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Influence of Thermal Modification on Surface Properties and Chemical Composition of Beech Wood (*Fagus sylvatica* L.)

Utjecaj toplinske modifikacije na površinska svojstva i kemijski sastav bukovine (*Fagus sylvatica* L.)

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ABSTRACT • Thermal modification leads to the degradation of the compounds in wood, thereby changing the chemical composition of wood, which can affect the further wood finishing. In order to determine the effect of thermal modification on wood finishing, it is important to know the properties of its surface. In this research, the influence of thermal modification on pH, surface free energy, contact angle of coating and chemical composition of beech wood was studied. The results of this study show that acidity and water contact angle on beech wood was higher and polar component of surface free energy was lower after thermal modification. Furthermore, contact angle of waterborne coating on beech wood was increased by increasing the modification temperature and the content of extractives soluble in hot water and in organic solvent was increased after thermal modification of beech wood.

Key words: thermal modification, contact angle, surface free energy, wood chemical composition

SAŽETAK • Toplinska modifikacija uzrokuje razgradnju spojeva u drvu, čime se mijenja kemijski sastav drva što može utjecati na njegovu površinsku obradu. Kako bi se utvrdio učinak toplinske modifikacije na površinsku obradu drva, važno je znati svojstva njegove površine. U ovom je radu istraživana utjecaj toplinske modifikacije na pH drva, njegovu slobodnu površinsku energiju, kvašenje premaza i na kemijski sastav bukovine. Rezultati istraživanja pokazuju da je toplinska modifikacija povećala kiselost drva i kut kvašenja vode na bukovini i smanjila polarne komponente slobodne površinske energije. Nadalje, kut kvašenja vodenog premaza na bukovini povećao se s povećanjem temperature modifikacije, a sadržaj ekstraktiva topljivih u vrućoj vodi i organskom otapalu povećao se nakon toplinske modifikacije bukovine.

Ključne riječi: toplinska modifikacija, kut kvašenja, slobodna površinska energija, kemijski sastav drva

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1 INTRODUCTION

1. UVOD

Thermally modified wood, also known as the heat treated wood, has large application outdoors due to reduced hygroscopicity, improved dimensional stability, improved biological durability and attractive appearance, especially for facades, decking and garden furniture. Despite some improved properties compared to unmodified wood, thermally modified wood is still susceptible to surface degradation by weathering when exposed to outdoor conditions. Therefore, it is necessary to protect the surface of the thermally modified wood to prevent discolouration and formation of surface cracks (Militz, 2002; Miklečić *et al.*, 2010). In order to determine the effect of thermal modification on wood finishing, it is important to know the properties of surface of thermally modified wood such as pH (Ljuljka *et al.*, 1996), wettability (Pétrissans *et al.*, 2003) and surface free energy (De Meijer *et al.*, 2000). In previous research, Bonstra *et al.* (2007) reported that high temperatures lead to the increase of wood acidity. Moreover, according to research of Gérardin *et al.* (2007) and Petrič *et al.* (2012), thermal modification reduces the surface free energy of wood. However, there is no information in literature on the influence of thermal modification on contact angle of waterborne coatings. Furthermore, the change of chemical composition of wood after thermal modification can disrupt the interaction between coating and wood surface. This applies particularly to extractives, which have influence on coating adhesion strength and wettability (Ghofrani *et al.*, 2015).

The aim of this study was to analyse the influence of thermal modification on the surface pH, free energy and contact angle of waterborne coating of beech wood. These characteristics of wood surface could affect the interaction between wood and coating. Furthermore, we wanted to analyse the influence of thermal modification on the change of chemical composition of wood.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

Radial-textured samples of unmodified and thermally modified beech wood (*Fagus sylvatica* L.) with no visible defects were used in this study. Beech wood is the most widely distributed three species in Croatia and it is often modified to open up new fields of application. The samples had 4-5 annual rings per centimetre, and the width of annual ring was 2-2.5 mm with 30-48 % share of latewood. All wood samples were conditioned to 8.4 % moisture content at $(23 \pm 2) ^\circ\text{C}$ and $(50 \pm 5) \%$ relative humidity (RH).

Eight wood samples with dimensions of 1020 mm x 150 mm x 28 mm ($L \times R \times T$) have been modified using high temperature and vapour in commercial heat treatment chamber in the industrial process of modification without the use of chemicals. Two temperatures were used for the modification: $190 ^\circ\text{C}$ - lighter samples

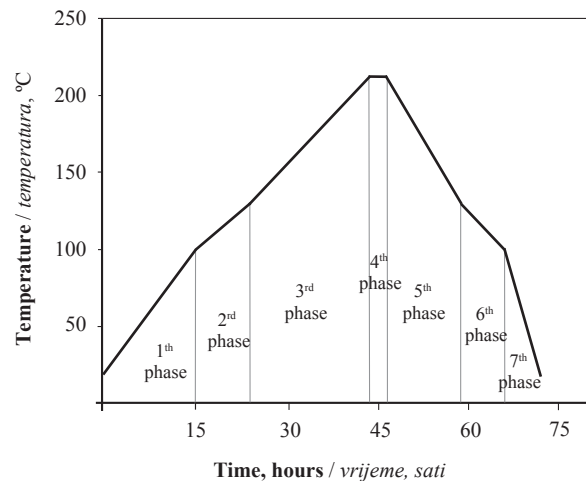


Figure 1 Phases of industrial thermal modification of wood samples

Slika 1. Faze toplinske modifikacije uzoraka drva u industrijskom procesu

(S) and $212 ^\circ\text{C}$ - darker samples (T), as used in ThermooWood process (Finish Thermowood Association). The process of thermal modification lasted 74 hours (Figure 1) and was conducted in seven phases.

2.1 Determination of wood pH

2.1. Određivanje pH drva

For the determination of wood pH, a water extract from the wood was prepared according to the methods of Pedieu *et al.* (2008). For each type of tested wood, a sample of 25 g was milled and dried at $(103 \pm 2) ^\circ\text{C}$ to the constant weight, and then conditioned in a desiccator to $(23 \pm 2) ^\circ\text{C}$. Following conditioning, the sample was added into 250 mL of boiling deionised water and boiled for 20 min in the Erlenmeyer flask with a reflux condenser. The solution was then filtered and cooled to $23 ^\circ\text{C}$. The pH of the filtered sample was measured with pH meter *Mettler Toledo - SG7*. Three measurements were made for each type of wood sample.

2.2 Determination of wood surface free energy

2.2. Određivanje površinske energije drva

The surface free energy of unmodified and thermally modified wood samples was calculated from the average contact angles using the Owens Wendt Rabel and Kaelble (OWRK) method (Wu, 1971) and using the Lifshitz-van der Waals - Acide Base (LW-AB) method (Good, 1992). The contact angle used for calculating the surface free energy was measured by the Wilhelmy method. According to that method, a wood sample is immersed in a liquid of known surface tension to a certain depth and the force acting on a vertically immersed plate is measured (Hakkou *et al.*, 2005). In this study, deionised water and formamide as polar liquids and diiodomethane as nonpolar liquid were used (Table 1).

For the determination of surface free energy, four unmodified (N) and thermally modified wood samples were prepared at $190 ^\circ\text{C}$ (S) and $212 ^\circ\text{C}$ (T) with dimensions of 100 mm x 30 mm x 2 mm. Each sample was then sawn up into three samples with dimensions of 20

Table 1 The values of surface tension and surface tension components of water, formamide and diiodomethane presented in mJ/m²

Tablica 1. Vrijednosti površinske napetosti i komponenti površinske napetosti vode, formamida i diiodometana prikazane u mJ/m²

Liquid <i>Tekućina</i>	γ_L	LW-AB method				OWRK method	
		γ_i^{LW}	γ_i^+	γ_i^-	γ_i^{AB}	γ_L^d	γ_L^p
Deionised water / <i>deionizirana voda</i>	72.8	21.8	25.5	25.5	51.0	22.0	50.2
Formamide / <i>formamid</i>	58.0	39.0	2.3	39.6	19.0	32.3	26.0
Diiodometane / <i>dijodometan</i>	50.8	50.8	0.00	0.00	0.00	50.8	0.00

Table 2 Composition of waterborne polyacrylate coating

Tablica 2. Sastav vodenoga poliakrilatnog premaza

Name of component <i>Naziv sastavnice</i>	Type of component <i>Vrsta sastavnice</i>	Content, % <i>Sadržaj, %</i>
Binder / <i>vezivo</i>	Esters of acrylic and metacrylic acid and styrene <i>estri akrilne i metakrilne kiseline i stiren</i>	70.00
Solvent / <i>otapalo</i>	Deionised water / <i>deionizirana voda</i>	19.00
Coalescent / <i>koalescent</i>	Isopropyl alcohol, butyl glycol / <i>izopropilni alkohol, glikol butil</i>	0.80
Rheological additive / <i>reološki aditiv</i>	Nonionic / <i>neionski</i>	0.40
Defoaming agent / <i>sredstvo protiv pjenjenja</i>	Silicone type / <i>tip silikona</i>	0.30
Wetting agent / <i>Sredstvo za vlaženje</i>	Silicone type / <i>tip silikona</i>	0.15
Wax / <i>vosak</i>	Paraffin and high-density polyethylene <i>parafin i polietilen velike gustoće</i>	8.20
Other components / <i>ostale sastavnice</i>	No dana / <i>nema podataka</i>	0.85

mm x 30 mm x 2 mm (L x R x T) and sanded with 80, 120 and 180 grid paper. The cross section of the prepared samples was immersed in nitrocellulose lacquer (2 mm) to exclude the absorption of test liquids, and then the samples were conditioned for 24 hours at (23 ± 2) °C and (50 ± 5) % RH. The first sample was used to determine the advancing contact angle of deionised water, the second of formamide (99+ %, J. T. Baker, USA) and the third of diiodomethane (99+ % Across Organics Belgium). The measurements were carried out at (23 ± 2) °C and (50 ± 5) % RH with the tensiometer (Krüss K100) by immersing the wood samples in a radial direction with the following parameters: speed before touching the liquid 6 mm/min, touch sensitivity 0.01 g, immersion velocity 12 m/min, immersion depth before measuring 2 mm, maximum immersion depth 7 mm.

2.3 Determination of contact angle of waterborne coating

2.3. Određivanje kuta kvašenja vodenog premaza

The contact angle was measured by the sessile drop method using a *Krüss Drop Shape Analysis System - DSA100*. Two unmodified (N) and thermally modified wood samples were prepared at 190 (S) and 212 °C (T) with dimensions of 30 mm x 20 mm x 5 mm (L x R x T). The samples were sanded with 80, 120 and 180 grid paper and conditioned for 72 hours at (23 ± 2) °C and (50 ± 5) % RH followed by measurement. For each sample, three drops of 5 µL of waterborne polyacrylate coating (Table 2) were deposited on the wood sample at different locations.

The value of contact angle was taken after 2 seconds of contact of the coating drop and the wood sample, because the preliminary results showed that this period of time is necessary in order to obtain drop sta-

bilisation. The obtained contact angle was the mean value of the left and right contact angle of the drop.

2.4 Determination of wood chemical composition

2.4. Određivanje kemijskog sastava drva

The unmodified and thermally modified samples were milled and sieved to obtain a fraction between 1.19-1.25 mm. The extractives content in the wood samples soluble in organic solvent was determined according to ASTM D1107 with a mixture of ethanol-benzene (1:1, v/v %), and the extractives content soluble in hot water was determined according to ASTM D1110. The obtained extract was dried in an oven at (103 ± 2) °C to constant weight and the extractives content was determined after isolation and drying to constant mass using the gravimetric method. The lignin content in the wood was determined by Klason method according to TAPPI T222om-11 on the extracted samples with a mixture of ethanol-benzene in which the water content was measured. Similarly as the lignin content, cellulose content was determined on the extracted samples with a mixture of ethanol-benzene in which the water content was measured according to the method of Miranda *et al.* 2012 (as cited in Kürscher and Hoffer, 1929). The lignin and cellulose content was determined gravimetrically in relation to absolutely dry extracted sample. In determining of extractive, lignin and cellulose content, two measurements were made for each type of wood sample.

3 RESULTS AND DISCUSSION

3. REZULTATI I DISKUSIJA

The pH results presented in Table 3 show that thermal modification caused an increase in acidity of

beech wood. As a reason for the increasing of wood acidity, Bonstra *et al.* (2007) indicated the formation of formic and acetic acid in the wood when it is subjected to high temperatures. They obtained a slightly higher acidity of thermally modified wood (pH = 3.5-4), but this may be due to the use of different wood species and different parameters during the process of thermal modification. From the obtained results, it can be concluded that there was no significant difference between the lower and higher temperature of modification, suggesting that already at 190 °C major changes in the pH of beech wood occurred. An increase in the acidity of thermally modified wood can have a negative effect on curing of coatings and on the interaction of thermally modified wood with metal objects.

The contact angle values of water, formamide and diiodomethane on unmodified and thermally modified wood are presented in Table 4. The results show that the water contact angle on thermally modified beech wood was higher compared to formamide and diiodomethane. Similar results were obtained for spruce wood (*Picea abies* Karst.) thermally modified in initial vacuum (Petrič *et al.*, 2012). Furthermore, the increasing of the modification temperature caused increasing of the water contact angle. Hakkou *et al.* (2005) reported that after heat treatment in the temperature range between 100 and 160 °C, the wood wettability changed suddenly.

Table 3 pH values of unmodified beech wood (N), thermally modified beech wood at 190 °C (S) and thermally modified beech wood at 212 °C (T)

Tablica 3. pH vrijednost nemodificirane bukovine (N), bukovine toplinski modificirane na 190 °C (S) i na 212 °C (T)

Type of wood <i>Vrsta drva</i>	pH
N	4.9 (0.00)*
S	4.3 (0.01)
T	4.4 (0.01)

* The values in parentheses are standard deviations. / *Vrijednosti u zagradama standardne su devijacije.*

One of the reasons of higher contact angle of water on the modified wood can be partial degradation of hemicellulose associated with the reorganisation of lignocellulosic compounds in the wood, which is the main cause of hydrophobicity of thermally modified wood (Pétrissans *et al.*, 2003; Hakkou *et al.*, 2005; Gérardin *et al.*, 2007). Furthermore, increasing of the contact angle of water can also cause extractives for which Ayrlimis *et al.* (2009) found that during the thermal modification migrate towards the wood surface and inactivate it. Extractives on the wood surface can also contaminate the test liquid, which can affect the measurement of the water contact angle with Wilhelmy method (Walinder and Johansson, 2001).

Smaller contact angle of formamide on thermally modified wood compared to unmodified wood was unexpected. It was expected that the ratio of the contact angle of formamide on thermally modified wood as

compared to unmodified wood would be similar to the contact angle of water as reported by Gérardin *et al.* (2007) on beech wood (*Fagus sylvatica* L.) and pine wood (*Pinus sylvestris* L.) and Pavlić (2009) on pine wood (*Pinus sylvestris* L.), because formamide is a polar liquid like water. One of the reasons for a lower contact angle may be less polarity of formamide compared to water. Petrič *et al.* (2012) reported that the contact angle of formamide can be affected by increased porosity of thermally modified wood and specific chemical reactions in the wood caused by thermal modification. Swelling of the polysaccharide cell wall caused by dimethyl formamide as determined by Inari *et al.* (2007) may be the cause of low contact angle of formamide compared to the contact angle of water. They also noticed that the chemical modification of wood with phenolic isocyanate in dimethyl formamide had a stronger impact on lignin in thermally modified wood than on lignin in unmodified wood. Table 4 also shows that the contact angle of diiodomethane increased with thermal modification of beech wood and was higher on thermally modified wood at 190 °C than at 212 °C. In the literature there are various data for the contact angle of diiodomethane on wood, from values of more than 70° on spruce wood (*Picea abies* L.) and meranti wood (*Shorea* spp.) (De Meijer *et al.*, 2000) to values not significantly higher than 0° on viscoelastic thermal compressed wood (Petrič *et al.*, 2009). From the three test liquids, the smallest dissipation of the contact angle measurements was recorded for the water. A marked increase in the contact angle of water on thermally modified wood will result in poor wetting of aqueous coatings, which may affect the adhesion and properties of coated thermally modified wood during use.

Table 4 Average values of the contact angle (Θ_a) on unmodified (N) and thermally modified beech wood at 190 °C (S) and 212 °C (T)

Tablica 4. Srednje vrijednosti kontaktnog kuta (Θ_a) na nemodificiranoj bukovini (N) i na bukovini toplinski modificiranoj na 190 °C (S) i 212 °C (T)

Type of substrate <i>Tip podloge</i>	Contact angle / kontaktni kut, Θ_a (°)		
	Water <i>Voda</i>	Formamide <i>Formamid</i>	Diiodomethane <i>Dijodometan</i>
N	55.9 (3.41)*	38.3 (6.66)	34.2 (9.97)
S	73.0 (1.15)	31.1 (6.12)	45.7 (4.60)
T	81.1 (2.40)	32.4 (5.96)	35.6 (5.99)

* The values in parentheses are standard deviations. / *Vrijednosti u zagradama standardne su devijacije.*

Results of the surface free energy, dispersing and polar component of the surface free energy of unmodified and thermally modified wood (Table 5) were calculated according to Owens Wendt Rable Kaebi method and to the Lifshitz-van der Waals - Acid Base method. The contact angle results on the wood surface, from which the surface free energy is calculated, depend on a number of variables such as measurement methods, the preparation of the wood surface, measuring time, moisture content, course-grained, early and late wood, surface roughness, surface contamination. With such a large number of influencing variables, comparison of

the results of the surface free energy from the literature can only provide limited information. According to OWRK method, a reduction of the surface free energy of thermally modified beech wood compared to unmodified wood was obtained with a slight increase of disperse and a high decrease of the polar component with an increase of modification temperature (Table 5). Gérardin *et al.* (2007) obtained similar results for thermally modified beech (*Fagus sylvatica* L.) and pine wood (*Pinus sylvestris* L.) and Petrič *et al.* (2012) for thermally modified spruce wood (*Picea abies* Karst.). Results according to LW-AB method also show a reduction of the surface free energy of thermally modified wood compared to unmodified wood. However, only on the samples modified at a higher temperature (212 °C), a strong reduction of the polar component was obtained (Table 5). These results indicate that there is a difference between these two methods of calculating the surface free energy of wood, which should be taken into consideration when they are compared. The resulting reduction of the surface free energy of thermally modified wood is too small to have a greater influence on wetting and adhesion of coatings. However, a marked decrease of the polar component indicates that the polar liquids, such as waterborne coatings, will poorly wet the surface of thermally modified wood, which may result in poorer adhesion.

Figure 2 shows that the wetting of the waterborne coating was better on the surface of the unmodified wood than on the surface of thermally modified wood i.e. it had a higher contact angle on thermally modified wood. The increase of the contact angle of waterborne coating on thermally modified wood was expected because of increasing of the contact angle of water on thermally modified wood (Table 4). Furthermore, the increasing of the coating contact angle on thermally modified wood can be caused by reducing the polar component of the surface free energy (Table 5). It can also be noted that the contact angle of the coating was increased with the increase of the modification temperature, which can be the result of increasing the crystallinity of cellulose (Pétrissans *et al.*, 2003) and increasing the extractive content in thermally modified wood (Figure 3).

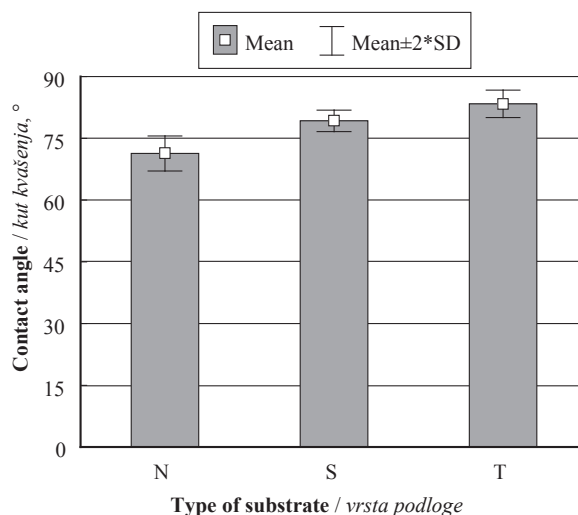


Figure 2 Contact angle of waterborne polyacrylate coating on unmodified (N) and thermally modified beech wood at 190 °C (S) and 212 °C (T)

Slika 2. Kut kvašenja vodenoga poliakrilatnog premaza na nemodificiranoj bukovini (N) i na bukovini toplinski modificiranoj na 190 °C (S) i 212 °C (T)

Figure 3 presents the content of extractives (soluble in hot water and organic solvent), cellulose and lignin before and after thermal modification of beech wood. It can be seen that the content of extractives soluble in hot water was increased after modification regardless of the modification temperature, while the content of extractives soluble in organic solvent and lignin was increased with the increase of the modification temperature. Similar results were obtained for thermally modified Norway spruce (*Picea abies* L.), Scots pine (*Pinus sylvestris* L.) and Radiata pine (*Pinus radiata* D.) (Boonstra and Tjeerdsma, 2006) and for Turkey oak (*Quercus cerris* L.) (Todaro *et al.*, 2013). According to the research of Esteves and Pareira (2009), most extractives disappear or decompose during thermal modification; however, new compounds are formed, which are isolated as a result of degradation of the compounds in the cell walls of the wood. Boonstra and Tjeerdsma (2006) noted that increasing of the extractives content also attributed to the degradation of the cell walls of the

Table 5 Surface free energy of unmodified (N) and thermally modified beech wood at 190 °C (S) and 212 °C (T) obtained by OWRK method

Tablica 5. Slobodna površinska energija nemodificirane bukovine (N) i bukovine toplinski modificirane na 190 °C (S) i 212 °C (T) dobivene OWRK metodom

Type of substrate Tip podloge	Surface free energy / Slobodna površinska energija, mJ/m ²							
	OWRK method			LW-AB method				
	S_{spolar}	$S_{sdispers}$	S_{stotal}	γ_{sv}^{LW}	γ_{sv}^{+}	γ_{sv}^{-}	γ_{sv}^{AB}	γ_{tot}
N	13.9	38.7	52.6	42.4	20.9	0.4	6.1	48.5
S	6.8	39.9	46.7	36.7	2.4	4.7	6.8	43.4
T	2.6	46.3	48.9	41.8	0.1	4.0	1.4	43.2

S_{spolar} – polar component / polarna komponenta

$S_{sdispers}$ – dispersion component / disperzijska komponenta

S_{stotal} – total surface free energy / ukupna slobodna površinska energija

γ_{sv}^{LW} – Lifshitz–van der Waals component / Lifshitz–van der Waalsova komponenta

γ_{sv}^{+} – Lewis acid parameter / Lewisov kiselinski parametar

γ_{sv}^{-} – Lewis base parameter / Lewisov bazni parametar

γ_{sv}^{AB} – Lewis acid–base component / Lewisova kiselinsko–bazna komponenta

γ_{tot} – total surface free energy / ukupna slobodna površinska energija

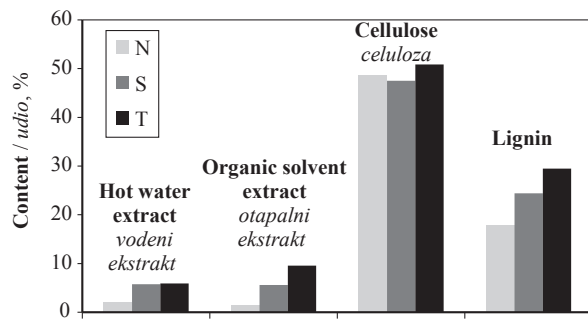


Figure 3 Percent content of extractives, cellulose and lignin in unmodified (N) and thermally modified beech wood at 190 °C (S) and 212 °C (T)

Slika 3. Postotni udio ekstraktivnih tvari, celuloze i lignina u nemodificiranoj bukovini (N) i u bukovini toplinski modificiranoj na 190 °C (S) i 212 °C (T)

wood. Therefore, it can be assumed that increasing of extractives content after thermal modification of beech wood indicates a greater degradation of the wood. Kamdem *et al.* (2002) suggested that higher lignin content does not mean the creation of new lignin during thermal modification than a reduction of other compounds in the wood. Furthermore, higher lignin content after thermal modification can be explained by the formation of some compounds by the thermal decomposition of carbohydrate, which can be contained in the isolated lignin (Yildiz *et al.*, 2006). The content of cellulose was slightly changed after thermal modification of beech wood, indicating that the cellulose is stable at high temperatures up to 212 °C.

4 CONCLUSION

4. ZAKLJUČAK

In this research, it was found that thermal modification caused higher acidity of beech wood, while there were no significant differences in wood pH between modification temperature at 190 °C and 212 °C.

Furthermore, thermal modification caused higher contact angle of water and lower polar component of wood surface free energy, which led to poor wetting of the thermally modified beech wood with waterborne coating.

The results showed that there is a difference between OWRK and LW-AB methods of calculation of wood surface free energy.

The contact angle of waterborne coating was increased on thermally modified beech wood with the increase of the modification temperature.

The content of extractives soluble in hot water and in organic solvent was higher after thermal modification. However, the content of extractives soluble in organic solvent increased with the increase of the modification temperature, which can be an indicator of wood degradation at high temperatures.

Klason method of lignin isolation proved not suitable for lignin isolation from thermally modified wood because with this method wood compounds formed by the thermal decomposition can be isolated.

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