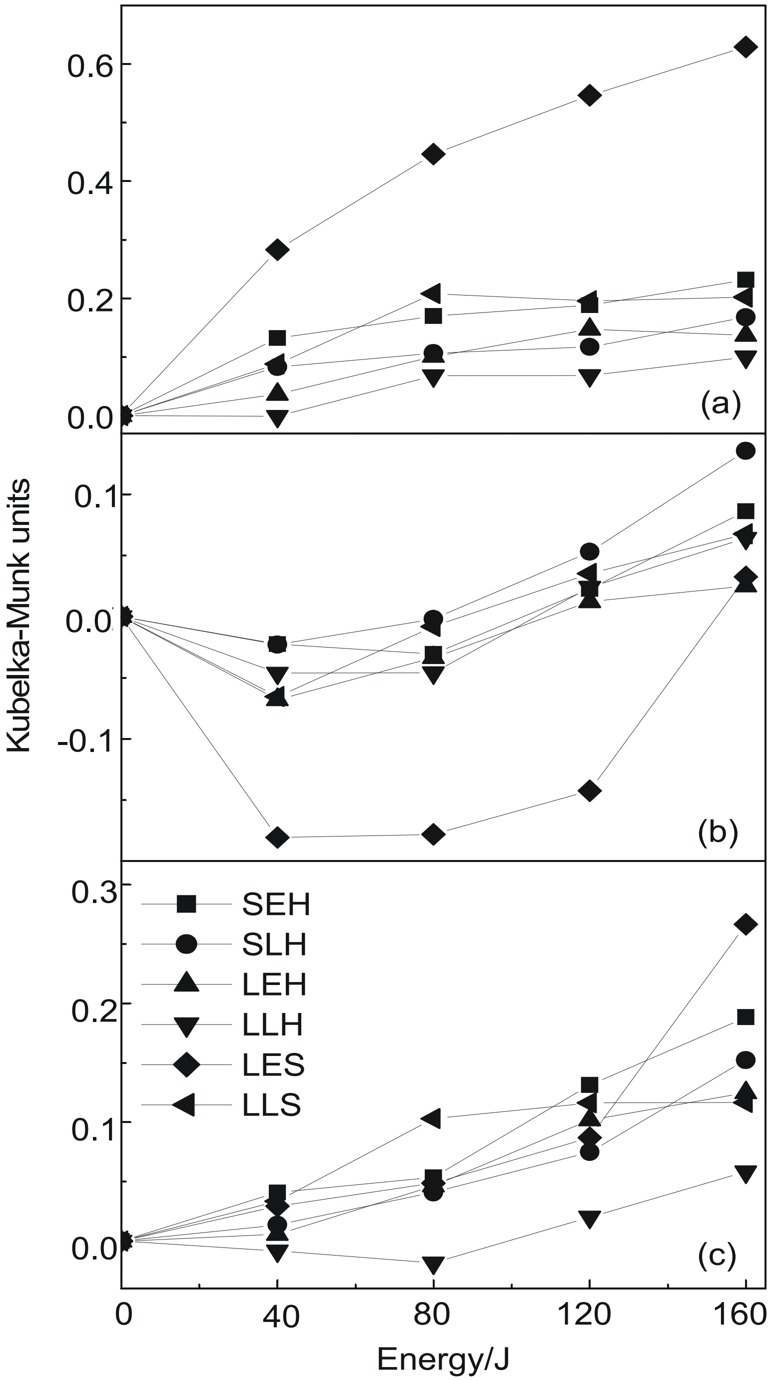


Figure 3. Difference spectra of larch (latewood of sapwood) between 3800 cm^{-1} and 2250 cm^{-1} irradiated with different impulse numbers from UV lasers

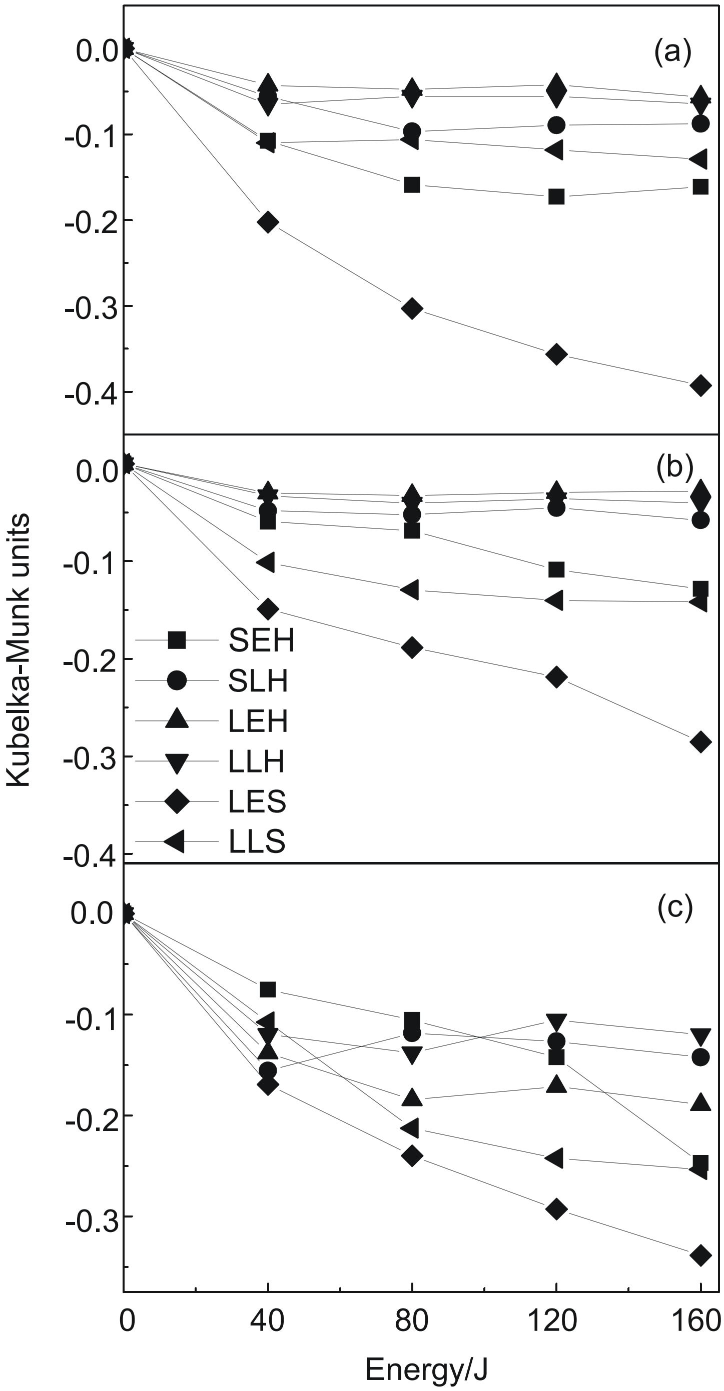
3.2 Changes in the spectra between 1850 and 850 cm^{-1}

The absorption region between 1800 and 1550 cm^{-1} behaved differently after irradiating the samples with different energies. In the band of non-conjugated carbonyl groups (1780-1700 cm^{-1}) a broad absorption increase can be observed around 1740 cm^{-1}, as a result of irradiating the samples with KrF laser at both energy levels *(Figure 4(a))* in agreement with earlier results (Papp et al. 2001). A decrease in absorbance around 1650 cm^{-1} (conjugated carbonyl groups and adsorbed water in wood capillaries) can be observed in the spectra for low irradiation energy, which is followed by increase for at high energy levels *(Figure 4(b))*. The difference spectra became positive after irradiating the sample with 160 J. The decrease can be attributed to loss of water as well as of conjugated C=O groups. But at higher energies the number of conjugated carbonyl groups increases, and this rise exceeds the rate of decrease. In the range of 1620-1560 cm^{-1} (syringyl units and carboxyl ions of lignin), our observations contradict the literature dealing with time-dependent processes of change in absorption (Hon – Feist 1986). In softwood, the intensity is growing, which is slower at low energies and more pronounced at high energy levels *(Figure 4(c))*. Since the syringyl content of lignin in softwood is low, the increase of carboxyl ions at low energy exceeds the decomposition of rings, and this is the reason why there is no decrease in absorption even at 40 J. The only sign of the decomposition of syringyl units is the slower increase in intensity. The characteristic absorption band of aromatic rings around 1510 cm^{-1} decreases even at 40 J, but this decrease is slower at higher energies *(Figure 5(a))*. The bands between 1460 cm^{-1} and 1315 cm^{-1} are practically unchanged during fractional treatment. The band around 1273 cm^{-1}, belonging to the guaiacyl units of lignin decreases *(Figure 5(b))*, in agreement with the literature (Hon – Chang 1984; Hon 1994). The absorption continuously decreases around 1234 cm^{-1} in the earlywood of larch sapwood, while there is no change in the other samples. The intensity of absorption around 1170 cm^{-1}, belonging to cellulose and hemicellulose C-O-C groups decreases constantly *(Figure 5(c))*, but the rate of decrease is slower at higher energies. The absorption at 1130 cm^{-1}, 1090 cm^{-1} and 1045 cm^{-1} increases for all of the samples. There is no change at 897 cm^{-1}, which band belongs to C1-H bond of the pyranose ring of cellulose.



Legend: first letters: S – Scots pine, L – Larch
second letters: E – Earlywood, L – Latewood
third letters: H – Heartwood, S – Sapwood

Figure 4. Difference spectra of softwood as a function of energy for the bands at 1740 cm^{-1} *(a), at 1650* cm^{-1} *(b) and at 1600* cm^{-1} *(c)*



Legend: first letters: S – Scots pine, L – Larch
second letters: E – Earlywood, L – Latewood
third letters: H – Heartwood, S – Sapwood

Figure 5. Difference spectra of softwood as a function of energy for the bands at 1510 cm^{-1} (a), at 1273 cm^{-1} (b) and at 1170 cm^{-1} (c)

4 CONCLUSIONS

Broad absorption bands that belong to the same chemical groups located at various positions of wood constituents (i.e. OH-groups around 3700-3050 cm^{-1}, CH_n-groups around 2930-2895 cm^{-1}, non conjugated carbonyl groups around 1780-1700 cm^{-1}) show no consistent change of absorption at different energy dozes. The intensity of OH bands in the treated samples can be higher or lower depending on the amount of radiation energy. Furthermore, within the wide band the rate of increase and decrease is different at different wave number ranges. In the CH_n region and in the band of non-conjugated carbonyl groups only absorption increase can be observed for softwood. 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. 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} bands), no uniform changes were observed during the irradiation. The initial decrease was followed by increase.

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