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Thermal modification of wood and a complex study of its properties by magnetic resonance and other methods

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Abstract   Thermal modification of wood is an effective method to improve some of the properties of wood. It is reported on studies of vacuum thermal-treated wood species by magnetic resonance methods. Wood species such as Scots pine (*Pinus sylvestris*), birch (*Betula pendula*), Russian larch (*Larix sibirica*), Norway spruce (*Picea abies*), small-leaved lime (*Tilia cordata*) were vacuum treated by heat at 220 °C with various durations up to 8 h. This selection of wood species was investigated by electron paramagnetic resonance, nuclear magnetic resonance and microscopy methods before and after the thermal treatment. Electron paramagnetic resonance experiments revealed changes in the amount of free radicals in samples with the thermal treatment duration. Additional information on magnetic relaxation of ^{1}H nuclei in samples at room temperature was obtained. Optical microscope analysis helped to detect structural changes in the thermally modified wood. Important properties of wood such as wood hardness and humidity absorption were also studied. The original results that were obtained correlate and complement each other, and clarify changes in the wood structure that appear with the heat treatment.

Introduction

Recent improvements of the thermal treatment methods of wood expand its application to different fields (Esteves and Pereira 2009). Heat-treated wood has a number of advantages that appear after physical and chemical modifications. A

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proper thermal treatment changes wood colour (Luostarinen et al. 2002; Sandoval-Torres et al. 2012), increases hydrophobic properties (Petrissans et al. 2003), reduces equilibrium moisture content value and reduces the mass (Hill 2006). Changes were observed in wood elasticity and strength (Boonstra et al. 2007; Kamdem et al. 2002) and dimensional stability (Hill 2006) that increases the effectiveness of wood for construction. Heat treatment also improves the decay resistance to biological attack (Kamdem et al. 2002; Doi et al. 1999). The corresponding chemical modifications depend on the heating regimes and the heating atmosphere and involve degradation of hemicellulose, changes of lignin and cellulose structures and chemical wood composition due to wood extractives loss (Hill 2006).

A large number of wood treatment studies are based on the information of the final mechanical or chemical wood characteristics (Boonstra et al. 2007; Shi et al. 2007; Terziev and Daniel 2002). However, the nature of heat induced processes inside the wood and the resultant changes are still not fully understood. Magnetic resonance methods are very well known as non-invasive techniques that allow to obtain information on structure and processes inside samples.

Earlier electron paramagnetic resonance (EPR) studies involved wood polymers cellulose (Ogiwara et al. 1974) and lignin (Steelink 1966; Oniki 1998), the influence of wood coatings, polymer oxidation (Hon et al. 1982; Kluzina and Mikhailov 1990), UV irradiation (Kuzina et al. 2004), etc. Many of them reported on the single free radical signal near $g = 2$ (Hon et al. 1980; Brai et al. 2009) and the temporary signal growth after UV irradiation. Steelink (1966) observed stable radicals in lignin. Ogiwara et al. (1974) reported on hyperfine structure of cellulose EPR spectra at 77 K temperature and that photoirradiation induces stable radicals. Hon et al. (1982) studied the formation of free radicals on the wood surface after photoirradiation at 77 K. These free radicals interact with oxygen molecules and form peroxide radicals. Oniki (1998) observed two types of radicals in lignin that appear after oxidation, being produced by syringyl end groups. Oxidation processes in UV- and γ-irradiated cellulose also produce alkyl radicals, and some of which remain at room temperature (Kluzina and Mikhailov 1990). The same group of authors identified the radicals with conjugated carbon–carbon bonds in lignin, which they detected by D-band EPR spectroscopy (Kuzina et al. 2004). Dependence of the EPR signal amplitude on wood sample moisture content (MC) is reported but not explained (Humar et al. 2006).

Brai et al. (2009) studied the microwave power saturation of free radicals EPR signal in wood samples. They observed EPR signal saturation above 2–5 mW power, depending on wood species. The authors also noticed that the saturation curves were sensitive to the wood decay state because of the changes in electronic relaxation times T_1 and T_2.

Only few short notes are available on thermally modified wood studies by EPR spectroscopy (Deka et al. 2008; Sivonen et al. 2002; Altgen et al. 2012). Sivonen et al. (2002) also found that the EPR signal changed with the temperature of the heat treatment. They noticed that the concentration of free radicals grows with the temperature and the generated free radicals are stable. They related this to the reduction of methoxyl group concentration with temperature. It was also found that

free radical concentration changes with the duration of the drying process of steam-dried wood (Liping et al. 1992), but no explanations were given.

Ahajji et al. (2009) reported on a linear correlation between the EPR signal of wood extractives (beech and spruce were heat treated for 1 h at 210–250 °C) and on colour changes. The observed EPR signal corresponded to phenoxyl free radicals, and the total amount of phenoxyl radical contents accounted for lignin and/or wood extracts increases with the heat treatment. It is known that the level of stable free radicals increases in wood as the thermal modification progresses (Viitaniemi et al. 2001).

Altgen et al. (2012) performed X-band EPR studies on heat-treated beech and spruce samples. Wood strips were thermally modified for 1.5–72 h at 180 °C or 1–10 h at 220 °C in the oven. The linear correlation between the EPR signal intensity and mass loss during heat treatment is reported. The increase of EPR signal intensity after the heat treatment is related to the formation of stable radicals in the wood. It was suggested that stable radicals are present in lignin (Sivonen et al. 2002; Steelink 1966), but the obtained linear correlation is unexpected when it is assumed that mass loss appears after the decomposition of cell wall polysaccharides. Altgen et al. (2012) suggested that this was probably caused by the interaction between radicals generated in polysaccharides and lignin. They also report on polynomial EPR signal amplitude correlations with the durability of thermally modified beech and spruce wood, and on the logarithmic relationship between the EPR signal amplitude and flexural strength, wood moisture and colour changes of the same samples. However, the reasons for these relationships remain unclear. The same group of authors also considered EPR spectroscopy as a potential method for the quality control of thermally modified wood but noted that the obtained correlations between the EPR signal and other wood properties are still not well understood (Willems et al. 2015). They also stated that EPR signal intensity of hardwoods is higher than that of softwoods because of differences in lignin composition.

Many EPR studies were performed on wood samples impregnated with various copper-based preservatives. It was found that copper (II) EPR parameters depend on the moisture content in some solutions such as CuS (Humar et al. 2001). The effect of various fungi on wood impregnated with copper-based solutions was studied via determination of copper and manganese EPR spectra parameter changes (Humar et al. 2002, 2004). X-band EPR measurements were taken before and after fungi exposure. The results indicate that oxalic acid production by the fungi plays an important role: helping to increase the leaching of heavy metals from the wood. Some fungi types are found to transform copper into non-toxic state which is important for further bio-recycling of waste wood.

Studies on colour stability of thermally modified, copper ethanolamine treated and untreated spruce samples under UV light irradiation show that the colour becomes more photostable after heat or copper treatment (Deka et al. 2008). EPR and IR spectroscopy measurements also indicate that it was a result of lignin modifications and monomers of phenolic compounds.

The majority of nuclear magnetic resonance (NMR) studies are mostly based on ^{13}C CP MAS studies of organic compounds of wood or impregnated wood with liquids or coatings (Maunu 2002; Eberhardt et al. 2007; Peemoeller et al. 2013).

Eberhardt et al. (2007) studied proton NMR of air-dried and oven-dried pine samples saturated by wood extractives and dichloromethane-d2 at 0.5 T external magnetic field. The distribution of ^{1}H nuclear magnetization relaxation time T_2 appeared to be ca. 0.5 ms for air-dried samples and 0.1 ms for oven-dried ones. Saturation of samples with wood extractives leads to shorter proton T_2 values for air-dried wood and longer T_2 values for oven-dried samples, but in both cases the linear correlation between T_2 and extractives content was observed. Peemoeller et al. (2013) detected a liquid-like wood polymer with proton relaxation time T_2 of ca. 500 μs above 45 °C temperature using pulsed NMR technique at 30 MHz frequency.

The structure and interaction between organic compounds were investigated. Some ^{13}C CP MAS studies report on specific changes in organic polymers during heat treatment (Maunu 2002; Sivonen et al. 2002). Sivonen et al. (2002) showed that the crystallinity index of cellulose increases after the heat treatment and has the highest value of 65 % at 230 °C. Tjeerdsma et al. (1998) noticed that the heat treatment leads to deacetylation of hemicelluloses and depolymerization of lignin. The uniform $T_{1\rho}$ relaxation of ^{1}H nuclei in lignin and cellulose is believed to confirm the strong link between both polymers (Košíková et al. 1999).

It is known that the probe liquid nuclei close to the solid surface have shorter NMR relaxation times than nuclei of bulk liquid in wood. Menon et al. (1987) measured T_2 and T_1 relaxation times of water protons inside the cedar and fir samples with various moisture contents at room temperature and 90 MHz frequency. The observed transverse magnetization evolution during CPMG measurements is a three component exponential decay function. The slowest component ($T_2 \sim$ 100–700 ms) was detected only for samples saturated by water. Fast ($T_2 \sim$ 2–7 ms) and medium ($T_2 \sim$ 10–40 ms) components are related to the water in the cell walls and to the molecules bound on the surface, respectively. With the decrease of wood MC, the slow and medium components disappear. The spin–lattice relaxation time T_1 values of ^{1}H nuclei in water were also found to decrease along with the MC from 400 ms (saturated by water) to 100 ms (9 % MC) for cedar samples. Riggin et al. (1979) also noted that ^{1}H FID due to water had increased time constants from about 80 μs (5 % MC) to 0.8 ms (30 % MC) in spruce. Results were independent of the Larmor frequency (5 and 17 MHz), and above 30 % MC the FID signal from water has at least two different relaxation times. Relaxation times T_1 and T_2 of ^{1}H nuclei in beech and pine samples were measured at 200 MHz (Gilardi et al. 1994). Authors also report on fast $T_2 = 30$ μs and slow $T_2 = 200$ ms components of transverse magnetization relaxation in beech at 7 % MC. The slow component disappears for dry samples. The observed proton spin–lattice relaxation time (T_1) was 900 ms. Both relaxation times T_1 and T_2 values tend to increase after brown-rot and white-rot wood decay.

In this paper, EPR studies of a large variety of thermally modified wood species are reported. Complementary ^{1}H NMR relaxation experiments were performed. The samples were also studied by optical microscopy. The original results of the effect of heat treatment on wood are reported. They reveal mechanisms of wood treatment, and suggestions on the related processes are made. Impact of heat treatment on humidity absorption and hardness of the wood samples is reported.

Materials and methods

Samples

A selection of wood species from the Central European part of Russia was studied in the frame of this work. The selection of sapwood samples included Scots pine (*Pinus sylvestris*), birch (*Betula pendula*), Russian larch (*Larix sibirica*), Norway spruce (*Picea abies*) and small-leaved lime (*Tilia cordata*). For preliminary experiments, oak (*Quercus robur*) was also used. Fresh air-dried wooden bars with typical values of moisture content MC of ca. 15 ± 1 % were cut along their fibres into pieces with $3(W) \times 3(H) \times 5(L)$ cm^3 dimensions prior to thermal treatment. The length L of the samples is oriented parallel to the longitudinal direction of wood, the width W and the height H—to the radial and tangential directions, correspondingly.

Moisture content MC values of samples were obtained by two methods. The first one is based on dielcometer method, and the used Hydro Easy Condtrol device provides MC values with 1 % inaccuracy. The second method is based on the samples mass measurements by laboratory scales, and MC values were determined by the standard equation: $MC = ((m - m_0)/m_0) \cdot 100$ %, where m is the mass of wet wood, m_0 is the mass of the dried wood.

Thermal treatment and sample storage

A combination of Aktan VTSh-K24-25 vacuum oven and VRO 5/21 rotary vane vacuum pump was used for the thermal treatment of wood pieces at a temperature of 220 °C and with pressure values lower than 50 mbar. The duration of this process varied from 40 min to 8 h for all wood species. The samples were located on the metal shelves inside the oven and enabled a heat transfer. At least 3 copies of each species were treated for each duration. After the treatment, wood pieces were cooled down to room temperature and stored under conditions of constant air relative humidity in a number of airtight boxes.

The mass loss (ML) after the heat treatment was calculated as the relative difference in dry mass of samples before and after the treatment.

Constant air relative humidity values inside the storage boxes were ensured by following saturated saltwater solutions (O'Brien 1948): $2ZnCl \cdot 3H_2O$ (3 %), $CaCl_2 \cdot 6H_2O$ (28.7 %), $Ca(NO_3)_2 \cdot 4H_2O$ (51 %), NaCl (75 %), KNO_3 (93 %). Treated sample copies were stored in different storage boxes. The samples stored at 3 % relative humidity were then used in EPR and NMR experiments. The samples stored in wet conditions (28.7–93 %) were used in humidity absorption and wood hardness measurements.

Electron paramagnetic resonance

Varian E-12 X-band spectrometer was used in the EPR experiments. Prior to the measurements, the samples were cut to $0.35(W) \times 0.35(H) \times 5(L)$ cm^3 dimensions

and conditioned in the 3 % relative humidity airtight box. The samples used in preliminary EPR experiments to determine the effect of MC on the EPR signal were not conditioned at 3 % relative humidity. The moisture content MC of samples was controlled before and after experiments in order to avoid unreliable data. The samples were placed in the 5 mm i.d. glass test tube that was mounted in the standard EPR cavity. A small piece of $Gd_3Ga_5O_{12}$ crystal or $MgO:Mn^{2+}$ was also attached to the glass tube and used as reference samples for proper EPR spectra comparison obtained at various receiver amplification levels. They were chosen to avoid overlaps of EPR spectra with free radicals signal of wood samples ($g = 2.002$). Microwave power of 1 mW and 100 kHz modulation frequency were used for all EPR spectra measurements.

Nuclear magnetic resonance

A home-built pulsed NMR spectrometer (Alakshin et al. 2013) with a resistive magnet (up to 0.8 T) was used in the NMR experiments. Solenoid copper coil with 4 mm i.d. was used as a detection coil. The resonant circuit was matched to 50 Ohm by inductive coupling. The duration of 90° pulse was 4 μs. The ^1H NMR relaxation measurements on birch samples were taken at 11.8 MHz frequency and at room temperature.

The sample dimensions for these experiments were $0.25(W) \times 0.25(H) \times 1.5(L)$ cm^3, and thermally treated samples were conditioned in 3 % relative humidity airtight box prior to the measurements. The samples MC values were also checked before and after the experiments. Standard 90°–180° pulse sequence was used to obtain the spin-echo signal and for the spin–spin relaxation time T_2 measurements of ^1H nuclei from the wood sample tissues. Spin–lattice relaxation times T_1 were measured by the "saturation-recovery" technique.

Optical microscopy

The Zeiss Axio microscope was used to observe the samples surface. A number of four samples for each wood species were studied to explore the impact of the thermal treatment: samples with 40-min, 4- and 8-h durations of treatment and untreated ones. The standard sample preparation technique for optical microscopy measurements was used. Samples were cut to $1(W) \times 1(H) \times 1(L)$ cm^3 cubes, soaked in a water for 24 h, and then their surface was cut by a sharp blade. Obtained images were processed and quantitatively analysed with *ImageJ* software using a standard technique (Pires et al. 2013).

Humidity absorption

After 60 days of samples storage under different constant relative humidity conditions, they were exposed to air for immediate MC measurements. The measured equilibrium MC values were then compared to the ones before the storage and to the default equilibrium values (Simpson and TenWolde 1999).

Wood hardness

The Brinell scale with a 10-mm steel ball was used in the mechanical tests of wood surface indentation hardness in radial direction. The home-built press allowed to apply a constant force of 1000 N to wood samples surface through the steel ball, and the obtained cavity area was measured. All samples were oven-dried prior to the experiments in order to neglect the effect of moisture content on wood hardness. The hardness values were then found using a standard equation for the Brinell hardness HB (Holmberg 2000).

Results and discussion

Mass loss

Mass loss with vacuum heat treatment duration at 220 °C is presented in Fig. 1 for pine, birch, larch, spruce and lime samples. The level of mass loss increases with the treatment duration and shows asymptotic behaviour. Its rate depends on the wood species. The mass loss of larch and spruce samples reaches its maximum values faster than the other investigated wood species. The obtained changes of the birch samples dry mass do not reach their asymptotic values after the 8-h vacuum heat treatment.

Allegretti et al. (2012) investigated vacuum thermal treatment of spruce and fir boards in the 160–220 °C temperature range at various vacuum pressures. They observed an asymptotic trend of dry mass loss ML with the increase of the treatment
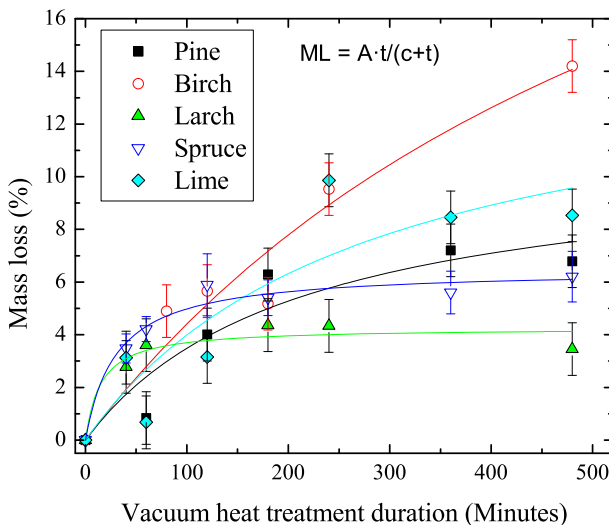

Fig. 1 Mass loss of pine, birch, larch, spruce and lime samples during the vacuum thermal treatment at 220 °C. *Solid lines* represent the asymptotic behaviour of the obtained data

duration t: $ML = A \cdot t/(c + t)$. They noted that the effect of time on mass loss is weaker for lower pressure treatment. The fit of the current mass loss results by the above asymptotic function (R^2 between 0.829 and 0.974) is also shown in Fig. 1. These results are different from the mass loss in wood after the plain air thermal treatments. Heat treatment in air results in higher rates of mass loss that are close to linear (Esteves et al. 2008) due to the oxygen presence and corresponding oxidation reactions.

Electron paramagnetic resonance

The typical measured EPR spectrum from wood samples at room temperature is shown in Fig. 2. For all wood species, the EPR spectra contain one line of free radicals with $g = 2.002$. The obtained lines are narrow, and the linewidth value lies within a range of 4–8 G depending on species.

In previous articles on wood EPR studies (Sivonen et al. 2002; Liping et al. 1992), the dependence of free radical signals on the wood sample MC was revealed, but explanation was never given. Moreover, different behaviour of the wood free radical signal amplitude on MC was obtained, and the nature of this phenomenon remains unclear.

At first, the influence of the wood moisture on the EPR signal amplitude was measured on oak samples in preliminary experiments. A number of untreated oak samples were conditioned at various air humidities prior to the measurements, and this let us compare samples with a different moisture content value. The results are shown in Fig. 3a. Higher moisture content values lead to a significant decrease in free radicals signal in EPR spectra. It is clear that EPR signal is strongly dependent on the wood sample moisture content MC, and further EPR experiments should be carried out on samples conditioned at the same relative humidity values.
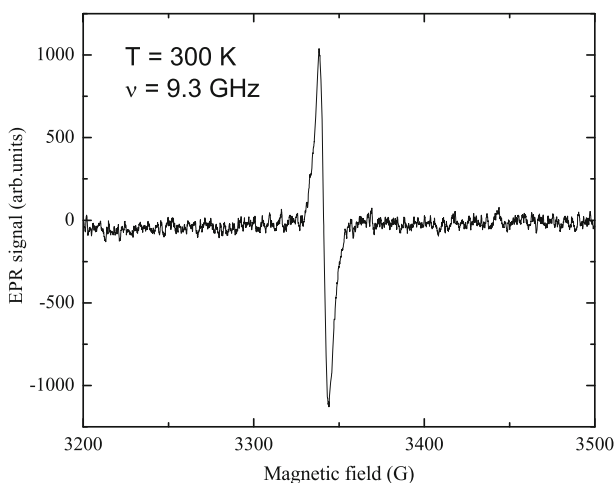

Fig. 2 Typical X-band EPR spectrum of larch wood samples obtained at room temperature
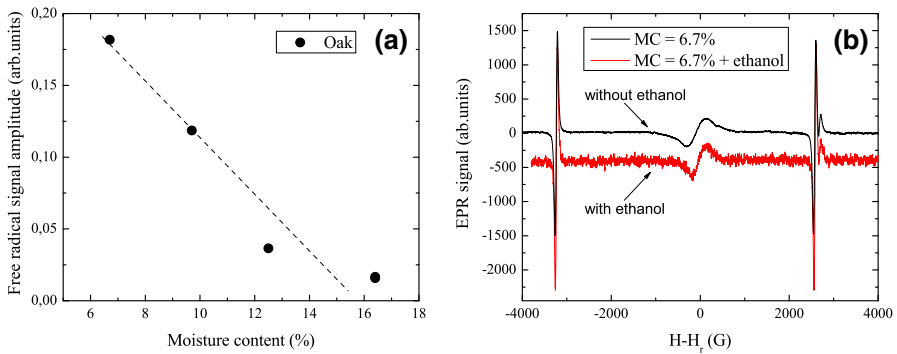
Fig. 3 **a** Normalized EPR signal amplitude of oak samples and its correlation with moisture content MC. *Dashed line* represents close to a linear behaviour of the obtained data. **b** Measured EPR spectra of identical oak samples with MC = 6.7 %: one sample was soaked in ethanol up to 21.7 % moisture content prior to measurements. Two narrow lines on the sides correspond to Mg^{2+}:MgO and were used for EPR spectra normalization

It is supposed that the obtained dependence of the EPR signal amplitude on sample MC is linked to the electric properties of water molecules—a water molecule is a dipole. It is also well known that many wood polymers as cellulose, lignin, etc., consist of polar parts as $\equiv$C–OH and $\equiv$C–COOH groups that can easily enough be broken. These sites can attract water molecules. In addition, long polymer molecules contain a lot of unstable interchain hydrogen bonds. In order to prove this suggestion, an additional EPR experiment was performed with a wood sample soaked in a weakly polar liquid 96 % ethanol. Figure 3b displays registered EPR spectra of the oak sample with MC = 6.7 % and of the same sample soaked in ethanol to 21.7 %. Both EPR spectra are identical, and there is no impact of ethanol on the free radical signal amplitude. This result confirms the electric interactions affect the EPR signal amplitude in the presence of bulk water in wood samples.

The procedure of sample conditioning in storage boxes with a constant and low value of 3 % relative air humidity was done prior to all further EPR and NMR experiments on heat-treated wood samples. The MC values of samples were checked to be similar before and after the measurements to diminish the effect of MC on the EPR signal. Measured EPR signal amplitudes against the applied thermal treatment duration for various wood species are shown in Fig. 4. The measured signal values were normalized on the maximum obtained one for each wood species. The linewidth of obtained free radical signal does not change after the thermal treatment for all samples.

The correlation between the free radicals signal amplitude and the heat treatment duration is linear for all studied samples up to 6-h treatment. This fact leads to an obvious conclusion that the vacuum thermal treatment applied to the wood results in a constant break of chemical bonds in wood polymers. It is known that hemicellulose and cellulose are sensitive to the heat treatment temperature of 220 °C used in the current work (Esteves and Pereira 2009). Hemicellulose molecules are less stable and degrade easily with appearance of methoxyl groups
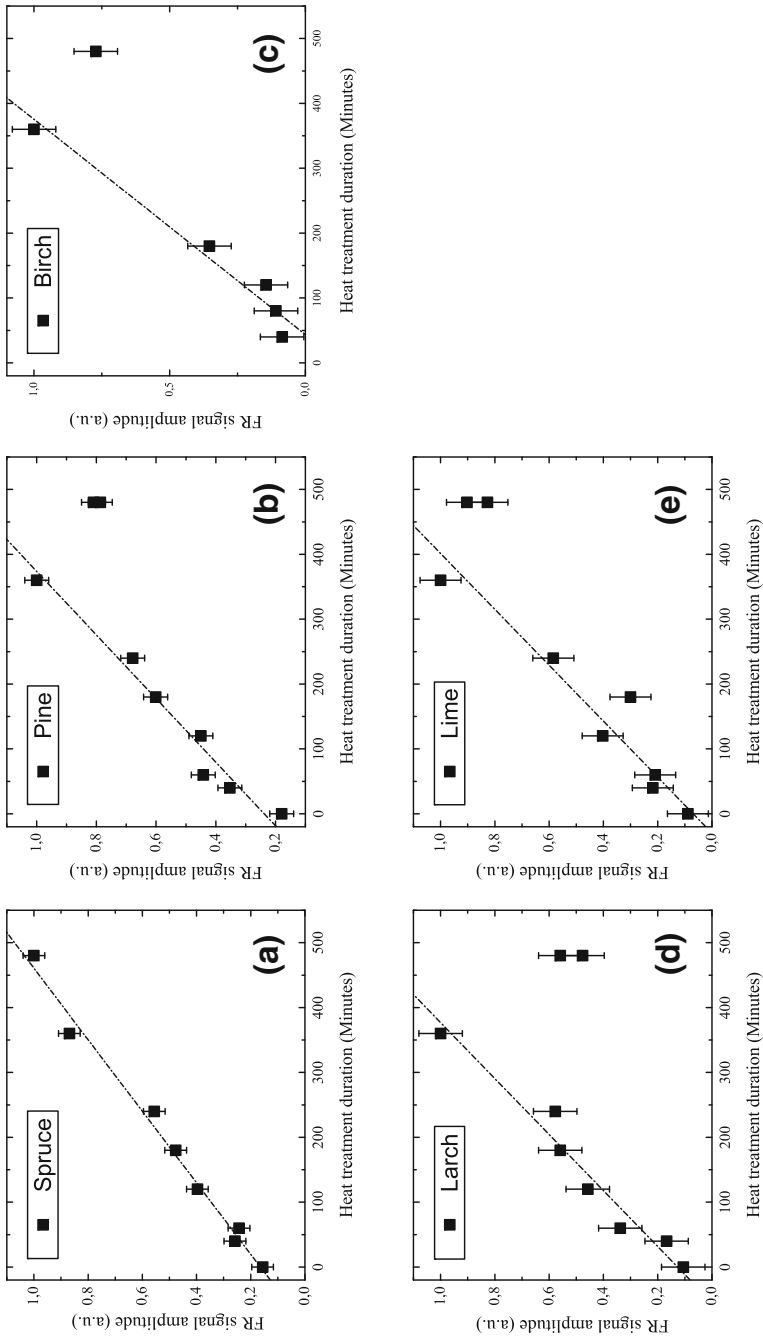
Fig. 4 Normalized EPR signal amplitude of spruce (**a**), pine (**b**), birch (**c**), larch (**d**) and lime (**e**) samples and its correlation with the vacuum thermal treatment duration at 220 °C. *Dashed line* represents the linear behaviour of the obtained data

and volatile compounds. Water molecules detach from cellulose and depolymerization process with rise of free radicals occurs. At the same time, cellulose crystallinity increases due to the destruction of low-order cellulose.

While the EPR signal amplitude demonstrates the linear behaviour with the vacuum heat treatment duration, its correlation with the mass loss is strongly nonlinear. The EPR signal amplitude values grow faster than the mass loss (see Fig. 1) during the treatment, especially for the mass loss values close to the maximum ones. This leads to a fact that the structural changes connected with volatile compounds influence samples mass changes but do not play a significant role in the free radicals formation. The smallest correlation between the mass loss and the EPR signal is observed for larch and spruce samples. Heat treatment in air at atmospheric pressure leads to results different from the vacuum treatment. Altgen et al. (2012) reported on linear correlation between the mass loss and the EPR signal intensity of air heat-treated beech and spruce samples. It is suggested that completely different obtained correlations are the consequence of oxygen presence in the air. The oxygen molecules induce various oxidation reactions, as formation of acetic acid, for example. Acetic acid acts as a depolymerization catalyst that leads to the formation of higher amount of volatile compounds and a higher mass loss as a consequence. The degradation of wood polymers during vacuum treatment progresses with lower mass loss changes.

The values of the EPR signal amplitude of majority of wood species treated for 8 h are much lower than expected from the linear behaviour (see Fig. 4b–e). These data points were compared with the measured EPR spectra of sample copies and additional samples in order to assure correctness of the current EPR data. It appears that this result is totally reproducible. This can be possible if the 8-h vacuum heat treatment at 220 °C leads to severely destructive changes in the samples.

Nuclear magnetic resonance

A large number of NMR studies of wood samples and extracted wooden polymers as cellulose, lignin, hemicellulose and others were done earlier. Many of them include NMR experiments on coated or impregnated wood samples or soluble extractives, but the information of the thermal treatment impact on the wood tissues is insufficient and limited. The majority of NMR experiments on heat-treated wood was performed using ^{13}C CPMAS spectroscopy methods that can provide information on some chemical structure modifications and interactions of some wood polymers (Maunu 2002). It is determined that despite the degradation of some mechanical properties, the crystallinity of cellulose increases at high treatment temperature. The amount of ^{1}H nuclei significantly exceeds the number of ^{13}C isotopes in organic compounds of wood, and investigations into their magnetic relaxation properties can provide new and complementary information about inner processes and changes in wood during the heating process.

The current EPR spectra show that the amount of free radicals in wood samples significantly grows after the heat treatment. The proton NMR signal spin kinetics of the wood tissue ^{1}H nuclei was studied in order to find another possible impact of the heat treatment. NMR measurements were taken for a number of selected birch
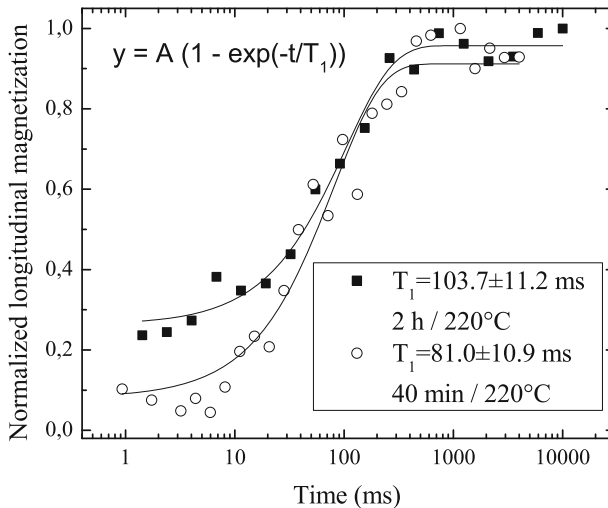
Fig. 5 Longitudinal magnetization recovery curves of ^1H nuclei in thermally treated birch wood samples (*filled symbols*—220 °C/2 h, *open symbols*—220 °C/40 min) at 12 MHz frequency and room temperature (400 averages). *Solid line* represents the approximation curve. Obtained T_1 relaxation times do not change under used thermal treatment conditions

samples with different treatment duration and temperature including untreated ones. The typical longitudinal magnetization recovery curves obtained by 400 averages are shown in Fig. 5. A mono-exponential function fits the obtained longitudinal magnetization recovery curves. The ^1H nuclei spin–lattice relaxation time T_1 values for all investigated samples are close to the average value $T_1 = 95.7 \pm 11.8$ ms. The obtained T_1 values of ^1H nuclei in birch samples are of the same order as for dry samples of cedar (Menon et al. 1987) and are lower than the ones obtained for beech samples (Gilardi et al. 1994). Longitudinal magnetization recovery mechanism is independent from the wall structure (Menon et al. 1987), and its interpretation is complicated by the coupling to the solid protons.

Figure 6 displays typically measured ^1H nuclei transverse magnetization decay after 1000 averages with repetition time TR = 300 ms. It is also a mono-exponential process with the average spin–spin relaxation time $T_2 = 252.2 \pm 46.5$ µs. The transverse magnetization relaxation time T_2 of ^1H nuclei in birch is close to the fast component observed by other groups (Riggin et al. 1979; Menon et al. 1987; Gilardi et al. 1994). This fast component corresponds to the protons of the water molecules in the cell walls and cannot be associated with the hydrogen nuclei in the wood, because their relaxation is relatively fast with the apparent relaxation time of ca. 7 µs (Riggin et al. 1979). Slower components (1–1000 ms) of transverse magnetization relaxation are not observed due to the absence of the bulk water inside the wood samples and water molecules on the wood pores surface.

The ^1H magnetization relaxation rates of water in cell walls do not change after the vacuum thermal treatment and do not depend on this process. In the current experiments, ^1H relaxation times T_1 and T_2 of water in cell walls do not correlate
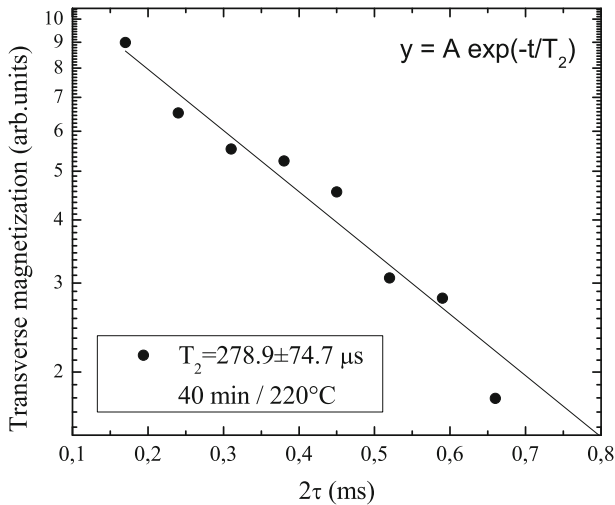
Fig. 6 Typical transverse magnetization decay of ^{1}H nuclei in thermally treated birch wood samples (220 °C/40 min) at 12 MHz frequency and room temperature (1000 averages, TR = 300 ms). *Solid line* represents the approximation curve

with the amount of free radicals in the samples as well. Despite the heat treatment process, the T_1 and T_2 relaxation time values remain similar to the untreated dry wood samples. The information on the obtained transverse magnetization decay curves of ^{1}H nuclei and relaxation time T_2 values allows assessing the location of water molecules inside the wood samples. Short relaxation times (hundreds of μs) point to the water molecules presence in the cell walls while slower relaxation (tens and hundreds of ms) provides information on the water molecules absorbed on the wood pores surface.

Optical microscopy

Optical microscope imaging was performed to assess the visual changes of wood structure during the heat treatment. Obtained examples of cross-sectional images of wood species are shown in Figs. 7, 8 and 9. Wood pores and capillaries are visible on the images. The colour of all samples changes and darkens with the heat treatment. Destructive changes appear after thermal modification. Especially, severe deformations of capillary walls are observed after 8-h treatment.

After a proper image analysis, the pore size distributions for each registered image were plotted. The changes of the wood pore cross-sectional area distribution are shown in Figs. 8 and 9. This method allows observing changes only for the pores bigger than 5 μm in diameter. Pores cross-sectional area distributions in birch and lime ($R^2 = 0.98$) samples follow log-normal law, while normal distribution is obtained for spruce, larch and pine ($R^2 = 0.94$) samples. Table 1 represents changes of the obtained distribution parameters as mean values x_c and full width at half-maximum pore sizes during the vacuum heat treatment at 220 °C. Pore distributions
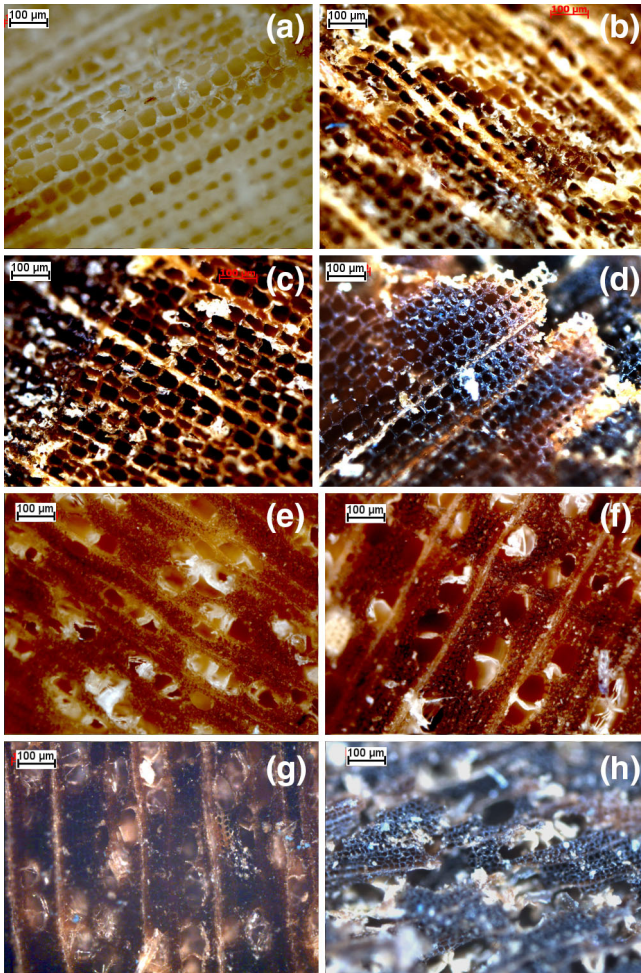
Fig. 7 Optical microscope images of the untreated and at 220 °C thermally treated pine samples: **a** untreated, **b** 40 min, **c** 4-h and **d** 8-h treatment; birch samples: **e** untreated, **f** 40-min, **g** 4-h and **h** 8-h treatment

in pine, spruce and larch behave similarly after the heat treatment. The obtained distributions point out that spread of pore sizes decreases after the thermal modification. For example, FWHM value decreases three times in larch samples after 8-h vacuum heat treatment and the amount of the smallest and the biggest observed pores decreases. Similar effect of pore diameter changes in thermally modified spruce was also observed by Zauer et al. (2015). The authors have found that the pore size distribution becomes narrower after the heat treatment, and they connect it with the cell wall shrinking. The pore sizes distribution becomes wider for birch and lime samples after the treatment. Slight increase in the pore dimensions in pine wood after heat treatment was registered by gradient ^{2}H NMR of
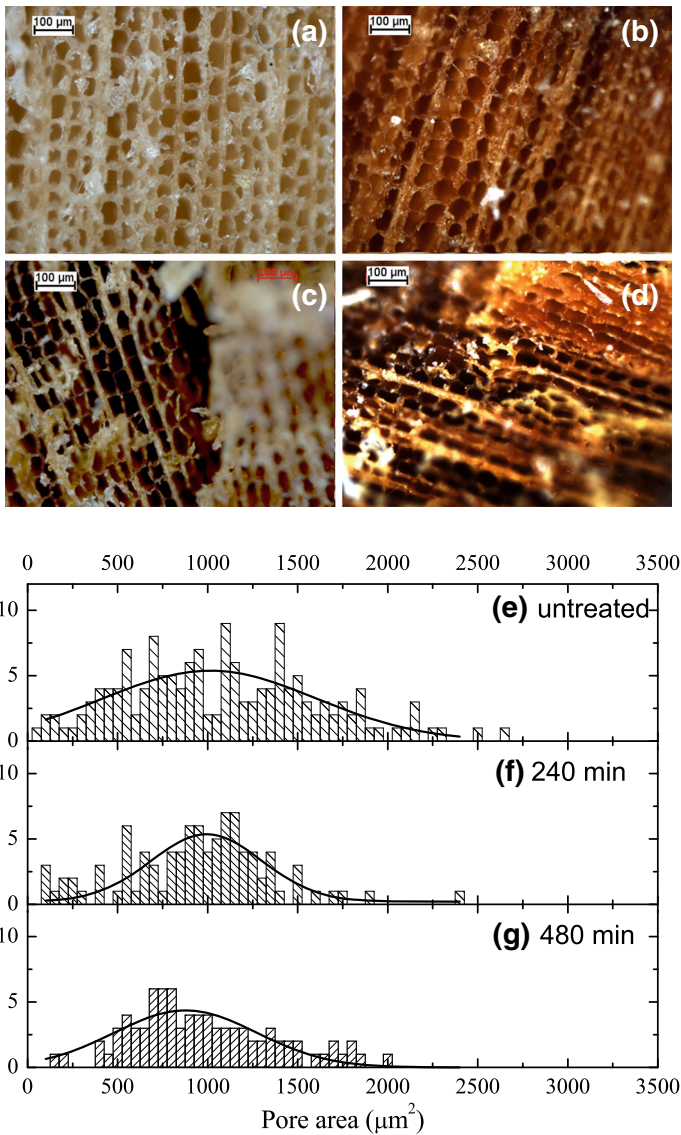
Fig. 8 Optical microscope images of the untreated and at 220 °C thermally treated larch samples:
a untreated, b 40-min, c 4-h and d 8-h treatment and pore area size distributions: e untreated, f 4-h and
g 8-h treatment

a liquid probe (Hietala et al. 2002), the authors also linked this to the removal of
cellular wall components. The deformation of cell walls is connected with changes
of the polymers structure and evacuation of volatile components. Mass loss
indicates on the latter process while the increase in stable free radicals obtained by
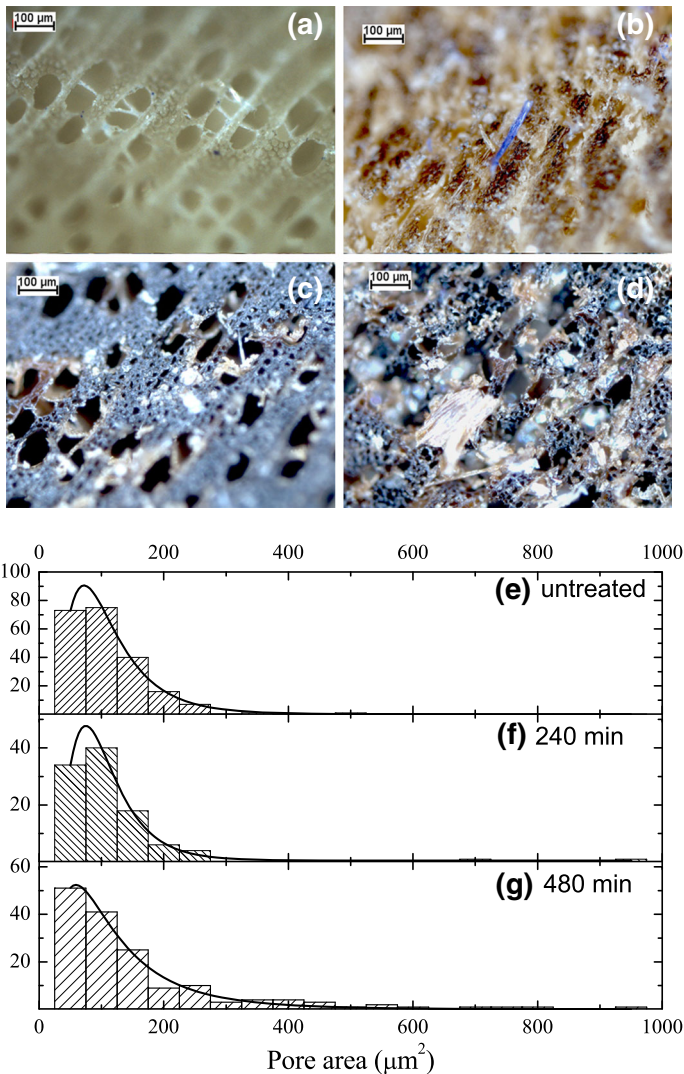EPR experiments reveals changes of the wood polymers.

Fig. 9 Optical microscope images of the untreated and at 220 °C thermally treated lime samples: **a** untreated, **b** 40-min, **c** 4-h and **d** 8-h treatment and pore area size distributions: **e** untreated, **f** 4-h and **g** 8-h treatment
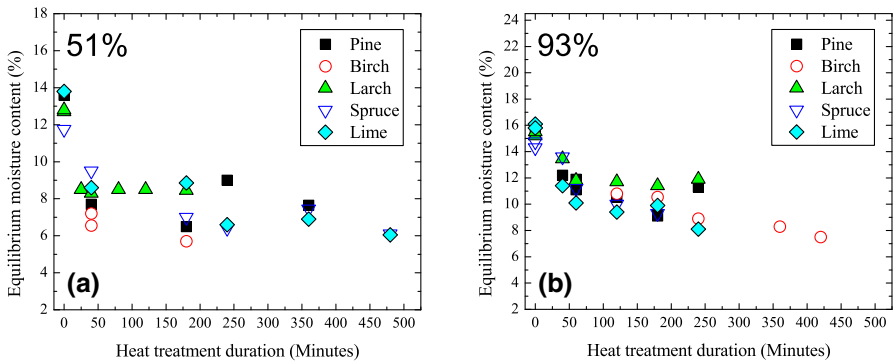
Humidity absorption

Preparation of sample copies allowed investigating the influence of vacuum heat treatment on the wood resistance to the moist external conditions. After 2 months of storage in humid airtight boxes, the samples reached their equilibrium MC values.

Figure 10 displays how equilibrium MC value changes for wood samples after vacuum thermal treatment of various durations and following storage at 51 and at

Table 1 Changes of the pore sizes distribution parameters during the vacuum heat treatment at 220 °C

Samples	Parameter (μm^2)	Treatment time (h)		
		0	4	8
Pine	FWHM	303.8 ± 38.9	508.5 ± 24.2	263.6 ± 14.3
	x_c	777.2 ± 41.7	861.9 ± 41.1	393.4 ± 17.2
Spruce	FWHM	404.9 ± 38.4	423.3 ± 40.2	283.7 ± 14.2
	x_c	462.3 ± 19.0	578.9 ± 20.0	534.0 ± 7.1
Larch	FWHM	1184.7 ± 102.5	673.3 ± 57.6	394.3 ± 27.9
	x_c	1011.2 ± 47.9	985.9 ± 28.8	930.3 ± 27.1
Lime	FWHM	54.3 ± 0.5	47.6 ± 0.8	75.5 ± 2.3
	x_c	98.0 ± 0.9	95.9 ± 0.9	101.9 ± 3.1
Birch	FWHM	20.4 ± 0.1	–	53.6 ± 1.2
	x_c	73.5 ± 0.2	–	115.1 ± 2.5

Fig. 10 Equilibrium moisture content MC values of vacuum heat-treated wood samples change with treatment duration. MC values are shown after samples storage at 51 % **a** and 93 % **b** relative humidity for 60 days at room temperature

93 % relative humidity of air. Measured MC values are lower than the calculated ones from Simpson and TenWolde (1999). For example, estimated moisture content of untreated wood is 22 at 93.0 % relative humidity. The longer the treatment, the lower the equilibrium MC value obtained. For example, the equilibrium MC changed for spruce from 15.5 to 9.1 at 93.0 % relative humidity and from 13.6 to 7.65 at 51 % relative humidity. However, there is no significant change in equilibrium MC observed for heat treatment longer than 2 h.

Similar changes with a slight deviation were obtained for other wood species (see Fig. 10a, b). It can be seen that at 93 % relative humidity the equilibrium moisture values reduce: for larch from 15.2 to 11.4 %, for spruce from 14.75 to 9.3 %; and for lime from 16.1 to 8.1 %. At 51 % relative humidity, it changes from 9 to 6.2 % for birch, from 12.7 to 8.45 % for larch, from 11.75 to 6.1 % for spruce and from 13.45 to 6.05 % for lime. These values are qualitatively in agreement with measured
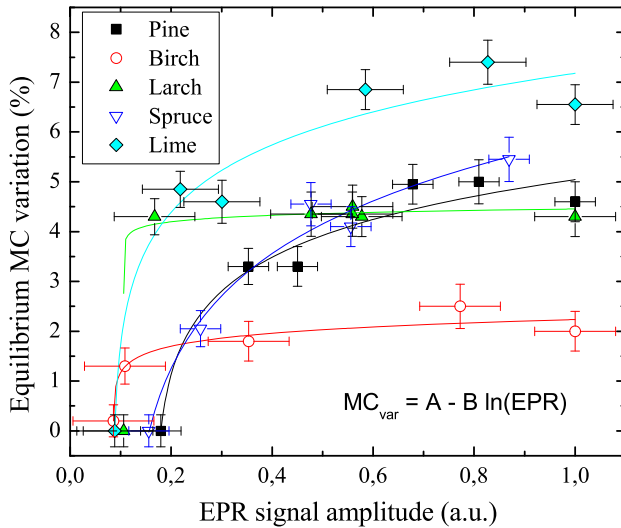
Fig. 11 Correlation between equilibrium moisture content variation MC_{var} at 50 % relative humidity and room temperature and the normalized EPR signal amplitude of vacuum heat treated at 220 °C spruce, lime, pine, birch and larch samples. *Solid lines* represent the logarithmic regression $MC_{var} = a - b \cdot \ln(EPR)$

equilibrium moisture of various wood species obtained by other groups in different storage conditions (Kamdem et al. 2002; Gündüz et al. 2008). From the plots, it is clear that after certain vacuum heat treatment duration the value of equilibrium MC cannot be improved further. Similar behaviour was found in eucalypt wood by Esteves et al. (2007). Concerning destructive changes after long thermal treatment, it can be concluded that optimal duration for vacuum thermal treatment of studied wood species is between 3 and 6 h at 220 °C temperature. These duration values can be different for wood samples of bigger size.

The variation of the obtained equilibrium moisture content MC_{var} is plotted against the relative EPR signal amplitude values in Fig. 11. A good correlation between equilibrium moisture content and results of EPR experiments is observed with a logarithmic equation $MC_{var} = a - b \cdot \ln(EPR)$: the coefficient of multiple correlation $R^2 = 0.996$ (larch), $R^2 = 0.979$ (spruce), $R^2 = 0.963$ (lime), $R^2 = 0.960$ (pine) and $R^2 = 0.939$ (birch). Similar type of regression is reported for thermally treated beech and spruce samples (Altgen et al. 2012). EPR techniques can be used to assess or predict equilibrium MC of vacuum heat-treated wood samples. However, the relationship between the equilibrium MC and the free radicals concentration in wood remains unclear.

Wood hardness

Figure 12a displays the measured values of radial wood hardness for a number of vacuum heat-treated and untreated samples. The obtained hardness values are close to the ones presented in the literature (Shi et al. 2007; Terziev and Daniel 2002).
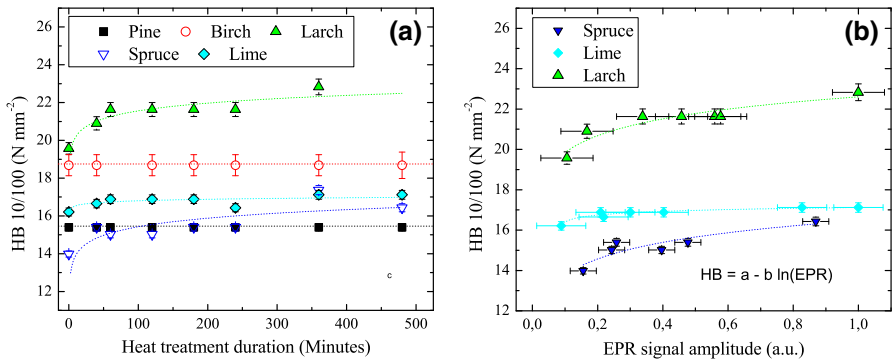
Fig. 12 a Changes of the radial Brinell hardness of wood species after vacuum thermal treatment at 220 °C. **b** Correlation between the radial Brinell hardness of spruce, lime and larch samples and normalized EPR signal amplitude. *Solid lines* represent the logarithmic regression HB = a − b·ln(EPR)

Two types of heat impact on wood surface hardness are found. The current mechanical tests show that surface of larch, lime and spruce samples becomes more rigid after approximate 1-h vacuum heat treatment at 220 °C. After this duration, mechanical properties do not vary much with further treatment. The maximum obtained enhancement of the larch and lime hardness by heat treatment is near 15 %. Influence of heat on hardness of other studied species as pine and birch appears to be negligible. There are a large number of published articles on Brinell hardness changes after heat treatment with controversial results. Shi et al. (2007) reported an increase in radial hardness of 7 % for spruce, 19 % for fir, 36 % for birch, increase of 19 % and then decrease of 24 % for pine after 2- to 3-h treatment at 200 °C. Ates et al. (2009) detected 10–30 % decrease in radial hardness of pine after 2 and 8 h processing at 230 °C. Boonstra et al. (2007) obtained 48 % increase in pine hardness after 90 min treatment at 180 °C.

The correlation between the obtained Brinell hardness of larch, spruce and lime against the relative EPR signal amplitude values is plotted in Fig. 12b; the EPR signal values for 8-h vacuum treatment are excluded. The results also fit with a logarithmic equation HB = a − b·ln(EPR) as well as results of equilibrium moisture content measurements. The corresponding coefficients of multiple correlation are $R^2 = 0.943$ (lime), $R^2 = 0.919$ (larch) and $R^2 = 0.834$ (spruce). According to Altgen et al. (2012), mechanical properties as bending strength decrease with the EPR signal increase by a logarithmic law for heat-treated spruce and beech. It is noted that the influence of stable radicals on mechanical properties of wood is not direct. The absence of any changes of wood hardness with EPR signal for birch and pine leads to an important conclusion that applied vacuum heat treatment destroys polymers, chemical agents and possibly some extractives which are not responsible for the wood hardness. These can be hemicellulose or low-order cellulose chains, for instance. Overall cellulose and lignin mechanical properties enhance after the thermal treatment. This fact is also in agreement with the results obtained by Sivonen et al. (2002) that heat processing at 180–230 °C increases the level of cellulose crystallinity in pine. Since the correlation between the EPR signal

amplitude and wood hardness was found for larch, lime and spruce, it is possible to use EPR technique to assess the wood hardness.

Conclusion

The current investigation of various thermally treated wood species by magnetic resonance methods revealed important changes in wood structure which were not available for observation by other methods. It has been proven that free radicals EPR signal amplitude strongly depends on the MC of the wood samples and decreases as MC value grows. Additional EPR experiments with absorbed ethanol indicate a possible connection of this effect with the electric dipole properties of H_2O molecules. The observed linear increase in free radicals EPR signal from wood samples with the thermal treatment duration implies an increase in chemical bond ruptures in the wood tissues. The nonlinear correlation between the EPR signal amplitudes and the mass loss is reported. Despite the amount of free radicals in the wood, the ^1H NMR relaxation times T_1 and T_2 do not change with the applied heat treatment. The obtained relaxation time values indicate that the obtained NMR signal corresponds to the water molecules adsorbed on the wood tissues surface.

Observed changes in pore size distributions by microscopy methods indicate cell wall shrinking and deformation. This process is indirectly related to the mass loss and formation of stable free radicals detected by EPR method.

It was found that the equilibrium moisture content variation during vacuum heat treatment correlates with the EPR signal amplitude with a logarithmic regression for all used samples. Similar logarithmic correlation with the EPR results is observed for the radial Brinell hardness changes in larch, lime and spruce samples. These relationships remain unclear, but EPR technique can be used to assess mechanical properties of wood samples.

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