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# Sadržaj
# Contents

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# Heat-Treated Wood Reinforced High Density Polyethylene Composites

## Kompoziti visoke gustoće na bazi polietilena ojačani toplinski modificiranim drvom

**ABSTRACT** • *This study investigated the effect of untreated and heat-treated ash and black pine wood flour concentrations on the selected properties of high density polyethylene (HDPE) composites. HDPE and wood flour were used as thermoplastic matrix and filler, respectively. The blends of HDPE and wood flour were compounded using single screw extruder and test samples were prepared through injection molding. Mechanical properties like tensile strength (TS), tensile modulus (TM), elongation at break (EatB), flexural strength (FS), flexural modulus (FM) and impact strength (IS) of manufactured composites were determined. Wood flour concentrations have significantly increased density, FS, TM and FM and hardness of composites while reducing TS, EatB and IS. Heat-treated ash and black pine flour reinforced HDPE composites had higher mechanical properties than untreated ones. Composites showed two main decomposition peaks; one coming from ash wood flour (353-370 °C) and black pine wood flour (373-376 °C), the second one from HDPE degradation (469-490 °C). SEM images showed improved dispersion of heat-treated ash and black pine wood flour. The obtained results showed that both the untreated and heat-treated ash/black pine wood flour have an important potential in the manufacture of HDPE composites.*

*Keywords: HDPE; wood flour; thermal modification; heat treatment; polymer composite*

**SAŽETAK** • *U radu je opisano istraživanje utjecaja koncentracije drvnog brašna od nemodificiranog i toplinski modificiranog drva jasena i crnog bora na odabrana svojstva kompozita visoke gustoće na bazi polietilena (HDPE). HDPE i drvno brašno upotrijebljeni su kao termoplastična matrica i punilo. Mješavine HDPE-a i drvnog brašna pripremljene su uz pomoć ekstrudera s jednim vijkom, a ispitni su uzorci izrađeni injekcijskim prešanjem. Istraživanjem su određena mehanička svojstva proizvedenih kompozita poput vlačne čvrstoće (FS), modula elastičnosti pri vlačnom ispitivanju (FM), istezanja pri lomu (EatB), čvrstoće na svijanje (FS), modula elastičnosti pri tlačnom ispitivanju (FM) i udarne čvrstoće (IS). Koncentracije drvnog brašna značajno su povećale gustoću, tvrdoću, FS, TM i FM, a smanjile TS, EatB i IS. HDPE kompoziti ojačani drvnim brašnom od toplinski modificiranog drva jasena i crnog bora imali su bolja mehanička svojstva od kompozita ojačanih drvnim brašnom od nemodificiranog drva jasena i crnog bora. Kompoziti su pokazali dva glavna područja razgradnje: prvo, razgradnju drvnog brašna drva ariša (353 – 370 °C) i drvnog brašna drva crnog bora (373 – 376 °C) te, drugo, razgradnju HDPE-a (469 – 490 °C). SEM slike potvrdile su poboljšanu raspodjelu drvnog brašna od toplinski modificiranog drva jasena i crnog bora. Rezultati su pokazali da drvno brašno od nemodificiranoga i toplinski modificiranog drva jasena i crnog bora imaju velik potencijal u proizvodnji HDPE kompozita.*

*Ključne riječi: HDPE; drvno brašno; toplinska modifikacija; toplinski tretman; polimerni kompoziti*

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## 1 INTRODUCTION
1. UVOD

Polymer composites can be manufactured using polymer matrix such as polyethylene, polystyrene, polypropylene and polyvinyl chloride and organic filler (wood fiber, wood flour and agricultural residues) or inorganic filler (talc, mica, calcium carbonate). Recently, the use of organic fillers has been increased due to many advantages such as low cost, low density, high specific properties, non-abrasive nature, renewability, biodegradability and availability. Therefore, several studies were conducted to manufacture polymer composites using organic fillers including wood flour, wheat straw, nutshell flour, sunflower stalk, flax, jute, sisal, bagasse, ramie and kapok (Yang *et al.*, 2005; Mengeloglu and Karakus, 2008; Kaymakci *et al.*, 2013; Donmez Cavdar *et al.*, 2014; Aydemir *et al.*, 2015). Some of the studies focused on industrial products and they have been applied in industrial fields such as outdoor furniture, automobile parts, structural panels, etc. Wood, as organic filler, is the most feasible material to produce the polymer composites. However, because of the moisture absorption in wood, as all organic fillers, it suffers a number of disadvantages. Poor resistance against fungal and insect attack, swelling, and shrinkage resulting from water absorption and desorption are some of these shortcomings. Many studies have been carried out to improve the unfavorable properties of wood (Kaboorani *et al.*, 2008; Arwinfar *et al.*, 2016). These include chemical and thermal modifications. Chemical modification of wood itself can be done, for example, by acetylation with acetic anhydride (Cetin and Ozmen, 2011; Ozmen *et al.*, 2013), acetyl chloride, or isopropenyl acetate, which are usually coated on the surface of wood fibers. Others are chemical modifications such as surface treatments, corona or plasma discharge, and enzymatic treatment (Follrich *et al.*, 2010; Aragal *et al.*, 2012). The chemical modifications only provide an improvement on the surface of materials used and their outdoor performances are generally not good enough in application areas. Heat treatment of wood, called thermal modification, has been reported to be an effective method to provide a sustainable improvement of the physical properties such as dimensional stability and/or durability of wood. Many researchers have used heat treatment process to improve wood properties (Yildiz *et al.*, 2006; Shi *et al.*, 2007; Gunduz and Aydemir, 2009; Kabir *et al.*, 2012; Segerholm, 2012; Li *et al.*, 2013; Boruvka *et al.*, 2015). Heat treatment of wood reduces hydrophilicity of wood. In addition, heat treatment modifies the polar nature of wood possibly resulting in better compatibility between wood and the polymer matrix, thus leading to high quality and thermally stable composites. The changes in wood chemistry can be utilized to improve compatibility between wood and the polymer matrix (Aragal *et al.*, 2012). Some studies focused on the use of the heat-treated wood in the production of polymer composites (Aydemir *et al.*, 2015; Kaboorani *et al.*, 2008; Arwinfar *et al.*, 2016; Kaboorani and Faezipour, 2009; Aydemir *et al.*, 2019); however, the literature data on the properties of polymer composites with heat-treated wood is scarce.

The aim of this study was to evaluate the effect of heat-treated/untreated ash wood and black pine wood flour concentrations on the selected properties of high density polyethylene (HDPE) composites. Density, hardness, tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus and impact strength properties and thermogravimetric analyzer (TGA), scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis were studied.

## 2 MATERIALS AND METHODS
2. MATERIJALI I METODE

### 2.1 Materials
2.1. Materijali

High density polyethylene (HDPE-I-668) was supplied by PETKIM Inc. in Turkey. HDPE has a density of 0.96 g/cm³, melting point of 134 °C, MFI/230 °C/ 2.16 kg = 0.36 g/10 min. Untreated and heat-treated (at 212 °C for 3 h under water vapor) ash (*Fraxinus excelsior* L.) and black pine (*Pinus nigra* Arn.) woods were supplied from NovaWood Inc. in Turkey. The densities of untreated ash and black pine wood were 0.70 g/cm³ and 0.50 g/cm³ and after thermal treatment, the densities changed to 0.65 g/cm³ and 0.47 g/cm³, respectively. All wood types were grounded with a lab-type grinder, and the size of the filler for both untreated and heat-treated wood flour was 80 mesh.

### 2.2 Processing of polymer composite materials
2.2. Priprema kompozita

The experimental design of the study is presented in Table 1. During the manufacturing process, depending on the formulation, the high density polyethylene (HDPE), untreated and heat-treated ash and black pine wood flours, as fillers, were mixed in a high intensity mixer to produce homogeneous blend. The blends were compounded in a laboratory scale single screw extruder (TTB, Tecnomatic Inc, Turkey) at 40 rpm screw speed. Temperatures were set at 180 °C from feed zone to die zone. Extruded samples were collected, cooled and granulated into pellets. The pellets were then oven-dried at 80 °C for 24 h and stored in sealed plastic bags for injection molding. The pellets were injection molded into tensile, flexural test samples using an HDX-88 injection molding machine at a barrel temperature of between 180 °C and 200 °C (injection pressure: 100 bar, injection speed: 80 mm/sec., screw speed: 40 rpm, cooling time about 30 s).

### 2.3 Density
2.3. Gustoća

Density of the manufactured polymer composites were determined using water displacement technique and analyzed utilizing central composite design (CCD) (ASTM D792-13).

### 2.4 Mechanical properties
2.4. Mehanička svojstva

To evaluate the effect of heat-treated and untreated wood flours on the mechanical, thermal and morphological properties of HDPE composites, testing of

**Table 1** Experiment design
**Tablica 1.** Plan eksperimenta

| ID | HDPE, % | Untreated wood flour, % *Nemodificirano drvno brašno, %* | | Heat-treated wood flour, % *Toplinski modificirano drvno brašno, %* | |
|---|---|---|---|---|---|
| | | Ash wood *Drvo jasena* | Black pine wood *Drvo crnog bora* | Ash wood *Drvo jasena* | Black pine wood *Drvo crnog bora* |
| Control *Kontrolni uzorci* | 100 | | | | |
| UAC1 | 90 | 10 | | | |
| UAC2 | 80 | 20 | | | |
| UAC3 | 70 | 30 | | | |
| TAC1 | 90 | | | 10 | |
| TAC2 | 80 | | | 20 | |
| TAC3 | 70 | | | 30 | |
| UBPC1 | 90 | | 10 | | |
| UBPC2 | 80 | | 20 | | |
| UBPC3 | 70 | | 30 | | |
| TBPC1 | 90 | | | | 10 |
| TBPC2 | 80 | | | | 20 |
| TBPC3 | 70 | | | | 30 |

the flexural, tensile and notched impact properties were conducted in a climate-controlled testing laboratory. Flexural properties such as flexure strength (*FS*) and flexure modulus (*FM*) were determined in accordance with ASTM D 790. The flexural specimens (4×15×160 mm) with 80 mm span length were tested in the three points loading with a crosshead speed of 2 mm/min on a Zwick Roell Z010 Universal testing machine. The same instrument was also used for the tensile testing. Tensile properties, such as tensile strength (*TS*) and tensile modulus (*TM*), were conducted according to ASTM D 638. Samples (4 mm × 18.6 mm × 165 mm) were tested at a crosshead speed of 5 mm/min. The tensile modulus of the samples was taken as the slope of the curve at stress levels between 0.05 % and 0.2 %. Notched impact tests (sample dimension was 4 mm × 15 mm × 50 mm) were performed according to ASTM D 256. The notches were added using a Polytest notching cutter by RayRan and notched samples were tested on a HIT5.5P impact testing machine, manufactured by Zwick. Six specimens prepared according to the applicable standards were used in all mechanical testing.

## 2.5 Hardness
2.5. Tvrdoća

Inspired by the Shore-D method, the hardness property of specimens was tested according to ASTM D 2240. Six specimens with dimension of 50 mm × 13 mm × 5 mm were tested for each composite formulation.

## 2.6 Thermogravimetric analysis (TGA)
2.6. Termogravimetrijska analiza (TGA)

Thermogravimetric analysis (TGA) measurements were carried out using Shimadzu TGA-50 on samples of about 10 mg. Each sample was scanned over a temperature range from room temperature to 700 °C at a heating rate of 10 °C/min under nitrogen with a flow rate of 20 ml/min to avoid sample oxidation. Three samples randomly picked from the ground test specimens were used.

## 2.7 Scanning electron microscope (SEM) analysis
2.7. Pretražna elektronska mikroskopija (SEM)

The fractured surface of the samples was also studied by using Tescan MAIA3 XMU scanning electron microscope. All SEM characterization was conducted on the fractured section of the tensile test samples. The samples were first dipped into liquid nitrogen and snapped to half to prepare the fractured surfaces.

## 2.8 X-ray diffraction (XRD)
2.8. Rendgenska difrakcija (XRD)

XRD was performed with a high resolution X-ray diffractometer (Model XPert PRO, Philips PANalytical, Netherlands) with Ni-filtered Cu Ka (1.540562 Å) radiation source operated at 45 kV voltage and 40 mA electric current. The samples were scanned from 5° to 40° 2θ range with a step of 0.02° and a step time of 2.5 s. A silicon zero-background plate was used to make sure there was no peak associated with the sample holder. The same sample holder and the same position of the holder were used for all tests. The crystallinity index (*CI*) of the powdered samples was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved X-ray scattering curve (Rabiej, 2003). Three specimens for each test were scanned with XRD. *CI* values were found using Eq. 1:

$$CI \ (\%) = \frac{\sum A_c}{\sum (A_c + A_a)} \qquad (1)$$

Where $A_c$ is the integrated area underneath the respective crystalline peaks, and $A_a$ is the integrated area of the amorphous halo.

## 2.9 Statistical analysis
2.9. Statistička analiza

Design-Expert® Version 7.0.3 statistical software program was used for statistical analysis. The effects of wood concentration on the physical, mechanical, thermal and morphological properties of the

obtained samples were evaluated. All samples were analyzed with the one-way variance analysis (ANOVA), and then Duncan test was applied to determine whether the samples differed significantly among the groups. All statistical analysis was conducted at 99 % significance level ($p < 0.01$).

## 3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

### 3.1 Densities, hardness (Shore D) and mechanical properties
3.1. Gustoća, tvrdoća (Shore D) i mehanička svojstva

Densities in the range of 0.87-0.93 g/cm³ were measured based on heat-treated/untreated ash wood flour concentrations in polymer composites. Density variations in HDPE composites are presented in Table 2. Density of polymer composites manufactured with the addition of 10 % ash wood flour was decreased. Density of the ash wood flour reinforced HDPE composites was increased with the other wood concentrations. However, the increases in the density of the composites were found to be not statistically significant and their densities exhibited similar results.

Densities in the range of 0.87-0.93 g/cm³ were measured based on heat-treated/untreated black pine wood concentrations in polymer composites. The densities of black pine wood reinforced HDPE composites, similar to density of ash wood flour reinforced HDPE composites, were firstly decreased with the addition of 10 % black pine wood but then were increased with the addition of other wood concentrations. Compared to heat-treated and untreated black pine wood, densities of the composites were found to have similar results. Wood flour is a compressible material and the density of the wood cell wall is about 1.44-1.50 g/cm³ (Kellog, 1981). The porous anatomy of the solid wood results in overall densities of about 0.32-0.72 g/cm³, when dry (Simpson and TenWolde, 1999). However, the high pressures found during plastics processing can collapse the hollow fibers that comprise the wood flour or fill them with the molecular weight additives and polymers. Consequently, adding wood fibers to commodity plastics increases their density (Simpson and TenWolde, 1999). Increased density of the thermoplastic composites with lignocellulosic filler was also reported by Rosa *et al.* (2009).

The effect of both heat-treated/untreated wood and wood concentration on the hardness (Shore D) of wood reinforced HDPE composites is shown in Table 2. The results showed that hardness of polymer composites manufactured with the addition of 10 % heat-treated/untreated ash wood flour was decreased but the addition of other wood concentration did not provide a significant change in the hardness of HDPE composites. It is believed that hardness properties of wood reinforced HDPE composites decreased due to density of

**Table 2** Duncan test results and standard deviation of density, hardness (shore D) and mechanical properties of neat HDPE and composites
**Tablica 2.** Rezultati Duncanova testa i standardne devijacije gustoće, tvrdoće (Shore D) i mehaničkih svojstava čistog HDPE-a i kompozita

| Samples Uzorci | d, g/cm³ | Shore-D | TS, MPa | TM, MPa | EatB, % | FS, MPa | FM, MPa | IS, kJ/m |
|---|---|---|---|---|---|---|---|---|
| Control Kontrolni uzorci | 0.93 A (±0.1) | 65 AB (±2) | 20 D (±0.1) | 580 F (±12) | 460 F (±2) | 40 G (±0.2) | 1750 G (±22) | 5 G (±0.5) |
| UAC1 | 0.87 A (±0.1) | 63 A (±1) | 20 D (±0.2) | 429 AB (±19) | 34 D (±9) | 30 AB (±0.5) | 996 A (±35) | 15 F (±0.7) |
| UAC2 | 0.90 A (±0.1) | 65 AB (±3) | 19 B (±0.3) | 452 AB (±18) | 18 C (±4) | 32 D (±0.5) | 1186 B (±10) | 12 D (±0.6) |
| UAC3 | 0.92 A (±0.1) | 66 B (±6) | 18 A (±0.3) | 513 CD (±28) | 10 A (±1) | 34 E (±0.6) | 1359 D (±54) | 10 C (±0.7) |
| TAC1 | 0.88A (±0.1) | 63 A (±1) | 22 F (±0.2) | 458B (±11) | 33 D (±5) | 31 C (±0.6) | 1136 B (±33) | 12 D (±0.8) |
| TAC2 | 0.91 A (±0.1) | 65 B (±5) | 22 F (±0.3) | 524 D (±14) | 12 AB (±2) | 35 F (±0.2) | 1470 E (±22) | 9 C (±0.2) |
| TAC3 | 0.92A (±0.1) | 65 B (±3) | 21EF (±0.2) | 594 E (±34) | 9 A (±1) | 39 G (±1.4) | 1726 G (±39) | 8 B (±0.5) |
| UBPC1 | 0.87 A (±0.1) | 63 A (±1) | 21 EF (±0.1) | 422 A (±19) | 33 D (±6) | 30 A (±0.6) | 1058 A (±40) | 16 F (±0.8) |
| UBPC2 | 0.89 A (±0.1) | 65 B (±4) | 20 D (±0.1) | 455 AB (±24) | 19 C (±3) | 30 BC (±0.7) | 1137 B (±50) | 13 E (±0.5) |
| UBPC3 | 0.93 A (±0.1) | 67 C (±6) | 19 C (±0.2) | 575 E (±43) | 8 A (±1) | 35 F (±0.4) | 1604 F (±81) | 10 C (±0.9) |
| TBPC1 | 0.87 A (±0.1) | 64 A (±3) | 21 E (±0.1) | 448 AB (±14) | 42 E (±5) | 29 A (±0.3) | 1020 A (±12) | 12 D (±0.4) |
| TBPC2 | 0.90 A (±0.1) | 65 B (±2) | 20 D (±0.2) | 490C (±21) | 16 BC (±2) | 33 D (±0.1) | 1261 C (±26) | 9 C (±0.7) |
| TBPC3 | 0.93 A (±0.1) | 67 C (±9) | 19 B (±0.1) | 566 E (±29) | 8 A (±1) | 36 F (±0.2) | 1623 F (±26) | 7 A (±0.3) |

polymer composites manufactured with the addition of 10 % wood flour. The lowest and highest hardness was determined as about 63 for the UAC1, TAC1, UBPC1 and TBPC1 and as 67 for the TBPC3, respectively. The hardness of HDPE composites showed that the filler concentration has a more important impact than heat treatment. Heat-treated ash and black pine wood flour reinforced HDPE composites had a positive effect on hardness. Consequently, the heat treatment did not provide any improvement to the hardness with the filler concentration of 10 % and 30 %. Similar results for wood reinforced polymer composites were also observed by Hua *et al.* (2011), Kord (2011), Medupin *et al*. (2013) and Sathishkumar (2014).

The obtained data for the *TS* of neat HDPE and the composites are presented in Table 2. Tensile strength (*TS*) of HDPE composites manufactured using untreated ash wood flour was 20 MPa, 20 MPa, 19 MPa and 18 MPa for 0 %, 10 %, 20 % and 30 % wood concentration, respectively. Adding untreated ash did not provide a significant increase in the tensile strength of HDPE composites and the tensile strength of HDPE composites was reduced by untreated ash wood flour concentration ($p<0.01$). This reduction might be caused by the poor adhesion between hydrophilic filler wood and hydrophobic PE matrix. Reduced *TS* values due to the lack of compatibility between filler and polymer were also reported by others (Alsewailem and Binkhder, 2014; Obasi, 2015). The addition of heat-treated ash wood flour into neat HDPE generally improved the tensile strength ($p<0.01$). In the studied heat-treated wood concentration range, the addition of more heat-treated wood into HDPE composites provided higher *TS* values as compared to composites manufactured with untreated ash wood. Arwinfar *et al.* (2016) also reported that the addition of heat-treated wood into polymer matrix increased tensile strength. Tensile strength (*TS*) of HDPE composites manufactured using untreated black pine wood was 20 MPa, 21 MPa, 20 MPa and 19 MPa for 0 %, 10 %, 20 % and 30 % wood concentration, respectively (Table 2). The tensile strength of HDPE composites manufactured with the addition of 10 % heat-treated/untreated black pine wood was increased but the addition of more wood concentration into HDPE matrix did not provide any improvement in *TS*. It is believed that tensile properties of wood reinforced HDPE composites was decreased due to density of polymer composites manufactured with the addition of 10 % wood flour. Similar results were also reported by Robin and Breton (2001). It can be said that wood species exhibited a different effect on the tensile strength of the polymer composites. However, adding untreated ash and black pine wood flour did not provide a significant improvement in the similar tensile strength. Tensile strength of untreated and heat-treated black pine wood reinforced composites generally exhibited similar results and it can be said that both heat-treated and untreated black pine wood did not have a significant effect on the tensile strength.

In the case of tensile modulus (*TM*), adding untreated and heat-treated wood flour to neat HDPE gen-erally has not a significant effect on *TM,* and *TM* of all HDPE composites was lower than neat HDPE expected for TAC3; *TM* of HDPE composites was significantly increased while heat-treated and untreated ash wood flour concentration was increased from 10 % to 30 % ($p<0.01$). The obtained data for *TM* of ash wood flour reinforced HDPE composites is presented in Table 2. HDPE composites manufactured using heat-treated ash wood flour showed higher *TM* than untreated ash wood flour. Heat-treated ash wood flour had a positive effect on *TM*. Similar to *TM* of ash wood flour reinforced HDPE composites, *TM* was significantly increased by untreated and heat-treated black pine wood concentration ($p<0.01$). Heat-treated black pine wood reinforced composite showed higher *TM* than untreated ones. Wood species did not have a significant effect on the tensile modulus of the composites and *TM* of all HDPE composites was found to be lower than its neat HDPE. In conclusion, the *TM* of HDPE composite reinforced with both heat-treated/untreated ash and black pine wood flours was increased with wood concentrations. Similar results were also reported by Robin and Breton (2014) and Kaboorani *et al*. (2008).

The results for elongation at break (*EatB*) values can be seen in Table 2. Both ash and black pine wood flour concentrations had a negative effect on *EatB* of HDPE polymer composites ($p<0.01$), respectively and *EatB* values were generally reduced with the increased concentration of ash and black pine wood flour due to increasing stiffness of the composites. As a result, the elongation at break values reduced with adding both untreated and heat-treated wood flour. The elongation at break decreased from 460 % to 10 % and 9 % for untreated and heat-treated ash wood flour concentration, and 8 % for untreated and heat-treated black pine wood flour, increasing from 0 to 30 wt% in neat HDPE, respectively. Usually in the composites, lower elongation at break values was observed with increased modulus (Mengeloglu and Karakus, 2008 and 2008a).

The results of the flexural strength (*FS*) are presented in Table 2. The *FS* values of HDPE polymer composites were significantly increased by untreated and heat-treated ash wood flour concentration (p<0.01), but the *TM* of all composites was found to be lower than its neat HDPE. HDPE composites manufactured using heat-treated ash wood flour generally showed higher *FS* than when using untreated ash wood flour. Adding heat-treated ash wood flour generally had a positive effect on *FS*. Similar to *FS* of ash wood flour reinforced HDPE composites, *FS* was significantly increased by heat-treated and untreated black pine wood concentration ($p<0.01$), but the *FS* of all composites was found to be lower than its neat HDPE. Heat-treated black pine wood reinforced composites generally provided higher *FS* than the composites with untreated ones, and *FS* values of all HDPE composites were found to be similar to each other. The addition of heat-treated wood flour in composites had a positive effect on *FS,* but the addition of untreated and heat-treated wood flour did not improve *FS* of neat HDPE, and all *FS* values of the composites were found to be lower

than *FS* of neat HDPE. Wood species generally did not have a significant effect on the *FS* of HDPE composites. As a result, the *FS* of HDPE composite reinforced with both heat-treated/untreated ash and black pine wood flour was increased with wood concentrations. Composites produced with 30 % heat-treated ash and black pine wood flour provided significantly higher *FS* values compared to other composites. In previous studies, the effects of different lignocellulosic fillers on selected properties of polymer composites were investigated and it is reported that flexural strength of the polymer composites was increased with increasing lignocellulosic filler content (Kiziltas *et al.,* 2014; Donmez Cavdar *et al.,* 2015). For polyolefin-based plastic lumber decking boards, ASTM D 6662 (2001) standard requires the minimum *FS* of 6.9 MPa (1.000 psi). All composites produced in this study provided *FS* values (29.68-33.87 MPa and 31.12-38.59 MPa) for heat-treated and untreated ash wood flour, respectively, and (29.52-35.24 MPa and 29.36-35.57 MPa) for untreated and heat-treated black pine wood, respectively, that are well over the requirement by the standard.

A similar trend in *FS* was observed for flexural modulus (*FM*) as shown in Table 2. Both heat-treated and untreated ash and black pine wood flour concentration had a significant effect on *FM* of HDPE composites ($p<0.01$ and $p<0.01$, respectively). The presence of both untreated/heat-treated ash and black pine wood flour improved *FM* values, however *FM* values of all HDPE composites were found to be lower than *FM* of neat HDPE. ASTM D 6662 (2001) standard requires the minimum *FM* of 340 MPa (50.000 psi) for polyolefin-based plastic lumber decking boards. All composites produced in this study provided *FM* values of 996-1359 MPa and 1136-1726 MPa for untreated and heat-treated ash wood flour, respectively, and 1058-1604 MPa and 1020-1623 MPa for untreated and heat-treated black pine wood, respectively. These values are well over the required standards.

The results for impact strength (*IS*) are presented in Table 2. The results showed that IS of the composites manufactured with the addition of 10 % heat-treated/untreated ash and black pine wood flour was increased, but it was decreased with the addition of more wood concentration into neat HDPE. Both untreated/heat-treated ash and black pine wood flour concentration had a significant effect on IS of HDPE composites ($p<0.01$). Generally, with the rise of both untreated/heat-treated ash and black pine wood flour concentration, IS values were decreased. HDPE polymer composites manufactured using untreated ash and black flour pine wood

showed higher IS than heat-treated ones. Similar results were also reported by Aydemir *et al.* (2015) and Huang *et al.* (2012). They found that the increase in *IS* occurred because adding wood flour played an important role in strengthening and enhanced two-phase interface area interaction of the composite. However, while wood flour concentrations increased, interface compatibility was a major problem. Thus, impact strength of the wood polymer composites was found to decrease by Huang *et al.* (2012) and Tisserat *et al.* (2013). Boonstra *et al.* (2007) found that heat treatment decreases the impact strength of the wood due to the significantly lower density of the treated specimens, and therefore it can be said that neither heat treatment nor wood flour concentration have a significant effect on the impact strength of HDPE composites.

**3.2 Thermal and morphological properties of wood reinforced HDPE composites**
3.2. Toplinska i morfološka svojstva drvom ojačanih HDPE kompozita

The curves for thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) of HDPE composites manufactured using untreated/heat-treated ash and black pine wood flour are presented in Figure 1. The summary of thermal stability for neat HDPE, the composites with 30 % untreated ash wood flour (UAC3) and heat-treated ash wood flour (TAC3), and the composites with 30 % untreated black pine wood flour (UBPC3) and heat-treated black pine wood flour (TBPC3) are given in Table 3. Neat HDPE showed single stage degradation at the set temperature of 469 °C and total mass loss of 99 %. The TGA curves of the wood exhibit two mass loss peaks (Yang *et al.*, 2005; Karakus *et al.*, 2016). The first occurs at about 100 °C and is mainly caused by evaporation of moisture and other volatiles from the wood. The second peak, at approximately 200 °C to 400 °C, is due to the degradation of hemicelluloses, cellulose, and lignin. Hemicellulose degrades between 150 °C and 350 °C, cellulose decomposes between 240 °C and 350 °C, and lignin between 250 °C and 500 °C (Kaboorani and Faezipour, 2009; Byren and Nagle, 1997). HDPE composites provided two main decomposition peaks. The first peak of around 353-370 °C and 373-376 °C referred to ash wood and black pine wood flour reinforced HDPE composites, respectively, while the second peak came from HDPE and was around 469-490 °C. Residue after 500 °C was increased with the addition of wood concentration to HDPE matrix. The mass loss for the samples with both untreated ash and black pine wood flour at 500 °C was 93.8 % and 92.6 %, respectively.

**Table 3** Summary of thermal stability for neat HDPE and their composites
**Tablica 3.** Sažetak rezultata toplinske stabilnosti čistog HDPE-a i kompozita

| **Samples** / *Uzorci* | *T10 %*, °C | *T50 %*, °C | *T90 %*, °C | *DTGmax*, °C | **Weight loss, %** / *Gubitak mase, %* |
|---|---|---|---|---|---|
| HDPE | 449 | 481 | 499 | 491 | 99 |
| UAC3 | 303 | 441 | 493 | 486 | 94 |
| TAC3 | 356 | 475 | 503 | 489 | 95 |
| UBPC3 | 306 | 451 | 494 | 487 | 93 |
| TBPC3 | 343 | 476 | 511 | 490 | 95 |
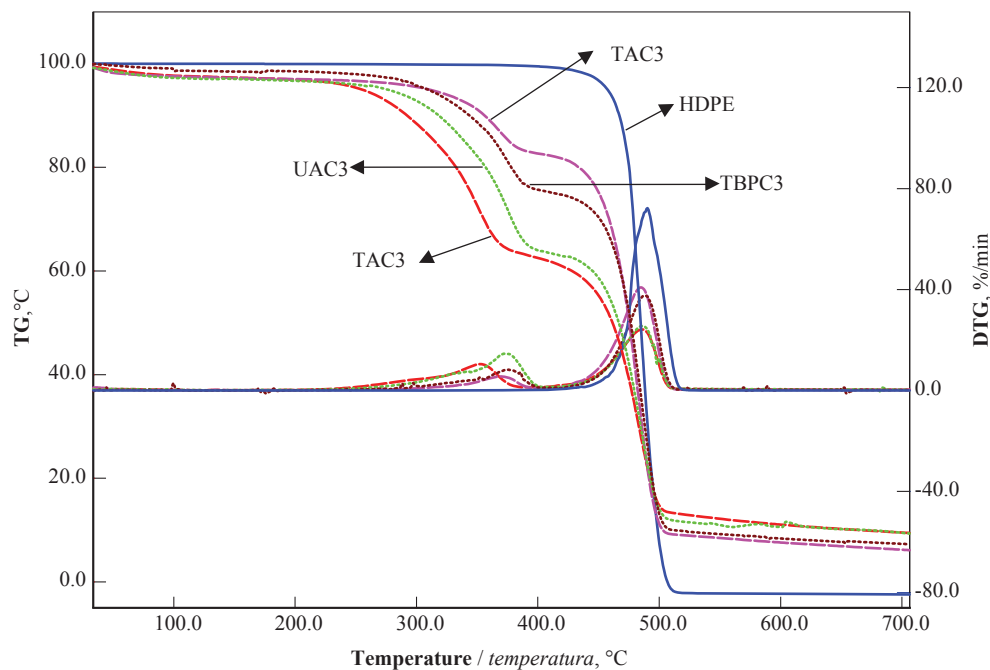
**Figure 1** TGA results of wood reinforced HDPE composites
**Slika 1.** TGA rezultati drvom ojačanih HDPE kompozita

Figure 1 also shows that the samples with untreated ash wood and heat-treated black pine wood flour exhibited higher thermal stability as compared to the samples with the heat-treated ash and untreated black pine wood flour. Thermal stability of the composites produced from heat-treated wood increased. The increase could also be attributed to better adhesion between wood and the matrix (HDPE) because the pretreatment possibly lowered the polarity of wood and made wood more compatible with the matrix. Similar results were also reported by Li *et al.* (2013).

Morphology of the untreated/heat-treated ash and black pine wood flour reinforced HDPE composites was also studied. SEM micrographs of neat HDPE, the samples with 30 % untreated ash and heat-treated ash wood flour, and the samples with 30 % untreated black pine and heat-treated black pine wood flour are given in Figure 2. Fractured surface of neat HDPE is presented in Figure 2a. Furthermore, neat HDPE exhibits ductile mode of failure. Figure 2b and 2c shows the wood fillers and their size in the samples with the heat-treated and untreated ash wood flour. The mode of failure becomes more brittle with HDPE composites with untreated wood (Ghasem, 2013; Atli *et al.*, 2018). In addition, the surfaces of the composites with untreated wood have prominent holes due to particle pull out resulting from poor adhesion (Figure 2b and 2d) (Mengeloglu and Karakus, 2012). Under tensile stress, the particles were easily pulled out from the matrix. This may mean that the interface could not effectively transfer the stress. This observation is in agreement with the lower modulus values recorded for the untreated wood composites (Table 2). Furthermore, for the heat-treated ash and black pine wood flour reinforced composites (Figure 2d and

2e), the holes are not quite prominent and particles pull out appears relatively less compared to the untreated ones. The particle surface is slightly rough and nearly uniformly dispersed and embedded within the matrix. Similar results for untreated and heat-treated wood reinforced HDPE composites were also reported by Arwinfar *et al.* (2016) and Aragal *et al.* (2012).

### 3.3 XRD Analysis of neat HDPE and wood reinforced HDPE polymer composites
3.3. XRD analiza čistog HDPE-a i drvom ojačanih HDPE kompozita

X-ray diffractograms of HDPE and its composites are presented in Figure 3. Neat HDPE and its composites showed peaks around 2θ = 22.1° and 24.50°. The peaks for the (110) and (200) planes of HDPE shifted little when the wood flour was added and an important change in the diffraction peak intensity was not observed with the presence of wood flour.

Crystallinity index (*CI*) of neat HDPE and its composites was calculated with XRD peaks. With the addition of wood flour, the *CI* changed in all the XRD. *CI* was calculated as 61.2 % for neat HDPE, 41.6 % for untreated ash wood flour reinforced HDPE polymer composites (UAC3), 44.8 % for heat treated ash wood flour reinforced HDPE composites (TAC3), 43.9 % for untreated black pine wood reinforced HDPE composites (UBPC3), and 46.2 % for heat treated black pine wood reinforced HDPE composites (TBPC3). It was determined that crystallinity of cellulose in wood increased with thermal modification. It is believed that mechanical properties of wood flour reinforced HDPE composites had a positive effect due to high crystallinity properties of polymer composites manufactured with heat treated wood. After thermal modification of wood at high temperature (at 180 °C and above), the
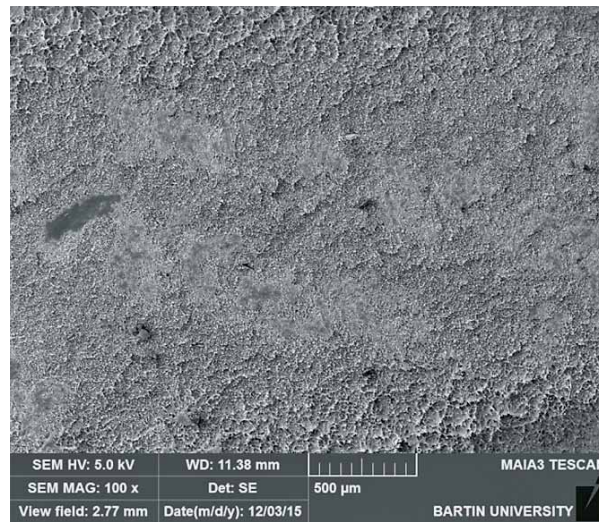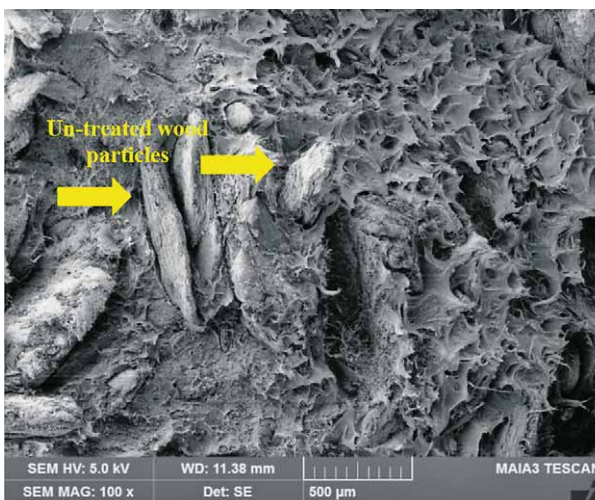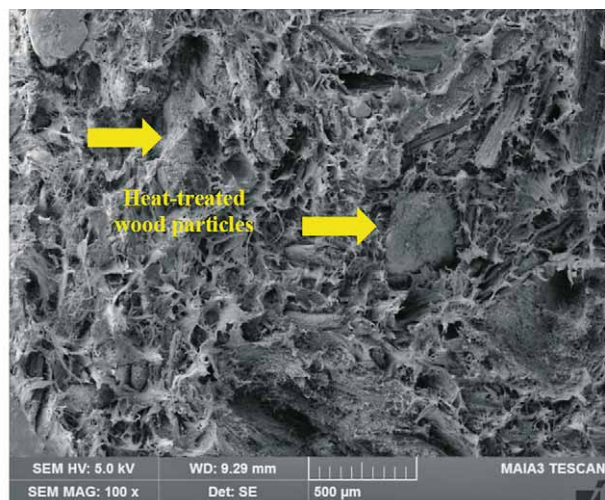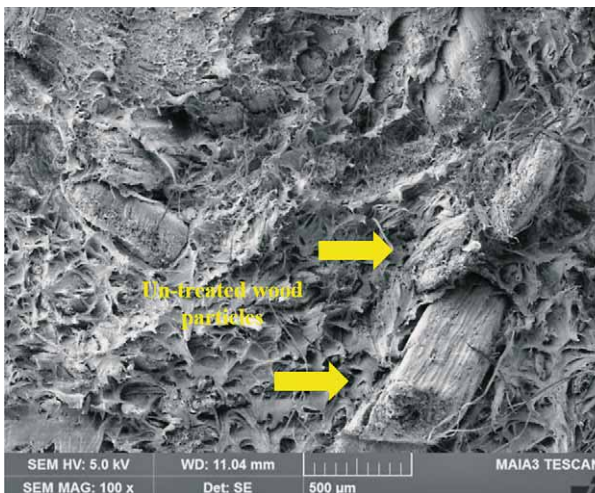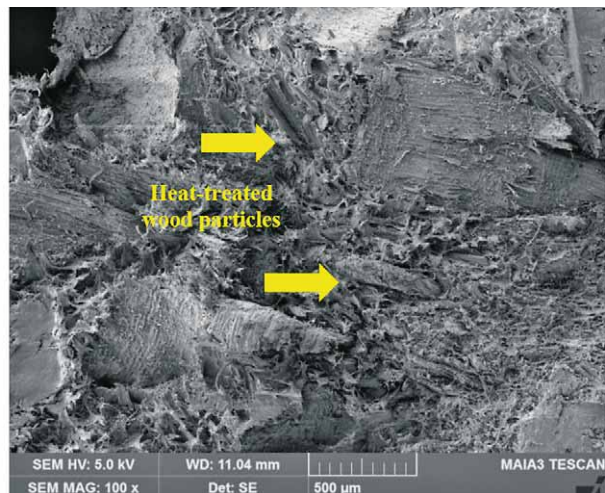
**Figure 2** SEM micrographs of (a) neat HDPE, (b) untreated ash (UAC3), (c) heat treated ash (TAC3), (d) untreated black pine (UBPC3), (e) heat treated black pine (TBPC3)
**Slika 2.** SEM mikrografije (a) čistog HDPE-a, (b) nemodificiranog drva ariša (UAC3), (c) toplinski modificiranog drva ariša (TAC3), (d) nemodificiranog drva crnog bora (UBPC3), (e) toplinski modificiranog drva crnog bora (TBPC3)

crystallinity ratio of the heat-treated wood increased slightly due to the degradation of the hemicelluloses and the crystallinity ratio of softwood was found to increase more in comparison with hardwood (Aydemir *et al.*, 2015). Consequently, it can be said that the crys-

tallinity of black pine wood increased with thermal modification more than that of ash wood and, therefore, the effect of pine wood on the mechanical properties of the composites was determined to be higher than that of ash wood.
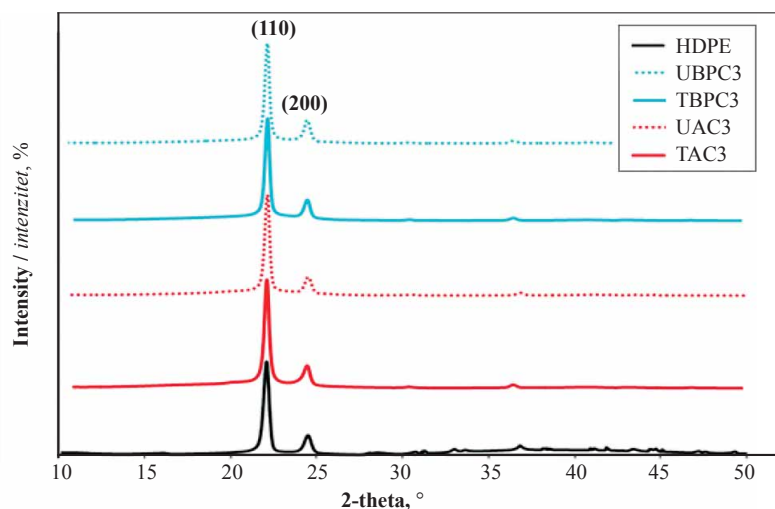
**Figure 3** X-ray diffractograms of HDPE and its composites
**Slika 3.** Rendgenski difraktogrami HDPE-a i kompozita

## 4 CONCLUSIONS
4. ZAKLJUČAK

This study evaluated the effect of untreated and heat-treated ash and black pine wood flour concentrations on the physical, mechanical, thermal and morphological properties of HDPE composites. Physical properties (density), mechanical properties (tensile, flexural, impact strength and hardness), thermal properties (TGA) and morphological properties (SEM) were determined. According to the obtained results, mechanical properties of all HDPE composites were found to be lower than those of neat HDPE. Statistical analysis showed that density, flexural strength, flexural modulus tensile modulus and hardness values of polymer composites significantly increased with the rising percentages of ash and black pine wood flour. Both heat-treated ash and black pine wood flour reinforced HDPE composites had a positive effect on hardness. Heat-treated ash and black pine wood flour reinforced HDPE composites had a positive effect on mechanical properties compared to untreated ones. The increase in wood concentration improved flexural strength, tensile modulus, flexural modulus and hardness while reducing tensile strength, elongation at break and impact strength. However, impact strength values of HDPE composites produced from heat-treated ash and black pine wood flours were slightly lower. Heat treatment had a negative effect on impact strength. HDPE showed single stage degradation while both ash and black pine wood flour reinforced HDPE composites showed a two-step mass loss thermal degradation. The first peak of around 353-370 °C and 373-376 °C referred to ash wood and black pine wood flour reinforced HDPE composites, respectively, while the second peak came from HDPE and was around 469-490 °C. Residue after 500 °C was increased with the addition of wood concentration to HDPE matrix. The crystallinity of the composites with heat-treated wood was found to be higher than that of untreated wood-HDPE composites according to the data obtained with XRD. According to the study results, it can be concluded that heat-treated wood flour can be used as an alternative raw material in the application areas of wood-HDPE composites.

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# Examining Parameters of Surface Quality Performance of Paulownia Wood Materials Modified by Thermal Compression Technique

## Ispitivanje parametara površinske kvalitete toplinski prešanog drva paulovnije

**ABSTRACT** • *The aim of this study was to evaluate the effect of thermal compression process on some surface properties of paulownia solid wood materials. The widest surface of wood samples was mechanically compressed at high temperatures. The duration was 45 min. Four different process combinations were created, including two temperatures (150 °C and 170 °C) and two pressure levels (20 bar and 22.5 bar). The surface roughness, wettability and color properties of treated and untreated samples were compared. The roughness properties, both parallel and perpendicular to grain direction, were determined according to JIS B 0601:1994 standard. The contact angle changes of water dripped to the surface were measured according to time. For color properties, a spectrophotometer was used according to CIE L\*a\*b\* system. The color changes were classified according to a grading method from literature. The most remarkable results on wettability were observed. The contact angle values significantly increased with this method. Although higher temperature increased the contact angle values, higher pressures did not change the values. When the surface roughness values were generally considered, this technique could decrease the values up to 40 % ratio according to the control group. Only the combination of 150 °C and 20 bar did not significantly change the values. Lastly, the results of color properties showed that all treatment parameters significantly affected total color change values of samples. Grading results were similar and the color change of modified samples graded as the lowest color difference, except with the combination of 150 °C and 20 bar. The combination of 170 °C and 22.5 bar (highest treatment conditions) significantly changed all color characteristics of samples, except b\* parameter. The results of this research showed that mechanical thermal compression method could change surface properties of this fast-growing species.*

*Keywords: thermal compression; paulownia; wettability; contact angle; surface roughness*

**SAŽETAK** • *Cilj ovog rada bio je procijeniti učinak toplinskog prešanja na neka površinska svojstva drva paulovnije. Najveća površina uzoraka bila je prešana pri visokim temperaturama. Prešanje je trajalo 45 minuta. Primijenjene su četiri različite kombinacije uvjeta prešanja, uključujući dvije vrijednosti temperature (150 i 170 °C)*

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*i dva različita tlaka (20 i 22,5 bara). U eksperimentu su uspoređeni hrapavost površine, kvašenje i boja prešanih i neprešanih uzoraka. Hrapavost je mjerena paralelno i okomito na smjer vlakanaca prema normi JIS B 0601:1994. Mjerena je i promjena kontaktnog kuta vode na površini u vremenu. Boja je određivana spektrofotometrom prema sustavu CIE L\*a\*b\*. Promjene boje klasificirane su primjenom klasifikacijske metode iz literature. Najveće su promjene primijećene među vrijednostima kvašenja. Vrijednosti kontaktnog kuta značajno su se povećale prešanjem. Iako je viša temperatura utjecala na povećanje vrijednosti kontaktnog kuta, veći tlakovi nisu promijenili vrijednosti kontaktnog kuta. Ako se općenito uzmu u obzir vrijednosti hrapavosti površine, upotrijebljena bi tehnika prešanja mogla smanjiti vrijednosti hrapavosti do 40 % s obzirom na kontrolne uzorke. Samo kombinacija od 150 °C i 20 bara nije znatnije promijenila ispitivane vrijednosti. Glede boje, rezultati su pokazali da su svi parametri prešanja bitno utjecali na ukupne vrijednosti promjene boje uzoraka. Rezultati ocjenjivanja boje bili su slični, a promjene boje prešanih uzoraka ocijenjene su kao najmanje, osim za kombinaciju 150 °C i 20 bara. Pogotovo je kombinacija 170 °C i 22,5 bara (najviši parametri prešanja) značajno promijenila sve parametre boje uzorka, osim parametra b\*. Rezultati ovog istraživanja pokazali su da bi metoda toplinskog prešanja mogla promijeniti površinska svojstva drva ove brzorastuće vrste.*

**Ključne riječi:** *toplinsko prešanje; paulovnija; kvašenje; kontaktni kut; hrapavost površine*

# 1 INTRODUCTION
1. UVOD

Fast-growing tree species and their wood have become more preferable in recent years. However, usage area of their wood is limited due to low characteristic features. Therefore, several modification methods have been tried to increase the characteristics of these wood species. Thermal treatments as a modification method are more widely used in commercial products because the methods can be easily applied to many wood species. The methods generally change physical and mechanical properties of material while increasing some physical properties such as stability and durability. As fast-growing species already have low mechanical properties, many studies about thermal treatments focused to modify physical properties.

As a fast growing tree species, Paulownia is a deciduous species capable of achieving very high growth rates under favorable conditions. The wood of paulownia is soft, lightweight, ring-porous, straight-grained and mostly knot-free wood with a satiny luster (Kalaycioglu *et al.*, 2004). According to Kaygin *et al.* (2015), density, hardness on every surface, bending strength and modulus of elasticity properties of paulownia (*Paulownia elongata*) were found lower than those of poplar (*Populus tremula*) and juniper (*Juniperus excelsa*). Although the characteristics of paulownia subspecies (*P. elongata, P. tomentosa, P. fortunei* etc.) and origins (China, Turkey) are different, they are still lower than those of many other species (Kaymakci *et al.*, 2013).

Referring to Flynn and Holder (2001) and Clad and Pommer (1980), Akyildiz and Kol (2010) indicated that paulownia wood is used for a variety of applications such as furniture, construction, musical instruments, shipbuilding, aircraft, packing boxes, coffins, paper, plywood, cabinetmaking, and molding.

Thermal compression is a kind of modification method. The material is compressed with heated plates and kept at a constant pressure for a while in this method. It is related to viscoelastic behavior, internal and microscopic structure of wood material. Steam (Kutnar and Kamke, 2012), oil (Welzbacher *et al*., 2007) and other

pre- or post-treatments can be applied for increasing the effect of densification. The additional treatments can give better results; however, the additional process may bring risks and costs for industrial applications.

The temperature, pressure and duration levels determine the material characteristics particularly density and surface properties such as roughness, wettability, appearance. Surface properties of wood are a determinant characteristic for use and surface treatments. It is affected by anatomic properties such as anisotropy, cell dimensions, annual ring, grain direction, and treatments such as coating and modification methods. İmirzi *et al.* (2014) compared the surface roughness properties of untreated and thermally compressed (with densification term) Scots pine wood. They found that the treated samples had smoother surfaces after some machining process (planing, circular sawing, sanding). Candan *et al.* (2013) studied thermal compression of paulownia wood boards and they found that the process could not generate an enhancement in the dimensional stability, while moisture content values decreased. However, the process caused increasing of surface density and hardness values. Otherwise, in several papers it was reported that other thermal modification methods applied to several wood species (both softwood and hardwood) changed the color of the material (González-Peña *et al.*, 2009; Brischke *et al.*, 2007).

The aim of this study was to examine surface quality performance of Paulownia as a fast-growing species after mechanical thermal compression. In this context, the properties of the treated samples such as surface roughness, wettability and color were investigated and compared with the untreated samples and process parameters.

# 2 MATERIALS AND METHODS
2. MATERIJALI I METODE

## 2.1 Wood material and thermal compression method
2.1. Drvni materijal i metoda toplinskog prešanja

Paulownia (*Paulownia* spp.) lumbers were commercially purchased from Rize, Turkey. Lumbers were

planed and cut to obtain small and clear (defect-free) samples with dimensions of 50 mm by 50 mm by 18 mm. Thermal compression process was mechanically performed in hot-press. The compression was applied to the widest surfaces of samples. Four treatment combinations with two-treatment temperatures (150 °C and 170 °C) and two pressure levels (20 bar and 22.5 bar) were used with 45 min duration. All experimental design is shown in Table 1. In addition, a control group with untreated samples was used to investigate the possible changes. All samples were conditioned at (20±2) °C and (65±5) % relative humidity (RH) in a climate chamber until equilibrium moisture content was reached after thermal modification.

## 2.2 Surface roughness measurement
2.2. Mjerenje hrapavosti površine

The measurements were performed both parallel (//) and perpendicular (⊥) to the grain of each samples. Four roughness parameters were characterized by JIS B 0601 (1994) standard. The investigated parameters were arithmetical average roughness (*Ra*), maximum height (*Ry*) and ten-spot average roughness (*Rz*). Mitutoyo SJ-301 surface roughness tester, known as a stylus type profile-meter, was used for the tests (Anon., 2002). The measurements were performed with 0.5 μm accuracy. The speed of stylus type pin was 10 mm/min and λc value was 12.5 mm.

## 2.3 Wettability measurement
2.3. Mjerenje kvašenja

Contact angle (*CA*) values were obtained to determine the wettability characteristics of the samples. They were determined using KSV Cam-101 Scientific Instru-

ment (Helsinki, Finland) device. 5μL droplet of distilled water was used as the liquid. After the water droplet was dripped on the pressured surface, the camera of the device captured 30 images at 1-second intervals. *CA* values from the images were measured with image processing software. The mean of two-contact angle values (left and right) were used to analyze each image.

## 2.4 Determination of color characteristics
2.4. Određivanje svojstava boje

The color measurements were carried out using a Minolta CM-2600d spectrophotometer (Konica Minolta, Japan) equipped with an integrating sphere according to the *CIE L\*a\*b\** system. The system consists of three parameters: *L\**, *a\** and *b\**. The *L\** axis represents the lightness and varies from 0 (black) to 100 (white). The symbol +*a\** is for red, -*a\** for green, +*b\** for yellow and –*b\** for blue. Moreover, brightness (R457 nm) was determined according to ISO 2470 standard), while whiteness and yellowness were determined according to ASTM E313 standard. Total color change Δ*E\** was calculated using the *L\**, *a\** and *b\** data of each sample according to the equation given below (Eq. 1) (In equation, each "Δ" indicates the difference of each parameter). Additionally, the magnitude of Δ*E* results were classified according to the grading rules suggested by Cividini *et al.* (2007) (Table 2).

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \qquad (1)$$

For comparison of all groups, multiple comparisons were first subjected to an analysis of variance (ANOVA), and significant differences between average values of control and treated samples were determined using Duncan's multiple range test with SPSS Software. *p*-values of 0.05 were considered to determine significance level.

## 3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Control and treated sample groups were compared and homogeneity groups were determined for each test according to the Duncan's multiply range test. The surface roughness results are shown in Table 3.

As seen in Table 3, some statistically significant differences ($p < 0.05$) were found to exist as determined by Duncan's multiple-comparison tests. When

**Table 1** Experimental design of thermal compression process
**Tablica 1.** Plan eksperimenta toplinskog prešanja

| Panel group *Grupa ploče* | Treatment conditions / *Parametri prešanja* | | |
|---|---|---|---|
| | Temperature, °C *Temperatura,* °C | Pressure, bar *Tlak,* bar | Duration, min *Trajanje,* min |
| Control | - | - | - |
| A | 150 | 20.0 | 45 |
| B | 150 | 22.5 | 45 |
| C | 170 | 20.0 | 45 |
| D | 170 | 22.5 | 45 |

**Table 2** Total color change (Δ*E*) grading rules (Cividini *et al.*, 2007)
**Tablica 2.** Pravila ocjenjivanja ukupne promjene boje (Δ*E*) (Cividini *et al.*, 2007.)

| Δ*E* value Δ*E vrijednost* | Observation / *Zapažanje* | Change level\* *Stupanj promjene\** |
|---|---|---|
| 0.2 > Δ*E* | Not visible difference / *nema vidljivih razlika* | 0 |
| 0.2 < Δ*E* < 2 | Small difference / *male razlike* | 1 |
| 2 < Δ*E* < 3 | Color difference visible with high quality screen *razlika boje vidljiva uz pomoć ekrana visoke kvalitete* | 2 |
| 3 < Δ*E* < 6 | Color difference visible with medium quality screen *razlika boje vidljiva putem ekrana srednje kvalitete* | 3 |
| 6 < Δ*E* < 12 | High color difference / *izrazita razlika u boji* | 4 |
| Δ*E* > 12 | Different colors / *različite boje* | 5 |

\*The change levels were determined for this paper. / *Stupnjevi promjene određeni za ovaj rad.*

**Table 3** The effect of thermal compression with different durations on surface roughness of paulownia wood*
**Tablica 3.** Utjecaj toplinskog prešanja i njegova trajanja na hrapavost površine drva paulovnije*

| Temperature, °C *Temperatura,* °C | Pressure, bar *Tlak,* bar | Ra (μm) | | Ry (μm) | | Rz (μm) | |
|---|---|---|---|---|---|---|---|
| | | // | ⊥ | // | ⊥ | // | ⊥ |
| Control / *Kontrolni uzorci* | | 3.95[b] (0.90) | 5.23[bc] (1.15) | 21.78[ab] (3.86) | 37.39[b] (5.78) | 14.34[ab] (2.91) | 26.21[cd] (3.44) |
| 150 | 20.0 | 4.00[b] (1.00) | 6.10[c] (2.09) | 24.76[b] (6.00) | 40.82[b] (10.43) | 15.96[b] (4.16) | 28.28[d] (6.42) |
| 150 | 22.5 | 2.71[a] (0.49) | 4.07[ab] (0.77) | 17.84[a] (3.04) | 30.54[a] (5.58) | 11.40[a] (1.84) | 22.16[bc] (3.21) |
| 170 | 20.0 | 3.32[ab] (0.91) | 3.81[a] (1.38) | 19.88[a] (4.68) | 27.58[a] (7.85) | 12.63[a] (3.27) | 19.75[ab] (5.50) |
| 170 | 22.5 | 2.63[a] (0.98) | 3.09[a] (0.70) | 18.49[a] (4.69) | 25.42[a] (5.69) | 11.53[a] (3.70) | 22.16[bc] (4.16) |

*Mean (standard deviation) and the same letter on numbers in the same column show that there is no difference in group homogeneity for each parameter ($p<0.05$). / *Srednja vrijednost (standardna devijacija) i isto slovo uz brojeve u istom retku pokazuju da nema razlike u homogenosti grupa za svaki parametar ($p<0,05$).*

all values generally considered, surface roughness values decreased up to 40 %. Only combination of 150 °C and 20 bar did not significantly change the values. When the values were considered in detail, the values of Control and 150 °C - 20 bar groups were higher than other treatment groups for all directions. When the pressure effect was investigated (at the same temperatures), there was significant change at the temperature of 150 °C, while there was no significant change at 170 °C. When the temperature effect was investigated (at the same pressures), there was significant change with temperature increment at 20 bar pressure, while there was no significant change at 22.5 bar. In addition, similar changes were obtained in both directions.

Dogu *et al.* (2017) similarly applied thermal compression method to paulownia wood with only 20 bar pressure at the same temperatures. They observed that slightly more cellular damage occurred in the treated samples and found that distribution of deformation was not uniform in the growth rings of the treated samples. Their comment might explain the similarity of roughness values between Control and 150 °C 20 bar groups. Although there are more differences between Control and 170 °C 20 bar roughness values, they were only limited to perpendicular direction. However, the pressure levels and/or duration can be increased to affect the material properties and to obtain smoother surface, because the material thickness can decrease by half, as stated in some studies. Although useful results were obtained with stylus-based technique, the measurements were realized with different steps through a line with perpendicular and parallel directions to grain. Areal measurement might be required for wider evaluation.

The contact angle (*CA*) results of the samples are presented in Table 4.

As seen in Table 4, statistically significant differences ($p < 0.05$) were found to exist as determined by Duncan's multiple-comparison tests. The contact angle (*CA*) values for all treated samples increased with increasing thermal compression treatment, especially with increment in temperature according to control (untreated) samples. It was found that the *CA* values were in-

**Table 4** The effect of thermal treatment with different durations on wettability of paulownia wood*
**Tablica 4.** Utjecaj toplinskog prešanja i njegova trajanja na kvašenje drva paulovnije*

| Temperature, °C *Temperatura,* °C | Pressure, bar *Tlak,* bar | Contact angle, ° *Kontaktni kut,* ° |
|---|---|---|
| Control / *Kontrola* | | 30.63[a] (11.79) |
| 150 | 20.0 | 59.98[b] ( 9.28) |
| 150 | 22.5 | 53.80[b] (14.21) |
| 170 | 20.0 | 82.59[c] (16.16) |
| 170 | 22.5 | 84.78[c] (12.05) |

* Mean (standard deviation) and the same letter on numbers in the same column show that there is no difference in group homogeneity for each parameter ($p<0.05$). / *Srednja vrijednost (standardna devijacija) i isto slovo uz brojeve u istom retku pokazuju da nema razlike u homogenosti grupa za svaki parametar ($p<0,05$).*

creased when the treatment temperature increased. However, significant differences were not observed with changing pressure for both temperatures. It can be said that thermal compression gained the hydrophobic character to the wood surface. At 170 °C, the *CA* values reached nearly 90°, which may show enough hydrophobicity for a wood material. Hakkou (2005) indicated that investigation of the effect of temperature on wettability showed that it changes suddenly for temperatures between 130 °C and 160 °C, indicating that higher temperatures, generally used for heat treatment, are not necessary to modify wood hydrophilic properties.

Examining other studies, Mirzaei *et al.* (2012) found that, by the rise of the treatment temperature, the contact angle values of paulownia wood samples were increased to 100 °C and 150 °C with a 30-minute hydrothermal treatment. Candan *et al.* (2011) found similar decrease in wettability of poplar wood under similar treatment conditions, namely 170 °C and 190 °C for 60 minutes without pressure. The obtained contact angle values are suitable for many surface treatments. However, Laskowska and Sobczak (2018) increased pressure 20 times more with shorter durations. They found similar decrease in wettability of oak wood under similar treatment conditions, namely 150 °C and 450 bar for 8 min treatment.

**Table 5** Color change of each group*
**Tablica 5.** Promjena boje svake grupe*

| Temperature, °C *Temperatura,* °C | Pressure, bar *Tlak,* bar | L* | a* | b* | Brightness *Svjetlina* | Whiteness *Bjelina* | Yellowness *Žućenje* |
|---|---|---|---|---|---|---|---|
| Control / *Kontrolni uzorci* | | 77.12 (0.69)ᶜ | 5.07 (0.74)ᵃ | 15.37 (0.83)ᵃ | 39.07 (1.41)ᶜ | 51.74 (1.16)ᶜ | 36.89 (2.22)ᵃ |
| 150 | 20.0 | 65.10 (6.94)ᵇ | 6.94 (1.54)ᵇ | 23.75 (1.52)ᵇ | 20.70 (6.27)ᵇ | 34.78 (8.24)ᵇ | 60.73 (8.20)ᵇ |
| | 22.5 | 66.38 (2.63)ᵇ | 6.72 (0.88)ᵇ | 22.87 (1.51)ᵇ | 21.86 (3.27)ᵇ | 35.91 (3.47)ᵇ | 57.73 (5.02)ᵇ |
| 170 | 20.0 | 61.08 (7.11)ᵇ | 7.53 (1.18)ᵇ | 22.84 (2.50)ᵇ | 17.55 (5.43)ᵇ | 29.97 (8.75)ᵇ | 62.01 (5.32)ᵇ |
| | 22.5 | 52.16 (2.86)ᵃ | 9.32 (0.89)ᶜ | 23.71 (1.84)ᵇ | 10.67 (1.48)ᵃ | 20.39 (2.60)ᵃ | 72.74 (4.54)ᶜ |

\* Mean (standard deviation) and the same letter on numbers in the same column show that there is no difference in group homogeneity for each parameter ($p<0.05$). / *Srednja vrijednost (standardna devijacija) i isto slovo uz brojeve u istom retku pokazuju da nema razlike u homogenosti grupa za svaki parametar ($p<0,05$).*

**Table 6** Total color change ($\Delta E$) according to each treatment parameter*
**Tablica 6.** Ukupna promjena boje ($\Delta E$) za pojedini parametar prešanja

| Variables / *Varijable* | | $\Delta E$ values *$\Delta E$ vrijednosti* | Change level *Stupanj promjene* |
|---|---|---|---|
| Control | 20.0 bar - 150 °C | 15.12 (7.22)ᶜᵈ | 5 |
| Control | 22.5 bar - 150 °C | 13.30 (3.26)ᵇᶜᵈ | 5 |
| Control | 20.0 bar - 170 °C | 18.70 (5.40)ᵈ | 5 |
| Control | 22.5 bar - 170 °C | 26.77 (2.50)ᵉ | 5 |
| 20.0 bar - 150 °C | 22.5 bar - 150 °C | 6.49 (4.01)ᵃ | 3 |
| 20.0 bar - 170 °C | 22.5 bar - 170 °C | 9.40 (7.74)ᵃᵇᶜ | 4 |
| 20.0 bar - 150 °C | 20.0 bar - 170 °C | 7.28 (4.16)ᵃᵇ | 4 |
| 22.5 bar - 150 °C | 22.5 bar - 170 °C | 14.69 (3.79)ᶜᵈ | 5 |

\* Mean (standard deviation) and the same letter on numbers in the same column show that there is no difference in group homogeneity for each parameter ($p<0.05$). / *Srednja vrijednost (standardna devijacija) i isto slovo uz brojeve u istom retku pokazuju da nema razlike u homogenosti grupa za svaki parametar ($p<0,05$).*

The color change results of samples are presented in Table 5 and total color changes of each treatment parameter related to control group and to each other are presented in Table 6.

As seen in tables, thermal compression process changed the color tones and brightness of samples when the results were compared with control (untreated) samples. Results showed that 170 °C and 22.5 bar process conditions significantly changed all color characteristics of samples, while only *b*\* parameter was similar with other process conditions. As seen in Table 6, all treatment parameters significantly affected total color change values of samples. The changes were more pronounced at the temperature of 170 °C. Otherwise, the pressure increment was only significant at the temperature of 170 °C, when the total color change was compared with control samples.

The color values of the samples changed significantly when the temperature changed; additionally, the change was higher at the temperature of 170°C. Kaygin *et al.* (2009) found similar changes of *L*\*, *a*\* and *b*\* on paulownia samples although they carried out conventional heat treatment at 160 °C, 180 °C and 200 °C without pressure.

Atik *et al.* (2013) and Akkus and Budakci (2015) similarly found that the color change increased with temperature increment, although they used different species. Their results showed that the higher tempera-

ture was applied to the material, the greater decrease was observed in the lightness value, as in this study. The color change, especially getting dark, (*L*\* value decrement) can extend the use of this fast-growing wood species, paulownia, as it can be considered exclusive in the market.

# 4 CONCLUSIONS
4. ZAKLJUČAK

In this study, one of the thermal modification techniques, mechanical thermal compression, was used for trying to change some surface characteristics of a fast-growing wood species - paulownia. Results showed that some significant changes of surface roughness, wettability, color properties were observed with some temperature and pressure combinations.

The observed changes showed that the properties of a fast-growing tree species, paulownia, can change. If these properties may be determined as reasonable for some uses, the market share of paulownia can increase. Kaymakci *et al.* (2013) pointed out that this situation can play a major role for countries that have poor wood resources for lumber production. Future studies should focus on changing modification possibilities by observing together anatomical structure and mechanical properties, because the applied pressure and temperature levels may be critical for the above properties.

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# Effect of Using Urea Formaldehyde Modified with Extracts in Plywood on Formaldehyde Emission

## Učinak upotrebe urea-formaldehida modificiranog ekstraktima na emisiju formaldehida furnirske ploče

**ABSTRACT •** *Formaldehyde-based adhesives are used in the forestry industry. This is because formaldehyde is inexpensive, easy to use and resistant to moisture; it also has particular mechanical effects. Formaldehyde has both advantages and disadvantages. It is known that various diseases such as lung cancer occur in humans as a result of the release of formaldehyde into the air during and after board production. In this study, a urea formaldehyde glue mixture was prepared by using four different fillers (extract of maritime pine (Pinus pinaster) and elm (Ulmus glabra) bark, extract of hazelnut (Corylus avellana) husk and acorn tannins) at two different ratios. The bonding shear strength of pine (Pinus sylvestris) and spruce (Picea orientalis) plywood produced with urea formaldehyde adhesive was tested according to EN 314-1 standard. All plywood, except the plywood with acorn tannin, met the requirements of the standard. A formaldehyde emission test of the plywood was carried out in accordance with EN 713-3 standard. With this approach, it is possible to quickly determine formaldehyde emissions. Experimental results were obtained for subsequent measurements, including chamber tests. It was observed that the elm bark extract reduced the formaldehyde emission of pine plywood by 40 %, while other fillers reduced it by 3-37 %.*

*Keywords: formaldehyde emission; plywood; elm bark; hazelnut husk; tannin; urea formaldehyde*

**SAŽETAK •** *U drvoprerađivačkoj industriji upotrebljavaju se ljepila na bazi formaldehida zato što je taj aldehid jeftin, jednostavan za uporabu, otporan na vlagu i ima posebne mehaničke učinke. Formaldehid ima određenih prednosti i nedostataka. Poznato je da se u ljudi koji rade u drvoprerađivačkoj industriji pojavljuju različite bolesti poput raka pluća, što može biti posljedica ispuštanja formaldehida u zrak tijekom i nakon proizvodnje ploča. Za ovo je istraživanje pripremljena smjesa urea-formaldehidnog ljepila dodavanjem četiriju različitih punila: ekstrakta kore primorskog bora (Pinus pinaster) i brijesta (Ulmus glabra), ekstrakta ljuske lješnjaka (Corylus avellana) i tanina žira u dva različita omjera. Posmična čvrstoća furnirske ploče od borovine (Pinus sylvestris) i smrekovine (Picea orientalis), proizvedene uporabom urea-formaldehidnog ljepila, ispitana je prema normi EN 314-1. Sve furnirske ploče, osim onih s taninom iz žira, zadovoljile su zahtjeve norme. Ispitivanje emisije formaldehida iz furnirskih ploča provedeno je prema normi EN 713-3. Tim je pristupom moguće brzo odrediti emisije formaldehida. Dobiveni su eksperimentalni rezultati za naknadna mjerenja, uključujući ispitivanje u komori. Primijećeno je da je ekstrakt kore brijesta smanjio emisiju formaldehida furnirske ploče od borovine za 40 %, dok su ostala punila smanjila tu emisiju za 3 – 37 %.*

*Ključne riječi: emisija formaldehida; furnirska ploča; kora drva brijesta; ljuska lješnjaka; hrapavost površine*

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# 1 INTRODUCTION
## 1. UVOD

The increasing demand for wood products and the decrease in the presence and quality of wood raw materials have gradually increased the importance of composite wood products. Wood-based composite panels such as plywood, particleboard and fibreboard are among the most widely used materials in the whole world (Aydın *et al.*, 2010). These materials are used widely for construction, decoration and furnishing of homes, offices, schools, as well as other non-industrial workplaces, and many of these materials have high formaldehyde emissions (FE) due to the use of such things as solvent-borne paints and adhesives (Böhm *et al.*, 2012).

Most adhesives used in plywood production are urea formaldehyde (UF), phenol formaldehyde (PF) and melamine formaldehyde (MF) adhesives (Ružiak *et al.*, 2017). The use of urea-formaldehyde adhesive, as the main adhesive used by the forest industry, is due to its excellent adhesion to lignocellulosic materials, excellent intrinsic cohesion, ease of handling and application, lack of colour in the finished product and low cost. However, lack of resistance to weather and water and its susceptibility to emission of formaldehyde vapours are two main disadvantages of UF adhesive (Aydin *et al.*, 2006).

Formaldehyde is produced by oxidizing methane or methanol in the presence of a catalyst. 70 % of this production is only used in the synthesis of formaldehyde-based adhesives (Stefanowski, 2018). This is because their prices are low, they do not absorb moisture, are resistant to mechanical effects and are easy to use (Çolak, 2002). Additionally, FE is elevated, even in the absence of adhesives in wood. Certain reports have mentioned that FE is produced from wood during hot-pressing of composite panels, and it is generally accepted that FE from the wood is an insignificant contributor to the total measurable level of FE in a composite wood product (Böhm *et al.*, 2012).

A variety of test methods have been developed for determining the initial emittable formaldehyde concentrations from wood-based products. Each method has its own special set of board conditioning and test conditions that have both positive and negative attributes. Large chamber tests, such as the European large chamber test, are expensive, time-consuming and need a large quantity of the sample. Consequently, it is impractical to use this technique for quality assurance in commercial production. Other methods, such as gas analysis, using a perforator or a desiccator, are widely used in quality production control for factories and save time in comparison to the referenced methods (chambers), which need 7-28 days (Böhm and Salem, 2012). Regarding equipment cost, analysis time and informative value in combination, the most promising method for rapid formaldehyde emission analysis is the flask method. This method has been used consistently for formaldehyde emission, not at least because of its experimental simplicity and good correlation with other emission test methods. The flask method may be used to quickly determine the effectiveness of formaldehyde emission reduction attempts while developing a low-emission binder system (Dorner *et al.*, 2012).

Formaldehyde emissions cause different disturbances in humans within certain values. Irritations in eyes, nose and throat are caused at 0.1-5 ppm; tears, nasal, throat burning and breathing difficulty are caused at 10 ppm; fatal lung cancer and other serious diseases occur at 25 ppm and above. Oral administration of a 37 % aqueous solution of formaldehyde results in death (URL1, 2018). Formaldehyde is classified as a carcinogen known by the State of California, Proposition 65 (2008) and the International Health Research Agency (IARC), a division of the World Health Organization (WHO) (IARC, 2004). The National Institute of Health National Toxicology Program (NTP) states that formaldehyde is reasonably expected as a human carcinogen (Salem and Böhm, 2013a).

It is an important problem to reduce or wipe out the emission of formaldehyde in panels produced with synthetic adhesives. Formaldehyde emissions can be reduced in a number of ways, such as lowering the formaldehyde ratio during composition and addition of fillers (lignin, tannin, etc.) (Çolakoğlu, 1993).

One of the possible available materials for production of adhesive mixture fillers is the bark of domestic wood materials. Wood bark is a waste product that results out of wood raw material processing (Ružiak *et al.*, 2017). Çöpür *et al.* (2007) also reported that the internal bond strength of chipboards made of hazelnut husk and urea formaldehyde adhesive meets the general-purpose particleboard standard requirement, which is the European Norm. Therefore, hazelnut husk may be used as an important filler in plywood production.

The key factors for successful utilisation of bark and hazelnut husk for adhesives are polyphenol compounds known as tannins (Ogunwusi, 2013). Formaldehyde emission from tannin-bonded panels is almost completed due to the free formaldehyde residue remaining after pressing. Flavonoid-methylene bonds (Figure 1) are resistant to any hydrolysis process due to their phenolic nature (Pizzi *et al.*, 1994).

Tannin-based adhesives have been studied by many researchers. For example, Moubarik *et al.* (2013) studied a corn starch-mimosa tannin-UF adhesive mixture produced for reduction of formaldehyde emissions of the particles produced. In another study, by adding
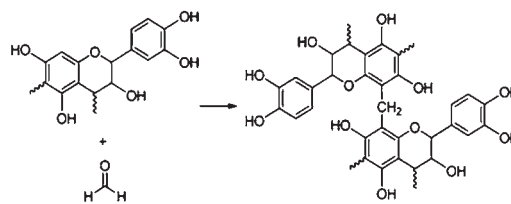


**Figure 1** Reaction between tannin and formaldehyde (Arbenz and Avérous, 2015)
**Slika 1.** Reakcija između tanina i formaldehida (Arbenz and Avérous, 2015.)

**Table 1** Variables applied in extraction process
**Tablica 1.** Varijable primijenjene u postupku ekstrakcije

| Species / *Vrste* | Temperature, ºC *Temperatura, °C* | Ratio (*w/v*) *Omjer (w/v)* | Time, hour *Vrijeme, h* | Particle moisture content, % *Sadržaj vode u česticama, %* |
|---|---|---|---|---|
| Maritime pine bark *kora primorskog bora* | 95 | 1/6 | 2 | 17.18 |
| Elm bark / *kora brijesta* | 95 | 1/6 | 2 | 12.67 |
| Hazelnut husk / *ljuska lješnjaka* | 75 | 1/50 | 3 | 15.68 |
| Acorn tannin / *tanin žira* | Supplied from a commercial company / *nabavljen od komercijalne tvrtke* | | | |

hybrid bark extract to UF adhesive, Zhang *et al.* (2014) reduced plywood formaldehyde emission. Gangi *et al.* (2013) also added tannin to PF and MF adhesive, which produced a decrease in the formaldehyde emission of plywood. Elbadawi *et al.* (2015) produced particleboard by adding extracts of acacia barks as a 35 % solution to 3 different proportions (5-10-15 %) of UF adhesive. There was an increase in the mechanical properties at a rate of 5 %. Nemli and Çolakoğlu (2005) produced particleboard by adding different amounts of mimosa bark. UF adhesive was used in particleboard production. They observed a decrease in formaldehyde emission. Aydin *et al.* (2017) turned walnut, fir, spruce and chestnut shells into a flour and used it as filler in plywood produced with a UF adhesive. Chestnut and fir reduced formaldehyde emission. Pirayesh *et al.* (2013) produced particleboard using a UF adhesive. They also used walnut and almond shells at different proportions. Formaldehyde emission and mechanical properties decreased with the increase in the walnut and almond shell ratio in the particleboard.

In this study, the effects of the use of bark extracts, hazelnut husk extracts and acorn tannin as fillers on the bonding shear strength and formaldehyde emission of plywood panels were evaluated. For this aim, besides the use of wheat flour as the control group, extract of maritime pine and elm bark, hazelnut husk extract and acorn tannins were used. Moreover, it was aimed to use wood barks and hazelnut husk as value-added raw material for the industry.

## 2 MATERIALS AND METHODS
## 2. MATERIJALI I METODE

To be used as a filler in producing plywood, maritime pine *(Pinus pinaster)* bark, elm *(Ulmus glabra)* bark and hazelnut *(Corylus avellana)* husk were obtained from Trabzon in northern Turkey. Acorn tannin was purchased from a commercial company. Scots pine *(Pinus sylvestris)* and spruce *(Picea orientalis)*



**Figure 2** Hot water extraction
**Figure 2.** Ekstrakcija vrućom vodom

veneers used in plywood production were obtained from Karadeniz Technical University.

### 2.1 Extraction process
### 2.1. Postupak ekstrakcije

The barks and hazelnut husk peeled from wood were exposed to natural drying for 14 days. Then, a ring-type flaker was used to break the chips down to particle size before extraction. The bark and husk particles were extracted with hot water in a boiler at the solid / liquid (*w/v*) ratios presented in Table 1.

In order to prevent the volatile compounds from escaping with the effect of heat, the extraction process as seen in Figure 2 was carried out by adding ice onto the lid during the extraction process and until the contents were cooled down in a closed boiler.

Removal of barks and husk from the solution was carried out with a 60-mesh sieve. Then, it was boiled in a steel-bottom boiler to remove the water and increase the solid matter content. After most of the water was removed, and the density of the solution increased, it was poured into an aluminium tray and dried in an oven at 70 °C until it was completely dry. The samples taken from the oven were ground in a ring mill and turned into powder. The moisture of the extracts was measured with a Precisa brand moisture analyser. The extracts that were obtained are shown in Figure 3.



**Figure 3** 1 – Elm bark extract, 2 – Maritime pine bark extract, 3 – Hazelnut husk extract
**Slika 3.** 1 – ekstrakt kore brijesta, 2 – ekstrakt kore primorskog bora, 3 – ekstrakt ljuske lješnjaka

**Table 2** Glue mixture of test groups
**Tablica 2.** Smjesa ljepila ispitnih grupa

| | Glue mixture *Smjesa ljepila* | Test groups / *Ispitna grupa* | | | | |
|---|---|---|---|---|---|---|
| | | A (control / *kontrola*) | B (maritime pine bark / *kora primorskog bora*) | C (elm bark *kora brijesta*) | D (hazelnut husk *ljuska lješnjaka*) | E (acorn tannin *tanin žira*) |
| Ingredient (parts by weight) *Sastojak (maseni udio)* | UF adhesive (55 % solids content) *UF ljepilo (55 % suhe tvari)* | 100 | 100 | 100 | 100 | 100 |
| | Wheat flour / filler *pšenično brašno / punilo* | 30/0 30/0 | 25/5 27.5/2.5 | 25/5 27.5/2.5 | 25/5 27.5/2.5 | 25/5 27.5/2.5 |
| | Hardener (NH₄Cl) / *otvrdnjivač* (NH₄Cl) | 10 | 10 | 10 | 10 | 10 |

**Table 3** Technical characteristics of UF adhesive
**Tablica 3.** Tehnička svojstva UF ljepila

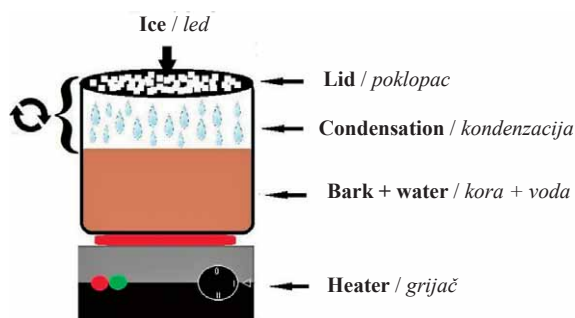| UF adhesive characteristics *Svojstva UF ljepila* | UF adhesive (limit value) *UF ljepilo (granične vrijednosti)* |
|---|---|
| Solid content / *suha tvar,* % | 55±1 |
| Density / *gustoća,* 20 °C, g/cm³ | 1.214 |
| Viscosity / *viskoznost,* 20 °C, cps | 140 |
| Flowing point / *točka tečenja,* 20 °C, s | 29 |
| Gel time / *vrijeme želiranja,* s | 22 |
| pH, 20 °C | 8.32 |
| Free formaldehyde / *slobodni formaldehid,* % | Max. 0.8 |
| Storage time / *vrijeme skladištenja,* 20 °C | 60 days |

## 2.2 Chemical analysis of extracts
2.2. Kemijska analiza ekstrakata

The extracts for pH measurement of the particles were prepared according to TAPPI T m45 (1992). Five grams of the samples of each group were extracted with 150 ml of distilled water for 24 hours. After filtering, pH measurements were carried out.

The Stiasny number method was used to determine the polyphenol content of the extracts. Fifty ml of 0.4 % w/w tannin solution was pipetted into a 150-ml flask. Aqueous formaldehyde (37 %, 5 ml) and hydrochloric acid solution (10 N, 5 ml) were then added, and the mixture was heated under reflux for 30 min. The reaction mixture was filtered through a sintered glass filter (40–100 μm) while it was still hot. After this, the precipitate was dried in an oven at 105 °C to constant weight. The Stiasny number is the ratio of the oven-dried weight of the precipitate to the total dissolved solids content of the tannin extract, expressed as a percentage (Pizzi and Mittal, 2010).

The total phenolic content of the extract samples prepared according to the Folin-Ciocalteu method is presented as gallic acid equivalent (mg GAE / g).

## 2.3 Preparation of glue mixture
2.3. Priprema smjese ljepila

Fillers by 2.5 % and 5 % (by replacing wheat flour) of the UF (55 % solid content) adhesive (Table 3) were added to the UF glue mixture. The glue mixture recipe used in plywood production is given in Table 2.

The fillers obtained from the tree barks and hazelnut husk were added gradually to the UF adhesive during the preparation of the glue mixtures of all test groups, and the glue mixtures were mixed to obtain a homogenous adhesive. Finally, the hardener (NH₄Cl) was added to these mixtures.

## 2.4 Determination of bonding shear strength and formaldehyde emission of plywood
2.4. Određivanje posmične čvrstoće spoja i emisije formaldehida furnirske ploče

In this study, scots pine and spruce veneers of 2 mm thickness and 50 cm × 50 cm dimensions were dried at 110 °C to 4-6 % humidity. Gluing of the veneers was carried out in a 4-roller gluing machine, and 160 g/m². The boards prepared after gluing were pressed in a single-layer hydraulic press with a pressing area of 70 cm × 89 cm. Pressing conditions: temperature 110 °C, pressure 8 kg/cm², time 6 minutes. The produced test boards were stacked on top of each other for 1 week without using stacking slats to eliminate the difference in temperature and humidity between the inner and outer layers. Thus, form changes were prevented by ensuring the cooling of the plywood under equal conditions.

Bonding shear strength test was carried out according to EN 314-1 standard. According to this standard, the bonding shear strength test sample was prepared for 3-layer plywood (EN 314-1, 1993). The test samples prepared from plywood in each group produced with the urea formaldehyde adhesive were kept in water at 20 °C for 24 hours, and 30 samples from each group were examined.

The formaldehyde emission values of the produced plywood were determined using the flask method in accordance with EN 717-3 (1996) standard. Two replicate tests were conducted for determination of formaldehyde emissions. The flask method is an inexpensive and simple method for testing formaldehyde release, and it is suitable for testing of uncoated boards (Aydin *et al*., 2017).

## 2.5 Statistical analysis
2.5. Statistička analiza

Simple analysis of variance was used to reveal the effects of the fillers on formaldehyde emission in addition to the bonding shear strength of plywood. The analysis of variance was carried out using the test groups common to the plywood whose effects were in-

**Table 4** Chemical contents of extracts
**Tablica 4.** Kemijski sastav ekstrakta

| Species / *Vrsta* | pH | Total phenol mg GAE/g *Ukupni fenoli* mg GAE/g | Stiasny number*, % *Stiasnyjev broj*, %* | Extraction yield, % *Stupanj ekstrakcije, %* |
|---|---|---|---|---|
| Maritime pine bark / *kora primorskog bora* | 4.42 | 101.1238±4.0 | 9 | 7.5 |
| Elm bark / *kora brijesta* | 5.79 | 407.05 | 50 | 5.18 |
| Hazelnut husk / *ljuska lješnjaka* | 6.47 | 14.04 | 31 | 13.3 |
| Acorn annin / *tanin žira* | 3.97 | 710.3 | - | - |

*Stiasny number of raw barks and hazelnut husk was measured. / *Izmjeren je Stasnyjev broj sirove kore i ljuske lješnjaka.*

vestigated. If the differences obtained by the analysis of variance were found to be significant, Student-Newman-Keuls test was used to compare the means of variance sources, and the homogeneity of the groups was determined. The SPSS 23 for Windows statistical package program was used for the statistical analyses.

## 3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

### 3.1 Chemical analysis of extracts
3.1. Kemijska analiza ekstrakta

Table 4 shows the total polyphenol content, pH value and extraction yield of the extracted barks and husk, in addition to the Stiasny values of the raw barks and husk.

In the extraction process, the highest yield was obtained from the hazelnut husk, while the lowest yield was obtained from the elm bark. Extraction yields highly depended on the wood bark species. Usually, water extracts present more impurities than urea, carbonate and urea+sulphite extracts (Bertaud *et al*., 2012). Extractives obtained through hot water extraction contain hemicellulose, some acetic acid and even lignin. It is worth noting that the amount of water used during extraction has little influence on the extractive yield (Feng *et al*., 2013).

When the Stiasny number of the unextracted bark and husk was evaluated, the highest Stiasny number was obtained from the elm bark, and the lowest Stiasny number was obtained from the maritime pine bark. The Stiasny number gives the reactivity of our extracts to formaldehyde, and this information may help us determine if the extracts can be used as adhesives (Chupin *et al*., 2013). Yazaki and Collins (1994) assessed the minimum Stiasny value to produce high-quality adhesives as 65 %. However, Ping *et al*. (2011) produced good-quality adhesives while obtaining a Stiasny number of 46 %.

The highest total phenol content was determined in the acorn tannin, followed by the elm bark extract. The lowest total phenol content was detected in the hazelnut husk. Generally, the bark of older trees provides a higher tannin and extractive content. The outer bark of some conifers contains the greatest percentage of extractable total phenols, followed by inner bark, heartwood and sapwood. The yield of tannin from bark depends on species, age, parts of the tree and storage time after tree felling (Feng *et al*., 2013).

### 3.2 Bonding shear strength
3.2. Posmična čvrstoća spoja

Figure 4 shows the changes in the bonding shear strength depending on the glue mixture. The bonding shear strength of groups B and D in pine plywood was significantly higher than the control group. There was no statistically significant difference between the other groups and the control. Elbadawi *et al*. (2015) stated that the curing rates of formaldehyde-based adhesives were very dependent on the pH of the environment in which they cure. If the pH is low, then pre-curing may be performed. When an adhesive pre-cures, the board's layer is weak and flaky. In a study that produced plywood using maritime pine bark extract, it was stated that the adhesion quality was shown by variables such as the polymerization degree, structure and composition of the carbohydrates and reactive polyflavonoids in the extract (Yazaki, 1994).

In spruce plywood, the bonding shear strength of groups B and E was significantly lower than the control group. There was no statistically significant difference between the other groups and the control group. It has been stated in the literature that maritime pine bark tannins can change the reaction balance according to the chemical properties of the tree species since they have a phloroglucinol A ring structure (Pizzi, 1979). Since acorn tannin has the highest polyphenol content and lowest pH value, it creates a thick glue line by shortening the curing time and lowering the urea / formaldehyde mole ratio as its high polyphenol content causes a negative effect on adhesion (Çolak, 2002; Nemli, 2002).

The filler ratios used in the pine and spruce plywood did not significantly affect the bonding shear strength.

Considering the difference in the bonding shear strength of the groups using fillers, as stated in the literature, the presence of pits, peaks and cracks on the surface in the microscopic examination of the veneers may be caused by the presence of irregular fibres and other defects. It is known in the literature that these surface conditions cause blockages that prevent the glue from fully wetting and lead to stresses when the glue hardens (Aydın *et al*., 2001). It was observed that surface defects, porous and fibrous structures were removed with the use of a filler, and it was stated in the literature that better adhesion occurs, and glue leakage is prevented (Tan and Çolakoğlu, 2010).
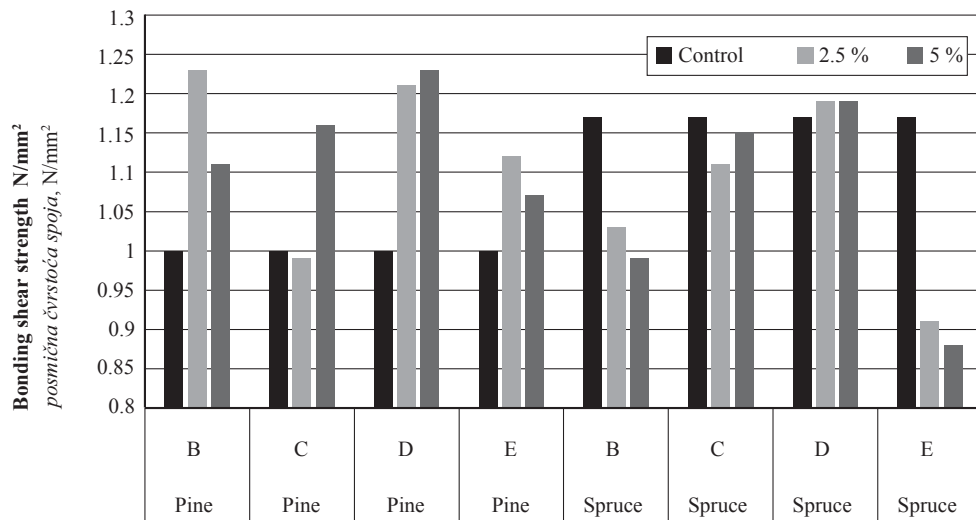
**Figure 4** Bonding shear strength values
**Figure 4.** Vrijednosti posmične čvrstoće spoja

### 3.3  Formaldehyde emission
3.3.  Emisija formaldehida

Formaldehyde emission for the plywood groups was determined by the flask method. The formaldehyde emission values of the test panels are given in Figure 5.

The formaldehyde emission of the filler-added groups was lower in both plywood types than the control group. The fact that fillers cause low formaldehyde emissions is due to the reaction of natural phenolic tannins with formaldehyde (Zhang *et al*. 2014). Aydin *et al*. (2017) added different bark flours to an adhesive, and the resulting plywood reduced formaldehyde emissions. Similarly, Zhang *et al*. (2014) added bark extract to an adhesive and observed a decrease in the formaldehyde emission of plywood.

The formaldehyde emission in pine plywood was lower than that in spruce plywood. In plywood produc-
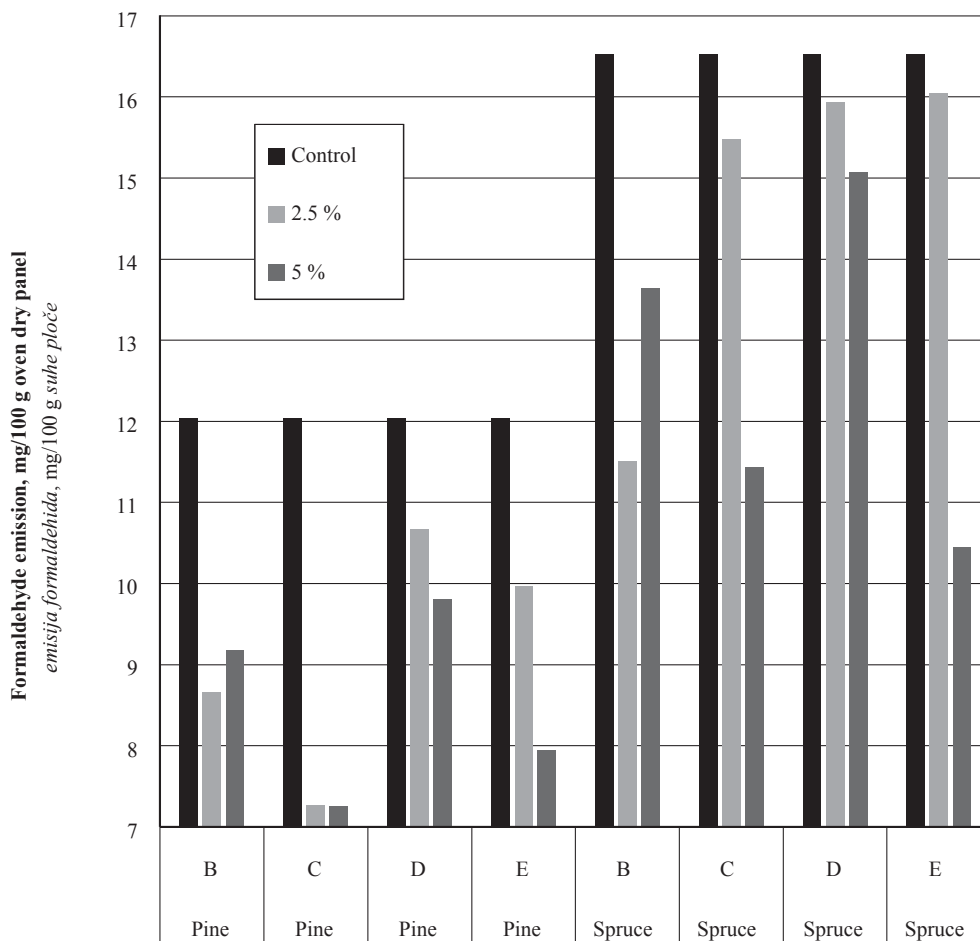


**Figure 5** Formaldehyde emission values
**Figure 5.** Vrijednosti emisije formaldehida

tion, the pressing temperature causes acetyl groups to be removed from the veneers to turn into acetic acid, which has a formaldehyde-binding effect. Additionally, it was found in the literature that the amount of formaldehyde decomposed from plywood surfaces depends on the anatomical structure, porosity and diffusion resistance of the tree from which the outer layer is produced (Çolakoğlu, 1993). Salem *et al.* (2012) stated that there are two main factors affecting the formaldehyde emission of particleboard. The first one was that the formaldehyde present in the adhesive interacted in a distinct way with each wood species and the second one that FE values were affected by the anatomy of the respective wood species. It was found in previous studies that plywood panels were manufactured with PF adhesive, and formaldehyde emission was close to that of solid wood, because the C-C bonding in the PF adhesive was very stable against hydrolytic attacks. It is important to point out here that such low free formaldehyde values may be emitted from the wood itself, and the boards are considered formaldehyde free (Salem *et al.* 2013b).

In pine plywood, the lowest formaldehyde emission was determined in group C. Elm bark extract has a high polyphenol content and a high pH value. As a result of this, acetyl groups that are esterified with sugar units in hemicellulose in a high-temperature alkaline environment are subjected to hydrolysis, and acetyl groups have a binding effect on formaldehyde (Çolak, 2002). In groups other than the control group, the highest formaldehyde emission value was found in group D with the lowest polyphenol content. Among the filler-used groups, group B had a higher formaldehyde emission at a rate of 5 % than group E, while group E had a higher formaldehyde emission than group B at 2.5 %.

The formaldehyde emissions of spruce plywood using 5 % filler were compared. In the groups other than the control group, the highest formaldehyde emission was determined in group D, and the lowest formaldehyde emission in group E. The hazelnut husk extract had the lowest quantity, and the acorn tannin extract had the highest quantity of polyphenols. Among the groups in which fillers were used, when the ratio decreased to 2.5 %, the lowest formaldehyde emission was found in group B. Since maritime pine tannin has a structure of phloroglucinol ring A, it was stated in the literature that it can change the reaction balance according to the chemical properties of the tree species (Pizzi, 1979).

In both types of plywood, it was determined that, as the filler ratio increased, the emission of formaldehyde in groups C, D and E decreased. In previous studies, Nemli (2002) stated that formaldehyde emission decreased with increasing bark ratio in particleboards produced using mimosa bark.

Pirayesh *et al.* (2013) reported that walnut/almond shell usage rate and formaldehyde emission are inversely proportional in particleboard production. Especially the tannin content in the bark affected the formaldehyde emission.

As a result of the test performed in the group using maritime pine bark, it was observed that the increase in the filler ratio increased the formaldehyde emission.

## 4 CONCLUSIONS
4. ZAKLJUČAK

Maritime pine bark, elm bark and hazelnut husk were obtained from Trabzon in northern Turkey. Hot water extracts were obtained from these agricultural wastes. The acorn tannin was purchased from a commercial company. Then, the extracts and acorn tannins were added into the urea formaldehyde glue mixture at the rates of 5 % and 2.5 % (replacing wheat flour) of the UF (55 % solid content) adhesive. The bonding shear strength and formaldehyde emission of the plywood produced with the modified UF adhesive were investigated.

The use of maritime pine bark extract and hazelnut husk extract in pine plywood increased the bonding shear strength significantly. In spruce plywood, the use of maritime pine bark extract and acorn tannin significantly reduced the bonding shear strength. Except for the group in which acorn tannin was used in spruce plywood, all groups met the requirements of EN 314-1 standard.

The reason for choosing the flask method in measuring formaldehyde emission was to compare the effects of the filling materials on formaldehyde emission. The use of the elm bark extract reduced the formaldehyde emission of pine plywood by 40 %. The use of 5 % acorn tannin reduced the formaldehyde emission by 34 % in pine plywood and 37 % in spruce plywood. The other fillers reduced the formaldehyde emission in the range of 3 % to 31 %.

The formaldehyde emission problem in the wood-based board sector is an issue that needs to be seriously addressed due to the increasing legal requirements that are developed in parallel with the increasing importance given to the environment and human health.

It was found that the extract obtained from the waste wood barks and hazelnut husk can be used as additives to substitute wheat flour in a glue mixture. It may be concluded from this study that elm bark extract may be used in a glue mixture as a formaldehyde scavenger in plywood panels.

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# Thermal Behavior of Insulation Fiberboards Made from MDF and Paper Wastes

## Toplinska svojstva izolacijskih vlaknatica izrađenih od otpadnog MDF-a i papira

**ABSTRACT** • *Today, recycling is becoming increasingly important. In recycling process, the product performance should also be considered. In this study, manufacturing insulation fiberboard, as a practical wood product from recycled fibers, was investigated. For this purpose, two types of waste (MDF wastes and waste paper) were recycled to fibers and used for producing insulation fiberboards. The target fiberboard density was 0.3 g/cm³. The ratio of waste paper to MDF waste recycled fibers (WP/RF) was considered at two levels of 70/30 and 50/50. Poly vinyl acetate adhesive was used as a variable in the board manufacturing process. The mechanical properties, dimensional stability, thermal conductivity, and fire resistance of the boards were evaluated. Besides, the thermal stability of fiberboards was studied using thermal analysis including thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The results showed that the insulation fiberboards had admissible mechanical properties and dimensional stability. The manufactured boards displayed low thermal conductivity, which proved to be well competitive with other insulation materials. The fiberboards manufactured with PVAc adhesive and WP/RF ratio of 50/50 had higher fire resistance compared to other treatments. Additionally, results of thermal analysis showed that the use of PVAc adhesive and WP/RF ratio of 50/50 leads to improved thermal stability. Overall, the recycled fibers from MDF and paper wastes appear to be appropriate raw materials for manufacturing thermal insulation panels, and use of PVAc adhesive can significantly improve thermal and practical properties of insulation fiberboards.*

*Keywords:* insulation fiberboards; recycling; thermal stability; MDF wastes; waste paper

**SAŽETAK** • *Danas recikliranje postaje sve važnije, a u tom postupku treba uzeti u obzir i svojstva proizvoda koji se recikliranjem dobivaju. U ovom je radu istražena proizvodnja izolacijske ploče vlaknatice kao praktičnoga drvnog proizvoda od recikliranih vlakana. Za tu su namjenu u vlakna reciklirane dvije vrste otpada (MDF otpad i papirni otpad), koje su iskorištene za proizvodnju izolacijskih ploča vlaknatica. Ciljana gustoća ploče vlaknatice bila je 0,3 g/cm³. Planirani je omjer vlakana recikliranih od otpadnog papira i MDF otpada (WP/RF) iznosio 70 : 30 i 50 : 50. U procesu proizvodnje ploča upotrijebljeno je polivinilacetatno ljepilo. Eksperimentom su određena ova mehanička svojstva ploča: dimenzijska stabilnost, toplinska vodljivost i vatrootpornost. Osim toga, uz pomoć toplinske analize koja je podrazumijevala termogravimetrijsku analizu (TGA) i diferencijalnu toplinsku analizu (DTA) istražena je toplinska stabilnost ploča vlaknatica. Rezultati su pokazali da izolacijske ploče vlaknatice imaju odgovarajuća mehanička svojstva i dimenzijsku stabilnost. Usto, proizvedene su ploče imale nisku toplinsku vodljivost, što potvrđuje njihovu konkurentnost s ostalim izolacijskim materijalima. Ploče vlaknatice proizvedene*

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s PVAc ljepilom i uz omjer WP/RF od 50 : 50 imale su veću vatrootpornost od ploča proizvedenih ostalim postupcima (omjerima sastojaka). Usto, rezultati toplinske analize pokazali su da upotreba PVAc ljepila i omjer WP/RF od 50 : 50 pridonose poboljšanoj toplinskoj stabilnosti. Zaključno, reciklirana vlakna od MDF otpada i otpadnog papira čine se prikladnom sirovinom za proizvodnju termoizolacijskih ploča, a uporaba PVAc ljepila može znatno poboljšati toplinska i uporabna svojstva takvih izolacijskih ploča vlaknatica.

**Ključne riječi:** izolacijske ploče vlaknatice; recikliranje; toplinska stabilnost; MDF otpad; otpadni papir

# 1 INTRODUCTION
## 1. UVOD

MDF (medium-density fiberboards) is known as one of the most essential raw materials for the construction and furniture industry (Pan *et al.,* 2018). Due to the growing consumption of MDF, a huge amount of waste has been generated. Despite the well-known problems of toxic gas emissions to human health and environmental problems, in some countries, such as Iran, waste MDF is still burned, instead of being recycled. Due to the decline in the quality of MDF boards made from recycled fibers, manufacturers are reluctant to recycle this waste. The change in the chemical composition and the urea-formaldehyde resin residues on the surface of the recycled wood fibers leads to an increase in fiber pH. (Lykidis and Grigoriou, 2008; Medved and Resnik, 2004). Considering the incompatibility of the recycled fibers with urea-formaldehyde resin, one of the possible solutions could be to use the recycled fibers to produce binderless boards. Therefore, insulation fiberboard production is an additional alternative to add value to these materials. Insulation fiberboard is a free-formaldehyde, green material made of natural fibers with a low density between 0.1 to 0.35 g/cm³. One of the most critical applications of insulation fiberboard could be its use as thermal insulator in buildings (Epinoza-Herrera and Cloutier, 2009). Due to climate change trends and the importance of reduced energy consumption, it is necessary to develop materials with high thermal insulation ability to sustain proper temperature in interior environments (Sable *et al.,* 2015; Torres Rivas *et al.,* 2018). The materials used as the building thermal insulation must have high specific heat capacity, low density, and low thermal conductivity (Pavelek and Adamova, 2019). Plastic foam and mineral wools are usually used as thermal insulation in building construction. Regarding the petroleum basis of plastic foam and health risks of mineral wools, it is necessary to find a safer and more environmentally friendly alternative for insulation purposes (Kawasaki and Kawai, 2006). Over the past years, raising awareness of environmental issues and harmful effect of chemicals on human health and other organisms have led to the development of green materials (Pavelek and Adamova, 2019). In the previous researches, agricultural and forestry wastes as the insulation materials have been investigated (Asdrubali *et al.,* 2015; Lin *et al.,* 2017; Tsalagkas *et al.,* 2019). One of the important sources of natural fibers, which has not been given enough attention so far, is MDF wastes. However, the high flammability of the natural fibers restricted their applications (Cai *et al.,* 2016). Thermal stability and

fire-resistance of insulation materials is a necessary factor. TGA-DTA and fire retardant tests can be useful techniques to evaluate the performance of insulation materials. TGA measures the mass losses of materials under the influence of elevated temperatures, so it can partially simulate the thermal degradation occurring in fire events (Ramiah, 1970). In this study, the fiberboards were manufactured by a mixture of recycled fibers from MDF and paper wastes to achieve better formation of natural bonds. Waste paper, due to its large number of hydroxyl groups, allows natural bonds to be formed, thus contributing to better formation of fiberboard.

The aim of this study is to investigate the fiberboard produced from recycled fibers without chemicals, along with protecting the natural environment and sustainable use of resources.

# 2 MATERIALS AND METHODS
## 2. MATERIJALI I METODE

### 2.1 MDF wastes recycling process
### 2.1. Proces recikliranja MDF otpada

For this study, MDF wastes and original fibers were obtained from Pars Neopan MDF factory in Iran (Nashtarood). This factory uses a mixture of hardwoods as raw material. These wastes always remain after size cutting of produced MDF boards.

Poly vinyl acetate resin was supplied by Shomal Chemical Industry, a manufacturer of resins and adhesives. The properties of PVAc are shown in Table 1.

**Table 1** Properties of PVAc resin
**Tablica 1.** Svojstva PVAc smole

| Solid Content, %<br>*Sadržaj suhe tvari, %* | Ash<br>*Pepeo, %* | Color<br>*Boja* | Form<br>*Oblik* |
|---|---|---|---|
| 40 | 0.2 | White / *bijela* | Liquid / *tekućina* |

A laboratory chipper crushed the wastes of MDF, and then the chips were treated with hot water at 100 °C for 30 min. After that, the wet chips and waste paper were transferred to the pulper, and the fibers were mechanically released.

### 2.2 Process of manufacturing insulation fiberboards
### 2.2. Proces proizvodnje izolacijskih ploča vlaknatica

Fibers and water were added to the mixture with a weight ratio of 0.03:1 (treatments with adhesive materials), and then 40 g PVAc solution was added to the mixture, too. The obtained pulp was poured to the forming

| 1-Chipping the MDF wastes<br>*1-Usitnjavanje MDF otpada* | 2-Treating the MDF wastes<br>whit hot water<br>*2-Tretiranje MDF otpada*<br>*vrućom vodom* | 3-Pulping MDF and paper<br>wastes<br>*3-Priprema kaše od MDF*<br>*otpada i otpadnog papira* | 4-Mixing the fibers and PVAc<br>with water<br>*4-Miješanje vlakana i PVAc*<br>*ljepila s vodom* |
| 5-Forming<br>*5-Formiranje* | 6-Cold pressing<br>*6-Hladno prešanje* | 7-Drying in oven<br>*7-Sušenje u sušioniku* | 8-Final insulation<br>fibreboard<br>*8-Izolacijska ploča*<br>*vlaknatica* |

**Figure 1** MDF wastes recycling and production process stages of insulation fiberboards
**Slika 1.** Recikliranje MDF otpada i proizvodni proces izolacijskih ploča vlaknatica

equipment, which let water draining, by gravity and low pressure of hand molding. At the end of this step, the thickness of the board reached 30 to 40 mm. The board was pressed at 3.5 bar pressure to a final thickness of 12 mm in a cold press. Finally, the wet board was dried for 24 h at 100 °C, then cooled, weighed and measured, and its density was calculated (the density of insulation fiberboards must be around 0.3 g/cm³). The manufactured boards were conditioned at 20 °C and 65 % humidity for two weeks before trimming to prepare test samples. The MDF wastes recycling and production process stages are shown in Figure 1.

### 2.3 Morphology of fibers
2.3. Morfologija vlakana

Franklin method was used for the separation of wood fibers to study the morphology of fibers. Specimens of virgin and recycled fibers were macerated in a mixture (1:1) of 30 % hydrogen peroxide and acetic acid in a 64 °C oven for 24 hours. After maceration, the samples were washed with distilled water. For measuring fiber dimension, the microscopic images were captured by Motic microscope. After that, the fiber dimensions were measured in Image j software. The dimension of 50 fibers was measured for each kind of fibers.

### 2.4 Physical and mechanical properties
2.4. Fizička i mehanička svojstva

Thickness swelling (*TS*) after immersion in water for 2 h, modulus of rupture (*MOR*), modulus of elasticity (*MOE*) and internal bonding (*IB*) were calculated according to JISA 5905:2003.

### 2.4.1 Thickness swelling after immersion in water
2.4.1. Debljinsko bubrenje nakon potapanja u vodi

First the thickness of the center part of the test piece shall be measured to the nearest 0.05 mm by a dial gauge or a micrometer, next the test piece shall be

placed in water horizontally in depth of about 3 cm below the water surface at a temperature of 20±1 °C. After immersion in water for 2 h, the test piece shall be taken out of water, the water on the test piece shall be removed, and the swelling in thickness after immersion in water shall be calculated by Eq. 1:

$$\text{Swelling in thickness after immersion in water (\%)} = \frac{t_2 - t_1}{t_1} \cdot 100 \qquad (1)$$

Where, $t_1$ – thickness of test piece before immersion (mm)
$t_2$ – thickness of test piece after immersion (mm)

### 2.4.2 Bending strength
2.4.2. Čvrstoća na savijanje

Using the test apparatus, as shown in Figure 2, a load of about 10 mm/min at a mean deforming rate on the surface of test piece was applied. The maximum load (*P*) shall be measured, and the bending strength shall be obtained from Eq. 2:

$$\text{Bending strength}\left(\frac{N}{mm^2}\right) = \frac{3 \cdot P \cdot L}{2 \cdot b \cdot t^2} \qquad (2)$$

Where, $P$ – maximum load (*N*)
$L$ – span (mm)
$b$ – width of test piece (mm)
$t$ – thickness of test piece (mm)

### 2.4.3 Internal bonding
2.4.3. Čvrstoća na raslojavanje

The test piece shall be adhered to a steel block. The tensile load is applied vertically to the surface test
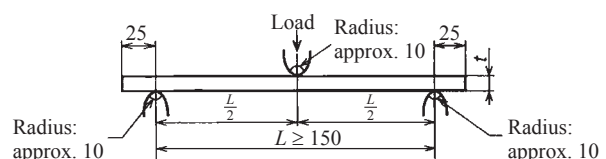
**Figure 2** Bending strength test apparatus
**Slika 2.** Uređaj za ispitivanje čvrstoće na savijanje

of the test piece, the maximum load (*P*) at the time of the fracture of the adhesion part shall be measured, and the internal bond shall be calculated by Eq. 3:

$$Internal\ bond \left(\frac{N}{mm^2}\right) = \frac{P}{b \cdot L}$$

Where, *P* – maximum load at time of fracture of adhesion part (*N*)
  *b* – width of sample (mm)
  *L* – length of sample (mm)

### 2.5 Thermal conductivity
2.5. Toplinska vodljivost

Thermal conductivity coefficient (*λ*) of the insulation fiberboards was measured across the thickness of the panel using a heat flux meter custom-made apparatus.

The full size of the specimens was 500 mm × 500 mm but heat flow was measured in the 120 mm × 120 mm midrange of the sample. The temperature difference between the hot and cold plate was set to 10 °C. For each panel type, the thermal conductivity test was carried out on three specimens.

### 2.6 Fire resistance
2.6. Vatrootpornost

Fire resistance was assessed by the ignitability of products subjected to direct impingement of flame. The test procedure was performed according to STN EN ISO 11925-2:2010.

The test sample with a size of 170 mm × 150 mm was exposed to a small flame with a height of 30 mm for a specified time. The burner must be inclined by an angle of 45° to the vertical axis.

The flame is applied to the sample for 60 s. The measured properties consisted of mass reduction, inflammation time, fire endurance and burnt area.

### 2.7 Thermal stability analysis
2.7. Analiza toplinske stabilnosti

For investigating the thermal behavior of insulation fiberboards, Simultaneous Thermal Analysis (TGA/DTA) was done using Linseis Analyzer (STA PT 1000).

10 mg of each sample was placed on a balance located in the furnace, and heat was applied over the temperature range of room temperature to 600 °C. The analysis was performed under a nitrogen atmosphere flowing at 20 mL/min and a scanning rate of 20 °C/min.

### 2.8 Statistical analysis
2.8. Statistička analiza

The effect of the recycled fiber proportion and the adhesive utilization on the properties of insulation fiberboards was assessed by one-way ANOVA statistical analysis. Also, Duncan's Multiple Range Test (DMRT) was used to check for significant differences between treatment groups.

## 3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

### 3.1 Morphology of fibers
3.1. Morfologija vlakana

The appearance of virgin and recycled fibers is shown in Figure 3. It is obvious that recycled fibers have been damaged as compared to virgin fibers. Fiber degradation occurs due to the pressure and high temperature applied to the fibers during the process of making the initial boards, gluing step, loss of wood polymers, heating and mechanical recycling operations (Lykidis and Grigoriou, 2008).

The measured values of length and diameter of the fibers are presented in Table 2. The results showed that the length and especially the diameter of recycled fibers are less than those of virgin fibers due to the destruction of fibers in the initial board manufacturing and recycling process. The length of the fibers plays an important role in the physical and mechanical properties and its reduction leads to a decrease in the quality of the manufactured boards (Dix *et al.,* 2001a).

### 3.2 Physical and mechanical properties of insulation fiberboards
3.2. Fizička i mehanička svojstva izolacijskih ploča vlaknatica

Statistical analysis of physical and mechanical properties is summarized in Table 3.

**Table 2** Morphology of virgin and recycled fibers
**Tablica 2.** Morfologija djevičanskih i recikliranih vlakana

| Fibers / *Vlakna* | Length, mm *Duljina*, mm | Diameter, mm *Promjer*, mm |
|---|---|---|
| Virgin fibers *djevičanska vlakna* | 2.8 | 0.52 |
| Recycled fibers *reciklirana vlakna* | 1.62 | 0.33 |



**Figure 3** Appearance of virgin and recycled fiber surface (unit mm, magnification 40x)
**Slika 3.** Izgled površine djevičanskih i recikliranih vlakana (jedinica: mm, povećanje: 40 puta)

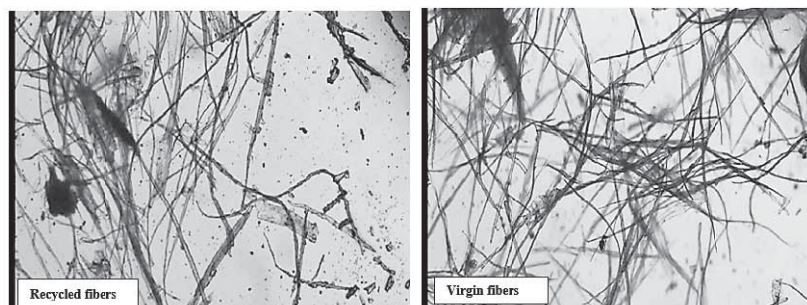**Table 3** Statistical analysis of physical and mechanical properties of insulation fiberboard produced with different treatments (*TS* – thickness swelling, *MOR* – modulus of rupture, *MOE* – modulus of elasticity, *IB* – internal bonding)
**Tablica 3.** Statistička analiza fizičkih i mehaničkih svojstava izolacijskih ploča vlaknatica proizvedenih različitim tretmanima (*TS* – debljinsko bubrenje, *MOR* – modul loma, *MOE* – modul elastičnosti, *IB* – čvrstoća na raslojavanje)

| Properties / *Svojstva* | Variables / *Varijable* | Mean square *Srednji kvadrat* | *df* (within groups) *df (unutar grupa)* | sign. |
|---|---|---|---|---|
| *TS*, % | Proportion of fibers / *udio vlakana* | 29.67 | 1 | 0.000 |
| | Adhesive utilization / *uporaba ljepila* | 48.15 | 1 | 0.000 |
| | Interaction effect / *međudjelovanje* | 8.56 | 1 | 0.008 |
| *MOR*, MPa | Proportion of fibers / *udio vlakana* | 41.19 | 1 | 0.000 |
| | Adhesive utilization / *uporaba ljepila* | 373.71 | 1 | 0.000 |
| | Interaction effect / *međudjelovanje* | 2.839 | 1 | 0.001 |
| *MOE*, MPa | Proportion of fibers / *udio vlakana* | 1970114.01 | 1 | 0.000 |
| | Adhesive utilization / *uporaba ljepila* | 1153714.08 | 1 | 0.000 |
| | Interaction effect / *međudjelovanje* | 148632.73 | 1 | 0.000 |
| *IB*, MPa | Proportion of fibers / *udio vlakana* | 0.432 | 1 | 0.000 |
| | Adhesive utilization / *uporaba ljepila* | 0.98 | 1 | 0.000 |
| | Interaction effect / *međudjelovanje* | 0.09 | 1 | 0.000 |

The analysis showed that the effect of different ratios of fibers and adhesive utilization on both physical and mechanical properties of insulation fiberboards was significant at a 99 % confidence interval (Sig <0.01). Duncan's multiple range classification of the effect of different treatments is shown in Table 4.

As shown in Table 4, instead of thickness swelling of the insulation fiberboards, which is better than values defined in the standard, the other measured properties are lower than those specified in the standard, but they are relatively acceptable regarding their low density and manufacturing condition (without synthetic resin and hot pressing). The application of the manufactured fiberboards is restricted; they are intended to be used as insulator, and they cannot be used in applications where high strength is required. The use of PVAc adhesive resulted in the improvement of the physical and mechanical properties of insulation fiberboards. PVAc can improve the adhesion of fibers (Sable et al., 2015). PVAc, as an insulator, provides not only mechanical strength but also prevents the exposure of fibers to the atmosphere and leads to high stability in the environment (Hosseini and Entezami, 2005). In terms of thickness swelling and internal bonding, WP/RF ratio of 50/50 is suggested. However, considering *MOR* and *MOE*, WP/RF ratio of 70/30 leads to better results due to more flexibility of waste paper as compared to fibers recycled from MDF wastes, which is the result of a lower amount of lignin and decreased stiffness of waste paper. As the results show, an increased amount of waste paper leads to a decrease in the internal bonding of boards because of heterogeneous forming of boards, which results in a lack of proper bonding between the different components of two types of fiber (Rassam, 2008). Paper fibers also have a higher specific surface area than that of wood fibers because of their small size and high slenderness ratio, which results in better absorption of the adhesive and prevents uniform spreading between the fibers. Because of this phenomenon, the internal adhesion of boards with a higher proportion of waste paper is reduced (Ghahri, 2017). Each type of fiber has its own unique characteristics due to their different preparation methods. Considering MDF fibers, hemicelluloses and lignin of the intercellular material have been partially degraded, also due to the mechanical method of fiber separation, fractures occurred in the fibers and the dissolved lignin resulted in fusion and reconnection of the fibers in hot press (Ghahri, 2017). However, in the case of paper fibers, chemical and semi-chemical pulping have a profound effect on cellulose fibers and cell walls. These include the removal of large amounts of hemicelluloses and lignin from the reticular cell walls and their conversion into larger pores reticular

**Table 4** Average values of Duncan's multiple range classification of the effect of different treatments on properties of produced insulation fiberboards: N-70-30 (without adhesive, WP/RF ratio of 70/30), N-50-50 (without adhesive, WP/RF ratio of 50/50), W-70-30(with PVAc adhesive, WP/RF ratio of 70/30) and W-50-50 (with PVAc adhesive, WP/RF ratio of 50/50)
**Tablica 4.** Srednje vrijednosti Duncanove višestruke klasifikacije učinka različitih tretmana na svojstva proizvedenih izolacijskih ploča vlaknatica: N-70-30 (bez ljepila, omjer WP/RF 70 : 30), N-50-50 (bez ljepila, WP/RF omjer 50 : 50), W-70-30 (s PVAc ljepilom, WP/RF omjer 70 : 30) i W-50-50 (s PVAc ljepilom, WP/RF omjer 50 : 50)

| Property *Svojstvo* | N-70-30 | N-50-50 | W-70-30 | W-50-50 | Standard values (Thickness of 12 to 19 mm) *Standardne vrijednosti (debljina od 12 do 19 mm)* |
|---|---|---|---|---|---|
| *TS*, % | 10.17(b) | 6.88(ab) | 7.46(ab) | 6.12(a) | 12 |
| *MOR*, MPa | 18(c) | 11(d) | 19.5(b) | 13.7(a) | 20 |
| *MOE*, MPa | 1520.66(b) | 1034.11(c) | 1860.01(a) | 1630.49(b) | 2200 |
| *IB*, MPa | 0.09(b) | 0.099(b) | 0.209(b) | 0.41(a) | 0.55 |

system that creates space and locality for water absorption. The partial removal of lignin and hemicellulose polymers results in the availability of large numbers of hydroxyl groups in the cell wall of the fibers, which leads to excellent hydrogen bonding of the fibers and subsequently dimensional stability of the produced fiberboards. Waste paper fibers and recycled fibers from MDF wastes have different morphology. The waste paper fibers lose much lignin, while the recovered fibers from MDF wastes have more lignin, which makes them stiffer as compared to paper fibers (Hwang et al., 2005). When the combination of paper fibers and recycled fibers from MDF wastes are used for fiberboard manufacturing, inter-fiber bonds are formed better.In addition, the paper fibers have a bearded state due to refining operations, which makes them more likely to have hydrogen bonds (Rassam, 2008).

### 3.3 Thermal conductivity of insulation fiberboards
3.3. Toplinska vodljivost izolacijskih ploča vlaknatica

Thermal conductivity is an indicator of the value of a material as a heat insulator (Xu *et al.,* 2004). Wood based panels manufacturing methods, wood based materials and wood particle sizes were indicated as having a large effect on thermal conductivity (Tsalagakas *et al.,* 2019). As it can be observed in Figure 4, the insulation fiberboards made from PVAc adhesive and the WP/RF ratio of 50/50 is a better insulator compared to other treatments. The use of PVAc decreased thermal conductivity.

Utilization of waste paper and fibers recycled from MDF wastes as a component appears to be an appropriate choice for manufacturing insulation fiberboards. Paper has been employed as insulation material due to its low thermal conductivity value. The thermal conductivity of paper varies upon the paper sheet density, filler content, nature of fibers, etc. (Tsalagakas *et*

*al.,* 2019). The measured thermal conductivity ( of the obtained boards was within the interval of 0.025-0.037 W/m·K, which is in the range of building bio-based insulation materials (Theasy *et al.,* 2017). Due to the different structure of the two types of fibers (obtained from waste paper and MDF wastes) and process of manufacturing, the structure of the insulation fiberboards is very porous. Low thermal conductivity of the insulation fiberboards is due to the low conductivity of the air trapped in the pores. The large number of spaces and voids inside the insulators impeded heat transfer, resulting in considerably lower thermal conductivity (Sihabut and Laemsak, 2010). The thermal conductivity of air is lower than that of solid materials (Nguyen *et al.,* 2018). For better comparison, the measured values of for different kinds of insulators, according to the results reported by other researchers, are presented in Table 5.

### 3.4 Fire resistance of insulation fiberboards
3.4. Vatrootpornost izolacijskih ploča vlaknatica

According to Table 6, samples lose their weight about 3 % to 15 % of the weight of the initial value after 60 s of flame exposure.

The results of flame resistance values of insulation fiberboards showed that the lowest mass reduction was related to fiberboards manufactured with PVAc adhesive and WP/RF ratio of 50/50 (lower amount of paper), which can confirm the positive effect of the use of adhesive on the thermal stability of insulation fiberboards. It is obvious that the use of PVAc can increase the fire resistance of insulation boards. PVAc is degraded by elimination of acetic acid, yielding a char that provides a transitory phase as the filler particles fuse into a ceramic mass (Al-hassany et al., 2010). Insulation fiberboards manufactured without adhesive and WP/RF ratio of 50/50 (N-50-50) had the lowest ther-
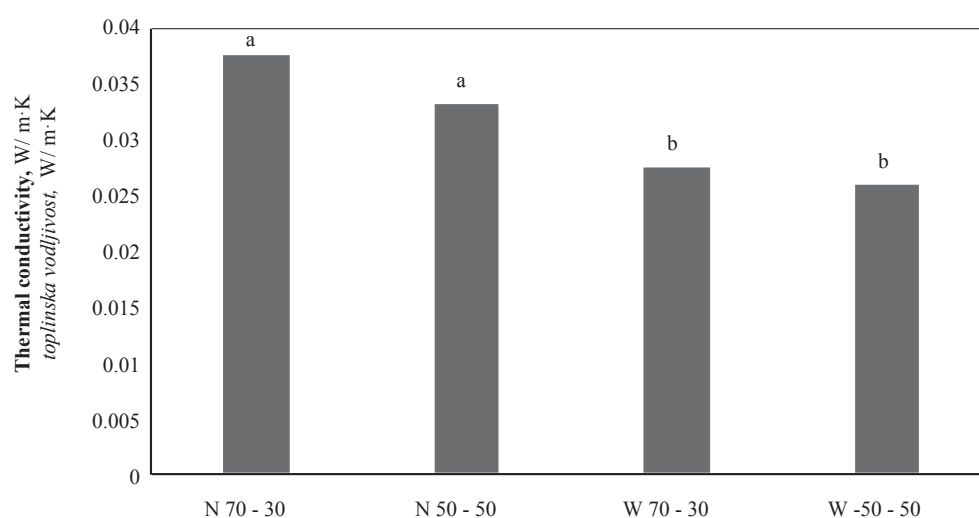


**Figure 4** Thermal conductivity values of insulation fiberboards made by different treatments (Duncan's multiple range classifications are shown above the columns: N-70-30 (without adhesive, WP/RF ratio of 70/30), N-50-50 (without adhesive, WP/RF ratio of 50/50), W-70-30(with PVAc adhesive, WP/RF ratio of 70/30) and W-50-50 (with PVAc adhesive, WP/RF ratio of 50/50)
**Slika 4.** Vrijednosti toplinske vodljivosti izolacijskih ploča vlaknatica izrađenih različitim tretmanima (Duncanove višestruke klasifikacije prikazane su iznad stupaca): N-70-30 (bez ljepila, omjer WP/RF 70 : 30), N-50-50 (bez ljepila, omjer WP/RF 50 : 50), W-70-30 (s PVAc ljepilom, omjer WP/RF 70 : 30) i W-50-50 (s PVAc ljepilom, omjer WP/RF 50 : 50)

**Table 5** Thermal conductivity of different kinds of insulators
**Tablica 5.** Toplinska vodljivost različitih vrsta izolacijskog materijala

| Material / *Materijal* | Thermal conductivity coefficient, W/m·K *Koeficijent toplinske vodljivosti*, W/m·K | Literature / *Literatura* |
|---|---|---|
| Wood with density of 0.45 to 0.65 g/cm³ / *drvo gustoće 0,45 - 0,65* g/cm³ | 0.13 | Xu *et al.*, 2004 |
| Wood with density of 0.2 to 0.5 g/cm³ / *drvo gustoće 0,2 - 0,5* g/cm³ | 0.01 | Kawasaki and Kawai, 2006 |
| Plywood with density of 1.7 g/cm³ / *furnirska ploča gustoće* 1,7 g/cm³ | 0.071 | Xu *et al.*, 2004 |
| Insulation board with density of 0.26 g/cm³ *izolacijska ploča gustoće 0,26* g/cm³ | 0.044 | Xu *et al.*, 2004 |
| Concrete with density of 0.2 g/cm³ / *cement gustoće 0,2* g/cm³ | 1.2 | Xu *et al.*, 2004 |
| Bricks with density of 1.7 g/cm³ / *cigla gustoće 1,7* g/cm³ | 0.53 | Xu *et al.*, 2004 |
| Waste paper / *otpadni papir* | 0.05- 0.06 | Tsalagakas *et al.*, 2019 |
| Waste newspaper particle board *iverica od otpadnoga novinskog papira* | 0.025 | Theasy *et al.*, 2017 |
| Insulation boards from oil palm fronds *izolacijske ploče od palminih listova* | 0.034 | Sihabut and Laemsak, 2010 |
| Insulation boards from empty fruit branches *izolacijske ploče na bazi grana voćaka* | 0.038 | Sihabut and Laemsak, 2010 |
| Rock wool / *kamena vuna* | 0.037 | Sihabut and Laemsak, 2010 |
| Bark based panels from popular *ploče na bazi kore topolovine* | 0.069-0.093 | Tsalagakas *et al.*, 2019 |
| Wooden matts from wood shaving and kenaf fibers *drveni tepisi na bazi blanjevine i vlakana od kenafa* | 0.069 | Tsalagakas *et al.*, 2019 |

**Table 6** Average values of fire resistance properties of insulation fiber boards and Duncan's multiple range classification of the effect of different treatments: N-70-30 (without adhesive, WP/RF ratio of 70/30), N-50-50 (without adhesive, WP/RF ratio of 50/50), W-70-30(with PVAc adhesive, WP/RF ratio of 70/30) and W-50-50 (with PVAc adhesive, WP/RF ratio of 50/50)
**Tablica 6.** Srednje vrijednosti svojstava vatrootpornosti izolacijskih ploča vlaknatica i Duncanova višestruka klasifikacija učinka različitih tretmana: N-70-30 (bez ljepila, omjer WP/RF 70 : 30), N-50-50 (bez ljepila, omjer WP/RF 50 : 50), W-70-30 (s PVAc ljepilom, omjer WP/RF 70 : 30) i W-50-50 (s PVAc ljepilom, omjer WP/RF 50 : 50)

| Property / *Svojstvo* | N-70-30 | N-50-50 | W-70-30 | W-50-50 |
|---|---|---|---|---|
| Mass reduction, % / *smanjenje mase, %* | 7.44(c) | 15.21(d) | 4.71(b) | 2.62(a) |
| Inflammation time, s / *vrijeme zapaljenja*, s | 5(a) | 2(a) | 9(b) | 8(b) |
| Fire endurance, s / *vatrootpornost*, s | 75(b) | 120(c) | 15(a) | 10(a) |
| Burnt area, % / *izgorjela površina*, % | 21(b) | 38(c) | 4(a) | 1(a) |

mal stability as compared to other treatments due to low internal bonding and weakness in bonding formation. Reducing internal bonding between fibers and the fuzzy surface of boards caused more surface burns and lead to an increased mass reduction of the boards, which is an important criterion for assessing fire resistance of boars (Hojati et al., 2018).

### 3.5 Thermal stability of insulation fiberboards
3.5. Toplinska stabilnost izolacijskih ploča vlaknatica

Figures 5 and 6 show the TGA–DTG and DTA curves of insulation fiberboards, respectively.

Thermal degradation mechanism of wood occurred in three regions, including 60-100 °C (evaporation of water and extractives), 130-350 °C (decomposition of major wood chemical constituents) and after 350 °C (complete decomposition of wood) (Feng *et al.,* 2012; Bodirlau *et al.,* 2009; Yunchu *et al.,* 2000). Above 200 °C, the pyrolysis speed increases, hemicelluloses and cellulose decompose into gases (Yunchu *et al.,* 2000). In a temperature range between (250 to 300 °C, lignin and cellulose are degraded, and tar, gas and char are produced during the pyrolysis (Hakiki- Uner

*et al.,* 2016). After heating to 350 °C, since the amount of flammable gas is very small, the flame burn transforms into the flameless charcoal burn. In this step, weight loss slows down (Yunchu *et al.,* 2000). After 430 °C, an exothermal peak of wood burn appears on the DTA curve (Figure 6).

Instead of the N-70-30 curve, which is related to insulation fiberboards made by WP/RF ratio of 70/30 and without adhesive, in other curves, the sharp exothermal peak is smoothed and the temperature of the peak is increased. This means that the utilization of a higher amount of wood fibers and adhesive increased the thermal stability of fiberboards, and the rates of heat released slowly down. The broadest peak is related to W-50-50 insulation fiberboards, which are manufactured by the use of PVAc adhesive and a lower amount of waste paper. Concerning the N-70-30 curve, the main component is waste paper. Waste paper is mainly composed of cellulose. The shape of this curve and the intensity of the decomposition peak are very similar to those of the cellulose curve (Sobol *et al.,* 2020). In fact, there is a larger share of cellulose in this sample and therefore its shape is different from other
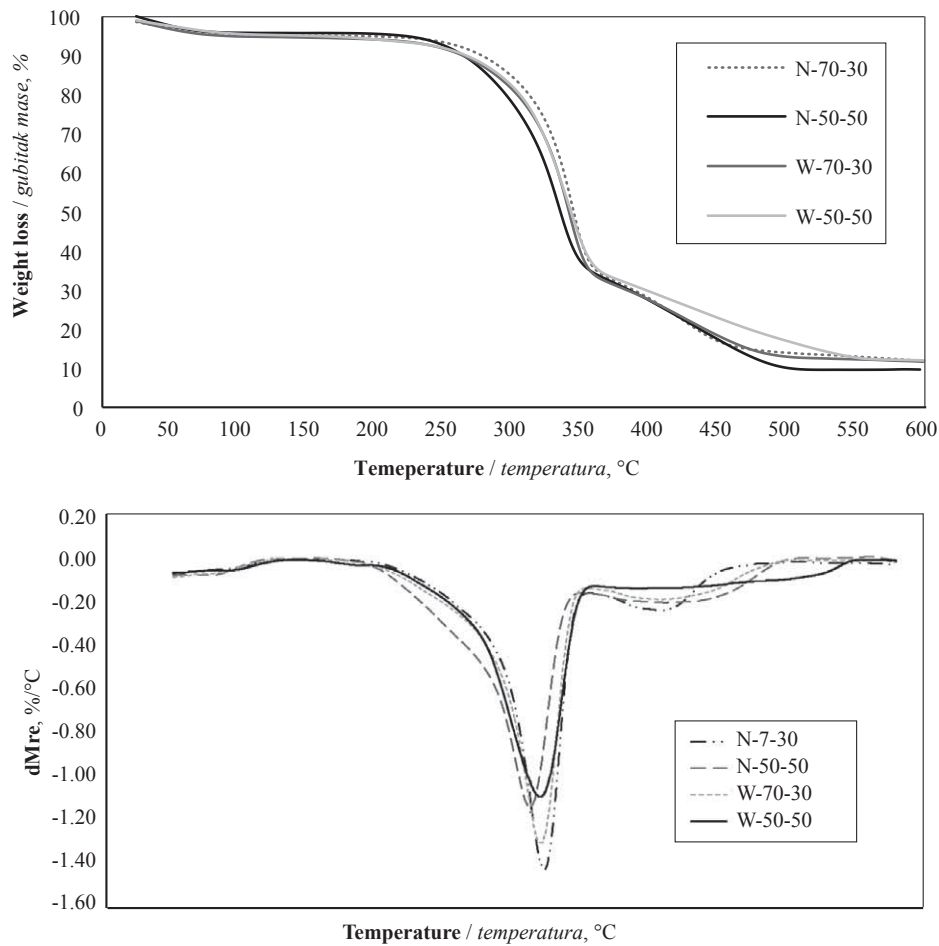
**Figure 5** TGA-DTG thermograms of insulation fiberboards: N-70-30 (without adhesive, WP/RF ratio of 70/30), N-50-50 (without adhesive, WP/RF ratio of 50/50), W-70-30 (with PVAc adhesive, WP/RF ratio of 70/30) and W-50-50 (with PVAc adhesive, WP/RF ratio of 50/50)
**Slika 5.** TGA-DTG termogrami izolacijskih ploča vlaknatica: N-70-30 (bez ljepila, omjer WP/RF 70 : 30), N-50-50 (bez ljepila, omjer WP/RF 50 : 50), W-70-30 (s PVAc ljepilom, omjer WP/RF 70 : 30) i W-50-50 (s PVAc ljepilom, omjer WP/RF 50 : 50)
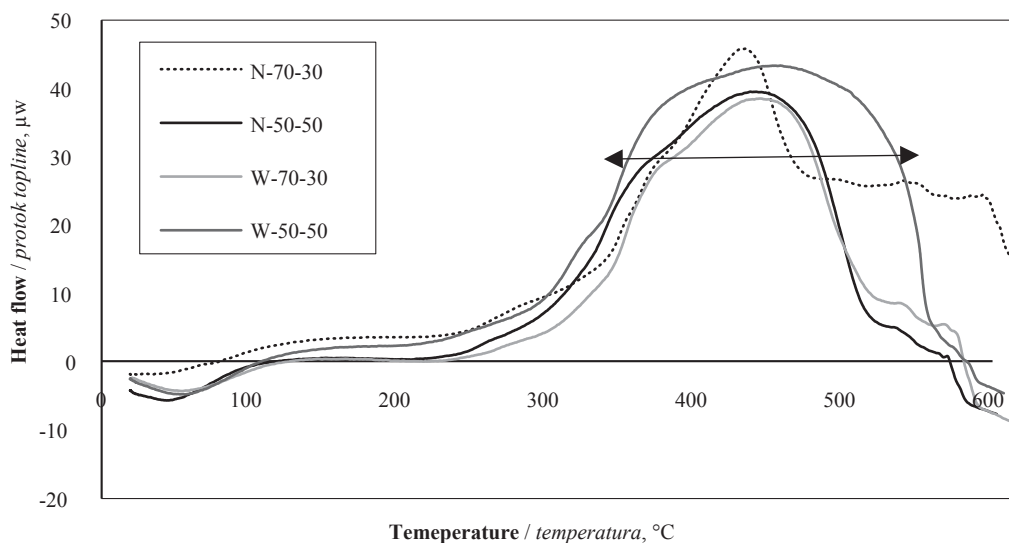


**Figure 6** DTA thermograms of insulation fiberboards: N-70-30 (without adhesive, WP/RF ratio of 70/30), N-50-50 (without adhesive, WP/RF ratio of 50/50), W-70-30 (with PVAc adhesive, WP/RF ratio of 70/30) and W-50-50 (with PVAc adhesive, WP/RF ratio of 50/50)
**Slika 6.** DTA termogrami izolacijskih ploča vlaknatica: N-70-30 (bez ljepila, omjer WP/RF 70 : 30), N-50-50 (bez ljepila, omjer WP/RF 50 : 50), W-70-30 (s PVAc ljepilom, omjer WP/RF 70 : 30) i W-50-50 (s PVAc ljepilom, omjer WP/RF 50 : 50)

**Table 7** TGA – DTA results from insulation fiberboards manufactured by waste MDF and paper fibers: N-70-30 (without adhesive, WP/RF ratio of 70/30), N-50-50 (without adhesive, WP/RF ratio of 50/50), W-70-30(with PVAc adhesive, WP/RF ratio of 70/30) and W-50-50 (with PVAc adhesive, WP/RF ratio of 50/50)
**Tablica 7.** TGA – DTA rezultati za izolacijske ploče vlaknatice proizvedene od vlakana MDF otpada i otpadnog papira: N-70-30 (bez ljepila, omjer WP/RF 70 : 30), N-50-50 (bez ljepila, omjer WP/RF 50 : 50), W-70-30 (s PVAc ljepilom, omjer WP/RF 70 : 30) i W-50-50 (s PVAc ljepilom, omjer WP/RF 50 : 50)

| Samples Uzorci | $T_i$-$T_f$, °C | $T_m$, °C | $W_{Ti}$, % | $W_{max}$. % (second region / drugo područje) | $W_{Tf}$, % | Residues, % Ostatak, % | DTA peak, °C |
|---|---|---|---|---|---|---|---|
| N-70-30 | 105.7-470 | 359.9 | 3.23 | 60.21 | 23.22 | 11.8 | 432 |
| N-50-50 | 100.3-500 | 355.4 | 4.16 | 59.21 | 26.94 | 9.7 | 445 |
| W-70-30 | 134.8-490 | 363.8 | 4.13 | 61.58 | 21.49 | 11.7 | 450 |
| W-50-50 | 125.5-550 | 358.3 | 3.79 | 20.21 | 22.86 | 12 | 460 |

$T_i$-$T_f$ – temperature corresponding to the beginning and end of decomposition, respectively / t*emperatura koja odgovara početku i kraju razgradnje*; $T_m$ – Temperature corresponding to the maximum rate of mass loss / *temperatura koja odgovara najvećem gubitku mase*; W – weight loss / *gubitak mase*

curves. Summary data of TGA-DTA for fibers can be observed in Table 7.

The results show that the degradation began faster with insulation fiberboard in which PVAc adhesive was used. In addition, when the lower percentage of waste paper was used, the degradation reaction occurred faster. $T_m$ as a crucial factor, was higher with insulation fiberboards made from WP/RF ratio of 70/30 with PVAc and lower with insulation fiberboards manufactured without adhesive and WP/RF ratio of 50/50. The maximum weight loss was observed in insulation fiberboard manufactured with PVAc adhesive and WP/RF ratio of 70/30. The lowest weight loss with a significant difference occurred in insulation fiberboards manufactured with PVAc adhesive and WP/RF ratio of 50/50 (W-50-50). The higher weight loss means lower thermal stability (Aydemir *et al.,* 2011). It can be said that the use of adhesive and a lower percentage of waste paper results in a higher thermal stability. There is not a significant difference in terminal mass residues of different treatments. The lowest mass residue (9.7 %) was observed with insulation fiberboard manufactured without adhesive and with 50 % waste paper, the reason probably being the weak bonding of this kind of board. Overall, it can be concluded that the use of adhesive results in increased thermal stability of insulation fiberboard. Also, the higher amount of waste paper decreased the thermal stability of insulation fiberboards. DTA peak temperature in N-70-30 fiberboards was significantly lower than in other treatments, which confirmed previously obtained results and showed that this treatment caused lower thermal stability of fiberboards. The thermal resistance of a compound is related to the breakdown of the weakest bond at a specific temperature as the temperature was raised (Bachari, 2015).

## 4 CONCLUSIONS
## 4. ZAKLJUČAK

This study showed that it is possible to manufacture insulation fiberboard from wastes of MDF and paper by the wet process.

According to the measured values, which were similar to mineral wool, it can be said that the manu-

factured insulation fiberboards can be properly used as a structural insulator.

The use of PVAc adhesive and a lower percentage of waste paper (WP/RF ratio of 50/50) in manufacturing fiberboard result in a higher fire resistance and thermal stability, in better functional properties and lower thermal conductivity values of insulation fiberboards.

Better insulators have better thermal stability.

Overall, it can be concluded that waste MDF and paper have good potential to be used as raw material for producing green insulation fiberboards. with better results obtained from treatment in which PVAc adhesive and the WP/RF ratio of 50-50 (waste paper to recycled MDF fibers) were used.

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# Performance of ANN in Predicting Internal Bonding of Cement Particleboard Manufactured from Giant Reed and Bagasse

## Primjena umjetne neuronske mreže u predviđanju čvrstoće na raslojavanje cementne iverice proizvedene od divovske trske i ostataka od prerade šećerne trske

**ABSTRACT** • *The present article investigates the microstructure of the cement matrices and the products of cement hydration by means of scanning electron microscopy, Fourier transform infrared spectroscopy and X-Ray diffraction. Then, the internal bonding strength (IB) is measured for the mixtures containing various amounts of nanosilica (NS), reed and bagasse particles. Finally, an Artificial Neural Network (ANN) is trained to reproduce these experimental results. The results show that the hardened cement paste including NS features the highest level of C-S-H. However, it has a lower level of C-S-H polymerization if reed or bagasse particles are applied. A relatively new dense microstructural degree is considered in the cement pastes containing NS, and a lower agglomeration is observed in the samples including reed or bagasse particles with NS. According to the microstructural analysis, the addition of NS to the samples containing reed or bagasse particles increases the unhydrated amount of $C_2S$ and $C_3S$ in the cement paste due to the decrease in the water needed for fully hydrated cement grains through portlandite ($Ca(OH)_2$), C-S-H and ettringite increase. Besides, it is shown that the ANN prediction model is a useful, reliable and quite effective tool for modeling IB of cement-bonded particleboard (CBPB). It is indicated that the mean absolute percentage errors (MAPE) are 1.98 % and 1.45 % in the prediction of the IB values for the training and testing datasets, respectively. The determination coefficients ($R^2$) of the training and testing data sets are 0.972 and 0.997 in the prediction of the bonding strength by ANN, respectively.*

*Keywords:* cement-bonded particleboard; nanosilica; internal bonding; hydration; ANN

**SAŽETAK** • *U radu se opisuje istraživanje mikrostrukture cementnih matrica i proizvoda hidratacije cementa uz pomoć pretražnoga elektronskog mikroskopa, Fourierove transformirane infracrvene spektroskopije i rendgenske difrakcije. Pritom je izmjerena i čvrstoća na raslojavanje (IB) za smjese koje sadržavaju različite količine čestica nanosilike (NS), trske i ostataka od prerade šećerne trske. Na kraju su uz pomoć umjetne neuronske mreže (ANN)*

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*reproducirani eksperimentalni podatci. Rezultati su pokazali da otvrdnuta cementna pasta s nanosilikom ima najvišu razinu C-S-H. Međutim, ako se rabe čestice trske ili ostataka od prerade šećerne trske, cementna pasta ima niži stupanj polimerizacije C-S-H. Detaljno je analiziran relativno nov stupanj gustoće mikrostrukture cementne paste koja sadržava nanosiliku, pri čemu su uočene i manje nakupine u uzorcima koji su, osim nanosilike, sadržavali i čestice trske ili ostataka od njezine prerade. Prema analizi mikrostrukture, dodatkom nanosilike uzorcima koji sadržavaju čestice trske ili ostataka od prerade šećerne trske povećava se nehidratizirana količina $C_2S$ i $C_3S$ u cementnoj pasti zbog smanjenja vode potrebne za potpunu hidratizaciju cementnih zrna putem portlandita $(Ca(OH)_2)$ te povećanjem C-S-H i etringita. Osim toga, pokazalo se da je ANN model predviđanja koristan, pouzdan i vrlo učinkovit alat za modeliranje čvrstoće cementne iverice na raslojavanje. Srednja apsolutna pogreška (MAPE) u predviđanju čvrstoće na raslojavanje za eksperimentalne i izmjerene skupove podataka iznosi 1,98 %, odnosno 1,45 %. Koeficijenti korelacije $R^2$ eksperimentalnih i izmjerenih skupina podataka u predviđanju čvrstoće na raslojavanje uz pomoć ANN modela iznose 0,972 odnosno 0,997.*

**Ključne riječi:** *cementna iverica; nanosilika; čvrstoća na raslojavanje; hidratacija; ANN*

# 1 INTRODUCTION
## 1. UVOD

Mineral-bonded particleboards are panel products manufactured from the compressed particles of the wood or non-wood materials and a mineral binder such as cement. Among these panels, cement-bonded particleboards are well known and are applied in different components of the final industrial products. The increasing population and demands for wood-based composite materials have encouraged the researchers to study the application of the non-wood-based biomass in different composites. Annual plant and lignocellulosic waste materials can be substituted for wood to produce agro-based panels. Nowadays, more than 30 plants are used as renewable materials in various composed-productions around the world (Bektas *et al.*, 2005). Therefore, it seems that substitution of raw materials such as agricultural waste will play an important role in the composite production industries such as particleboards in the future (Nemli *et al.*, 2009). One of the lignocellulosic renewable biomasses is reed (*Arundo donax*) stalks. This species is known as a weedy and invasive plant in several countries (Quinn and Holt, 2008) and is considered as one of the 100 world's most aggressive species (Lowe *et al.*, 2000). In addition, since this species is a fast renewable alternative, it can meet the demand for biomass production via cultivation of *A. donax* on in a wide scale. However, using this material is accompanied by drawbacks that can strongly affect the properties of the lignocellulosic-based composite materials, including the adverse effects of certain extractives during cement hardening, undefined standard method to assess the compatibility of these materials with cement, etc.

In order to improve the compatibility between cement and lignocellulosic materials and cement-bonded particleboard properties, researchers studied the effect of many variables, including particle size, different kinds of wood or lignocellulosic materials with or without additives, water-, acid- or alkaline-solution leaching, etc. on the cement hydration behavior and cement-bonded particleboard (CBPB) properties. According to Eusebio (2004), bagasse particles passed through a 2 mm-sized mesh with the bagasse–cement ratio of 1:2 that should be selected to make CBPB with the density of 1.00 g/cm³. Bilba *et al.* (2003) treated bagasse particles thermally at the temperature of 200 °C to improve the bagasse–cement complex and showed the hydration behavior of the cement. Sedan *et al.* (2008), Arsene *et al.* (2007) and Troedec *et al.* (2011) showed that the alkaline and pyrolysis pre-treatments of the fiber can enhance the flexural strength of the composites, while the acid treatment decreases the properties of the panels. Further improvement of the porosity, durability and strength of the panels can be achieved by adding pozzolanic materials such as fly ash, slag, silica fume and metakaolin (Filho *et al.*, 2003; Juarez *et al.*, 2007). Juarez *et al.* (2007) treated the fibers with paraffin and added fly ash as a pozzolan admixture to the composite matrix. The performance of the composite was acceptable; so the paraffin treatment reduced the water absorption of the fibers, while the tensile strength was at the sufficient level (Coatanlem *et al.*, 2006). Coatanlem *et al.* (2006) showed that CBPB properties are improved by saturating the wood particles with sodium silicate due to the formation of ettringite needles enhancing the bonds between wood particles and cement paste.

The diversity of the phenomena potentially occurring in the cement-wood particleboard reinforced by NS is such that linking the *IB* to its physical origin is hardly achievable. For instance, changes in *IB* can be induced by different stress concentrations due to the volume and shape of macropores, difference of the effective w/c ratio owing to the absorption of water by wood particles, change of hydration degree of the cement paste, consumption of Portlandite by pozzolanic reactions strengthening the interface between the paste and the wood particles or leakage of soluble organic matters poisoning the hydration of the cement. Hence, it seems that there are many effective factors related to the physical and mechanical properties of CBPB, so that it is necessary to optimize panel production by changing the main effective variables to reduce the negative effect of the poisoning compounds, increasing the performance of the panels in different applications and decreasing the production cost of the panels.

On one hand, common statistical methods involve a great deal of work, and on the other hand, they

neither predict the properties of the panels nor optimize the production process. However, ANNs have emerged as one of the most useful methods for modeling and optimization in recent years, especially for non-linear problems (Desai *et al.,* 2008). They are especially useful for simulating experimental designs, which are difficult to be explained by physical models. They demonstrate a linkage between input and output data using a series of non-linear functions. The number of layers in the network and the number of neurons in each layer known as architecture are the most important steps in choosing a neural network modeling.

There are a few studies related to the wood-based panel properties based on ANNs such as modeling formaldehyde emission (Akyuz *et al.,* 2017), predicting effect of adding paraffin on physical properties of medium density fiberboard (Gurgen *et al.*, 2019), predicting the internal bond strength of the particleboard under outdoor exposure (Watanabe *et al.,* 2015; Korai and Watanabe, 2016), optimizing the process parameters in wood-based panel production (Cook *et al.,* 2000; Ozsahin, 2013), obtaining the values of the internal bond of the particleboard using the manufacturing parameters (Cook and Chiu, 1997), predicting the particleboard mechanical properties (Fernandez *et al.,* 2008), so on.

Even though there is sufficient literature on the properties of the wood-based panels, only a few systematic investigations are reported so far to correlate the production parameters and properties of CBPBs and predict the panel properties. Hence, in this study, a design is developed from the experimental data that performs experiments to explore the correlation between the production variables including Nano $SiO_2$ content, particle size and weight ratio of bagasse to reed particles and multi-layer perceptron (MLP) model to predict the panel properties.

## 2 MATERIALS AND METHODS
2. MATERIJALI I METODE

### 2.1 Microstructural investigations
2.1. Istraživanje mikrostrukture

Reed stalks were collected from a suburb near Zabol City in Sistan-and-Baloochestan Province of Iran. Bagasse particles were obtained from Pars Paper Co. Ltd., Haft Tapeh, Iran. Reed stalks and bagasse particles were milled into fine particles using a hammer mill, and then, the oversized particles were eliminated by an analytical sieve shaker using a sieve with the mesh size of 40. The commercial grade Portland cement (Type II) was purchased from Sistan Cement Industry Co., Ltd., Iran, to be used as a binder for making cubic samples with the dimensions of 2 cm × 2 cm × 3 cm. Nano-$SiO_2$ powder was purchased from Plasma Chem. GmbH, Berlin, Germany, under the trade name AEROSIL® 200 to be used as an accelerator additive, and its average BET surface area was (200±25) $m^2$/g, with the average particle size of 7-14 nm and the purity 99.80 %. In order to disperse Nano in cement well, the Nano was added to the distilled water and ultrasoni-

cated (frequency: 20 kHz; generating power: 600 W) for 6 min to form nanoparticle suspensions. The prepared suspensions were then used as "mixing water" for preparing cement pastes. The nano-$SiO_2$ powder was used as a replacement of the cement at the weight percentage of 6 % (by dry weight of the cement).

The cement complex was divided into four different mixtures, i.e. the pure cement paste, cement mixed with Nanosilica, cement+Nanosilica mixed with reed fine particles and cement-Nanosilica mixed with bagasse fine particles. Due to the high absorption of the reed and bagasse particles, the cement paste samples were prepared with a high water to cement ratio of 50:50.

After curing the samples for 15 days, scanning electron microscopy (SEM) was employed to study the microstructural changes in the samples with or without Nanosilica. Samples were metallized by a 1-2 nm thick conductive layer of Au under a vacuum medium after being mounted in the standard form. The morphology was observed by AIS 2100, Seron Technology, Korea. The transmission Fourier-Transform Infrared Spectroscopy (FTIR) technique was used to measure the infrared active cured-cement samples. For this purpose, 1 mg of the powdered samples was blended with 99 mg KBr as an infrared transparent soft salt in order to obtain the same concentration and avoid variations of the transmittance between the samples. The mixtures were then pressed into a solid disc and then scanned between 400 $cm^{-1}$ and 4000 $cm^{-1}$, with a total of 20 scans and a resolution of 8 $cm^{-1}$ to identify their specific functional groups by a Bruker Optics TENSOR 27 FTIR spectrometer. To consider the crystallinity of the samples, their X-ray diffraction (XRD) patterns were recorded by an Equinox 3000 (INEL, France) wide angle X-ray diffractometer using a CuKα radiation source with the wavelength of λ=0.154 nm.

### 2.2 Board preparation
2.2. Priprema ploče

The raw materials used in this study were bagasse (sugar cane) and reed (*Arondodonax*) particles prepared using a disc mill (DM 200, produced by Retsch Co., Germany) and screened by an analytical sieve shaker using sieves to obtain five particle sizes: (1) very large, S1 (10 mm pass/8 mm on); (2) large, S2 (8 mm pass/6 mm on); (3) medium S3 (6 mm pass/4 mm on); (4) small S4 (4 mm pass/2 mm on), and very small S5 (2 mm pass). The particles were further oven dried to 5 % moisture content (*MC*). A commercial grade Portland cement, type II, was used as a bonding agent. The cement ratio of the lignocellulosic particles applied in this study was 1:3 based on the oven dry weight. Calcium chloride ($CaCl_2$ – 5 % based on the weight of the cement) was added to the cement complex as the accelerator of the cement hydration. The nominal board density of 1150 kg/$m^3$ was selected with the weight ratio of bagasse/reed particles at five levels of 2.55:97.45, 6.94:93.06, 13.38:86.62, 19.81:80.19 and 24.20:75.80. In order to produce CBPB, the particles were wetted by water containing $CaCl_2$ and then

mixed with cement containing Nano SiO$_2$ at five levels (the cement weight 0.48, 1.5, 3, 4.5 and 5.52 %) as the third variable of the study. After stirring them for 15 minutes, one-layered mats were formed among two steel plates with the dimensions of 350 mm × 350 mm.

The complex was pressed under a hydraulic press with the thickness of 12 mm and kept under constant pressure for 24 h using a press clamp. When the panels were removed from the press, in order to minimize the cement capillary desiccation and improve the hydration process, panels were sprayed by distilled water (25 ml for every panel) and wrapped in a plastic bag before being stored to be cured at 60 °C for 4 h. Then, bag-wrapped samples were conditioned for 28 days at (25±2) °C with (60±10) % RH. According to the experimental design and levels of variables, 20 panels were manufactured. After being manufactured, the panels were trimmed and tested for the internal bonding (*IB*) according to EN 319 (1999). The bonding strength test was performed using a HONSFILD material testing device.

The variance analysis was used to determine the effect of the production parameters on the *IB* of the panels. For this purpose, the response surface methodology (RSM) was applied.

### 2.3 Artificial neural network analysis
2.3. Analiza uz pomoć umjetne neuronske mreže

The MATLAB Neural Network Toolbox was used to predict the internal bonding strength values of CBPB in response to other levels of the selected variables that were not obtained from the experimental study. In the ANN modeling of the present work, silica content, particle size and bagasse/reed particles ratio were considered as the prime processing variables. Hence, our aim was to reveal the optimum level of each selected variable for each CBPB to obtain the highest internal bonding strength values. The data were obtained from the experimental study.

The performances of the ANN model are evaluated by computing mean-square errors (*MSE*), root-mean-square errors (*RMSE*), mean absolute percentage error (*MAPE*) and the coefficient of determination (*R*$^2$) (Zhang *et al.*, 1998).

In order to minimize *MSE* and determine the weight and bias values, ANNs training process was followed with MATLAB software package.

Since the error between the actual and predicted outputs must be minimized, the trial and error method was selected to design the back propagation ANN model among several different ANN structures (Zhang *et al., 1998*), and the parameters including the number of inputs, hidden and output layers and neurons in each layer, transfer functions, number of learning cycles, initialization of the weights and the biases, etc. Levenberg – Marquardt algorithm (trainlm) was used as the training algorithm. However, avoiding overfitting is another important point when applying ANN models. A method for improving generalization is called early stopping, which is provided for all of the supervised network creation functions in Neural Network Toolbox. Therefore, to determine the effects of the particle size, bagasse/reed particles ratio and nanosilica content on the internal bonding strength, and simultaneously to use early stopping method in order to avoid overfitting, the experimental data were divided into three groups: training (for adjusting the weights of the network), validation (for preventing the network in local minima) and testing. Among these data, fourteen samples (70 % of the data) were selected for ANN training process, three samples being selected (15 % of the data) for the validation set, and the remaining three samples (15 % of the data) for the testing set. The data sets used in the training, test and prediction model are illustrated in Tables 1 and 2.

A typical multi-layered ANN architecture and the optimum architecture of the ANN model are schematically shown in Figures. 1a and b in terms of the parameters mentioned above. To determine the number of the

**Table 1** Training data set and *IB* prediction model results
**Tablica 1.** Eksperimentalni podatci i rezultati modela predviđanja čvrstoće na raslojavanje

| Nano content<br>*Sadržaj nanočestica* | Particle size<br>*Veličina čestica* | Weight ratio (bagasse/reed)<br>*Maseni udio*<br>*(ostatci od prerade šećerne trske / trska)* | Internal bonding, MPa<br>*Čvrstoća na raslojavanje,* MPa | | |
|---|---|---|---|---|---|
| | | | **Measured**<br>*Izmjerena* | **Predicted**<br>*Predviđena* | **Error, %**<br>*Pogreška, %* |
| 1.5 | 2-4 | 19.81:80.19 | 0.42 | 0.4489 | -0.0289 |
| 1.5 | 6-8 | 6.94:93.06 | 0.18 | 0.1932 | -0.0132 |
| 1.5 | 6-8 | 19.81:80.19 | 0.32 | 0.3170 | 0.0070 |
| 3 | <2 | 13.38:86.62 | 0.26 | 0.2508 | 0.0091 |
| 3 | 4-6 | 2.55:97.45 | 0.32 | 0.3915 | -0.0715 |
| 3 | 4-6 | 13.38:86.62 | 0.47 | 0.4995 | -0.0295 |
| 3 | 4-6 | 13.38:86.62 | 0.48 | 0.4995 | -0.0195 |
| 3 | 4-6 | 13.38:86.62 | 0.49 | 0.4995 | -0.0095 |
| 3 | 4-6 | 13.38:86.62 | 0.495 | 0.4995 | -0.0045 |
| 3 | 4-6 | 13.38:86.62 | 0.50 | 0.4995 | -0.0005 |
| 3 | 4-6 | 24.20:75.80 | 0.65 | 0.6370 | 0.0130 |
| 4.5 | 2-4 | 6.94:93.06 | 0.25 | 0.2424 | 0.0075 |
| 4.5 | 6-8 | 6.94:93.06 | 0.22 | 0.2413 | -0.0213 |
| 5.52 | 4-6 | 13.38:86.62 | 0.33 | 0.3608 | -0.0309 |

**Table 2** (A) Testing data set and (B) validation data set of *IB* prediction model results
**Tablica 2.** (A) Skup izmjerenih podataka i (B) skup podataka za provjeru valjanosti rezultata modela predviđanja čvrstoće na raslojavanje

| Nano content *Sadržaj nanočestica* | Particle size *Veličina čestica* | Weight ratio (bagasse/reed) *Maseni udio (ostatci od prerade šećerne trske / trska)* | Internal bonding, MPa *Čvrstoća na raslojavanje,* MPa | | |
|---|---|---|---|---|---|
| | | | Measured *Izmjerena* | Predicted *Predviđena* | Error, % *Pogreška, %* |
| (A): Testing data set and *IB* prediction model results *(A): Skup izmjerenih podataka i rezultati modela predviđanja čvrstoće na raslojavanje* | | | | | |
| 0.45 | 4-6 | 13.38:86.62 | 0.21 | 0.2245 | -0.0145 |
| 1.5 | 2-4 | 6.94:93.06 | 0.20 | 0.2311 | -0.0311 |
| 3 | 4-6 | 13.38:86.62 | 0.493 | 0.4995 | -0.0065 |
| (B): Validation data set and *IB* prediction model results *(B): Skup podataka za provjeru valjanosti i rezultati modela predviđanja čvrstoće na raslojavanje* | | | | | |
| 4.5 | 8 | 19.81:80.19 | 0.43 | 0.4335 | -0.0035 |
| 3 | 9.36 | 13.38:86.62 | 0.19 | 0.1955 | -0.0055 |
| 4.5 | 4 | 19.81:80.19 | 0.52 | 0.5045 | +0.0155 |
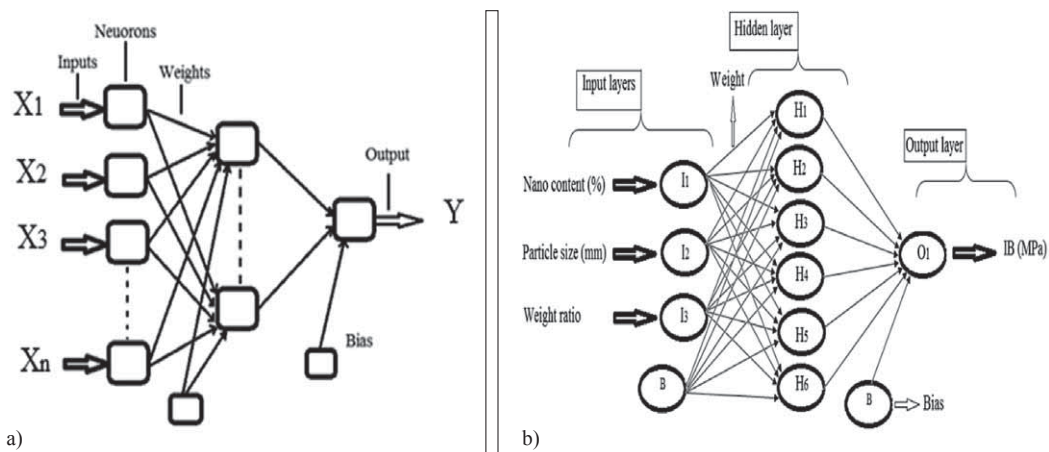


**Figure 1** (a) A typical multi-layered ANN architecture and (b) ANN architecture used as prediction model for *IB*
**Slika 1.** (a) Tipična višeslojna ANN arhitektura i (b) ANN arhitektura upotrijebljena kao model predviđanja čvrstoće na raslojavanje

hidden layer neurons, 6 neurons were finally considered in this layer after following the method of trial and error and repetition in the training of the network by changing the number of neurons from 0 to 20 in the hidden layer. In this condition, the network showed the best performance, so that as the number of neurons decreased or increased in the hidden layer, the efficiency of the network decreased and the network did not learn.

Before training the network, the data sets were normalized using their minimum and maximum values within the range of -1 to 1 by applying the hyperbolic tangent sigmoid function in order to prevent any calculation error related to different parameter magnitudes. The normalized data were finally converted into the original scale using a reverse normalizing process to evaluate the results with MATLAB software. The ANN's training process was discontinued after 3 epochs because of the mean square error of 0.000658. Figure 2 estimates the error along with iterative process to determine the best network architecture.
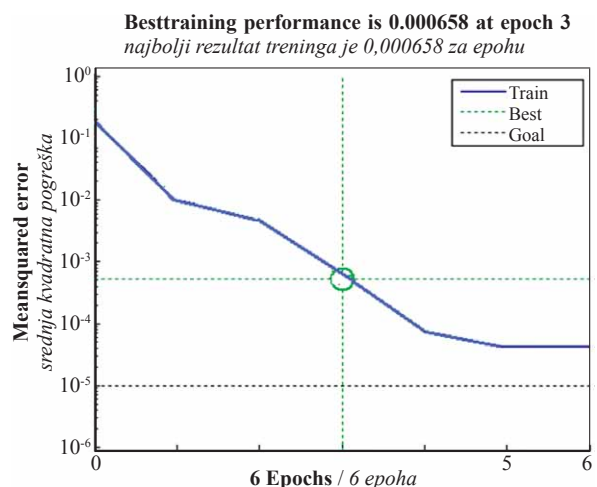


**Figure 2** Evolution of error during iterative process for ANN
**Slika 2.** Evolucija pogreške tijekom iterativnog postupka za ANN

# 3 RESULTS AND DISCUSSION
## 3. REZULTATI I RASPRAVA

### 3.1 Microstructural study
### 3.1. Istraživanje mikrostrukture

SEM examinations were performed to study the morphology and microstructure of the pure cement sample, samples with nanosilica, samples with nanosilica and bagasse fine particles and samples with nanosilica and reed fine particles for 15 days. In Figure 3A (pure sample), a large amount of $Ca(OH)_2$ (CH) crystals and a high level of porosity can be observed in the composite mass of the calcium silicate hydrate (C-S-H) with a foil-like or platy shape and monosulphate, showing that without nanosilica, large air pores with many plate-like hydrates are formed in the hardened cement, and that $Ca(OH)_2$ has enough space to grow.

Due to the availability of the void space for uninhibited growth situations, as NS is added to the cement paste, CH formation changes and dense and compact structures of other hydration products are produced such as C-S-H and monosulphate, while $Ca(OH)_2$ crystals are reduced (Figure 3B). In fact, nano-$SiO_2$ additives can fill the pores in the cement by activating pozzolanic reaction, reacting with CH in the solution to produce more C-S-H, so that the micro-structure of the samples with nano-$SiO_2$ is denser than that of the samples without nano-$SiO_2$. In fact, most of the ettringite and C-S-H crystals were covered by the added NS and this addition accelerated the hydration process. This created more compaction, so that the hydration products were produced fully, they filled the pores and $Ca(OH)_2$ was not observed. This improved the mechanical properties of the cement complex.

SEM images provide evidence of a denser structure of hydrated products in the cement paste containing NS, and the occurrence of micro- or/and nano-cracks in the cement paste reinforced by reed is likely due to a lower effective water to cement ratio as a part of water has been absorbed by reed. (Figures 3C and 3D).

As the addition of organic and hydrophilic lignocellulosic-based materials greatly increases the viscosity of the cementitious mixtures (Spiesz and Brouwers, *2014*; Rupasinghe *et al., 2017*), the increase in the porosity of hardened cement at microscale is expected due to the formation of a large amount of air cavities entrapped in the cementitious system. Since the organic materials are not saturated, they absorb some water from the cement paste, thus reducing its effective water-to-cement ratio and increasing its viscosity.

On the other hand, evaluation of the hydration process of the cement paste mixed with accelerators can show the changes in the properties of not only cement paste but also cement-binder-based panels. According to Xie *et al.* (2016*)*, the intensity of the changes in the hydration behavior of lingo-cement systems is related to differences in the existing amount of poisonous component in the lignocellulosic materials such as sugars, which delay the hydration process. In order to accelerate the hydration process and according to the first step of this study (Nazerian *et al., 2018*), it was

determined that the addition of pozzolanic materials such as $SiO_2$ can accelerate the hydration process, so that adding 3 % nano $SiO_2$ (based on cement weight) to the cement paste even containing bagasse or reed fine particle raised the maximum hydration temperature, while the time of reaching the main rate peak shortened. Also, the increase of $SiO_2$ replacement shortened the setting time.

Besides, due to the nucleation effect of nanosilica in the system and the corresponding increase in the cement hydration and C-S-H generation, the formation of air voids can be limited using an optimal nanosilica content. Since the water defining the water/cement ratio includes the water required to saturate the dry reed particles, the effective water to cement ratio is likely decreased by adding reed particles. It might be decreased to the point that the hydration of the cement becomes incomplete. With respect to the fact that one of the most important cement hydration products is C-S-H as a product of this pozzolanic reaction, which is made by mixing calcium hydroxide (CH) and silica in the presence of water due to the lake of sufficient water, CH production decreases in the hydration process, so that less C-S-H is formed.

Since the structure of cement systems is very sensitive to the moisture movement during the hydration (due to the existence of hydrophilic fiber elements), the lower effective w/c ratio may also explain the occurrence of microcracks induced by shrinkage (Jennings *et al., 2007*) that are visible on SEM images, as shown in Figure 3C. The positive influence of NS addition is due to the filling ability and the Pozzolanic activity, which results in C-S-H formation (Raiess Ghasemi *et al., 2010*). Hence, it seems that the addition of nano $SiO_2$ can compensate for the negative effect of using reed particles in the cementitious systems.

The addition of nanosilica formed a dense and uniform structure in the hardened cement by increasing the C-S-H gel content. However, a stronger water absorption ability in the spongy structure of bagasse compared to denser reed particles leads to a higher decrease in the system water, which makes the cement grains unhydrated (Figure 3D). Hence, cement hydration and generation of CH are delayed or limited. As CH decreases, the formation of C-S-H gel dense structure is limited as a result of the reaction of NS with CH, and hence, the porosity of the hardened cement is relatively large.

Figure 4 shows the FTIR spectra of the pure cement paste (CP), cement-nanosilica (CN) mixture and cement paste reinforced by reed (CNR) and bagasse (CNB) fibers with nanosilica after being cured for 15 days. The broad absorption bands of IR spectra are observed in the range of 3800–3000 cm$^{-1}$, corresponding to the stretching vibrations of both structural and free –OH groups of water, CH and CSH gel with maxima close to 3446 cm$^{-1}$ (Xu *et al., 1999*; Kontoleontos *et al., 2012*,). The intensity of the band at 3446 cm$^{-1}$ for CP, CN and CNB was similar, while that of CNR decreased a little compared to others. In addition, the IR spectra of this band shifted slightly to 3420 cm$^{-1}$ and became broader and smaller. According to Xu *et al.* (1999),
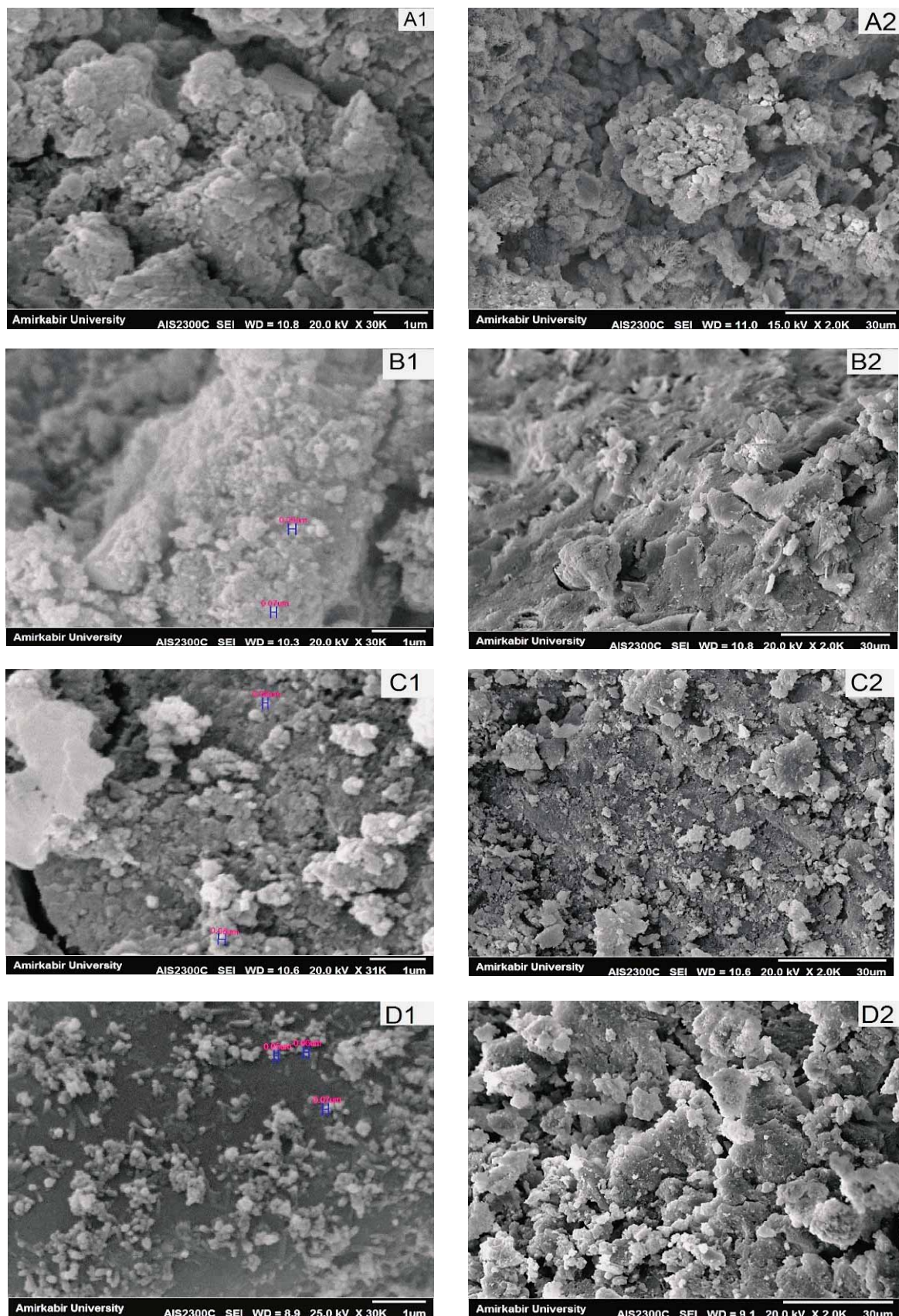
**Figure 3** SEM micrographs: (A) pure hardened cement paste, (B) 6 % nanosilica-cement paste, (C) 6 % nanosilica-cement paste-reed fiber, and (D) 6 % Nanosilica-cement paste-bagasse fiber, after 15 days of curing
**Slika 3.** SEM mikrografije: (A) čista otvrdnuta cementna pasta, (B) 6 %-tna nanosilikatno-cementna pasta, (C) 6 %-tna nanosilikatno-cementna pasta – vlakna trske i (D) 6 %-tna nanosilikatno-cementna pasta – vlakna ostataka od prerade šećerne trske 15 dana nakon otvrdnjivanja
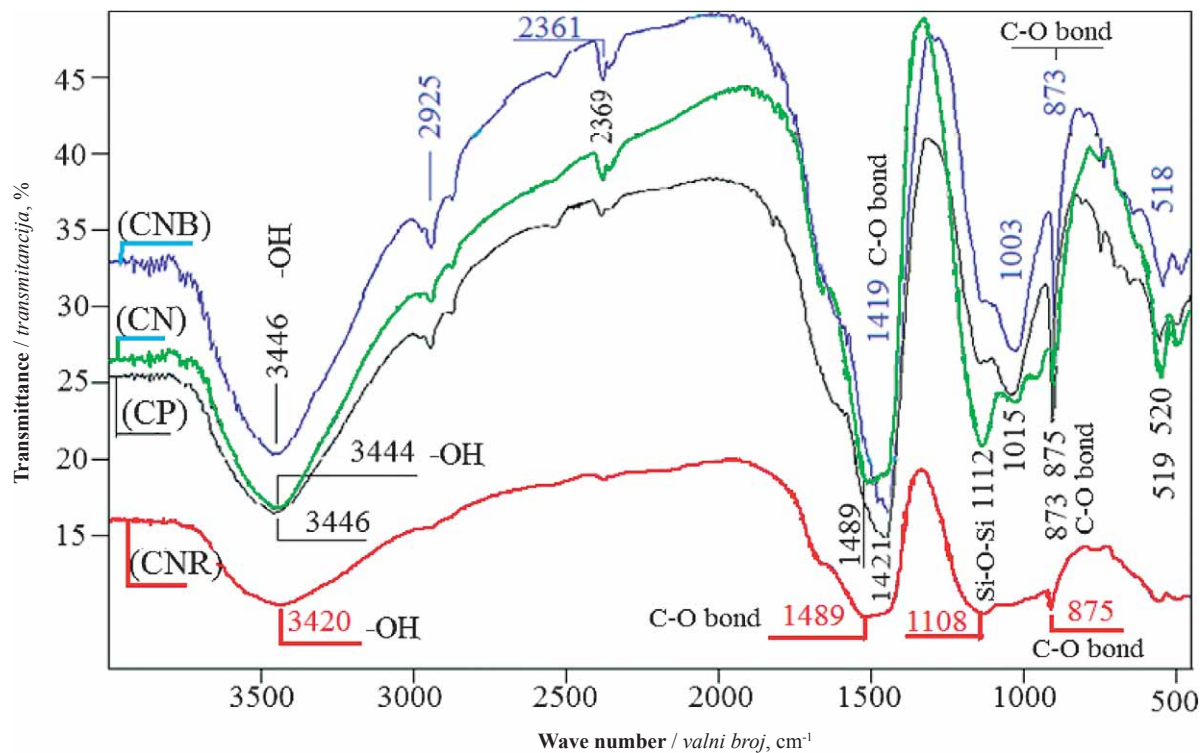
**Figure 4** FTIR of (CP) pure cement, (CN) cement + Nano SiO$_2$, (CNR) cement + Nano SiO$_2$ +reed, (CNB) cement + Nano SiO$_2$ + bagasse
**Slika 4.** FTIR (CP) čistog cementa, (CN) cementa + nano SiO$_2$, (CNR) cementa + nano SiO$_2$ + trska, (CNB) cementa + nano SiO$_2$ + ostatak od prerade šećerne trske

Bjornstrom *et al.* (2004) and Kontoleontos *et al.* (2012) a decrease in the amount of bonded-OH groups and free water or the equivalent reduction in Ca(OH)$_2$ content and an increase in C-S-H content in CNR are the reasons of the changes in IR spectra.

According to the spectra, the gelation mechanism and siloxane bond (Si-O-Si) formation, due to the absorption band with the wave number of 1112 cm$^{-1}$, occurred in the samples containing nanosilica (CN), which is more than that in the CP (the presence of valley in the curve (CP)). This can be related to the fact that the reduction of the repulsion effect of Ca$^{2+}$ and Al$^{3+}$ formed from cement dissolution as a gelling agent on the nanosilica inter-particles net accelerates the gelation process (Innocentini *et al.*, 2002), in which hydroxyl groups (Si-OH) on the surface of silica are converted into siloxane bonds, and a three-dimensional network is formed (Anjos *et al.*, 2008), affecting the strength of the hardened cement.

According to the FTIR spectrum of CP and CNB systems, two distinct peaks are observed around 1420 cm$^{-1}$ and 873 cm$^{-1}$ related to the stretching and bending-in-plane vibrations of the C–O bonds of CH and CaCO$_3$, resulting from the reaction between Ca(OH)$_2$ and CO$_2$ in the air (Yılmaz and Olgun, 2008; Chang and Chen, 2006; Fernandez-Carrasco and Vazquez, 2009). The intensity of the band at 1420 cm$^{-1}$ is assumed to be closely related to the ratio and depth of the carbonation (Chang and Chen, 2006; Fernandez-Carrasco and Vazquez, 2009). The bands at 1420 cm$^{-1}$ and 873 cm$^{-1}$ shifted slightly to 1489 cm$^{-1}$ and 875 cm$^{-1}$ in the FTIR spectra of CN and CNR samples after being cured for 15 days, re-

spectively. The intensities of the bands at 1489 cm$^{-1}$ and 1420 cm$^{-1}$ of CNR were smaller than those of CNB, CN and CP, indicating the decrease in the carbonation ratio and depth in these samples. Similarly, the bending-in-plane vibrations of the C–O bonds at 873 cm$^{-1}$ (Chang and Chen, 2006) had lower intensities in the IR spectra of the CNR sample. According to these bands, carbonation increases as NS is added. In addition, CP paste exhibits a higher rate of carbonation than other cement complexes. The small OH bands from Ca(OH)$_2$ of the samples containing nanosilica may be due to their reaction with SiO$_2$–based CSH. This means that nanosilica enhances the crystallinity of portlandite and increases the density of the structure of the cement complex at microscale and improves the mechanical properties of the hardened cement.

Figure 5 shows the XRD analysis of the hydration behavior of the hardened cementitious samples in four compositions: pure cement (A), cement with nanosilica (B), cement with nanosilica and reed fine particles (C) and cement with nanosilica and bagasse fine particles (D). Comparing XRD spectra of (A), (B), (C) and (D) compositions, the peaks of calcium hydroxide (Ca(OH)$_2$) at 17.8°, 28.5°, 34°, 50.5°, 54° and 62.7°(2θ) (Singh *et al.,* 2016; Nakanishi *et al.,* 2016) appear in the XRD spectrum of (A), they become more intense in the samples (B) and (C), while they disappear or weaken in the cement pastes containing nanosilica with bagasse. In fact, the intensity of these peaks is largest for portlandite in the cement with nanosilica, reducing gradually as reed and bagasse particles are applied. Due to the high performance of SiO$_2$ to form pozzo-
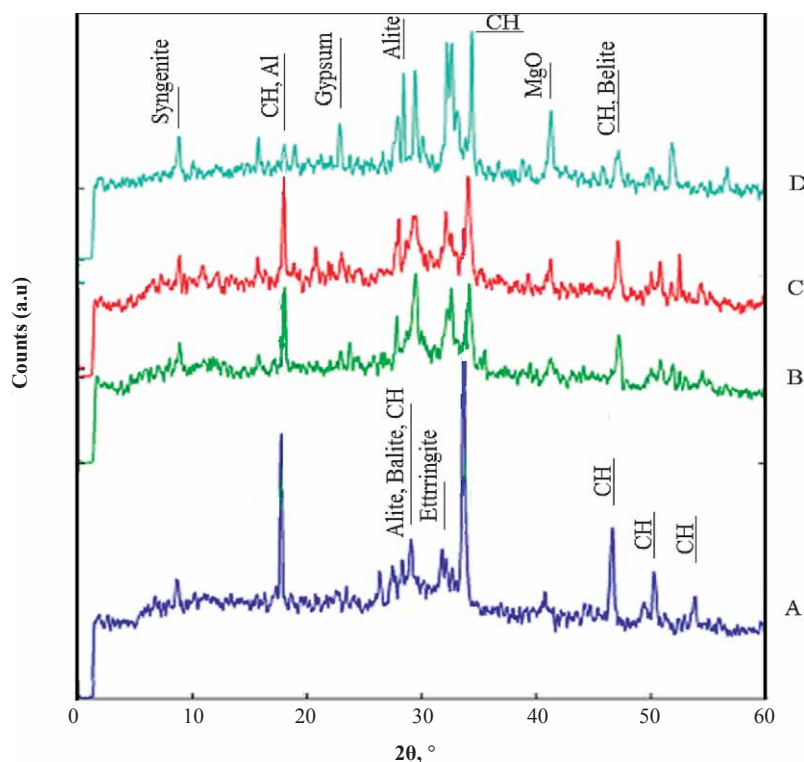
**Figure 5** XRD analysis of (A) pure cement, (B) cement + Nano SiO$_2$, (C) cement + Nano SiO$_2$ + reed, (D) cement + Nano SiO$_2$ + bagasse
**Slika 5.** XRD analiza (A) čistog cementa, (B) cementa + nano SiO$_2$, (C) cementa + nano SiO$_2$ + trska, (D) cementa + nano SiO$_2$ + ostatak od prerade šećerne trske

lanic reactions with CH, the intensity of these peaks is observed in the samples (C) and (D) and increases largely in the sample (B).

Apparently, these spectroscopic results foresee the weaker strength of CBPB made with bagasse particles resulting from insufficient formation of hydrate products at the bagasse particles interface. On the other hand, compared to pure cement pastes (A), the decrease in the calcium hydroxide XRD peaks in the cement pastes containing nanosilica illustrates that CH can react with SiO$_2$ and form more CSH gel as it was mentioned in previous studies (Rupasinghe *et al.,* 2017; Lavergne *et al.,* 2019).

A peak near 42.9° (2θ) can be related to periclase MgO (Stutzman *et al.,* 2016), which may slowly react with water and trigger an expansion of the concrete, though the porosity and local low relative humidity likely prevent such a phenomenon. Furthermore, Portlandite features a peak near 47° (2θ). These peaks at 47° (2θ) look smaller or wider for mixes containing CH: it might be due to the smaller amount of CH or the size of CH crystal being nearly at nanometric scale. The peak near 34° (2θ) is reduced by NS in a similar manner. These two peaks can disappear as the pozzolanic reaction entirely consumes the CH (Maddalena *et al.,* 2019).

It is found that the intensity of the peaks is similar around 9° (2θ) for syngenite, while the intensity of the peaks around 18° (2θ) for portlandite, 23° (2θ) for gypsum and 33° (2θ) for aluminate in the pure cement (Stutzman *et al.,* 2016) reaches the minimum, and then increases slightly as nanosilica and bagasse particles are added. Some of these peaks increased as reed parti-

cles were added. Due to the increment of the final amount of cement hydration products, the intensity of these peaks disappeared or decreased. It can be attributed to the fact that nanosilica can improve the hydration of cement, enabling the production of more hydration products such as ettringite. Ettringite needles are formed due to better bonds between reed or bagasse particles and cement paste (Coatanlem *et al.,* 2006).

It is known that C$_3$S (alite) and C$_2$S (belite) are fundamental contributors to the early strength development of the cement paste due to the reaction of C$_3$S and C$_2$S with sufficient water and with C-S-H gel formation acting as a binder. The addition of silica accelerates the formation of C-S-H gel. However, comparing XRD spectra of samples, alite peaks at 27.5° (2θ) and 29.2° (2θ) and ettringite peak at 32° (2θ) and belite peaks around 29° and 48° (2θ) (Wei *et al.,* 2003) appear in the spectrum of the cement paste containing 6 % nanosilica with reed and bagasse particles at the maximum intensity, while these peaks decrease in the cement pastes containing only 6 % nanosilica to the minimum intensity in the pure cement as shown in Figure 5.

In fact, in this analysis, XRD peak patterns corresponding to the phases C$_2$S and C$_3$S increase as lignocellulosic particles are used due to the decrease of the hydration process. Due to the high specific surface area and the high ability of nano particles to absorb water molecules on one hand, and the high absorbent characteristics of carbohydrate chains, as well as the existence of a spongy tissue in the inner layer of reed or bagasse cane on the other hand, the amount of water is not sufficient to complete the hydration process and

form C-S-H gel. Hence, substitution of cement with nanosilica and addition of lignocellulosic particles to the cement paste matrix result in the excessive consumption of water and absorption of a part of the water for hydration. Therefore, this observation agrees with the statement that a threshold of nanosilica content needs to be considered to enhance the hydrated cement paste properties through pozzolanic reactions (Mondal *et al., 2*010; Kim *et al.,* 2010).

### 3.2 Experimental results
3.2. Eksperimentalni rezultati

Apparently, these spectroscopic results foresee the weaker strength of CBPB made with bagasse particles resulting from insufficient formation of hydrate products at the bagasse particles interface. On the other hand, compared to pure cement pastes (A), the decrease in the calcium hydroxide XRD peaks in the cement pastes containing nanosilica illustrates that CH can react with $SiO_2$ and form more CSH gel, as mentioned in previous studies (Rupasinghe *et al.,* 2017; Lavergne *et al.,* 2019).

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In fact, in this analysis, XRD peak patterns corresponding to the phases $C_2S$ and $C_3S$ increase as lignocellulosic particles are used due to the decrease of the hydration process. Due to the high specific surface area and the high ability of nano particles to absorb water molecules on one hand, and the high absorbent characteristics of carbohydrate chains as well as the existence of a spongy tissue in the inner layer of reed or bagasse cane on the other hand, the amount of water is not sufficient to complete the hydration process and form C-S-H gel. Hence, substitution of cement with nanosilica and addition of lignocellulosic particles to the cement paste matrix result in the excessive consumption of water and absorption of a part of the water for hydration. Therefore, this observation agrees with the statement that a threshold of nanosilica content needs to be considered to enhance the hydrated cement paste properties through pozzolanic reactions (Mondal *et al.,* 2010*;* Kim *et al.,* 2010).

The calculated *RMSE, MAPE* and $R^2$ statistics of the ANN model are listed in Table 4. As seen in Table 4, *RMSE, MSE, MAPE* and $R^2$ were found to be 0.0256, 0.00066, 1.988 % and 0.9727 for the training data, 0.02, 0.004, 2.894 % and 0.9970 for the validation data, and 0.202, 0.0004, 1.455 % and 0.9972 for the testing data. One of the most important evaluation criteria is *MAPE*. It is generally used to determine the prediction accuracy as the primary criterion. According to Table 4, *MAPE* values of the model range from 1.455 % to 2.894 % for IB. The error values are satisfactory. The results of the *MAPE* have ascertained that the performance of the model developed for the prediction of *IB* is quite good.

Another important evaluation criterion is $R^2$, which shows the extent of similarity or relationship be-

**Table 3** ANOVA results for *IB* (only significant terms)
**Tablica 3.** ANOVA rezultati za čvrstoću na raslojavanje (samo značajni rezultati)

| Source | SS | DF | MS | F value | Prob>F |
|--------|-----|-----|------|---------|--------|
| Model | 0.37 | 7 | 0.053 | 563.25 | < 0.0001 |
| A | 0.018 | 1 | 0.018 | 197.24 | < 0.0001 |
| B | 9.370E-003 | 1 | 9.370E-003 | 100.23 | < 0.0001 |
| C | 0.14 | 1 | 0.14 | 1524.21 | < 0.0001 |
| A² | 0.086 | 1 | 0.086 | 919.53 | < 0.0001 |
| B² | 0.13 | 1 | 0.13 | 1339.66 | < 0.0001 |
| AC | 1.800E-003 | 1 | 1.800E-003 | 19.25 | 0.0009 |
| BC | 2.450E-003 | 1 | 2.450E-003 | 26.21 | 0.0003 |

**Table 4** Evaluation results in terms of performance criteria of ANN model
**Tablica 4.** Rezultati evaluacije kriterija izvedbe ANN modela

| Data sets | *IB*, MPa | | | |
|---|---|---|---|---|
| *Skup podataka* | *RMSE* | *MSE* | *MAPE, %* | *R²* |
| Training / *trening* | 0.0256 | 0.0006 | 1.988 | 0.9727 |
| Validation *validacija* | 0.0200 | 0.0004 | 2.894 | 0.9970 |
| Testing / *testiranje* | 0.0202 | 0.0004 | 1.455 | 0.9972 |



tween the actual data and the predicted data. If $R^2$ value is less than 0.82, the relationship is poor, if it is between 0.82 and 0.90, the relationship is good, and if it is more than 0.91, the relationship is excellent (Shenk and Westerhaus *1996*). As shown in Table 4 and Figure 6, $R^2$ values are greater than 0.91, which means that the predictive success of the model is good. According to the statistical analyses, *RMSE*, *MSE*, *MAPE* and $R^2$ are acceptable for the internal bonding and meet the accuracy of the ANN learning and testing stages (Table 4). As confirmed by the results, the ANN approach has a sufficient validity rate to predict the internal bonding value of the cement-bonded particleboard.

There is limited information on the prediction of the mechanical properties of non-wood based cement-bonded composites. However, several studies have been conducted on some strength properties of the wood-based panels. Fernandez *et al.* (2008) obtained the $R^2$ values of 0.75 and 0.76 to predict the *MOR* and *MOE* of the particleboard by ANN, respectively. In another study, $R^2$ value of the regression model was 0.70 to predict the internal bonding of the particleboard (Cook and Whittaker, 1992). Eslah *et al.* (2012) found the R² values of 0.79 and 0.69 to predict the *MOR* and *MOE* of the particleboard, respectively, using the regression model. Watanabe *et al.* (2015) obtained the $R^2$ value of 0.93 to predict the internal bonding strength of the particleboard by ANN (15). Ozsahin (2013) determined the $R^2$ values as 0.973, 0.983 and 0.853 to predict the moisture absorption, thickness swelling and thermal conductivity of OSB by ANN. Thus, it can be seen that the $R^2$ values obtained by ANN models developed in this study are higher compared to those obtained by the above-mentioned modeling applications to predict the cement-based wood composites.

The model outputs of the training, validation and testing data and their comparisons with the actual outputs of the internal bonding strength are given in Figure 7 for each data set.

Also, the comparison of the actual values and the ANN prediction values are illustrated graphically in Figure 8 for all data. The results of the graphical comparisons showed similar internal bonding properties between the experimental study and the outputs obtained by ANN model and guaranteed the validity of the model. The results indicate that there is a permanent agreement between the outputs of the ANN model and the experimental data. This implies that the ANN model can be
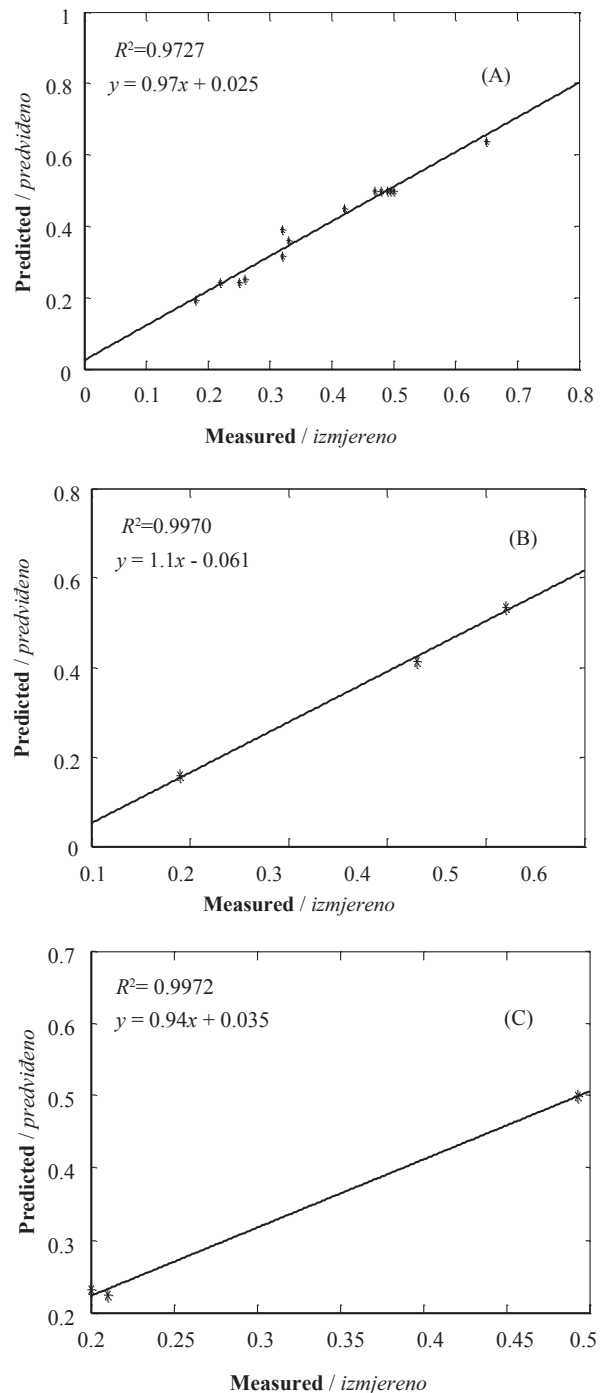
**Figure 6** Presentation of fit between actual and predicted values of *IB* for training (a), validation (b) and testing data (c)
**Slika 6.** Prikaz podudaranja stvarnih i predviđenih vrijednosti *IB-a* (a) za trening, (b) za validaciju te (c) za ispitne podatke

used to optimize the internal bonding strength value of the panels. Hence, values estimated by ANN model can be used to produce panels rather than the measured data, which reduces the testing time and cost.

Generally, all outputs of the effects of the production factors on the internal bonding strength of the panels can be estimated by the designed model for innumerable combinations. According to Figure 9, the predictive changes in the internal bonding are presented graphically for different nano contents and lignocellulosic particle sizes when bagasse/reed weight ratio is 13.38 %.
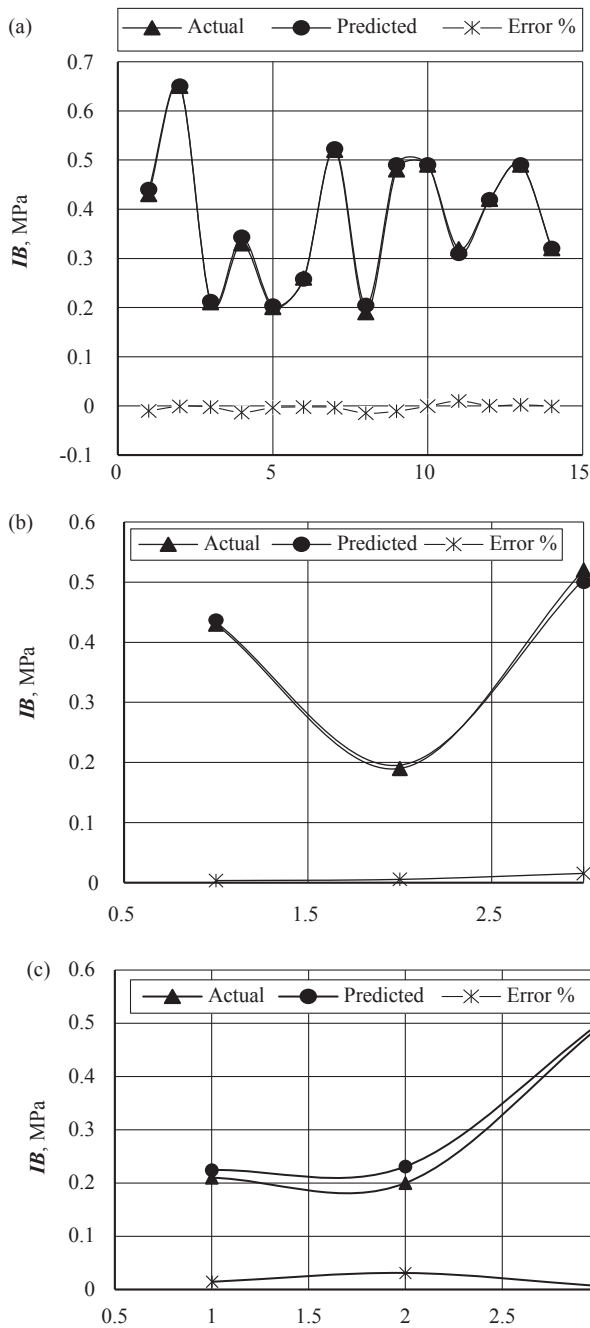
**Figure 7** Comparison of actual and model outputs of training (a), validation (b) and testing data (c)
**Slika 7.** Usporedba stvarnih i modeliranih rezultata (a) treninga, (b) validacije, (c) ispitnih podataka
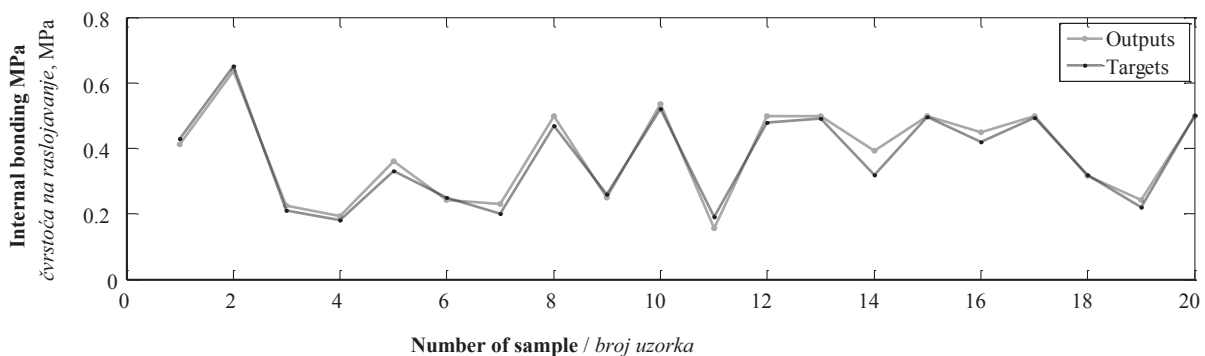
Besides, in other cases (Figure 10), the particle size was 6 mm, and the nano content and bagasse/reed weight ratio changed. As a result, the predictive changes in the internal bonding for different particle sizes and bagasse/reed weight ratios are given graphically in Figure 11.

Using the ANN model, it is possible to conceive the relative effect of all selected variables using the contour plots in the 2-D graph. To generate plots and determine the effect of the parameters on the dependent variables, the third variable of each plot is held at the medium value and the other two parameters range from minimum to maximum values. As shown in Figures. 9, 10 and 11, the plots of the suggested model indicated optimum values of the internal bonding as dependent variables for all combinations of the manufacturing parameters with a low deviation.

Figure 9 represents quantitatively the counter plot of the *IB* developed by the ANN model in an estimated response in the manufacturing process (nano content and particle size) depicted at a fixed bagasse/reed particle weight ratio. As shown, it is found that the *IB* was improved up to 0.56 MPa as the nano content increased up to 4.5 % and the particle size ranged from 4.5 to 5.5 mm. This situation can be related to the sufficient amount of the generated C–S–H seeds due to the hydration products grown on their surfaces and the formation of a dense C–S–H gel.

It is well known that silica can effectively increase pozzolanic reaction. Due to the shortage of silica, the cement paste may not be able to drive the pozzolanic reaction sufficiently. During the mixture of water and cement, a high amount of the soluble paste calcium hydroxide (CH) is formed which does not react with any component in the paste and increases the porosity of the cement paste. The solubility of this component of the hydrated cement is high and it increases diffusivity by more than an order of magnitude when it is present in the paste (Bentz and Barboczi, 1992).

Since silica has adequate time to react with calcium hydroxide produced by the hydration of the cement (Chowdhury *et al.,* 2015), the replacement of the cement with enough nanosilica may consume the paste CH through an early pozzolanic reaction between CH and surface of nanosilica to form C-S-H seeds, thus significantly lowering the diffusivity (Burris and Riding, 2014). According to this hypothesis, with a higher



**Figure 8** Comparison of actual and model outputs of all data
**Slika 8.** Usporedba stvarnih i modeliranih rezultata svih podataka

**Bagasse/reed ration at 0 level (13.38 %)**
*omjer ostatka od prerade šećerne trske i trske na razini 0 (13,38 %)*
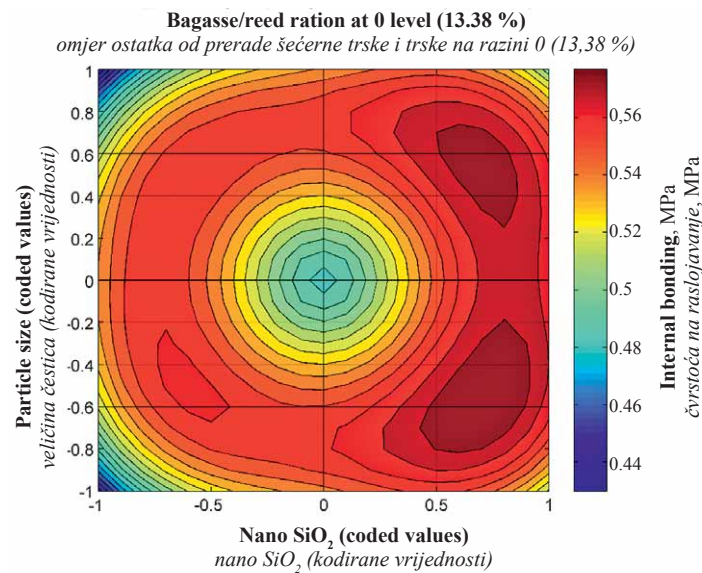


**Figure 9** Comparison of actual and model outputs of all data
**Slika 9.** Usporedba stvarnih i modeliranih rezultata svih podataka

**Particle size at 0 level (6 mm)**
*veličina čestica na razini 0 (6 mm)*
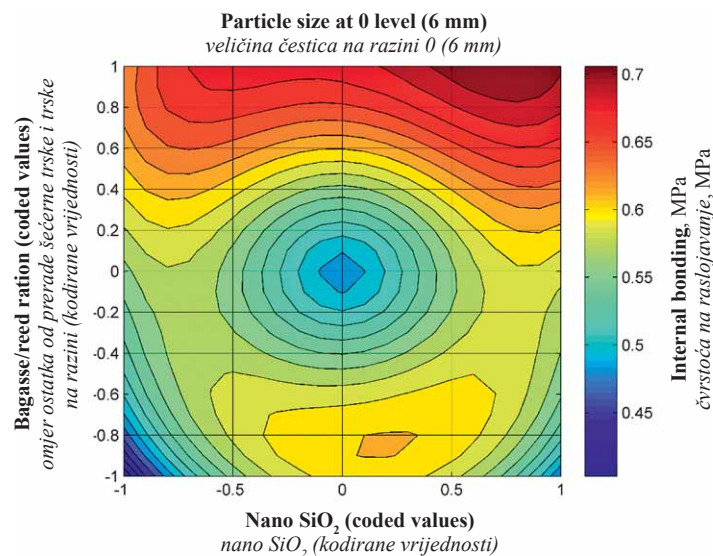


**Figure 10** Predictive changes in IB for different nano content and bagasse/reed ratio
**Slika 10.** Predviđene promjene čvrstoće na raslojavanje za različite sadržaje nanočestica i omjer ostatka od prerade šećerne trske i trske

**Nano SiO$_2$ (3 %)**
*nano SiO$_2$ (3 %)*
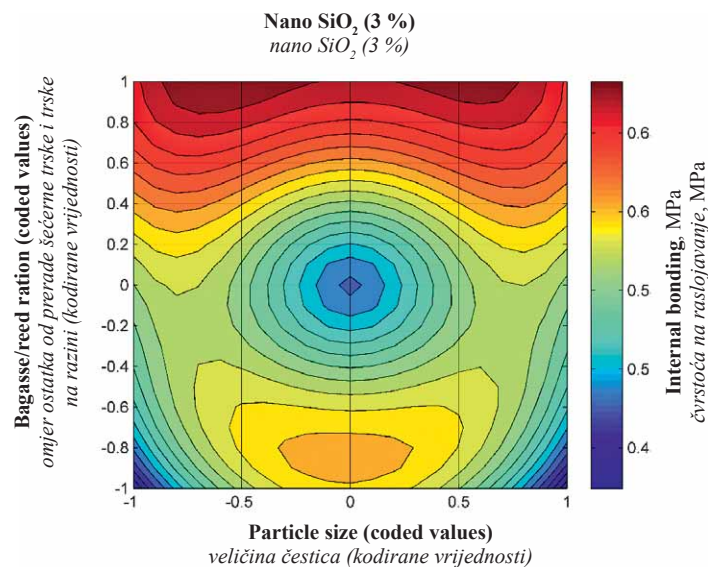


**Figure 11** Predictive changes in IB for different particle size and bagasse/reed ratio
**Slika 11.** Predviđene promjene čvrstoće na raslojavanje za različite veličine čestica i omjer ostatka od prerade šećerne trske i trske

amount of nanosilica, a sufficient amount of the generated C-S-H seeds enables the growth of the hydration products on their surfaces and results in the formation of a dense C-S-H gel (Birgisson *et al.,* 2012). This process decreases the CH content and porosity due to the higher calcium silicate hydrate density resulting from the pozzolanic reaction. Simultaneously, the increase in IB due to nanosilica addition can be related to the formation of less micro- or nanopores in the microstructures of the cement complex through the growth of the silica chains as fillers in C-S-H (Jeffrey *et al.,* 2009). On the other hand, according to Yu et al., the addition of nanosilica greatly increases the viscosity of the cement-water system, and a large amount of air can be entrapped into the complex, which in turn increases the porosity of the hardened concrete (Yu *et al.,* 2014). However, this statement cannot be true when the microstructure of the panels particles and the space among these particles.

Finer and shorter particles have a higher specific surface area, which can expose more surface to the cement paste with a high pH ($\approx$12.5). Hence, more polysaccharides, mainly hemicelluloses and extractives, can be dissolved in this alkaline solution so that oligo- or monosaccharides are formed. These materials (known as poisonous materials) can prevent the nucleation process of C-S-H gel on the grain cement. As C-S-H seeds increase, the retarding effects of these materials can be neutralized at the time of mixing cement with water and can be reversed by adding supplementary C-S-H after the retarding effect has already been established. The addition of nano $SiO_2$ provides an alternate pathway for increasing the C-S-H content in cement paste and the rate of the hydration process (Rao *2003*). At the same time, it reduces the $Ca(OH)_2$ content that cannot drive the pozzolanic reaction, if there is not enough nanosilica.

As it is well known, calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) are the main products obtained by the hydration process of the cement paste. Calcium silicate hydrate affects the mechanical properties of the cement paste through the hydration of $C_3S$ and $C_2S$, while calcium hydrate containing about 20-25 % of the volume of the hydration products does not affect the cementing property. With respect to the morphological properties, calcium hydroxide component is relatively weak and brittle so that the propagation of the cracks under the tensile loading situation can be easily increased through the area enriched by it (Tasdemir *et al.,* 1996). Nanosilica added to the mixture can activate the cement compounds chemically; so reactions are accelerated by calcium hydrates available on the cement paste and calcium silicate hydrate is produced, which enhances the cementitious complex strength.

According to Tasdemir *et al.* (1996), in the presence of nanosilica, the cracks usually develop through the cement grain. However, in the absence of nanosilica, the cracks usually spread around the coarse grain resulting in a more tortuous fracture path (Norsuraya *et al.,* 2016). This different crack pattern can be attributed to the stronger and more homogeneous interfacial zone as a result of a denser C-S-H formation in the interfacial zone than CH formation due to the addition of nanosilica.

Generally, many combinations of the studied parameters can be used for predicting *IB* by the designed model if all outputs are applied. According to Figure 10, the predictive changes in *IB* are indicated for nano content and bagasse/reed ratio when the particle size is >6 and <8 mm. The superior *IB* strength (>0.7 MPa) was predicted at the nano content >4.5 % and at the bagasse/reed particle weight ratio >19.81:80.19. This can be attributed to the fact that among the agricultural residues, bagasse is one of the herbaceous species with the highest ash and silica content in ash (~53.10 %, Frias and de Rojas, 2013; ~59%, Pilu *et al.,* 2012). However, the amount of ash (6.1 %, Galletti *et al.,* 2015; 3.6-4.2 %, Spatz *et al.,* 1997) and silica content in ash (49.4 %) are much lower for reed than for bagasse. Hence, according to the differences between qualitative studies shown in Figures 3, 4 and 5, it can be hypothesized that changing the content of portlandite, ettringite, alite, belite and other compounds produced by hydration process results in variations in the strength, so that raising the pozzolanic reaction in bagasse particles increases the strength of the cement due to the presence of a high level of pozzolanic materials (includes ash, fly ash, condensed silica fume etc.).

The cross-section of reed culms consists of a hypodermal texture with sclerenchyma fibers covered by a very hard, brittle and smooth glossy surface layer and thick parenchyma cells in the inner ring containing a large number of vascular bundles, characterized by heavily lignified bundle sheaths (60), resulting in reinforcement against reversible (elastic) and specially irreversible (plastic) deformation during the cold pressing process of panel manufacturing. On one hand, a drastic increase in the surface smoothness of the reed particles can adversely influence the strength because of the decreased mechanical interlocking between the cement and the particles, and on the other hand, the non-deformability of the reed particles can decrease the contact between particle-cement-particle and increase the empty space between particles.

Furthermore, the value range of the manufacturing variables might give a better understanding to specify the *IB* with the nano content of 3 % (coded values of 0), the bagasse/reed ratio of 19.81:80.19 and the particle size >4 to <6 mm (Figure 11). This combination produces panels with the *IB* values >0.65 MPa. For the present study, it is possible to say that approximately a higher *IB* value can be obtained with a higher bagasse/reed ratio. If the model is considered to work with an average error (*MAPE*) of 1.455 % for the testing data set, this result is acceptable and can be considered as a reasonable outcome.

The panels made from fine particles have structures without any macroscopic empty space in between; meanwhile, the panels prepared with coarser particles consist of structures with empty spaces in between. Basically, this increases the *IB* strength. However, smaller particles have higher specific surface area. Increasing the surface covered by binder, *IB* decreases. Hence, despite the largest surface covered by binder in coarser particles on one hand, and the smallest voids within the finer particles on the other hand, the greatest *IB* strength

was determined when medium-sized particles were used rather than less coarse particles.

Due to the difference in the cross-section of particles with different sizes, it can be assumed that the *IB* strength is correlated with the binder penetration in the longitudinal direction of particles and with the amount of the binder on the particle surface, i.e. with the cohesion strength of the bond between the binder and the particles. Fine particles expose higher cross-sectional surface area, so they can absorb more cement paste through the cross-section and also more poisonous component can enter into the solution. These factors decrease the amount of the cement paste on particles and delay the hydration process of the cement paste, and consequently, decrease the cohesion strength. Due to the over-penetration of water into particles, water content in the cement paste is insufficient; hence, cement grains cannot be hydrated completely.

## 4 CONCLUSIONS
## 4. ZAKLJUČAK

The microstructural compositions of the pure cement pastes, cement paste with 5.5 % hydrated nanosilica, cement paste with 5.5 % nanosilica containing bagasse and cement paste with 5.5 % nanosilica containing reed particles were examined for 15 days using SEM, FTIR and XRD. It is evident from SEM analyses that a large amount of portlandite $(Ca(OH)_2)$ crystals can be observed as plate-like-hydrates forming a high amount of porosity in the pure cement containing less calcium silicate hydrate (C-S-H), while the addition of nanosilica to the cement paste decreases the CH crystal formation and increases the density and the compaction structure of other hydration products such as CSH. By adding bagasse or reed particles, the porosity of the hardened cement increases due to the formation of a large amount of air cavities. The addition of nanoparticles can compensate for the negative effect of using lignocellulosic particles in cementitious systems.

According to the results of FTIR and XRD analysis, portlandite, ettringite and C-S-H gels as hydration products increased to a maximum level as nanosilica was added, and the poisonous effect of using lignocellulosic material was compensated by the hydration process of cement paste. However, unhydrated products such as C2S and C3S increased simultaneously due to the higher hydrophilicity of nanosilica and lignocellulosic particles. It is expected that using a higher level of water can be effective in increasing the hydration products.

The influence of different dosages of nanosilica (0.45, 1.5, 3, 4.5, and 5.52 wt %), particle size of bagasse and reed as lignocellulosic materials (2 mm pass/ 0 on, 4 mm pass/2 on, 6 mm pass/4 on, 8 mm pass/6 mm on and 8 mm on) and different weight ratios of bagasse to reed particles (2.55:97.45, 6.94:93.06, 13.38:86.62, 19.81:80.19 and 24.20:75.80) on the internal bonding strength of the cement-bonded particleboard was studied using ANN. The maximum internal bonding strength of 0.60MPa is exhibited by cement-bonded par-

ticleboards manufactured with the optimized parameters including the nanosilica content of 3.5 %, the particle size of 5.5 mm and the bagasse:reed ratio of 19.81:80.19.

The effect of the bagasse:reed ratio on the *IB* of the CBPB is more than that of nanosilica and particle size. The acceptable predictions of the observed CBPB internal bonding by the model indicate that ANNs can be a favorable tool for understanding those complexes. Consequently, the model can be used by producers to choose the internal bonding optimally as an important function of the measured properties of the cement-bonded lignocellulosic panels.

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# The Effect of Artificial Weathering on Surface Properties of Thermally Modified Oriental Beech Wood

## Utjecaj umjetnog izlaganja vremenskim utjecajima na svojstva površine toplinski modificirane bukovine

**ABSTRACT** • *The study aimed to determine some surface parameters such as surface roughness and color changes of thermally modified Oriental beech (Fagus orientalis L.) wood samples after 750 hours of artificial weathering. The results of the study showed that artificial weathering led to an increase in surface roughness of Oriental beech wood. Thermal modification interval of 210 °C - 230 °C gave a smoother surface than unmodified samples after artificial weathering. Artificial weathering caused darker, reddish, and yellowish tone of unmodified and thermally modified Oriental beech wood. According to the study findings, surface properties of thermally modified Oriental beech wood were better than those of unmodified Oriental beech.*

**Keywords:** *thermal modification; Oriental beech wood; color; surface roughness; artificial weathering; construction materials*

**SAŽETAK** • *Cilj rada bio je proučiti neka površinska svojstva uzoraka toplinski modificirane bukovine (Fagus orientalis L.) poput hrapavosti površine i promjena boje nakon 750 sati umjetnog izlaganja uzoraka vremenskim utjecajima. Rezultati su pokazali da umjetno izlaganje vremenskim utjecajima uzrokuje povećanje hrapavosti površine uzoraka bukovine. Toplinskom modifikacijom pri temperaturi od 210 – 230 °C postiže se glađa površina od one koju imaju nemodificirani uzorci nakon umjetnog izlaganja vremenskim utjecajima. Umjetno izlaganje vremenskim utjecajima uzrokuje tamnjenje uzoraka te povećanje udjela crvenoga i žutog tona na nemodificiranoj i toplinski modificiranoj bukovini. Dobiveni rezultati pokazuju da su svojstva površine toplinski modificirane bukovine bolja od površinskih svojstava nemodificirane bukovine.*

**Ključne riječi:** *toplinska modifikacija; bukovina; boja; hrapavost površine; umjetno izlaganje vremenskim utjecajima; konstrukcijski materijali*

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## 1 INTRODUCTION
1. UVOD

Wood has been preferred in the field of construction sector and furniture manufacture since ancient times, due to its natural beauty, thermal insulation, high strength, ease of use and processing (Su, 1997). However, wood is readily decomposed by environmental factors, including water, solar rays, bacteria, fungi and insects, fire, etc. (Kiguchi and Evans, 1998). This problem may be decreased by using chemical or thermal treatments. There has been a rise in the chemical treatment of wooden materials to enhance its mechanical, physical, and other properties for building proposes (Su, 1997; Yalinkilic *et al.,* 1999; Brelid *et al.,* 2000). However, the harms of chemicals used in treatment to increase the durability of wood are discussed. The demand for treating wood with environmentally friendly substances is increasing.

Methods called heat treatment or thermal modification are made to improve the properties of wood without using chemicals (Johansson, 2008). Heat treatment at high temperatures causes serious changes in the properties of wood. Therefore, it can be said that a new material has been formed as a result of heat treatment (Sundqvist, 2004). Thermal modification can be made in order to ensure the dimensional stability of the wood by reducing the water absorption rate, as well as to protect against biological organisms (Akgul and Korkut, 2012). However, since thermal modification negatively affects the mechanical and physical properties of wood, it has some commercial disadvantages (Gunduz and Aydemir, 2009).

It is common to use wood outdoors in architecture. However, wooden surfaces exposed to outdoor weather conditions can quickly deteriorate. Since the lignin in wood easily absorbs ultraviolet (UV) light, the fact that lignin absorbs UV light causes significant depolymerization in the main structural components of wood (Evans *et al.,* 2002). Some adverse conditions arising from weather conditions occur in the physical, mechanical, chemical and biological properties of wood and wood-based materials (Grelier *et al.,* 2000; Zhang and Kamdem, 2000; Evans *et al.,* 2005; Williams, 2005). It has been revealed as a result of scientific studies that the heat-treated wood material shows better resistance against weather conditions than the untreated wood (Temiz *et al.,* 2006; Nuopponen *et al.,* 2004; Ayadi *et al.,* 2003). Due to the chromophoric lignin structure, the heat-treated wood material can interfere with the light absorption process and induce photostability (Srinivas and Pandey, 2012).

Turkoglu *et al.* (2015) exposed heat-treated wood to natural weathering for six months. After six months of natural weathering, they experimented with some surface properties of wood such as surface roughness, gloss, and color changes. After the natural weathering process, the experimental results showed that the surface properties of wood have improved after the heat treatment. They also concluded that, after heat treatment at high temperatures, natural weathering affects the surface

properties of wood to a lesser extent. Kucuktuvek *et al.* (2017) investigated surface roughness characteristics of heat-treated Scots pine wood after weathering. They reported that heat-treated Scots pine wood had smooth surface after weathering. Toker *et al.* (2016) studied total color changes of heat-treated Oriental beech (*Fagus orientalis* L.) and Scots pine (*Pinus sylvestris* L.) woods after weathering. They found that total color changes of heat-treated Oriental beech (*Fagus orientalis* L.) and Scots pine (*Pinus sylvestris* L.) woods were lower than those of un-heated wood after weathering. Baysal *et al.* (2014), in an experimental study, investigated the gloss, surface roughness, and color change of the wooden test specimens after 500 hours of artificial weathering of heat-treated Scots pine (*Pinus sylvestris*). They stated that the surface properties of thermally modified Scots pine showed better surface properties as a result of artificial weathering than unmodified control samples. Garcia *et al.* (2014) reported that heat-treated teak sapwood (*Tectona grandis*) showed higher performance against color change after artificial weathering compared to control samples. Thus, wood material can become even more valuable as a result of heat treatment. The advantages of heat treatment can be listed as improved dimensional stability due to reduced hygroscopy, higher performance against degradation by microorganisms and insects, and dark color which is attractive to some users (Huang *et al.,* 2012).

The number of scientific studies examining the change in the surface properties of wood materials treated above 200 °C after artificial weathering is limited. For this reason, in this study, Oriental beech wood (*Fagus orientalis* L.), which was heat-treated at temperatures above 200 °C, is aimed to investigate color and surface roughness after artificial weathering.

## 2 MATERIALS AND METHODS
2. MATERIJALI I METODE

### 2.1 Sample preparation
2.1. Priprema uzoraka

Wood samples of 6 mm × 75 mm × 150 mm (radial by tangential by longitudinal) sized Oriental beech wood (*Fagus orientalis* L.) were prepared from air-dried wood. Wood samples were kept at 20 °C and 65 % relative humidity for 2 weeks before the tests started.

### 2.2 Thermal modification
2.2. Toplinska modifikacija

The thermal modification was done in a laboratory oven with temperature control. Three different temperatures (210 °C, 220 °C and 230 °C) were applied to Oriental beech samples under atmospheric pressure and heat treatment was performed in three different times (0.5, 1, and 1.5 hours). Five replications were made for each treatment group.

### 2.3 Artificial weathering
2.3. Umjetno izlaganje vremenskim utjecajima

Artificial weathering test according to ASTM G154-60 (2006) standard was made on a QUV weathering device (Q-Lab, USA) equipped with eight UVA

340 lamps. After the wooden specimens were exposed to 8-hour UV-ray irradiation cycles, 4 hours of condensation was applied on the QUV device for a total of 750 hours. The average radiation is at 340 nm wavelength ($\lambda_{max}$ = 340 nm) and its maximum intensity is 0.89 W/m$^2$. The temperature during the light irradiation period and the condensation period was around 60 °C and 50 °C, respectively.

## 2.4 Surface roughness
2.4. Hrapavost površine

According to DIN 4768 (1990) standard, roughness measurements were made with Mitutoyo Surftest SJ-301 device. In this study, the surface roughness parameter, such as average peak-valley height ($Rz$), was calculated. The surface roughness profile was scrutinized using the stylus with a diamond tip of 5 µm radius and 90° conical angle. The feed speed of the stylus was 0.5 mm/s1 along 8 mm sampling length (Zhong *et al.*, 2013). Five replications were made for each treatment group. Surface roughness measurements were made parallel to the fibers.

## 2.5 Color test
2.5. Određivanje boje

The three-dimensional CIELAB color space was used to quantify the color (Figure 1). Here, while the $L*$ axis represents lightness, $a*$, and $b*$ denote color coordinates. The parameters $+a*$ and $-a*$ represent red and green, respectively, while the parameter $+b*$ represents yellow and $-b*$ represents blue. The $L*$ parameter can range from 100 (white) to zero (black) (Zhang 2003). The colors of the specimens were measured with measurement geometry of d/8° and a D65 illuminant by a colorimeter (X-Rite SP Series Spectrophotometer, X-ride Pantone, MI, USA). The color coordinates were measured on the surface of samples at the same five points before and after artificial weathering. The measuring spot was adjusted to be equal or not more than one-third of the distance from the center of this area to the receptor field stops. Five replications



**Figure 1** Three-dimensional *CIEL\*a\*b\** color space (Hunt, 1995)
**Slika 1.** Trodimenzionalni prostor boje *CIEL\*a\*b\** (Hunt, 1995.)

were made for each treatment group. Color measurements were made parallel to the fibers.

The color difference, ($\Delta E*$) was determined for each wood as shown in the following Eqs. (ASTM D 1536–58 1964):

$$\Delta a* = a_f* - a_i* \tag{1}$$

$$\Delta b* = b_f* - b_i* \tag{2}$$

$$\Delta L* = L_f* - L_i* \tag{3}$$

$$\Delta E* = [(\Delta a*)^2 + (\Delta b*)^2 + (\Delta L*)^2]^{1/2} \tag{4}$$

Where: $\Delta a*$, $\Delta b*$, and $\Delta L*$ are the changes between the initial and final interval values.

## 2.6 Statistical evaluations of test results
2.6. Statistička analiza ispitnih rezultata

Experimental results were examined statistically. This examination was made with variance analysis and Duncan test. Duncan test with a 95 % confidence level of surface roughness and total color change test results were evaluated with a computerized statistical program. Homogeneity groups (HG) revealed whether the results were statistically significant. The exponential letters ($x^{a,b,c,d}$) are given as homogeneity groups in Table 1 and 2.

# 3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA
## 3.1 Surface roughness
3.1. Hrapavost površine

The $Rz$ values used for surface roughness parameter before and after artificial weathering are presented in Table 1.

Before artificial weathering, the average $Rz$ value of the unmodified control sample was 13.6. The test results indicated that, except for 0.5 h at 220 °C heat treatment, surface roughness values of all thermally modified Oriental beech wood samples were increased before weathering. Thermal modification gave a smoother surface than unmodified Oriental beech after artificial weathering. The increase in smoothness or reduction in roughness can be crucial for the use of solid wood. Wooden materials with rough surfaces require much more sanding than those with a smooth surface, which leads to a decrease in thickness of the material and, therefore, increases the losses due to the sanding process (Dundar *et al.*, 2008). Besides, it ensures that losses in the planer are reduced, and high-quality surfaces are obtained (Sevim Korkut *et al.*, 2008).

Surface roughness is considered to be a significant parameter to determine the wood surface quality, and many parameters affect the wood surface quality (Yildiz *et al.*, 2013). The weathering exposure increased the roughness of the un-heated and thermal treated Oriental beech. After artificial weathering, the increasing range of $Rz$ was from 26.03 % to 75.26 % for thermal modified Oriental beech wood samples, while the increase of $Rz$ by 106.63 % was observed for unmodified Oriental beech. This is because artificial
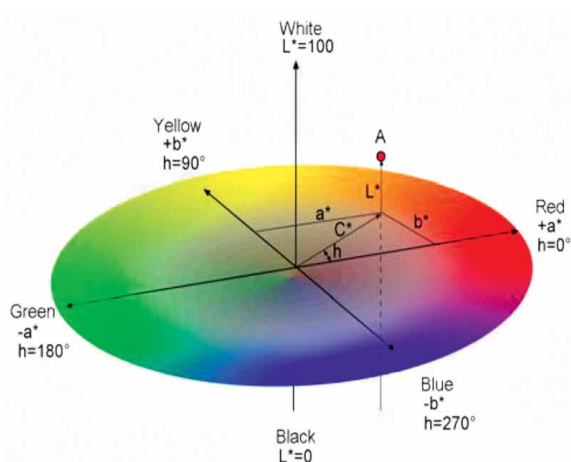
**Table 1** Surface roughness values of Oriental beech samples before and after artificial weathering
**Tablica 1.** Vrijednosti hrapavosti površine uzoraka bukovine prije i nakon umjetnog izlaganja vremenskim utjecajima

| Thermal treatment, °C *Toplinska obrada, °C* | Hours *Sati* | Before artificial weathering *Prije umjetnog izlaganja vremenskim utjecajima* | After 750 h artificial weathering *Nakon 750 h umjetnog izlaganja vremenskim utjecajima* | |
|---|---|---|---|---|
| | | $Rz$, μm (Mean / *srednja vrijednost*) | $Rz$, μm (Mean / *srednja vrijednost*) | $Rz$, μm Increases / *Povećanje*, % |
| Unmodified (Control) *Nemodificirani (kontrolni) uzorci* | - | 13.60 (2.76)* | 28.10 (3.63) | (+)106.63[a]** |
| 210 | 0.5 | 16.92 (2.45) | 27.65 (4.47) | (+)63.42[bc] |
| | 1.0 | 16.82 (3.52) | 26.15 (3.64) | (+)55.12[c] |
| | 1.5 | 20.17 (1.73) | 25.96 (0.89) | (+)28.70[d] |
| 220 | 0.5 | 10.27 (2.47) | 18.00 (4.02) | (+)75.26[b] |
| | 1.0 | 13.86 (2.60) | 22.13 (2.96) | (+)59.73[bc] |
| | 1.5 | 14.76 (3.32) | 18.97 (4.55) | (+)28.54[d] |
| 230 | 0.5 | 20.51 (5.49) | 31.49 (2.00) | (+)53.50[c] |
| | 1.0 | 17.54 (3.73) | 23.50 (2.42) | (+)33.99[d] |
| | 1.5 | 17.25 (3.81) | 21.74 (5.32) | (+)26.03[d] |

\* The values in parenthesis are standard deviations. Five replications were made for each group. / *Vrijednosti u zagradama standardne su devijacije.* \*\*The exponential letters are given as homogeneity groups (HG). / *Slova označuju homogene grupe (HG).*

weathering affects primarily the surface of wood, and causes slow abrasion of wood fibers from the surface (Williams *et al.,* 2001). According to the results of the study, rising temperature and prolonged modification time led to a lower surface roughness of Oriental beech after artificial weathering. Turkoglu *et al.* (2015) investigated the effect of weathering on the roughness of thermally treated Oriental beech. They reported that heat-treated samples reduced the effects of weathering on surface roughness. Baysal *et al.* (2014) explained that the unheated Scots pine wood gave a rougher surface than the heat-treated Scots pine wood after artificial weathering. The findings of this study are compatible with the above-mentioned researchers' results.

## 3.2 Color changes
3.2. Promjena boje

Table 2 shows the color changes of thermally modified Oriental beech before and after artificial weathering.

As could be expected, $L^*$ values of heat-treated Oriental beech wood were lower than those of un-heated (control) wood. This is because thermal modification caused the decrease of $L^*$ values of Oriental beech wood. Therefore, Oriental beech wood becomes darker after thermal modification. This tonality is generally developed with increasing temperature and durations. These findings are generally compatible with previous

**Table 2** Color changes of Oriental beech samples before and after artificial weathering
**Tablica 2.** Promjena boje uzoraka bukovine prije i nakon umjetnog izlaganja vremenskim utjecajima

| Thermal treatment, °C *Toplinska obrada, °C* | Hours *Sati* | Before artificial weathering *Prije umjetnog izlaganja vremenskim utjecajima* | | | After 750 h artificial weathering *Nakon 750 h umjetnog izlaganja vremenskim utjecajima* | | | Color changes *Promjena boje* | | | Total color changes *Ukupna promjena boje* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $L_i^*$ | $a_i^*$ | $b_i^*$ | $L_f^*$ | $a_f^*$ | $b_f^*$ | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta E^*$ |
| Unmodified (Control) *Nemodificirani (kontrolni) uzorci* | - | 71.28 | 9.76 | 18.32 | 57.22 | 13.36 | 27.95 | -14.06 | 3.60[a] | 9.63[a] | 17.42[a]* |
| 210 | 0.5 | 44.66 | 7.94 | 16.11 | 42.37 | 12.29 | 22.56 | -2.29 | 4.35 | 6.45 | 8.11[b] |
| | 1.0 | 43.70 | 7.74 | 15.80 | 41.49 | 10.17 | 20.04 | -2.21 | 2.43 | 4.24 | 5.36[c] |
| | 1.5 | 43.08 | 7.32 | 14.44 | 39.2 | 11.68 | 17.51 | -3.88 | 4.36 | 3.07 | 6.59[bc] |
| 220 | 0.5 | 41.34 | 7.87 | 14.94 | 37.5 | 12.01 | 20.31 | -3.84 | 4.14 | 5.37 | 7.79[b] |
| | 1.0 | 34.74 | 7.02 | 12.48 | 34.67 | 8.5 | 14.56 | -0.07 | 1.48 | 2.08 | 2.55[e] |
| | 1.5 | 34.42 | 6.76 | 12.45 | 33.68 | 7.6 | 13.43 | -0.74 | 0.84 | 0.98 | 1.49[e] |
| 230 | 0.5 | 37.27 | 7.59 | 13.57 | 35.33 | 9.17 | 17.54 | -1.94 | 1.58 | 3.97 | 4.69[cd] |
| | 1.0 | 28.85 | 5.30 | 8.46 | 26.43 | 6.45 | 9.39 | -2.42 | 1.15 | 0.93 | 2.83[de] |
| | 1.5 | 34.05 | 7.22 | 13.10 | 33.28 | 8.51 | 15.17 | -0.77 | 1.29 | 2.07 | 2.56[e] |

\*The exponential letters are given as homogeneity groups (HG). Five replications were made for each group. / *Slova označuju homogene grupe (HG). Za svaku je grupu pripremljeno pet uzoraka.*

studies (Aksoy *et al.,* 2011; Baysal *et al.,* 2014; Militz, 2002; Yildiz *et al.,* 2011; Toker *et al.,* 2016). The decreases of *L\* values* of thermally modified wood can be attributed to changes in lignin structure and noncellulosic polysaccharides (Grelier *et al.,* 2000; Petric *et al.,* 2004; Hon and Chang, 1985). While the (+) values of *a\** show that Oriental beech turned to red, (+) values of *b\** show that Oriental beech turned to yellow. According to our results, the thermally modified wood surface turned to red and yellow after thermal modification. Baysal *et al.* (2014) found that, while *a\** values decreased with the increase in temperature and time, the *b\** values increased initially and then decreased at temperatures used. Akgul and Korkut (2012) investigated the color characteristics of thermally treated Uludag fir wood. According to their findings, with higher treatment temperature and durations, yellow tone initially increased and then decreased. Gunduz and Aydemir (2009) studied color characteristics of heat-treated Hornbeam wood. They found that, while the *b\** values increased slightly at low temperature and durations, higher temperatures caused the decrease of *b\** values of Hornbeam wood. Our results showed that artificial weathering caused the decrease of *L\** values of thermally modified and unmodified wood. Negative values of Δ*L\** were observed after weathering. Our results showed that decreases in *L\** values of thermally treated wood were lower compared to those of un-heated wood. For example, while Δ*L\** of unmodified wood was 14.06, it was between (-0.07) and (-3.88) for thermally modified wood. Baysal *et al.* (2014) investigated lightness values of thermally modified wood after artificial weathering. They determined that Δ*L\** values of thermally modified wood were lower compared to unmodified wood after artificial weathering. Our results are compatible with Baysal's findings (2014).

The color change results of the study showed that thermally modified and unmodified wood surface turned to red after weathering. After weathering, Δ*a\** changed between 0.84 to 4.36. Sivrikaya *et al.* (2015) studied color changes of thermally modified Scots pine wood after artificial weathering. They reported that the Δ*a\** values of Scots pine increased after weathering. Baysal *et al.* (2014) studied Δ*a\** changes of thermally modified wood. They determined that thermally modified Scots pine wood gave positive Δ*a\** values after artificial weathering. Our results are compatible with the aforementioned studies. According to our results, thermally modified and unmodified wood showed positive Δ*b\** values after artificial weathering. It can be due to the modification of some chromophoric groups of lignin (Grelier *et al.,* 2000). Moreover, Δ*b\** of unmodified wood was higher compared to thermally modified wood. Baysal *et al.* (2014) studied color changes of Scots pine after artificial weathering. They determined that Scots pine gave positive Δ*b\** values after artificial weathering. Also, they found that, in general, Δ*b\** values decreased with increasing temperature and durations. Our results are compatible with the Baysal *et al.* (2014) findings. Δ*E\** values of thermally modified Oriental beech were lower compared to unmodified wood. For example, Δ*E\**

of unmodified wood was 17.42, while it varied between 1.49 and 8.11 in thermally modified wood. There was a statistically significant difference between Δ*E \** values of the unmodified (control) and thermally modified Oriental beech wood (*p*≤0.05). In general, total color changes in wood decreased with temperature and duration after artificial weathering.

# 4 CONCLUSIONS
4. ZAKLJUČAK

Thermal modification reduced the surface roughness and color changes of Oriental beech after artificial weathering compared to untreated beech wood. The surface of heated and un-heated wood was darkened due to artificial weathering exposure. However, thermally modified wood gave a lighter surface than unmodified wood after artificial weathering. Oriental beech wood tended to be reddish and yellowish after artificial weathering. Total color changes of heat treated Oriental beech wood were lower compared to those of un-heated wood. Generally, higher treatment temperature and treatment time resulted in lower surface roughness and total color changes of Oriental beech wood after artificial weathering.

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# Possibility of Use of NCC-Reinforced Melamine-Urea-Formaldehyde Adhesive in Plywood Manufacturing

## Mogućnost uporabe melamin-urea-formaldehidnog ljepila ojačanog nanocelulozom u proizvodnji furnirskih ploča

**ABSTRACT** • *The possibility of using nanocellulose (NCC) as a filling substance for melamine-urea-formaldehyde (MUF) adhesive was investigated for the process of manufacturing plywood. The adhesive mixtures were prepared with various nanocellulose concentrations. The amount of introduced filler had a significant effect on both resin and plywood characteristics. Fourier transform infrared spectroscopy (FTIR) did not show any major changes between experimental and reference variants. The viscosity of resin increased after the introduction of nanocellulose. The addition of NCC in the amount of 5 g and 10 g per 100 g of solid resin led to an improvement in bonding quality, modulus of elasticity and bending strength. Further increase of NCC concentration caused a deterioration of manufactured plywood properties. In summary, the addition of proper amount of nanocellulose resulted in manufacturing plywood with improved properties.*

*Keywords: plywood; melamine-urea-formaldehyde adhesive; nanocellulose; filler*

**SAŽETAK** • *U radu je prikazano istraživanje mogućnosti uporabe nanoceluloze (NCC) kao punila za melamin-urea-formaldehidno ljepilo (MUF) koje se upotrebljava u proizvodnji furnirskih ploča. Smjese ljepila pripremljene su dodavanjem različitih koncentracija nanoceluloze. Količina dodanog punila znatno je utjecala na svojstva smole i furnirske ploče. Furierovom infracrvenom spektroskopijom (FTIR) nisu utvrđene veće promjene između eksperimentalnih i referentnih varijanti. Viskoznost smole povećala se nakon dodatka nanoceluloze. Dodatak 5 i 10 g nanoceluloze na 100 g otvrdnute smole rezultirao je poboljšanjem kvalitete vezanja, modula elastičnosti i čvrstoće na savijanje. Daljnje povećanje koncentracije nanoceluloze uzrokovalo je pogoršanje svojstava proizvedenih furnirskih ploča. Ukratko, dodatak odgovarajuće količine nanoceluloze rezultirao je furnirskom pločom poboljšanih svojstava.*

*Ključne riječi: furnirska ploča; melamin-urea-formaldehidno ljepilo; nanoceluloza; punilo*

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## 1 INTRODUCTION
1. UVOD

Nanotechnology is a relatively new science that has already become the frontier of the 21st century. It is defined as the field focused on the control and understanding of the matter at a dimensional range between 1 and 100 nm (Hulla *et al*., 2015). From the beginning, nanotechnology has been playing the role of a scientific platform joining and linking together various disciplines (Szczesna-Antczak *et al*., 2012). The objects with the dimensions between 1 and 100 nm have unique mechanical, optical, magnetic and electrical properties (Wegner and Jones, 2005). Thus, the nanoscience also provides many opportunities for wood-based materials manufacturing (Candan and Akbulut, 2013). It seeks to develop advanced materials having significantly improved chemical, physical properties and functions (Wegner and Jones, 2006).

Wood-based materials such as plywood, particleboards, medium- and high density fiberboards are becoming more popular in recent years. The production of plywood, which is a multilayer composite made of glued wood veneers, reached about 157 million m³ in 2017 and it is still growing (Bekhta *et al*., 2020; Sydor *et al*., 2020). Due to its favorable mechanical properties and dimensional stability, it founds an application in many industry branches (Kawalerczyk *et al*., 2019a). In structural applications, plywood is used in walls, ceilings and roof constructions; in furniture as a basic material for both upholstered and case furniture (Bekhta *et al*., 2009b; Majewski, 2019). Moreover, it is also appreciated as a packaging material due to its ease of processing, lightness and durability, and in transport as a flooring material or in trailers construction. The properties of plywood and consequently its application depend on the quality of veneers and the type of used adhesive (Kawalerczyk *et al*., 2020c; Mirski *et al*., 2011).

Amino resins are synthetic adhesives widely used in wood-based material industry. Their participation in the general range of wood adhesives market is estimated at 85 % (Jóźwiak, 2018; Kamoun *et al*., 2003). The three main types: UF (urea-formaldehyde), MF (melamine-formaldehyde) and MUF (melamine-urea-formaldehyde) may be distinguished as the most commercially available (Gonçalves *et al*., 2019; Mirski *et al*., 2020). The widespread use of MUF adhesives in recent years results from the higher bond quality, water resistance and lower formaldehyde emission in comparison with UF resin (Lei and Frazier, 2015; Tohmura *et al*., 2001). The adhesives mixtures applied in plywood manufacturing have to contain various kinds of fillers. They are insoluble, non-volatile substances added in order to adjust the viscosity, reduce raw material costs and increase bonding between the wood components (Kawalerczyk *et al*., 2019b; Ong *et al*., 2018).

In recent years an interesting concept of using cellulose as a modifier for polymers has been increasingly investigated. It is the most important constituent of the plants cell walls and, moreover, it is also synthe-

sized in tunicate sea animals and some bacteria (Henriksson and Berglund, 2007; Janardhnan and Sain, 2011). The attention received by cellulosic particles results from their high surface area, high stiffness and strength. Many studies on using nanocellulose (NCC) as an environmentally friendly modifier of wood adhesives have already been carried out (Ayrilmis *et al*., 2016a; Gardner *et al*., 2008; Vineeth *et al*., 2019).

The effect of nanocellulose addition to amino resins was investigated by Veigel *et al*. (2012). They found that the modification increased the viscosity of liquid adhesive and caused a significant improvement in both particleboard and oriented strand board (OSB) strength properties. Studies conducted by Mahrdt *et al*. (2016) confirmed that the introduction of cellulosic particles led to the increase in particleboard strength values. Furthermore, the influence of nanocellulose on multilayered wood-based material has also been investigated. Zhang *et al*. (2011) noted a major enhancement in plywood shear strength and the reduction in formaldehyde emission because of the silanized nanocellulose added to UF adhesive. However, studies conducted by Kawalerczyk *et al*. (2020b) did not confirm the effect on the reduction of the harmful formaldehyde emission with the use of non-modified nanocellulose. Ayrilmis *et al*. (2016b) concluded that cellulosic particles added to UF adhesive can reduce the VOCs (volatile organic compounds) emitted from LVL (laminated veneer lumber). The price of nanocellulose may be a limiting factor for some applications but there are many studies on finding the way to obtain it with more cost-effective methods (Babicka *et al*., 2020; Kawalerczyk *et al*., 2021).

Despite the fact that MUF adhesives are becoming more popular, especially for applications in kitchens, floors and some structural materials, and although they are increasingly replacing pure UF adhesives, no studies have examined the effect of their nanocellulose-reinforcement on the properties of manufactured plywood panels (Lei and Frazier, 2015). Thus, the aim of the present study was to investigate the effect of adding NCC to MUF adhesive on the plywood performance.

## 2 MATERIALS AND METHODS
2. MATERIJALI I METODE

### 2.1 Materials
2.1. Materijali

Rotary cut birch (*Betula* L.) veneer sheets were purchased from the market with the dimensions of 320 mm × 320 mm × 1.3 mm, moisture content of (5 ± 1) %, without any defects, and they were used for the research purpose. The commercial MUF adhesive with the following characteristics: solid content of 64 - 69 %, gel time at 100 °C of 63 s, viscosity between 1000 and 2500 mPa·s, density of 1.27 g/m³ and pH of 9.5 - 10.7 was purchased for the experiment. The 20 % aqueous solution of ammonium nitrate ($NH_4NO_3$) was added as a hardener taking into account the environmental aspects (Aras *et al*., 2015). In order to adjust

and regulate the viscosity of adhesive mixture, the rye flour was introduced in accordance with the industrial formulations. Nanocellulose, added as a modifier, was purchased from Nanografi Nanotechnology Co. Ltd. (Ankara, Turkey). As declared by the producer, the dimensions of the particles were 300 - 900 nm in length and 10 - 20 nm in width.

**2.2 Methods**
2.2. Metode

A 10 % aqueous suspension of nanocellulose was prepared with the use of magnetic stirrer (600 rpm, 10 min), because cellulosic nanoparticles had to be processed in wet state. The experimental adhesive mixtures with the addition of NCC suspension, flour and hardener were homogenized using CAT-500 homogenizer at 1000 rpm for 2 minutes. The control adhesive was prepared in accordance with an industrial formulation. The compositions of both experimental and reference mixtures are summarized in Table 1.

No additional water was added in experimental variants because the nanocellulose was introduced in the state of water suspension. The viscosities of adhesives mixtures and their changes in 6 h were investigated using Brookfield DV-II + Pro viscometer. In order to assess the chemical bonding between the resin and nanocellulose, Fourier transform infrared spectroscopy was carried out. Reference and experimental adhesive mixtures were cured at 140°C and grinded. The obtained powders with a fraction of 0.125 mm were mixed with KBr at 1/200 mg ratio. Spectra were registered using a Nicolet iS5 spectrophotometer (Thermo Fisher Scientific) with Fourier transform at the range of 500 - 4000 cm$^{-1}$ at the resolution of 4 cm$^{-1}$, registering 16 scans.

The adhesive mixtures were spread on the surface of external veneers in the amount of 170 g/m$^2$. The veneer sets were assembled perpendicularly to each other. Three-layer plywood panels with the dimensions of 320 mm × 320 mm were produced in a hydraulic laboratory press with the following pressing parameters: temperature of 140 °C, unit pressure of 1.3 MPa and pressing time of 4 min. Three replicate panels were produced for all the test groups. Manufactured plywood was tested in order to investigate the following properties:
- formaldehyde (HCHO) emission with the flask method according to EN 717-3 (1996) initially and after 30 days of panels conditioning while left open at (20 ± 3) °C and (65 ± 2) % relative humidity,

- shear strength after 24 h of soaking in water at (20 ± 3) °C and after preparation including boiling in water for 6 h and cooling in water at (20 ± 3) °C for 1 h according to EN 314-1 (2004),
- modulus of elasticity and bending strength parallel and perpendicular to the grains of face layer according to EN 310 (1993).

On the basis of the results obtained in above tests, the proper composition of adhesive mixture was selected. The experimental adhesive labeled "N5" showing the best reinforcing effect was applied in the amount of 170, 160, 150, 140 and 130 (g/m$^2$) in order to investigate the possibility of reducing the adhesive consumption in plywood production. The pressing process was conducted at 140 °C with the unit pressure of 1.3 MPa for 4 min. Manufactured plywood panels were tested in terms of shear strength both after 24 h of soaking in water at (20 ± 3) °C and after pretreatment consisting of boiling in water for 6 h and cooling in water at (20 ± 3) °C for 1 h according to EN 314-1 (2004). The obtained results were compared with a reference variant, which was labeled "170 REF" in further part of the paper.

The evaluation of mechanical properties and bonding quality involved 12 samples of each variant. The results were subjected to the multivariate statistical analysis ANOVA. The Tukey test with a significance level of α = 0.05 was applied to distinguish the homogeneous groups with the use of Statistica 13.0 software.

**3 RESULTS**
3. REZULTATI

Figure 1 illustrates the time-viscosity dependence. The results indicate that nanocellulose-reinforced MUF resins were characterized by significantly increased viscosity in comparison with reference mixture.

The viscosity of adhesive mixture containing the maximal amount of cellulosic nanoparticles was 46 % and 33 % higher when compared to resin only filled with rye flour initially and after 6 hours of measurements, respectively. The increasing values of all resins viscosity during the test time resulted from the progressive polycondensation reactions and the constant water absorption by hydrophilic fillers. The viscosity of the glue mixture increased with the increasing percentage of nanocellulose addition similarly to investigations reported by Damásio *et al.* (2017). One factor that may

**Table 1** Compositions of adhesive mixtures
**Tablica 1.** Sastav smjesa ljepila

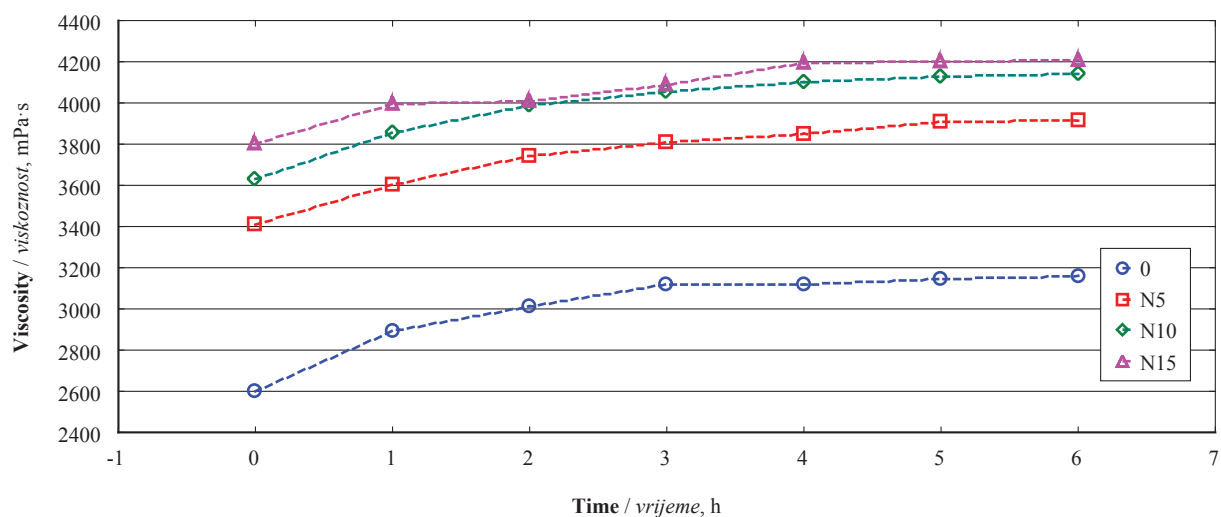| Variant label *Oznaka varijante* | Quantity (g/100 g of solid MUF resin) *Količina (g/100 g otvrdnute MUF smole)* | | | |
|---|---|---|---|---|
| | NCC suspension *NCC suspenzija* | Rye flour *Raženo brašno* | H$_2$O | Hardener *Otvrdnjivač* |
| 0 | 0 | 20 | 10 | 2.5 |
| N5 | 5 | 10 | 0 | 2.5 |
| N10 | 10 | 10 | 0 | 2.5 |
| N15 | 15 | 10 | 0 | 2.5 |

**Figure 1** Viscosity of adhesives mixtures
**Slika 1.** Viskoznost smjesa ljepila

have contributed to this major increase in viscosity is the highly hydrophilic nature of cellulose. It tends to absorb water due to its chemical structure – the surfaces of cellulose are covered in hydroxyl groups on the equatorial positions of glucopyranose ring (Yamane *et al*., 2006). Another factor is the increased chemical reactivity of nanoparticles in general (Shahbazi *et al*., 2013). The introduction of nanocellulose probably caused a substantial interfibrillar interaction. The number hydroxyl groups located on the surfaces of individual fibrils can cause a considerable interaction between them, which can lead to the formation of temporary bonds (Iotti *et al*., 2011).

A similar effect was also observed in case of the NCC-reinforcement of UF and PF adhesives (Kawalerczyk *et al*., 2020b, a; Mahrdt *et al*., 2016). Hong and Park (2017) distinguished the viscosity of adhesive as one of the most important factors affecting the strength properties of cured bonds. Studies conducted by Derkyi *et al*. (2008) also confirmed that the rheological properties of UF resin had a significant effect on plywood bonding quality. The adhesive characterized by too low viscosity penetrates extensively into porous surface of the veneer during application and pressing. Consequently, the layer remaining on the veneer surface is no longer sufficient to ensure good quality of the bond (Sellers, 1985). The viscosity may also be a factor limiting the amount of nanocellulose added to the adhesive. The lack of water in the mixture can affect the crosslinking of adhesive and moreover, the addition of highly hydrophilic filler can prevent water from evaporating during the pressing process (Mahrdt *et al*., 2016; Réh *et al*., 2019). Furthermore, it is also hard to evenly spread the adhesive characterized by too high viscosity and adjust it to the applying equipment. In case of this research, both reference and experimental mixtures obtained values that allowed the application without any difficulties.

Since the reinforcing effect of nanocellulose is associated with chemical bonding, the Fourier transform infrared spectroscopy (FTIR) was carried out in order to investigate the chemical interactions. The
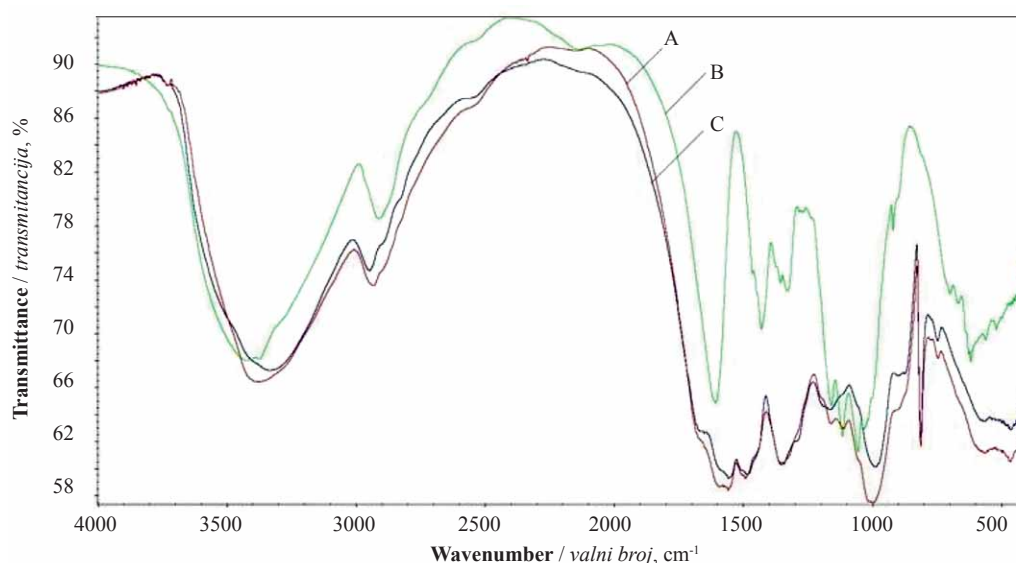


**Figure 2** FTIR spectra of: A – modified resin labeled N5; B – nanocellulose; C – unmodified MUF resin
**Slika 2.** FTIR spektri: A – modificirana smola označena kao N5; B – nanoceluloza; C – nemodificirana MUF smola
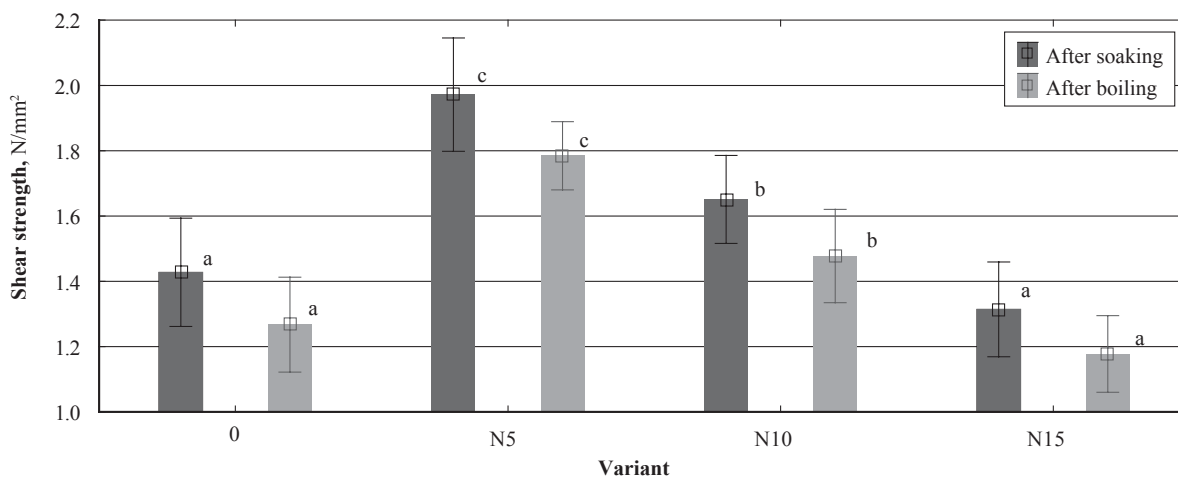
**Figure 3** Shear strength of plywood (a, b, c letters indicate homogeneous groups)
**Slika 3.** Čvrstoća na smik furnirske ploče (a, b i c slova označuju homogene grupe)

transmittance spectra of cured modified and non-modified resins are presented in Figure 2. Spectra of all modified resins regardless of the variant had the same course.

The broad band at 3400 cm$^{-1}$ was assigned to the O-H stretching of hydroxyl groups in each sample. The C-H stretching of methylene groups was recorded in the range from 2920 cm$^{-1}$ to 2890 cm$^{-1}$ (Luo *et al.*, 2015). The slight difference in intensity of C-H band was probably inducted by the hydrogen bonding in MUF and NCC sample. For MUF and MUF+NCC samples, the peak at 1690 cm$^{-1}$ corresponded to C=O groups in amide (Müller *et al.*, 2009; Pandey and Pitman, 2003). In the case of NCC sample, the peak at 1620 cm$^{-1}$ was assigned to O-H vibration of absorbed water (Wulandari *et al.*, 2016). The peak at 1320 cm$^{-1}$ corresponded to C-H and C-O vibrations contained in the polysaccharide rings and it was observed at spectra of NCC and MUF+NCC. Spectra of MUF and MUF+NCC were characterized by a peak around 1560 cm$^{-1}$, which was assigned to the C-N stretching of secondary amines. Moreover, the peak at 1360 cm$^{-1}$ was assigned to the C-N stretching of CH$_2$-N witch confirmed presence of amine groups (Luo *et al.*, 2015). The peak at 1060 cm$^{-1}$ corresponded to vibration from the pyranose ring (spectra of NCC) (Wulandari *et al.*, 2016). In the case of triazine rings, the peak at 1190 cm$^{-1}$ was observed. It was assigned to C-N stretching vibrations (Yuan *et al.*, 2016). Spectra of MUF + NCC was characterized by occurrence of a peaks at 1060 cm$^{-1}$ and 1120 cm$^{-1}$, which corresponded to pyranose rings and aliphatic ring, respectively (Luo *et al.*, 2015). These peaks were not observed at MUF spectra. Presumably, it resulted from the fact that interactions occurred between nanocellulose and MUF resin chemical. The peak at 810 cm$^{-1}$ was assigned to the typical stretching of the triazine ring of melamine and it was observed at spectra of MUF resin and MUF+NCC (Gao *et al.*, 2012; Kandelbauer *et al.*, 2007; Reimschuessel and McDevitt, 1960; Sun *et al.*, 2011).

The transmittance spectra of reference and reinforced adhesive revealed mostly the characteristic functional groups of MUF resins. According to literature, the interfacial bonding of nanocellulose with resins can be attributed to the reaction between the methylol groups of resin and hydroxyl groups of cellulose (Singha and Thakur, 2008).

Glue line quality is one of the most important properties of plywood affecting both its physical and mechanical characteristics (Bekhta *et al.*, 2009a). Thus, the shear strength test was carried out since it is the fundamental indicator of the adhesive performance in plywood panels (Bekhta *et al.*, 2016; Rohumaa *et al.*, 2013). The results of bonding quality are summarized in Figure 3.

In order to fully evaluate how changes in adhesive formulation influenced the mechanical properties of plywood, such as bending strength (*MOR*) and modulus of elasticity (*MOE*), investigations were made both parallel and perpendicular to the grains of the face layer. The results are presented in Figure 4.

On the basis of the research conducted, it was confirmed that the key to obtain optimum reinforcement effect was the amount of added nanoparticles (Ferreira 2017). The major improvements in shear strength values were obtained in variants where the percentages of added NCC were 5 and 10 %. The best results were observed in case of variant labeled N5 and the increase was 38 % and 41 % in comparison with reference panels after soaking and after boiling, respectively. The introduction of 10 g of cellulosic nanoparticles also led to the increase of bonding quality compared to the mixture filled only with flour. As expected based on the previous research, as the amount of nanocellulose increased, the shear strength value constantly decreased (Kawalerczyk *et al.*, 2020b, a; Veigel *et al.*, 2012). Bonding quality of panels labeled N15 was decreased by about 8 % both after soaking and boiling in water. However, all plywood samples met the requirements of EN 314-2 (1993) and their shear strength exceeded 1 N/mm$^2$.

Mechanical properties, such as modulus of elasticity and bending strength (also called modulus of rupture) of the NCC-modified plywood show significantly
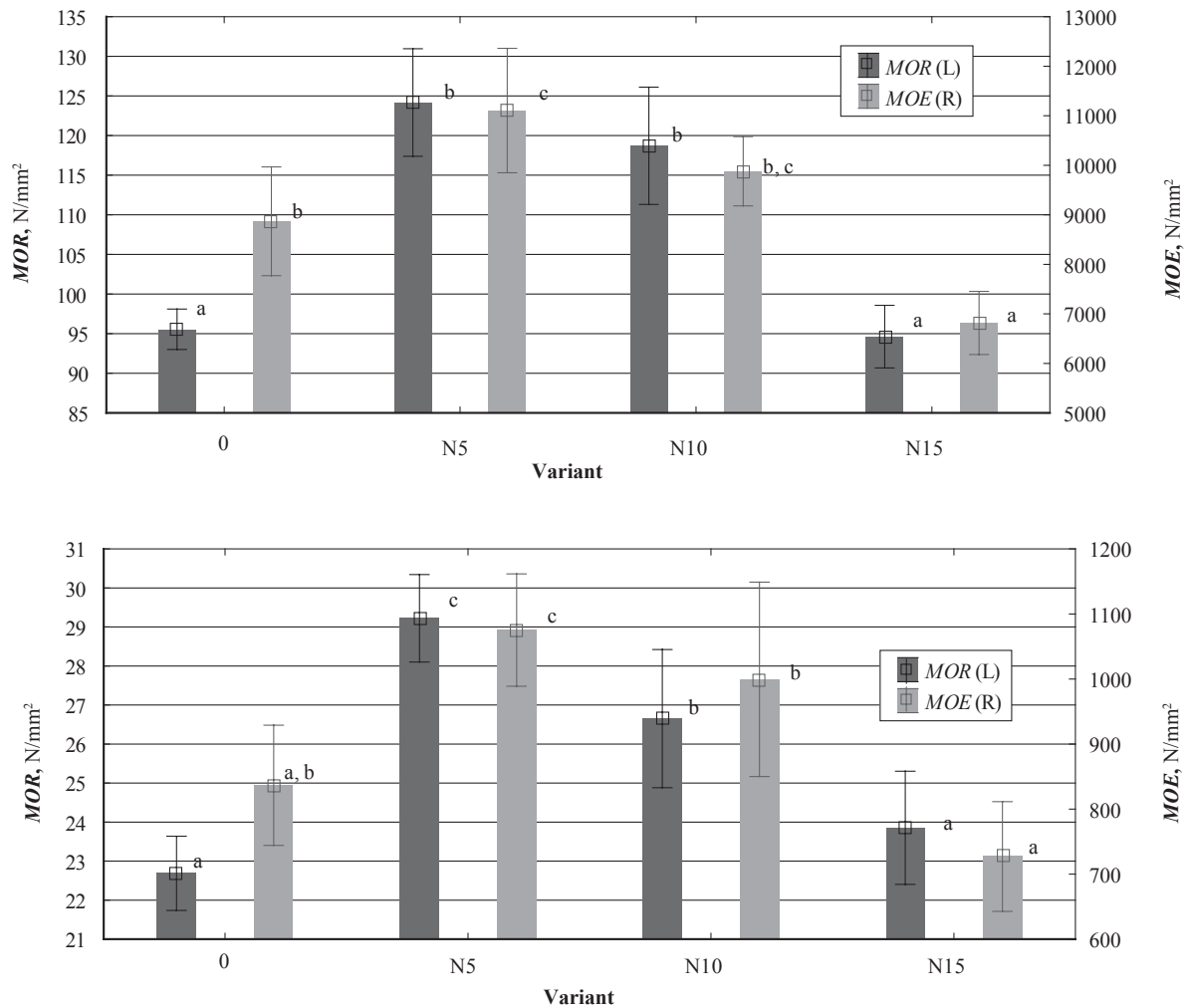
**Figure 4** Bending strength (*MOR*) and modulus of elasticity (*MOE*) of plywood tested: (a) parallel and (b) perpendicular to grains of face layer (a,b,c letters indicate homogeneous groups)
**Slika 4.** Čvrstoća na savijanje (*MOR*) i modul elastičnosti (*MOE*) ispitivane furnirske ploče: (a) u smjeru žice površinskog sloja i (b) okomito na smjer žice površinskog sloja (a, b i c slova označuju homogene grupe)

higher average values than reference plywood. The most satisfactory results were obtained in case of plywood modified with the smallest addition of nanocellulose. Modulus of elasticity and bending strength increased by approx. 27 % in comparison with control samples. Further addition of modifier at the level of 10 g also caused an improvement in plywood performance but, as expected from shear strength values, the maximum concentration of nanocellulose caused a notable decrease of panel strength properties.

The addition of nanocellulose to MUF resin shows similar results to the effect on UF resin modification (Kawalerczyk *et al*., 2020b). Zhang *et al*. (2011) introduced silane-modified NCC in plywood manufacturing and observed that bonding quality increased by about 24 %. Furthermore, investigations of Damásio *et al*. (2017) showed that the shear strength of a glue line increased by 56 % after the addition of 8 % CNF (cellulose nanofibrils). Ayrilmis *et al*. (2016a) stated that the enhancement in UF-glue joints strength resulted from their increased ducticility. Veigel *et al*. (2012) also confirmed the reinforcing nature of nanocellulose. Properties of manufactured particleboards and OSB (oriented strand boards) were improved when the CNF

was added to UF resin. The reason for that major reinforcing effect is, as reported by Vineeth *et al*. (2019), the improvement in fracture energy and fracture toughness. Veigel *et al*. (2011) showed that the addition of nanocellulose in the amount of 2 % resulted in the increase of the toughening effect up to 45 %. The enhancement can be also attributed to the chemical bonding between the methylol groups of resin and the free hydroxyl groups contained in cellulosic chain (Fornué *et al*., 2011). Moreover, Hu *et al*., (2014) confirmed that the presence of cellulose nanocrystals increase the wood-adhesive bonding and interactions. Another aspect leading to the reinforcing effect of the introduction of nanocellulose is the changes in resin morphology. Major fragility of amino resins results from their tendency to develop microcracks (Thomas *et al*., 2019). They deteriorate the mechanical performance of manufactured materials, and limiting their occurrence has a significant effect on the strength properties of glue lines (Kawalerczyk *et al*., 2019b). Kawalerczyk *et al*. (2020a) investigated the effect of nanocellulose addition on phenol-formaldehyde resin morphology. Studies have shown that the modification enhanced the structure of cured resin and made it significantly less
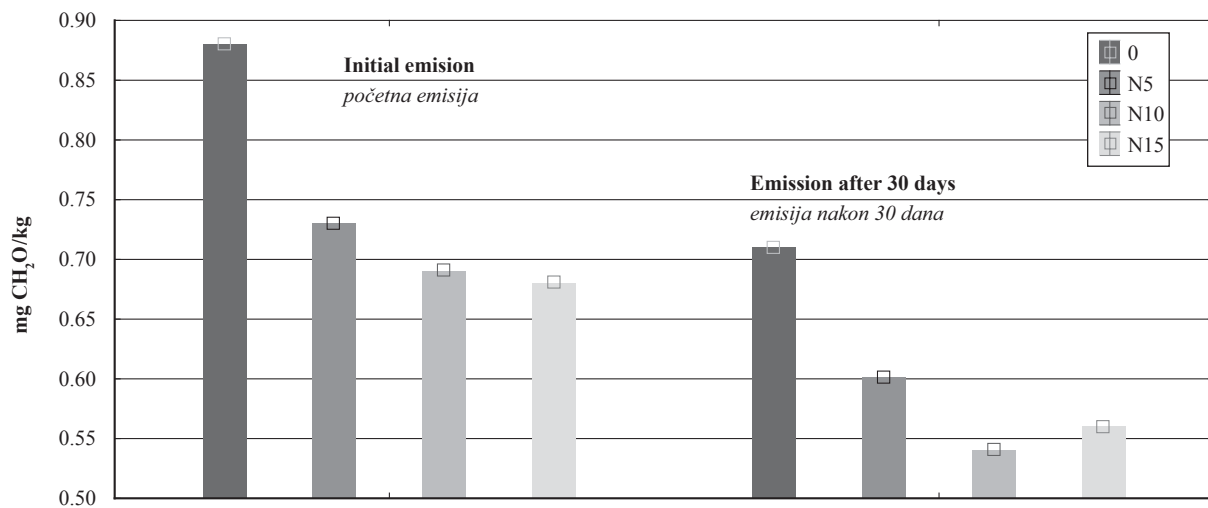
**Figure 5** Formaldehyde emission from plywood
**Slika 5.** Emisija formaldehida iz furnirske ploče

porous, more solid and compact. The deterioration observed in bonding quality, MOR and MOE resulted from too high concentration of nanoparticles, which consequently led to the formation of agglomerates. It has particularly negative effect since the nanofillers act like carriers of stress along the glue line and the occurrence of agglomerates cause the accumulation of load at certain points of the bond (Singha and Thakur, 2008).

A major disadvantage of amino resins is a harmful formaldehyde emission (Dziurka and Mirski, 2014). According to literature, there are three main sources of emitting formaldehyde from adhesives: hydrolytic degradation of cured resin, residual formaldehyde contained in the resin and condensation reaction between hydroxymethyl groups and other aromatic carbon or two hydroxymethyl groups (Tohmura *et al.*, 2001). Since building materials including wood-based materials are considered to be one of the most common sources of formaldehyde emission, it is important to reduce it. The results of HCHO emissions are presented in Figure 5.

Plywood panels manufactured with the use of NCC-modified resin were characterized by significantly lower formaldehyde emissions. As the concentration of cellulosic nanoparticles increased, the amount of emitted HCHO was substantially reduced. Thus, the best results were observed in case of variant N15, where the decrease was 23 %. Studies conducted by Zhang *et al.* (2011) have shown very similar effects. Authors stated that the addition of modified NCC led to reduced HCHO emission due to physical adsorption and chemisorption. Moreover, *Li et al.* (2015) hypothesized that the decreased formaldehyde emissions can be attributed to increased viscosity of an adhesive. According to the author's theory, the glue mixture characterized by low viscosity penetrates into the wood pores, which consequently increases the emission of plywood. It was also reported that the monomeric formaldehyde and polyoxymethylene glycols contained in the resin can easily interact with OH groups of nanoparticles (Candan and Akbulut, 2013; Dudkin *et al.*, 2006).

Furthermore, cellulose itself is able to irreversibly bound formaldehyde in small quantities (Bekhta *et al.*, 2019; Kamath *et al.*, 1985). Another reason for this reduction can be the unique characteristics of nanoparticles such as chemical activity, tremendous surface area or physical properties. Liu and Zhu (2014) explained that the decrease in HCHO emissions results from the ability of nanoparticles to absorb free formaldehyde from adhesives.

The resin costs are more than 60 % of the total wood-based materials manufacturing costs (Cao *et al.*, 2018). Both the modification of veneer surface and the modification of adhesives are investigated factors that can possibly lead to the reduction of the binding agent consumption. The possibility to reduce the amount of applied resin was determined on the basis of shear strength test and the results are presented in Figure 6.

As the amount of applied glue mixture decreased, the bonding quality also decreased. The shear strength values were reduced since the quantity of applied resin was insufficient to fully and evenly cover the veneer surface (Bekhta and Marutzky, 2007). Introducing nanocellulose in the amount of 5 g per 100 g of solid MUF resin had a positive effect on its properties, durability and morphology, and consequently it allowed to reduce adhesive spread rate by 30 %. The experimental plywood glued with reference resin mixture in the amount of 170 g/m² was characterized by equally good shear strength as panels manufactured with the use of NCC-reinforced adhesive in the amount of 140 g/m². The differences between these two variants were not statistically significant and the p-value was 0.999020 and 0.999987 after soaking and after boiling, respectively. However, further decrease of adhesive spread rate led to a notable deterioration in bonding quality, but the results still met the requirements of EN 314-2 (1993). The modification of resin seems to be more effective than surface modification, e.g. veneer compression (Bekhta and Marutzky, 2007). Corresponding results were obtained by Dukarska and Czarnecki (2016) in studies concerning the nano-SiO₂ addition to MUPF (melamine-urea-phenol-formaldehyde) adhesive. The
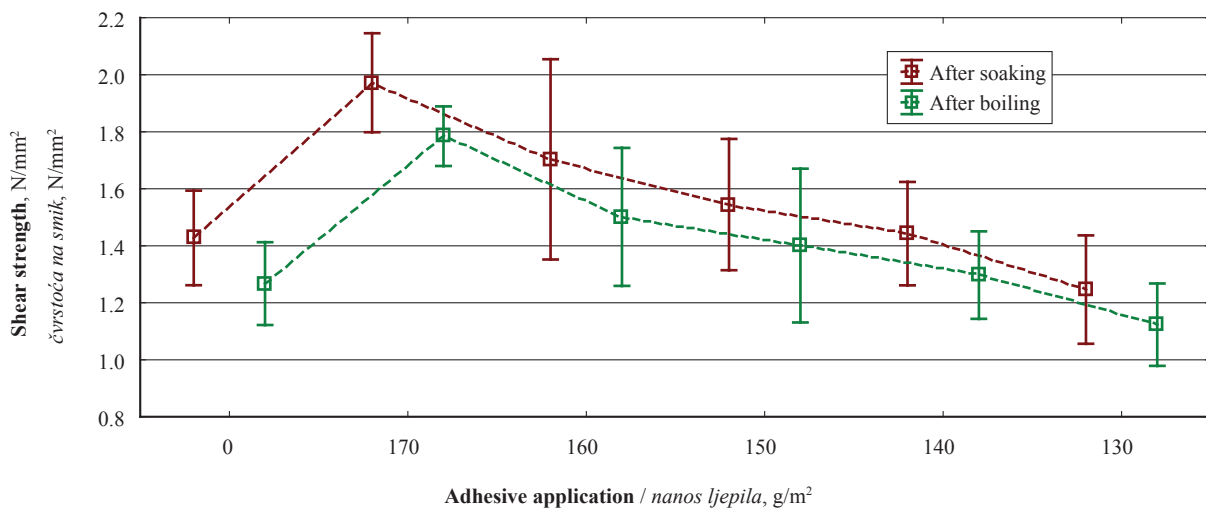
**Figure 6** Reduction of adhesive application in manufactured plywood
**Slika 6.** Smanjenje nanosa ljepila u proizvodnji furnirske ploče

introduction of fumed nanosilica allowed to decrease the resin spread rate in plywood production by 30 %. In future, it would be interesting to investigate how the reduction of MUF adhesive consumption influences the emission of free formaldehyde.

## 4 CONCLUSIONS
4. ZAKLJUČAK

The time-viscosity dependence showed a significant increase after the addition of nanocellulose. As the amount of added nanomodifier increased, the viscosity values also increased.

The Fourier transform infrared spectroscopy (FTIR) did not show any major changes between experimental and reference samples, thus it did not explain the chemical interaction between nanocellulose and melamine-urea-formaldehyde resin.

The addition of small amounts of nanocellulose (5 g and 10 g) led to the improvement in bonding quality and mechanical properties such as modulus of elasticity and bending strength. The best results were obtained in case where the concentration of NCC was up to 5 g per 100 g of solid resin.

The MUF adhesive modification with nanocellulose caused a decrease in the amount of emitting formaldehyde.

The addition of nanocellulose allowed the reduction in adhesive consumption by 30 %.

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# First and Second Phase of Human Centered Design Method in Design of Exterior Seating Furniture

## Prve dvije faze dizajniranja vanjskog namještaja primjenom metode dizajna usmjerene prema korisniku

**ABSTRACT** • *The article describes a part of the designing process of exterior furniture that utilizes HPL (high pressure laminate) with the reduced use of construction metal elements, using user-centered design methods. The process is divided into several phases. This article primarily uses human-centered design and describes the process of researching user attitudes and market research, as important methods in the overall design process. The observed results are crucial especially when introducing new products based on products already existing on the market. The contemporary market is filled up with a surplus of products that are not so customer-oriented, and customers are often lost in their choice. Currently, there is a tendency on the market to personalize each product to the customer, so this becomes one of the main designer's methods in designing a product. The designer can personalize a product based on the user and market research. New products can be different in the approach to customer's needs and attitudes in cases that the designing process follows the current needs. Also, it is important to present it properly to the public. It is necessary to create a representative customer, who can represent the potential group. This young woman has specific characteristics that can be used in the rest of the designing process – her relationship with nature and sitting outdoors, her relationship with furniture and her ability to purchase a new product.*

*Keywords:* exterior furniture; human centered design; wood; user research; market research; furniture design

**SAŽETAK** • *U članku se opisuje dio postupka projektiranja vanjskog namještaja za koji se iskorištava HPL (visokotlačni laminat), uz smanjenu upotrebu metalnih građevnih elemenata i uz primjenu metode dizajna usmjerene prema korisniku. Proces je podijeljen na nekoliko faza. U ovom je radu težište na dizajnu podređenom čovjeku, pri čemu se opisuje i postupak istraživanja stajališta korisnika i istraživanje tržišta kao važne metode u cjelokupnom procesu dizajniranja. Uočeni su rezultati presudni za uvođenje novih proizvoda utemeljenih na već postojećim proizvodima na tržištu. Suvremeno je tržište preplavljeno proizvodima koji nisu osobito orijentirani prema kupcu, a kupci se pri izboru često gube u tom mnoštvu ponude. Trenutačno je na tržištu zamjetna težnja da se svaki proizvod prilagodi kupcu, pa to postaje jedno od glavnih dizajnerskih polazišta pri dizajniranju proizvoda. Zahvaljujući istraživanju tržišta i zahtjeva korisnika, dizajner može prilagoditi proizvod svakom pojedinom kupcu. Također, sve je više dokaza da se konkurentnost nekih tvrtki temelji na inovativnoj upotrebi dizajna usmjerenoga*

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*prema korisniku. Ako postupak dizajniranja prati trenutačne potrebe i ako se pravilno prezentira u javnosti, novi se proizvodi mogu razlikovati po pristupu potrebama i stajalištima svakog kupca.*

***Ključne riječi:*** *vanjski namještaj; dizajn usmjeren prema čovjeku; drvo; istraživanje zahtjeva korisnika; istraživanje tržišta; dizajn namještaja*

# 1 INTRODUCTION
## 1. UVOD

From the outside perspectives, it is often difficult to fully understand how exterior (or site) design integrates the elements of furniture that are used for various design purposes and create a sense of place. Such an understanding can open up creative possibilities for designers of outdoor areas and enable them to shape spaces that can succeed in achieving their aims over the long term (Yücel, 2013). Also, there is growing evidence that the competitiveness of some companies is based on an innovative use of user-oriented design (Montresor and Vezzani, 2019).

Today´s customers prefer to sit outside, in the parks, outdoor public spaces or in the gardens and on terraces. These habits are the main reasons for using special materials and special types of technologies together with new design methods during the product production.

While designing, it is necessary to investigate all aspects that influence the acceptance of new product innovations (Mulder-Nijkamp, 2020). It is also always important to do research in the public, because the people are the ones who are going to use the final product and it should always serve its user (Parsons, 2009).

Previous results show that the most common material for exterior furniture is wood in combination with a metal supportive structure (Vuković, 2018). Using solid wood helps the design of exterior furniture to develop in more imaginative and user-friendly ways, but it brings further technical problems in joining two different materials (Fictum *et al*., 2018). The goal of this study is to make the first two parts of the human centered design process of a bench according to the Czech Technical Standards (WEB 1). These parts are made by using High Pressure Laminate (HPL) in combination with solid wood, while reducing the use of metal fasteners. This article focuses on user-centered design methodology, which uses user and market research as the main design methods that lead to creating the imagined user – the "Persona". The research was carried out in 2017 with the aim of designing a new product for today's customer. The obtained data from the user research was implemented into the designing process. The user research was made by HCD (Human Centered Design) principles in the first part – Empathy. This phase of research is often a neglected part of design, but it is an important source of information for each designer.

HPL and solid wood were chosen as the main materials mostly due to their good properties for their intended use. In addition, the Ready-to-Assemble (RTA) furniture principles were used in the project. This approach makes transport of the furniture easier and more efficient, reduces the price of logistics and overall saves money to our potential customer. Also, it was decided that the exterior seating furniture would be designed for a private owner and not as seating for open urban spaces.

## 1.1 Human centered design
### 1.1. Dizajn usmjeren prema čovjeku

In the recent years, entrepreneurship has become a popular topic and has attracted many young people to start their own companies. In entrepreneurship, design is generally viewed as essential to innovation, replacing the conventional role of the engineer (Xihui and Rieple, 2019), and Human-Centered Design (HCD) is one of the unavoidable design methodologies.

Human-Centered Design, (in the market research phases called User-Centered Design) is a set of principles used during formation of a product, its related services and surrounding environment that also includes the organization and the interactions between the product and its intended user. The reason for its name is that the whole process starts and ends with people. These techniques are based on the behavior and needs of a person (Norman, 2010), because the idea of sustained development cannot be effectively implemented without including social needs and people-oriented designing (Rzeszotarska-Palka and Czalczynska-Podolska, 2019). Users attempt to meet their unfulfilled needs by designing and developing new products and processes (in open design platforms and due to the digital fabrication technologies like 3D printing) and thus provide new concepts and design ideas (Naik *et al.*, 2020).

In this project, some techniques of HCD were used. Its first step is the necessity to respect the opinions and attitudes of the people. Thus, the whole research is conditioned by empathy toward the customer (Weinschenk, 2012). The next step is to create. This crucial part is the most well-known phase during the designer's work. This phase is not just about sketching or modeling; the team creates charts, a two-axis matrix and diagrams. After creating, the product has to be realized. Product designer uses models, prototypes, scale models, virtual models or part-models (Fernandes *et al*., 2017). In this part, it is necessary to create a timeline. In the end, it is important to let users evaluate the resulting product. This evaluative research serves as a feedback and helps to address issues of the product design (Creative Commons, 2013).

# 2 MATERIALS AND METHODS
## 2. MATERIJALI I METODE

## 2.1 Design process
### 2.1. Proces dizajna

Designers´ practices have been constantly evolving in the last two centuries. During the last decades new technologies, processes and approaches have in-

fluenced them (Menichinelli *et al.,* 2020). That is the reason why there are many processes of design in the world now. Nevertheless, the HCD is considered as the most useful in today's society (as part of the Design Thinking Theory). Design Thinking leverages the body of design theory literature and adapts it to interpret how design-driven innovation can happen in the context of business (Verganti *et al.,* 2020). Its principles were created by Creative Commons (2013) and published by IDEO organization, IDE organization, Heifer International and ICRW organization: "Design focused on human". The process is divided into three steps: *Listening*, *Creation*, and *Realization*. These steps are very comprehensive. This process was modified into five-step process as a result of the needs of modern design: Empathy, Define, Ideation, Prototyping, Testing.

Design Thinking (also HCD) supports the mindset of co-creation pedagogy as both their key characteristics and methods arise from equal, multidisciplinary co-creation and person-centered approaches (Jussila *et al.*, 2020).

### 2.2 User research
2.2. Istraživanje mišljenja korisnika

The research of user's opinion, attitudes and needs can fall either into the first or second step: Empathy and Define. The empathy is necessary during the design process because, if someone wants to design a new product, it is not sufficient to create just a "good product". A designer has to know his/her possible client, or at least to imagine his/her profile. The client determines the success rate of a new product in a market and the designer needs to know the users (Weinschenk, 2012).

Quantitative exploratory metrics were used to collect the necessary data. Due to the envisaged product, it was necessary to obtain larger and reliable data. For this purpose, individual e-questionnaires were used. The assumed hypothesis of this executed research was that people actively use their exterior furniture (whether in their private or in public spaces) and that they prefer the materials chosen for the new product. After the research was done, the resulting data were evaluated, and the "Persona" was created.

In the user research, a lot of data regarding our respondents were collected. Respondents were also potential users and buyers. After the data evaluation, a profile of the "Persona" was created, which facilitated the process of designing a new product for exterior use – namely the bench.

*Basic Survey Information*

There were 127 respondents for the study research. The respondents were randomly selected, so that the questionnaire results would remain unbiased and impartial. The user research was divided into six blocks:

1. Personal information
2. Questions about spending their time in exterior
3. Used outdoor furniture material
4. Customers own outdoor furniture
5. Purchase of a new exterior furniture
6. RTA principles

There were series of questions associated with each block. The questionnaire was developed by the team of authors and it was shared online through social networks, so the sample of people who can answer the questions or the answer rate could not be counted. In this part of the study, quantitative exploration type of investigation was used. In the questionnaire, the potential user was asked several types of questions - open answers, single choice answers and multiple-choice answer. A basic statistical method was used for analyzing the results obtained. Arithmetic mean and user sets were used. Nominal and ordinal values were monitored, as well as rations. All data were processed in Microsoft Excel.

Due to the type of sharing the questionnaire, people at the age of 65+ were not in the focus group. Seniors have needs other than the focus group and that is why they need other specific properties of furniture.

### 2.3 Market research
2.3. Istraživanje tržišta

Five companies were chosen as the example of the selected type of furniture in 2018 (before the designing started). The main indicators of the chosen type of furniture were: use of RTA principles, materials and technology of exterior furniture. The team of authors described here primarily worked with online data resources of companies from Europe and USA.

## 3 RESULTS
3. REZULTATI

### 3.1 User research results (Empathy)
3.1. Rezultati istraživanja korisnika (empatija)

Block 1: Personal information

This section of user research serves to create a Persona and to segment customers into different categories – market segregation.

The group of respondents contained 68 % of women and 32 % of men. Age diffusion is shown in Figure 1.

The research revealed that the respondents had predominantly secondary education and their average gross monthly wage was up to CZK 15,000 (about 642 Euros).

The question regarding the transport showed that the connection between the time spent outside (to possibly use exterior furniture) and the type of transport was verified. It was discovered that people who use public transport and bicycles have more opportunities to spend their time outdoor and therefore use outdoor furniture more frequently. More than half of our respondents (55.2 %) mainly used public transport, 28.8 % used a car and 14.4 % most often just walked. The bicycle as a mean of transport was used by only 1.6 % of respondents.

The last question divided the respondents according to their interests. More than 60 % of respondents said that their main interests included watching movies, hiking and traveling.
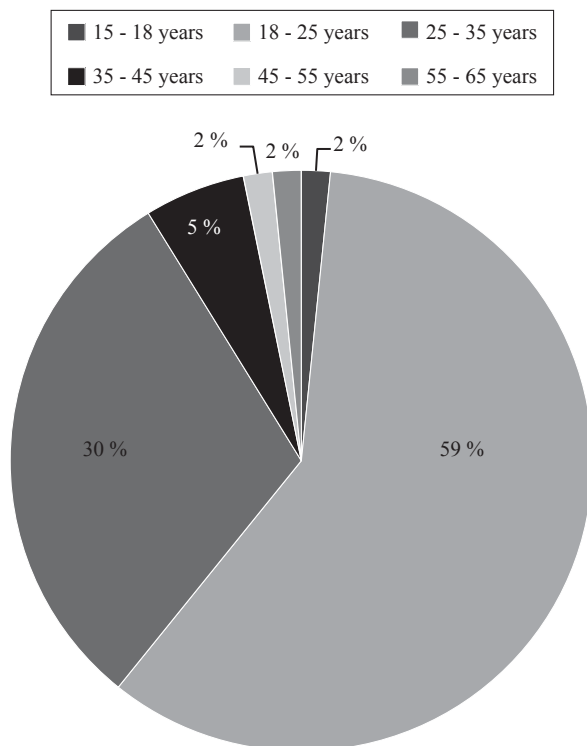
**Figure 1** Age of respondents
**Slika 1.** Dob ispitanika

Block 2: Questions about spending time in exterior

Most respondents (85.6 %) spent their time outdoors mostly hiking and walking. The second favorite places of interests are outdoor restaurants and bars with 55.2 %. The last significant group of 48.8 % is made of respondents who do outdoor sport.

Respondents mostly use their own exterior furniture (41 %). 38 % of respondents mostly use the exterior furniture in bars and restaurants.

Block 3: Used outdoor furniture

The goal of this section was to find out whether the used material made impact on the overall popularity of the product, namely if the users were more enticed to sit on the furniture and use it. Also, the section describes defects or deficiencies that the users have noticed with this furniture. According to the research results, it is clear that the used material is an important factor – 59 % of respondents said that this factor was meaningful. It is justified by hygiene and comfort – in the winter. The user does not want to use metal furniture or furniture that can spoil the user clothes.

The most common defects found by respondents were table instability and the inconvenience of single-seat sitting. See Figure 2 for more details.

The preferred furniture appearance was the natural appearance (the exposed material) as indicated in 56.5 % of user's responses. In 41.9 % of responses, neutral colors were preferred. Only in 1.6 % of cases respondents preferred an over dimensioned look. As for the preferences according to the material, the most popular material used was solid wood (73 % of responses). The second place was taken by a combination of wood and metal materials (65.3 % of responses).

Block 4: User's own exterior furniture

Only 66.4 % of respondents had their own exterior furniture. This question block was only filled by 65.3 % of respondents due to this limitation.

According to Figure 3, it was found out that the majority of respondents owned a complete outdoor set (table and several chairs) or only a chair or a bench.

According to the research carried out, the exterior furniture was placed mainly in the garden, 51 % of respondents. 43 % of respondents said that their furniture was placed on their terrace or balcony.
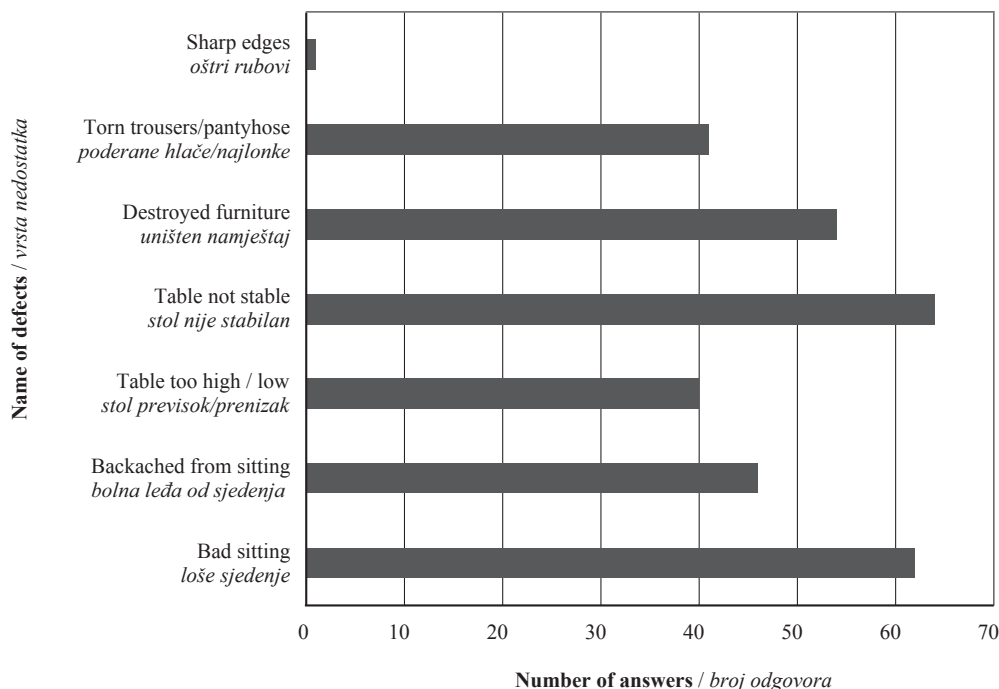


**Figure 2** Most common defects of exterior furniture
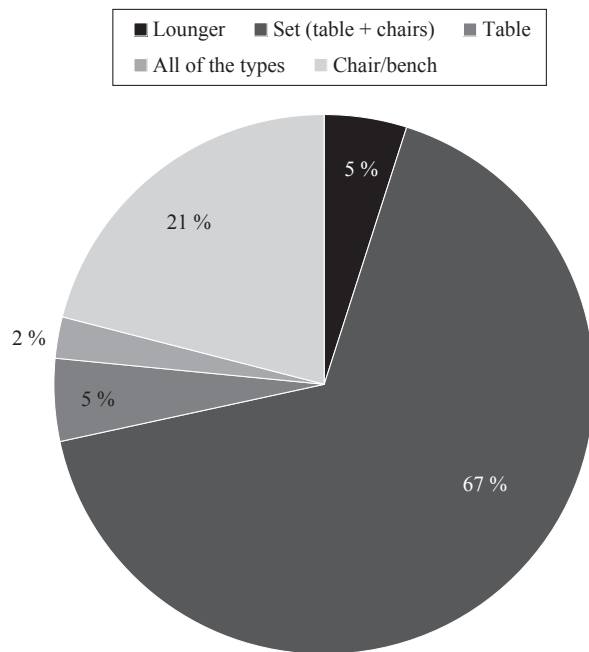**Slika 2.** Najčešći nedostatci namještaja

**Figure 3** User´s own exterior furniture
**Slika 3.** Korisnikov postojeći vanjski namještaj

All 84.3 % respondents were satisfied with their own furniture. The most common reason for user´s dissatisfaction was the furniture age.

Block 5: Purchase of new design furniture

The first question of this block was the most important feature of user´s new furniture products. The furniture functionality was selected as the most important feature (with 43.3 % of responses), see Figure 4.
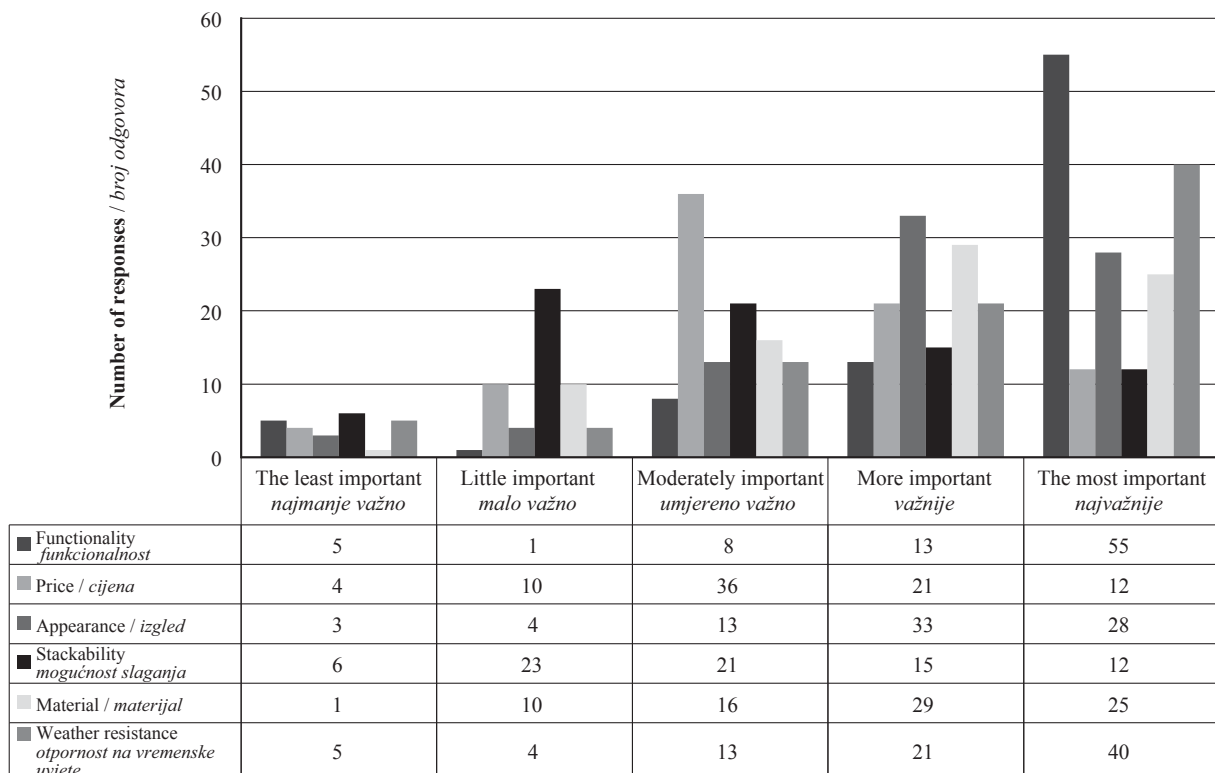
Answers to the question of how much money users are willing to pay for a new chair were scattered. One third of answers fell into a category of 500 – 1, 000 CZK (22 – 46 Euros) per chair, which is the largest part of the answers.

The most popular choice was a hobby market, in 28.7 % of responses. According to the respondents, the second place was taken by IKEA. Our respondents buy furniture roughly once in five years.

Block 6: RTA Principles

According to the research results, 76.8 % of respondents preferred to buy demountable furniture, where customers assemble the furniture by themselves. At the same time, 94.4 % of respondents did not find assembly of the furniture complicated. Assembly instructions were found to be understandable enough by ¾ of respondents. Unfortunately, more than half of respondents did not care about this type of furniture and did not tighten joints, even if this was stated in the assembly instructions.

**3.2 The Persona (Define)**
3.2. Osoba (definiranje)

This part of the process is an integral part of the design process. Persona shows the average user/customer and helps the final design. A designer always tries to help with the design for a specific person. The created Persona is based on the first part of this study: the user research. In order to create an imaginary person´s profile, it is necessary to think of some missing information – this information cannot be obtained from our respondents: especially the name.



| | The least important *najmanje važno* | Little important *malo važno* | Moderately important *umjereno važno* | More important *važnije* | The most important *najvažnije* |
|---|---|---|---|---|---|
| Functionality *funkcionalnost* | 5 | 1 | 8 | 13 | 55 |
| Price / *cijena* | 4 | 10 | 36 | 21 | 12 |
| Appearance / *izgled* | 3 | 4 | 13 | 33 | 28 |
| Stackability *mogućnost slaganja* | 6 | 23 | 21 | 15 | 12 |
| Material / *materijal* | 1 | 10 | 16 | 29 | 25 |
| Weather resistance *otpornost na vremenske uvjete* | 5 | 4 | 13 | 21 | 40 |

**Figure 4** Features of new furniture according to its importance for users
**Slika 4.** Obilježja novog namještaja prema njihovoj važnosti za korisnike

Table 1 The Persona – Helena Valesova
**Tablica 1.** Osoba – Helena Valesova

| | Name / *Ime* | Helena Valesova |
|---|---|---|
|  | Age / *Dob* | 23 years / *23 godine* |
| | Education / *Obrazovanje* | Secondary school / *srednja škola* |
| | Interests / *Interesi* | Nature, hiking, music, films *priroda, planinarenje, glazba, film* |
| | Transport type / *Vrsta prijevoza* | Public / *javni* |
| | Earnings / *Dohodak* | Up to 15 000 CZK (642 EUR) |

Helena spends most of her time outdoors hiking and walking, or in outdoor bars and restaurants. Helena uses her own outdoor furniture or furniture in restaurants. The material used for furniture influences Helena. She prefers wooden furniture or a combination of wood and metal. Helena's biggest problem during her use of exterior furniture was her back aching while sitting on the furniture and instability of her table.

Helena has her own exterior furniture, namely she owns a set of chairs and a table. She is satisfied with her furniture and she placed it in her garden.

When Helena is buying her new exterior furniture, the most important features are furniture functionality and its weather resistance. She will probably buy these new products in a hobby market or similar stores and she is willing to spend in the range of 500-1500 CZK per one chair. Helena buys new furniture once in 5 years.

Helena likes to assemble her new furniture and its assembly is not a complication for her. At the same time, installation instructions do not seem to be complicated or confusing either. Regrettably, she does not tighten up the furniture joints on a regular basis.

For clarity, a summary in Table 2 is provided.

### 3.3 Market research results
3.3. Rezultati istraživanja tržišta

Products in the market research were selected based on the data obtained in the user research. Each example corresponds to at least one of the requirements by the Persona.

Request: RTA principle

A sample product used for sitting was manufactured by Semigoods Company (WEB 2). Designers used High Pressure Laminate as a construction material on all sides of the chair and they added solid wood as a natural and interesting element of the product. They found that the properties of solid wood and HPL were very good - strong and durable. However, solid wood was more suitable for the contact with the human body due to better thermal insulation.

This company used metal elements to join all parts of the product, but this product was chosen due to the design. It complied with the RTA principles, but it

Table 2 Summary table
**Tablica 2.** Zbirna tablica

| Characteristic of Helena / *Helenine karakteristike* | Her relationship with outside furniture / *Njezin odnos prema vanjskom namještaju* | - the used material influences Helena – she prefers wood and metal / *Heleni je važan materijal od kojega je namještaj izrađen – ona više voli drvo i metal*<br>- she used outside furniture from bars or restaurants and her own / *Helena se koristila vanjskim namještajem u barovima ili restoranima i vlastitim*<br>- the biggest problem during using for her is uncomfortable sitting / *najveći problem tijekom uporabe za Helenu je neudobno sjedenje* |
|---|---|---|
| Her own furniture / *Helenin vlastiti namještaj* | In the garden / *Vrtni namještaj* | Set of chairs and table / *garnitura stolica i stolova* |
| Buying new outside furniture / *Kupnja novoga vanjskog namještaja* | The most important factors / *Najvažnija obilježja* | - weather resistance / *otpornost na vodu*<br>- functionality / *funkcionalnost* |
| | Where will she buy? / *Gdje će ga kupiti?* | Hobby (or similar) stores / *Hobi ili slične trgovine* |
| | How much will she spend? / *Koliko će novca potrošiti?* | 500 – 1500 CZK (147 – 440 HRK) |
| RTA principle / *RTA načelo* | Does she like it? / *Sviđa li joj se?* | Yes, instructions are not complicated / *da, upute nisu složene* |
| | Does she care about joins? / *Je li joj važan način sastavljanja?* | No / *ne* |

**Figure 5** One of the chosen products due to RTA principles used, design by Semigoods Company (WEB 2)
**Slika 5.** Jedan od proizvoda odabranih zbog primijenjenog RTA načela; dizajn Semigoods (WEB 2)



**Figure 7** Bench Arki-Bench by Pedrali, chosen due to used HPL material (WEB 4)
**Slika 7.** Klupa Arki-Bench tvrtke Pedrali izabrana zbog upotrijebljenog HPL materijala (WEB 4)

did not meet the requirements of the persona due to its price – the bench cost was 1500 Euros.

Request: Functionality, stackability, comfortable sitting, weather resistance

Chairs Bohem are a collection made by mmCité Company (WEB 3), designed by Aleš Kachlík. The designer created retro style sitting with the aim of providing comfortable sitting. The chair is made of galvanized power-coated steel structure. The seats and backrests are made of sheet aluminium or plywood. The chair is available in two heights. All of the products from this collection are fully stackable.

The next example is bench Arki-Bench. This product was made by Pedrali Company. It was chosen due to the material used – the seating part is made of HPL, the rest of the product is made of massive wood.

## 4 DISCUSSION CONCLUSIONS
## 4. RASPRAVA I ZAKLJUČAK

The HCD principles have brought the necessary information for the design process. The information gained from users was necessary to determine the final



**Figure 6** Collection Bohem by mmCité, chosen due to functionality, comfortable sitting and stackability (WEB 3)
**Slika 6.** Kolekcija Bohem tvrtke mmCité odabrana zbog funkcionalnosti, udobnog sjedenja i lakoće sastavljanja (WEB 3)

design for the new products – outdoor bench made of HPL. Everything discovered during the user and market research was incorporated during the whole design process. The number of respondents was sufficient in order to get a complete picture of the situation. With this type of questions, the designer would better understand the specific requirements and preferences of potential users.

During the market research, it was found out that some products with a few of the used principles (e.g. RTA) already exist; however, a product combining all of the principles used within this project was not recognized.

The results of the user research showed that today´s customer wants to buy a new functional and weather resistant exterior furniture in a hobby market or similar store. The customer will spend about 22 – 40 Euros per one chair and he/she will buy a new product every five years. If the assembling is not complicated, the customer prefers to assemble his/her new furniture. According to the user research, it would be better to design products where it is not necessary to tighten up the furniture joints on a regular basis, because most of respondents said that they do not do it regularly.

The market research showed that there are many different uses of HPL, RTA principles or minimization of metal elements in furniture, but the used combination of the above materials was not found. The biggest challenge of the designing process will be to meet all the requirements while respecting the price range. No matching products were found at the requested price. The price was determined on the basis of the user research so it depends on the chosen group.

The new product will be a bench or sitting chair made of a combination of materials in natural colors – no specific colorful surfaces. For the user, the price and functionality of the product is very important, and the biggest problem while sitting on the chairs is users' backache.

All the data will be used in the designing process of a new product for exterior use – innovative design bench oriented to the user.

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# Investigation of the Effect of Using Activated Sludge Treated with Acetic Acid on Physical and Strength Properties of Recycled Pulp

## Istraživanje utjecaja uporabe aktivnog mulja tretiranog octenom kiselinom na fizička svojstva i čvrstoću reciklirane celuloze

**ABSTRACT** • *This study aimed to scrutinize chemical treatment of Mazandaran Wood and Paper mill activated sludge with 3 % acetic acid for the manufacture of environmentally eco-friendly bio composite. In this study, the paper pulp required was obtained from the waste newsprint paper. The activated sludge was treated in a beaker for 3 min in 3 % acetic acid and then in a water bath at 75 and 100 °C for 45 and 90 min. After that, the treated activated sludge was mixed and refined with waste newsprint paper pulp at ratios of 0, 5, 10, 15 and 20 %. The test specimens were prepared according to TAPPI standard and the physical properties (water absorption and porosity) and mechanical (tensile strength, tear strength, ring crush test, burst strength and folding strength) were measured. The results showed that the activated sludge treatment caused the increase in tear strength, ring crush test, burst strength and porosity as well as the decrease in water absorption, tensile strength and folding strength. FT-IR spectrum of the treated samples showed that the treatment with acetic acid strengthened and activated the functional groups on the surface of activated sludge fibers. The activated sludge added at a level of 5 % at 100 °C for 90 min as well as at a level of 20 % at 75 °C for 45 min was more suitable than other treatments.*

*Keywords:* activated sludge; acetic acid; newsprint paper; eco-friendly bio composite; resistance features

**SAŽETAK** • *Cilj ovog rada bio je proučiti kemijsku obradu aktivnog mulja proizvedenog u tvornici drva i papira Mazandaran izvedenu 3 %-tnom octenom kiselinom za proizvodnju ekološki prihvatljivog biokompozita. Celulozna kaša potrebna za istraživanje dobivena je od otpadnoga novinskog papira. Aktivni mulj obrađen je 3 %-tnom octenom kiselinom u čaši, i to u trajanju 3 minute, a zatim u vodenoj kupelji temperature 75 i 100 °C u trajanju od 45 i 90 min. Nakon toga taj je aktivni mulj pomiješan i rafiniran s celuloznom kašom od otpadnoga novinskog papira u omjerima od 0, 5, 10, 15 i 20 %. Ispitni su uzorci pripremljeni prema TAPPI normi, nakon čega su izmjerena njihova fizička svojstva (upijanje vode i poroznost) te mehanička svojstva (vlačna čvrstoća, čvrstoća na kidanje, tlačna čvrstoća prstena, čvrstoća na pucanje i preklopna čvrstoća). Rezultati su pokazali da je kemijska obrada aktivnog mulja pridonijela povećanju čvrstoće uzoraka na kidanje, otpornosti na tlačnu silu, čvrstoći na pucanje i poroznost te smanjenju upijanja vode, kao i vlačne i preklopne čvrstoće. FT-IR spektri tretiranih uzoraka poka-*

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zali su da obrada octenom kiselinom ojačava i aktivira funkcionalne skupine na površini vlakana aktivnog mulja. Aktivni mulj dodan u omjeru od 5 % pri 100 °C i u trajanju 90 minuta te u omjeru od 20 % pri 75 °C i tijekom 45 minuta bio je prikladniji od ostalih uzoraka.

***Ključne riječi:*** *aktivni mulj; octena kiselina; novinski papir; ekološki prihvatljiv biokompozit; otpornost*

# 1 INTRODUCTION
1. UVOD

Today, population growth and rising standards, paper consumption and production, as well as production of other industrial and agricultural products have risen and as a result, the amount and variety of solid waste produced has increased. Therefore, environmental pollution from agricultural and industrial waste is a global concern and safe management of hazardous waste will be one of the greatest challenges facing humanity. Therefore, finding a suitable social, technical, economic and environmental solution to have a greener and cleaner environment is a global concern. Several countries are trying to solve this problem by recycling waste (Lertsutthiwong *et al*., 2008; Pappu *et al*., 2007). Mazandaran Wood and Paper Industries Complex annually produce 75000 tons, 52000 tons, 38000 tons of fluting paper, newsprint and printing and writing paper, respectively. In addition, solid waste, paper mill sludge, waste from the pulp and paper process or paper recycling due to the large amounts produced leads to a lot of pressure on the environment at the paper mills. Some paper mills burn sludge to decrease the produced sludge volume, although the space required for this operation is rare and expensive. The paper mill sludge also contains 45-55 % moisture and 20 % solids, which causes problems for transport. The landfill of paper mill waste, in addition to not being economical, causes environmental issues and groundwater pollution. On the other hand, a large area of land is required for the landfill of fibers (Horace *et al*., 1999; Smook, 1995). On average, sludge production (organic and inorganic) in the wood and paper mill of Mazandaran is 1700 tons per month. In addition, sludge dry percentage is about 25 % (along with the moisture), so the dry sludge produced per month and day are about 425 and 4 tons, respectively. Semi-dry activated sludge contains organic and inorganic substances such as sodium, sulfur, extractives, fats, waxes, sterols, and fiber fines, and calcium carbonate (due to filler) along with the tree bark. Moreover, active sludge contains hazardous chemical compounds that can decrease the amount of harmful chemical compounds by chemical treatment (Son *et al*., 2001)

Ghasht Roodkhani *et al*. (2010) reported that the values of tensile, tear, burs, folding strength, and density of the mixed papers compared to the control sample decreased, while the values of bulk, thickness, brightness, and opacity increased. Nazeri *et al*. (2008) showed that the increase in CMP (Chemical Mechanical Pulp) fine amount leads to increase the air resistance and opacity and also decrease roughness, so variations in CMP fines have no effect on brightness. Tudarvari *et al*. (2016) examined the effect of fiber

length variations of different OCC (Old Corrugated Container) pulp-recycled papers on strength properties. The results showed that OCC pulp produced from different paper sources have different fiber length distribution that has a significant impact on the fluting paper strength properties. The OCC pulp with higher amounts of long fiber and lower amounts of fines has good strength properties (tensile strength, burst strength, and tear strength) for producing fluting paper. Girones *et al*. (2010) stated that increasing the amount of sludge in composites will result in a composite with lower tensile strength. Therefore, in composites that are exposed to tensile force, the paper mill sludge acts as a filler, and when the material is subjected to bending force, the sludge acts somewhat like a reinforcement. Ismail and Bakar (2004) reported that increasing the amount of paper sludge in composites increases water absorption and decreases tensile strength. Ismail and Bakar (2005) reported that the ester treatment and acetylation of the sludge of the paper mill in the manufacture of composites improves the tensile strength and Young's modulus and also reduces water absorption.

The aim of this research is to use activated sludge as an additive with different ratios and also to use modified activated sludge with acetic acid to improve the physical-mechanical properties of paper produced from recycled fibers and activated sludge.

# 2 MATERIALS AND METHODS
2. MATERIJALI I METODE

## 2.1 Sample preparation
2.1. Priprema uzoraka

In this study, 10 kg of waste newspaper with dimensions of 5 cm × 5 cm was prepared by hand. The newspaper pieces were kept in water for 24 hours and then converted into a pulp in a disintegrator (British Pulp Evaluation Apparatus manufactured by Mavis Engineering Ltd.London N.1. England) at 300 rpm for 30 min. In addition, the waste dry sludge was prepared from Mazandaran wood and paper mill located in the Sari's Pahne Kola and transferred to the laboratory, and then about 2 kg was soaked in water for 24 hours. After that, both materials were mixed by the disintegrator at around 300 rpm. Then, the newspaper paste was dewatered with 40-mesh and sludge with 200-mesh. The waste newspaper paste and activated sludge were calculated and mixed in the amount required for the experiment (handsheet) according to Table 1. The waste newsprint pulp and activated sludge were refined using a refinery PFI (No. 221; Beating Performance Adjusted by the Norwegian Pulp and Paper Research Institute, Trondheim, Norway) at 300 rpm. Then, the water was added to the mixture obtained up to a volume of 10 liters. Furthermore, about 300 cc of the obtained solu-

**Table 1** Percentage of activated sludge and waste newsprint pulp
**Tablica 1.** Postotni udio aktivnog mulja i celulozne kaše od otpadnoga novinskog papira

| Test samples *Ispitni uzorci* | Activated sludge, % (Treated** and untreated) *Aktivni mulj, % (tretirani** i netretirani)* | Waste newspaper pulp *Celulozna kaša od otpadnoga novinskog papira* |
|---|---|---|
| Control / *Kontrolni uzorci* | 0 | 100 |
| 1 | 5 | 95 |
| 2 | 10 | 90 |
| 3 | 15 | 85 |
| 4 | 20 | 80 |

**Treated in a bain-marie (warm water bath) at different temperatures and times (75, 100 °C and 45, 90 min) / *tretiran metodom bain-marie (kupelj s toplom vodom) pri različitim temperaturama i uz različita vremena trajanja (75 i 100 °C te 45, 90 minuta)*

tion was removed/isolated for weight control. Then, the test samples of the waste newsprint pulp with 100, 95, 90, 85 and 80 % ratios and untreated activated sludge in 5 levels (0, 5, 10, 15, 20 %) according to the TAPPI T205 sp-12 (2015) with a basis weight of 120 g/$m^2$ were prepared. The thickness of the handmade specimens was measured using a thickness gauge (E.J.CADY & CO. CHICAGO, USA) to the nearest 0.001 millimeter.

**2.2 Chemical treatment of activated sludge**
2.2. Kemijska obrada aktivnog mulja

To improve the mixing conditions with newspaper, paste and activated sludge, sludge samples with the ratios listed in Table 1 were placed separately in beakers containing 3 % acetic acid for 30 min. Then, they were treated in a Bain Marie bath (45, 90 min and 75, 100 °C). Test specimens were prepared and pressed according to TAPPI T205 sp-12 (2015) standard with a base weight of 120 g/$m^2$ and then dried. Finally, the strength and water absorption properties of handsheets were measured.

**2.3 Mechanical and physical properties of handsheets**
2.3. Mehanička i fizička svojstva laboratorijskih listova papira

The properties of 210 handsheets were calculated. Tensile strength, burst resistance, tear strength, ring crush test (RCT), and water absorption indices were used in accordance with TAPPI T494 om-13 (2015),

TAPPI T403 om-10 (2015), and TAPPI T496 sp-(2015) standards, TAPPI T818 cm-07 (2015) and TAP-PI T441 om-13 (2015), respectively.

**2.4 Attenuated total reflection (ATR) spectroscopy**
2.4. Pojačana infracrvena spektroskopija (ATR)

ATR spectroscopy was used to determine the status of the active groups present in the handheld samples made from untreated and acetic acid-treated paper paste and sludge. For this purpose, the JASCO FTIR-4700 device made in Japan (Japan Spectroscopic CO., LTD. Hachioji city Tokio Japan) was used.

**2.5 Statistical analysis**
2.5. Statistička analiza

In this study, the effect of activated sludge on physical and strength properties of recycled pulp obtained by mixing activated sludge and newspaper waste-paper was statistically evaluated. Statistical analysis was performed using SPSS software (IBM Corporation, v.23, Armonk, NY, USA) in the form of one-way analysis of variance. Finally, the means were grouped using Duncan's test at a confidence level of 5 %.

**3 RESULTS AND DISCUSSION**
3. REZULTATI I RASPRAVA

The results of statistical analysis showed that there was a significant difference in the physical and mechanical properties of the handsheets from activated sludge treated with acetic acid (at different temperatures and times) and untreated at the 5 % level (Table 2).

**3.1 Comparison of FT-IR spectra of activated sludge samples**
3.1. Usporedba FT-IR spektara uzoraka aktivnog mulja

FT-IR spectra of control, untreated and acetic acid-treated sludge are presented in Figure 1. The parts of the spectra with the wavenumber between 2700 and 3700 $cm^{-1}$ and 2100 and 2500 $cm^{-1}$ are shown separately.

**3.2 Tear strength**
3.2. Čvrstoća na kidanje

The average thickness of the handsheets was about 300 μm (0.3 mm). The results of analysis of variance showed that there was a significant difference in the strength properties of the paper samples ($p < 0.05$). The results showed that by increasing activated sludge, the tear strength in the paper made decreased. Since the

**Table 2** One-way ANOVA properties of activated sludge treated with acetic acid
**Tablica 2.** Svojstva jednosmjerne analize varijance aktivnog mulja tretiranoga octenom kiselinom

| Characteristic variable *Karakteristična varijabla* | RCT | | Water absorption (Cobb 60) *Upijanje vode (Cobb 60)* | | Tear strength *Čvrstoća na kidanje* | | Tensile strength *Vlačna čvrstoća* | | Burst strength *Čvrstoća na pucanje* | | Folding strength *Preklopna čvrstoća* | | Porosity *Poroznost* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatments *Vrsta obrade* | *F* | Sig.* | *F* | Sig. | *F* | Sig. | *F* | Sig. | *F* | Sig. | *F* | Sig. | *F* | Sig. |
| | 18.151 | 0.0001 | 132.717 | 0.0001 | 16.092 | 0.0001 | 14.617 | 0.0001 | 8.746 | 0.0001 | 6.779 | 0.0001 | 35.228 | 0.0001 |

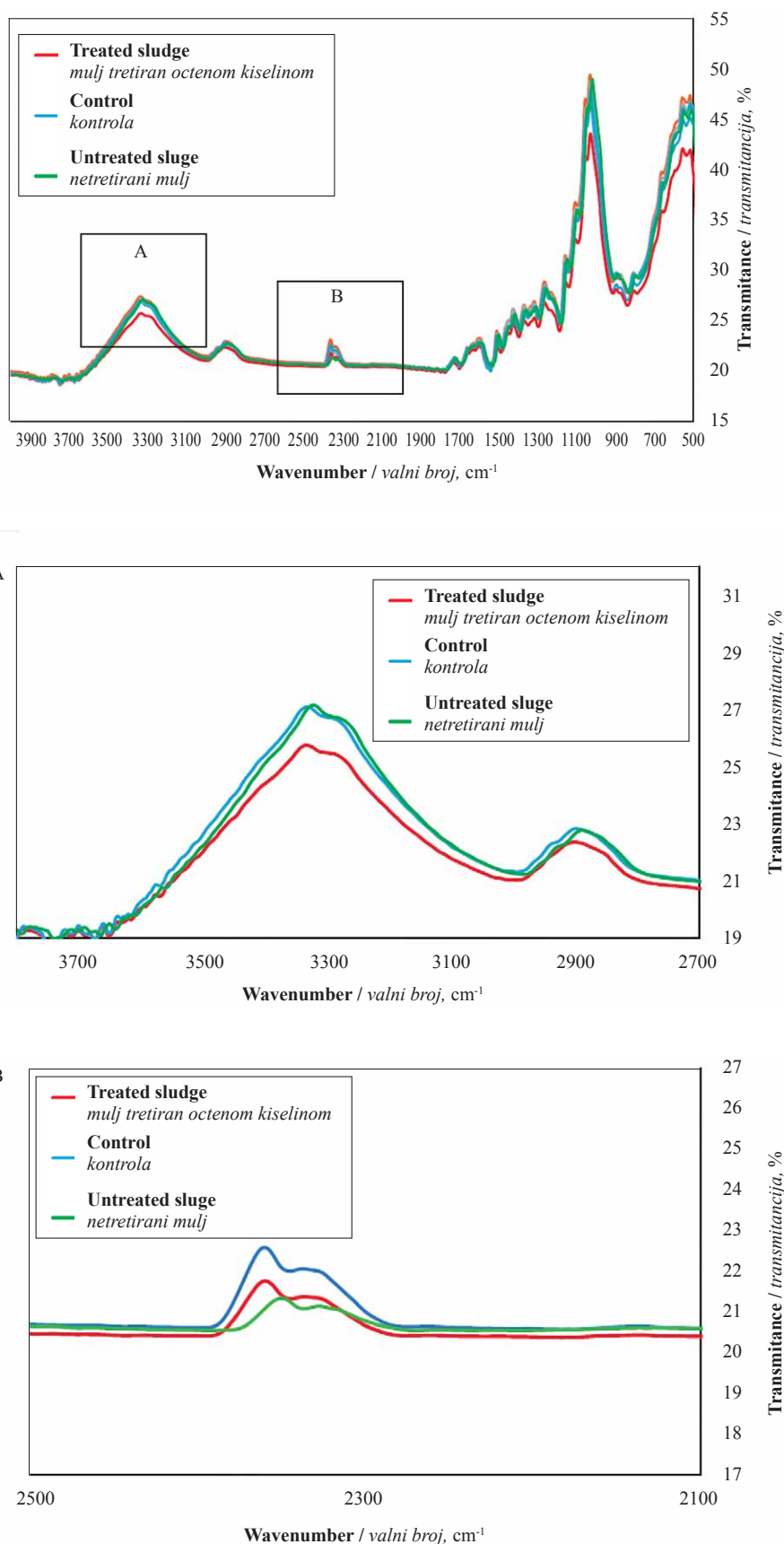* Sig. - significant / *značajno*

**Figure 1** FT-IR spectra of control, untreated and acetic acid-treated sludge
**Slika 1.** TGA FT-IR spektri kontrolnoga i netretiranog mulja te mulja tretiranoga octenom kiselinom
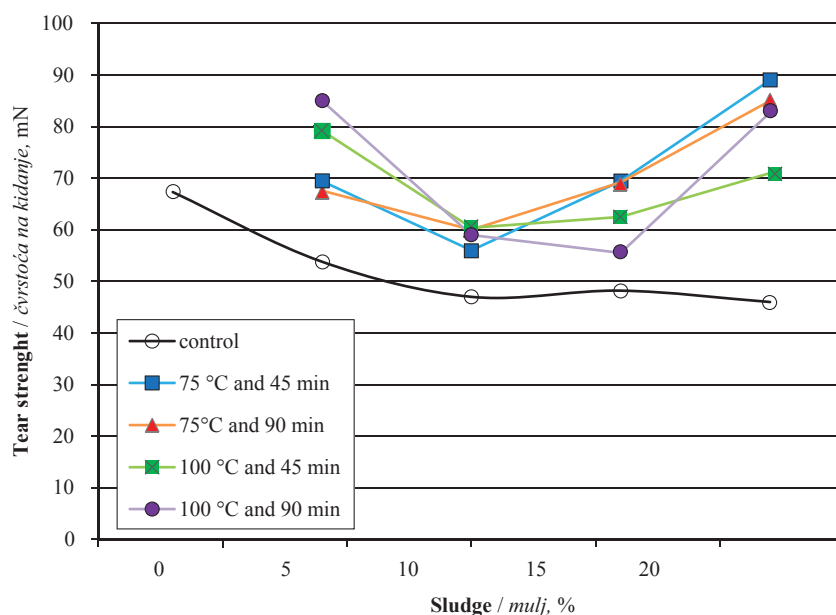
**Figure 2** Comparison of tear strength of samples made by adding activated sludge to waste newsprint paper
**Slika 2.** Usporedba čvrstoće na kidanje uzoraka napravljenih dodavanjem aktivnog mulja otpadnome novinskom papiru

fiber length, the linear density of fibers and fines in activated sludge are lower than in the waste newsprint paper components, the addition of untreated activated sludge to the samples decreased the tear strength. Comparing the spectrum of untreated activated sludge and control, the attenuation of the peak related to hydroxyl groups is visible, which indicates less resistance of paper made with untreated activated sludge. Significant changes after modification in different bands are attributed to different components, which include cellulose, hemicellulose, and lignin. The decrease in spectrum intensity at 3300 cm$^{-1}$ wavelength due to treatment can be attributed to hydroxyl (OH) groups (Sabazoodkhiz *et al.,* 2017). The hydroxyl tensile region is of particular importance for explaining hydrogen bonding patterns (Clausen *et al.,* 2010) (Figure 1). Bagherzadeh *et al*. (2013) stated that the decrease in strength is impaired by increasing the filler surface area, because the filler materials in the paper act as a separator, reducing the fiber connections and thus reducing the tear strength. (Bagherzadeh, 2013). Barzan *et al*. (2015) also reported that, compared to control treatment paper, handmade papers filled with extracted calcium carbonate reduced tear resistance by approximately 19 %.

The activated sludge treated with 3 % acetic acid significantly increased the tear strength. The acetic acid treatment can indicate the improvement of fiber surface and better paper formation, and provides a more suitable substrate for the physical and mechanical properties of paper. The most suitable treatment results, with the highest tear strength, were achieved with the samples treated with acetic acid at 75 ° C for 45 min. The results showed that by adding the treated activated-sludge (acetic acid) to the untreated samples with a ratio of 5 to 20 %, the tear strength initially de-

creased and then showed a significant increase of up to 20 %. Moreover, a mixing ratio of 5 and 20 % of the treated activated-sludge (with acetic acid) was always more tear resistant than the control sample. And also, by adding 5 % (at 100 °C for 90 min) and 20 % (at 75 °C for 45 min) of the treated activated sludge, the most suitable tear strength was observed. Additionally, the absorption peak intensity of 1791 cm$^{-1}$ in the treated samples was less than 1544 cm$^{-1}$, which indicates the presence of a reaction between acidic groups in acetic acid and hydroxyl groups in wood paste, which creates a high-intensity ester functional group. (Neeru *et al.,* 2013) (Figure 1).

### 3.3 Tensile strength
3.3. Vlačna čvrstoća

The results showed that the increasing activated sludge increased the tensile strength of the resulting paper. Due to the low fiber lengths and fines in activated sludge and also higher specific surface, the addition of untreated activated sludge to the specimens increased the specific surface and tensile strength of the test specimens. The tensile strength index of the samples can be seen in Figure 3. Tensile strength is one of the most important strengths of the paper that protects it against tensile stresses. Paper weight, fiber roughness, and fiber width are the factors affecting tensile strength. Tensile strength increases with increasing fiber length, increasing refining intensity and press pressure, and performing surface sizing on paper (Scott, 2007). The results showed that the tensile strength index increased by adding untreated activated sludge to the recycled fiber pulp. It appears that the reason of this increase can be attributed to the high specific surface area of the activated sludge (Nazeri *et al.,* 2008). Primary and secondary materials improve the
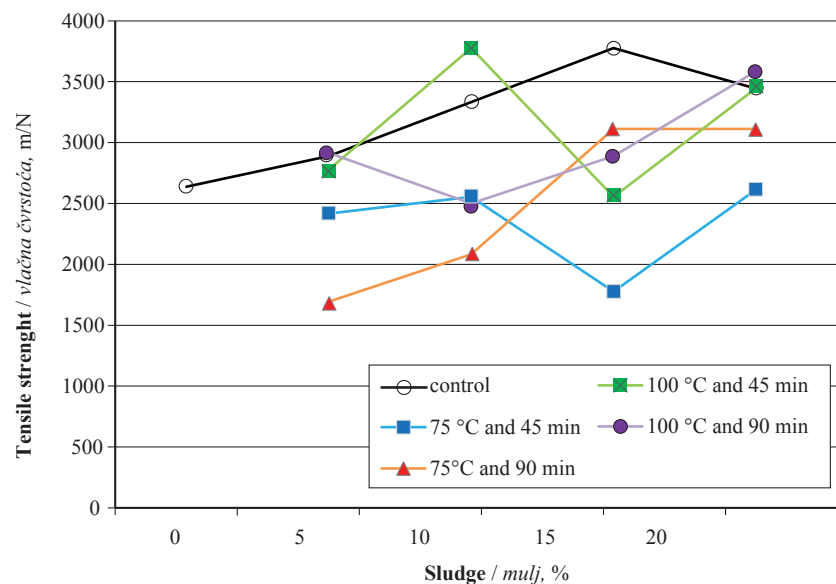
**Figure 3** Comparison of tensile strength of samples made by adding activated sludge to waste newsprint paper
**Slika 3.** Usporedba vlačne čvrstoće uzoraka napravljenih dodavanjem aktivnog mulja otpadnome novinskom papiru

strength properties of the paper (Krogerus *et al.*, 2002). Son *et al.* (2004) showed that the swelling and tensile properties of the composites improved slightly with the addition of paper sludge compared to the control samples (Son *et al.,* 2004). Additionally, activated sludge treated with 3 % acetic acid resulted in a slight decrease in the tensile strength of some of the treated samples. Among the treatments, the most appropriate treatment and the highest tensile strength were observed in samples treated with acetic acid at 100 °C for 45 min with a mixing ratio of 10 %, at 100 °C for 90 min with a mixing ratio of 20 %, at 75 °C for 90 min with a mixing ratio of 15 %, and 15 % in the control sample. In contrast, the results of other studies have shown that the treatment of esterification and acetylation improved the tensile strength and length change in the fracture zone as well as the Young's modulus in composites and reduced water absorption (Ismail and Bakar, 2005).

The removal of the corresponding peak in the adsorption region of 1248.34 cm⁻¹ in activated sludge can be due to the flexural vibrations of phenolic hydroxyl. Additionally, the removal of peaks in the adsorption zones of 1237.03 cm⁻¹ is closely related to the C=O, C=C, and C=O bonds of the carbonyl units, and the adsorption region of 1412.12 cm⁻¹ is related to aromatic C-H and C-H associated with type II alcohols; C=O is also treated in activated sludge and attenuates or removes carbonyl groups (Figure 1) (Mehmood *et al.,* 2019).

**3.4 Ring crush test (RCT)**
3.4. Otpornost na tlačnu silu

The results showed that, by increasing activated sludge, the ring crush of the resulting samples decreased. Since the lengths and fines of fibers in activated sludge are shorter than in waste newsprint paper components, the addition of untreated activated sludge to the specimens causes the short fibers and some components of fine sludge to be placed in the Z direction of the treated specimens, which will decrease the ring

crush. Activated-sludge treated with 3 % acetic acid decreased in some treatments and slightly increased in ring crush test. Among the treatments, the best treatment and the highest ring crush test in the acetic-acid treated samples were at 100 °C for 90 min (Figure 4). The results showed that the addition of 5 to 20 % activated-sludge treated with acetic acid to the untreated samples resulted in a significant increase in the ring crush. In addition, the mixing of 15 % and 20 % of activated sludge treated with acetic acid consistently showed the highest increase in ring crush than the control sample. The data analysis illustrated that there is a significant difference between the mean ring crush tests of treatments at the 1 % level.

**3.5 Burst strength**
3.5. Čvrstoća na pucanje

The results showed that, by increasing the activated sludge, the resistance to bursting of the made samples decreased. This can be due to the presence of more fillers between the fibers, such as calcium carbonate (polymorphism of calcite), and the small particle size of calcium carbonate fillers in untreated activated sludge, which reduces the level of bonds. In contrast, the addition of activated sludge and weakening of the bond between the fibers reduces the mechanical strength (Akbari *et al.,* 2017). Additionally, it seems that the short length of fibers in activated sludge and the use of recycled fibers can be another reason to reduce the mechanical properties (Miri *et al.,* 2016). Additionally, except in samples treated with 3 % acetic acid activated-sludge at 100 °C for 90 min, the resistance to bursting decreased slightly in other treatments (Figure 5). The results showed that by adding 5 to 20 % of acetic-acid treated activated-sludge to the untreated samples, the resistance to bursting of the samples increased markedly up to 20 %. The burst strength of the sample from the mixing of 15 to 20 % showed a significant increase as well. The best tensile strength in
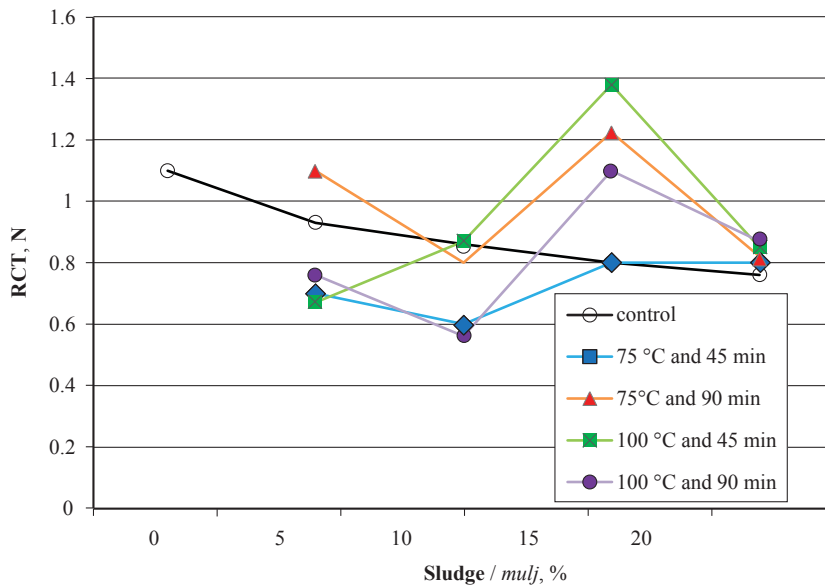
**Figure 4** Comparison of ring crush test of samples made by adding activated sludge to waste newsprint paper
**Slika 4.** Usporedba otpornosti na tlačnu silu uzoraka napravljenih dodavanjem aktivnog mulja otpadnome novinskom papiru

samples treated with acetic acid was at 100 °C for 90 and 45 min. Hemicellulose and lignin are affected by the treatments, which reduces the amount of hydroxyl groups and has a significant effect on lignin (Mehmood *et al.,* 2019). Aliphatic is seen in the absorption range of 3312 cm$^{-1}$ (Figure 1).

### 3.6 Water absorption (Cobb 60)
3.6. Upijanje vode (Cobb 60)

The results of analysis of variance showed that there was a significant difference in the physical prop-

erties (water absorption) of the made paper samples (p < 0.05). The results showed that, by increasing the activated sludge, the water absorption percentage of the samples made increased. Since the fines and specific surface of the activated sludge are higher than those of waste newsprint paper components, the addition of untreated activated-sludge to the samples increased the water absorption of the samples (Figure 6). Therefore, hydrophilic structures in activated sludge as well as moisture absorption by recycled newspaper fibers can be a reason to reduce the strength properties and in-
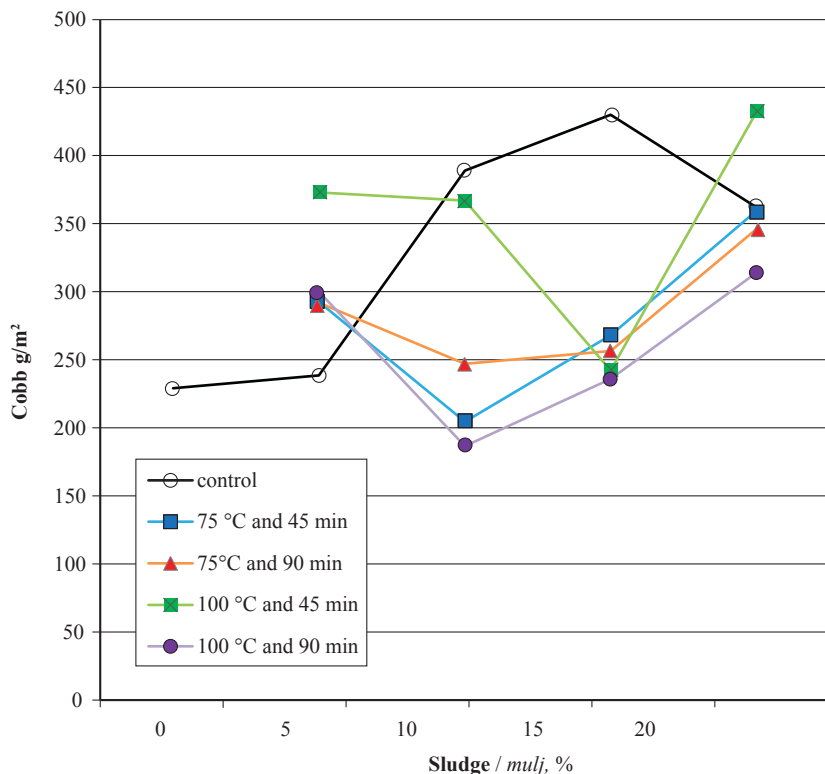


**Figure 5** Comparison of burst strength of samples made by adding activated sludge to waste newsprint paper
**Slika 5.** Usporedba čvrstoće na pucanje uzoraka napravljenih dodavanjem aktivnog mulja otpadnome novinskom papiru
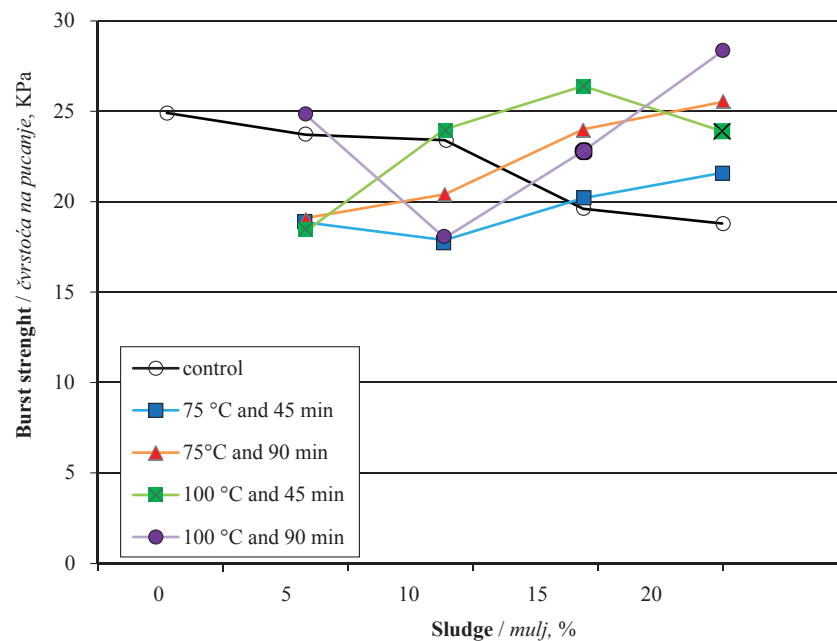
**Figure 6** Comparison of burst strength of samples made by adding activated sludge to waste newsprint paper
**Slika 6.** Usporedba čvrstoće na pucanje uzoraka napravljenih dodavanjem aktivnog mulja otpadnome novinskom papiru

crease water absorption. The chemical treatment of activated sludge with 3 % acetic acid showed a significant increase in water absorption of the samples. Moreover, among the treatments, the highest water absorption was observed in samples treated with acetic acid at 100 °C for 45 min. The results showed that, by adding 5 to 20 % of the activated sludge treated with acetic-acid to the untreated samples, the water absorption of the samples was firstly decreased and then significantly increased up to 20 %. The water absorption in the treated samples with mixing ratios was always lower than the control samples. The lowest and the best water absorption was observed in samples treated with acetic acid at 100 °C for 90 min. Additionally, the region of the 2300 cm$^{-1}$ peak belonged to the carbonyl groups, which indicates hemicellulose leaching (Pandey *et al.,* 2012) (Figure 1). Ismail and Bakar (2004) reported that increasing the amount of paper sludge in composites increased the Young's modulus and water absorption.

## 4 CONCLUSIONS
4. ZAKLJUČAK

The main purpose of this study was to improve the physical and mechanical properties of paper made from activated sludge and recycled fibers by acetic acid treatment.

The addition of the untreated activated-sludge of the paper mill to the waste newsprint paper decreased some mechanical resistances up to 20 % and increased tensile strength up to 27 %; it also increased the physical properties such as the water absorption up to 55 % and porosity of the specimens up to 4 %.

The addition of the activated-sludge treated with 3 % acetic acid to the waste newsprint paper increased the maximum mechanical strength up to 35 % and de-

creased the water absorption by up to 50 % and the tensile strength up to 20 %. In addition, a significant increase in tear strength and ring crush test, as well as a decrease in water absorption, are important features for the specimens made.

The best mixing ratio for the specimens made included activated-sludge treated with 3 % acetic acid in a mixing ratio of 5 and 20 % with the waste newspaper at 100 and 75 °C for 90 and 45 min, respectively, and especially 75 °C for 45 min.

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# Potencijal i uloga biomase u hrvatskoj i europskoj energetskoj tranziciji

## Potential and Role of Biomass in Croatian and European Energy Transition

**SAŽETAK** • *Republika Hrvatska kao punopravna članica Europske unije trenutačno sudjeluje u energetskoj tranziciji, odnosno u procesu dekarbonizacije gospodarstva transformacijom energetskog sektora u kojemu obnovljivi izvori energije zamjenjuju fosilna goriva. U tom procesu biomasa kao najsloženiji oblik obnovljive energije ima važnu ulogu s obzirom na brojne pozitivne okolišne i ekonomsko-socijalne aspekte uporabe. Sukladno ciljevima EU-a, Hrvatska je ostvarila potrebnih 20 % udjela proizvodnje iz obnovljivih izvora, no udio proizvodnje energije iz biomase još nije zadovoljavajući. Najiskorištavaniji izvor biomase jest kruta biomasa, posebice peleti, proizvođači kojih su izvozno orijentirani. Unatoč tome, Hrvatska još uvijek ovisi o uvozu biomase, kao i sve članice EU-a. Stoga je za unapređenje proizvodnje i potrošnje energije od biomase potrebna sinergija i zajedničko djelovanje svih sudionika energetskog sektora, a donositelji odluka odgovarajućim mjerama trebaju stvoriti preduvjete za razvoj tržišta biomase. U ovom se radu na temelju analize tržišta biomase te njezine uloge u nacionalnim i europskim energetskim politikama analizira trenutačni položaj i značenje biomase u energetskoj tranziciji Hrvatske. Na temelju provedenog istraživanja može se zaključiti da je jasno vidljiv pomak prema niskougljičnoj energetici, u čemu upravo biomasa ima važnu ulogu, iako je stopa upotrebe biomase u Hrvatskoj još uvijek ispod ambicioznog scenarija koji predviđa EU.*

***Ključne riječi:*** *biomasa; energetska tranzicija; Hrvatska; Europska unija; Europski zeleni plan*

**ABSTRACT** • *The Republic of Croatia, as a full member of the European Union, is currently participating in the energy transition, i.e. the process of decarbonization of the economy through the transformation of the energy sector in which renewable energy sources replace fossil fuels. In this process, biomass as the most complex form of renewable energy plays an important role given the many positive environmental and economic-social aspects of use. In accordance with the goals of the European Union, Croatia has achieved the required 20 percent share of production from renewable sources, but the share of energy production from biomass is still unsatisfactory. The most commonly used sources of biomass are solid biomass, especially pellets whose producers are export-oriented. Nevertheless, Croatia is still dependent on biomass imports, as is the case at EU level. Therefore, the improvement of production and consumption of energy from biomass requires synergy and joint action of all stakeholders in the energy sector, and decision-makers should create appropriate preconditions for the development of the biomass market. This paper analyzes the current position and importance of biomass in the energy transition of Croatia, based on the analysis of the biomass market, and its position in national and European energy policies. The research concludes that, although the rate of biomass use in Croatia is still below the ambitious scenario envisaged by the European Union, there is a clear shift towards low-carbon energy in which biomass plays a significant role.*

***Keywords:*** *biomass; energy transition; Croatia, European Union; European Green Deal*

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## 1. UVOD
1 INTRODUCTION

Nova industrijska strategija Europske unije (EU), četvrta industrijska revolucija (4IR), zelena i kružna ekonomija te bioekonomija, energetska tranzicija, resursna učinkovitost i klimatska neutralnost najvažnije su sastavnice novoga industrijskog doba koje obilježavaju gospodarske, društvene i okolišne promjene te tehnološka otkrića. Da bi tu viziju nove industrijske ere pretvorila u stvarnost, Europa će trebati upravljati brzom i sveobuhvatnom transformacijom, boriti se za globalnu konkurentnost i baviti se niskougljičnom energijom i sirovinama, što će zahtijevati djelovanje i suradnju donositelja politika na svim razinama. Prema Europskoj komisiji, Europski zeleni plan nudi rješenja za ta pitanja (EK, 2019a). Riječ je o novoj strategiji rasta kojom se EU nastoji preobraziti u pravedno i prosperitetno društvo s modernim, resursno učinkovitim i konkurentnim gospodarstvom u kojemu 2050. neće biti netoemisija stakleničkih plinova i u kojemu gospodarski rast nije povezan s iskorištavanjem resursa (EK, 2019a). Ambicije se neće moći ostvariti bez strateškog pristupa obnovljivim izvorima energije (OIE).

Naime, obnovljiva energija jedan je od ključnih prioriteta energetske unije (EK, 2019b), a OIE-ovi imaju središnju ulogu upravo u Europskome zelenom planu (EK, 2019a). U tom je kontekstu Direktiva 2009/28/EZ o promicanju uporabe energije iz obnovljivih izvora (RED I) bila osnovni element politike Energetske unije i ključni pokretač na putu ostvarenja ciljeva obnovljive energije do 2020. (EK, 2019b). Međutim, stupanjem na snagu Direktive (EU) 2018/2001 o promicanju uporabe energije iz obnovljivih izvora (RED II) u prosincu 2018. uspostavljen je novi okvir za ostvarivanje obvezujućeg cilja EU-a od najmanje 32 % obnovljive energije u konačnoj brutopotrošnji energije do 2030. godine. Prema važećoj Direktivi, „povećana uporaba energije iz obnovljivih izvora ima glavnu ulogu u promicanju sigurnosti opskrbe energijom, održive energije po pristupačnim cijenama, tehnološkog razvoja i inovacija te tehnološkog i industrijskog vodstva, osiguravajući pritom okolišne, društvene i zdravstvene koristi te važne mogućnosti za zapošljavanje i regionalni razvoj, ponajprije u ruralnim i udaljenim područjima". Osim toga, OIE-ovi su usko povezani s energetskom učinkovitošću, pokretač su dekarbonizacije energetskog sustava Unije i izvor gospodarskog rasta, pridonose smanjenju onečišćenja zraka te zbog njih ekonomije država članica Unije imaju lakši pristup povoljnoj i čistoj energiji (EK, 2017).

Na tom tragu osmišljen je i treći cilj ažurirane europske biogospodarske strategije – „Održivo biogospodarstvo za Europu: Jačanje veze gospodarstva, društva i okoliša" (engl. *A sustainable Bioeconomy for Europe: Strengthening the connection between economy, society and the environment*) (EK, 2018a), prema kojemu je smanjenje ovisnosti o neobnovljivim, neodrživim resursima, bilo iz domaćih izvora ili iz uvoza, važno za postizanje energetskih i klimatskih ciljeva EU-a

jer se očekuje da će ključna sastavnica u kombinaciji izvora energije 2030. ostati bioenergija, na koju trenutačno otpada najveći udio energije iz obnovljivih izvora u EU-u. Nadalje, prema Europskoj komisiji (2019b), glavni OIE-ovi koji su 2017. iskorištavani u potrošnji energije bili su biomasa u sektoru grijanja i hlađenja, hidroenergija i energija vjetra u sektoru električne energije te biogoriva u sektoru prometa. O važnosti biomase svjedoči i *činjenica da su prema Strategiji pametne specijalizacije Republike Hrvatske (NN, 32/*2016) upravo biomasa i bioproizvodi glavni inovacijski pokretači na znanju utemeljene bioekonomije. Osim toga, područje biomase otvara razvojne mogućnosti određenim industrijskim sektorima koje će trebati usmjeriti prema različitim nišama i novim tehnološkim smjerovima (NN, 32/2016), a prema procjenama sektora, u industrijama EU-a u kojima se pretežito koristi biomasa moglo bi se do 2030. otvoriti milijun novih radnih mjesta (EuropaBio, 2016.).

Nadalje, prema Zakonu o obnovljivim izvorima energije i visokoučinkovitoj kogeneraciji (NN 100/2015), biomasa se definira kao biorazgradivi dio proizvoda, otpada i ostataka biološkog podrijetla iz poljoprivrede (uključujući tvari biljnoga i životinjskog podrijetla), šumarstva i srodnih proizvodnih djelatnosti, uključujući ribarstvo i akvakulturu, kao i biorazgradivi dio industrijskoga i komunalnog otpada. Sukladno definiciji, „biomasa ima golem potencijal za daljnji razvoj koji treba slijediti neka osnovna načela, kao što su visoka učinkovitost, konkurentnost i održivost", a „korištenje biomase za proizvodnju topline na najbolji način zadovoljava navedene principe" (Šegon *et al.*, 2014.). U tom smislu Republika Hrvatska (RH) ima snažan potencijal za iskorištavanje biomase za energetske namjene, što se može zaključiti iz sve većeg broja projekata s primjenom biomase u proizvodnji električne i toplinske energije. Raste broj kogeneracijskih postrojenja i elektrana na biomasu koje svojom proizvodnjom toplinske energije opskrbljuju i javne ustanove u svojoj blizini, a radi se i na projektima kojima se kućanstva potiču na zamjenu starih kotlova kotlovima na biomasu, čime se jača svijest o važnosti obnovljivih izvora energije i energetske učinkovitosti.

Trenutačno su EU-u *i većina država članica na dobrom putu da ostvare svoje obvezujuće ciljeve za 2020.* (Eurostat, 2020.). Međutim, europska je industrija izgubila svoj položaj u razvoju OIE-ova. U svijetu je porast proizvodnje obnovljive energije ponajprije posljedica agresivne proizvodnje solarnih panela u Kini (po dampinškim cijenama). Naime, iako je Europa rano zauzela (a Kina poslije preuzela) vodeću ulogu u razvoju solarnih panela i ćelija, o čemu svjedoči činjenica da je pet europskih tvrtki bilo među najvećim proizvođačima od 2001. do 2004., u međuvremenu se situacija promijenila (Bjerkem *et al.*, 2019.). Očekuje se da će do 2022. na SAD, Indiju i Kinu otpadati dvije trećine globalnog širenja OIE-ova. Osim toga, Kina je i u hidroenergetici, bioenergiji i električnim vozilima vodeća zemlja na globalnom tržištu (Bjerkem *et al.*, 2019). Stoga je neupitna važnost ekonomske analize OIE-ova, a time i biomase.

## 2. BIOMASA U SKLOPU EUROPSKOGA ENERGETSKOG OKVIRA
## 2 BIOMASS WITHIN EUROPEAN ENERGY FRAMEWORK

U sektoru energije iz obnovljivih izvora u Europi je zaposleno više od 1,1 milijuna osoba, a najveći su poslodavci industrija za proizvodnju energije od vjetra, solarnih fotonaponskih tehnologija i krute biomase (EK, 2016.). Naime, nastojanja EU-a da do 2020. postigne svoje energetske i klimatske ciljeve rezultirala su novim industrijama, radnim mjestima u Europi i većim tehnološkim inovacijama, što je smanjilo troškove tehnologije, a kao najbolji primjer Europska komisija (2018b) navodi upravo „revoluciju u području energije iz obnovljivih izvora". Stoga je u posljednjih desetak godina usvojen niz komunikacija, strategija, direktiva i akcijskih planova „u kontekstu vodstva EU-a u prijelazu na pametniju i čišću energiju za sve i provedbe Pariškog sporazuma" (EK, 2016.).

Kronološki, u skladu s čl. 194. st. 1. Ugovora o funkcioniranju Europske unije (UFEU), promicanje obnovljivih oblika energije jedan je od ciljeva energetske politike Unije. Nadalje, kao jedan od prvih konkretnih koraka, Direktivom 2009/28/EZ uspostavljen je regulatorni okvir za promicanje uporabe energije iz obnovljivih izvora. Njime je utvrđen obvezujući nacionalni cilj glede udjela obnovljive energije u potrošnji energije i u sektoru prometa koji je trebao biti postignut do 2020. Zatim je u ožujku 2010. objavljen dokument „Europa 2020: strategija za pametan, održiv i uključiv rast" (EK, 2010.). U toj strategiji Komisija predlaže sedam vodećih inicijativa za postizanje napretka u svakoj od prioritetnih tema, među ostalim za resursno učinkovitu Europu koja je podrazumijevala „smanjenje emisije stakleničkih plinova za najmanje 20 % u odnosu na razinu iz 1990. ili za 30 %, ako su uvjeti dobri; povećanje udjela OIE u krajnjoj potrošnji energije na 20 %; i povećanje energetske učinkovitosti za 20 %".

Potom je 2011. usvojen „Plan za prijelaz na konkurentno niskougljično gospodarstvo do 2050." (engl. *A Roadmap for moving to a competitive low carbon economy in 2050*), a u lipnju 2012. donesena je komunikacija pod nazivom „Obnovljiva energija: važan čimbenik na europskom energetskom tržištu" (engl. *Renewable Energy: a major player in the European energy market*), u kojoj su nabrojene mogućnosti za politiku OIE-ova za razdoblje nakon 2020. godine.

Nakon toga je EK u siječnju 2014. donio komunikaciju „Okvir za klimatsku i energetsku politiku u razdoblju 2020. – 2030.", u kojoj su donesene smjernice za buduću energetsku i klimatsku politiku Unije i u kojoj se promišlja o tome kako će se te politike razvijati nakon 2020. Komisija je predložila da bi cilj Unije za 2030. u smislu udjela energije iz obnovljivih izvora potrošene u Uniji trebao iznositi barem 27 %, a Europsko vijeće taj je prijedlog potvrdilo, što znači su članice trebale odrediti i ambicioznije vlastite nacionalne ciljeve kako bi najprije ostvarile, a potom i nadmašile svoje planirane doprinose cilju Unije za 2030. Nadalje, 2014.

jedan je od deset političkih prioriteta tadašnjeg predsjednika EK-a Jeana-Clauda Junckera bila Energetska unija. Na tom je tragu u veljači 2015. EK objavio „Paket mjera za Energetsku uniju – Okvirnu strategiju za otpornu energetsku uniju s naprednom klimatskom politikom" (engl. *Energy Union package – A Framework Strategy for a Resilient Energy Union with a Forward-Looking Climate Change Policy*). U tom je paketu mjera istaknuto da strategija Energetske unije ima pet usko povezanih dimenzija osmišljenih za postizanje veće energetske sigurnosti, održivosti i konkurentnosti. To su energetska sigurnost, solidarnost i povjerenje, potpuno integrirano europsko energetsko tržište, energetska učinkovitost, dekarboniziranje gospodarstva i istraživanje, inovacije i konkurentnost. Dodatno je naglašeno da EU ima pravila o energiji utvrđena na europskoj razini, ali u praksi postoji 28 nacionalnih zakonodavnih okvira, zbog čega je nužno razvijati integrirano energetsko tržište kako bi se potaknulo tržišno natjecanje i postigla veća učinkovitost tržišta.

Kao sljedeći korak EK je u studenom 2016. objavio komunikaciju naslova „Čista energija za sve Europljane" (engl. *Clean Energy For All Europeans*), kojom je predstavio regulatorne prijedloge i mjere za olakšavanje prijelaza na čistu energiju, usmjerene na modernizaciju gospodarstva i poticanje ulaganja u sektore povezane s čistom energijom. Taj paket mjera imao je tri glavna cilja: davanje prioriteta energetskoj učinkovitosti, postizanje globalnog vodstva u području OIE-ova te osiguranje poštenog rješenja za potrošače.

U studenom 2018. objavljena je dugoročna strategija „Čist planet za sve – Europska strateška dugoročna vizija za prosperitetno, moderno, konkurentno i klimatski neutralno gospodarstvo" (engl. *A Clean Planet for all – A European strategic long-term vision for a prosperous, modern, competitive and climate neutral economy*), čija je svrha „potvrditi vodeću ulogu Europe u oblikovanju globalne klimatske politike te predstaviti viziju koja može pomoći da se do 2050. na troškovno učinkovit način i putem društveno pravedne tranzicije postigne nulta neto stopa emisija stakleničkih plinova" (EK, 2018b). Nadalje, EU je krajem 2018. usvojio već spomenutu Direktivu 2018/2001/EU o promicanju uporabe energije iz obnovljivih izvora, čijim je stupanjem na snagu uspostavljen novi okvir za ostvarivanje obvezujućeg cilja Unije od najmanje 32 % obnovljive energije u konačnoj brutopotrošnji energije do 2030. (EK, 2019b). Paralelno je usvojena i Uredba (EU) 2018/1999 Europskog parlamenta i Vijeća o upravljanju Energetskom unijom i djelovanjem u području klime u kojoj se propisuje izrada integriranih nacionalnih energetskih i klimatskih planova za desetogodišnje razdoblje. Prvi integrirani energetski i klimatski plan trebao bi obuhvatiti razdoblje od 2021. do 2030. godine.

Konačno, prvi važan korak novoizabrane predsjednice EK-a Ursule von der Leyen bio je Europski zeleni plan, nova strategija rasta za postizanje održivoga gospodarstva EU-a, u kojoj je istaknuto da se „mora razviti energetski sektor koji se uglavnom temelji na obnovljivim izvorima, uz brzo postupno ukidanje upotrebe ugljena i dekarbonizaciju plina" (EK, 2019a). U sklopu

Europskoga zelenog plana fokus je stavljen na sedam područja, među ostalim i na čistu energiju. Prema toj bi politici države članice 2023. morale ažurirati svoje nacionalne energetske i klimatske planove koji bi održavali nove klimatske ambicije (EK, 2019c). Na tom je tragu deset godina nakon „Strategije Europa 2020", 10. ožujka 2020., objavljena „Nova industrijska strategija za Europu" (engl. *A New Industrial Strategy for Europe*), kojom se želi osigurati klimatska neutralnost i digitalno vodstvo, a kako bi postala konkurentnija, zelenija i kružnija, potrebno je osigurati sigurnu opskrbu čistom i pristupačnom energijom te sirovinama.

Iz opsežnog pregleda europskoga energetskog okvira vidljivo je istodobno povezano djelovanje EU-a na različitim područjima s ciljevima i planovima koji su kroz godine konkretniji, detaljniji i razrađeniji. Osim toga, svaka članica ima svoje nacionalne energetske politike koje su oblikovane upravo na europskom tragu, ali i u skladu s nacionalnim mogućnostima i interesima.

## 3. BIOMASA U HRVATSKOJ ENERGETSKOJ POLITICI
## 3 BIOMASS WITHIN CROATIAN ENERGY POLICY

Sudjelovanjem u energetskoj tranziciji EU-a Hrvatska kao punopravna članica mora usklađivati energetsku politiku i zakonodavni okvir sa zakonodavstvom EU-a te ostvarivati svoje interese u području energetike, a oni su utvrđeni strategijom, zakonima i drugim propisima koji se odnose na obavljanje energetske djelatnosti. Međutim, i prije nego što je postala članica EU-a Hrvatska je tijekom pretpristupnih pregovora i priprema za članstvo izradila Program korištenja OIE i Akcijski plan za OIE kako bi utvrdila dugoročnu perspektivu razvoja njihove infrastrukture (u sklopu zatvaranja poglavlja 15. Energetika pretpristupnih pregovora) (Ministarstvo gospodarstva, 2013.), a reforma energetskog sektora u Hrvatskoj započela je donošenjem Zakona o energiji 2001. (NN 68/2001) i paketa energetskih zakona kojima se uređuje obavljanje pojedinih energetskih djelatnosti.

Prema Zakonu o energiji (NN 68/2001 i 177/2004) „osnovni akt kojim se utvrđuje energetska politika i planira energetski razvitak je Strategija energetskog razvoja" kojom se „utvrđuju nacionalni energetski programi, potrebna ulaganja u energetiku, poticaji za ulaganja u obnovljive izvore i kogeneraciju i za povećanje energetske učinkovitosti te unapređenje mjera zaštite okoliša", a donosi je Hrvatski sabor na prijedlog Vlade RH za razdoblje ne kraće od deset godina. Do sada je Sabor usvojio tri energetske strategije. Prva od njih – Strategija energetskog razvitka, donesena je 2002. i imala je „energetsku, ekonomsku, zakonodavnu, organizacijsku, institucionalnu i obrazovnu dimenziju s ciljem da pripremi energetski sektor Hrvatske za što lakše i efikasnije uključivanje u EU" (NN 38/2002-839).

Međutim, s obzirom na to da je u međuvremenu RH postala kandidatkinja za punopravno članstvo u

EU, da je prihvatila sporazum o Energetskoj zajednici te potpisala i ratificirala Kyotski protokol uz Okvirnu konvenciju UN-a o promjeni klime te da je bila suočena s velikom nestabilnošću cijena energije na svjetskom tržištu, 2009. usvojena je druga, unaprijeđena strategija – Strategija energetskog razvoja RH (NN 130/2009-3192), koja je imala tri osnovna cilja: sigurnost opskrbe energijom, konkurentnost energetskog sustava i održivost energetskog razvoja. Prema toj Strategiji (NN 130/2009-3192), Hrvatska pripada zemljama s velikim potencijalom biomase te je sebi postavila cilj da u 2010. iskorištava oko 15 PJ energije iz biomase, a u 2020. oko 26 PJ. Predviđeno je da će se dio te biomase upotrebljavati u brojnim elektranama na biomasu ukupne snage oko 85 MW u 2020., a radi povećanja energetske učinkovitosti prednost *će* imati postrojenja s istodobnom proizvodnjom električne i toplinske energije. Tom je Strategijom (NN 130/2009-3192) predviđeno i sinergijsko djelovanje razvojnih politika nekoliko ministarstava putem poticajnih mjera državne, industrijske, poljoprivredne i energetske politike kojima će se omogućiti razvoj hrvatske drvoprerađivačke industrije, gospodarenje šumama i iskorištavanje šumske biomase te poticati pošumljavanje i uzgajanje kultura kratkih ophodnji, kao i uporaba biomase u proizvodnji električne i toplinske energije u kogeneracijama i elektranama na biomasu.

Nakon što je 1. srpnja 2013. pristupila EU-u, RH je, zajedno s drugim članicama, preuzela obvezu povećanja potrošnje energije iz obnovljivih izvora, u skladu s Direktivom 2009/28/EZ o poticanju uporabe energije iz obnovljivih izvora, prema kojoj bi u 2020. udio energije iz OIE-ova u neposrednoj bruto potrošnji na razini EU-a trebao iznositi najmanje 20 %. Kako bi se taj cilj ostvario, svaka je članica morala donijeti nacionalni akcijski plan za OIE-ove u kojemu se određuje ukupni nacionalni cilj vezan za OIE-ove (Ministarstvo gospodarstva, 2013.). U skladu s tim, Hrvatska je Nacionalni akcijski plan za OIE do 2020. godine usvojila 2013.

Potom je Ministarstvo zaštite okoliša i energetike RH započelo izradu treće Strategije energetskog razvoja Republike Hrvatske do 2030., s pogledom na 2050. godinu. Sukladno smjernicama Povjerenstva za izradu Strategije, Energetski institut „Hrvoje Požar" izradio je Zelenu i Bijelu knjigu (2019a i 2019b), koje su bile analitička podloga za izradu Strategije. U skladu s navedenim, u svibnju 2019. objavljeni su Nacrt prijedloga Strategije i Strateška studija utjecaja na okoliš (Ministarstvo zaštite okoliša i energetike, 2019a i 2019b). Na postojeće nacionalne strategije i planove nadovezuje se i Integrirani nacionalni energetski i klimatski plan za razdoblje od 2021. do 2030. godine, u kojemu se daje pregled nacionalnih ciljeva za svaku od pet ključnih dimenzija Energetske unije te odgovarajuće politike i mjere za ostvarivanje tih ciljeva (Ministarstvo zaštite okoliša i energetike, 2019c).

Konačno, 28. veljače 2020. usvojena je Strategija energetskog razvoja RH do 2030., s pogledom na 2050. godinu (NN 25/2020-602), prema kojoj iskorištavanje biomase dobiva novi kontekst s kružnim gospodarstvom i biogospodarstvom te se potražnja za bioma-

som kao sirovinom proširuje iz dotadašnjih vrijednosti na nove, inovativne dobavne lance i proizvode utemeljene na biološkoj osnovi. Poljoprivreda, šumarstvo i ribarstvo te industrije utemeljene na tim sektorima, kao i održavanje krajolika (prometnih, energetskih i ostalih infrastruktura, vodotokova, urbanih zelenih površina), uz gospodarenje otpadom, *čine* sirovinsku osnovu obnovljivih bioloških resursa biogospodarstva ili biomasu. Pri tome bi prednost u iskorištavanju biomase trebalo dati proizvodima s većom dodanom vrijednosti ili primjenom kaskadnog korištenja, ali i uskladiti s nacionalnim kapacitetom gospodarstva i sa znanstvenoistraživačkom zajednicom te sa strateškim razvojnim ciljevima.

Na energetski sektor, pa tako i na OIE-ove i biomasu, uvelike utječe Zakon o obnovljivim izvorima energije i visokoučinkovitoj kogeneraciji iz 2015. (NN 100/2015) te izmjene i dopune Zakona koje su stupile na snagu krajem 2018. (NN 111/2018). Donošenjem tog Zakona Hrvatska je prvi put na jednome mjestu uredila područje OIE-ova i time potvrdila da su iskorištavanje obnovljivih izvora i proizvodnja energije iz visokoučinkovitih kogeneracija važni za nacionalno gospodarstvo. Navedenim Zakonom te njegovim izmjenama i dopunama utvrđene su i mnogobrojne prednosti za investitore olakšavanjem razumijevanja procesa izgradnje proizvodnih postrojenja i ulaskom u sustav poticanja, čime se omogućuje veća transparentnost i bolja informiranost svih sudionika na tržištu.

Jedan od aktualnih zakona u RH jest i Zakon o drvenastim kulturama kratkih ophodnji (NN 15/2018-313), usvojen 2018. radi stvaranja uvjeta za proizvodnju biomase iz kultura kao obnovljivoga i ekološki prihvatljivog energenta na načelima gospodarske održivosti, socijalne odgovornosti i ekološke prihvatljivosti. Taj je Zakon prvi takav propis u Hrvatskoj, a njegovom se primjenom stvara mogućnost za iskorištavanje šumskih i poljoprivrednih zemljišta koja nisu pogodna za poljoprivrednu proizvodnju ili su zapuštena. Time se potiče razvoj zemljišta kao resursa za proizvodnju energije i stvara dodana vrijednost, ali i otva-

raju nova radna mjesta putem samozapošljavanja i zapošljavanja u ruralnim područjima.

## 4. ANALIZA HRVATSKOG TRŽIŠTA BIOMASE U USPOREDBI S TRŽIŠTEM EUROPSKE UNIJE
## 4 ANALYSIS OF CROATIAN BIOMASS MARKET IN RELATION TO EUROPEAN UNION MARKET

Posljednjih je godina iskorištavanje OIE-ova u zemljama EU-a u snažnom porastu, što se ponajprije može pripisati programu Strategije Europa 2020. (prema kojoj je jedan od utvrđenih obveznih ciljeva povećanje udjela OIE-ova u potrošnji energije u EU-u na 20 %) i Direktivi o energiji iz obnovljivih izvora, usvojenoj 2009. (kojom su za svaku državu utvrđeni nacionalni ciljevi u području energije iz obnovljivih izvora uzimanjem u obzir njihove polazišne točke i ukupnog potencijala za energiju iz obnovljivih izvora). Napredak u ostvarenju tih ciljeva vidljiv je na slici 1., koja prikazuje koliko je opsežna upotreba obnovljive energije te stupanj do kojega su obnovljiva goriva zamijenila fosilna i time pridonijela dekarbonizaciji europskoga gospodarstva.

Hrvatska je svoj cilj od 20 % ostvarila još 2004., kada je bila četvrta članica po visini udjela energije iz obnovljivih izvora u bruto finalnoj potrošnji. Taj je udio 2017. porastao na 27,28 %, a i tada je Hrvatska po visini udjela i dalje ostala među prvih deset zemalja članica, i to na osmome mjestu. Prema podatcima Eurostata za 2018., udio energije iz obnovljivih izvora iznosio je 28 %, te je Hrvatska ponovo zauzela osmo mjesto među zemljama članicama EU-a. Ako se takav rast potrošnje energije iz obnovljivih izvora nastavi i u idućem razdoblju, Hrvatska ne bi trebala imati poteškoća u ostvarivanju ciljeva za iduće desetljeće. Osim toga, hrvatska proizvodnja i potrošnja energije iz drva i biomase posljednjih godina ostvaruju porast, iako niskom prosječnom godišnjom stopom. Prema podatcima Energetskog instituta „Hrvoje Požar", u razdoblju
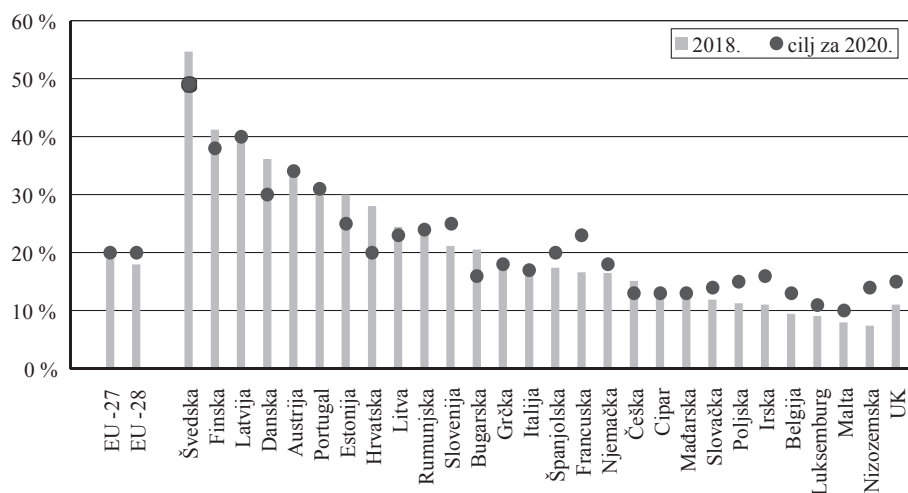


**Slika 1.** Udio energije iz obnovljivih izvora unutar EU-28 u 2018. godini u bruto finalnoj potrošnji (Eurostat)
**Figure 1** Share of renewable energy in EU28 in 2018 in gross final consumption (Eurostat)
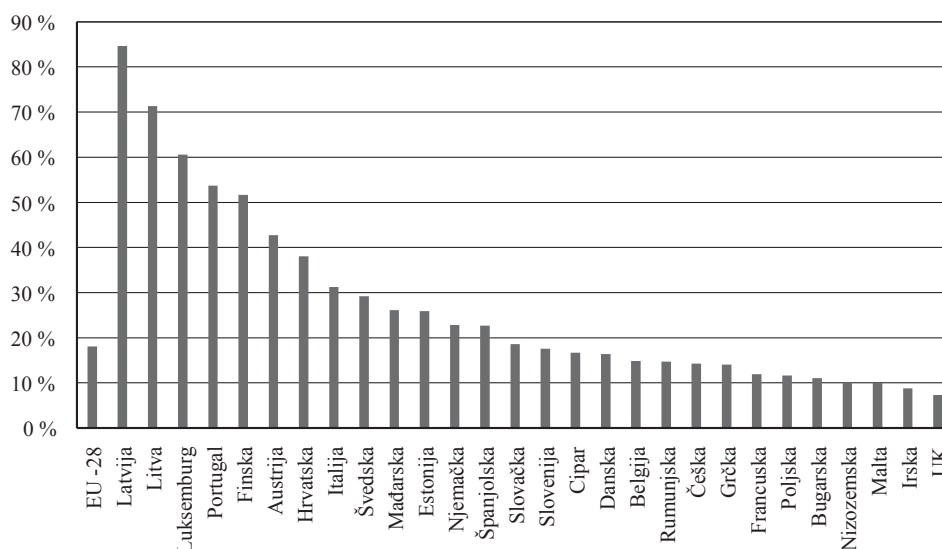
**Slika 2.** Udio proizvedene primarne energije iz biomase i obnovljivog otpada u ukupnoj proizvodnji primarne energije zemalja EU-28 u 2017. (izračun autorica prema podatcima Eurostata i udruge Bioenergy Europe)
**Figure 2** Share of primary energy produced from biomass and renewable waste in total primary energy production of EU28 in 2017 (calculation by authors according to Eurostat and Bioenergy Europe)

2013. – 2018. ostvaren je porast proizvodnje s prosječnom godišnjom stopom od 0,5 % te porast potrošnje s prosječnom godišnjom stopom od 0,6 %. Unatoč porastu proizvodnje, Hrvatska u proizvodnji primarne energije iz biomase ima vrlo mali udio s obzirom na razinu EU-a (Energetski institut „Hrvoje Požar", 2019c). Tako je 2016. udio proizvodnje primarne energije iz biomase i obnovljivog otpada u usporedbi s EU-om, prema podatcima Bioenergy Europe (Statistical Report, 2018 Edition), iznosio 1,17 %. Kao dominantan izvor biomase pojavljuje se kruta biomasa, a sve veću važnost dobiva proizvodnja peleta, koja ostvaruje stalni trend rasta. Energija iz biomase prevladava u općoj potrošnji, dok je u industriji i sektoru prometa biomasa, odnosno biogorivo još uvijek najslabije iskorištavan energent u neposrednoj potrošnji. Uvoz i izvoz biomase ostvaruju stabilan trend rasta, iako uvoz ostvaruje veću prosječnu godišnju stopu rasta od izvoza. Ista je situacija i na razini EU-a, koji još uvijek uvelike ovisi o uvozu goriva, pa tako i o uvozu biomase.

Kad je riječ o potrošnji energije iz obnovljivih izvora, podatci Europske udruge za biomasu Bioenergy Europe (Statistical Report, 2019.) pokazuju da je na razini EU-a 2017. biomasa činila 8,6 % ukupne bruto finalne potrošnje EU-a. Hrvatski udio potrošnje biomase u ukupnoj bruto finalnoj potrošnji EU-a manji je od 1 %, dok je najveći udio imala Njemačka. Na razini Hrvatske udio potrošnje biomase u ukupnoj bruto finalnoj potrošnji iznosio je 14,7 %.

Nadalje, prema podatcima Bioenergy Europe (Statistical Report, 2019.) primarna proizvodnja energije iz obnovljivih izvora jedina je kategorija koja se u EU-28 povećava, a glavnu ulogu u tome imaju biomasa i vjetar; biomasa i dalje ima vodeće mjesto (s udjelom od 18 % u proizvodnji primarne energije u EU-28 u 2017.). Stoga su OIE-ovi ključni *činitelj* za osiguranje energetske neovisnosti EU-a. Doista, u EU-28 primarna se proizvodnja fosilnih goriva drastično smanji-

la – za gotovo 50 % u 2017. u usporedbi sa 2000. godinom. U Hrvatskoj je udio proizvodnje primarne energije iz biomase i obnovljivog otpada u odnosu prema ukupnoj proizvodnji primarne energije iznosio 38,04 % (sl. 2.).

Prema podatcima Europskog vijeća za pelet EPC (akronim od engl. European Pellet Council) objavljenima u izvještaju udruge Bioenergy Europe, većina je zemalja članica EU-a u 2018. iskoristila više od polovice svojih kapaciteta za proizvodnju peleta. Nadalje, prema istom izvještaju, Hrvatska od 2010. bilježi stalan rast proizvodnje peleta, pri čemu su svi tržišni uvjeti postali povoljni (dostupnost sirovina i inozemna potražnja) te omogućuju razvoj proizvodnje, a očekuje se da će se taj rastući trend nastaviti.

Ukupni kapacitet proizvodnje na razini EU-a u 2018. iznosio je 23,4 milijuna tona, a proizvedeno je 16,9 milijuna tona peleta. Iako je najveći broj operativnih pogona za proizvodnju peleta bio u Španjolskoj, najveći kapacitet i ostvarenu proizvodnju imala je Njemačka. Hrvatska je 2018. ostvarila 82 % moguće proizvodnje peleta s obzirom na to da je naš kapacitet proizvodnje bio 370 000 tona, a proizvedeno je 305 000 tona peleta. Kapaciteti proizvodnje i stvarno ostvarena proizvodnja u zemljama članicama EU-a prikazane su na slici 3. Prema istom izvještaju, u EU-u je 2018. bilo 719 operativnih pogona za proizvodnju peleta, najviše u Španjolskoj, i to 80, dok je Hrvatska imala 21 instalirani pogon za proizvodnju peleta.

Unija još uvijek uvelike ovisi o uvozu goriva, posebice nafte i plina, a ista je situacija i s biomasom. Prema podatcima Eurostata u izvještaju Bioenergy Europe, u EU-u je 2018. ostvaren viši uvoz biomase od izvoza. Nadalje, 2018. godine najveće su izvoznice biomase od zemalja članica EU-a bile Latvija, Estonija i Austrija, dok su UK, Italija i Danska iste godine bile najveće uvoznice. Hrvatska je u području biomase i obnovljivog otpada izvozno orijentirana jer je promatrane godine u
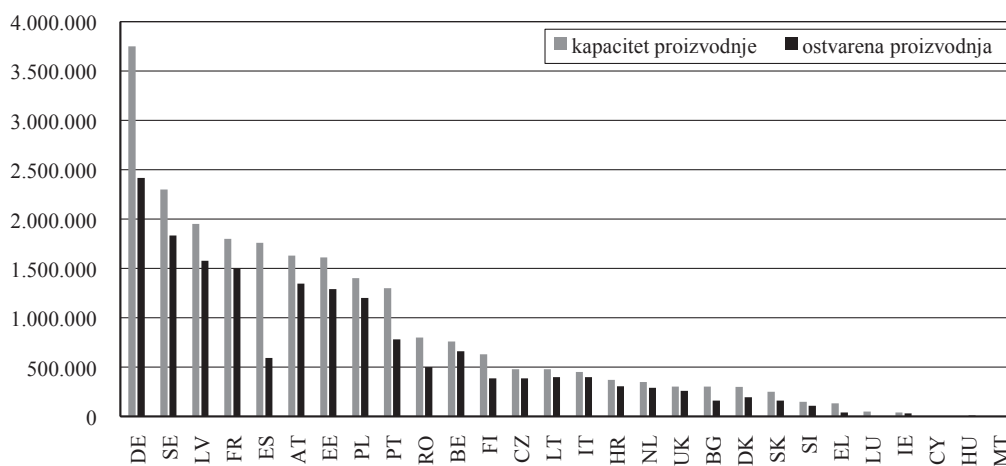
**Slika 3.** Proizvodnja peleta u EU-28 u 2018. godini, u tonama (European Pellet Council)
**Figure 3** Pellet production in tons in 2018 in EU28 (European Pellet Council)
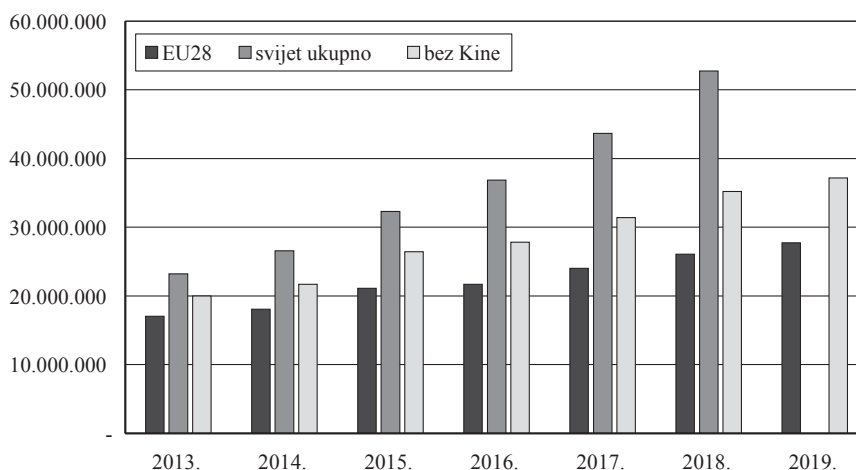


**Slika 4.** Potrošnja peleta u svijetu u razdoblju 2013. – 2019., u tonama (Bioenergy Europe)
**Figure 4** Global pellet consumption between 2013 and 2019, in tonnes (Bioenergy Europe)
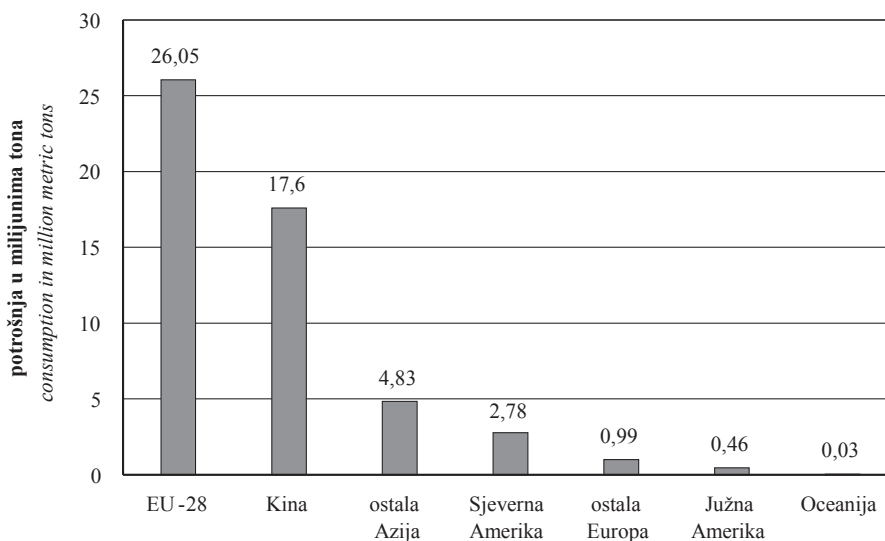


**Slika 5.** Potrošnja peleta u odabranim regijama svijeta u 2018., u milijunima tona (Statista)
**Figure 5** Consumption of wood pellets worldwide in 2018, by select region, in million metric tons (Statista)
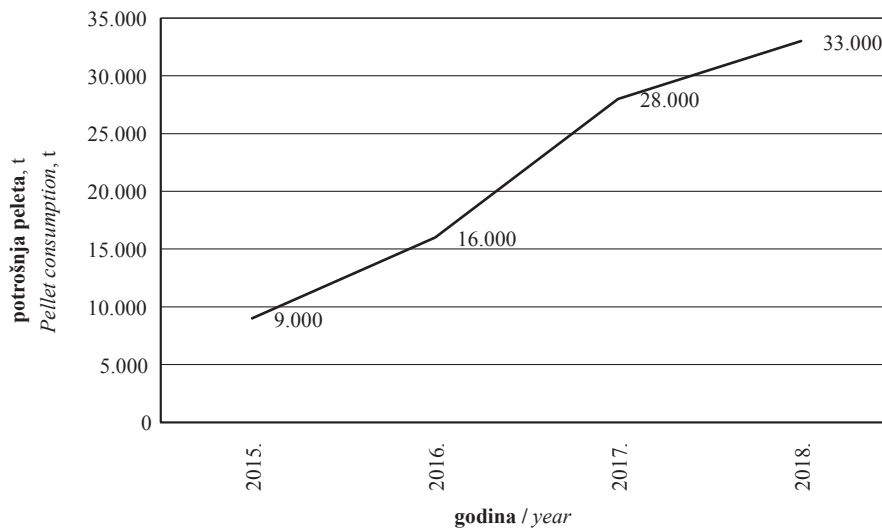
**Slika 6.** Potrošnja peleta u Hrvatskoj u razdoblju 2013. – 2018., u tonama (Bioenergy Europe)
**Figure 6** Pellet consumption in Croatia from 2013 to 2018, in tonnes (Bioenergy Europe)

Hrvatsku uvezeno 29 000 tona ekvivalentne nafte, a izvezeno 312 000 tona ekvivalentne nafte.

Kada je riječ o globalnoj potrošnji peleta u razdoblju 2013. – 2019., vidljiv je kontinuirani rast (sl. 4.). Nadalje, prema podatcima na slici 5., razvidno je da se velik dio potražnje drvenih peleta u 2018. odnosio na zemlje članice EU-a.

Nadalje, na slici 6. predočena je potrošnja peleta u Hrvatskoj u razdoblju 2015. – 2018., koja prema podatcima Bioenergy Europe bilježi evidentan porast.

Međutim, unatoč porastu potrošnje peleta, i dalje postoji velik potencijal za popularizaciju tog energenta u Hrvatskoj. Stoga je nužno pokrenuti kampanje koje će informirati javnost i educirati društvo o pozitivnim učincima koji proizlaze iz upotrebe peleta. Država može dati primjer poticanjem zelene javne nabave i upotrebom peleta kao energenta među javnim korisnicima, a jedna od mjera za povećanje potrošnje jest i porezno rasterećenje smanjenjem PDV-a na pelete, što bi pozitivno utjecalo i na proizvodnju peleta na domaćem tržištu. Također, za poticanje kućanstava na veću potrošnju peleta potrebno je provoditi projekte dodjele sredstava fizičkim osobama, odnosno građanima za nabavu i ugradnju kotlova i peći na pelete. Kako bi se stimuliralo tržište i povećala proizvodnja i potrošnja peleta, nužno je stvoriti povoljnu investicijsku klimu osiguravanjem subvencija za proizvođače, ali i uklanjanjem zakonodavnih, administrativnih i tehničkih prepreka koje znatno usporavaju i otežavaju ulaganja.

## 5. ZAKLJUČAK
## 5 CONCLUSIONS

U procesu dekarbonizacije gospodarstva i prelaska s fosilnih goriva na OIE-ove, biomasa zbog svoje obnovljivosti i održivosti ima važnu ulogu u energetskoj tranziciji RH. Sagledavanjem okolišnih i ekonomsko-socijalnih učinaka upotrebe biomase kao energenta može se zaključiti da, unatoč manjim negativnim utjecajima na okoliš, biomasa svojim pozitivnim utje-

cajem na okoliš, ekosustave i zdravlje ljudi uvelike pridonosi održivom razvoju i postizanju energetskih ciljeva, ali i razvoju hrvatskoga gospodarstva pridonoseći većem zapošljavanju i jačem regionalnom razvoju.

Iako je Hrvatska ostvarila europske ciljeve za potrebnih 20 % udjela proizvodnje iz obnovljivih izvora do 2020., provedenom analizom hrvatskog tržišta biomase može se zaključiti da je udio biomase u proizvodnji iz OIE-ova još uvijek premalen. Nadalje, biomasa kao OIE ima sve veću važnost unutar europskih, ali i nacionalnih zakonodavnih okvira koji prate europske smjernice razvoja. Na temelju provedenog istraživanja može se zaključiti da je jasno vidljiv pomak prema niskougljičnoj energetici, u čemu upravo biomasa ima bitnu ulogu, iako je stopa iskorištavanja biomase u Hrvatskoj još uvijek ispod ambicioznog scenarija koji predviđa EU. Mijenja se javna percepcija o mogućnostima i politikama sektora energije dobivene iz biomase, ali nedovoljnim intenzitetom. Međutim, treba uzeti u obzir činjenicu da je energetska tranzicija dugotrajan proces za koji ne postoje prethodna iskustva na kojima se ona može temeljiti, zbog čega je potrebno kontinuirano pratiti rezultate i dinamiku promjena u idućim godinama. Stoga, unatoč sve većem zanimanju za iskorištavanje biomase kao obnovljivog izvora energije za proizvodnju i potrošnju, i dalje postoji izniman potencijal za napredak i popularizaciju tog energenta u Hrvatskoj.

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# Drvo antiarisa (*Antiaris toxicaria var. africana Scott-Elliot ex A. Chev.*)

## NAZIVI

Vrsta *Antiaris toxicaria var. africana* Scott-Elliot ex A. Chev. iz porodice *Moraceae* poznata je pod brojnim sinonimima od kojih je vjerojatno najpoznatiji *Antiaris africana* Engl. Standardni trgovački naziv drva te botaničke vrste i njezinih podvrsta i varijeteta u Europi jest antiaris (engl.), ako (franc.) i Ako (njem.). Lokalni su trgovački nazivi tog drva Antiaris, Ogiovu, Oro (Nigerija); Akede, Fou, Handame, Mutie, Ogiovu, Pou, Sili, Tide, Zaadi (Obala Bjelokosti); Chenchen, Kyenkyen, Kodzo, Logotsi, Ofo (Gana); Diolosso (Kamerun); Bonkonko, Tsangu (Kongo); Bovili, Kakulu (Sijera Leone).

## NALAZIŠTE

Antiaris prirodno raste u skupinama unutar tropskih kišnih šuma zapadne Afrike od Senegala preko Sijera Leonea, Liberije, Obale Bjelokosti, Gane, Nigerije, Kameruna i Gabona do Konga.

## STABLO

Ta brzorastuća vrsta naraste 30 do 40 m visoko, deblo drveta dugačko je do 20 m, a prsni mu je promjer od 0,6 do 0,9 m, katkad i 1,5 m. Deblo je ravno i valjkasto, a žilište s vidljivim dijelovima postranoga korijenja doseže do 2,0 m visine. Kora antiarisa je glatka, sivocrvenkasta, s bijelim pločicama. Na starim se stablima ljušti, sočna je i ako se probuši dok je svježa, izlučuje mliječni sok. Debljina kore je od 1 do 2,5 cm.

## DRVO

### Makroskopska obilježja

Bjeljika je bjelkasta i široka do vrlo široka. Bojom se jedva razlikuje od žutobijele ili žutosmeđe srži, koja s vremenom potamni do zlatnosmeđe nijanse. Tekstura drva ravne žice jednostavna je, uzdužno fino izbrazdana i nije dekorativna. Međutim, radijalne površine dvostruko usukane žice izrazito su prugaste, lijepog izgleda i zlatnožutog sjaja. Miris svježeg drva je neugodan.

Zone rasta raspoznaju se po područjima s manje pora na poprečnom presjeku. Pore i drvni traci jedva su uočljivi golim okom, a dobro se vide tek pod povećalom. Na radijalnim se površinama sjaje drvni traci visoki do 1 mm. Pore na uzdužnim površinama izgledaju kao fine, ravnomjerno raspoređene brazdice.

### Mikroskopska obilježja

Pore drva su krupne, difuznog rasporeda, uglavnom pojedinačne, ponegdje u parovima ili skupinama. Promjer pora kreće se od 100...190...260 mikrometara. Rijetko su raspoređene, tj. od 3 do 5 ili 8 na 1 mm² poprečnog presjeka. Volumni udio pora je 13 do 18 %. Katkad imaju tile. Uzdužni je parenhim paratrahealno vazicentričan i konfluentan, s volumnim udjelom u drvu od 12 do 18 %. Drvi su traci difuznog rasporeda i slabo heterogeni. Visoki su 560...835...1120 mikrometara, odnosno od 15 do 35 ili 55 stanica, a široki su 20...50...65 mikrometara, odnosno od 2 do 4 ili 6 stanica. Gustoća trakova iznosi 4 do 6 ili 7 trakova na 1 mm tangentnog smjera, a volumni udio trakova u drvu je oko 19 %. Vlakanca su libriformska, septirana i difuzno raspoređena. Mogu se uočiti i izolirane vlaknaste traheide. Debljina dvostruke stijenke vlakanaca kreće se od 2,9...4,3...5,9 mikrometara, a promjer lumena je od 17,8...22,3 (29,9) mikrometra. Dužina vlakanaca iznosi 640...1050...1375 mikrometara, a volumni udio vlakanaca u drvu je 45...56 %. Smjer vlakanaca je ravan i blago dvostruko usukan.

Rijetko se mogu naći radijalni međustanični kanali te pojedinačni kristali romboidnih i drugih oblika u uzdužnome i radijalnom parenhimu.

### Fizička svojstva

| | |
|---|---|
| Gustoća standardno suhog drva ($\rho_o$) | 410...500 kg/m³ |
| Gustoća prosušenog drva ($\rho_{12-15}$) | 440...500...580 kg/m³ |
| Gustoća sirovog drva ($\rho_s$) | 700...800 kg/m³ |
| Poroznost | oko 73 % |
| Radijalno utezanje ($\beta_r$) | 3,0...3,7...4,4 % |
| Tangentno utezanje ($\beta_t$) | 5,3...6,5...7,8 % |
| Volumno utezanje ($\beta_v$) | 8,4...10,4...12,5 % |

### Mehanička svojstva

| | |
|---|---|
| Čvrstoća na tlak | 32...42...50 MPa |
| Čvrstoća na savijanje | 40...59...76 MPa |
| Čvrstoća na vlak, paralelno s vlakancima | 19...42...81 MPa |
| okomito na vlakanca | 1,9...2,4 MPa |
| Tvrdoća HB paralelno s vlakancima | 30…36…45 MPa |
| Tvrdoća HB okomito na vlakanca | 9…16…25 MPa |
| Modul elastičnosti | 5800...8400 MPa |

## TEHNOLOŠKA SVOJSTVA

### Obradivost

Drvo se ručno i strojno dobro i bez problema obrađuje pri kutu rezanja od 15 do 20° i brzini rezanja 25 do 30 m/s. Površina drva s dvostruko usukanom žicom tijekom blanjanja ima tendenciju kidanja. Drvo se lako reže, ljušti i cijepa. Pogodnije je za rezanje nego za ljuštenje. Čavle i vijke bez poteškoća prihvaća i drži. Za obradu su potrebni oštri alati.

### Sušenje

Drvo antiarisa dobro se i brzo suši, uz moguće promjene oblika tijekom sušenja. Preporučuje se sušenje u sušionicama.

### Trajnost i zaštita

Drvo je podložno napadu ksilofagnih kukaca suhog drva, kao i termita (razred S). Slabo je otporno na gljive uzročnice truleži (razred otpornosti 5). Lako se impregnira jer je permeabilno (razred 1).

### Uporaba

Rabi se kao furnir pri izradi furnirskih i drugih ploča, od tog se drva izrađuju unutarnja stolarija i unutarnje obloge, proizvode se kutije i sanduci, služi za izradu dijelova namještaja, drvne galanterije, ploča vlaknatica i iverica te drvenih roleta (sjenila).

### Sirovina

Isporučuje se u obliku trupaca dužine 4,0 … 9,0 m, srednjeg promjera od 60 do 120 cm te kao piljena građa i furnir.

### Napomena

Antiaris nije na popisu ugroženih vrsta međunarodne organizacije CITES, a na popisu međunarodne organizacije IUCN Red list navodi se kao stabilna vrsta. Drvo je poznato kao nadomjestak za drvo abachija (*Triplochiton scleroxylon* K. Schum.), limbe (*Terminalia superba* Engl. & DIels) i kota (*Pterygota macrocarpa* K. Schum.). Tijekom obrade drva antiarisa može se pojaviti iritacija kože i sluznica.

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# Vrste drva s naslovnica časopisa

# DRVNA INDUSTRIJA

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## Upute

Predani radovi smiju sadržavati najviše 15 jednostrano pisanih ISO A4 listova (210 mm × 297 mm) s dvostrukim proredom (30 redaka na stranici), uključujući i tablice, slike te popis literature, dodatke i ostale priloge. Dulje je članke preporučljivo podijeliti na dva ili više nastavaka. Tekst treba biti u docx formatu, u potpunosti napisan fontom Times New Roman (tekst, grafikoni i slike), normalnim stilom, bez dodatnog uređenja teksta. Prva stranica poslanog rada treba sadržavati puni naslov, ime(na) i prezime(na) autora, podatke o zaposlenju autora (ustanova, grad i država) te sažetak s ključnim riječima (duljina sažetka približno 1/2 stranice A4). Posljednja stranica treba sadržavati titule, zanimanje, zvanje i adresu (svakog) autora, s naznakom dopisnog autora s Uredništvom. Znanstveni radovi moraju biti sažeti i precizni. Osnovna poglavlja trebaju biti označena odgovarajućim podnaslovima. Napomene se ispisuju na dnu pripadajuće stranice, a obrojčavaju se susljedno. One koje se odnose na naslov označuju se zvjezdicom, a ostale uzdignutim arapskim brojkama. Napomene koje se odnose na tablice pišu se ispod tablica, a označavaju se uzdignutim malim pisanim slovima, abecednim redom. Latinska imena trebaju biti pisana kosim slovima (italicom), a ako je cijeli tekst pisan kosim slovima, latinska imena trebaju biti podcrtana. U uvodu treba definirati problem i, koliko je moguće, predočiti granice postojećih spoznaja, tako da se čitateljima koji se ne bave područjem o kojemu je riječ omogući razumijevanje ciljeva rada. Materijal i metode trebaju biti što preciznije opisane da omoguće drugim znanstvenicima ponavljanje pokusa. Glavni eksperimentalni podaci trebaju biti dvojezično navedeni. Rezultati trebaju obuhvatiti samo materijal koji se izravno odnosi na predmet. Obavezna je primjena metričkog sustava. Preporučuje se upotreba SI jedinica. Rjeđe rabljene fizikalne vrijednosti, simboli i jedinice trebaju biti objašnjeni pri njihovu prvom spominjanju u tekstu. Za pisanje formula valja se koristiti Equation Editorom (dodatkom u MS Wordu). Jedinice se pišu normalnim (uspravnim) slovima, a fizikalni simboli i faktori kosima (italicom).

Formule se susljedno obrojčavaju arapskim brojkama u zagradama, npr. (1) na kraju retka. Količina slika mora biti ograničena samo na one koje su prijeko potrebne za objašnjenje teksta. Isti podaci ne smiju biti navedeni i u tablici i na slici. Slike i tablice trebaju biti zasebno obrojčane, arapskim brojkama, a u tekstu se na njih upućuje jasnim naznakama ("tablica 1" ili "slika 1"). Naslovi, zaglavlja, legende i sav ostali tekst u slikama i tablicama treba biti napisan hrvatskim i engleskim jezikom. Slike je potrebno rasporediti na odgovarajuća mjesta u tekstu, trebaju biti izrađene u rezoluciji 600 dpi, crno-bijele (objavljivanje slika u boji moguće je na zahtjev), formata jpg ili tiff, potpune i jasno razumljive bez pozivanja na tekst priloga. Svi grafikoni i tablice izrađuju se kao crno-bijeli prilozi (osim na zahtjev). Tablice i grafikoni trebaju biti na svojim mjestima u tekstu te originalnog formata u kojemu su izrađeni radi naknadnog ubacivanja hrvatskog prijevoda. Ako ne postoji mogućnost za to, potrebno je poslati originalne dokumente u formatu u kojemu su napravljeni (MS Excel ili Statistica format). Naslovi slika i crteža ne pišu se velikim tiskanim slovima. Crteži i grafikoni trebaju odgovarati stilu časopisa (fontovima i izgledu). Slova i brojke moraju biti dovoljno veliki da budu lako čitljivi nakon smanjenja širine slike ili tablice. Fotomikrografije moraju imati naznaku uvećanja, poželjno u mikrometrima. Uvećanje može biti dodatno naznačeno na kraju naslova slike, npr. "uvećanje 7500 : l". Diskusija i zaključak mogu, ako autori žele, biti spojeni u jedan odjeljak. U tom tekstu treba objasniti rezultate s obzirom na problem postavljen u uvodu i u odnosu prema odgovarajućim zapažanjima autora ili drugih istraživača. Valja izbjegavati ponavljanje podataka već iznesenih u odjeljku Rezultati. Mogu se razmotriti naznake za daljnja istraživanja ili primjenu. Ako su rezultati i diskusija spojeni u isti odjeljak, zaključke je nužno napisati izdvojeno. Zahvale se navode na kraju rukopisa. Odgovarajuću literaturu treba citirati u tekstu, i to prema harvardskom sustavu (ime – godina), npr. (Krpan, 1970). Nadalje, bibliografija mora biti navedena na kraju teksta, i to abecednim redom prezimena autora, s naslovima i potpunim navodima bibliografskih referenci. Popis literature mora biti selektivan, a svaka referenca na kraju mora imati naveden DOI broj, ako ga posjeduje (http://www.doi.org) (provjeriti na http://www.crossref.org).

## Primjeri navođenja literature

Članci u časopisima: Prezime autora, inicijal(i) osobnog imena, godina: Naslov. Naziv časopisa, godište (ev. broj): stranice (od – do). Doi broj.

*Primjer*

Kärki, T., 2001: Variation of wood density and shrinkage in European aspen (*Populus tremula*). Holz als Roh- und Werkstoff, 59: 79-84. http://dx.doi.org/10.1007/s001070050479.

*Knjige:* Prezime autora, inicijal(i) osobnog imena, godina: Naslov. (ev. izdavač/editor): izdanje (ev. svezak). Mjesto izdanja, izdavač (ev. stranice od – do).

*Primjeri*

Krpan, J., 1970: Tehnologija furnira i ploča. Drugo izdanje. Zagreb, Tehnička knjiga.

Wilson, J. W.; Wellwood, R. W., 1965: Intra-increment chemical properties of certain western Canadian coniferous species. U: W. A. Cote, Jr. (Ed.): Cellular Ultrastructure of Woody Plants. Syracuse, N.Y., Syracuse Univ. Press, pp. 551- 559.

Ostale publikacije (brošure, studije itd.)

Müller, D., 1977: Beitrag zür Klassifizierung asiatischer Baumarten. Mitteilung der Bundesforschungsanstalt für Forstund Holzvvirt schaft Hamburg, Nr. 98. Hamburg: M. Wiederbusch.

*Web stranice*

***1997: "Guide to Punctuation" (online), University of Sussex, www.informatics.sussex.ac.uk/department/docs/punctuation/node 00.html. First published 1997 (pristupljeno 27. siječnja 2010).

Autoru se prije konačnog tiska šalje PDF rada. Rad je potrebno pažljivo pročitati, ispraviti te vratiti Uredništvu s popisom ispravaka te s popunjenim obrascem za dopuštenje objavljivanja i izjavi o autorskim pravima. Ispravci su ograničeni samo na tiskarske pogreške: dodaci ili znatnije promjene u radu naplaćuju se. Autori znanstvenih i stručnih radova besplatno dobivaju po jedan primjerak časopisa. Autoru svakog priloga također se dostavlja besplatan primjerak časopisa. Dodatne informacije o načinu pisanja znanstvenih radova mogu se naći na web adresi: **www.ease.org.uk/publications/author-guidelines**

# Instructions for authors

## General terms

The Journal of Drvna industrija (Journal of Wood Industry) publishes scientific papers (original scientific papers, short note, preliminary papers and review papers), other contributions and professional information related to structure, properties and protection of wood and wood materials, application of wood and wood materials, mechanical woodworking, hydrothermal treatment and chemical processing of wood, all aspects of wood materials and wood products production and trade in wood and wood products, and other events connected to the wood industry.

Submission of a paper implies that the work has not been submitted for publication elsewhere or published before (except in the form of an abstract or as part of a published lecture, review or thesis, in which case it must be stated in a footnote); that the publication is approved by all co-authors (if any) and by the authorities of the institution where the research has been carried out.

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The scientific papers shall be published in English with an extended summary in Croatian. The titles, headings and all the relevant results shall be presented bilingually. Other articles are generally published in Croatian. The Editor's Office shall provide the translation into Croatian for foreign authors. The scientific papers will be subject to a thorough review by at least two selected referees.

The Editorial Board shall make the choice of reviewers, as well as the decision about the classification of the paper and its acceptance (based on reviewers' recommendations). All contributions are subject to proofreading. The editors will require authors to modify the text in the light of the recommendations made by reviewers and language advisers, and they reserve the right to suggest abbreviations and text improvements.

Authors are fully responsible for the contents of their contributions. It shall be assumed that the author has obtained the permission for the reproduction of portions of text published elsewhere, and that the publication of the paper in question does not infringe upon any individual or corporate rights.

Papers shall report on true scientific or technical achievement. Authors are responsible for the terminological and metrological consistency of their contributions.

The contributions are to be submitted by e-mail to the following address: drind@sumfak.hr

## Details

Papers submitted shall consist of no more than 15 single-sided ISO A4 (210 mm × 297 mm) sheets of 30 double-spaced lines, including tables, figures and references, appendices and other supplements. Longer papers should be divided into two or more continuing series. The text should be written in .docx format, fully written using Times New Roman font (text, graphs and figures), in normal style without additional text editing.

The first page of the paper submitted should contain full title, name(s) of author(s) with professional affiliation (institution, city and state), abstract with keywords (approx. 1/2 sheet A4). The last page should provide the full titles, posts and address(es) of each author with indication of the contact person for the Editor's Office.

Scientific papers shall be precise and concise. The main chapters should be characterized by appropriate headings. Footnotes shall be placed at the bottom of the same page and consecutively numbered. Those relating to the title should be marked by an asterix, others by superscript Arabic numerals. Footnotes relating to the tables shall be printed under the table and marked by small letters in alphabetical order. Latin names shall be printed in italics and underlined.

Introduction should define the problem and if possible the framework of existing knowledge, to ensure that readers not working in that particular field are able to understand author's intentions.

Materials and methods should be as precise as possible to enable other scientists to repeat the experiment. The main experimental data should be presented bilingually.

The results should involve only material pertinent to the subject. The metric system shall be used. SI units are recommended. Rarely used physical values, symbols and units should be explained at their first appearance in the text. Formulas should be written by using Equation Editor (MS Word add-in). Units shall be written in normal (upright) letters, physical symbols and factors in italics. Formulas shall be consecutively numbered with Arabic numerals in parenthesis (e.g. (1)) at the end of the line.

Discussion and conclusion may, if desired by authors, be combined into one chapter. This text should interpret the results relating to the problem outlined in the introduction and to related observations by the author(s) or other researchers. Repeating the data already presented in the "Results" chapter should be avoided Implications for further studies or application may be discussed. A conclusion shall be expressed separately if results and discussion are combined in the same chapter. Acknowledgements are presented at the end of the paper.

The paper will be sent to the author for proofreading, in PDF format before printing. The paper should be carefully corrected and sent back to the Editor's Office with the list of corrections made and with the filled form for publishing permission and copyright statement.

Corrections should be limited to printing errors; amendments to or changes in the text will be charged.

Each contributor will receive one (1) copy of the journal.

Further information on the way of writing scientific papers can be found on the following website: www.ease.org.uk/publications/author-guidelines

## Tables and figures guidelines

The quantity of figures shall be limited to those absolutely necessary for clarification of the text. The same information must not be presented in both a table and a figure. Figures and tables should be numbered separately with Arabic numerals, and should be referred to in the text with clear remarks ("Table 1" or "Figure 1"). Titles, headings, legends and all the other text in figures and tables should be written in both Croatian and English.

Figures should be inserted into the text. They should be of 600 dpi resolution, black and white (color photographs only on request and extra charged), in jpg or tiff format, completely clear and understandable without reference to the text of the contribution.

All graphs and tables shall be black and white (unless requested otherwise). Tables and graphs should be inserted into the text in their original format in order to insert them subsequently into the Croatian version. If this is not possible, original document should be sent in the format in which it was made (MS Excel or statistica format). The captions to figures and drawings shall not be written in block letters. Line drawings and graphs should conform to the style of the journal (font size and appearance). Letters and numbers shall be sufficiently large to be readily legible after reduction of the width of a figure or table. Photomicrographs should have a mark indicating magnification, preferably in micrometers. Magnification can be additionally indicated at the end of the figure title, e.g. "Mag. 7500:1".

## Guidelines for writing references

Relevant literature shall be cited in the text according to the Harvard style ("name, year"), e.g. (Krpan, 1970). In addition, the bibliography shall be listed at the end of the text in alphabetical order of the author›s names, together with the title and full quotation of the bibliographical reference.

The list of references shall be selective, and each reference shall have DOI number (http://www.doi.org) (double-check at http://www.crossref.org).

## Example of references

*Journal articles:*
Author's second name, initial(s) of the first name, year: Title. Journal name, volume (ev. issue): pages (from - to). DOI number.
Example:
Kärki, T., 2001: Variation of wood density and shrinkage in European aspen (Populus tremula). Holz als Roh- und Werkstoff, 59: 79-84. http://dx.doi.org/10.1007/s001070050479.

*Books:*
Author's second name, initial(s) of the first name, year: Title. (ev. Publisher/editor): edition, (ev. volume). Place of publishing, publisher (ev. pages from - to).
*Examples:*
Krpan, J. 1970: Tehnologija furnira i ploča. Drugo izdanje. Zagreb: Tehnička knjiga.
Wilson, J.W.; Wellwood, R.W. 1965: Intra-increment chemical properties of certain western Canadian coniferous species. U: W. A. Cote, Jr. (Ed.): Cellular Ultrastructure of Woody Plants. Syracuse, N.Y., Syracuse Univ. Press, pp. 551-559.

*Other publications (brochures, studies, etc.):*
Müller, D. 1977: Beitrag zur Klassifizierung asiatischer Baumarten. Mitteilung der Bundesforschungsanslalt für Forst- und Holzwirtschaft Hamburg, Nr. 98. Hamburg: M. Wiederbusch.

*Websites:*
***1997: "Guide to Punctuation" (online), University of Sussex, www.informatics.sussex.ac.uk/department/docs/punctuation/node 00.html. First published 1997 (Accessed Jan. 27, 2010).