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Thermal Modification Intensity of Heat-treated Poplar Wood. Part 2: Characterization and Predication from Outside to Core Layers

Intenzitet toplinske modifikacije topolovine. Dio 2: Karakterizacija i predviđanje od vanjskoga prema unutarnjim slojevima

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ABSTRACT • *Based on the previous study of the heat-treated wood at 0-3 mm surface layer, this study focuses on the transition of thermal modification intensity on 160-220 °C heat-treated poplar from surface to core layers. The color change was evaluated by CIELAB, and surface hardness was detected via Shore D (HD) and pressing ball method (H_R); furthermore, the FT-IR was applied to detect the thermal degradation of wood components. The results show that the degradation of cell wall components in the surface layer of heat-treated poplar wood is greater than that in the core layers, and the thermal degradation intensity of the surface layer of the heat-treated poplar wood is greater than that of the other inner layers. Surface color and hardness properties of the heat-treated wood between S_0 and S_1-S_5 test surfaces were significantly different under the same heat treatment conditions; the surface hardness showed an increasing trend, and the H_R value of the $H_{220\text{-}2}$ core layer was 105.71 % higher than that of the surface layer. Heat treatment temperature is the main factor affecting the property of wood surface, while the effect of duration is smaller. The hemicellulose content change was mainly related to the degradation intensity on heat-treated wood at different locations. An accurate prediction model of surface color, hardness, and other properties of the heat-treated wood at different locations was established by Table Curve 3D software.*

KEYWORDS: *heat treatment; modification intensity; transition; hardness; color; surface layer; inner layers; poplar wood*

SAŽETAK • *Prethodno istraživanje toplinski modificiranog drva odnosilo se na površinski sloj od 0 do 3 mm, a ovo se istraživanje bavi prijelazom intenziteta toplinske modifikacije pri 160 – 220 °C s površinskoga prema*

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unutarnjim slojevima topolovine. Za evaluaciju promjene boje primijenjen je CIELab sustav, a tvrdoća površine utvrđena je Shore D (HD) metodom i metodom utiskivanja kuglice (HR). Osim toga, procjena toplinske razgradnje spojeva u drvu napravljena je FT-IR spektroskopijom. Rezultati pokazuju da je razgradnja stanične stijenke spojeva drva u površinskom sloju toplinski modificirane topolovine veća nego u središnjim slojevima te da je intenzitet toplinske razgradnje površinskog sloja topolovine veći od intenziteta razgradnje ostalih unutarnjih slojeva. Boja površine i svojstva tvrdoće toplinski modificiranog drva između S0 i S1-S5 ispitnih površina značajno su se razlikovali uz jednake uvjete toplinske modifikacije. Tvrdoća površine pokazala je rastući trend, a HR vrijednost H220-2 unutarnjeg sloja bila je 105,71 % vrijednosti površinskoga. Temperatura toplinske modifikacije glavni je čimbenik koji utječe na svojstva površine drva, dok je utjecaj trajanja modifikacije manji. Promjena sadržaja hemiceluloze uglavnom je povezana s intenzitetom razgradnje toplinski modificiranog drva na različitim lokacijama. Točan model predviđanja boje i tvrdoće površine te drugih svojstava toplinski modificiranog drva na različitim mjestima uspostavljen je uz pomoć Table Curve 3D softvera.

KLJUČNE RIJEČI: *toplinska modifikacija; intenzitet modifikacije; prijenos; tvrdoća; boja; površinski sloj; unutarnji slojevi; topolovina*

1 INTRODUCTION
1. UVOD

Wood, a renewable and green material, has unique material properties and excellent visual characteristics such as lightweight, good toughness, high plasticity, beautiful texture, rich color, and easy processing (Wang *et al*., 2019; Ansell, 2015). Wood is now widely used in the field of furniture and construction (Gurleyen *et al*., 2017; Yang *et al*., 2020). Due to the deepening conflict between the growing wood processing industry and the scarce natural forest resources, China has vigorously promoted the planting of fast-growing wood to alleviate it (Liu *et al*., 2019; Yang *et al*., 2020). According to the results of the Ninth National Forest Resources Inventory Report of the National Forestry and Grassland Administration (2018), the dominant tree species (groups) in China's artificial arbor forest area are *Cunninghamia lanceolata*, *Populus* spp., *Eucalytus* spp., *Larix* spp., *Pinus massoniana*, *Pinus tabuliformis*. In 2021, China's plantation area accounted for 73 % of the global plantation area (Wang and Shen, 2022). Poplar, as one of the major plantation woods in China, can provide a vast quantity of raw materials for processed products such as paper making and wood-based panels. Although poplar has a relatively short growth cycle and gives a high yield, it usually exhibits some dimensional instability and low-density problems, which limits its efficient utilization and large-scale application as a solid wood material (Pan *et al*., 2019; Yang *et al*., 2020).

Modification of fast-growing poplar wood can effectively improve its properties, and increase its economic benefits (Kamperidou *et al*., 2012; Shi and Li, 2014). The modification refers to the treatment of wood materials by chemical, physical or biological methods to change the internal composition or structure of the wood to enhance some aspects of wood performance (Hill, 2006), of which heat treatment is an environmentally friendly technology without any addition of chemicals. Heat-treated wood is popular for its excellent performance, green and safe process, and has developed remarkably (Gu *et al*., 2020).

Property changes of heat-treated wood and its modification mechanism have been widely studied. Most of the existing research is focused on the overall performance or surface properties of heat-treated wood. However, the process of thermal treatment is commonly applied to sawn wood of especially large dimensions, and the properties of the treated wood on different locations in the thickness direction vary with the progression of the heat treatment and mass transfer. Kadem *et al*. (2020) performed a transient analysis of heat and mass transfer processes during heat treatment and found that, as the sample thickness increased, there was a gradual difference in the temperature at the center of the sample, attributed to the lower thermal conductivity of the wood. Wang (2011) studied the thermal effects of vacuum heat treatment of rough-barked eucalyptus wood and found that the sample thickness has a significant effect on heat absorption per unit mass and that thickness differences lead to uneven heat transfer in thin slices. The modification intensity of wood is unequal at different locations or layers in the direction of thickness. Our previous study uncovered the surface properties change, including surface hardness, roughness, and abrasion of heat-treated poplar, and the discrepancy of those surface properties of heat-treated poplar at the 3 mm surface layer, showing that the most thermal degraded part located in the 1 mm outer surface layer, and the surface hardness, wet-ability, and bonding strength of the heat-treated wood could be remarkably enhanced by removing the outer surface layer (Chu *et al*., 2020).

The performance change of heat-treated wood from surface to core layers is still unknown. This study aims to reveal the variation of heat-treated poplar on different test layers located from the surface to the center core layers in the direction of thickness. Properties including surface color, Shore and pressing ball

hardness, and cell wall component changes were taken into consideration. Besides, the FT-IR and XRD were applied to detect the degradation of wood components and explore the mechanism of the modification intensity variation from outside to core layers, which provided the basis for evaluating the performance of the heat-treated poplar wood.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Sample preparation
2.1. Priprema uzoraka

The 12-year-old Zhonglin 46 poplars were selected, and the straight part of the air-dried lumber was cut into 200 mm × 150 mm ×30 mm boards. The moisture content of all the samples was around 10 %.

The heat-treated poplar wood was prepared by a self-made high temperature experiment device. The poplar wood samples were evenly put in the device, and the temperature inside the box was raised to 130 °C at a heating rate of 20 °C·min^{-1} and maintained for 30 minutes, and then raised to the target temperature (160 °C, 190 °C, and 220 °C) at a heating rate of 10 °C·min^{-1} and maintained for 2 h or 4 h. After that, the samples were removed to the climate chamber to achieve an equilibrium moisture.

Then the modified poplar wood was cut with a 3 mm gradient using a precise sliding saw on the tangential section, forming 6 different testing surfaces (S_0, S_1, S_2, S_3, S_4, S_5), and 5 testing layers (T_1, T_2, T_3, T_4, T_5), as shown in Figure 1.

2.2 Measurement of surface color and hardness changes
2.2. Mjerenje promjene boje i tvrdoće površine

According to the CIE1976LAB standard colorimetric system, a precision colorimeter (HP-200, Shenzhen Hampoo) was used to obtain the surface color parameters of different heat-treated wood layers, namely S_0 to S_5 of wood in each group. Five sites were randomly selected for each sample, and each group was repeatedly tested three times, and then the average value of the results was taken. Before the measurement, all the samples were subjected to humidification balance treatment in a conditioning chamber with a temperature of 20 °C and relative humidity of 65 %. Color difference value ΔE^* was calculated according to Eqs. (1) to (4).

$$\Delta L = L_t - L \quad (1)$$

$$\Delta a = a_t - a \quad (2)$$

$$\Delta b = b_t - b \quad (3)$$

$$\Delta E^* = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right]^{\frac{1}{2}} \quad (4)$$

Where L_t, a_t, b_t are the chromatic parameters of the poplar wood after HT, and L, a, b are the chromatic parameters of wood before HT.

Press ball hardness test adopts a high-precision double-column universal testing machine (AG-X plus, Shimadzu, Japan), using a hemispherical steel indenter mold, referring to the national standard GB/T1941-2009 wood hardness test method. The hemispherical steel indenter was pressed into the surface of the balanced specimen at a uniform speed of 1 mm/min, the pressing load was marked as P, and each experimental group was repeated 15 times. Based on the indentation load of the untreated Poplar wood, the pressing ball hardness (H_R) was calculated with Eq. (5) (Yu *et al.,* 2020).

$$H_R = \frac{P}{P_0} \quad (5)$$

Where P is the load at 1 mm on the surface of the heat-treated wood (N) and P_0 is the load at 1 mm on the surface of the untreated wood (N).

A Shore D hardness tester (HS-D, Wenzhou Baoyi) was used to test the surface hardness of the balanced samples. Ten positions were randomly selected on the surface of each sample for testing, and each experimental group was repeated three times. The surface hardness value (HD) was calculated as shown in Eq. (6).

$$HD = \frac{100 - L}{0.025} \cdot 100\% \quad (6)$$

Where L is the displacement of the Shore D hardness tester needle tip relative to the pressure foot surface when the tester pressure foot is completely attached to the surface of the sample, unit: mm.

2.3 Chemical analysis
2.3. Kemijske analize

According to Figure 1, the parts T_1 to T_5 of each sample were smashed into 100-120 meshed wood powder, and the absolutely dried samples were selected

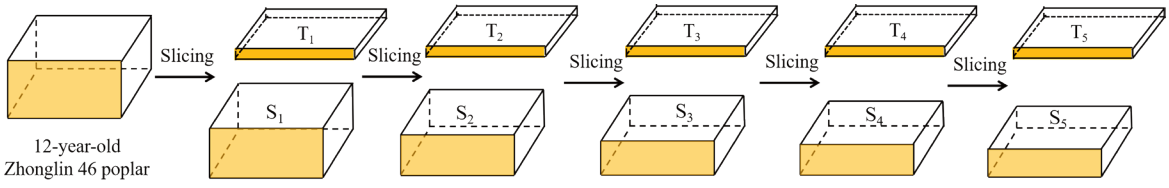

Figure 1 Flow chart of layering of heat-treated poplar board
Slika 1. Dijagram toka raslojavanja ploče od toplinski modificirane topolovine

for chemical analysis. The Fourier transform infrared spectra were collected in a Tensor-II (Bruck, Germany), the wave number interval was 400-4000 cm^{-1}, and the resolution was 4 cm^{-1}. Each sample was scanned and analyzed 32 times.

2.4 Data analysis and modeling of surface properties
2.4. Analiza podataka i modeliranje površinskih svojstava

For the surface color and hardness, multiple comparisons were first subjected to analysis of variance (ANOVA), and significant differences between the average value of untreated and heat-treated samples were determined using Duncan's multiple range test. Besides, differences between S_0~S_5 test surfaces of the wood treated under the same treatment condition were also determined, and then the Curve 3D software was used to establish the prediction models of ΔL^*, ΔE^*, H_R, and *HD* values.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Color and hardness of different test surfaces on heat-treated poplar wood
3.1. Boja i tvrdoća različitih ispitnih površina toplinski modificirane topolovine

The main purpose of heat treatment is to change the color of the wood, improve the single and light color of the fast-growing wood surface, and therefore enhance the decorative properties (Lei *et al*., 2021). The L^*, a^*, and b^* values of the test surfaces (S_0-S_5) at the position of different thicknesses on 160-220 °C heat-treated poplar wood are shown in Figure 2.

From Figure 2, it can be seen that the lightness value L^* of the heat-treated wood tends to decline with the increase of heat treatment temperature and duration, while the red-green value a^* and yellow-blue value b^* increase first, and then decline. The changing trend of chromatic parameters is consistent with the

Table 1 ANOVA analysis of color and hardness of different test layers of heat-treated poplar wood
Tablica 1. ANOVA analiza boje i tvrdoće različitih ispitnih slojeva toplinski modificirane topolovine

Source of difference *Izvor razlike*		**Sum of squares of deviations (SS)** *Zbroj kvadrata odstupanja (SS)*	**Degree of freedom (*df*)** *Stupanj slobode (df)*	**Mean square (*MS*)** *Srednji kvadrat (MS)*	***F*-value** *F-vrijednost*	***P*-value** *P-vrijednost*
ΔL^*	HT temperature *HT temperatura*	60035.16	2	30017.58	2814.75	1.40E-131
	HT duration / *HT trajanje*	603.13	1	603.13	56.56	2.95E-12
	Test layer location *lokacija ispitnog sloja*	1179.14	5	235.83	22.11	4.66E-17
	Deviation / *odstupanje*	1823.61	171	10.66		
	Summation / *zbroj*	173782.04	180			
ΔE^*	HT temperature *HT temperatura*	57552.64	2	28776.32	2934.01	4.45E-133
	HT duration / *HT trajanje*	601.92	1	601.92	61.37	4.78E-13
	Test layer location *lokacija ispitnog sloja*	1038.93	5	207.79	21.19	1.86E-16
	Deviation / *odstupanje*	1677.14	171	9.81		
	Summation / *zbroj*	188136.76	180			
H_R	HT temperature *HT temperatura*	1.17	2.00	0.59	36.53	8.13E-15
	HT duration / *HT trajanje*	0.67	1.00	0.67	41.70	4.70E-10
	Test layer location *lokacija ispitnog sloja*	7.38	5.00	1.48	92.19	5.02E-57
	Deviation / *odstupanje*	4.47	279.00	0.02		
	Summation / *zbroj*	241.60	288.00			
HD	HT temperature *HT temperatura*	79.32	2.00	39.66	11.88	1.12E-05
	HT duration / *HT trajanje*	56.45	1.00	56.45	16.91	5.15E-05
	Test layer location *lokacija ispitnog sloja*	932.93	5.00	186.59	55.91	3.97E-40
	Deviation / *odstupanje*	931.09	279.00	3.34		
	Summation / *zbroj*	638614.85	288.00			

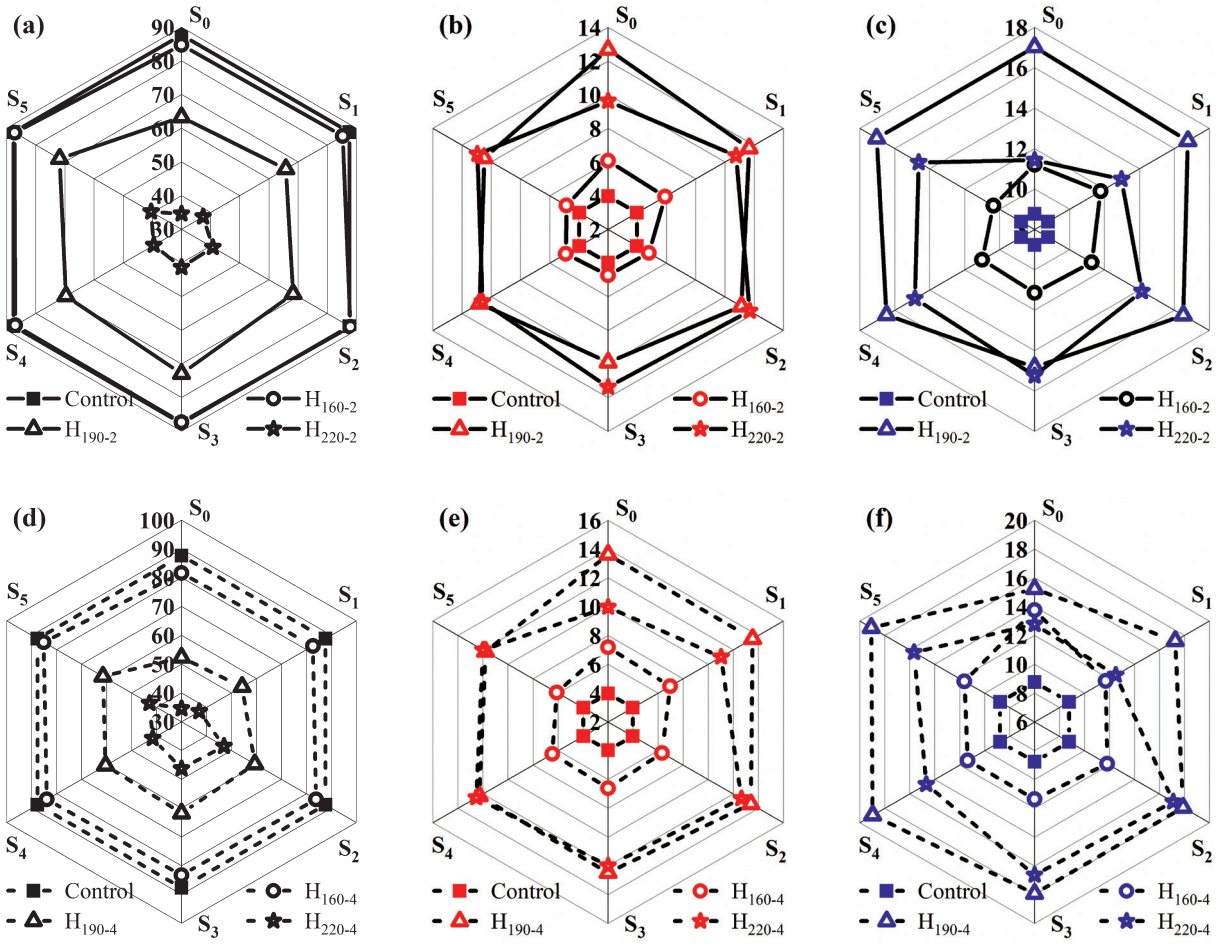

Figure 2 Chromatic parameters of different test surfaces on heat-treated poplar wood
Slika 2. Kromatski parametri različitih ispitnih površina toplinski modificirane topolovine

previous research (Hill, 2006; Chu *et al*., 2016; Gao *et al*., 2019). Interestingly, for all the heat-treated wood, the L^* value of the test surface increased as the position changed from S_0 to S_5, and this increment of the L^* value varies with the HT temperature and duration. For 160 °C and 190 °C heat-treated wood, the a^* value decreased as the position changed from S_0 to S_5, the greatest decreasing amplitude being 22.2 % in the $H_{160\text{-}2}$. The b^* value increased from S_0 to S_5 when the heat treatment temperature was 190 °C and 220 °C; the b^* value of the $H_{190\text{-}2}$ on S_0 surface was 28 % higher than that of the S_5 surface. It could prove that the heat-treated wood was not uniform regarding surface color in the direction of thickness, and the properties of real processing surface after cutting or sanding needed to be further studied. The lightness difference ΔL^* between the S_0 and S_5 of heat-treated wood increased with the HT temperature, in which the lightness of the S_5 surface of the $H_{220\text{-}4}$ increased by 24.1 % compared with that of the S_0 surface.

It could be clearer that the surface color and hardness changed as the position of different thickness ranged from S_0 to S_5, based on the lightness difference ΔL^* and the color difference ΔE^*. Two different methods, that is the surface pressing ball hardness and Shore hardness, were used to characterize the hardness of the test layers of heat-treated poplar wood at different positions, and the results are shown in Figure 3. ANOVA analysis of the chromatic parameters and surface hardness are shown in Table 1.

Figure 3 and Table 1 show that the HT temperature, duration, and test surface layer location all have significant effects on the surface hardness of the test layers. The change of the test surface position has a more significant effect on the surface hardness of the heat-treated wood, proving that the modification intensity of the heat-treated wood was different in the thickness direction. H_R and HD values of heat-treated poplar board decreased with increasing HT temperature, while it increased only slightly with increasing HT duration. As predicted, the H_R and HD values of the S_0 on the heat-treated poplar wood decreased significantly with increasing HT temperature in all groups. Interestingly, the other test surfaces S_1-S_5 also decreased but to a relatively lesser extent. There is a certain thickness of brittleness layer on the surface of the heat-treated wood, and its degree of thermal degradation and brittleness is higher than that of the internal material. The overall increasing trend of the surface hardness of the heat-treated wood from the surface to the core layer

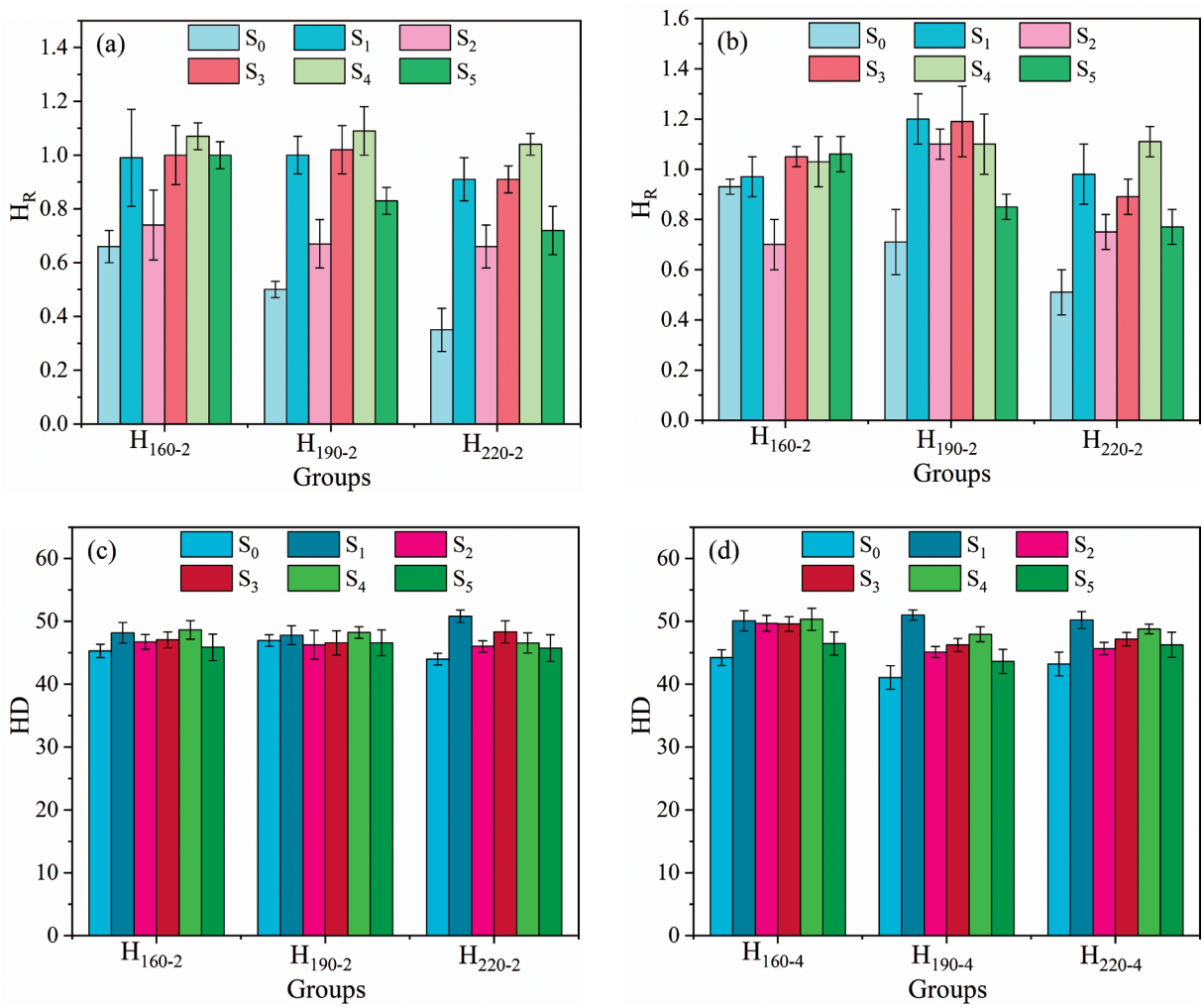

Figure 3 Surface pressure ball and Shore hardness of test layers in different positions of heat-treated poplar board
Slika 3. Tvrdoća površine izmjerena utiskivanjem kuglice i tvrdoća po Shroreu ispitnih slojeva na različitim mjestima toplinski modificirane topolovine

exhibited an "M" shape, and the difference between the surface and core layers increases with the increase of the HT temperature.

The ΔL^*, ΔE^*, H_R, and *HD* values of the test surfaces on S_0 to S_5 of the same experimental group were analyzed by SPSS. The S-N-K (Student Newman Keuls) method was selected for pairwise comparison, and the obtained data were marked with letters, as shown in Table 3. The HT temperature, duration, and test surface location all have significant effects on the color change of the heat-treated poplar boards, with the effect of HT temperature being the most significant. It is obvious that the ΔE^* values of the test surfaces at the same position gradually increase with the increase of the HT temperature. The extended HT duration increased the ΔE^* value, and the effect was less compared to the HT temperature, which is consistent with the findings of the ANOVA in Table 1.

The color change of heat-treated wood was closely related to treatment factors like treatment time, temperature, agent of treatment (Zhan *et al*., 2022). In addition, the effect of HT duration on wood color gradually decreases at higher HT temperatures. For example, the ΔE^* of $H_{160\text{-}2}$, $H_{160\text{-}4}$ was 4.46 and 8.58, while the ΔE^* of $H_{220\text{-}2}$, $H_{220\text{-}4}$ was 53.46 and 53.62, indicating that the color of poplar wood no longer changed significantly when the HT duration exceeded 2 h under the HT temperature of 220 °C. The ΔL^* and ΔE^* values, whose test surfaces of the wood board were treated by the same HT temperature and duration but located in a different position in the direction of thickness, were also significantly different. Except for $H_{160\text{-}2}$, there were significant differences regarding ΔL^* and ΔE^* values between the S_0 and S_1-S_5 surfaces of the heat-treated poplar boards at the 0.05 level. For $H_{160\text{-}2}$, the color change of S_0 and S_1 were statistically significantly different from that of S_2~S_5 surfaces.

Based on the result in Table 2, it could be concluded that the depth of the Shore hardness tester probe into the wood is about 1.3 mm, which is quite close to the depth of 1 mm pressure ball. The changing trend of H_R is basically consistent with that of *HD*. The H_R of the heat-treated wood S_0 and S_5 test surfaces showed significant differences at different HT conditions. As

Table 2 Color change and hardness of test surfaces at different positions of heat-treated poplar
Tablica 2. Promjena boje i tvrdoće ispitnih površina na različitim mjestima toplinski modificirane topolovine

Groups		ΔL^*	ΔE^*	H_R	HD	Groups		ΔL^*	ΔE^*	H_R	HD
H_{160-2}	S_0	-2.97^a	4.46^a	0.66^b	45.3^b	H_{160-4}	S_0	-6.05^a	8.58^a	0.93^b	46.96^a
	S_1	-2.32^a	4.34^a	0.99^a	48.18^a		S_1	-5.02^b	6.55^b	0.97^{ab}	47.80^a
	S_2	0.27^b	2.67^b	0.74^b	46.75^{ab}		S_2	-3.77^c	5.41^{cd}	0.70^c	46.28^a
	S_3	-0.32^b	2.57^b	1.00^a	47.05^{ab}		S_3	-4.38^{bc}	5.74^{bc}	1.05^a	46.59^a
	S_4	-0.60^b	2.61^b	1.07^a	48.65^a		S_4	-3.72^c	5.18^{cd}	1.03^a	48.25^a
	S_5	-0.41^b	1.94^b	1.00^a	45.88^b		S_5	-2.45^d	4.35^d	1.06^a	46.59^a
H_{190-2}	S_0	-24.37^a	27.20^a	0.50^d	43.99^d	H_{190-4}	S_0	-35.36^a	37.23^a	0.71^c	44.24^c
	S_1	-21.86^b	24.52^b	1.00^a	50.83^a		S_1	-33.39^b	35.76^a	1.20^a	50.09^a
	S_2	-19.33^c	22.02^c	0.67^c	46.03^c		S_2	-28.27^c	31.18^b	1.10^a	49.69^a
	S_3	-14.74^e	17.00^e	1.02^a	48.31^b		S_3	-25.89^d	28.76^c	1.19^a	49.60^a
	S_4	-17.99^d	20.73^c	1.09^a	46.56^c		S_4	-27.25^{cd}	30.27^{bc}	1.10^a	50.33^a
	S_5	-15.82^e	19.01^d	0.83^b	45.75^c		S_5	-26.18^{cd}	29.21^{bc}	0.85^b	46.46^b
H_{220-2}	S_0	-53.08^a	53.46^a	0.35^d	41.08^e	H_{220-4}	S_0	-53.13^a	53.6^{2}a	0.51^e	43.21^c
	S_1	-50.24^b	50.87^b	0.91^b	51.01^a		S_1	-50.52^b	51.15^b	0.98^b	50.23^a
	S_2	-46.88^c	47.84^c	0.66^c	45.11^c		S_2	-40.62^e	42.37^e	0.75^d	45.69^b
	S_3	-46.32^c	47.37^c	0.91^b	46.25^c		S_3	-41.37^e	42.88^e	0.89^c	47.19^b
	S_4	-48.14^c	48.98^c	1.04^a	47.96^b		S_4	-46.08^c	47.25^c	1.11^a	48.80^a
	S_5	-47.25^c	48.12^c	0.72^c	43.64^d		S_5	-44.82^d	46.05^d	0.77^d	46.28^b

Different superscript letters indicate significant differences at 0.05 statistical level.
Različita slova u eksponentu označavaju statistički značajne razlike pri razini od 0,05.

displayed in Table 2, the H_R and *HD* value of the heat-treated poplar wood has several levels with significant differences between the different positions of S_0~S_5 surfaces (except for H_{160-4}). When the HT temperature was relatively low, there were only two significantly different levels in the H_{160-2}, and differences between S_3-S_5 test surfaces were insignificant. As the HT temperature increased, the difference between the S_1 and core layers increased. For instance, the H_R value of the S_5 of H_{220-2} was 105.71 % higher than that of S_0, and four in five test surfaces were significantly different.

3.2 Chemical component change of different test surface layers
3.2. Kemijske promjene spojeva u različitim slojevima ispitne površine

The FT-IR spectrum of the changes in chemical functional groups of poplar wood before and after heat treatment are shown in Figure 4. The experiments in the spectral range of 4000-400 cm^{-1} mainly analyzed the changes of characteristic peaks in the range of 1800-1750 cm^{-1}. The shear vibration peak of cellulose at 1424 cm^{-1} changed to a lesser extent after heat treatment, so the peak here was selected for normalization of the spectrum (Wentzel *et al.,* 2019), and the ratios of the peaks are shown in Table 3.

The changes in the functional groups on the surface of the heat treatment were analyzed by combining Figure 4 and Table 3. The characteristic peak at 1735 cm^{-1} is the hemicellulose acetyl non-conjugated carbonyl group (Li *et al.,* 2009), and the intensity of this peak decreases with the increasing heat treatment temperature. This phenomenon is mainly caused by hemicellulose degradation, and the higher the heat treatment temperature, the more intense degradation.

The characteristic peak at 1163 cm^{-1} is attributed to the C-O-C stretching vibration of cellulose and hemicellulose. Moreover, the characteristic peak near 1058 cm^{-1} is the C-O stretching vibration of cellulose and hemicellulose, and the intensity of this peak increases during low temperature heat treatment, indicating the formation of alcoholic and aldehyde pyrolysis products during heat treatment (Gao, 2019). The characteristic peak near 1058 cm^{-1} reflects the C-O condensation vibration of cellulose and hemicellulose, and the intensity of this peak increases at low heat treatment temperatures, indicating the generation of alcoholic aldehydes pyrolysis products during heat treatment. However, its intensity decreases with increasing temperature, suggesting that the condensation reaction of alcohols and aldehydes occurs.

The carbonyl stretching vibration peak at 1650 cm^{-1} is attributed to lignin and is mainly present on the propyl-branched chain. A spectral peak at 1603 cm^{-1} corresponds to the stretching vibration peak of the benzene ring backbone of lignin conjugated to C=O, and 1264 cm^{-1} corresponds to the absorption peak of the C=O stretching vibration of the G ring and acyloxy bond in lignin (Gao *et al.,* 2020). The intensity of the

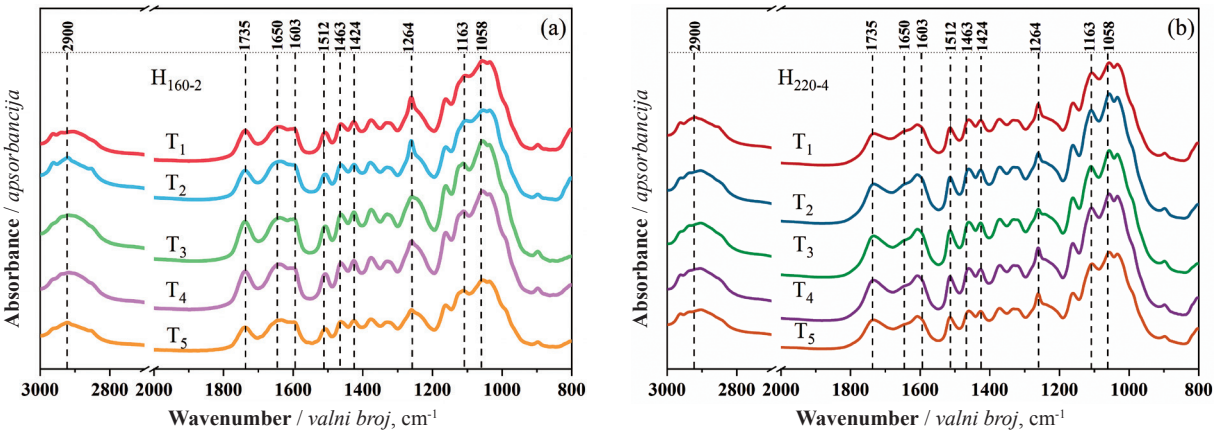

Figure 4 Infrared spectra of different surface layers of heat-treated poplar wood
Slika 4. Infracrveni spektri različitih površinskih slojeva toplinski modificirane topolovine

Table 3 Strength ratios of peaks normalized at 1424 cm^{-1}
Tablica 3. Omjeri intenziteta vrhova normalizirani na 1424 cm^{-1}

Groups		I1735	I1603	I1512	I1463	I1264	I1163	I1058
Control		0.865	0.801	0.737	0.974	1.840	0.904	2.560
H_{160-2}	T_1	0.782	0.824	0.725	0.944	1.620	1.577	2.542
	T_2	0.827	0.992	0.717	0.992	1.677	1.496	2.543
	T_3	0.808	0.859	0.712	0.955	1.311	1.537	2.446
	T_4	0.784	0.852	0.733	0.955	1.403	1.580	2.426
	T_5	0.780	0.954	0.721	0.963	1.358	1.505	2.339
H_{190-2}	T_1	0.773	0.864	0.733	0.962	1.553	1.538	2.659
	T_2	0.777	0.921	0.748	0.971	1.295	1.518	2.432
	T_3	0.787	0.806	0.755	0.968	1.387	1.535	2.626
	T_4	0.795	0.888	0.739	0.975	1.267	1.534	2.484
	T_5	0.855	0.796	0.763	0.980	1.434	1.546	2.579
H_{220-2}	T_1	0.709	0.847	0.810	0.985	1.518	1.358	2.234
	T_2	0.742	0.856	0.825	1.009	1.336	1.507	2.686
	T_3	0.770	0.867	0.819	1.000	1.566	1.588	2.942
	T_4	0.788	0.872	0.847	1.010	1.355	1.498	2.507
	T_5	0.819	0.896	0.850	1.016	1.383	1.466	2.425
H_{160-4}	T_1	0.816	0.810	0.741	0.966	1.425	1.598	2.534
	T_2	0.868	0.755	0.759	0.972	1.637	1.519	2.594
	T_3	0.801	0.768	0.755	0.960	1.470	1.536	2.377
	T_4	0.830	0.785	0.756	0.970	1.719	1.541	2.733
	T_5	0.741	0.856	0.759	0.966	1.345	1.517	2.236
H_{190-4}	T_1	0.846	0.787	0.757	0.978	1.375	1.551	2.603
	T_2	0.840	1.000	0.769	0.982	1.296	1.515	2.444
	T_3	0.852	1.000	0.723	0.992	1.287	1.525	2.451
	T_4	0.861	0.933	0.733	0.976	1.315	1.576	2.533
	T_5	0.864	0.950	0.721	0.979	1.443	1.600	2.721
H_{220-4}	T_1	0.707	0.900	0.833	1.013	1.360	1.387	2.280
	T_2	0.744	0.911	0.867	1.017	1.311	1.461	2.411
	T_3	0.766	0.886	0.864	1.011	1.250	1.457	2.310
	T_4	0.789	0.871	0.860	1.018	1.421	1.503	2.468
	T_5	0.771	0.866	0.843	1.000	1.465	1.449	2.543

peaks at 1650 cm^{-1} and 1264 cm^{-1} decreased with the increasing heat treatment temperature, while the intensity of the peak at 1603 cm^{-1} increased, indicating that the relative lignin content increased, while the branched-chain breakage occurred by thermal degradation and possibly cross-linked condensation reaction. The benzene ring carbon skeleton vibration peak of lignin at 1512 cm^{-1} and the C-H bending vibration peak in lignin and carbohydrates at 1463 cm^{-1} were enhanced with increasing heat treatment temperature and duration, which may be caused by the increase in relative lignin content due to hemicellulose degradation (Zang *et al.,* 2018).

As can be seen in Table 3, the characteristic peak at 1735 cm^{-1} showed a small difference between the surface and core layers at 160 °C treatment. With the increasing heat treatment temperature, the intensity of this peak showed an increasing trend from the surface layer to the core layer, and the characteristic peak at $H_{220\text{-}2}$ was 0.709 in the surface layer, which was 13.43 % lower than that in the core layer. Therefore, hemicellulose degradation was less at 160 °C treatment. The difference in the degree of hemicellulose degradation between the surface and core layers increased with the increase in temperature, while it decreased with increasing duration. At 160 °C treatment, the intensity of the characteristic peak at 1163 cm^{-1} in the surface layer was greater than that in the core layer. As the heat treatment temperature increased, the intensity of this absorption peak tended to enhance from the surface layer to the core layer, probably since the surface hydroxyl groups of cellulose and hemicellulose in the surface layer formed ether bonds earlier than those in the core layer at lower temperatures. However, it is also the ether bond in the surface layer that breaks first when the temperature increases, and the extension of the duration has minor effect on this peak. Only at the temperature of 220 °C, the absorption peak intensity of the core layer at 1058 cm^{-1} was significantly stronger than that of the surface layer. With the increase of heat treatment temperature, the hemicellulose and cellulose in the surface layer were the first to undergo ring-opening reactions to form alcohols and aldehydes. Then, with the further increase of temperature, the alcohols and aldehydes in the surface layer underwent condensation reactions and the core layer was less reactive than the surface layer, and the difference increased with the extension of the duration.

Under different heat treatment conditions, the variation of absorption peak intensity at 1512 cm^{-1} and 1463 cm^{-1} between the surface and core layers was light, indicating that the heat treatment had small effect on the lignin benzene ring skeleton. The intensity of the characteristic peak at 1264 cm^{-1} showed a decreasing trend from the surface layer to the core layer after 2 h duration, reflecting that the relative lignin content in the surface layer of the heat-treated wood was greater than that in the core layer; however, the intensity of the characteristic peak at 1264 cm^{-1} in the surface layer was gradually greater than that in the core layer with the extension of the duration, suggesting that the pyrolysis of lignin in the surface layer was greater than that in the core layer.

3.3 Prediction of surface properties on different test surface layers

3.3. Predviđanje površinskih svojstava na različitim ispitnim površinskim slojevima

Surface color and hardness of S_0 surface on the heat-treated wood are significantly different from those of the S_1~S_5 core layer surfaces, and the H_R of the S_0 surface is significantly different from all other test surfaces. Therefore, the S_0~S_5 test surfaces have a unique property variation that warrants a separate study. As the effect of HT temperature on the color of heat-treated wood is relatively small, this study mainly investigates the influence of HT temperature of the test surfaces at different positions. Table Curve 3D software was used to establish the prediction models of ΔL^* and ΔE^* values. The fitting surfaces are shown in Figure 5.

Table Curve 3D software was used to establish the prediction models of HT temperature (T) and test surfaces (F) with lightness change (ΔL^*) and color changes (ΔE^*). The fitting surfaces are shown in Figure 5.

The prediction models for ΔL^* and ΔE^* of the heat-treated poplar wood are:

$\Delta L^* = 160.69 - 1.09 * T - 43.92 * F - 1.15 \times 10^{-4} * T^2 + 1.43 * F^2 + 0.44 * T * F + 2.90 \times 10^{-6} * T^3 + 0.05 * F^3 - 0.01 * T * F^2 - 9.72 \times 10^{-4} * T^2 * F$ (R^2=0.966);

$\Delta E^* = 199.51 - 29876.22/T + 13.35 * F - 1308772.50/T^2 + 2.80 * F^2 - (8820.77 * F)/T + 1.84 \times 10^{-8}/T^3 - 0.04 * F^3 - (386.87 * F^2)/T + (1026586.80 * F)/T^2$ (R^2=0.966).

The model fits well and the empirical prediction model could be used to predict the changes in the surface color of poplar boards at different positions under different HT conditions.

This color difference on heat-treated wood in the direction of thickness could be explained by the diversity of chemical components degradation intensity, as well as extractives migration from the core layer to the surface layer. Shi and Bao (2021) found that the extractives of heat-treated wood migrate under hydrothermal conditions, which may cause differences in the color of different layers. Under the HT conditions, polysaccharides, especially the hemicellulose, degrade and, numerous hydroxyl groups are oxidized to carboxyl groups and carbonyl groups. As the HT proceeds, these degradation products continue to react and generate furfural and phenolic compounds with color-emitting or color-assisting groups. At the same time, lignin undergoes condensation and oxidation reactions with

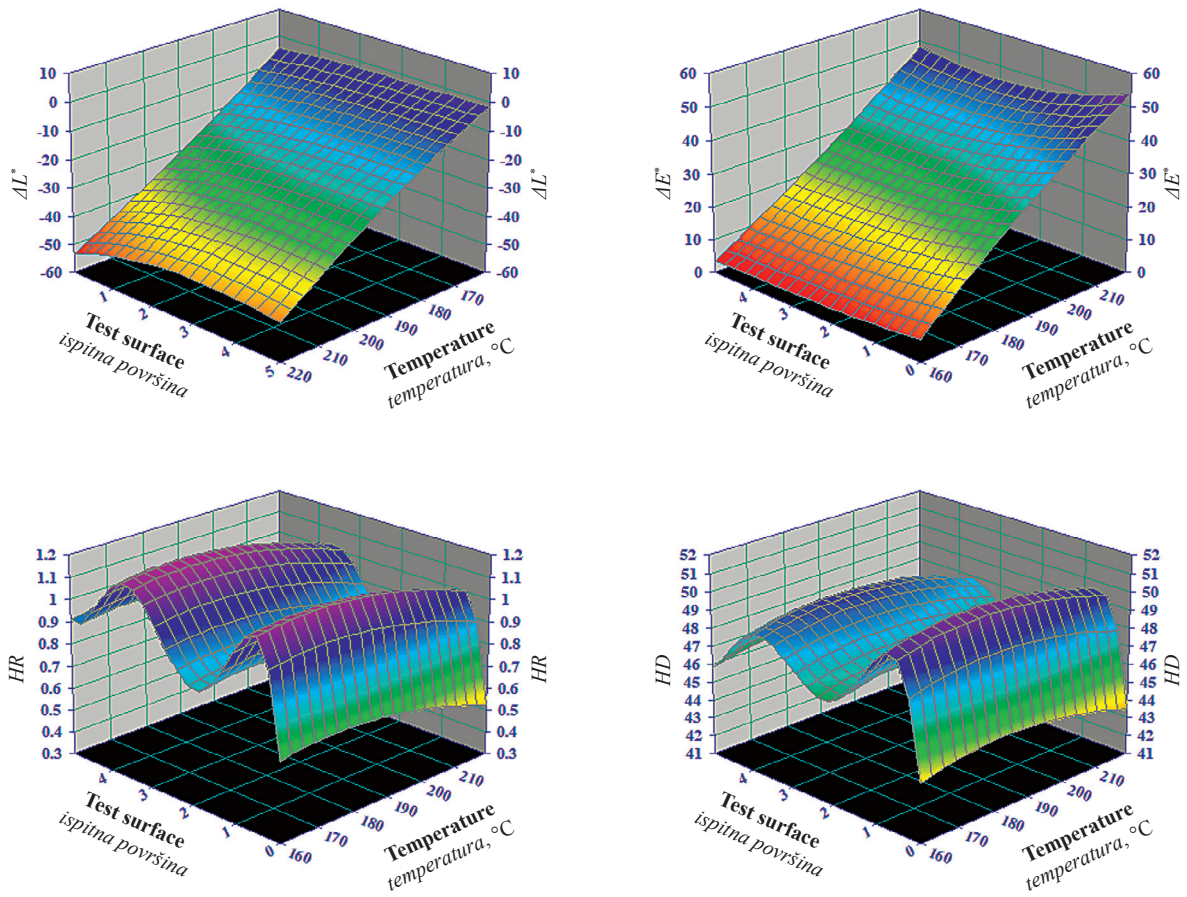

Figure 5 Fitting surface of ΔL^*, ΔE^*, H_R, HD of heat-treated poplar board
Slika 5. Fitanje površine ΔL^*, ΔE^*, H_R, HD za ploče od toplinski modificirane topolovine

degradation products under high temperature conditions, generating new color-emitting substances that change the color of heat-treated wood (Cao *et al.,* 2018; Konnerth *et al.,* 2010; Kamperidou, 2012).

Table Curve 3D software was used to establish the prediction models of HT temperature (T) and test surfaces (F) with the hardness of the heat-treated poplar board in terms of ball hardness (H_R) and Shore hardness (HD). The fitting surfaces are shown in Figure 5.

The prediction models for H_R and HD of the heat-treated poplar wood are:

H_R=-1.30-8.13*ln$T$+2.30*(ln$T$)^2+0.08*(ln$T$)^3-0.04*(ln$T$)^4+1.99*F-2.65*F^2+1.31*F^3-0.27*F^4+0.02*F^5 (R^2=0.729)

HD=-1015.94+407.34*ln$T$-39.11*(ln$T$)^2+21.68*F-25.39*F^2+11.24*F^3-2.11*F^4+0.14*F^5 (R^2=0.704)

The equations fit well, so the empirical prediction model can be used to predict the variation of hardness at different locations of poplar wood boards under different heat treatment conditions. Besides, the surface hardness of heat-treated wood is influenced by multiple factors. Konnerth *et al*. (2010) used hemicellulose for targeted hemicellulose removal and found that wood hardness is most sensitive to changes in cell wall hemicellulose content, so the reduction in wood hardness after heat treatment is mainly influenced by hemicellulose degradation. The difference in hardness between the surface and core layer increases with increasing temperature, probably because the hemicellulose, a cell wall filling material, decreased to a different extent. Altgen *et al*. (2018) found by infrared spectroscopy that wood undergoes cross-linking reactions in the cell matrix during heat treatment, and that differences in the degree of cross-linking between the surface layer and core layer may also contribute to their differences.

4 CONCLUSIONS
4. ZAKLJUČAK

The surface color and hardness of the heat-treated wood were not uniform from the surface layer to the core layer, and there were several levels with significant differences as the temperature increased. The surface color and hardness properties between S_0 and S_1~S_5 test surfaces were significantly different under different heat treatment conditions. The color difference of heat-treated poplar wood tended to decrease from the S_0 surface to the core layers, from 4.46 to 1.94 for $H_{160\text{-}2}$ and from 53.46 to 48.12 for $H_{220\text{-}2}$; the surface

hardness shows an increasing trend. $H_{160\text{-}2}$ increases from 0.66 to 1.0, an increase of 34 %. The hardness of the $H_{220\text{-}2}$ core surface layer increases by 105.71 % compared to the S_0 surface.

The degradation of cell wall components in the surface layer of heat-treated poplar wood was greater than that in the core layers. FT-IR showed that the thermal degradation of hemicellulose and lignin of the T_1 surface layer was greater than that in the core layers. The difference of the test surfaces could be predicted as it related to the location and heat treatment conditions. Table Curve 3D software was used to establish an accurate prediction model of the trend of surface color, hardness, and other properties at different locations of the heat-treated wood and different heat treatment temperatures.

In conclusion, this paper displayed the property difference of test surface from outside to core layers of the heat-treated wood and proved that the thermal modification intensity of the heat-treated poplar wood was different in the direction of thickness. Accurate models were established, which could be used to predict the surface color and hardness on each test surface of the heat-treated poplar wood in the direction of thickness.

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