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Comparing Wettability and Surface Free Energy of False Heartwood, Ripe Wood and Sapwood in Beech (*Fagus sylvatica* L.)

Usporedba stupnja kvašenja i slobodne površinske energije lažne srži, zrelog drva i bjeljike bukovine (*Fagus sylvatica* L.)

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ABSTRACT • *False heartwood is a common defect in beech wood. If the false heartwood is healthy and without microbial attacks, it is possible to utilize such material. Application of adhesives and coatings is an important part of the wood furniture industry. Studying wood surface properties provides answers to problems in application of glues, coating materials, and similar. Comparing wettability and surface free energy of false heartwood, ripe wood, and sapwood zones of beech was the focus of this paper. Two-way ANOVA with Duncan post-hoc test of multiple comparison was used for testing of the hypotheses and statistical evaluation of the results. The zones were also examined with light microscopy. Two testing liquids were used in wettability experiment – redistilled water and diiodomethane. Ripe wood showed the best wettability for both testing liquids among the wood zones. Significant differences in contact angles at the beginning of the wetting process, equilibrium contact angles, and surface free energies were found in almost all pairwise comparisons of the wood zone and testing liquid factors. The pairs where significant difference was not found were as follows: false heartwood and ripe wood in testing with redistilled water, and ripe wood and sapwood in testing with diiodomethane. Equilibrium times in all wood zones for both testing liquids were also statistically evaluated. Significant differences were found in all wood zones in testing with redistilled water. In testing with diiodomethane, equilibrium time for false heartwood was significantly different from ripe and sapwood zone equilibrium times.*

KEYWORDS: *beech; false heartwood; light microscopy; surface free energy; wettability*

SAŽETAK • *Lažna srž česta je greška bukovine, ali je i to drvo moguće iskoristiti ako je zdravo i nije napadnuto mikrobima. Primjena ljepila i premaza važni su postupci u drvnoj industriji i proizvodnji namještaja. Proučavanje svojstava površine drva daje odgovore na probleme u primjeni ljepila, premaznih materijala i sl. Fokus ovog rada je na usporedbi stupnja kvašenja i slobodne površinske energije drva u zoni lažne srži, zrelog drva i bjeljike bukovine. Za testiranje hipoteza i statističku procjenu rezultata primijenjena je dvosmjerna ANOVA s Duncanovim*

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post-hoc testom višestruke usporedbe. Zone drva istražene su i svjetlosnim mikroskopom. Pri ispitivanju stupnja kvašenja upotrijebljene su dvije ispitne tekućine – redestilirana voda i dijodometan. Zrelo drvo pokazalo je najbolju sposobnost kvašenja s obje ispitne tekućine. Značajne razlike u kontaktnim kutovima na početku kvašenja, ravnotežnim kontaktnim kutovima i slobodnim površinskim energijama zabilježene su u gotovo svim usporedbama zona drva i različitih ispitnih tekućina. Parovi u kojih nije utvrđena značajna razlika jesu lažna srž i zrelo drvo u ispitivanju redestiliranom vodom te zrelo drvo i bjeljika u ispitivanju dijodometanom. Također, statistički su procijenjena ravnotežna vremena u svim zonama drva za obje ispitne tekućine. U ispitivanju s redestiliranom vodom utvrđene su značajne razlike među ravnotežnim vremenom u svim zonama drva. U ispitivanju s dijodometanom ravnotežno vrijeme za lažnu srž značajno se razlikovalo od ravnotežnog vremena u zoni zrelog drva i bjeljike.

KLJUČNE RIJEČI: *bukovina; lažna srž; svjetlosni mikroskop; slobodna površinska energija; stupanj kvašenja*

1 INTRODUCTION
1. UVOD

Defects in wood are irregularities or abnormalities in wood structure. They usually change physical and mechanical properties of wood and therefore limit the use of such wood (Čunderlík, 2009). Nonetheless, defects in wood can create an interesting and aesthetically pleasing structure and are sought after for the manufacture of unique products. False heartwood is a hidden wood defect, and it is difficult to detect in a growing tree (Kúdela, 2011).

Other terms such as true heartwood, red heartwood, discoloured wood, wounded wood, pathological heartwood are also used for the different wood colourations found in hardwoods (Hörnfeldt *et al.,* 2010). The term "false heartwood" is used throughout this paper to cover all variants of wood colourations found in beech, in opposition to the normal heartwood colouration that beech does not produce (Hörnfeldt *et al.,* 2010; Shigo, 1986). Požgaj *et al.* (1993) divide false beech heartwoods according to their visible shape on the cross section. Round (simple, double, mosaic) red brown to pale brown heartwoods are considered "healthy" false heartwoods. Star shaped, flame shaped false heartwoods, and round false heartwoods with a different coloured zone and a sharp margin are "unhealthy" false heartwoods. Unhealthy and decayed false heartwood has significantly worse mechanical properties and it is not suitable for production of solid wood furniture (Požgaj *et al.,* 1993).

Numerous theories and interpretations of the formation of false heartwood are hypothetical even today (Prka *et al*., 2009). Many authors (Nečesaný, 1958; Bosshard, 1967; Paclt, 1953; Račko and Čunderlík, 2006) agree on the opinion that the primary cause of the false heartwood formation is a trunk injury during tree growth and the age of the beech tree. The trunk injury together with age influence the size and type of false heartwood. According to Chovanec (1969, 1974 and 1989) and Nečesaný (1958), the extent of false heartwood in the trunk depends on the age in which the wound was formed, the extent of the wound and the velocity of wound occlusion (Račko and Čunderlík, 2006). A healthy false heartwood is formed when parenchyma cells in the ripe wood zone die away. With the dyeing parenchyma cells, a film is created on the scalariform perforation plates. The false heartwood is then changing colour due to oxidization of extractives and tyloses form inside vessels (Kúdela, 2011).

Račko and Čunderlík (2006) evaluated the qualitative structure of beech logs produced in seven harvest areas in Slovakia, as well as the quality and quantity of beech false heartwood. The false heartwood was found in 30.7 % of the harvested logs. The average age of the logs ranged from 66.3 to 115.6 years. Račko and Čunderlík (2010) also investigated ripe wood as a limiting factor of false heartwood formation in beech. False heartwood started to form in approximately the 40th cambial age of the trunk, when there was already a 2.5 cm thick ripe wood zone present. Most of the trunks (89.5 %) had a smaller false heartwood zone compared to the size of ripe wood zone.

Another such research on the share of false heartwood in beech was performed by Prka *et al*. (2009) in central Croatia. In the respective cut classes, the share of logs containing false heartwood was as follows: 11.7 % in thinning cut, 54.7 % in preparatory felling, 71.3 % in seeding felling, and 84.6 % in final felling. The average age of the logs ranged from 76 to 106 years.

False heartwood often has a beautiful colour and texture (Hörnfeldt *et al*., 2010), which can be used as an aesthetic element in furniture. Some timber processors started looking for classical false heartwood timber to use its decorative characteristics. Furniture made of beech false heartwood is already well established and can be found in the individual production by carpenters as well as in the industrial production of kitchens, living- and bedrooms (Hansmann *et al*., 2009). Colour of the false heartwood can be effectively utilized for the production of decorative veneers (Kúdela, 2011).

According to Koch (2004), the industrially relevant properties of false heartwood are not adversely affected, except for the formation of tyloses. Požgaj *et al.* (1993) stated that, aside from colour and permeability, the physical and mechanical properties of healthy beech heartwood are the same as physical and mechanical properties of beech wood without false heartwood.

According to Pöhler *et al.* (2006), the mechanical and technological properties of red hearted beech give no evidence of different behaviour in comparison with the normal beech wood.

Applying adhesives or coating materials on beech boards or veneers with false heartwood, ripe wood, and sapwood might bring forth problems in woodworking processes. Differences in wood surface properties can cause different behaviour of coating materials on the wood substrate, different absorption of the adhesive or coating material, and this can cause defects in the final products. Therefore, it is important to study and understand wood surface properties, to ensure a final product of high quality.

Wetting of the wood surface with liquids is a very complex process. It depends on the chemistry and behaviour of liquids, substrate behaviour, and interactions between the wood substrate and liquids used (Kúdela *et al*., 2016). A good wettability is often a predictor of high-quality adhesive bonding (Piao *et al*. 2010). Contact angles measured at the interface with a liquid standard serve as a base for deriving wood surface thermodynamic characteristics – surface free energy and its components. Contact angles are also an important indicator to predict the adhesion performance of coating materials and glues to the substrate (Kúdela *et al*., 2016). The surface free energy of wood is a useful parameter that provides information on the interaction between the wood surface and an adhesive. Additionally, it has a great influence on the bonding strength of wood composites (Qin *et al*., 2015).

Evaluation of the relative wettability of a surface can be helpful for predicting or controlling the outcome of various industrial processes. Wettability can be generally defined as the tendency of a selected liquid to spread out and make intimate contact with a surface of interest (Hubbe *et al*., 2015). The best measure of wetting process quality is the contact angle between the solid substrate and the wetting liquid (Liptáková *et al*., 1998). Studying of wood wetting with liquids is obligatory for understanding interactions at the interface between wood and coating material, wood and gluing materials, and similar (Scheikl *et al*., 2001; Piao *et al*., 2010). Measurement of the contact angle formed by a droplet of a liquid placed on wood surface is a widely used method for the assessment of surface wettability and calculation of surface free energy (Štrbová *et al*., 2013). The contact angles are also useful for the assessment of other properties of the solid – liquid – gas system (Liptáková *et al*., 1998).

The aim of this study is to compare wettability and surface free energy of false heartwood, ripe wood, and sapwood zones of beech wood. In addition, microscopic structure of each zone was examined with light microscopy. The contact angle and surface free energy results were analyzed with a two-way ANOVA method and Duncan's post-hoc test of multiple comparison.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Four beech trees were harvested in September 2022, in the locality Štiavnické vrchy (Štiavnické mountains, in Slovakia). The logs were cut through into planks. From each log, planks containing false heartwood, ripe wood, and sapwood were selected (from here, false heartwood, ripe wood, and sapwood will be referred to as FHW, RW, and SW, respectively). These planks were cut into rectangular timber, separating the FHW, RW, and SW zones. Rectangular timber from each zone was selected and sawn into smaller samples with dimensions 150 mm x 20 mm x 40 mm, in longitudinal, radial, and tangential direction, respectively. From each log, one sample per FHW, RW, and SW was used. Twelve samples in total were used for this experiment. The average oven dried density of the samples was: 683 kg/m^3 in FHW, 669 kg/m^3 in RW, and 653 kg/m^3 in SW. All sides of the samples were milled.

The samples were oven dried at a temperature of (103±2) °C. After drying, the samples were weighed on a Radwag laboratory scale (model XA 60/220/X, Radwag, Radom, Poland) and measured with a digital slide calliper. The samples were then placed into a climatic chamber (relative air humidity was set to 45 % and air temperature to 20 °C), until they reached an equilibrium moisture content of 7.5 %. When the samples reached the equilibrium moisture content, they were weighed again, and the moisture content was calculated using the gravimetric method.

2.1 Wettability with liquids and wood surface free energy
2.1. Stupanj kvašenja tekućinama i slobodna površinska energija drva

Wood surface wetting process and contact angle measurement were performed with a Krüss DSA30 Standard drop shape analyzer (Hamburg, Germany) and the attached software package (Fig. 1). Following Kúdela (2014), two testing liquids with different polarities were used – redistilled water and diiodomethane. Redistilled water is a polar-apolar liquid with a polar component of surface free energy higher than the polar component of wood. Diiodomethane is a nonpolar liquid with a nonpolar component of surface free energy higher than the disperse component of wood (Kúdela *et al*., 2019). Parameters of both liquids are listed in Table 1.

Syringes were used to apply drops of the testing liquids on the wood surface. For each testing liquid, separate syringes were used. The drop volume was set to 1.8 µl. Testing liquids were applied on tangential

Table 1 Surface free energy and its components of the testing liquids
Tablica 1. Slobodna površinska energija ispitnih tekućina i njihove komponente

Testing liquid *Ispitna tekućina*	γ_L, mJ/m^2	γ_L^d, mJ/m^2	γ_L^p, mJ/m^2	γ^+, mJ/m^2	γ^-, mJ/m^2	η, Pa·s	**References** *Reference*
Redistilled water / *redestilirana voda*	72.80	21.80	51.00	25.50	25.50	0.010	Gardner (1996)
Diiodomethane / *dijodometan*	50.80	50.80	0.00	0.00	0.00	0.028	van Oss *et al*. (1998)

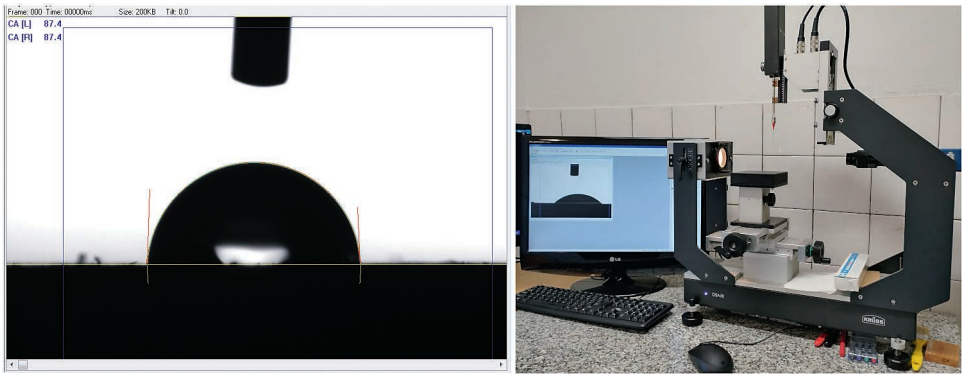

Figure 1 Contact angle measurement by the circle method on the left side of the figure; Krüss DSA30 Standard drop shape analyzer on the right side of the figure
Slika 1. Mjerenje kontaktnog kuta kapi (lijeva slika); Krüss DSA30 standardni analizator oblika kapi (desna slika)

surfaces of the samples. The drop shape analyzer recorded spreading and soaking of the testing liquids from the moment they were applied on the tangential surface until their complete soaking into the substrate. Spreading of the testing liquids along the fibres was analyzed. Scanning frequency (number of recorded frames per second) was set and adjusted according to the wetting intervals in FHW, RW, and SW. Measurement of the contact angles was computed in the DSA30 software, using the circle method.

Contact angles θ_0 were measured right after the drop application, in the very first moment of the testing liquid spreading. Equilibrium contact angles θ_e were determined according to Liptáková and Kúdela (1994), at a moment of spreading of the testing liquids, when the contact angle changed from an advancing angle to a receding angle. This equilibrium state was matched with the moment when the liquid stopped spreading onto the surface and started to recede. This moment was determined through the drop base diameter (Kúdela *et al*., 2015). Contact angles θ_0 and θ_e were used to calculate θ_w, the contact angle corresponding to an ideal smooth surface (Liptáková and Kúdela, 1994). The contact angle θ_w was calculated according to Eq. 1, 2, and 3 (Liptáková and Kúdela, 1994):

$$\cos\theta_0 = f_1 \cdot \cos\theta_w - f_2 \quad (1)$$

$$\cos\theta_e = f_1 \cdot \cos\theta_w + f_2 \quad (2)$$

Where:

θ_0 – contact angle at the beginning of the wetting process,

θ_e – equilibrium contact angle,

θ_w – equilibrium contact angle corresponding to a wood substance with surface characterized by roughness of molecular dimensions,

$f1$ – proportion of the substance at the spot occupied by the testing liquid,

$f2$ – proportion of void pores and cell capillaries and of cell walls under the drop (Kúdela, 2014).

Surface free energy values of the substrate γ_S were calculated according to the equation modified by Neumann *et al*. (1974), Eq. 4:

$$\cos\theta = \frac{(0.0137 \cdot \gamma_S - 2.00)\sqrt{\gamma_s \cdot \gamma_L} + \gamma_L}{\gamma_L \cdot \left(0.0137 \cdot \sqrt{\gamma_S \cdot \gamma_L} - 1\right)} \quad (4)$$

Dispersion and polar components γ_S^d and γ_S^p of the substrate surface free energy were calculated according to Kloubek (1974), Eq. 5 and 6:

$$\sqrt{\gamma_S^d} = \sqrt{\gamma_L^d} \cdot \frac{1+\cos\theta}{2} \pm \sqrt{\gamma_L^p} \cdot \sqrt{\frac{\gamma_S}{\gamma_L} - \left(\frac{1+\cos\theta}{2}\right)^2} \quad (5)$$

$$\sqrt{\gamma_S^p} = \sqrt{\gamma_L^p} \cdot \frac{1+\cos\theta}{2} \mp \sqrt{\gamma_L^d} \cdot \sqrt{\frac{\gamma_S}{\gamma_L} - \left(\frac{1+\cos\theta}{2}\right)^2} \quad (6)$$

According to Kúdela *et al*. (2016), a combined value of the surface free energy γ_{SC} was calculated by addition of the dispersion component γ_S^d, calculated from measurements with diiodomethane and polar component γ_S^p, calculated from the measurement with redistilled water. In total, 72 measurements were done per each zone, 18 measurements per one sample were done with both testing liquids. The spots where the testing liquid drop was placed did not overlap.

2.2 Data analysis
2.2. Analiza podataka

A two-way ANOVA was used for testing whether the variability of the results among samples was due to chance or was the effect of the observed factors or their

Table 2 Two-factor ANOVA design used for estimating how the mean of a quantitative variable changes according to the levels of two categorical variables
Tablica 2. Dvofaktorska ANOVA za procjenu promjene srednje vrijednosti kvantitativne varijable prema razinama dviju kategoričkih varijabli

Source of variation *Izvor varijacije*	**Sum of squares** *Zbroj kvadrata*	**Degree of freedom** *Stupanj slobode*	**Mean square** *Srednja vrijednost kvadrata*	***F*-test**	***p*-level**
Factor A effect / *utjecaj faktora A*	SS_A	df_A	MS_A	F_A	p_A
Factor B effect / *utjecaj faktora B*	SS_B	df_B	MS_B	F_B	p_B
Interaction AB effect *utjecaj interakcije faktora A i B*	SS_{AB}	df_{AB}	MS_{AB}	F_{AB}	p_{AB}
Error / *pogreška*	SS_E	df_E	MS_E		
Total / *ukupno*	SS_{Total}	df_{Total}			

Figure 2 FHW (A), RW (B), and SW (C) zone samples. Small blocks to cut out for microscopic examination are marked on the pictures on the right-hand side.
Slika 2. Uzorci zona FHW (A), RW (B) i SW (C). Mali blokovi za izrezivanje za mikroskopsko ispitivanje označeni su na slikama desno.

interaction. The null hypothesis of equal samples means was tested. The test criterion was *F*-statistic representing the ratio of two estimates of variance – an estimate of the variance among samples (*MS* effect) and an estimate of variance within samples (*MS* error). The design of the two-factor ANOVA is presented in Table 2.

If *MS* effect is significantly greater than *MS* error, then the null hypothesis is rejected in favour of the alternative hypothesis - de facto the given factors are responsible for differences among sample means. Subsequently, Duncan post-hoc test of multiple comparison was applied to identify significant pairwise differences. Sample means and 95 % confidence intervals for population means are presented graphically by box and whisker charts.

The analyses were carried out using statistical software STATISTICA 12. An alpha level of 0.05 traditionally used in similar studies as decision rule was applied. The output tables were edited in the Microsoft Excel spreadsheet editor.

2.3 Microscopic observation
2.3. Mikroskopska analiza

For microscopic observation, FHW, RW, and SW samples from one log were selected randomly. From each of the selected 150 mm × 20 mm × 40 mm samples, a 4 mm thick slice was sawn from the 20 x 40 mm side. This was done after the samples were oven dried. Two 7 mm × 4 mm × 3 mm small wood blocks were carefully cut from these slices. Radial and tangential microsections were our main object of observation; therefore, each of the small wood blocks was cut accordingly. In Figure 2, small wood blocks are marked on the FHW, RW, and SW zones.

The small wood blocks were embedded in epoxy resin and left to cure for two weeks. Approximately 15 µm thick microsections were cut from the wood-resin blocks on a sledge microtome (Reichert, Wien, Austria). The microsections were stained with a combination of Astra Blue and Safranin stains. This stain combination was used to detect axial parenchyma and nutrients inside ray parenchyma cells (Slováčková and Mišíková, 2023). Astra Blue and Safranin stain combination can also be used to distinguish cellulose from lignified cells (de Baerdemaeker *et al*., 2018). Safranin stains lignin regardless of whether cellulose is present, whereas Astra Blue stains cellulose only in the absence of lignin (Srebotnik and Messner, 1994; Schwarze and Engels, 1998). A combination of Safranin and Astra Blue is used to detect early stages of white rot, i.e., selective delignification (Srebotnik and Messner, 1994). With this stain combination, a fungal attack could be discovered, so it also confirmed that the false heartwood did not have a fungal attack. After staining, the microsections were mounted in Euparal (BioQuip Products Inc., Rancho Dominguez, CA, USA).

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Wettability and surface free energy
3.1. Stupanj kvašenja i slobodna površinska energija

Soaking of the testing liquids into the wood zone samples is presented Figure 3. One characteristic measurement per each wood zone for both testing liquids was selected to be presented in the figure. Measurements with average contact angles θ_0 and average soaking times (from the time of the placement of the testing liquid drop until the time of complete soaking into the wood substrate) were selected. Figure 3 presents the decrease of contact angles over time. The longest average soaking times for both testing liquids were observed in FHW, and the shortest times were observed in RW.

The mean values of θ_0 and θ_e contact angles measured in the respective wood zones are presented in Table 3 and Table 4. In measurement with redistilled water, the lowest mean contact angles were measured in FHW, and the highest values were measured in SW. In measurement with diiodomethane, the highest mean contact angles were measured in FHW, and the lowest in RW.

Concerning θ_0, detailed results of two-way ANOVA experiment are presented in Table 3. Based on computed p-values, the null hypothesis that there is no difference among the means was rejected. The observed differences of θ_0 among samples are the result of the interaction effect of the investigated factors – testing liquid and wood zone. In the detailed pairwise comparison, significant differences in mean θ_0 values were confirmed for most pairs based on the presented p-values.

Similarly in Table 4, when evaluating θ_e, significant differences of mean values among samples were tested (p=0.000), which is the result of the influence of the investigated factors. In a detailed pairwise comparison, the null hypothesis of equality of θ_e was ac-

Table 3 Results of Duncan post-hoc test of pairwise differences for dependent variable θ_0
Tablica 3. Rezultati Duncanova post-hoc testa razlikâ između parova za zavisnu varijablu θ_0

Two-way ANOVA with interaction: testing liquid*wood zone, $F = 7.48$, $df = 2$, $p = 0.001$ *Dvosmjerna ANOVA s interakcijom: ispitna tekućina* zona drva, $F = 7{,}48$, $df = 2$, $p = 0{,}001$*								
Testing liquid *Ispitna tekućina*	**Wood zone** *Zona drva*	**Mean value, °** *Srednja vrijednost, °*	(1) FHW	(2) RW	(3) SW	(4) FHW	(5) RW	(6) SW
Redistilled water *redestilirana voda*	(1) FHW	80.45		0.892	0.013	0.000	0.000	0.000
	(2) RW	80.58	0.892		0.014	0.000	0.000	0.000
	(3) SW	82.97	0.013	0.014		0.000	0.000	0.000
Diiodomethane *dijodometan*	(4) FHW	41.15	0.000	0.000	0.000		0.002	0.005
	(5) RW	37.97	0.000	0.000	0.000	0.002		0.654
	(6) SW	38.40	0.000	0.000	0.000	0.005	0.654	

Note: The pairs without a significant difference are printed in black. / *Napomena: parovi bez značajne razlike otisnuti su crnom bojom.*

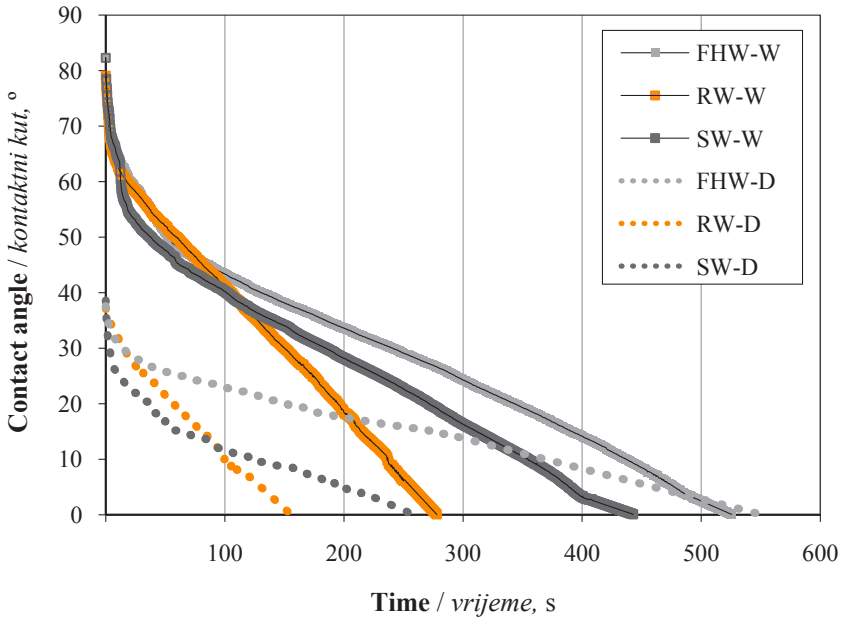

Figure 3 Contact angles over soaking time. Testing liquids are denoted next to wood zone abbreviations: W - measurement with redistilled water, D - measurement with diiodomethane.
Slika 3. Kontaktni kutovi tijekom kvašenja. Ispitne su tekućine označene uz kratice zone drva: W – mjerenje redestiliranom vodom, D – mjerenje dijodometanom.

Table 4 Results of Duncan post-hoc test of pairwise differences for dependent variable θ_e
Tablica 4. Rezultati Duncanova post-hoc testa razlikâ između parova za zavisnu varijablu θ_e

Two-way ANOVA with interaction: testing liquid*wood zone, $F = 7.64$, $df = 2$, $p = 0.000$ *Dvosmjerna ANOVA s interakcijom: ispitna tekućina* zona drva, F = 7,64, df = 2, p = 0,000*								
Testing liquid *Ispitna tekućina*	**Wood zone** *Zona drva*	**Mean value, °** *Srednja vrijednost, °*	(1) FHW	(2) RW	(3) SW	(4) FHW	(5) RW	(6) SW
Redistilled water *redestilirana voda*	(1) FHW	23.90		0.042	0.000	0.000	0.000	0.000
	(2) RW	25.55	0.042		0.043	0.000	0.000	0.000
	(3) SW	27.19	0.000	0.043		0.000	0.000	0.000
Diiodomethane *dijodometan*	(4) FHW	37.69	0.000	0.000	0.000		0.051	0.230
	(5) RW	36.03	0.000	0.000	0.000	0.051		0.393
	(6) SW	36.72	0.000	0.000	0.000	0.230	0.393	

Note: The pairs without a significant difference are printed in black. / *Napomena: parovi bez značajne razlike otisnuti su crnom bojom.*

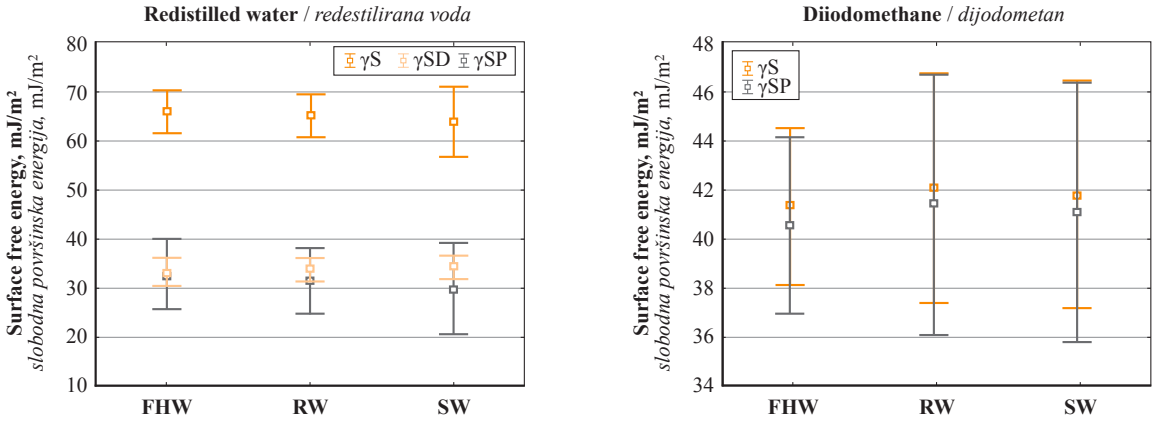

Figure 4 Box and whisker plot (sample mean ± 2·standard deviation) of surface free energy calculations with both testing liquids
Slika 4. Prikaz rezultata (srednja vrijednost uzorka ± 2·standardna devijacija) izračuna slobodne površinske energije s obje ispitne tekućine

cepted in only two cases – redistilled water FHW versus RW, and diiodomethane RW versus SW.

Results of surface free energy and its polar and disperse components are presented in Figure 4. In measurement with redistilled water, surface free energy and its polar component showed a decreasing trend through the wood zones. The highest surface free energy was found in FHW and the lowest surface free energy in SW. Disperse component of the surface free energy in measurement with redistilled water had a moderately increasing trend through the wood zones.

In measurement with diiodomethane, the highest surface free energy and its disperse components were found in RW. The lowest values were found in FHW. Since diiodomethane is a nonpolar liquid with only a disperse surface free energy component, the polar component of surface free energy in wood zones was zero and is therefore not included in Figure 4.

Results of analysis for surface free energy are presented in Table 5. The *F*-test of the interactive effect of the two investigated factors – testing liquid and wood zone – confirmed their significant influence (p=0.000) on the surface free energy values. Even in a simultaneous pairwise comparison using Duncan's test, almost all pairs were significantly different. As pairs with the same mean surface free energy values, the combinations - re-

Table 5 Results of Duncan post-hoc test of pairwise differences for dependent variable of surface free energy
Tablica 5. Rezultati Duncanova post-hoc testa razlikâ između parova za zavisnu varijablu slobodne površinske energije

Two-way ANOVA with interaction: testing water*wood zone, $F = 10.20$, $df = 2$, $p = 0.000$ *Dvosmjerna ANOVA s interakcijom: ispitna tekućina* zona drva, F = 10,20, df 2, p = 0,000*								
Testing liquid *Ispitna tekućina*	**Wood zone** *Zona drva*	**Mean value, mJ/m²** *Srednja vrijednost,* mJ/m²	(1) FHW	(2) RW	(3) SW	(4) FHW	(5) RW	(6) SW
Redistilled water *redestilirana voda*	(1) FHW	65.94		0.031	0.000	0.000	0.000	0.000
	(2) RW	65.05	0.031		0.002	0.000	0.000	0.000
	(3) SW	63.82	0.000	0.002		0.000	0.000	0.000
Diiodomethane *dijodometan*	(4) FHW	41.26	0.000	0.000	0.000		0.083	0.265
	(5) RW	42.01	0.000	0.000	0.000	0.083		0.475
	(6) SW	41.72	0.000	0.000	0.000	0.265	0.475	

Note: The pairs without a significant difference are printed in black. / *Napomena: parovi bez značajne razlike otisnuti su crnom bojom.*

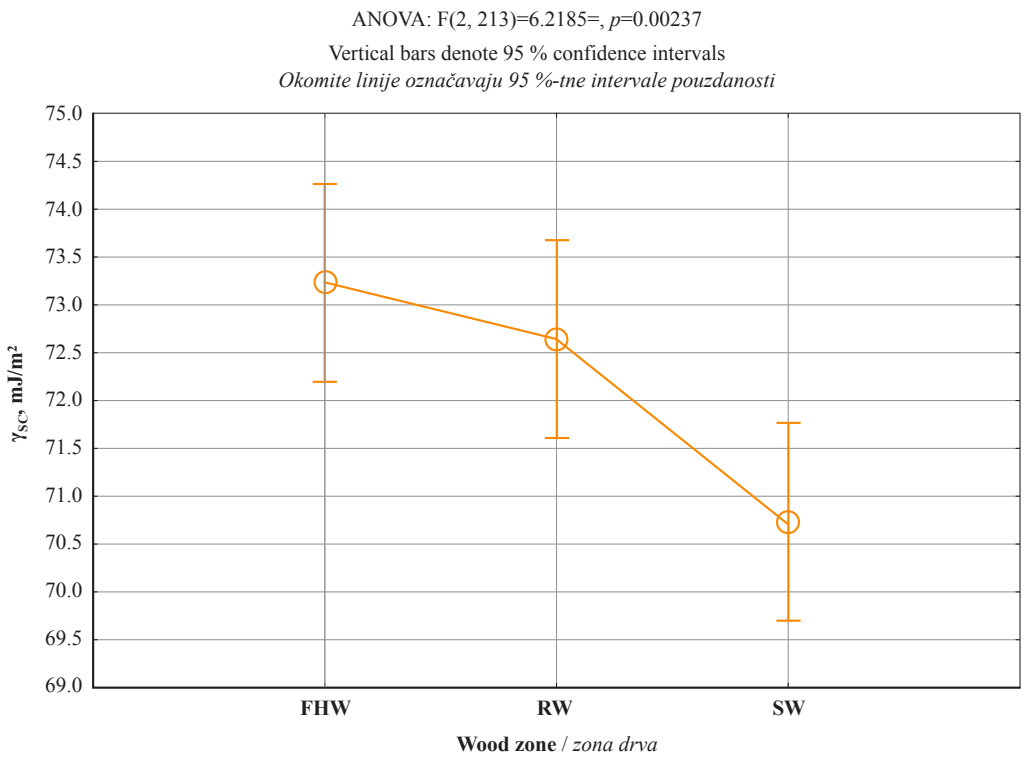

Figure 5 Result of One-way ANOVA and 95 % confidence intervals: dependence of combined surface free energy on wood zone

Slika 5. Rezultat jednosmjerne ANOVA analize i 95 %-tnog intervala pouzdanosti: ovisnost kombinirane slobodne površinske energije o zoni drva

distilled water FHW versus RW, and diiodomethane RW versus SW- were proven by the test.

Following Kúdela *et al*. (2016), the combined surface free energy values γ_{SC}, calculated by addition of the average value of dispersion component γ_S^d, calculated from measurements with diiodomethane and average value of polar component γ_S^p, calculated from the measurement with redistilled water, were as follows: 73.23 mJ/m^2 in FHW, 72.64 mJ/m^2 in RW, and 70.73 mJ/m^2 in SW. These values are slightly lower than the surface free energy value of normal beech wood of 78.3 mJ/m^2 reported by Kúdela *et al*. (2016). The surface of the samples used in the cited research was milled. The authors did not state the moisture content of the normal beech wood; a different moisture content value could have had an influence on the surface free energy value. The combined surface free energy values calculated on beech wood with FHW and normal beech wood confirm that the adhesion behaviour of beech wood with FHW is similar to normal beech wood. ANOVA was used for the analysis of the combined surface free energy values. The result is presented in Figure 5. The investigated factor wood zone showed that SW was significantly different (p=0.002) from FHW and RW.

Studies on adhesion behaviour of beech false heartwood show that the results of the adhesion behaviour of beech false heartwood are the same as those of normal beech wood (Pöhler *et al*., 2006). Aicher and Reinhardt (2007) examined delamination and dry shear strength tests on glued beech false heartwood. It was found that false heartwood did not have an influence on shear strength. Delamination tests revealed a distinct dependency of the glue line integrity on false heartwood and width of the adherents (Aicher and Reinhardt, 2007).

3.2 Microscopic observation
3.2. Mikroskopska analiza

The results of microscopic observation of FHW, RW and SW are presented in Figure 6 and Figure 7. The FHW zone microsection (shown in Figure 6A and 6B) absorbed only Safranin from the stain combination Astra Blue and Safranin. The formation of FHW is closely connected with the production of tyloses inside the vessels (Kúdela and Čunderlík, 2012). Numerous tyloses were observed inside the vessels of the samples used in this experiment. The tyloses are denoted in Figure 6A and 6B with black arrows. Tyloses were observed only in the FHW zone. Oxidized extractives were also observed; they are visible in the ray parenchyma cells in Figure 6A as a dark looking compound inside the ray parenchyma cell. Similar observation of the extractives inside ray parenchyma cells was made by Požgaj *et al.* (1993). Ray parenchyma cells containing oxidized extractives are denoted with a white arrow (outlined with black).

The RW microsections are shown in Figure 6C and 6D. RW microsections absorbed also blue stain

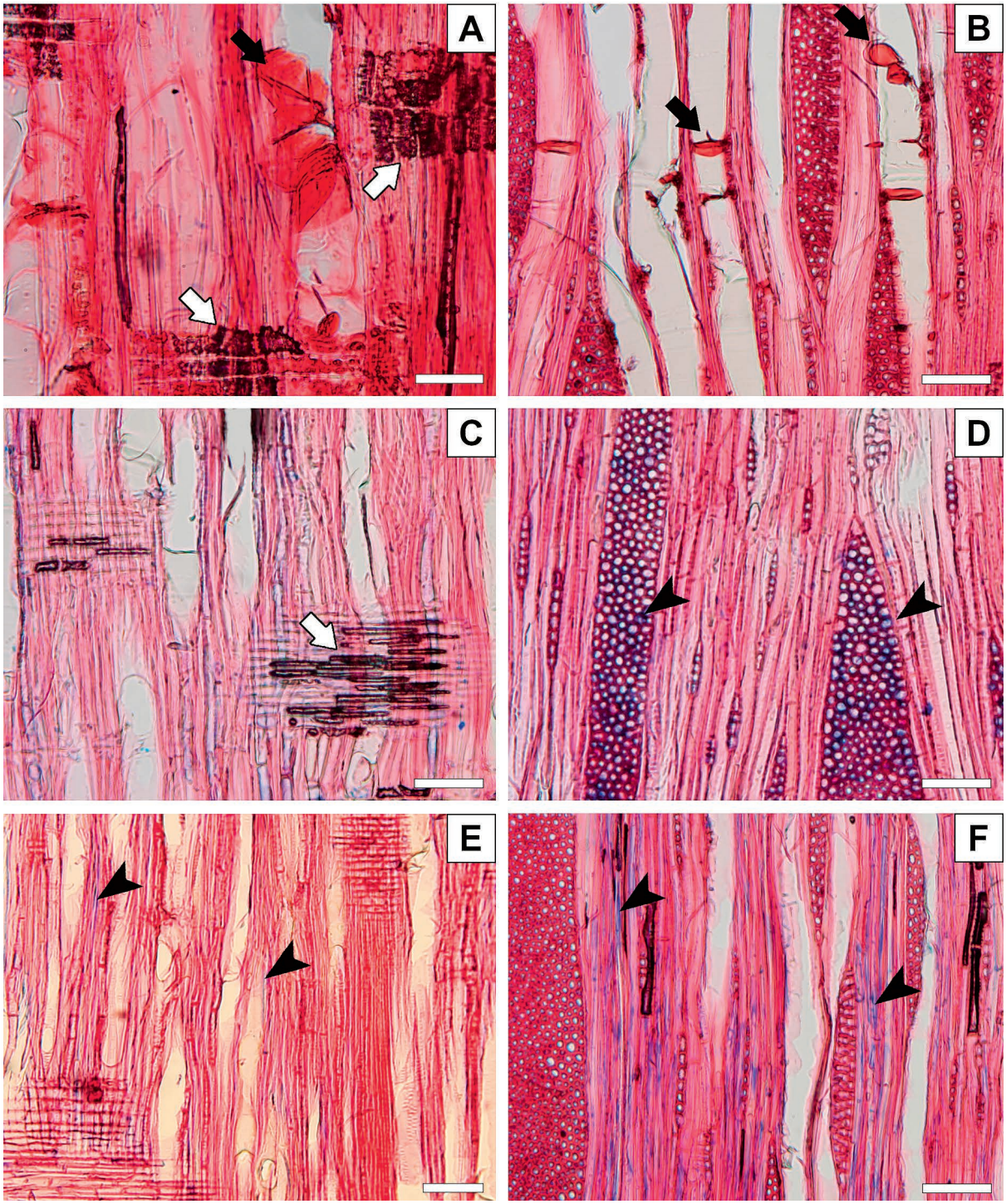

Figure 6 FHW (A and B), RW (C and D) and SW (E and F) microsections stained with Astra Blue and Safranin stain combination. A, C and E are radial microsections and B, D and F are tangential microsections. Scales are denoted with a white stripe in the lower right corners of the figures – 50 µm in 5A and 100 µm in the other figures.
Slika 6. FHW (A i B), RW (C i D) i SW (E i F) mikrografije obojene kombinacijom boja Astra Blue i Safranin. A, C i E radijalni su presjeci, a B, D i F tangentni presjeci. Skale su označene bijelom prugom u donjem desnom kutu slikâ – 50 µm u 6A i 100 µm u ostalim slikama.

from the stain combination. The axial parenchyma and ray parenchyma cells absorbed Astra Blue stain (denoted with arrow heads in Figure 6D, visible also in 6C). Because of the staining, both types of parenchyma cells can be clearly distinguished from the rest of the wood structure. The rest of the microsection absorbed red from Safranin stain. In Figure 6D, the blue stained ray parenchyma cells are dispersed throughout the wide ray. Figure 7 shows that in some rays, only the parenchyma cells on the outer part of wide rays absorbed the blue colour from the stain combination. Oxidized extractives in ray parenchyma cells appeared in radial RW microsections, Figure 6C. The oxidized extractives in RW microsections were

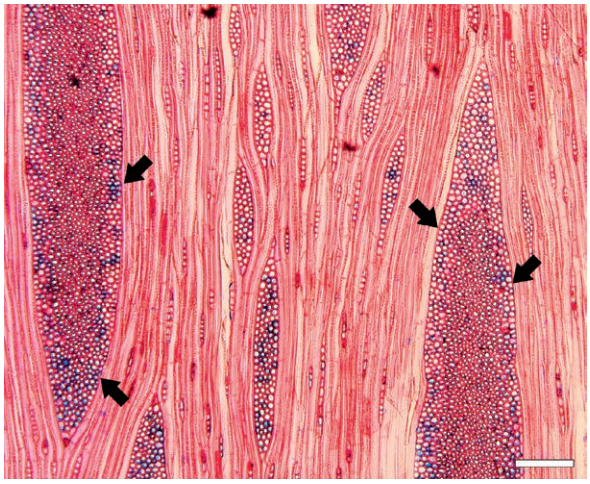

Figure 7 Tangential microsection of RW zone with blue stained ray parenchyma cells on the outer edges of the wide ray. Scale is denoted with a white stripe in the lower right corner of the figure and its size is 150 µm.
Slika 7. Mikrografija tangentnog presjeka RW zone s plavo obojenim stanicama parenhima na vanjskim rubovima širokih trakova. Skala je označena bijelom prugom u donjem desnom kutu slike, a veličina je 150 µm.

less pronounced than in FHW microsections. When a healthy FHW is formed, still active parenchyma cells in the RW zone become inactive. During the formation of FHW, extractives inside the parenchyma cells oxidize (Požgaj *et al*., 1993). The occurrence of oxidized extractives in ray parenchyma cells in RW could be a sign of FHW formation.

SW microsections (shown in Figure 6E and 6F) also absorbed blue stain from the stain combination and revealed axial parenchyma. This is denoted in Figure 6E and 6F with black arrowheads. The axial parenchyma in SW microsections appeared to be more saturated with the blue stain than in RW microsections. Extractives in ray parenchyma cells were not observed in SW microsections.

The difference between RW and SW zones is in the vitality of parenchymatic cells. This has a significant influence on the occurrence of defects in the wood structure. Parenchymatic cells in SW have a high vitality whereas parenchymatic cells in RW have a low vitality (Kúdela and Čunderlík, 2012).

Jankowska *et al*. (2018) studied the effect of extractives on wettability on 13 tropical wood species, European beech, and oak. The influence of extractives relative to wettability and surface free energy was confirmed. Oxidized extractives were observed in FHW and RW (Figure 6A and C). The results of Duncan's pairwise comparison suggest that there could be an influence of oxidized extractives on wettability and surface free energy of beech in FHW and RW, however further research needs to be performed to confirm this statement.

The research (Jankowska *et al*., 2018) also determined that a higher content of axial parenchyma resulted in a higher contact angle. Axial parenchymas were visible in RW and SW microsections (Figure 6C and 6F). They absorbed the blue stain from the Astra Blue – Safranin stain combination. Axial parenchyma was not visible in FHW microsections. The presence of axial parenchyma can possibly influence wettability and surface free energy of beech; the results of the Duncan's test for θ_0, θ_e, and for FHW and SW pair in redistilled water measurement, and all pairs in diiodomethane measurement support this statement. In measurement with redistilled water, the contact angles in RW and SW were higher than in FHW. However, in measurement with diiodomethane, the contact angles were higher in FHW than in RW and SW. To firmly confirm the statement, further research needs to be done.

3.3 Equilibrium time
3.3. Ravnotežno vrijeme

Equilibrium time is the time passing from the measurement of the contact angle θ_0 until the contact angle θ_e is described as the equilibrium time t_u. During the sessile drop experiments, different equilibrium times in different wood zones were noticed. Therefore, the effect of wood zone on the equilibrium times was analyzed. The analysis was performed using ANOVA, especially in the case of redistilled water and diiodomethane. In both cases, the investigated factor significantly affected the values of equilibrium time (p=0.000). Figure 8 presents the 95 % confidence intervals for equilibrium time means of individual wood zones. In the case of the redistilled water, significant differences were tested in all three wood zones. In the case of diiodomethane, FHW differed significantly from RW and SW.

In measuring with diiodomethane, the drop often showed only the receding angle; it started to soak into the wood substrate immediately after placing the diiodomethane drop. The equilibrium times were 0 seconds in 5.5 % of FHW measurements, 40 % of RW measurements, and 28 % of SW measurements. The average equilibrium time for FHW measured with diiodomethane was ten times higher than that for RW and SW. The significant differences in equilibrium time of FHW for both testing liquids were caused by the numerous tyloses present in FHW (Figure 6A and 6B). Tyloses obstruct the pass ability of vessels, hence false heartwood permeability for liquids is significantly decreased (Babiak *et al*., 1990; Kúdela and Čunderlík, 2012).

Kúdela *et al*. (2015) stated that the equilibrium time t_u depends on the liquid polarity, as well as on wood moisture content, polar share, and viscosity of the testing liquids. The variability of t_u values in one testing liquid is the result of unevenness of the wood surface and the random placement of the testing liquid drop on the wood surface (Kúdela *et al*., 2015).

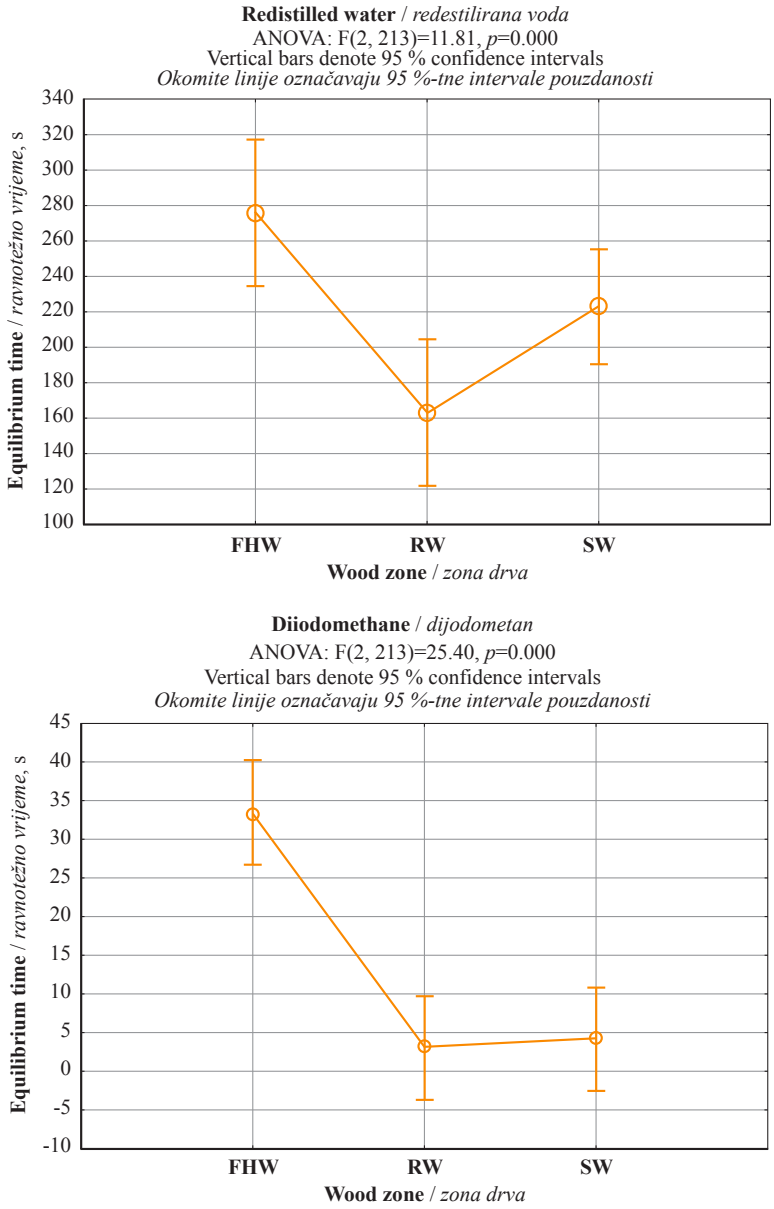

Figure 8 Result of One-way ANOVA and 95 % confidence intervals: dependence of equilibrium time on wood zone using two testing liquids - redistilled water and diiodomethane
Slika 8. Rezultat jednosmjerne ANOVA analize i 95 %-tnog intervala pouzdanosti: ovisnost ravnotežnog vremena o zoni drva za dvije ispitne tekućine – redestiliranu vodu i dijodometan

According to Kúdela *et al.* (2016), a poorer wetting performance is associated with a longer time necessary for the testing liquid drop to spread over the surface and higher contact angles. Significantly enhanced wettability with standard polar and non-polar liquids was reflected in higher surface free energy (Kúdela *et al.,* 2022). In our experiment, FHW had the longest average soaking and equilibrium times, a high combined surface free energy, lowest contact angles in measurement with redistilled water and highest contact angles in measurement with diiodomethane. FHW had also tyloses inside vessels and extractives in ray parenchyma. RW had the lowest average soaking times, lowest equilibrium time, higher combined surface free energy than SW, and low contact angles in both testing liquids. The average soaking times of SW were between RW and FHW average soaking times, SW had low equilibrium times, the highest contact angles in measurement with redistilled water and lowest combined surface free energy values. Out of the tested wood zones in beech wood, RW had the best wettability for both testing liquids. SW had the worst wettability for redistilled water; wettability for diiodomethane was similar to that of RW. It is difficult to state whether FHW had good or bad wettability. The combined surface free energy values and contact angles measured with redistilled water suggest that the wettability of FHW is similar to that of RW. However, the average soaking and equilibrium times were the longest among the wood zones.

4 CONCLUSIONS
4. ZAKLJUČAK

This paper focused on wettability and surface free energy of false heartwood, ripe wood, and sapwood in beech. Measurement of contact angles was performed with two testing liquids – redistilled water and diiodomethane (a polar-apolar and a nonpolar liquid). Two-way ANOVA and Duncan's post-hoc test of multiple comparison were used for statistical analysis of the results. False heartwood, ripe wood, sapwood wood zones and testing liquids were the main factors in Duncan's pairwise comparison test.

Ripe wood showed the best wettability for both testing liquids with a high surface free energy, lowest contact angles among the researched wood zones and shortest average soaking and equilibrium times. Sapwood showed the worst wettability in measurement with redistilled water. False heartwood showed similar wettability to ripe wood in measurement with redistilled water, although the average soaking and equilibrium times were the longest. The long times are caused by the presence of tyloses in false heartwood. These findings were supported by Duncan's post-hoc test. The false heartwood and ripe wood pair did not differ significantly, while sapwood was significantly different from ripe wood and false heartwood in measurement with redistilled water.

In measurement with diiodomethane, false heartwood showed the worst wettability, while the wettability of sapwood was similar to that of ripe wood. These results were also supported by Duncan's post-hoc test; the sapwood and ripe wood pair did not show a significant difference.

The long average soaking time of false heartwood needs to be taken into consideration in furniture production. An incorrect application of adhesives on veneers containing false heartwood could affect the glue line integrity of the final product.

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5 REFERENCES
5. LITERATURA

1. Aicher, S.; Reinhardt, H. W., 2007: Delamination properties and shear strength of glued beech wood laminations with red heartwood. Holz als Roh- und Werkstoff, 65: 125-136 (in German). https://doi.org/10.1007/s00107-006-0135-7
2. Babiak, M.; Čunderlík, I.; Kúdela, J., 1990: Permeability and structure of beech wood. IAWA Bulletin, 11(2): 115.
3. Bosshard, H., 1967: On the facultative formation of stained heartwood. Holz als Roh- und Werkstoff, 25: 405-416 (in German). https://doi.org/10.1007/bf02612900
4. Chovanec, D., 1969: Povrchové znaky poranenia buka. Lesnícky časopis, 15:372-383.
5. Chovanec, D., 1974: Možnosti zábrany vzniku bukového jadra. Lesnícky časopis, 20: 339-354.
6. Chovanec, D.; Čunderlík, I.; Válka, J., 1989: Znaky kvality bukových kmeňov. Vedecké a pedagogické aktuality, 1st ed. VŠLD Zvolen, pp. 103.
7. Čunderlík, I., 2009: Štruktúra dreva. Zvolen, Technical University at Zvolen, p. 136.
8. De Baerdemaeker, N. J. F.; Hias, N.; Bulcke, J. V. D.; Keulemans, W.; Steppe, K., 2018: The effect of polyploidization on tree hydraulic functioning. American Journal of Botany, 10: 161-171. https://doi.org/10.1002/ajb2.1032
9. Gardner, D. J., 1996: Application of the Lifshitz – van der Waals acid – base approach to determine wood surface tension components. Wood and Fiber Science, 28 (4): 422-428.
10. Hansmann, C.; Stingl, R.; Teischinger, A., 2009: Inquiry in beech wood processing industry concerning red heartwood. Wood Research, 54 (3): 1-12.
11. Hörnfeldt, R.; Drouin, M.; Woxblom, L., 2010: False heartwood in beech *Fagus sylvatica*, Birch *Betula pendula*, *B. papyrifera* and ash *Fraxinus excelsior* – an overview. Ecological Bulletins, 53: 61-76. http://www.jstor.org/stable/41442020
12. Hubbe, M. A.; Gardner, D. J.; Shen, W., 2015: Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies. BioResources, 10 (4): 8657-8749. https://doi.org/10.15376/biores.10.4.hubbe_gardner_shen
13. Jankowska, A.; Boruszewski, P.; Drożdżek, M.; Rębkowski, B.; Kaczmarczyk, A.; Skowrońska, A., 2018: The role of extractives and wood anatomy in the wettability and free surface energy of hardwoods. BioResources, 13 (2): 3082-3097. https://doi.org/10.15376/biores.13.2.3082-3097
14. Kloubek, J., 1974: Calculation of surface free energy components of ice according to its wettability by water, chlorbenzene and carbon disulfide. Journal of Colloid and Interface Science, 46: 185-190. https://doi.org/10.1016/0021-9797(74)90001-0
15. Koch, G., 2004: Eigenheiten des rotkernigen Buchenholzes – Institut für Holzbiologie and Holzschutz, Bundesforschungsanstalt für Forst- und Holzwirtschaft. http://www.buchenzentrum.de/pdfs/rotkern_koch_ef_2004.pdf (Accessed May 10, 2023).
16. Kúdela, J., 2011: Beech wood, its importance and utilization. In: Buk a bukové ekosystémy Slovenska, 1st ed. VEDA, Bratislava, pp. 527-552.
17. Kúdela, J.; Čunderlík, I., 2012: Beech wood – structure, properties and use. Zvolen, Technical University at Zvolen, pp. 152 (in Slovak).

18. Kúdela, J., 2014: Wetting of wood surface by liquids of a different polarity. Wood Research, 59 (1): 11-24.
19. Kúdela, J.; Wesserle, F.; Bakša, J., 2015: Influence of moisture content of beech wood on wetting and surface free energy. Acta Facultatis Xylologiae Zvolen, 57 (1): 25-35.
20. Kúdela, J.; Javorek, L.; Mrenica, L., 2016: Influence of milling and sanding on beech wood surface properties. Part II. Wetting and thermo-dynamical characteristics of wood surface. Annals of Warsaw University of Life Sciences – SGGW Forestry and Wood Technology, 95: 154-158.
21. Kúdela, J.; Reiprecht, L.; Vidholdová, Z.; Andrejko, M., 2019: Surface properties of beech wood modified by CO_2 laser. Acta Facultatis Xylologiae Zvolen, 61 (1): 5-18. https://doi.org/10.17423/afx.2019.61.1.01
22. Kúdela, J.; Kubovský, I.; Andrejko, M., 2022: Influence of irradiation parameters on structure and properties of oak wood surface engraved with a CO_2 laser. Materials, 15: 8384. https://doi.org/ 10.3390/ma15238384
23. Liptáková, E.; Kúdela, J., 1994: Analysis of the wood – wetting process. Holzforschung, 48 (2): 139-144. https://doi.org/10.1515/hfsg.1994.48.2.139
24. Liptáková, E.; Kúdela, J.; Sarvaš, J., 1998: Problems concerning equilibrium state on the phase boundary wood liquid material. In: Proceedings of 3rd IUFRO Symposium Wood structure and Properties 98. Slovakia, September, pp. 109-114.
25. Nečesaný, V., 1958: Jádro buku: struktura, vznik a vývoj. Bratislava, Slovak Academy of Sciences, pp. 231.
26. Neumann, A. W.; Good, R. J.; Hoppe, C. J.; Sejpal, M., 1974: An equation of state approach to determine surface tensions of low-energy solids from contact angles. Journal of Colloid and Interface Science, 49 (2): 291-303. https://doi.org/10.1016/0021-9797(74)90365-8
27. Paclt, J., 1953: Štúdia o nepravom jadre buka. Bratislava, IV. – V. Biológia, 8: 255-262.
28. Piao, C.; Winandy, J. E.; Shupe, T. F., 2010: From hydrophilicity to hydrophobicity: a critical review. Part I: Wettability and surface behavior. Wood and Fiber Science, 42 (4): 490-510.
29. Požgaj, A.; Chovanec, D.; Kurjatko, S.; Babiak, M., 1993: Štruktúra a vlastnosti dreva. Bratislava, Príroda, pp. 485.
30. Pöhler, E.; Klingner, R.; Künniger, T., 2006: Beech (*Fagus sylvatica* L.) – Technological properties, adhesion behaviour and colour stability with and without coatings of the red heartwood. Annals of Forest Science, 63: 129-137. https://doi.org/10.1051/forest:2005105
31. Prka, M.; Zečić, Ž.; Krpan, A. P. B.; Vusić, D., 2009: Characteristics and share of European beech false heartwood in felling sites of central Croatia. Croatian Journal of Forest Engineering, 30 (1): 37-49.
32. Qin, Z.; Chen, H.; Gao, Q.; Zhang, S.; Li, J., 2015: Wettability of sanded and aged fast-growing poplar wood surfaces: I. surface free energy. BioResources, 10 (1): 1008-1023. https://doi.org/10.15376/biores.10.1.1008-1023
33. Račko, V.; Čunderlík, I., 2006: Qualitative and quantitative evaluation of false heartwood in beech logs of various age and qualitative structure. Wood Research, 51 (3): 1-10.
34. Račko, V.; Čunderlík, I., 2010: Zrelé drevo ako limitujúci faktor vzniku nepravého jadra buka (*Fagus sylvatica* L.). Acta Facultatis Xylologiae Zvolen, 52 (1): 15-24.
35. Scheikl, M.; Wålinder, M.; Pichelin, F.; Dunky, M., 2001: Bonding process. In: Wood Adhesion and Glued Products, COST Action E13, State of the Art – Report, pp. 172.
36. Schwarze, F. W. M. R.; Engels, J., 1998: Cavity formation and the exposure of peculiar structures in the secondary wall (S2) of tracheids and fibres by wood degrading basidiomycetes. Holzforschung, 52 (2): 117-123. https://doi.org/10.1515/hfsg.1998.52.2.117
37. Shigo, A. L., 1986: A new tree biology dictionary: Facts, photos, and philosophies on trees and their problems and proper care. United States of America, Shigo and Trees., pp. 132.
38. Slováčková, B.; Mišíková, O., 2023: Observing the structure diversity of historic heirloom apple tree (*Malus domestica* Borkh.) wood in Central Slovakia. Diversity, 15 (1): 15. https://doi.org/10.3390/d15010015
39. Srebotnik, E.; Messner, K., 1994: A simple method that uses differential staining and light microscopy to assess the selectivity of wood delignification by white rot fungi. Applied and Environmental Microbiology, 60 (4): 1383-1386. https://doi.org/10.1128/aem.60.4.1383-1386.1994
40. Štrbová, M.; Wesserle, F.; Kúdela, J., 2013: Contact angle measurement on wood by drop shape analysis. In: Proceeding of Science for Sustainability International Conference for PhD Students, University of West Hungary, Györ.
41. van Oss, C. J.; Good, R. J.; Chaudhury, M. K., 1998: Additive and nonadditive surface tension components and the interpretation of contact angles. Langmuir, 4 (4): 884-891. https://doi.org/10.1021/la00082a018

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