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Changes in DRIFT spectra of wood irradiated by UV laser as a function of energy

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Abstract

We investigate the energy dependence of the UV laser irradiation on DRIFT spectra of wood. Changes in the spectra have been studied with 248.5 nm wavelength of UV laser radiation. To monitor the energy dependence, a different number of laser impulses were directed towards the sample's surface. It can be concluded that several chemical processes contribute to the effect of the UV laser radiation. The processes depend on several factors one of which is the amount of absorbed energy. The characteristics of wood species can be observed mainly at low energy irradiation in the changes of spectra since these characteristics disappear with increased energy, the absorption's changes have become more and more uniform. Recording the spectra of treated sample, the spectra show the degree of the surface's instantaneous degradation. The differences among the observed changes in spectra may originate from both the diversity of the original spectra (the features of wood species and surface properties) and the stage of degradation's degree of sample. Changes in absorption become less pronounced with increasing energy.

Keywords: Wood; Photodegradation; UV laser; Energy dependence; DRIFT spectroscopy

1. Introduction

The study of the UV photodegradation of wood has begun some decades ago [1,2]. The investigation should have two stages: first, the irradiation of the wood's surface by UV beam; second, the detection of the changes caused by the radiation. There are two ways of irradiation: in a natural environment one uses the Sun as a source or different kind of UV lamps in artificial circumstances. In both cases there is no way to measure exactly the energy of radiation on the sample's surface. In addition, the UV photodegradation is influenced by other factors (moisture, temperature, visible light and infrared radiation) and it is hard to exclude them. Using UV lasers instead of traditional lamps during the irradiation could solve all of the above-mentioned problems. Using lasers as radiation sources [3,4] the duration of the treatment can be shortened, the wavelength of the radiation can be known, and the energy can be determined as well as the intensity of radiation at the surface. In order to investigate the UV photodegradation's dependence on the radiation energy, we used an UV laser working at definite wavelengths. The infrared (IR) spectrum of wood and its constituents has already been studied in many aspects [5–7]. The diffuse reflection infrared Fourier transform (DRIFT) spectroscopy is a widely accepted method for analyzing the spectrum of wood, wood component and pulp and to follow the changes occurring on the surface of the wood [8–44]. The energy dependence of the changes in the DRIFT spectra of wood materials will be discussed below.

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2. Materials and methods

For the experiments, the samples were made of softwoods (larch: *Larix decidua*; scotch pine: *Pinus silvestris*) and of hardwoods (beech: *Fagus silvatica*; black locust: *Robinia pseudoacacia*). The samples used were disks with 12 mm diameter and 1.5–2 mm thickness and were chosen from planed, cutting age boles. Their surface contained only one tissue (early or latewood of heartwood or sapwood) so the surface was tangential. To have uniform moisture content, the samples were dried at 70–75 °C for 3 days. Drying of wood at temperatures above 40 °C causes loss of volatile substances also, so the results may involve possible influence.

Irradiation by UV light was performed using a krypton-fluoride excimer laser. The laser emitted light impulses with a wavelength of 248.5 nm and with duration of 15 ns/impulse. The high energy of the impulses was diminished using an energy filter and the samples' surface was 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 on 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 one sample should receive 20 mJ energy/impulse. Each sample was repeatedly irradiated; their IR spectra were recorded after every irradiation act. The effect of 2000 pulses per act at 10 Hz repetition rate irradiated each sample to have significant differences between the irradiated and untreated samples. So one sample received 40 J energy in one irradiation act, which means an energy density of 510 kJ/m^2. To be sure that we will have significant differences with these energy dozes several preliminary experiments were done. In these experiments, we have made about 50 repetitions to set up the above measurements. The presented results are related to individual sample, they are not an average of them. The irradiation was carried out at atmospheric pressure and in open space. The sample surface was not cooled and was not sanded.

DRIFT spectra were recorded between 3800 and 850 cm^{-1} with 4 cm^{-1} resolution and with 256 scans by using a Fourier-transform infrared (FTIR) spectrophotometer, Bio-Rad Digilab Division (FTS-65A). To exclude the direction dependence [35,36], the disks were placed always in the same position; they were hit by IR beam with the grain. Baseline correction was performed with straight-lines in two steps between: 3800 and 1900 cm^{-1}; 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 [23,24], the absorbance analogue unit in diffuse reflectance spectroscopy: $KM = a/b = (1-R)^2/2R$, where R is the fraction of incident light remitted by a sample with zero transmitted fraction of light, a and b are the linear absorption and remission coefficient, respectively) of untreated samples from the spectrum (measured in Kubelka–Munk unit) of treated samples. It is important that the absorbance be constant at places where there are no changes in the spectrum. On the basis of earlier studies [4] the absorbance maximum around 1373 cm^{-1} was chosen as reference point. Each spectrum obtained after UV treatment was multiplied by the factor obtained by dividing the absorbance at 1373 cm^{-1} measured before and after UV irradiation. Thus the intensity value on the difference spectra is given in Kubelka–Munk unit. Positive values refer to the increase, negative values to the decrease of absorbance, respectively.

3. Results and discussions

To reveal the qualitative features of the spectra and their changes, the spectra of earlywood of heartwood together with the relevant peak's wavenumbers for untreated and treated with 8000 impulses (160 J); samples are shown in Fig. 1 for larch (a) and beech (b). The main differences of composition between hardwood and softwood can be identified in these spectra, indifferently in the so-called 'fingerprint region', i.e. between 1800 and 850 cm^{-1} [37].

For the analysis of the spectral changes caused by the irradiation, the difference spectra were divided in two regions as spectra between: 3800 and 1800 cm^{-1}; 1800 and 850 cm^{-1}.

3.1. Changes in the spectra between 3800 and 1800 cm^{-1}

In the OH-band region (3700–3050 cm^{-1}) a decrease and an increase in the absorption can be observed depending on

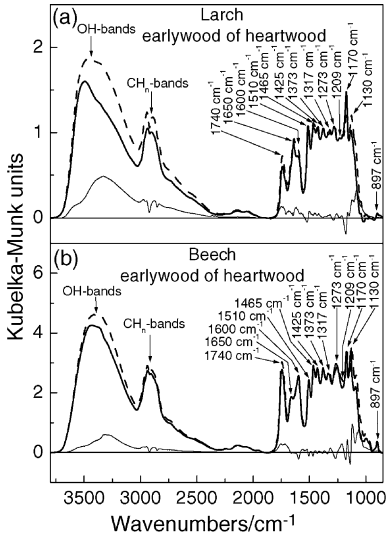

Fig. 1. DRIFT spectra of earlywood of heartwood for larch (a), and for beech (b) between 3800 and 850 cm^{-1}, without treating (solid) and irradiated with 160 J (dashed) and their difference (thin solid).

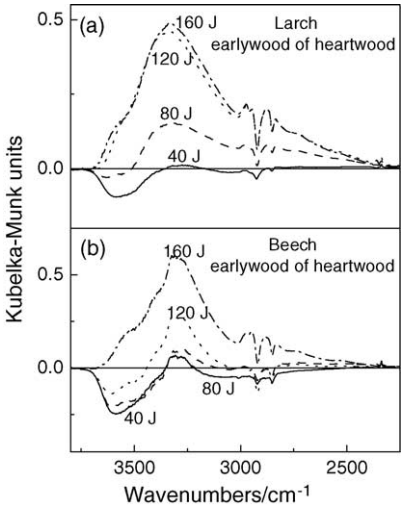

Fig. 2. Difference spectra of earlywood of heartwood for larch (a) and for beech (b) between 3800 and 2250 cm^{-1} irradiated with different impulse numbers from UV lasers.

the energy. For low energy, the left side of the band and even its centre are decreasing. For 40 and 80 J, this decrease is much more characteristic than the meaningless increase in the absorption on the right side of the band. Around the maxima and the right side of the band, the absorption is increasing by the increase in energy. In this range, the difference spectra are always positive for 120 and 160 J. At the same time, the definite decrease on the left side of the band is followed by an increase, and for 160 J, the difference spectra have became positive for all samples (Fig. 2).

It seems from our investigations that there are more processes in the OH-band region during irradiation. For low energy, these processes are dominant and cause a decrease in absorption on the left side range of band. This is very likely due to the decomposition of H-bridge bonds, which do not need large amount of energy to decompose. A band at about 3560 cm^{-1} was assigned to absorbed water weakly bound in [38], 3460–3412 cm^{-1} to O···H stretch in wood [39], 3570–3450 cm^{-1} to valence vibration of H bonded OH-groups (intramolecular) in cellulose [40], 3455–3410 cm^{-1} to O(2)H···O(6) intramolecular in cellulose [41], 3375–3340 cm^{-1} O(3)H···O(5) intramolecular in cellulose [41,42], 3310–3230 cm^{-1} O(6)H···O(3) intermolecular in cellulose [41–43], 3400–3200 cm^{-1} valence vibration of hydrogen bonded OH-group [40]. A summary of band assignments was published recently in Ref. [44]. With this parallel, the appearance of hydroxyl groups started, but this process is slower. It was shown in [30,31], that the intensity of bands varies depending on the particle size, or the particle size and concentration of wood powder influence the DRIFT spectra. One of the reasons that the sample surface became more and more rough is that the high energy density laser impulses reach the samples within a short period of time. So the sample is capable of adsorbing 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}) the rise is dominant in absorption for the softwood even for low energy, while for the hardwood a decrease in absorption was found for energy even up to 120 J, but for high energy (160 J) only an increase in absorption can be observed in the spectra of the investigated samples.

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

The absorption wavenumbers of the CO stretching in non-conjugated ketones, carboxyl groups and lactones are between 1730 and 1780 cm^{-1} [25] and the non-conjugated aliphatic carbonyls absorb between 1700 and 1750 cm^{-1} [26]. The tissues of woods behaved differently in this range (1780–1700 cm^{-1}). A broad absorption increase around 1740 cm^{-1} can be observed for latewoods after irradiating the samples with KrF laser at both energy levels (Fig. 3, left)

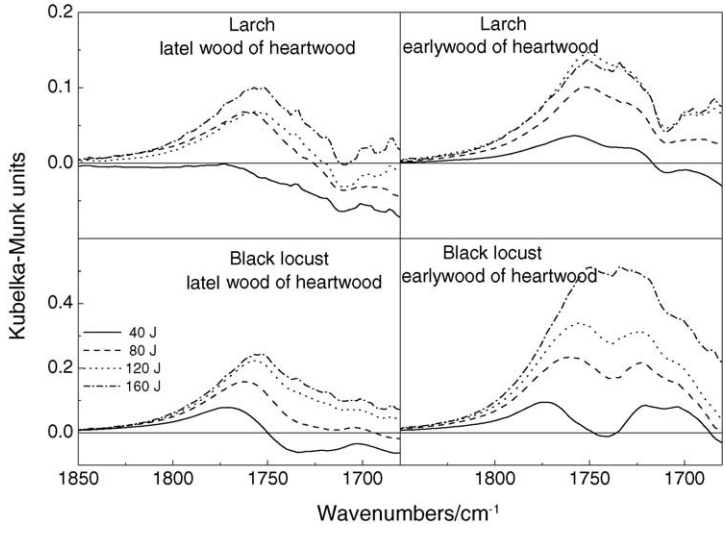

Fig. 3. Difference spectra of softwoods and hardwoods between 1850 and 1680 cm^{-1} irradiated with different impulse numbers from UV lasers.

in agreement with earlier results [4], while for earlywoods two different peaks appeared (around 1755 and 1725 cm^{-1}) in the difference spectra (Fig. 3, right). These two peaks are more pronounced for the hardwoods.

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 an increase for higher energies. The difference spectra became positive after irradiating the sample with 160 J. The decrease can be attributed to loss of water as well as to the conjugated C=O groups. But for higher energy the number of conjugated carbonyl groups is increasing and this rise depending on the wood's species, exceeds the rate of decrease (see Fig. 4(a) and (b)). In the range of 1620–1560 cm^{-1} (syringyl units and carboxyl ions of lignin), our observations contradict those of the literature dealing with time-depending processes of changes in absorption [9,17]. All of them reported the continuous decrease of intensity both for hardwood and softwood. In our experiments, the intensity was squarely growing in the case of softwoods [28], which was slower for low energy and more pronounced for high energy (Fig. 5(a)). In the case of hardwoods' tissues, the intensity was decreasing for low energy but it was followed by an increase for high energy (Fig. 5(b)). The likely reason is that due to photodegradation two rival processes are present. The decomposition of the syringyl units decreases the band intensity whereas the growing concentration of the carboxyl ions increases the band intensity. In softwood, the syringyl content of lignin is low, so that the increase of the number of carboxyl ions at low energy surmounts the effect of the decomposition of the rings. This is the reason why there is not only decrease but also a slower increase in the absorption even at 40 J. However, for hardwoods the syringyl content

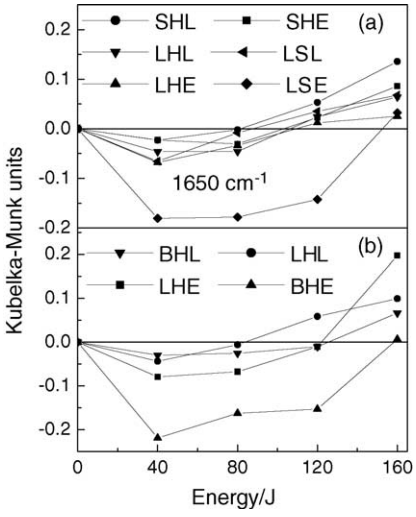

Fig. 4. Difference spectra of woods as a function of energy for the bands at 1650 cm^{-1} in the case of softwoods (a), and in the case of hardwoods (b). The abbreviated letters in (a): the first S, scotch pine; the second S, sapwood; the first L, larch; the last L, latewood; E, earlywood; H, heartwood, and in (b): B, beech; the first L, black locust, while for the others are the same as in (a).

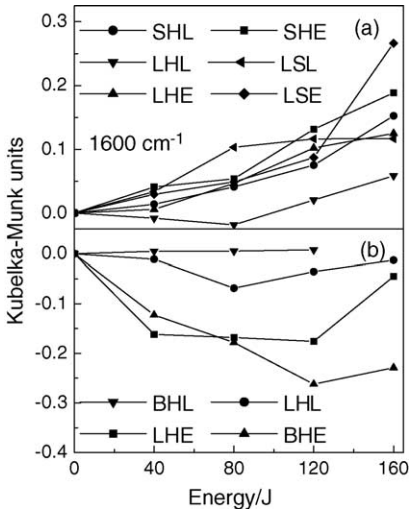

Fig. 5. Difference spectra of woods as a function of energy for the band at 1600 cm^{-1} in the case of softwoods (a) and in the case of hardwoods (b). The symbols are the same as in Fig. 4.

is higher and decomposition becomes dominant at low energies.

The characteristic absorption band of aromatic rings around 1510 cm^{-1} is decreasing for all of the samples even at 40 J, but this decrease is slower for higher energy. The bands between 1460 and 1315 cm^{-1} are practically unchanged during fractional treatment of softwoods; while in the case of hardwoods the initial decrease in intensity was followed by an increase around 1460 and 1425 cm^{-1} (Fig. 6(a)) and a remarkable intensity increase was observed around 1317 cm^{-1} (Fig. 6(b)) which is CH_2 rocking vibration derived from cellulose [40]. The band around 1273 cm^{-1} (Fig. 7), belonging to the guaiacyl units of lignin is decreasing in agreement with Refs. [2,8]. The absorption is continuously decreasing around 1234 cm^{-1} for earlywood of larch's sapwood, while there is no change for the other samples. Also continuous, but

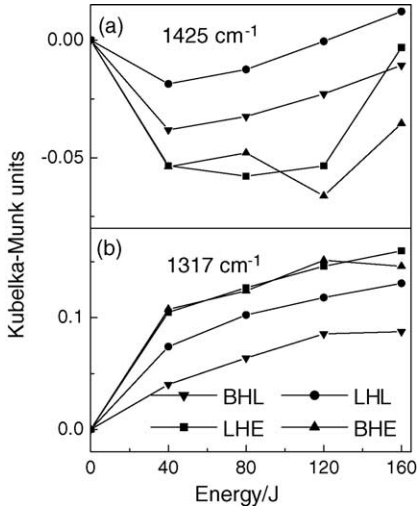

Fig. 6. Difference spectra of hardwoods as a function of energy for the bands at 1425 cm^{-1} (a) and 1317 cm^{-1} (b). The symbols are the same as in Fig. 4.

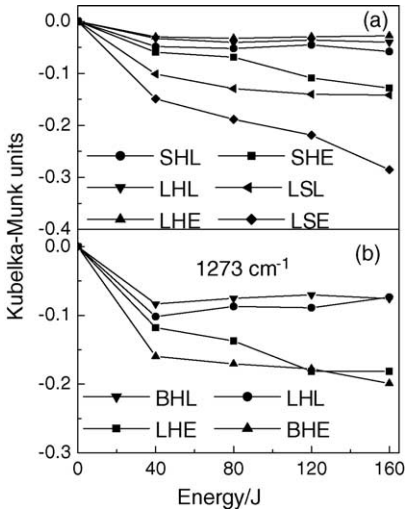

Fig. 7. Difference spectra of woods as a function of energy for the bands at 1273 cm^{-1} in the case of softwoods (a) and in the case of hardwoods (b). The symbols are the same as in Fig. 4.

increase in intensity can be observed for hardwood's tissues around 1209 cm^{-1}. The band, which is screened in the untreated spectra, appeared as a separate peak after the fourth act, for example in the spectrum of beech (Fig. 1(b)). The intensity of absorption around 1170 cm^{-1}, belonging to cellulose and hemicellulose C–O–C groups, is constantly decreasing but the rate of decrease is slower for higher energy. The intensity of the band belonging to more chemical groups at 1130 cm^{-1} was continuously increasing and its maxima were shifting to a lower wavenumber range for softwoods and the latewood black locust's heartwood. The absorption at 1090 and 1045 cm^{-1} is increasing for all samples. There is no change at 897 cm^{-1}, which band belongs to C_1–H bond of pyranose ring of cellulose.

4. Conclusions

Several chemical processes contribute to the effect of UV radiation on the surface of wood. The processes depend on many factors and one of them is the amount of absorbed energy. The UV radiation reaching the wood's surface diminishes at first the H-bridge bonds and degrades the aromatic rings of lignin. At the same time the products of degradation are appearing on the surface of wood. These two competing processes – a decrease of concentration of diminished bonds and an increase of concentration of degradation products – determine the intensity of the absorption band. The UV laser radiation results in similar processes on the surface of wood's samples independent of the tissues or kind of wood. The kindness characteristics can be observed mainly at low energy irradiation in the changes of spectra and these characteristics disappear with increase of energy, as the absorption's changes become more and more uniform. Recording the spectra of treated sample, the spectra show the degree of the surface's instantaneous degradation. The differences among the observed changes in spectra may originate both from diversity of original spectra (the kind of wood and surface properties), or from the stage of degradation's degree of sample. If the products of degradation are left on their surface, they defend the bonds of underlying layers from UV radiation and the degradation processes are weakening.

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References

[1] M.A. Kalinins, US Forest Service Research Paper 57 (1966) 23–61.
[2] D.N.-S. Hon, S.-T. Chang, J. Polym. Sci. 22 (1984) 2227–2241.
[3] E. Barta, L. Tolvaj, G. Papp, T. Nagy, S. Szatmári, O. Berkesi, Holz Roh Werkst. 56 (1998) 318.
[4] G. Papp, E. Barta, L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi, Tech. Lett. 5 (2001) 1–6.
[5] C.L. Hess, Tappi J. 35 (1952) 315–319.
[6] J. Marton, H.E. Sparks, Tappi J. 50 (1967) 363–367.
[7] A.J. Michell, Proceedings of the 10th Cellulose Conference, Syracuse, 1988.
[8] D.N.-S. Hon, Wood Fiber Sci. 26 (1994) 185–191.
[9] D.N.-S. Hon, W.C. Feist, Wood Sci. Technol. 20 (1986) 169–183.
[10] T.P. Schultz, W.G. Glasser, Holzforschung 40 (1986) 37–44.
[11] O.G. Dirckx, D.M. Masson, X.M. Deglise, Proceedings of the Wood and Pulping Chemistry Symposium, Paris, 1987.
[12] A.J. Michell, Wood Fiber Sci. 20 (1988) 272–276.
[13] N.L. Owen, D.W. Thomas, Appl. Spectrosc. 43 (1989) 451–455.
[14] E.S. Zavarin, S.J. Jones, L.G. Cool, J. Wood Chem. Technol. 10 (1990) 495–513.
[15] S. Backa, A. Brolin, Tappi J. 5 (1991) 218–226.
[16] H. Tylli, I. Forsskahl, C. Olkonnen, J. Photochem. Photobiol. A 76 (1993) 143–149.
[17] B.A. Horn, J. Qiu, N.L. Owen, W.C. Feist, Appl. Spectrosc. 48 (1994) 662–668.
[18] K.K. Pandey, K.S. Theagarajan, Holz Roh Werkst. 55 (1997) 383–390.
[19] B. Košíková, L. Tolvaj, Drev. Vysk. (Wood Res.) 43 (1998) 37–46.
[20] E. Barta, L. Tolvaj, T. Nagy, S. Szatmári, O. Berkesi, G. Papp, Drev. Vysk. (Wood Res.) 44 (1999) 13–19.
[21] G. Papp, L. Tolvaj, E. Bartha, Proceedings of the Fourth ICWSF, High Wycombe, 1999, pp. 494–501.
[22] Y. Sudiyani, Y. Imamura, S. Doi, S. Yamauchi, J. Wood Sci. 49 (2003) 86–92.
[23] P. Kubelka, JOSA 38 (1948) 448–451.
[24] P. Kubelka, JOSA 44 (1954) 330–335.
[25] K. Mitsui, A. Murata, L. Tolvaj, Holz Roh Werkst. 62 (2004) 164–168.
[26] U. Müller, M. Rätzsch, M. Schwanninger, M. Steiner, H. Zöbl, J. Photochem. Photobiol. B 69 (2003) 97–105.
[27] G. Papp, E. Preklet, B. Košíková, E. Barta, L. Tolvaj, J. Bohus, S. Szatmári, O. Berkesi, J. Photochem. Photobiol. A 163 (2004) 187–192.
[28] E. Barta, G. Papp, E. Preklet, L. Tolvaj, O. Berkesi, T. Nagy, S. Szatmári, Acta Silv. Lign. Hun. 1 (2005) 1–9.
[29] O. Faix, K. Németh, Holz Roh Werkst. 46 (1988) 112.
[30] O. Faix, J.H. Böttcher, Holz Roh Werkst. 50 (1992) 221–226.

[31] S.-T. Chang, C.-L. Wu, S.-Y. Wang, H.-T. Chang, Taiwan J. For. Sci. 13 (1998) 1–18.
[32] W. Cui, D. Kamdem, T. Rypstra, Wood Fiber Sci. 36 (2004) 291–301.
[33] F. Kimura, T. Kimura, D.G. Gray, Holzforschung 49 (1995) 173–178.
[34] F. Kimura, T. Kimura, D.G. Grey, Holzforschung 48 (1994) 343–348.
[35] S. Tsuchikawa, M. Torii, S. Tsutsumi, J. Near Infrared Spectrosc. 6 (1998) 47–53.
[36] S. Tsuchikawa, M. Torii, S. Tsutsumi, Holzforschung 55 (2001) 534–540.
[37] N.L. Owen, D.W. Thomas, Appl. Spectrosc. 43 (1989) 451–455.
[38] E.P. Kalutskaya, S.S. Gusev, Polym. Sci. USSR 22 (1981) 550–556.
[39] O. Faix, Holzforschung 45 (Suppl.) (1991) 21–27.
[40] D. Fengel, M. Ludwig, Das Papier 45 (1991) 45–51.
[41] N.V. Ivanova, E.A. Korolenko, E.V. Korolik, R.G. Zbankov, Zh. Prikladnoj Spektroskopii 51 (1989) 301–306.
[42] C.Y. Liang, R.H. Marchessault, J. Polym. Sci. 37 (1959) 385–395.
[43] E.P. Kalutskaya, S.S. Gusev, Polym. Sci. USSR 22 (1981) 550–556.
[44] M. Schwanninger, J.C. Rodrigues, H. Pereira, B. Hinterstoisser, Vib. Spectrosc. 36 (2004) 23–46.