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SURFACE PROPERTIES OF BEECH WOOD MODIFIED BY CO_2 LASER

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ABSTRACT

The paper is focused on the analysis of surface properties of beech wood modified by the CO_2 laser. Colour and morphological changes in the beech wood surface subjected to laser treatment under different irradiation doses were monitored. Experiments were carried out to investigate the wetting surfaces treated with standard liquids. Free surface energy values were also determined for these surfaces. The results showed that increasing the irradiation dose over a range of 0–75 J·cm^{-2} induced a significant increase in the total colour difference (ΔE^* = 45). This discolouration was caused by a significant decrease in brightness L^* from 73 to 30 and also by the decreased colour coordinates a^* a b^*. Significant morphological changes were not detected except at the highest irradiation dose with the entire surface layer being carbonised and the surface roughness increased. An increase in irradiation doses resulted in a decrease in the surface free energy values of beech wood. However, the wood surface modified this way still complied with the requirements for surface treatment with coating materials and for gluing.

Key words: beech wood, CO_2 laser, surface properties, colour, roughness, waviness, wetting, surface free energy

INTRODUCTION

In recent decades, there has been considerable interest in exploring the surface properties of wood in the context of its purpose-oriented modification. Various types of wood surface pre-treatments (thermal, thermo-hydro-mechanic, CO_2 laser, plasma, nanoparticles and others) modify, in different ways, the wood structure and properties (VARGA and VAN DER ZEE 2008, ČERMÁK and DEJMAL 2013, KAČÍK and KUBOVSKÝ 2011, DZURENDA 2014, KÚDELA and ANDOR 2018, REINPRECHT *et al*. 2018), This may have considerable impacts on the quality of the surface treatment and also on the quality of the glued joints.

Electromagnetic radiation of various wavelengths induces progressive degradation of wood surfaces, which in the initial phases is manifested through discolouration. In this process, important factors are the form of the radiation (CO_2 laser beam, UV, IR) and the wood species (PANDEY and VUORINEN 2008, KUBOVSKÝ and KAČÍK 2013, ZBOROWSKA *et al*. 2016, REINPRECHT 2016, KUBOVSKÝ *et al*. 2018, KÚDELA *et al*. 2018a). The purpose-oriented modification of wood surface properties induced with CO_2 laser beam, infrared (IR) and ultraviolet (UV) radiation is often performed based exclusively on empirical experience.

The technology of wood surface treatment with a laser beam, however, allows us to control the amount of energy supplied to the wood surface according to the required purpose-oriented impact on the wood surface structure. The amount of energy delivered onto the wood surface with a laser beam and the conversion of this energy into heat depend on the laser's power, the speed of the laser head's movement, the focal distance and the raster density (GURAU *et al*. 2018, LI *et al*. 2018, KÚDELA *et al.* 2018a). The energy absorbed into the main wood components is reflected in changes to these components in colour, morphology and water absorbance/repellence of the wood surface (WUST *et al*. 2005, ALIGIZAKI *et al*. 2008, KAČÍK and KUBOVSKÝ 2011, HALLER *et al*. 2014, VIDHOLDOVÁ *et al*. 2017, GURAU *et al*. 2018, LI *et al*. 2018, SIKORA *et al*. 2018, KÚDELA *et al.* 2018a).

KAČÍK and KUBOVSKÝ (2011) demonstrated a drop in polysaccharide amounts in wood irradiated with a CO_2 laser, depending on the amount of energy supplied. The degradation was especially evident in hemicelluloses and in part of the amorphous cellulose fraction. There were also changes to the lignin structure. WUST *et al*. (2005) also observed changes in the cellulose, hemicellulose and lignin distribution patterns across cell walls. These authors suggested intervals for irradiation parameters that will guarantee melting without pyrolysis. The results of the X-ray photo-electron spectroscopy (XPS) indicated an increased number of non-polar bonds C–C and C–H, with C–O bonds maintained without change (DOLAN 2014). Besides irradiation parameters, the degradation of the main wood components also significantly depends on the wood species (WUST *et al*. 2005, KAČÍK and KUBOVSKÝ 2011, HALLER *et al*. 2014, DOLAN 2014).

These changes in the chemical structure of wood irradiated with different electromagnetic radiation types cause the wood to darken. This is especially typical for the light-coloured wood species. The changes in the wood surface chemistry are also reflected in the changes to the wood surface morphology. The results of microscopic observations point out (HALLER *et al*. 2014, DOLAN 2014) that treating the wood surface with a laser beam may make the surface smoother because the cells melt down to a depth of several micrometres without carbonisation. Carving a wood surface with a laser may lead to an opposite effect (GURAU *et al*. 2018). The form of electromagnetic radiation delivered onto the wood surface has considerable influence.

Energy supplied in various forms also affects the wood surface wettability. A liquid's capacity to wet a solid surface is assessed based on the contact angle value. The contact angle is an important indicator in predicting adhesion strength of glues and coating materials and in predicting the effectiveness of wood thermal and chemical modification. Contact angle values measured at the interphase with liquid standards are also a point for determining the thermo-dynamical characteristics of wood surface properties – surface free energy and its components (BLANCHARD *et al.* 2009, WANG and PIAO 2011, PETRIČ and OVEN 2015, HUBBE *et al.* 2015, LASKOWSKA and SOBCZAK 2018, JANKOWSKA *et al*. 2018)

Contact angle values measured after different wood surface modifications are also indicative for prediction of whether the modified wood surface will be more or less water-absorbent than the original.

HALLER *et al*. (2014) give an example of pine wood surface melt under effects of CO_2 laser irradiation without carbonisation (treatment temperature below 200°C) and with worse water absorbance compared to the original, untreated surface (HALLER *et al*. 2014). The melt layer, which was several micrometres thick, substantially enhanced the surface water repellence, which was evident on the contact angle values exceeding 90° and on the lower rate of the drop soaking into the wood. DOLAN (2014) did not observe lower wetting performance for irradiated surfaces and even obtained some opposite results. Moreover, the laser-treated wood did not show significant changes in its surface energy. The total surface energy was low, with dominant disperse component. The polar (acid/base) ratio was

significantly reduced compared to the referential specimens. The Lewis base parameter of the acid/base component of surface free energy remained relatively high, while the Lewis acid parameter was lowered significantly, close to the zero value. The laser radiation parameters used in this case were not the same as those used by HALLER *et al*. (2014). The results of these two authors, however, point out that the purpose-oriented surface treatment can affect the surface water absorbance or repellence and the bond creation between the wood and film-forming material.

The aim of this study has been to investigate the selected surface properties of CO_2 laser modified beech wood – discolouration, roughness variation, wettability and surface free energy.

MATERIALS AND METHODS

Wood surface modification with CO_2 laser

The experimental measurements were carried out on beech wood test specimens with dimensions of 50 × 20 × 5 mm (Fig. 1a). The specimens were irradiated with a power laser LCS 400 (maximum power 400 W), following the methods designed by VIDHOLDOVÁ *et al*. (2017). The specimen surface was situated 127 mm under the focal point of focusing lens (the same distance for all specimens). Under this setting, the laser beam diameter on the specimen surface was 10 mm, with an effective power of 45 W. The power was measured with an appliance Coherent Radiation Model 201. The laser beam was perpendicular-oriented to the specimen surface, and the laser head was moving along the surface at a determined speed. To obtain uniform irradiation across the whole surface, the head was driven three times, parallel, with irradiated bands overlapping appropriately (Fig. 1b).

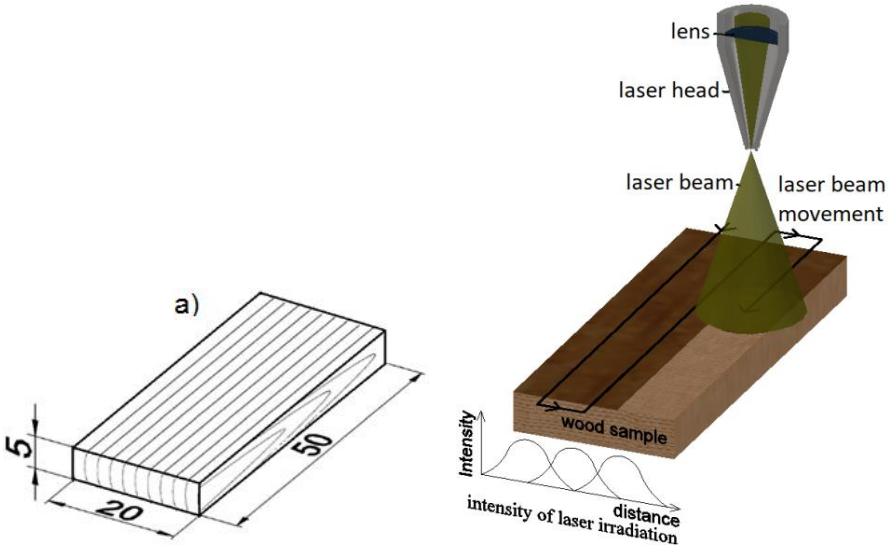

Fig. 1 Test specimen (a) and irradiation with a CO_2 laser beam (b).

There were eight testing groups, each consisting of five specimens. These groups were irradiated with different values of irradiation dose *H*. In addition, there was a group of referential specimens for comparison (Table 1). The irradiation dose *H* was controlled by adjusting the moving speed of the laser head from 6 to 58 mm·s^{-1}. The value was calculated according to the equation

$$H = \frac{P_e \cdot \tau}{A} = \frac{P_e \cdot x}{A \cdot v} \quad (1)$$

where P_e is the laser beam power on the specimen surface, τ is irradiation time during one head passage (the ratio between the specimen dimension x and rate v), and A is the area irradiated during one passage. Table 1 shows irradiation dose values for different rates of laser beam passage.

Tab. 1 Irradiation dose for specific head movement rate.

Specimen	Ref.	A	B	C	D	E	F	G	H
Scanning rate *v* [mm·s^{-1}]	0	58	42	36	30	24	18	12	6
Irradiation dose *H* [J·cm^{-2}]	0	7.8	10.7	12.5	15.0	18.8	25.5	37.5	75.0

Wood surface morphology

The changes to wood surface morphology induced with laser treatment were assessed based on roughness parameters *Ra*, *Rz*, and *RSm* and on the wood surface inspected with light microscopy. Roughness was measured on the radial surfaces parallel with and perpendicular to the grain with a profile-meter Surfcom 130A.

The surface roughness was evaluated in this way: the waviness was filtered from the profile, and the resulting curve was transferred onto the baseline. The overall measured length consisted of the initial segment, five sampling length segments l_r (cutoff λ_c), and the final segment l_p. The first and last segment served to eliminate the possible vibrations associated with starting and stopping the measuring. The sampling length values ranged within 0.025–8 mm in accordance with the preliminary measured values of the roughness parameters *R*a and *R*z.

Wood surface colour

In the test specimens, both the irradiated and referential ones, their colour space CIE $L^*a^*b^*$ was measured with a spectro-photometer Spectro-guide 45/0 gloss by BYK–GARDNER GmbH. The colour was measured at six spots on each specimen (uniformly distributed on the measured surface). The discolouration extent was expressed through the total colour difference ΔE^*, calculated according to the equation:

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

were $\Delta L^* = L_2^* - L_1^*$ (3)

$\Delta a^* = a_2^* - a_1^*$ (4)

$\Delta b^* = b_2^* - b_1^*$ (5)

where index 1 means the so-called referential value, measured on the non-irradiated wood surface, and index 2 indicates the coordinate value after the irradiation.

Wood surface wetting with liquids and wood surface free energy assessment

The wood wetting process associated with the contact angle measurements up to the complete drop soaking into the substrate was performed with a goniometer Krüss DSA30 Standard. Two testing liquids differing in polarity were used – redistilled water and diiodomethane. Using these two liquids follows KÚDELA (2014). Diiodomethane is a non-polar liquid with a non-polar component of surface free energy higher than the disperse component of wood. Redistilled water is a polar-apolar liquid with a polar component of surface free energy that is higher than the polar component of wood. Table 2 shows the testing liquids' parameters.

Tab. 2 Free surface energy of testing liquids γ_L and its components.

Testing liquid	Liquid character	γ_L	γ_L^D	γ_L^P	γ^+	γ^-
		[mJ·mm^{-2}]				
water	**polar**	72.8	21.8	51.0	25.5	25.5
diiodomethane	**non-polar**	50.8	50.8	0.0	0.0	0.0

From the moment of contact of the testing drop (volume 0.0018 ml) with the wood surface, the wood wetting and drop spreading along the fibre direction were inspected. The history of the drop shape, from the first contact up to the complete soaking, was recorded with a camera. The scanning frequency was set according to the wetting interval.

The drop shape was analysed, and the contact angle was determined based on two methods: drop perimeter (circle method) and drop height and diameter (height-width method, Fig. 2).

Fig. 2 Determining the contact angle value by the circle method (a) and by the height-width method (b).

The contact angle values θ_0 were measured at the beginning of the wetting process, meaning at the moment of the first contact between the drop and substrate. The drop width values d (drop diameter) were used for identifying the moment of reversion of the acceding contact angle into the receding one. The drop's contact angle at this moment was considered the "equilibrium" contact angle – θ_e. The contact angle values θ_0 and θ_e obtained in this way were used for calculating the contact angle value θ_w corresponding to an ideal smooth surface, according to the methods described in LIPTÁKOVÁ and KÚDELA (1994). Subsequently, this angle was used to calculate surface free energy and its components. The contact angle was measured at six different measuring spots on each specimen.

As the wood was wetted with two different liquids, the wood surface free energy was determined separately for wetting with water and with diiodomethane, according to the adjusted equation originally proposed by NEUMANN *et al*. (1974):

$$\cos\theta = \frac{(0{,}0137 \cdot \gamma_S - 2{,}00) \cdot \sqrt{\gamma_S \cdot \gamma_L} + \gamma_L}{\gamma_L \cdot (0{,}0137 \cdot \sqrt{\gamma_S \cdot \gamma_L} - 1)} \tag{6}$$

with the disperse and polar components γ_S^d and γ_S^p calculated in the following way by KLOUBEK (1974).

$$\sqrt{\gamma_S^{\,d}} = \sqrt{\gamma_L^{\,d}} \cdot \left(\frac{1+\cos\theta}{2}\right) \pm \sqrt{\gamma_L^{\,p}} \cdot \sqrt{\frac{\gamma_S}{\gamma_L} - \left(\frac{1+\cos\theta}{2}\right)^2} \tag{7}$$

$$\sqrt{\gamma_S^{\,p}} = \sqrt{\gamma_L^{\,p}} \left(\frac{1+\cos\theta}{2}\right) \mp \sqrt{\gamma_L^{\,d}} \cdot \sqrt{\frac{\gamma_S}{\gamma_L} - \left(\frac{1+\cos\theta}{2}\right)^2}\,. \tag{8}$$

The resulting surface energy of beech specimens irradiated with different radiation doses was determined as the sum of the energy polar component obtained with water and the disperse component obtained with diiodomethane.

RESULTS AND DISCUSSION

Irradiation doses ranging from 7.8 to 75.0 J·cm^{-2} caused major changes to the studied wood surface properties. The first one, detected visually, was surface discolouration. The results of the one-way variation analysis have unambiguously confirmed a significant influence of radiation intensity on the coordinate values L^*, a^*, and b^*. Table 3 lists the basic statistical characteristics for these coordinates. The original beech colour coordinates values were from the interval reported by BABIAK *et al.* (2004) and VIDHOLDOVÁ *et al*. (2017). The average lightness in the referential specimens L^* was 73.4, and this value decreased significantly with increasing radiation dose. The lowest lightness value (30) was measured in specimens irradiated with 37.5 J·cm^{-2}. The dose of 70 J·cm^{-2} did not further decrease lightness, and even an opposite trend was observable. The surface of the specimens in this group was entirely carbonised, and the carbonised layer displayed a tendency for light reflexion.

With irradiation dose increase as great as 12.5 J·cm^{-2}, the values of coordinates a^* and b^* increased moderately, shifting towards red and yellow, which caused gradual colouring of the wood to dark brown. Further irradiation dose increases initiated a reverse trend. The values of both coordinates decreased noticeably, close to zero at the highest irradiation dose, with the coordinates shifting towards green and blue. The wood surface colour was modified from dark brown to black. Our results agree with those obtained by VIDHOLDOVÁ *et al*. (2017). This discolouration is documented in Table 3. The differences in the coordinates ΔL^*, Δa^*, and Δb^* and the total colour difference ΔE^* are illustrated in Fig. 3. The total colour difference ranged from the second to sixth degree of the six-degree colour evaluation scale designed by ALLEGRETTI *et al.* (2009). This means the discolouration ranges from just visually observable up to a completely new colour.

Qualitatively similar results for beech wood were also obtained by KAČÍK and KUBOVSKÝ (2011) and KÚDELA *et al*. (2018). In our case, there were more conspicuous changes in the colour coordinates a^* and b^* corresponding to the identical irradiation dose. These deviation, however, may be due to the different directions of the laser head displacement parallel to the grain in our case, perpendicular to the grain in the literature referred to above and also due to the shorter distance between the specimens and the focusing lens in our case.

The figure in Table 3 illustrates that the wood surface discolouration was not homogeneous. We may suppose two reasons: first, uniform irradiation intensity was not possible across the whole specimen width, and second, the beech wood surface structure is heterogeneous. The irradiated surfaces were radial, with alternating early and late wood. Despise being a diffuse-porous wood species, beech wood displays certain differences in structure and properties between early and late wood that play a major role in creating inhomogeneous colour patterns.

The microscopic observation revealed that the colour inhomogeneity was, apart from alternating early and late wood, also caused by pith rays consisting of thin parenchyma cells and representing in beech wood a 20–27% share (KÚDELA and ČUNDERLÍK 2012). The pith rays were intensively darkening with increasing irradiation doses. In the case of group E, the pith rays exhibited marked dark spots and even carbonisation (Fig. 4).

The beech wood surface modification induced with CO_2 laser treatment was manifested not only through discolouration but also through morphological changes evaluated based on the specified roughness parameters. Table 4 lists the basic statistical characteristics of the roughness parameters *Ra*, *Rz*, and *RSm*, measured parallel with and perpendicular to the grain, for all the irradiation modes.

Tab. 3 Beech specimen surface colour and basic statistical characteristics for the coordinates L^*, a^* and b^*, after CO_2 laser treatment with different irradiation doses. (number of the measurements n= 30).

Colour coordinates	Basic statistical characteristics	Irradiation dose H (J·cm^{-2})								
		0	7.8	10.7	12.5	15.0	18.8	25.5	37.5	75.0
		Ref.	A	B	C	D	E	F	G	H
										
L^*	$\bar{x}$	73.39	71.88	66.28	65.36	61.28	53.32	41.48	29.71	31.98
	s	1.53	2.26	1.66	1.95	4.50	2.63	2.55	0.77	0.77
a^*	$\bar{x}$	7.44	7.45	8.59	8.43	8.11	7.78	6.60	2.48	0.45
	s	0.62	0.85	0.45	0.50	0.45	0.26	0.46	0.42	0.14
b^*	$\bar{x}$	18.42	17.67	19.04	18.26	17.29	15.74	12.70	4.20	1.84
	s	1.23	1.28	0.79	0.84	1.15	0.77	1.09	0.75	0.54

$\bar{x}$ – average, s – standard deviation

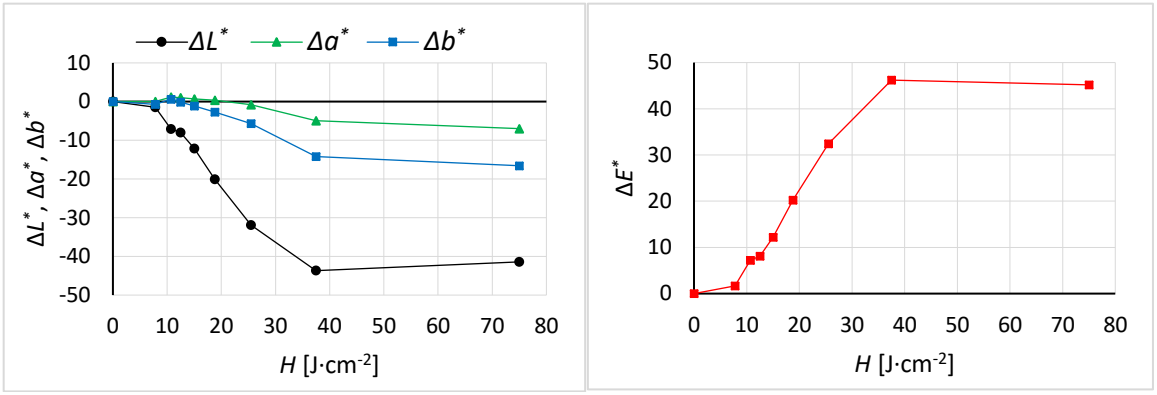

Fig. 3 Beech wood discolouration induced with different irradiation doses.

All the roughness parameters displayed high values and high variability. The roughness of our referential specimens was significantly higher than the roughness of milled or sanded wood as reported in KÚDELA *et al*. (2018b). The specimens discussed in this paper were cut with a fine circular saw, without any subsequent surface machining, which resulted in this difference.

The impacts of irradiation mode and anatomical direction were evaluated with the aid of a two-way variance analysis. The results have confirmed that both factors significantly affected all the roughness parameters. The roughness perpendicular to the grain was significantly higher than that parallel to the grain, but these differences were smaller than the analogical differences obtained for sanded or planed surfaces. The mechanical machining-sawing partially eliminated these differences.

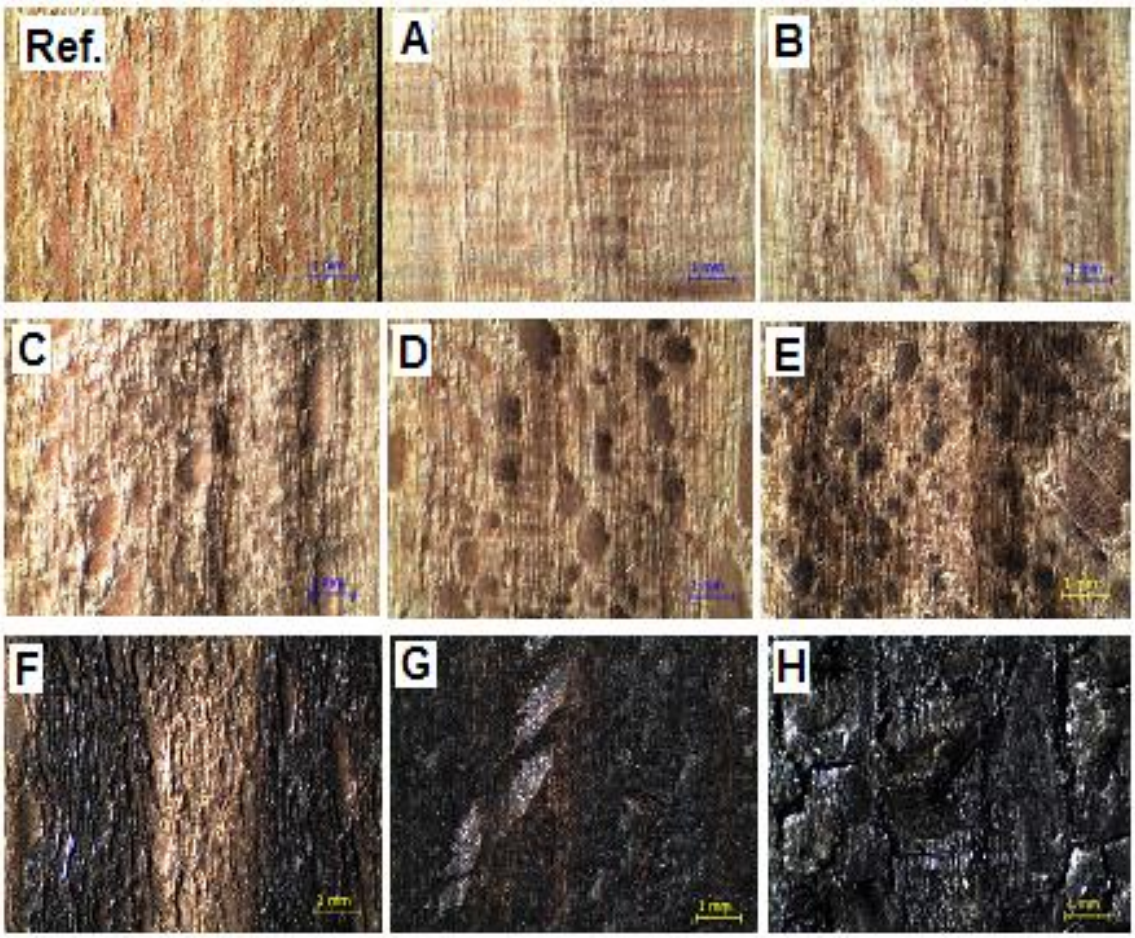

Fig. 4 Beech wood surface discolouration and altered morphology resulting from CO_2 laser irradiation with different amounts of supplied energy.

Table 4 indicates that the values of roughness parameters did not vary with varying irradiation doses in groups A–G. The laser beam seemed to have smoothing effects because the fibres released during sawing were removed and the surface cells were melted. The results demonstrate, however, that this phenomenon was in many cases masked by the mechanical pre-treatment of the specimen surface. This is true for all roughness parameters in both anatomical directions. The maximum irradiation dose, however, enhanced roughness in both directions because the specimen surface was carbonised and cracked (Fig. 4).

In terms of roughness, in case of a natural surface, it is also necessary to include the technical parameters of the cutting tool used for machining the surface before CO_2 laser treatment and the technological parameters of this laser treatment (CZANADY and MAGOSS 2011, GURAU 2013, FOTIN *et al.* 2013, KÚDELA *et al.* 2018a, b and others). The results of these authors as well as our results show that this process is intricate because it involves interactions between the wood surface and the mechanical cutting tool and the electromagnetic radiation within IR range. The wetting process in CO_2 laser-modified wood was evaluated through contact angles θ_0, θ_e, and θ_w. The results revealed that the changes to the beech wood surface morphology and chemistry induced by CO_2 laser treatment were also present where the wood surface was wetted with standard liquids. The water drop applied onto the wood surface was spreading continually over the surface, and, at the same time, it was soaking into the substrate.

Tab. 4 Basic statistical characteristics of beech wood surface roughness parameters after treatment with a CO_2 laser with different irradiation doses. (number of the measured segments n = 10).

Roughness parameters	Basic statistical character.	Irradiation dose H (J·cm^{-2})								
		0	7.8	10.7	12.5	15	18.8	25.5	37.5	75
		Ref.	A	B	C	D	E	F	G	H
		Parallel to grain								
Ra	$\bar{x}$ [µm]	8.231	7.578	7.222	8.261	7.397	7.276	8.168	7.093	11.867
	s [µm]	1.297	1.750	2.199	1.821	1.192	2.054	1.388	0.787	3.132
Rz	$\bar{x}$ [µm]	52.729	51.711	48.188	56.680	48.279	44.260	59.263	45.318	75.525
	s [µm]	8.905	14.130	17.030	13.970	11.343	12.378	13.315	8.387	26.443
RSm	$\bar{x}$ [µm]	800.279	804.770	717.811	723.610	734.087	37.897	739.712	661.479	627.802
	s [µm]	94.588	168.755	139.810	144.987	117.519	104.693	243.112	157.336	158.642
		Perpendicular to grain								
Ra	$\bar{x}$ [µm]	10.834	9.592	10.257	10.372	9.134	9.756	10.260	10.378	20.385
	s [µm]	1.641	1.891	1.319	1.738	1.761	1.758	1.387	1.659	4.395
Rz	$\bar{x}$ [µm]	78.951	66.190	70.333	73.450	66.531	66.893	74.251	68.599	126.420
	s [µm]	8.989	7.883	10.504	8.904	11.111	14.248	11.245	9.627	22.570
RSm	$\bar{x}$ [µm]	414.860	426.991	421.662	385.777	438.277	457.596	435.423	421.507	530.772
	s [µm]	56.139	73.941	61.517	37.822	11.243	142.841	105.182	85.636	131.627

$\bar{x}$ – average, s – standard deviation

The average time necessary to reach the equilibrium t_e during wetting of beech wood radial surface with water ranged from 12 to 43 seconds for all variants investigated. The only exception was group H, with an average time t_e of 1.5 sec. The beech wood surface treatment with CO_2 laser also significantly affected the contacts angle values θ_0, θ_e, and θ_w. Fig. 5 illustrates their dependence on the irradiation intensity.

In all test groups, with the exception of *H*, the average values of the contact angle θ_0 ranged from 60° to 65°. Despite significant differences detected between certain diameters, no dependence of the contact angle θ_0 values has been confirmed. Such dependence was found for the contact angles θ_e and θ_w. Fig. 5 shows that these two contact angles were considerably lower than θ_0 and that they increased proportionally with increasing irradiation intensity. In the case of *H*, all the contact angles were evidently lower. The specimens in this group had a continual carbonised layer on their surfaces, and this layer exhibited its own specific qualitative properties.

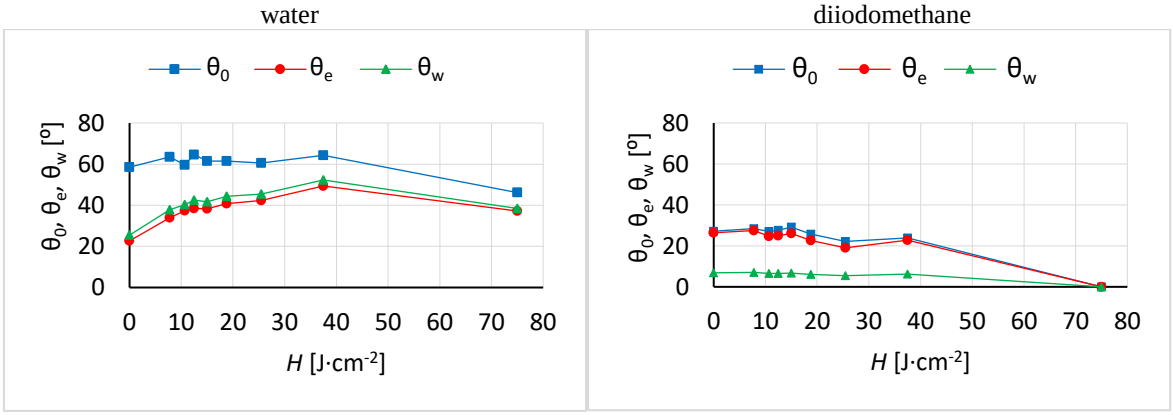

Fig. 5 Beech wood wetting dependence on irradiation dose.

Beech wood wetting with diiodomethane differed from water in quantity and quality. The wetting rate in diiodomethane was much faster, and the average times t_e for the tested groups were about one second. The average contact angle θ_0 values in groups Ref to D did not show significant changes with increasing irradiation dose. Further radiation dose increases induced contact angle decrease, in the case of group *H* down to zero. Consequently, the wetting was perfect. The course of contact angle θ_e values was qualitatively similar. The angle θ_w calculated for an ideal smooth surface was evidently lower, with the average values ranging from 5.5° to 7°. In group H, this angle was also zero.

The values of contact angles θ_0 and θ_e have been confirmed depending on the physical-chemical properties of the liquid and on the chemical properties of the wood surface. Supposing that the contact angle values θ_w are exclusively the result of the chemical composition of the two neighbour phases (LIPTÁKOVÁ and KÚDELA 1994, KÚDELA and LIPTÁKOVÁ 2006), the different values corresponding to different irradiation doses confirm major chemical changes to the wood surface due to varied irradiation doses.

The contact angle values also express the extent of water absorbance/repellence. Consequently, based on the contact angle θ_0 values, we may state that the water absorbance in the irradiated surface has not been reduced substantially. Similar results were obtained by DOLAN (2014), who investigated wetting of CO_2 laser-modified poplar and pine wood surfaces with several liquids (water, form-amide, diiodomethane). This author observed that the best liquid for wood wetting was water, having the highest polar component, and the poorest one was diiodpomethane, being an non-polar substance. The same fact has been confirmed in our case.

However, the assessment of water absorbance/repellence based on the contact angle θ_w values and on the time necessary for the drop to soak into the wood resulted in finding that the wood surface water absorbance decreased with increasing irradiation dose, which is in accord with HALLER *et al*. (2014). Nevertheless, in no case were our contact angles more than 90°, unlike the angles measured by the last cited authors.

The contact angle values θ_w were used for calculating the wood surface free energy γ_S with its disperse and polar components γ_S^d and γ_S^p. The surface free energy calculated based on wetting with water was the highest in the case of the referential specimens, displaying an average value of 67.5 $mJ \cdot m^{-2}$ – the same as the value obtained for milled radial beech wood surface by KÚDELA *et al*. (2016c). The polar component was somewhat higher (36.0 $mJ \cdot m^{-2}$) than the disperse one (31.5 $mJ \cdot m^{-2}$) (Fig. 6). With irradiation dose increasing, the surface free energy decreased proportionally, primarily due to the decrease in the polar component. The disperse component showed a moderate increase, just at the lowest irradiation dose. Later, however, no changes were detected. The surface free energy determined based on diiodomethane was evidently higher, consisting almost exclusively of the disperse component (Fig. 6).

Our results have confirmed that different liquid standards used for assessment of wood surface properties exhibited different performance at the wood-liquid interface. This was due to different surface free energy values and different disperse and polar components of these liquids. Following KÚDELA (2014), the final surface free energy was determined as the sum of the polar component derived from the wetting with water and disperse component obtained with diiodomethane. The surface free energy determined in this way was higher, with dominant disperse component, than the surface free energy calculated separately for the separate liquids (Table 5).

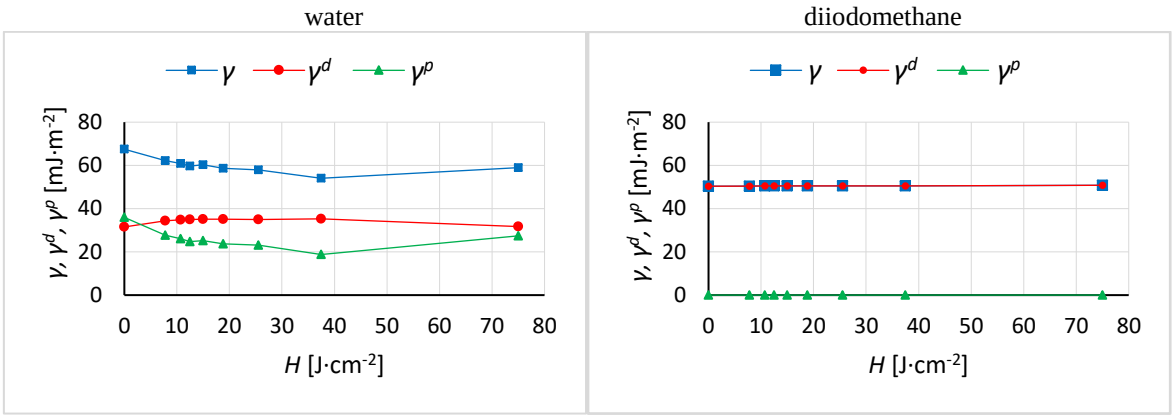

Fig. 6 Beech wood surface free energy and its disperse and polar component corresponding to different irradiation doses.

Tab. 5 The final values of surface free energy with the disperse and polar components for beech wood irradiated with varied energy amounts.

Free surface energy and its components	Irradiation dose H (J·cm^{-2})								
	0	7.8	10.7	12.5	15.0	18.8	25.5	37.5	75.5
	Ref.	A	B	C	D	E	F	G	H
γ	86.39	78.18	76.61	75.20	75.62	74.15	73.60	69.25	78.17
γ^d	50.43	50.41	50.46	50.46	50.45	50.50	50.54	50.48	50.80
γ^p	35.96	27.77	26.15	24.73	25.17	23.65	23.06	18.77	27.37

The changes to beech wood surface properties discussed in this paper were caused by the structural changes in the main wood components. KAČÍK and KUBOVSKÝ (2011) found no significant degradation of saccharides in wood irradiated with a CO_2 laser with a power less than 20 J·cm^{-2} (corresponding to groups A–E in our case). In this case, the wood surface modification does not show carbonisation symptoms. This means that the temperature in the surface layers did not exceed ca 200°C (HALLER *et al*. 2014). The irradiation dose of more than 25 J·cm^{-2} caused a dramatic loss of polysaccharides as the result of degradation of hemicelluloses and a part of the amorphous cellulose fraction. The ratio between the cellulose and hemicelluloses increased significantly, too, and the wood surface was gradually noticeably carbonised. In our study, this was the case of specimens belonging to groups F–H, with the surface layer of *H* specimens carbonised continually. The XPS results also indicate changes to the lignin structure (DOLAN 2014). Chemical reactions in lignin cause browning, especially in light-coloured wood species, including beech. Important agents are also extractive substances (CHANG *et al*. 2010, TOLVAJ *et al*. 2011, SIKORA *et al*. 2018), which are sensitive not only to UV radiation but potentially also to IR radiation (KÚDELA *et al*. 2018b). Identifying the nature of changes induced with specific irradiation types is not a simple problem. To address it, thorough chemical analyses on wood surfaces treated in this way are necessary.

CONCLUSION

In beech wood surface modification with different irradiation doses, the energy from a CO_2 laser was applied onto the wood surface, transformed into heat, and induced changes to the wood surface chemical structure, and, consequently, its properties.

The beech wood surface discolouration depended on the amount of supplied energy. Increasing the irradiation dose within 0–75 J·cm^{-2} resulted in significant changes in the colour coordinates L^*, a^*, and b^*. With increasing irradiation dose, lightness decreased (from 73 to 30), with the colour coordinates a^* and b^* clearly shifting towards green and blue, which also produced a dramatic increase in the total colour difference ΔE^*.

Important morphological changes, manifested in increased roughness, occurred only under the highest irradiation dose, mainly due to the surface layer carbonisation.

The beech wood surface free energy was calculated as the sum of polar component determined based on wood wetting with water and the disperse component determined based on wetting with diiodomethane. This energy decreased with increasing irradiation dose, especially due to the reduced polar component. Despite this fact, the laser-modified beech wood surfaces (except the carbonised one with a dose of 75 J·cm^{-2}) seem to comply with the requirements for the surface treatment with coating materials and for gluing.

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