

## Effect of Thermo-Vacuum Treatment on the Color and Chemistry of Larch Wood

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The objective of this study was to investigate the color and chemical changes of thermo-vacuum treated larch wood. Specimens were heat treated in a vacuum at various temperatures for 4 h. The color parameters of untreated and heat-treated samples were measured using the CIELab color system. Changes in the chemistry of larch wood were investigated using X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) spectroscopy, and UV-Vis spectroscopy. The results showed that the color of larch wood became darker at higher treatment temperatures. The O/C ratio decreased with an increase in treatment temperature. The C1 peaks showed that there was an elevated content of lignin and extractives on the wood surface after heat treatment. There were more free radicals for thermally treated wood samples, as demonstrated by the increase in the intensities of the ESR signals. Some groups of lignin that contribute to the darkness of the wood increased after thermo-vacuum treatment. Changes in surface chemistry may be the cause of discolorations that occurred during thermo-vacuum treatment.

*Keywords:* Larch wood; Thermo-vacuum treatment; Color; Surface chemistry

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### INTRODUCTION

Heat treatment is a well-developed and innovative method for improving the properties of wood without using any chemicals (Esteves *et al.* 2008; Akyildiz *et al.* 2009; Esteves and Pereira 2009; Dubey *et al.* 2012; Huang *et al.* 2012). Although the study of heat treatment was started by Stamm (1946), it has been systematically studied and industrialized only in the last dozen years. There are several different industrial heat treatment processes: “Thermowood” in Finland by the use of steam (Viitanen *et al.* 1994), Plato wood in the Netherlands with a combination of steam and heated air (Tjeerdsma *et al.* 1998), retification or *bois perdure* in France (Dirol and Guyonnet 1993), oil heat treatment in Germany (Rapp 2001), and the Termovuolo process by applying vacuum (Allegretti *et al.* 2012; Ferrari *et al.* 2013). Changes in color and surface chemistry caused by heat treatment have been intensely investigated (Bryne *et al.* 2010; Matsuo *et al.* 2011; Tuong and Li 2011).

The color of wood is determined by chemical components, including cellulose, hemicelluloses, lignin, and extractives. The darkening and reddening of wood as a result of heat treatment has been studied by previous researchers (Johansson and Morén 2006; Aksoy *et al.* 2011). The discoloration mechanism is complex: Sundqvist and Morén (2002) attribute the formation of color to the degradation of extractives, hemicelluloses, and lignin by hydrothermal treatment. The results obtained from Sehlstedt-Persson (2003) indicate that the formation of color could result from the hydrolysis of hemicelluloses by

the heat treatment of extractive free wood. The cleavage of ether linkages or the condensation of lignin (Wikberg and Maunu 2004), and the formation of oxidation products of phenolic substances (Bekhta and Niemz 2003) can all contribute to color changes.

The investigation of the surface chemical structure of some wood species has been carried out with X-ray photoelectron spectroscopy (XPS) before and after heat treatment (Inari *et al.* 2006; Gerardin *et al.* 2007). Electron spin resonance (ESR) is the instrument of choice for studying several aspects of wood chemistry (Solala *et al.* 2012; Xue *et al.* 2012), especially the formation of free radicals in wood. Sivonen *et al.* (2002) studied the formation and stability of free radicals in pine formed by thermal treatment. The intensities of the ESR signals from thermally treated wood samples increase with increasing thermal treatment temperature. The occurrence of condensation reactions and the formation of other aromatic structures have been studied by UV analyses during heat treatment (Boonstra and Tjeerdma 2006; Chen *et al.* 2012a).

Larch is one of the most important plantation tree species in northeast China. Larch wood has a high usage potential for solid wood products used for the construction, decoration, and furniture industries because of its high hardness, beautiful texture, and strong decay resistance (Li 2006). Consumers often like the darker tonality of wood due to the better decorative function. In order to meet the needs of customers, heat treatment has been used as a way to make wood darken and redden (Bekhta and Niemz 2003; Esteves and Pereira *et al.* 2009). Thermo-vacuum treatment has been reported as a method of darkening the wood color by some researchers (Allegretti *et al.* 2012; Ferrari *et al.* 2013). The color of alder birch wood is darkened by thermo-vacuum treatment and the discoloration mechanisms are analyzed using wet chemical analysis and FTIR (Yang *et al.* 2015). The discoloration mechanisms of heat-treated wood under vacuum are still not clear; therefore further studies still need to be done to elucidate the discoloration mechanisms. For this purpose, larch wood was heat treated under vacuum and the wood color and chemical changes were studied. The aim of this study was to investigate the color and chemical changes of thermo-vacuum treated larch wood and better understand the discoloration mechanisms by using XPS, ESR, and UV-Vis Spectra.

## EXPERIMENTAL

### Materials

Larch wood was obtained from Qingyuan County in Liaoning Province, China. Larch wood was sawn and processed with a planer to obtain specimens with a length of 400 mm (longitudinal), a width of 40 mm (radial), and a thickness of 40 mm (tangential). The specimens were free of macroscopic defects such as knots and splits.

### Methods

Prior to heat treatment, all specimens were oven-dried at  $103 \pm 2$  °C to 0% moisture content and then placed in a vacuum pressure furnace. Heat treatment was conducted at temperatures of 160, 180, 200, 220, and 240 °C for 4 h under the absolute pressure range from 0.01 to 0.05 MPa with reference to atmospheric pressure. At the end of each heat treatment, the furnace was turned off and the wood was kept inside until the temperatures reached 40 °C; then, the wood was removed and stored. The untreated specimens were used as control test samples.

Color values were measured by the CIELab system with a Minolta spectrophotometer (model CM-2600d, Japan) before and after heat treatment. The sensor head was 8 mm in diameter. Measurements were made using a D65 illuminant and a 10° standard observer. 10 samples were treated at each temperature and color was measured at 3 locations on each sample, and the mean value was calculated. The three coordinates of CIELab represent the lightness ( $L^*$ =0 indicates pure black and  $L^*$ =100 indicates pure white), its position between red and green ( $a^*$  negative values indicate green, while positive values indicate red), and its position between yellow and blue ( $b^*$  negative values indicate blue and positive values indicate yellow). The total color difference ( $\Delta E^*$ ) was calculated according to the following equation,

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  are the color changes between the untreated and heat-treated samples.

The results were analyzed using one-way ANOVA ( $P = 0.05$ ) from the SPSS statistical software program, and significant differences were determined by the Tukey multiple comparison test ( $\alpha = 0.05$ ).

Wood samples for the XPS study were collected from the same radial surface of samples used for color change measurements and processed with sizes of 5 mm × 5 mm × 1 mm (L × R × T) in the laboratory. X-ray photoelectron spectroscopy was performed on a Kratos Axis Ultra spectrometer (Kratos Analytical Ltd., UK) using a monochromatic Al K $\alpha$  X-ray source ( $\lambda = 1486.7$  eV) with a power of 225 W. Spectra were analyzed using CasaXPS software (2.3.12Dev7, UK). A high-resolution spectrum of the C1s region from 280 to 300 eV was collected at a pass energy of 20 eV and resolution of 0.05 eV/step, for quantitative measurements of binding energy and atomic concentration. Chemical bond analysis of the carbon was accomplished by fitting the C1s peak and de-convoluting it into three sub-peaks.

Wood samples for the ESR and UV-Vis study were ground into powder and passed through a 100-mesh screen, but not a 120-mesh screen. A total of 0.02 g of powder from untreated and treated wood was used to study the intensities of the free radicals. ESR measurements were carried out on a JEOL JES-FA 200 ESR spectrometer (Japan; sweep width 15 mT, microwave frequency 9.06 GHz, microwave power 0.998 mW, modulation amplitude 0.1 mT, time constant 0.3 s, sweep time 4 min). Intensities of the free radical signals were measured from the amplitude of the free radical signal. Spectral measurements in the range 240 to 800 nm were performed on a Cary 5000 UV-Vis spectrophotometer (Varian, USA).

## RESULTS AND DISCUSSION

### Color Changes of the Treated Wood

The color change data of heat-treated larch wood are presented in Table 1. According to the results, the color of thermo-vacuum treated wood became increasingly darker, compared with the original color, with increased treatment temperature. Similar results have been reported by Matsuo *et al.* (2011). Compared with the untreated samples, the lightness values ( $L^*$ ) decreased by 13.2%, 22.4%, 22.5%, 28.2%, and 43.8% with increasing temperature of heat treatment, respectively. Similar results have been reported

by Allegretti *et al.* (2012) for spruce and fir wood by thermo-vacuum treatment. Both  $a^*$  and  $b^*$  values gradually increased as the increasing treatment temperature. The former increased from 7.9 to 17.0 and the latter increased from 28.8 to 39.0. Similar results have been obtained in previous studies (Mottonen and Karki 2008; Gunduz *et al.* 2010). In this study,  $\Delta E^*$  values increased from 13.3 to 35.8 with the increase of treatment temperature from 160 °C to 240 °C. There is a similar trend with the results studied by Ferrari *et al.* (2013) for some European softwood and hardwood species using thermo-vacuum treatment. The mechanism of color change is complex: Sehlstedt-Persson (2003) indicates that the formation of color could result from the hydrolysis of hemicelluloses by the heat treatment of extractive free wood. The results obtained by McDonald *et al.* (1997) show that the Amadori-Maillard reaction results in the discoloration of wood. Sundqvist and Moren (2002) evaluate the effects of wood polymers and extractives on the color during hydrothermal treatment and show the extractives involve in the color formation of hydrothermal treated wood.

**Table 1.** Color Change Values of Heat-treated Wood

Treatment	$L^*$	$a^*$	$b^*$	$\Delta E^*$
Control	75.5 ( $\pm 5.0$ )a	7.9 ( $\pm 3.5$ )a	28.8 ( $\pm 2.8$ )a	—
160 °C	65.5 ( $\pm 5.3$ )b	13.3 ( $\pm 3.6$ )b	35.6 ( $\pm 1.7$ )b	13.3 ( $\pm 5.7$ )a
180 °C	58.6 ( $\pm 5.9$ )c	13.7 ( $\pm 2.2$ )bc	36.6 ( $\pm 4.5$ )b	19.5 ( $\pm 6.2$ )b
200 °C	58.5 ( $\pm 6.0$ )cd	14.4 ( $\pm 3.6$ )c	36.8 ( $\pm 4.0$ )b	20.0 ( $\pm 6.5$ )bc
220 °C	54.2 ( $\pm 6.1$ )d	15.4 ( $\pm 2.9$ )cd	37.7 ( $\pm 3.2$ )b	24.3 ( $\pm 7.0$ )c
240 °C	42.4 ( $\pm 7.0$ )e	17.0 ( $\pm 2.1$ )d	39.0 ( $\pm 3.0$ )b	35.8 ( $\pm 5.4$ )d

Standard deviations are shown in parentheses.

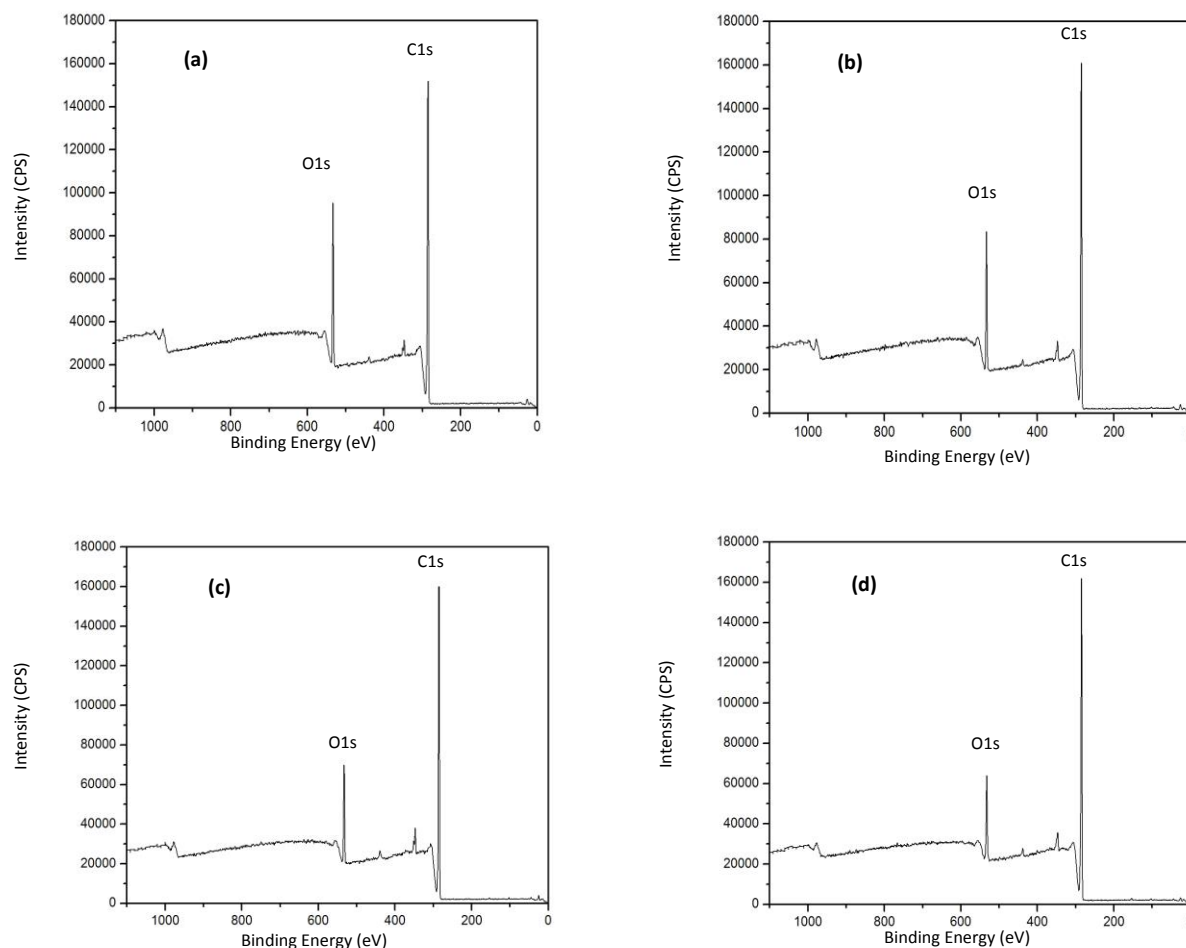
Means followed by the same letter are not significantly different by Tukey test at 0.05 probability level.

### XPS Analysis

The main reason for performing XPS analysis was to obtain information concerning the chemical environment and atomic concentrations present in untreated and heat-treated larch wood. Figure 1 shows a typical XPS survey spectrum of larch wood before and after thermo-vacuum treatment, and Table 2 lists the experimental atomic composition as determined from the XPS spectra analysis and the calculated oxygen to carbon (O/C) ratio for all samples. The XPS spectra revealed that carbon and oxygen were the major elements, and their peaks appeared at about 284 and 532 eV, respectively. A small amount of calcium and silicon was detected on the surface from their characteristic emission peaks at 347 and 98 eV, respectively. Table 2 shows some increase in the percentage of carbon atoms and at the same time some decrease in the percentage of oxygen atoms for each heat-treated wood sample in comparison with the control sample.

**Table 2.** Relative Amount of Atoms and O/C Ratio Determined by XPS for Heat-treated and Untreated Wood

Samples	C (%)	O (%)	N (%)	Ca (%)	Si (%)	O/C (%)
Control	84.3	14.5	0.2	0.8	0.2	17.2
160 °C	86.3	12.5	0.1	1.0	0.2	14.5
200 °C	87.8	10.5	0.2	1.2	0.2	12.0
240 °C	89.1	9.3	0.2	1.0	0.4	10.4

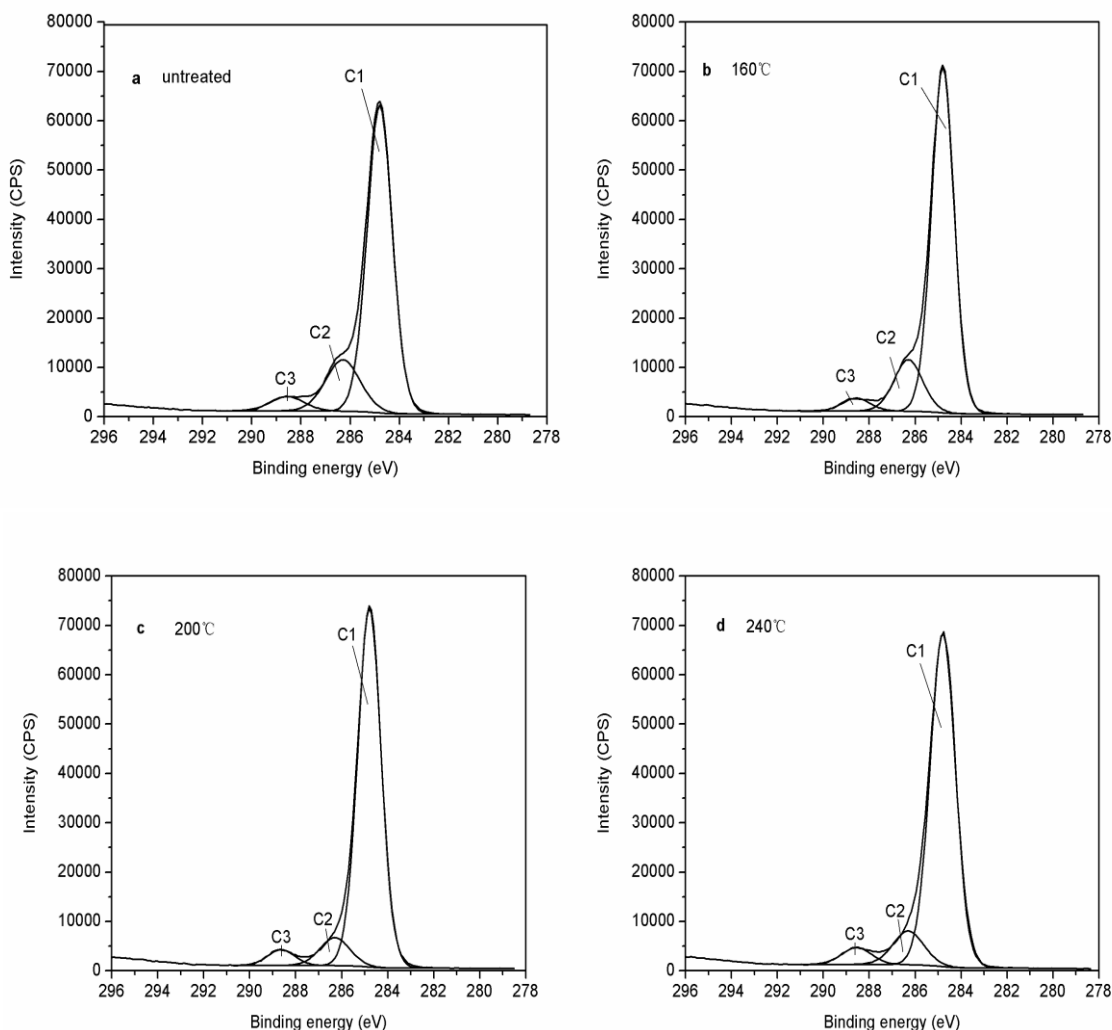


**Fig. 1.** XPS survey spectra of untreated and heat-treated larch wood: (a) control; (b) heat-treated at 160 °C for 4 h; (c) heat-treated at 200 °C for 4 h; and (d) heat-treated at 240 °C for 4 h

Using the total area of peaks and the respective photoemission cross-sections, a quantitative determination of oxygen to carbon (O/C) ratios for heat-treated and control samples is presented in Table 2. The results showed that O/C ratios were reduced from 17.2% to 10.4% with the increase of heat treatment temperature. The O/C atomic ratio of lignin is 0.33, extractives is 0.1, and cellulose is 0.83 (Kamdem *et al.* 1991). The decrease in O/C ratios might result from the formation of volatile by-products and an increase in lignin proportion on wood surface (Sernek *et al.* 2004; Nguila *et al.* 2006; Kocaefe *et al.* 2013). There was a high carbon content in untreated and heat-treated wood samples, which could indicate that the lignin and extractives (or their degradation products) content was higher on the wood surface, especially extractives. The XPS results obtained by Bryne *et al.* (2010) show that the high carbon content on wood surface is due to the migration of low-oxygenated species (presumably extractives) to the surface. In addition, the high carbon content might result from the new products with lower oxygen content due to the dehydration of wood components (Tuong and Li 2011).

Figure 2 shows the types and amounts of carbon-oxygen bonds on C1s spectra of treated and control samples. According to the relevant literature, the assignment of deconvoluted peaks C1s for lignocellulosic materials, which correspond to the four types

of carbon atoms, is well-established: C1, C2, C3, and C4 (Kamdem *et al.* 2001; Nzokou and Kamdem 2005). C1 corresponds to carbon only bonded to other carbon atoms and/or hydrogen atoms, which arises mainly from lignin and wood extractives. C2 has one link to a single non-carbonyl oxygen atom, which has been shown to be mainly derived from cellulose. C3 bonds to one carbonyl oxygen or two non-carbonyl oxygen atoms (Kamdem *et al.* 1991). As for C4, it was neglected here because it was low in content.



**Fig. 2.** C1s spectra of untreated and heat-treated larch wood: (a) control; (b) heat-treated at 160 °C for 4 h; (c) heat-treated at 200 °C for 4 h; and (d) heat-treated at 240 °C for 4 h

Table 3 shows the variation of peak area contributions of the C1, C2, and C3 components before and after thermo-vacuum treatment. C1 were the most important contributions for the surfaces of untreated and heat-treated samples. The C1 peak area increased by 4.5%, 12.4%, and 9.3% with the increasing treatment temperature, respectively. The C2 peak area decreased by 13.9%, 51.7%, and 41.7% with the increasing of treatment temperature, respectively. Nishimiya *et al.* (1998) attributed C1 and C2 to the aromatic carbon and aliphatic carbon of wood, respectively. The increase in the C1 peak area indicates higher concentration of lignin-derived aromatic carbon due to

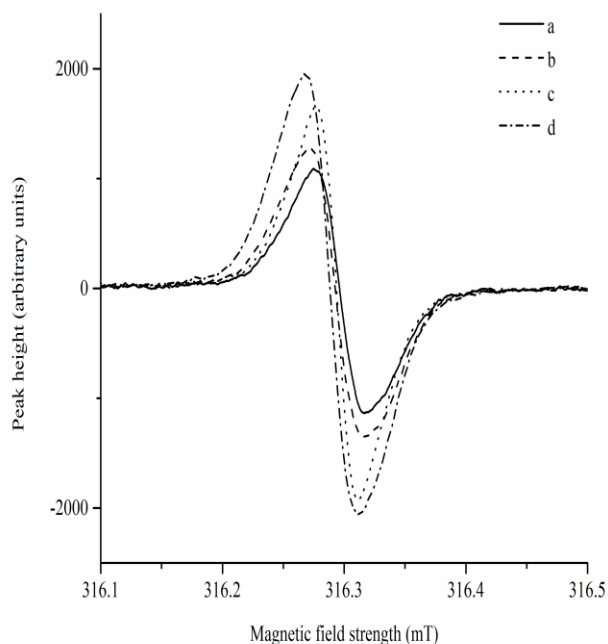
the partial degradation of hemicelluloses. The decrease in the C2 peak area indicates the reduction of aliphatic carbon of wood. As stated above, the results may be related to changes in the surface extractives or to the changes in chemical functional groups by the degradation of wood components during heat treatment (Weiland and Guyonnet 2003; Hakkou *et al.* 2005).

**Table 3.** C1s Division Peak Percentage Content of Wood Surface Due to Heat Treatment

Samples	C1 (%)	C2 (%)	C3 (%)
Control	77.2	18.0	4.9
160 °C	80.7	15.5	3.8
200 °C	86.8	8.7	4.5
240 °C	84.4	10.5	5.1

### ESR Analysis

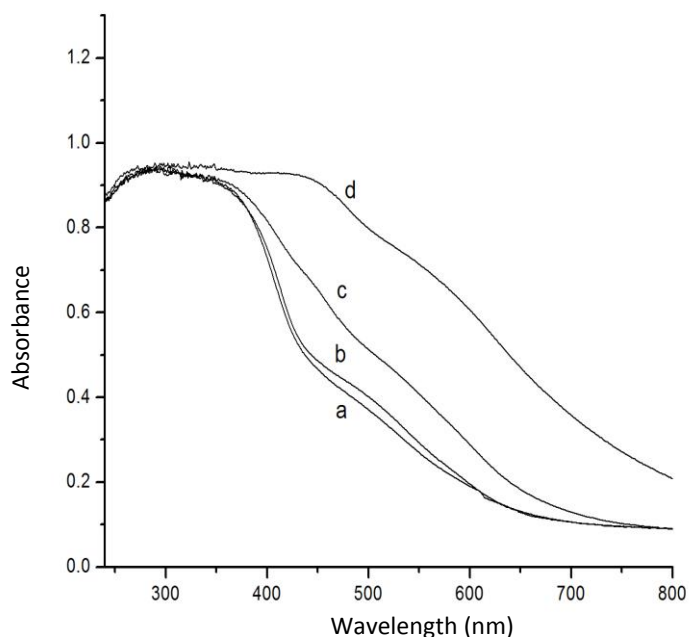
The ESR spectra of untreated and heat-treated larch wood are shown in Fig. 3. The signals grew with increasing temperature of heat treatment. The intensities of the ESR signals of thermo-vacuum treated wood samples were higher than those of untreated samples, indicating that more free radicals were formed during heat treatment, which was in agreement with previous results (Sivonen *et al.* 2002; Petric *et al.* 2004). The g-value of the free radical peaks was 2.003, attributable to the phenoxy free radicals generated from lignin (Sivonen *et al.* 2002; Kuzina *et al.* 2004; Baur and Easteal 2014). The further reaction of phenoxy free radicals may result in the formation of quinones that are responsible for darkening the wood (Petric *et al.* 2004; Evans 2012).



**Fig. 3.** ESR spectra of free radicals for different treatment temperatures: (a) control; (b) heat-treated at 160 °C for 4 h; (c) heat-treated at 200 °C for 4 h; (d) heat-treated at 240 °C for 4 h

## UV-Vis Spectra Analysis

The UV-Vis diffuse reflectance spectra obtained from the untreated and heat-treated samples are shown in Fig. 4. There was no obvious difference in the absorptions of the UV region. The absorptions at 280 and 350 nm increased slightly after heat treatment, which was attributed to  $\beta$ -5, the unsaturated  $C_\alpha = C_\beta$  bond, and the  $\beta$ -C = O structure of lignin and the conjugated carbonyl group in the side chains of lignin and double bonds, respectively (Chen *et al.* 2012b). The absorptions after heat treatment in the visible region (400 to 700 nm) were obviously increased, which indicated that some coloring reactions could occur during heat treatment. The absorptions in the 400 to 500 nm region could be attributed to quinones, which were formed from the reaction of the aromatic hydroxyl groups of lignin during heat treatment (Chen *et al.* 2012b).



**Fig. 4.** UV-Vis diffuse reflectance spectra of untreated and heat-treated larch wood: (a) control; (b) heat-treated at 160 °C for 4 h; (c) heat-treated at 200 °C for 4 h; and (d) heat-treated at 240 °C for 4 h

## CONCLUSIONS

1. It was found that thermo-vacuum treatment darkened larch wood. The values of  $L^*$  decreased and the chromaticity indices  $a^*$  and  $b^*$  increased after heat treatment.
2. The results of the XPS spectral analysis show that the O/C ratios decreased after heat treatment. The increase in the C1 peak area indicates higher concentration of lignin-derived aromatic carbon due to the partial degradation of hemicelluloses.
3. The results of the ESR study of the thermo-vacuum treatment of wood suggest that phenoxy free radicals are generated during heat treatment. The signals grow with increasing temperature of heat treatment. The reaction of phenoxy free radicals might be one cause of wood discoloration during heat treatment.



4. The formations of degradation and condensation products were demonstrated by the increasing absorption of the UV-Vis spectra after heat treatment.

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