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Aytaç Aydın[1], Sebahattin Tiryaki[2]

Impact of Performance Appraisal on Employee Motivation and Productivity in Turkish Forest Products Industry: A Structural Equation Modeling Analysis

Utjecaj ocjene rada na motivaciju i produktivnost zaposlenika u turskoj industriji proizvoda na bazi šuma: analiza strukturnih jednadžbi modela

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ABSTRACT • *The present study investigates the influence of performance appraisal on employee motivation and productivity in Turkish forest products industry using a structural equation model. The questionnaires prepared for this purpose were applied to 432 people that work in 14 forest products industry businesses operating throughout Turkey. A total of nine hypotheses were established to determine the relationship between performance appraisal and employee motivation and productivity. The results indicated that five hypotheses were accepted, while four of them were rejected. In the light of the findings of this study, it may be generally said that the effect of performance appraisal on employee motivation and productivity was high. In other words, performance appraisal was found to be a major factor on employee motivation and productivity. The present study is expected to help managers and decision makers in selecting suitable motivating factors in order to retain and satisfy their employees. Consequently, this study will fill an important gap in the area of performance appraisal in the forest products industry by structural equation modeling and presents the opportunity for further studies.*

Keywords: *employee performance, forest product industry, organizational performance, structural equation modeling*

SAŽETAK • *Studija je prikaz istraživanja utjecaja ocjene rada na motivaciju i produktivnost zaposlenika u turskoj industriji proizvoda na bazi šuma primjenom modela strukturnih jednadžbi. Na upitnike pripremljene za tu namjenu odgovarale su 432 osobe zaposlene u 14 tvrtki u sektoru industrije na bazi šuma diljem Turske. Pritom*

[1] Author is assistant professor at Karadeniz Technical University, Faculty of Forestry, Department of Forest Industry Engineering, Trabzon, Turkey. [2]Author is lecturer at Karadeniz Technical University, Arsin Vocational School, Department of Material and Material Processing Technologies, Arsin/Trabzon, Turkey.
[1] Autor je docent Tehničkog sveučilišta u Karadenizu, Šumarski fakultet, Odjel za industrije bazirane na šumi, Trabzon, Turska.[2] Autor je predavač Tehničkog sveučilišta u Karadenizu, Arsin škola, Odjel za procese obrade materijala, Arsin, Trabzon, Turska.

je postavljeno devet hipoteza za utvrđivanje odnosa ocjene rada i motiviranosti i produktivnosti zaposlenika. Rezultati su pokazali da je pet hipoteza prihvatljivo, a četiri su odbijene. U svjetlu nalaza ove studije može se reći da je učinak ocjenjivanja na motiviranost zaposlenika i produktivnost vrlo visok. Drugim riječima, ocjena rada najviše utječe na motiviranost zaposlenika i na njihovu produktivnost. Očekuje se da će rezultati studije pomoći menadžerima i donositeljima odluka u odabiru odgovarajućih motivacijskih čimbenika kako bi zadržali i zadovoljili svoje zaposlenike. Stoga će ova studija ispuniti jaz koji postoji u području ocjenjivanja rada u drvnoj industriji modeliranjem strukturnih jednadžbi te će otvoriti mogućnosti daljnjeg istraživanja.

Ključne riječi: *uspješnost zaposlenika, drvna industrija, organizacija, modeliranje strukturnih jednadžbi*

1 INTRODUCTION
1. UVOD

Employee performance plays an important role in achieving organizational goals. In other words, employee performance is directly linked to the success of any organization. Therefore, organizations try to improve their productivity by providing an improvement in employee performance throughout the world. In this regard, various strategies have been developed to measure employee performance; one of them is performance appraisal (PA) (Wholey, 1999; Gichuhi *et al.,* 2013).

The PA can be defined as a strategic and important approach that requires a regular inspection of the performance of employees in the organizations for performing the assigned tasks and responsibilities (Salau *et al.,* 2014). This strategy aims to measure, assess and improve the performance of employees to achieve various objectives (Singh *et al.,* 2010). The majority of organizations also use the PA approach to determine the factors such as salary increases, promotions, the need for individual development and training of employees (Gürbüz and Dikmenli, 2007). PA is thus accepted to be an important tool in order to improve both organizational performance and individual performance of employees. Such advantages of PA make it an important tool to reach organizational goals in many sectors (Vasset *et al.,* 2011).

It is also important to emphasize that human capital (employees) in the organizations is considered as one of the most critical factors in gaining sustainable competitive advantage in the competitive situation of today's world. The organizations that have skilled and motivated employees may be regarded as advantageous in reaching such goals. Thus, many organizations endeavor to improve the human resource management and its functions (Chang and Han, 2006; Fakhimi and Raisy, 2013). In this respect, PA may be regarded as one of major functions of human resources managers.

PA intends to evaluate the performance of employees as objectively as possible. Kumbhar (2011) reported that a well-designed PA system helps develop employee performance-related criteria, provides a feedback mechanism and enables a more equitable reward system. It was also stated that employees' productivity increases when a fair system is available for PA in any organizations. In this regard, PA undertakes a critical task for organizations in order to reach their strategic objectives (Kumbhar, 2011). On the other hand, some researchers have pointed out that a rewarding system, applied as a result of PA, contributes to an increase in employee motivation through influencing directly the performance of employees (Prowse and Prowse, 2009; Ochoti *et al.,* 2012). Ali and Ahmed (2009) mentioned that rewards are managerial tools that help to reach organizational goals by affecting individual or group behavior. Therefore, most organizations use various types of rewards such as pay, promotion, bonuses in order to motivate employees and increase employees performance (Ali and Ahmed, 2009).

Furthermore, PA is a continuing procedure that measures expertise and achievements of employees based on an acceptable accuracy and equality. The employees are subjected to an appraisal process periodically after they are hired. The appraisal activities serve as a guide for managers in making a decision on employees' current job performance, awards, career goals and other job-related actions based on performance (Gürbüz and Dikmenli, 2007). However, the factors such as differences in the level of education, hiring temporary workers, employment, work experience, time pressures, and shift work might affect the appraisal process as well as employee motivation and productivity (Vasset *et al.,* 2011).

Jelačić *et al.* (2008) found that the factors such as employment assurance, job organization and workplace activity affect employee motivation in forest products industry. In another study, no differences were found in terms of motivation factors among employees of Slovenian and Croatian wood industry companies. Besides, it was stated that managers should ensure the safety of employees and pay attention to their mutual relations (Kropivšek *et al.,* 2011). Hitka and Štipalova (2011) compared the motivation of employees in the wood industry and other manufacturing enterprises for various categories throughout Slovakia. It was observed that the diversity of the importance of motivational factors is less significant in the category of employees. In another study on the impact of the economic crisis period on the motivation of forest products industry employees, it concluded that employee motivation does not differ in the period before and after the crisis (Hitka *et al*., 2014). Lorincova (2016) mentioned that increasing professional satisfaction of employees in the furniture industry may lead to an increase in motivation and business productivity.

In addition to the above mentioned investigations, a comprehensive analysis that considers the influence of PA on employee motivation and productivity is needed. Structural equation modeling (SEM) is an appropriate approach for this purpose. SEM is a versatile multivariate statistical approach that enables re-

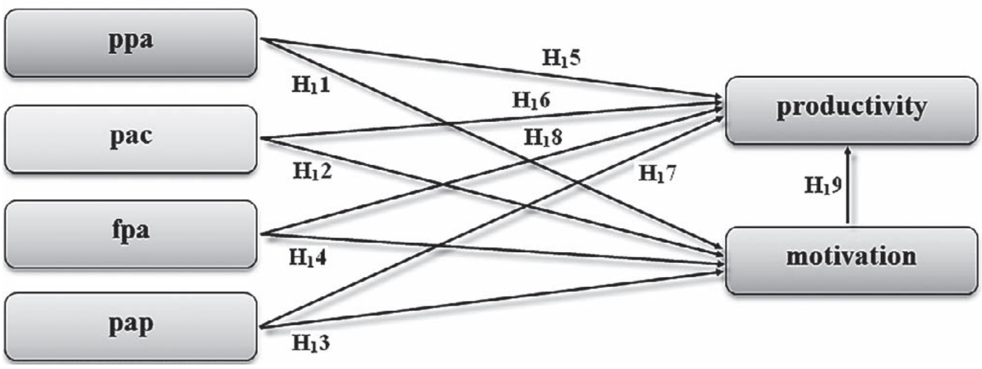

Figure 1 Conceptual model
Slika 1. Konceptualni model

searchers to effectively evaluate the relationships between observed and latent (unobserved) variables (Chan *et al.,* 2007). The emergence of this approach has been regarded as a significant development and it has been widely employed in various scientific disciplines (Xiong *et al.,* 2015). SEM is a combination of regression analysis, correlation, factor analysis, and path analysis. In comparison to other multivariate techniques, SEM is capable of estimating multiple and interrelated relationships and representing unobserved concepts in these relationships. This method also considers measurement errors in estimation. Further, it defines a model explaining an entire set of relationships (Xiong *et al.,* 2014). Because of these advantages, SEM has been increasingly employed in many disciplines, such as banking industry (Osibanjo *et al.,* 2014), education sector (Phin, 2015), service sector (Suki, 2014), business safety (Hsu *et al.,* 2012), tourism sector (Hallak *et al.,* 2012), food industry (Booth *et al.,* 2013), and health sector (Bazarganipour *et al.,* 2013), for uncovering the relationships among different kinds of variables.

1.1 Objectives and hypotheses
1.1. Ciljevi i hipoteze

Although there are many applications to examine the effect of PA on motivation and productivity in various disciplines, limited information is available to investigate the influence of PA on employee motivation and productivity in forest products industry by the SEM. This study, therefore, analyses the relationships among various factors that affect motivation and productivity of employees of Turkish forest products industry by means of SEM to create a model of factors that both directly and indirectly affect employee motivation and productivity.

Additional objectives of this study were:

- to detect the factors that increase employee motivation and productivity;
- to investigate the relationship between employee motivation and productivity;
- to assess the effect of the PA on the motivation and productivity of employees.

In this regard, the following hypotheses were established based on independent and dependent variables.

H_1 1, 2, 3, 4: There is a relationship between employee motivation and the purpose of PA (ppa), PA criteria (pac), PA practices (pap), Feedback in PA (fpa);

H_1 5, 6, 7, 8: There is a relationship between employee productivity and the purpose of PA (ppa), PA criteria (pac), PA practices (pap), Feedback in PA (fpa);

$H_1$9: There is a relationship between employee motivation and employee productivity.

In this perspective, we proposed the model composed of all the hypotheses that describe the relationships between two variables, as depicted in Figure 1.

From the model in Fig. 1, it can be seen that the purpose of the PA (ppa), PA criteria (pac), feedback in PA (fpa), and PA practices (pap) are considered as independent variables.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Population and sample
2.1. Populacija i uzorak

The participants of the present investigation are composed of businesses that have ISO 9001:2008 Quality Management System (QMS) certifications and operate in forest products industry throughout Turkey. A previous study conducted by Serin (2004) has revealed that businesses that employ more than 100 employees give more significance to total quality management applications because they have a more institutional structure. Fourteen companies that meet these criteria agreed to implement the study. The survey was conducted between March 2015 and December 2015.

Among the 14 participating businesses, 7 deal with furniture, 6 with board products and 1 with paper. Surveys were administered to 432 people, including senior, middle and lower level employees.

2.2 Data collection instruments
2.2. Način prikupljanja podataka

A questionnaire prepared by compiling data from the surveys found in the literature was used in this study (Tarlığ, 2006; Yılmaz, 2006). The survey is comprised of two sections. The first section contains 7 questions related to personnel information, while the other section includes Likert-type (5 scales) 51 questions related to the PA, employee motivation and employee productivity.

After the surveys were completed, the data obtained were entered into SPSS (Statistical Software for Social Sciences). Analyses for reliability and validity were then performed by AMOS (Analysis of Moment Structures) package program.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1. Demographic characteristics
3.1. Demografska obilježja ispitanika

In this section, demographic information of the participants such as age, education, gender, marital status, wages, working experience and position in the company were determined. Results regarding demographic information for participant employees are given in Table 1.

Table 1 shows that 49.4 % of the participants had vocational school and higher education levels. The majority of participants (82 %) were male, while 70.4 % were married. In addition, 43.8 % of the participants were employees, 49.1 % of them had 6 years and over of working experience.

3.2 Validity and reliability
3.2. Vrijednost i pouzdanost

For the present study, Cronbach alpha coefficient was used for reliability analysis. According to the results of the analysis conducted, general Cronbach alpha coefficient was found to be 0.950. This coefficient varies within a range of 0 to 1, and a value over 0.90 means an excellent agreement (Kalaycı, 2009).

Moreover, factor analysis was carried out to measure structural validity. However, it is important to state that conformity of the data set for the factor analysis is tested with Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy prior to the analysis. KMO should be over 0.5 for validity (Sharma, 1996). This value was found to be 0.917 for this study (Bartlett's Test of Sphericity Sig.:0.001). Thus, it can be said that the study was suitable for performing factor analysis. In the application of the factor analysis, varimax orthogonal rotation method and basic components analysis were considered. In this respect, factors that include less than three variables and variables that load on more than one factor were discarded. Furthermore, eigenvalues statistics was used in order to determine the number of factors. Dunteman (1989) reported that factors with an eigenvalue higher than 1 are considered significant. Table 2 presents the results of exploratory factor analysis related to the scale.

Upon application of factor analysis, from the scale consisting of 51 items, 18 items that do not match the structure of the scale or load on more than one factor were discarded. The remaining 33 items formed a structure that consists of 6 sub-factors with eigenvalues higher than 1. Total expressiveness of this six-factored structure was found to be 59.942 %.

3.3 Measurement model
3.3. Model mjerenja

Measurement model structure obtained as a result of factor analysis was tested by confirmatory factor analysis for investigating the structure validity. In order to test the conformity of the model, confirmatory factor analysis was performed by the AMOS. Standard prediction values, *t* values and reliability level of the variables in the model are given in Table 3.

In analyzing the standard prediction values of the variables, it was shown that the values vary between 0.491 and 0.846. Besides, the *t* values of these predic-

Table 1 Demographic information
Tablica 1. Demografski podatci

Demographic variables *Demografske varijable*		*N*	%	**Demographic variables** *Demografske varijable*		*N*	%
Educational status *Obrazovanje*	Literate / *pismen*	4	0.9	**Salary (TL)** *Plaća*			
	Primary education / *osnovno obrazovanje*	69	16.0		≤ 999	58	13.4
	High school / *srednje obrazovanje*	146	33.8		1000-1.499	165	38.2
	Vocational school / *stručno obrazovanje*	59	13.7		1.500-1.999	87	20.1
	University / *visoko obrazovanje*	149	34.5		2.000-2.499	65	13.0
	Postgraduate / *poslijediplomsko obrazovanje*	5	1.2		≥ 2.500	56	13.0
Total / *Ukupno*		432	100	**Total** / *Ukupno*		431	99.8
Gender *Spol*	Male / *muški*	357	82.7	**Age** *Dob*	16-19	7	1.6
	Female / *ženski*	71	16.4		20-24	46	10.6
Total / *Ukupno*		428	99.1		25-29	103	23.8
Working experience *Radni staž*	0-5	185	42.8		30-34	111	25.7
	6-10	143	33.1		35-39	93	21.5
	11-20	58	13.4		40-49	67	15.5
	≥ 21	11	2.5		≥ 50	5	1.2
Total / *Ukupno*		397	91,9	**Total** / *Ukupno*		432	100
Position *Pozicija*	Upper level / *viša razina*	38	8.8	**Marital status** *Bračni status*	Married *oženjen/udana*	304	70.4
	Middle level / *srednja razina*	175	40.5		Single / *samac*	119	27.5
	Worker / *radnik*	189	43.8		Other / *ostalo*	1	0.2
Total / *Ukupno*		402	93.1	**Total** / *Ukupno*		424	98.1

Table 2 Results of scale's exploratory factor analysis
Tablica 2. Rezultati faktorske analize

	Variables *Varijable*	**Factor load** *Težina čimbenika*	**Eigen value** *Vlastita vrijednost*	**Announced variance** *Predviđena varijanca* %	**Cronbach's Alpha** *Cronbachov alfa*
	PA purpose / *Svrha ocjene rada*		4.358	13.201	0.873
q3	In PA studies, the employees' ability for own business regulation and planning is measured / *Pri ocjeni rada mjerena je sposobnost zaposlenika za samostalno reguliranje i planiranje poslovanja.*	0.73			
q2	In PA studies, the employees' ability to make decisions are measured / *Pri ocjeni rada mjerena je sposobnost zaposlenika da donose odluke.*	0.73			
q1	In PA studies, the employees' job information is measured *Pri ocjeni rada mjerena je informiranost zaposlenika o poslu.*	0.71			
q4	In PA studies, the employees' labor and the ability to use correctly the resources are measured / *Pri ocjeni rada mjeren je rad zaposlenika i sposobnost ispravne uporabe resursa.*	0.69			
q5	In PA studies, the employees' ability to communicate effectively is measured / *Pri ocjeni rada mjerena je sposobnost zaposlenika da učinkovito komuniciraju.*	0.69			
q6	In PA studies, the employees' cooperation understanding is measured / *Pri ocjeni rada mjereno je razumijevanje suradnje zaposlenika.*	0.64			
q7	In PA studies, the employees' harmony with the environment and respectful behavior are measured / *Pri ocjeni rada mjerena je usklađenost zaposlenika s okolinom i njegovo ponašanje.*	0.63			
	PA criteria / *Kriteriji ocjene rada*		3.715	11.258	0.854
q26	My PA score significantly affects my salary. / *Ocjena moga rada znatno utječe na moju plaću.*	0.66			
q27	My PA score significantly affects my promotion / *Ocjena moga rada znatno utječe na moje promaknuće.*	0.64			
q16	PA system used in our business is generally sufficient. / S*ustav ocjenivanja rada koji se primjenjuje u našem poslovanju općenito je dovoljan.*	0.63			
q18	PA system used in our business is able to distinguish really successful staff from unsuccessful staff / S*ustavom ocjenivanja rada koji se primjenjuje u našem poslovanju moguće je razlikovati stvarno uspješne zaposlenike od neuspješnih.*	0.59			
q17	Getting high or low scores from PA is actually related to being successful or unsuccessful. / *Dobivanje visokih ili niskih ocjena rada stvarno je povezano s uspjehom ili neuspjehom.*	0.57			
q25	I need to work hard to go beyond a certain score in PA / *Moram naporno raditi kako bih postigao određene rezultate pri ocjenjivanju rada.*	0.56			
q20	My manager gives me a full score if I obtain an outstanding achievement in my work / *Moj menadžer daje mi najbolje ocjene ako postignem izvrsne rezultate u radu.*	0.56			
q14	PA criteria include necessary factors for me to succeed in my work. / *Kriteriji ocjenjivanja obuhvaćaju* čimbenike *potrebne za uspjeh u mom poslu.*	0.52			
	Feedback in PA / *Povratne informacije o ocjeni rada*		3.689	11.178	0.878
q33	In PA meeting, my manager tells me in what I am good / *Na sastanku vezanome za ocjenu moga rada menadžer mi kaže u* čemu *sam dobar.*	0.73			
q32	In PA interview, my manager clearly points to what I am missing. / *Na sastanku vezanome za ocjenu moga rada menadžer mi jasno kaže koji su moji nedostatci.*	0.73			
q35	In PA interview, my manager tells me my mistakes and failures *Na sastanku vezanome za ocjenu moga rada menadžer mi priopći koje su moje pogreške i konkretni nedostatci.*	0.73			

Table 2 Continue
Tablica 2. Nastavak

	Variables *Varijable*	**Factor load** *Težina čimbenika*	**Eigen value** *Vlastita vrijednost*	**Announced variance** *Predviđena varijanca* %	**Cronbach's Alpha** *Cronbachov alfa*
q36	In PA interview, my manager discusses with me about my mistakes I cannot correct. / *Na sastanku vezanome za ocjenu moga rada menadžer razgovara sa mnom o mojim pogreškama za koje ne znam kako ih ispraviti.*	0.70			
q34	In PA interview, my manager gives me the opportunity to express my ideas clearly. / *Na sastanku vezanome za ocjenu moga rada menadžer mi daje mogućnost da jasno izrazim svoje ideje.*	0.68			
q40	In PA interview, I identify common goals with my manager determining what I should do in future. / *Na sastanku vezanome za ocjenu moga rada zajedno sa svojim menadžerom identificiram ciljeve i dogovaramo ono* što *bih trebao* činiti *u budućnosti.*	0.54			
	PA practices / *Prakse ocjene rada*		3.153	9.555	0.830
q22	My manager uses PA as an element of threat. / *Moj menadžer koristi se ocjenom rada kao elementom prijetnje.*	0.83			
q21	I think my manager uses PA to reward some people he likes. *Mislim da se moj menadžer koristi ocjenom rada kako bi nagradio neke ljude koje voli.*	0.78			
q28	I think that my manager uses PA to punish persons he dislikes. *Mislim da se moj menadžer koristi ocjenom rada kako bi kažnjavao osobe koje mu se ne sviđaju.*	0.77			
q23	I think my manager evaluates my personality, not my performance. / *Mislim da moj menadžer procjenjuje moju osobnost, a ne moj posao.*	0.77			
q24	I think that people who obtain high PA score are the people who can present themselves well to the manager. / *Mislim da visoke ocjene dobivaju oni koji se menadžeru znaju prikazati dobrima.*	0.58			
	Productivity / *Produktivnost*		2.637	7.991	0.793
q47	PA system planned upon reaching a consensus with my superior improves my working efficiency. *Sustav ocjenjivanja rada kojim se planira postizanje dogovora s administratorom poboljšava moju radnu učinkovitost.*	0.79			
q48	Setting realistic goals and achievable targets for my work along with the company's goals and targets in my PA interview improves my working efficiency. / *Zadavanje realnih ciljeva i ostvarivih zadataka u skladu s ciljevima i zadaćama tvrtke poboljšava moju radnu učinkovitost.*	0.78			
q46	If feedback is high as a result of PA, it motivates employees and increases success. / *Ako je povratna informacija u skladu s ocjenom rada, ona motivira zaposlenike i povećava uspjeh.*	0.75			
q49	As a result of PA, eliminating my failures and determining my training needs in according with my deficiencies will improve my business efficiency. *Ispravljanje mojih nedostataka kao rezultat ocjene rada i određivanje mojih potreba za izobrazbom radi uklanjanja mojih nedostataka poboljšava moju učinkovitost u poslovanju.*	0.61			
	Motivation / *Motivacija*		2.228	6.753	0.788
q43	Motivation of a high performance person will be higher. *Motivacija pojedinca s visokim učinkom bit* će *veća.*	0.80			
q44	Performance of a high motivation person will be higher. *Produktivnost pojedinca s visokom motivacijom bit* će *veća.*	0.72			
q42	There is a positive effect of PA on motivation in terms of employees' self-expression, their regular communication, and sharing their problems / *Postoji pozitivan učinak ocjene rada na motivaciju u smislu samokritičnosti zaposlenika, njihove redovite komunikacije i dijeljenja njihovih problema.*	0.69			
	Announced Total Variances, % / *Predviđena varijanca* **Kaiser-Meyer-Olkin (KMO) value** / *KMO vrijednost* **Bartlett's Test of Sphericity (Sig.)** / *Bartlettov test sferičnosti*	- -	- -	59.942 0.917 0.001	

Table 3 Reliability values of the model
Tablica 3. Pokazatelji pouzdanosti modela

	Variables *Varijable*	**Std Loading** *Standardna devijacija*	***t****
Purpose of performance appraisal *Cilj procjene rada* (CR=0.88, AVE=0.50)	q3	0.710	14.217
	q2	0.737	-
	q1	0.728	14.593
	q4	0.726	14.554
	q5	0.698	13.972
	q6	0.695	13.913
	q7	0.646	12.896
Performance appraisal criteria *Kriteriji ocjene rada* (CR=0.90, AVE=0.51)	q26	0.795	12.754
	q27	0.696	12.945
	q16	0.729	-
	q18	0.715	14.207
	q17	0.660	13.103
	q25	0.648	10.851
	q20	0.661	13.134
	q14	0.592	11.732
Feedback in performance appraisal *Povratna informacija o ocjeni rada* (CR=0.88, AVE=0.55)	q33	0.800	-
	q32	0.723	15.800
	q35	0.725	15.872
	q36	0.692	14.991
	q34	0.765	16.934
	q40	0.730	16.001
Performance appraisal practices *Prakse u ocjeni rada* (CR=0.83, AVE=0.51)	q22	0.847	-
	q21	0.710	15.293
	q28	0.735	15.924
	q23	0.714	15.392
	q24	0.502	10.250
Productivity / *Produktivnost* (CR=0.80, AVE=0.50)	q46	0.710	12.724
	q47	0.724	-
	q48	0.754	13.295
	q49	0.629	11.463
Motivation / *Motivacija* (CR=0.84, AVE=0.63)	q42	0.753	-
	q43	0.766	13.818
	q44	0.718	13.209

* *P* values belonging to all *t* values is determined as 0.000. / *Vrijednosti P koje pripadaju svim vrijednostima t jednakima 0,000.*

tions were significant at 0.05 significance level. Therefore, it can be concluded that the validity of the model was provided.

Two types of reliability measures were used in the measurement model: the announced variance of the factors and the reliability coefficients of the factors. While the announced variance estimates of the factors show the total variance value explained by the observed variables of each factor, the reliability coefficients of the factors show the intrinsic reliability of the factors. As shown in Tables 2 and 3, the announced variance values of the factors are above the required lower limit (0.50 %) and the reliability coefficients of the factors are again above the lower limit (0.70).

The correlations among the purpose of performance appraisal, performance appraisal criteria, feedback in performance appraisal, performance appraisal practices, productivity and motivation are presented in Table 4 along with a discriminant validity test.

Table 4 Correlation matrix for the measurement model
Tablica 4. Korelacijska matrica za model mjerenja

Scales *Ljestvice*	**ppa**	**pac**	**fpa**	**pap**	**Productivity** *Produktivnost*	**Motivation** *Motivacija*
ppa	1					
pac	0.737	1				
fpa	0.595	0.771	1			
pap	0.253	0.408	0.336	1		
Productivity / *Produktivnost*	0.466	0.443	0.393	0.181	1	
Motivation / *Motivacija*	0.497	0.562	0.553	0.134	0.576	1

3.4 Structural model
3.4. Strukturni model

Table 5 gives the fit indexes belonging to the resulting findings as a result of the testing with the structural equation modeling analysis of the developed model.

As the fit indexes of the structural model were analyzed, it was seen that the model is within acceptable limits determined by the following literature (Anderson and Gerbing, 1984; Hancock and Mueller, 2006; Al-Refaie, 2015). AMOS program output of the model is shown in Figure 2.

Table 5 Fit indexes belonging to the results of the structural equation model
Tablica 5. Indeksi koji pripadaju rezultatima modela strukturne jednadžbe

Model	χ2	df	P-value	χ2/df	GFI	RMSEA
Default model	1026.554	480	0.001	2.139	0.877	0.051

Hypothesis was examined after the validity of the model was provided. The results of hypothesis tests are given in Table 6.

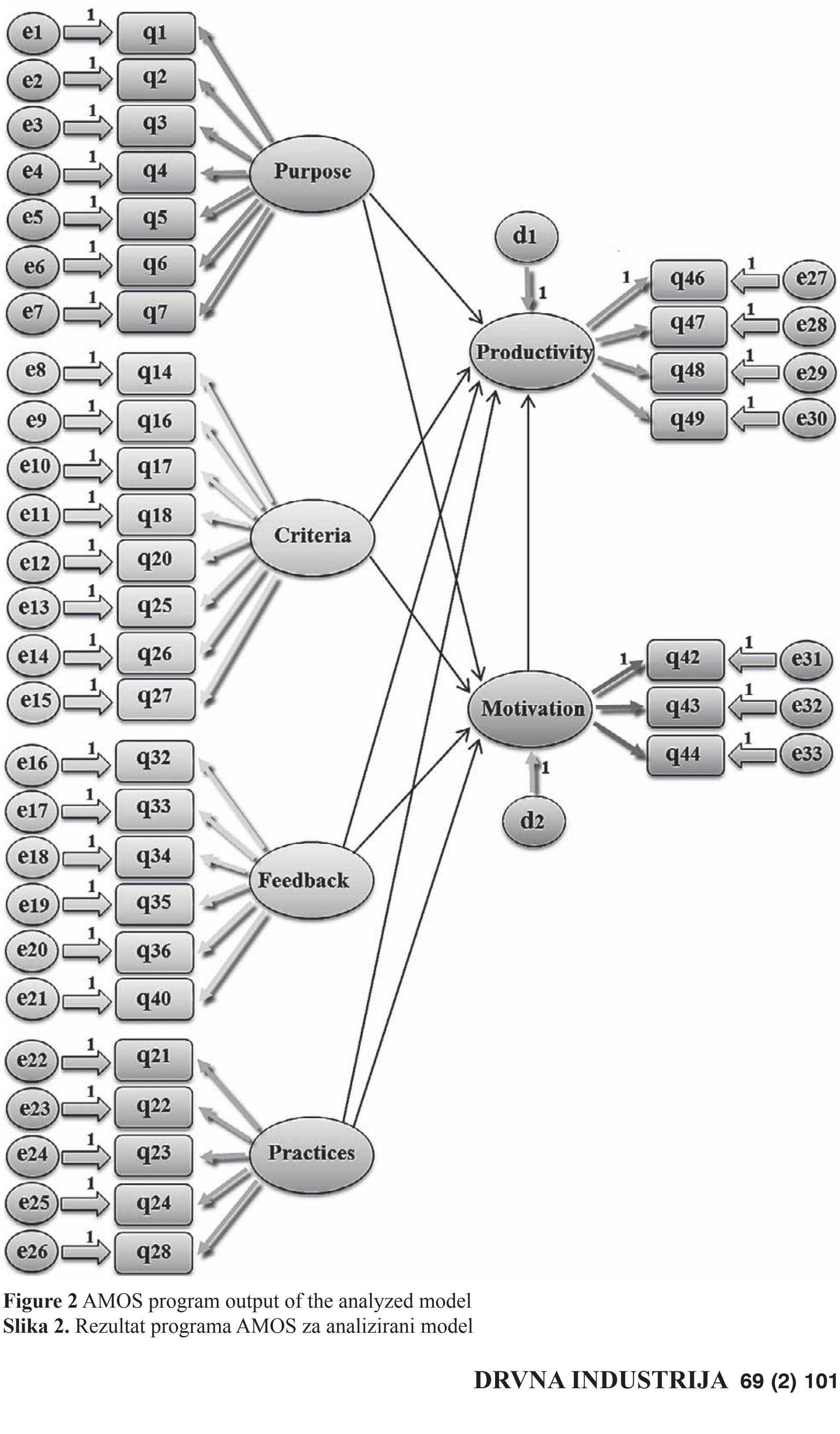

Figure 2 AMOS program output of the analyzed model
Slika 2. Rezultat programa AMOS za analizirani model

Table 6 Results of hypothesis tests
Tablica 6. Rezultati testiranja hipoteza

Hypothesis / *Hipoteza*		**Estimate (*r*)** *Procjena (r)*	**Decision** *Odluka*
$H_1$1:	Purpose of PA and employee motivation *Svrha ocjene rada i motivacija zaposlenika*	0.156	Rejected *odbijeno*
$H_1$2:	Criteria of PA and employee motivation *Kriteriji ocjene rada i motivacija zaposlenika*	0.276**	Supported *podržano*
$H_1$3:	Practices of PA and employee motivation *Prakse ocjene rada i motivacija zaposlenika*	-0.157*	Supported *podržano*
$H_1$4:	Feedback of PA and employee motivation *Povratne informacije o ocjeni rada i motiviranost zaposlenika*	0.278**	Supported *podržano*
$H_1$5:	Purpose of PA and employee productivity *Svrha ocjene rada i produktivnost zaposlenika*	0.187*	Supported *podržano*
$H_1$6:	Criteria of PA and employee productivity *Kriteriji ocjene rada i produktivnost zaposlenika*	0.005	Rejected *odbijeno*
$H_1$7:	Practices of PA and employee productivity *Prakse ocjene rada i produktivnost zaposlenika*	0.074	Rejected *odbijeno*
$H_1$8:	Feedback of PA and employee productivity *Povratne informacije o ocjeni rada i produktivnost zaposlenika*	-0.022	Rejected *odbijeno*
$H_1$9:	Employee motivation and employee productivity *Motivacija i produktivnost zaposlenika*	0.365*	Supported *podržano*

Note: $*p<0.05$, $**p<0.01$

When the results of the model were analyzed, it was seen that five of the nine hypothesis ($p<0.05$) were accepted, while four of them were rejected.

$H_1$1 examines the relationship between the purpose of PA and employee motivation. According to the model, there is no significant effect of the purpose of PA on employee motivation (estimate=0.156; $p>0.05$). Therefore, $H_1$1 hypothesis is rejected.

$H_1$2 examines the relationship between the criteria of PA and employee motivation. According to the model, there is a positive and significant impact of the criteria of PA on employee motivation (estimate=0.276; $p<0.05$). Therefore, $H_1$2 hypothesis is accepted. Accordingly, an increase of a standard unit in the criteria of PA constitutes an increase of 0.276 standard unit on employee motivation.

$H_1$3 examines the relationship between the practices of PA and employee motivation. According to the model, there is a negative and significant impact of the practices of PA on employee motivation (estimate=-0.157; $p<0.01$). Therefore, $H_1$3 hypothesis is accepted. Accordingly, an increase of a standard unit in the practices of PA constitutes a decrease of 0.157 standard unit on employee motivation.

$H_1$4 examines the relationship between the feedback of PA and employee motivation. According to the model, there is a positive and significant impact of the feedback of PA on employee motivation (estimate=0.278; $p<0.05$). Therefore, $H_1$4 hypothesis is accepted. Accordingly, an increase of a standard unit in the feedback of PA constitutes an increase of 0.276 standard unit on employee motivation.

$H_1$5 examines the relationship between the purpose of PA and employee productivity. According to the model, there is a positive and significant impact of the purpose of PA on employee productivity (estimate=0.187; $p<0.01$). Therefore, $H_1$5 hypothesis is accepted. Accordingly, an increase of a standard unit in the purpose of PA constitutes an increase of 0.187 standard unit on employee productivity.

$H_1$6 examines the relationship between the criteria of PA and employee productivity. According to the model, there is no significant effect of the criteria of PA on employee productivity (estimate=0.005; $p<0.05$). Therefore, $H_1$6 hypothesis is rejected.

$H_1$7 examines the relationship between the practices of PA and employee productivity. According to the model, there is no significant effect of the practices of PA on employee productivity (estimate=0.074; $p<0.05$). Therefore, $H_1$7 hypothesis is rejected.

$H_1$8 examines the relationship between the feedback of PA and employee productivity. According to the model, there is no significant effect of the feedback of PA on employee productivity (estimate=-0.022; $p<0.05$). Therefore, $H_1$8 hypothesis is rejected.

$H_1$9 examines the relationship between employee motivation and employee productivity. According to the model, there is a positive and significant impact of employee motivation on employee productivity (estimate=0.365; $p<0.01$). Therefore, $H_1$9 hypothesis is accepted. Accordingly, an increase of a standard unit in employee motivation constitutes an increase of 0.365 standard unit on employee productivity.

4 CONCLUSIONS
4. ZAKLJUČAK

In this study, the effects of PA applications applied in businesses that operate in the forest products industry on employee motivation and productivity were examined by means of a structural equation model. Upon analyzing the obtained results, it could be seen that the PA had a positive impact on employee productivity, while it did not have a significant impact on employee motivation. There was a positive effect of the criteria of PA on employee motivation, while there was no significant impact on employee productivity. There was a negative effect of the practices of PA on employee motivation, while there was no significant impact on employee productivity. The feedback studies in PA have been found to have a positive impact on employee motivation. However, it was shown that its impact on employee productivity was not significant. Besides, it was determined that employee motivation had a positive effect on employee productivity.

In the light of these results, the following suggestions have been made for the forest products sector.

- The purpose of the employee PA should be explained to the employees very thoroughly and thus their hesitations should be reduced or avoided. It should take into consideration that an increase in the employee motivation can be provided by using PA.
- PA criteria are required so that employees can reach achievable targets. Besides, it should be explained how to help the employees to provide the criteria. It should be noted that in this way an increase in employee productivity together with employee motivation can also be provided.
- In order to achieve the purpose of the PA, in making any decision about the employees, appraisal results should be used as the data source for education, career, job rotation, pricing, etc.
- By sharing the results of the PA studies with the employees, elimination of errors and deficiencies can be provided. In-service training activities can also be organized to solve employee errors.

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Corresponding address:

Assist. Prof. AYTAÇ AYDIN

Department of Forest Industry Engineering
Faculty of Forestry, Karadeniz Technical University
61080 Trabzon, TURKEY
e-mail: aytac@ktu.edu.tr

Rommel Crespo Gutiérrez[1], Luis Valenzuela[2], Hernán Poblete Wilson[3]

Mechanical Properties and Formaldehyde Release of Boards Manufactured with Hygrothermally Treated Tepa (*Laureliopsis Philippiana* Looser) Particles

Mehanička svojstva i oslobađanje formaldehida ploča proizvedenih od hidrotermički obrađenog iverja drva tepe (*Laureliopsis philippiana* Looser)

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ABSTRACT • *Three layer particleboards were manufactured using hygrothermally treated and untreated tepa (Laureliopsis philippiana) particles with urea-formaldehyde (UF) resin. Hygrothermal treatment consisted of autoclaving particles at 150 °C for 90 min (430 kPa) in a steam saturated atmosphere. A decrease in density and slenderness ratio in treated particles was observed. Modulus of elasticity (MOE) and modulus of rupture (MOR) in static bending, internal bond (IB), and formaldehyde release were determined. An increase in MOE, MOR and IB, as well as a decrease in formaldehyde release, was reported in boards made from heat treated particles.*

Key words: *Particleboard, hygrothermal treatment,* *Laureliopsis philippiana, urea-formaldehyde, particle geometry, mechanical properties, formaldehyde release*

SAŽETAK • *Za potrebe ovog ispitivanja proizvedene su troslojne ploče iverice od neobrađenoga i hidrotermički obrađenog iverja drva tepe (Laureliopsis philippiana) primjenom urea-formaldehidnog (UF) ljepila. Hidrotermička se obrada sastojala od zagrijavanja iverja pri 150 °C tijekom 90 minuta u atmosferi zasićenoj vodenom parom (pri tlaku 430 kPa). Nakon hidrotermičke obrade čestica uočeno je smanjenje gustoće i vitkosti čestica. Troslojnim su pločama ivericama određeni modul elastičnosti (MOE) i modul loma (MOR) pri statičkom savijanju, čvrstoća raslo-*

[1] Author is professor at School of Forest Engineering, Faculty of Environmental Sciences, State Technical University of Quevedo, Quevedo, Ecuador. [2]Author is professor at Department of Forest Management and Environment, Faculty of Forestry, University of Concepción, Concepción-Chile. [3] Author is a Contract Auditor for APA (The Engineered Wood Association), Valdivia-Chile.

[1] Autor je profesor Fakulteta znanosti o okolišu, Državno tehničko sveučilište u Quevedu, Quevedo, Ekvador. [2]Autor je profesor Odjela za gospodarenje šumama i okolišem, Šumarski fakultet, Sveučilište u Concepciónu, Concepción, Čile. [3]Autor je ugovorni revizor za APA-u (Društvo za obradu drva), Valdivia, Čile.

javanja (IB) i količina oslobođenog formaldehida. Za ploče izrađene od toplinski obrađenih čestica zabilježeno je povećanje mehaničkih svojstava (MOE, MOR) i čvrstoće raslojavanja te smanjenje količine oslobođenog formaldehida.

Ključne riječi: *ploča iverica, hidrotermička obrada, Laureliopsis philippiana, urea-formaldehid, geometrija čestica, mehanička svojstva, oslobođeni formaldehid*

1 INTRODUCTION
1. UVOD

The production of boards with *L. philippiana* particles using UF as adhesive does not produce favourable results. If an excess of catalysts is not used, bonding failures are produced in the core of the board, leading to blowout (Poblete and Peredo, 1990; Pinto and Poblete, 1992). The high pH value of this species prevents proper hardening of the adhesive (Poblete, 2001). Thermal treatment using pressurized vapour results in the formation of organic acids that catalyze the hydrolysis of hemicellulose, and to a lesser extent, amorphous cellulose (Mitchell, 1988). The formation of acetic and formic acids at temperatures between 100 and 200 °C reduces the pH value of wood (Garrote *et al.,* 1999; Nuopponen *et al*., 2004), encouraging the hardening of UF and improving mechanical properties.

The main objection to using thermally treated wood in the manufacturing of particleboards is the loss of mechanical strength. Paul and Ohlmeyer (2010) reported that the effects on the *MOE* in the boards are negligible, while the effects on IB strength, and particularly on *MOR*, are higher.

1.1 Effect of thermal treatment on mechanical properties of the boards
1.1. Utjecaj toplinske obrade na mehanička svojstva ploča

Thermal treatment of particles produces a 20 to 25 % increase in bending strength in boards manufactured with UF (Tomek, 1966). However, it has also been reported that *MOE*, *MOR* and density of thermally treated MDF decrease with increasing temperature (Ayrilmis *et al.,* 2009). Water steam treatment of particles and fibers at temperatures over 200 °C may result in a reduction of the wood-adhesive adhesion (Boonstra *et al.,* 2006), which reduces the IB of the boards (Mohebby *et al.,* 2008, Ayrilmis *et al.,* 2011), since thermal treatment may alter the adhesive distribution on the surface of the wood and the penetration within the porous structure of the wood (Sernek *et al.,* 2008). Paul *et al.* (2007) state that wood, usually hydrophilic, becomes hydrophobic after thermal treatment. The loss of mechanical properties can be related to the formation of soluble chemical products by the degradation of hemicellulose, such as formic acid and acetic acid, which accelerate the depolymerisation of carbohydrates (Garrote *et al.,* 2001; Sundqvist *et al*., 2006). The apparent contradictory results reported in the literature, may be because the thermal treatment of boards affects their whole structure and the interaction wood-adhesive-wood, degrading the adhesive bonds. Other important aspects are the temperature and conditions of thermal treatment employed. When high temperatures and pressures were employed, a higher degradation of the wood components is caused, reducing the mechanical properties.

1.2 Effect of thermal treatment on formaldehyde release
1.2. Utjecaj toplinske obrade na oslobađanje formaldehida

Roffael (2012) reported that, when defibration temperature is increased, it results in acidification of fibres and a reduction in the release of formaldehyde from MDF. Petersen *et al.* (1973) reported that particleboards manufactured from wood with low pH value emit lower quantities of formaldehyde than boards manufactured from wood with greater pH value.

1.3 Objectives
1.3. Ciljevi

The main objective of this study was to determine the effect of a hygrothermal treatment in steam saturated atmosphere on *L. philippiana* particles and the implications on properties of three layer particleboards. Specific objectives included the study of changes in particle geometry that can take place during gluing process. In particleboards, changes of *MOE* and *MOR* in static bending, IB, and formaldehyde release were determined.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Particles production and hygrothermal treatment
2.1. Proizvodnja iverja i hidrotermička obrada

L. philippiana wood was harvested from the XIV Region de Los Ríos near to the Andean mountains in Chile. The wood was cut into shavings and then, using a Pallmann PZ2 mill, particles were obtained. A quantity of the particles was treated in the autoclave at 150 °C for 90 min at 430 kPa pressure, in a steam saturated atmosphere.

2.2 Drying of particles
2.2. Sušenje iverja

Hygrothermally treated and non-treated particles were subjected to a drying process, in a Heraeus particle dryer with air circulation at 70 °C, until a moisture content of 4 % was reached.

2.3 Particle properties: dimensions, slenderness ratio, specific surface area and available adhesive quantity
2.3. Svojstva čestica: dimenzije, vitkost, specifična površina i raspoloživa količina ljepila

In order to quantify changes caused by the treatment, particles were subjected to the mechanical action of the blender without adhesive. After this procedure, 120 g of particles were sieved in a Retsch sieving machine using mesh size of 4.0, 2.8, 2.0, 1.4, 1.0, 0.5 and <0.5 mm. Each particle class was weighed to determine the proportional participation. In 30 particles of every class, length and thickness were determined using a micrometer and caliper. Basic density of the particles according to TAPPI T 258 om-94 was calculated. With the particle length, thickness and density data, slenderness ratio (Poblete and Peredo, 1990), specific surface area and available adhesive quantity (Poblete, 2001) were determined by the formulae:

$$\text{Specific surface area } (m^2/100g) = \frac{0.2}{\text{Thickness (mm) x Density } (g/cm^3)}$$

$$\text{Avaliable adhesive } (g/m^2) = \frac{\text{Density } (g/cm^3) \text{ x Thickness (mm) x Gluing factor (\%)}}{0.2}$$

2.4 Board manufacturing
2.4. Proizvodnja ploča

Hygrothermally treated and untreated *L. philippiana* particles were employed. The percentage of wood in the outer layer was 30 % and in the inner layer 70 %. UF (50 % solid) produced by Georgia Pacific Corp. with a molar ratio of 1:1.22 was applied as adhesive. This is a high emission resin, and was used without formaldehyde scavenger and without hardener in order to best determine the variation in formaldehyde release due to hygrothermal treatment. Particleboards with nominal densities of 600, 625, 650, 675 and 700 $kg \cdot m^{-3}$, with dimensions of 53 x 53 cm and 15 mm thickness were produced. The adhesive was applied at 8 % loading (dry basis) spraying it in a Drais FSP-80 blender. Pressing was conducted in a Bürkle LA-160 press at a temperature of 180 °C for 180 s. The maximum pressure used was 3 $N \cdot mm^{-2}$ for 30 s and half pressure of 1.5 $N \cdot mm^{-2}$ for 150 s. Two boards were produced for each nominal density, a total of 10 boards with non-treated particles and 10 boards with treated particles.

2.5 Mechanical properties of the boards
2.5. Mehanička svojstva ploča

Density (EN 323, 1993), *MOE* and *MOR* in static bending (EN 310, 1993), and *IB* (EN 319, 1993) were determined. The mechanical properties were carried out in a Metrotec HM-D/200 universal testing machine. The rate of loading was adjusted so that the maximum load was reached within 60 ± 30 s. The number of test specimens by treatment obtained in all board series for static bending (*MOE* and *MOR*) was 100 and for IB 90. The density was determined for every test specimen.

2.6 Formaldehyde release
2.6. Oslobođeni formaldehid

This was conducted according to the perforator method (EN 120, 1992). Three samples of the average nominal board density were analysed.

The perforator value was corrected in accordance with EN 312 (2010).

2.7 Statistical analysis
2.7. Statistička analiza

A simple linear regression analysis was conducted, relating each mechanical property to the density of the respective test specimen. Additionally, an analysis of variance was conducted with a 99 % confidence interval (p <0.01) (statistical program *R*), to determine differences among averages of properties. In the case of formaldehyde release determinations, because of the amount of tests, no statistical analysis was done, and for the results and discussion, the average of the three tests was considered.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Particle geometry, specific surface area and quantity of available adhesive
3.1. Geometrija čestica, specifična površina i količina raspoloživog ljepila

The change of the particles geometry comes along with a change in the slenderness ratio, specific surface area and available amount of adhesive. This modification of the geometry could have an effect on panel properties. As reported by Klauditz (Ginzel and Peraza, 1966) for the determination of the slenderness ratio, specific surface area of the particles and the available amount of adhesive, it is necessary to characterize the particles through the determination of basic density, thickness and length. The average weighted in accordance to the weight proportion of the particles in each sieve mesh for hygrothermally treated and untreated particles is presented in Table 1.

Table 1 Basic density, thickness, length, slenderness ratio, specific surface area and amount of available adhesive for hygrothermally treated and untreated *L. philippiana* particles
Tablica 1. Nominalna gustoća, debljina, duljina, vitkost, specifična površina i količina raspoloživog ljepila za hidrotermički obrađeno i neobrađeno iverje drva *L. philippiana*

Particles *Iverje*		**Basic density** *Nominalna gustoća* $kg \cdot m^3$	**Thickness** *Debljina* mm	**Length** *Duljina* mm	**Slenderness Ratio** *Vitkost iverja*	**Specific surface area** *Specifična površina* $m^2/100$ g	**Available adhesive** *Raspoloživo ljepilo* g/m^2
Surface Layer *Vanjski sloj*	Untreated *neobrađeno*	442	0.63	6.75	11.19	0.72	11.18
	Thermally treated *termički obrađeno*	428	0.60	6.48	10.85	0.78	10.25
Core Layer *Unutarnji sloj*	Untreated *neobrađeno*	442	0.90	14.55	16.00	0.50	15.98
	Thermally treated *termički obrađeno*	428	0.88	13.80	15.75	0.53	15.12

Table 2 Analysis of variance of the mean values of mechanical properties of boards manufactured with hygrothermally treated and untreated *L. philippiana* particles
Tablica 2. Analiza varijance vrijednosti mehaničkih svojstava ploča proizvedenih od hidrotermički obrađenoga i neobrađenog iverja drva *L. philippiana*

Mechanical property *Mehaničko svojstvo*	**Analysis of variance** / *Analiza varijance*						
	Untreated / *Neobrađeno*			**Hygrothermally treated** *Hidrotermički obrađeno*			***p*-value**
	$\bar{x}$ N·mm^{-2}	***sd*** N·mm^{-2}	cv %	$\bar{x}$ N·mm^{-2}	***sd*** N·mm^{-2}	**cv** %	
MOE in static bending / *MOE pri statičkom savijanju*	2023	386.5	19.11	3285	457.4	45.28	0.000*
MOR in static bending / *MOR pri statičkom savijanju*	12.62	3.07	24.34	20.03	3.81	19.00	0.000*
IB	0.24	0.18	76.41	0.47	0.15	31.39	0.000*

$\bar{x}$– mean / *srednja vrijednost*; *sd* – standard deviation / *standardna devijacija*; *cv* – coefficient of variation / *koeficijent varijacije*; * – Significant at *p* <0.01 / *signifikantno pri p<0,01*.

The results of hygrothermal treatment showed a decrease in the basic density of particles. As a consequence, thermally untreated particles presented a larger quantity of available adhesive, as total grams of adhesive per surface, square meter of particles. The decrease in the basic density of particles agrees with the decrease in density reported by other investigators (Schmidt, 1982; Feist and Sell, 1987). This effect is due to the thermal degradation of wood components, such as deacetylation of hemicellulose and lignin condensation, and to the lower equilibrium moisture content, since thermally treated wood becomes hydrophobic (Boonstra *et al.,* 2007).

Thickness and specific surface area of the particles did not change. Length, and hence slenderness ratio, decreased. This decrease was more significant in larger particles. Generally, it can be concluded that during the mechanical action of the gluing machine, it is the larger particles that undergo a reduction in size. The decrease in length of the particles may cause a change in the mechanical properties of the boards, causing a reduction of *MOE* and *MOR*, and increasing IB.

3.2 Mechanical properties of the boards
3.2. Mehanička svojstva ploča

Table 2 shows the averages, standard deviation, coefficient of variation and p values, according to the analysis of variance for boards manufactured with hygrothermally treated and untreated particles. The mechanical properties of the boards manufactured with hygrothermally treated and untreated particles present significant differences (*p* <0.01). The strength of the boards in static bending is correlated with the quality of the bonds achieved on the surface of the boards (Poblete, 2001).

The linear regression analysis registered significance at *p*<0.01. Coinciding with previous studies, when the density of the boards increased, the *MOE* and *MOR* also increased (Poblete, 2001). The regression analysis for the relationship between density and *MOE*

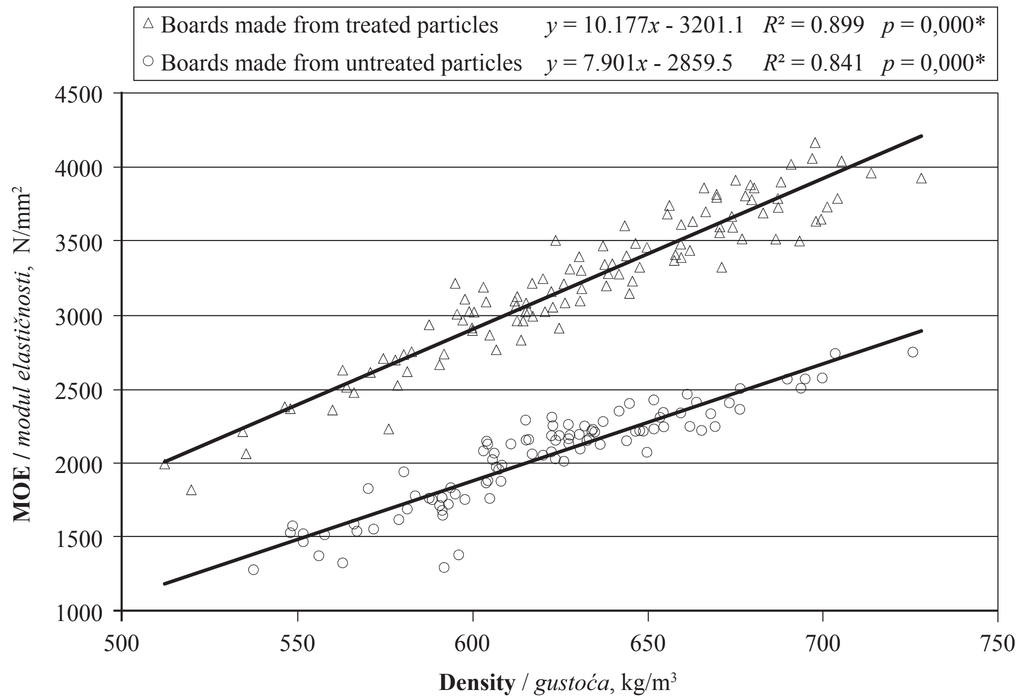

Figure 1 Relationship between *MOE* and density in *L. philippiana* boards manufactured with hygrothermally treated and untreated particles
Slika 1. Odnos modula elastičnosti i gustoće ploča proizvedenih od hidrotermički obrađenoga i neobrađenog iverja drva *L. philippiana*

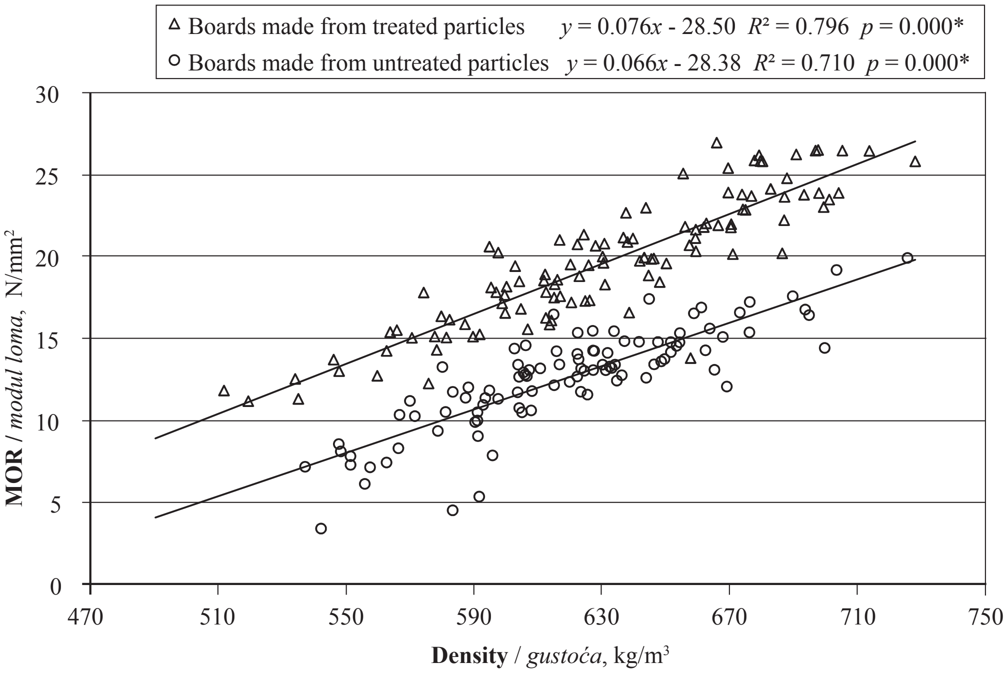

Figure 2 Relationship between *MOR* and density in *L. philippiana* boards manufactured with hygrothermally treated and untreated particles
Slika 2. Odnos modula loma i gustoće ploča proizvedenih od hidrotermički obrađenoga i neobrađenog iverja drva *L. philippiana*

is shown in Figure 1, and the relationship between density and *MOR* in Figure 2.

The regression for the relationship between density and *IB* is presented in Figure 3. Correlations were significant at p <0.01. *IB* is directly related with the bond quality of the particles in the core of the board (Poblete and Burgos, 2010). The results confirm the strong relationship between board density and *IB*, reported in many studies (Kollmann *et al*., 1975; Poblete, 1985; Poblete, 2001; Poblete and Burgos, 2010).

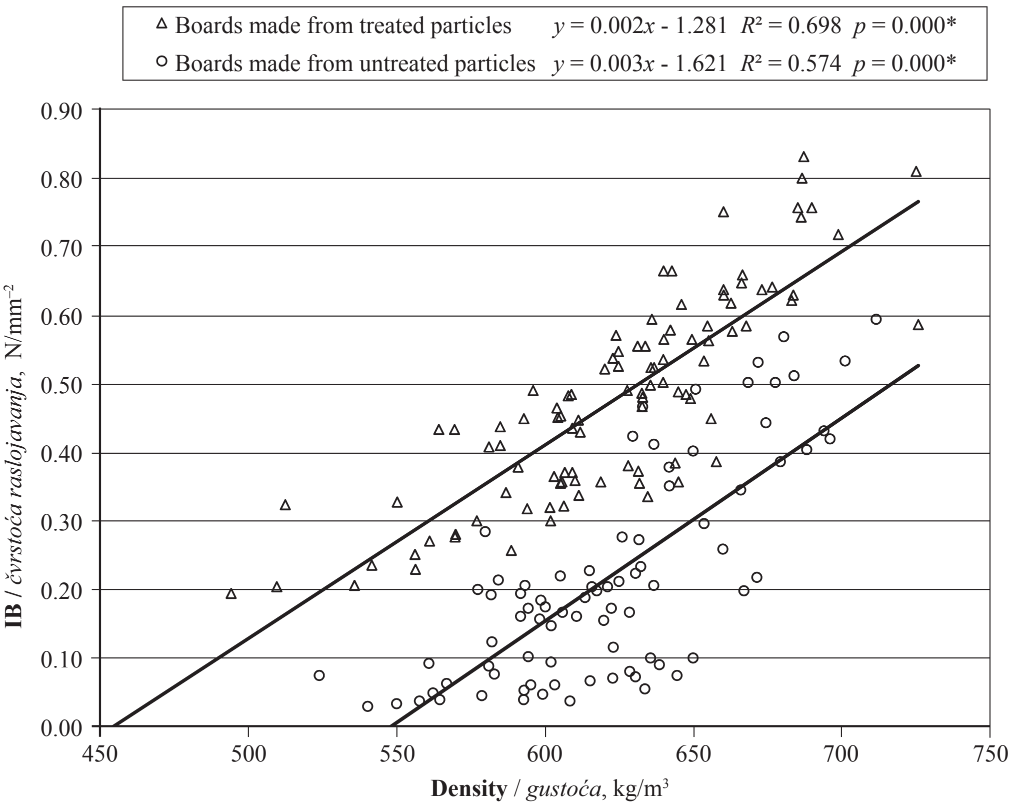

Figure 3 Relationship between density and *IB* of *L. philippiana* boards manufactured with hygrothermally treated and untreated particles
Slika 3. Odnos gustoće i čvrstoće raslojavanja ploča proizvedenih od hidrotermički obrađenoga i neobrađenog iverja drva *L. philippiana*

Table 3 Formaldehyde release average with and without moisture content correction
Tablica 3. Prosječna vrijednost oslobođenog formaldehida s korekcijom sadržaja vode i bez korekcije

Particles *Iverje*	**Equilibrium moisture content** *Ravnotežni sadržaj vode* %	**Formaldehyde release** / *Oslobođeni formaldehid* **mg/100 g**	
		Uncorrected value *Nekorigirana vrijednost*	**Corrected value** *Korigirana vrijednost*
Untreated / *Neobrađeno*	8.2	17.1	13.2
Thermally treated / *Toplinski obrađeno*	6.2	9.8	10.1

According to the analysis of variance, boards manufactured with treated *L. philippiana* particles presented better mechanical properties. In the static bending, the *MOE* increased by 38.4 %, while the *MOR* increased by 37.0 %. *IB* increased by 48.9 %. The increase in *MOE*, *MOR* and *IB* is in agreement with values reported by other studies (Tomek, 1966; Kakaras and Papadopoulos, 2004; Çolak *et al.,* 2007). When determining mechanical properties of particleboards, the wood-adhesive-wood interaction is evaluated, which is influenced by the type of adhesive and the environment in which it hardens. The pH value is what determines the success or failure of the bond. In a previous work about the effect of hygrothermal treatment on the chemistry of the same *L. philippiana* particles (Crespo *et al.,* 2013), a pH value of non-treated particles near neutral (6.7) was reported. This condition could inhibit UF curing if a hardener is not used. It should be noted that in this study a hardener was not applied. Pinto and Poblete (1992) studied *L. philippiana* particles, and acidified the environment with the addition of a catalyst, with positive effects on mechanical properties.

Çolak *et al.* (2007) have confirmed that the pH values of the particles obtained from vaporized logs decrease, generating an optimum pH environment during the curing of UF, and increasing the IB of the boards. Crespo *et al.* (2013) reported for the same *L. philippiana* particles that hygrothermal treatment decreased the pH value from 6.7 to 4.8, while the quantity of volatile acids, water soluble acids and buffering capacity, increased. These changes allow for better hardening of UF and a better wood-adhesive-wood bond, which explains the increase in bending strength properties and IB in the tested boards (Roffael and Parameswaran, 1986; Roffael, 1987).

The decrease in length and slenderness ratio in thermally treated particles observed in the current study may have also influenced the increase in IB of the boards. Coincidentally, Kakaras and Papadopoulos (2004) reported that treated particles produced an increase in the proportion of smaller particles, which is associated with an increase in IB. In the current study, considering that *MOE* and *MOR* increased, the contribution of the particles size reduction to the increase of IB is less than the change in acidity.

3.3 Formaldehyde release
3.3. Oslobađanje formaldehida

Table 3 shows the average values of formaldehyde release (perforator value) with and without moisture content correction.

The equilibrium moisture of the boards following acclimatization was different, and according to the standard (EN 312, 2010), the release value should be adjusted considering this parameter. Determinations with and without moisture content adjustments show that the hygrothermal treatment decreased the release of formaldehyde. Giebeler (1983) confirmed that, after the treatment of wood with moisture, heat and pressure, the most important improvement is the decrease by over 50 % in formaldehyde release of particleboards. Petersen *et al.* (1973) reported that boards manufactured from species with lower pH values (3.8) released less formaldehyde than boards made from species with higher pH values (4.8 and 5.5). There was no correction by moisture content of the boards reported in either of these studies. The results of Petersen *et al*. (1973) support that the decrease in the pH value of hygrothermally treated particles of *L. Philippiana,* which was reported by Crespo *et al*. (2013) in a former study, reduce the formaldehyde release of boards made from these particles.

Roffael (2012) reported that, when working with MDF manufactured with UF, an increase in defibration temperature from 140 to 175 °C results in a positive effect on formaldehyde release, which is attributed to the higher acidity of the thermo-mechanical pulp produced at 170 °C. Colak and Colakoglu (2004) claim that the acetic acid generated from the hydrolysis of non-cellulose polysaccharide acetyl groups reacts with the free formaldehyde in the resin, fixing this compound. As reported by Crespo *et al.* (2013) in a former study with the same particles of *L. philippiana*, hygrothermal treatment of particles increases the amount of volatile acids, water soluble acids and buffering capacity, significantly reducing the pH value. Considering the results of the current study, it can be confirmed that the reduction in formaldehyde release in boards manufactured with hygrothermally treated particles is due to the reduction in pH value, to the production of acids, and consequently to better setting of the UF.

4 CONCLUSIONS
4. ZAKLJUČAK

Hygrothermal treatment of *L. philippiana* wood particles resulted in lower basic density, length, slenderness ratio and quantity of available adhesive, while the specific surface area increased relative to untreated particles. The hygrothermal treatment increases mechanical properties in particleboards, while decreasing formaldehyde release. This effect is due to an acidification of the particles and an increase in the amount of extractable compounds. Overall, hygrothermal treatment of *L. philippiana* particles at 150 ºC for 90 min at the pressure of 430 kPa is a good alternative to improve mechanical properties, as well as to reduce formaldehyde release in particle boards manufactured from this species.

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Corresponding address:

Prof. ROMMEL CRESPO, Ph.D.

Universidad Técnica Estatal de Quevedo
QUEVEDO, ECUADOR.
e-mail: rscgtexcmex@hotmail.com

Miha Humar[1], Boštjan Lesar[1], Nejc Thaler[1], Davor Kržišnik[1], Nace Kregar[2], Simon Drnovšek[2]

Quality of Copper Impregnated Wood in Slovenian Hardware Stores

Kvaliteta drva impregniranoga bakrom u slovenskim trgovinama građevnog materijala

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ABSTRACT • *Ten different samples from Slovenian hardware stores were analysed. Samples were treated with copper based wood preservatives that were designed and advertised to be used in heavy duty applications in ground (use classes 4) and above ground (use classes 3.2). Retention and fungicidal properties were determined in order to establish the quality of treatment quality. Retention was determined by XRF analysis, while a modified EN 113 procedure was applied for the assessment of fungicidal properties. Two brown rot fungal species, Gloeophyllum trabeum and Fibroporia vaillantii, were used for durability testing. The results of the analysis clearly showed that only three of the inspected wood products met penetration requirements, and none of them had sufficient retention, which is also reflected in insufficient durability against wood decay fungi.*

Keywords: *wood, impregnation, penetration, quality control, degradation*

SAŽETAK • *Za potrebe ovog rada analizirano je deset različitih uzoraka iz slovenskih prodavaonica građevnog materijala. Uzorci su tretirani zaštitnim sredstvima na bazi bakra namijenjenim i preporučenim za zahtjevne uvjete primjene u tlu (uporabna klasa 4) i iznad tla (uporabna klasa 3.2). Određeni su retencija i fungicidna svojstva tih sredstava kako bi se utvrdila kakvoća zaštite drva. Retencija zaštitnog sredstva određena je uz pomoć XRF analize, dok je modificirani postupak EN 113 primijenjen za procjenu fungicidnih svojstava zaštitnih sredstava. Za testiranje trajnosti poslužile su dvije vrste gljivica smeđe truleži, Gloeophyllum trabeum i Fibroporia vaillantii. Rezultati analize jasno su pokazali da su samo na tri istraživana drvna proizvoda bili ispunjeni zahtjevi penetracije zaštitnog sredstva, a ni na jednome drvnom uzorku nije postignuta dovoljna retencija zaštitnog sredstva, što se očituje i nedostatnom trajnošću drva izloženoga djelovanju gljiva truležnica.*

Ključne riječi: *drvo, impregnacija, penetracija, kontrola kvalitete, degradacija*

1 INTRODUCTION
1. UVOD

The importance of wood in Europe is increasing and more and more wood is used in outdoor applications (Lacič *et al.,* 2014). Unfortunately, there are not many durable wood species available in Europe (Despot, 1998; Brischke, 2013). Hence, wood has to be protected in some way if used in outdoor applications. Since the majority of alternative wood preservatives have been banned (Regulation 528/2012), copper based preservatives are among the few alternatives that are suitable for protection of wood in outdoor applications (Humar *et al.,* 2001; Connell, 2004). However, as small customers are not able (or willing) to perform

[1] Authors are professor, assistant professor, assistant professor and PhD student at University of Ljubljana, Biotechnical Faculty, Ljubljana, Slovenia. [2]Authors are engineers employed in Bureau Veritas, Ljubljana, Slovenia.
[1] Autori su profesor, docent, docent i doktorand Sveučilišta u Ljubljani, Biotehnički fakultet, Ljubljana, Slovenija. [2]Autori su zaposlenici tvrtke Bureau Veritas, Ljubljana, Slovenija.

Table 1 Materials purchased in seven hardware stores in spring 2015.
Tablica 1. Materijali kupljeni u sedam trgovina građevnog materijala u proljeće 2015.

Abbre-viation *Oznaka*	**Form** *Oblik*	**Wood species** Vrsta drva	**Declared dimension** *Deklarirane dimenzije*	**Actual dimension** *Stvarne dimenzije*	**Price** / *Cijena*	
			mm	mm	€/piece	€/m³
A	Batten / *letva*	Scots pine / *obični bor*	90 × 90 × 1000	85 × 85 × 1000	5.59	690
B	Post / *stup*	Scots pine / *obični bor*	Φ 80 ×× 1250	Φ 76 × 1250	3.29	548
C	Post / *stup*	Scots pine / *obični bor*	Φ 60 ×× 1500	Φ 55 × 1470	2.89	723
D	Post / *stup*	Norway spruce / *visoka smreka*	Φ 80 ×× 1250	Φ 80 × 1250	4.99	792
E	Post / *stup*	Scots pine / *obični bor*	40 ×× 40 ×× 1500	40 × 40 × 1500	1.99	829
F	Batten / *letva*	Scots pine / *obični bor*	70 × 70 × 1000	66 × 66 × 1000	3.98	812
G	Batten / *letva*	Norway spruce / *visoka smreka*	50 × 70 × 2000	49 × 68 × 2000	5.69	813
H	Batten / *letva*	Scots pine / *obični bor*	70 × 70 × 1000	69 × 69 × 1000	4.15	847
I	Batten / *letva*	Norway spruce / *visoka smreka*	35 × 85 × 945	35 × 85 × 945	2.44	871
J	Post / *stup*	Norway spruce / *visoka smreka*	Φ 80 × 1300	Φ 80 × 1300	4.50	692

protection at home, they usually use wood from hardware stores. Unfortunately, this wood is not subjected to quality control protocols, so the quality of the impregnated wood does not always meet standards.

Quality control of wood in Europe is based on several standards. The essential one is EN 351-1 (CEN, 2007). This standard prescribes the penetration classes and the treated zone. There are six penetration classes defined, ranging from NP1 (no requirements) to NP6 (full sapwood penetration and 6 mm penetration to exposed heartwood). End users usually require spruce wood to meet penetration class NP3 (penetration of 6 mm), while penetration class NP5 (full sapwood penetration) is required for Scots pine wood. In contrast to penetration, end users and specifiers usually prescribe retention. The retention requirement is the uptake of the formulation/active ingredients, expressed in kg per m^3 of wood in the treated zone. This information is usually based on extensive field testing based on standard EN 599-1 (CEN, 2009), which prescribes which tests need to be performed for a particular use class. The list provided by the Nordic Wood Preservation Council (2008, 2015) is the reference most frequently applied by end users to prepare requirements for orders of impregnated wood. If wood is not treated correctly, failures can appear (Humar and Thaler, 2017), which leads to a bad reputation of wood preservation in general.

This research was performed in order to elucidate the quality of impregnated wood from hardware stores. Ten samples of copper treated wood that was advertised as being suitable for use in heavy-duty applications were purchased and analysed for suitability in outdoor applications.

2 MATERIAL AND METHODS
2. MATERIJAL I METODE
2.1 Material
2.1. Materijal

Ten different products were purchased in the period between March and April 2015 in seven hardware stores (Table 1 Materials purchased in seven hardware stores in spring 2015.). Each product consisted of three individual pieces-specimens. Specimens in the shop were selected at random. Wood was declared to be suitable for above- and in-ground applications. In addition, the shape of the posts clearly showed the potential use, and the colour and the declaration also clearly indicated that the wood had been treated with copper based preservatives.

The purchased material was marked and conditioned in the laboratory prior to analysis. Impregnated wood was cut into specimens suitable for further analysis, as explained in the following subchapters.

2.2 Methods
2.2. Metode

The quality of treatment is determined by the penetration and retention of the active ingredients (CEN, 2007). In order to elucidate these parameters, the poles and battens were cut into 3 cm thick cylinders. The first cylinder was located 10 cm from the edge. Cylinders were numbered. Odd numbered cylinders were used for penetration and retention analysis, while even numbered cylinders were used for durability testing. There were five cylinders per post used for penetration and retention and five for durability tests.

Penetration was determined visually. The depth of copper penetration was estimated on transverse planes, with a 1 % aqueous solution of potassium hexacyanoferrate being used as the colour reagent for copper. Even wood impregnated with a lower concentration of copper turned brown in the presence of this reagent (Humar and Lesar, 2009). In addition, samples were scanned. The penetration of other active ingredients was not determined. Average values were calculated based on eight individual measurements performed in every respective sample.

In order to determine retention and to confirm the penetration studies, the cylinders were cut into thin layers; 0-2 mm, 2-5 mm and 5-12 mm in depth, for elemental XRF analysis. Layers were cut from outer part to central part. The dimensions of the layers were determined based on a visual assessment of penetration. Each layer was milled in a SM 2000 Retch mill (Retch GmbH; Haan, Germany) and five parallel tablets (r = 16 mm; h = 5 mm) were pressed from the milled material with a Chemplex Sprectro pellet press (Chemplex Industries Inc., USA). The copper and chromium con-

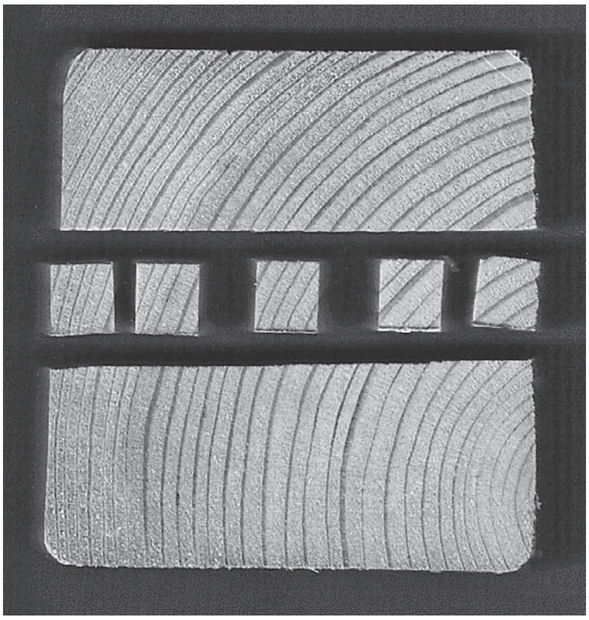

Figure 1 Position of the samples for durability testing. The outer specimens were used for assessment of fungicidal properties

Slika 1. Mjesto s kojega su uzeti uzorci za ispitivanje trajnosti; vanjski uzorci upotrijebljeni su za procjenu fungicidnih svojstava

tent in the tablets was determined with a Twin-X XRF spectrometer (XRF TwinX, Oxford instruments, UK). Measurements were performed with a PIN detector (U = 26 kV, I = 112 µA, t = 360 s). In addition, copper retention was determined on matched specimens to those used for determination of fungicidal properties. From the copper content in treated wood, individual retentions were calculated based on the chemical composition of the most frequently used preservative solutions in the region. Retention is expressed as the average value of at least ten individual measurements.

A decay test was performed according to a modified EN 113 (CEN, 2006) standard protocol using specimens from all posts/battens as follows. Disposable Petri dishes (Φ = 85 mm, h = 15 mm) containing 20 mL of 4 % potato dextrose agar (PDA, Difco, NJ, USA) were inoculated with two brown rot fungal species: *Gloeophyllum trabeum* (Pers.) Murrill (ZIM L018) and *Fibroporia vaillantii* (DC.) Parmasto (ZIM L037). The fungal isolates originated from the fungal collection of the Biotechnical Faculty, University of Ljubljana and are available to research institutions on demand (Raspor *et al*., 1995). *G. trabeum* was chosen because it is one of the most important softwoods degrading fungi and is considered to be copper sensitive. In contrast, *F. vaillantii* was chosen as a copper tolerant fungal strain. A plastic mesh was used to avoid direct contact between the samples and the medium. The assembled test dishes were then incubated at 25 °C and 80 % relative humidity (RH) for 12 weeks. Specimens of dimensions 10 mm × 10 mm × 20 mm were prepared and 5 replicates per fungal species were used for each group of treated woods (300 specimens in total). Specimens were made of the outer better-impregnated sapwood. Untreated Norway spruce and Scots pine specimens served as reference wood species to assess the validity of the test. After incubation, the fungal mycelium was removed and the samples were weighed to determine moisture content. After 24 hours of drying at 103 °C, mass loss was determined gravimetrically.

3 RESULTS AND DISCUSION
3. REZULTATI I RASPRAVA

XRF analysis confirmed the visual inspection that all of the treated wood used in this research had been treated with copper amine based wood preservatives. Selection of the preservative is in line with the intended use of the treated wood. Copper based wood preservatives are the most important option suitable for protection of wood in ground contact (Preston, 2000). However, as can be seen from the visual appearance of the cross-sections shown in Figure 2, the penetration of copper in most of the analysed treated wood does not meet the requirements. End users usually prescribe penetration class NP3 (penetration of at least 6 mm) for spruce wood and NP5 (full sapwood penetration) for Scots pine wood for in-ground applications. As can be seen from Table 2, only three samples met the penetration criteria. The copper penetrated more than 6 mm deep with sample G, made of Norway spruce wood. The other two samples were made of Scots pine wood (H and J). Since we did not perform analysis of the wood before impregnation, we were unable to determine the reasons for insufficient penetration. There are probably two main reasons: too high moisture content of wood before impregnation and/or inappropriate impregnation procedure (Wilkinson, 1979). As sometimes even the sapwood of refractory Scots pine sapwood was not fully impregnated, we presume that the anatomical features and presence of heartwood are not the key reasons for insufficient penetration and retention. However, inappropriate treatment results in the premature failure of wood (Humar and Thaler, 2017) and could negatively influence the public perception of wood preservation.

In addition to penetration, retention also determines the quality of the impregnated wood, so retention was determined in the second step. Retention of copper based wood preservatives in use class 3 (above-ground, uncovered) should exceed 8 kg/m^3; however, for in-ground applications (use class 4), retention of 16 kg/m^3 is required. As can be seen in Table 2, only one batten exceeded the limit for use class 3 conditions (sample G), while none of the posts met the criteria for use class 4 conditions.

Analysis of the retention in different layers indicated that the retention of active ingredients in the outer layers (outer 2 mm) exceeded the criteria for use class 3 conditions with 70 % of the samples (Figure 3 Retention of copper based wood preservatives in different layers of analysed impregnated wood. Grey lines indicate prescribed retention levels for use classes 3 and 4.). However, retention and, consequently, the copper concentration in inner layers decreased significantly with the majority of samples. This indicates that the concentra-

Table 2 Penetration and retention of copper based wood preservatives in the analysed impregnated wood (Values in bold indicate that the analysed treated wood meets the appropriate criteria. Standard deviation is given in parenthesis)
Tablica 2. Penetracija i retencija zaštitnog sredstva na bazi bakra u analiziranome impregniranom drvu (zadebljane vrijednosti pokazuju da analizirano zaštićeno drvo zadovoljava odgovarajuće kriterije; standardna odstupanja navedena su u zagradama)

Abbreviation *Oznaka*	**Form** *Oblik*	**Wood species** *Vrsta drva*	**Criteria** / *Kriteriji*	
			Penetration / *Penetracija* mm	**Retention** / *Retencija* kg/m^3
A	Batten / *letva*	Scots pine / *obični bor*	1.0	1.1 (0.2)
B	Post / *stup*	Scots pine / *obični bor*	7.7	4.7 (0.2)
C	Post / *stup*	Scots pine / *obični bor*	11.3	12.3 (0.5)
D	Post / *stup*	Norway spruce / visoka smreka	4.3	1.8 (0.1)
E	Post / *stup*	Scots pine / *obični bor*	5.0	5.6 (0.1)
F	Batten / *letva*	Scots pine / *obični bor*	14.7	4.4 (0.1)
G	Batten / *letva*	Norway spruce / *visoka smreka*	**6.3**	7.9 (0.3)
H	Batten / *letva*	Scots pine / *obični bor*	**21.7**	2.9 (0.1)
I	Batten / *letva*	Norway spruce / *visoka smreka*	3.7	7.2 (0.1)
J	Post / *stup*	Norway spruce / *visoka smreka*	**28.3**	12.6 (0.3)

tion of active ingredients in the preservative solution was sufficient but the procedure applied was inadequate or the moisture content of the wood was too high. However, with samples A, D and H, even the retention in the outer 2 mm did not exceed 5 kg/m^3, which is a catastrophic combination together with low retention.

In the final step, the efficiency of wood treatment against wood decay fungi was determined. Since all of the treated samples were made from conifers, only brown rot fungi were used. *G. trabeum* is a typical copper sensitive brown rot fungus. On the other hand, *F. vaillantii* has been proven to be a copper tolerant strain

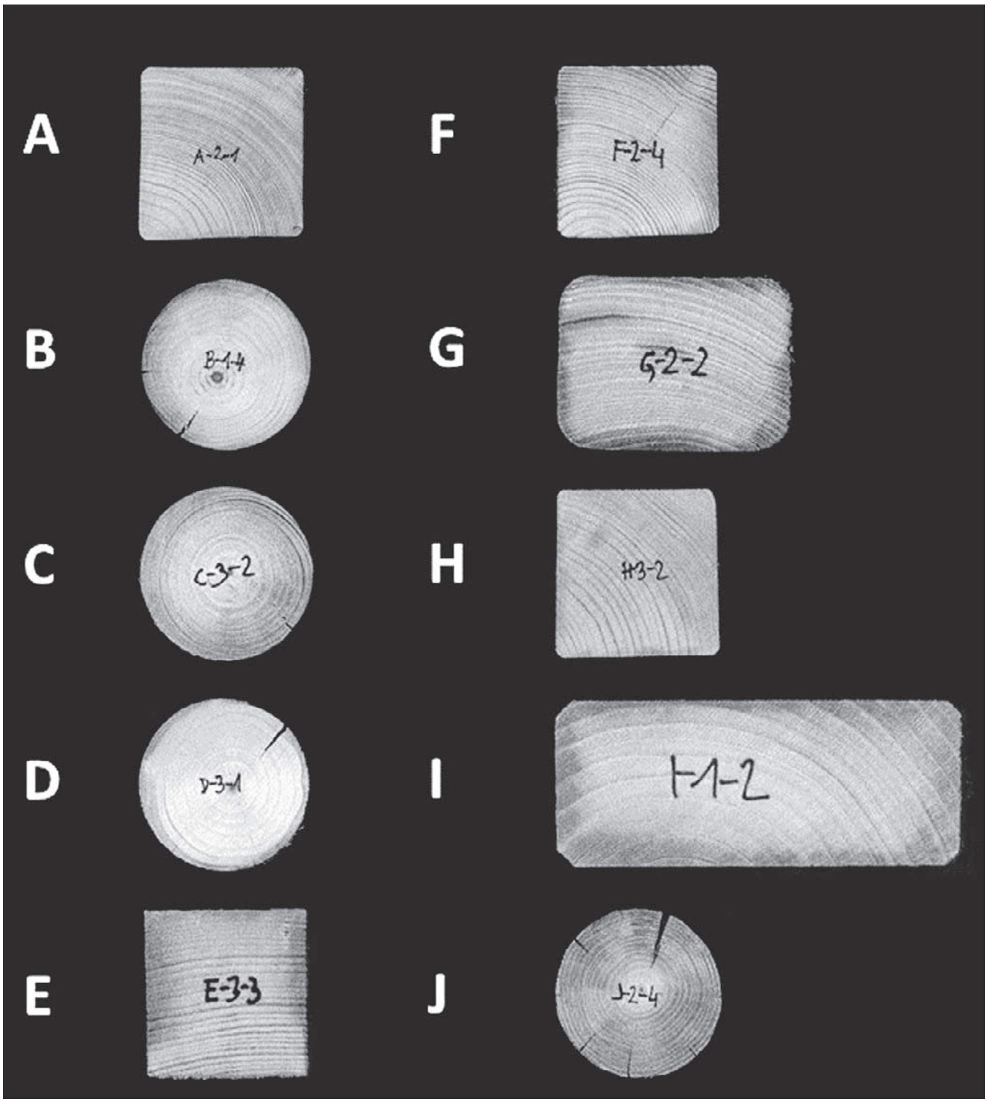

Figure 2 Cross-sections of analysed wood. The cross-sections are not in scale. Dimensions can be seen in Table 1
Slika 2. Presjeci analiziranog drva (poprečni presjeci nisu u mjerilu; dimenzije se mogu vidjeti u tablici 1.)

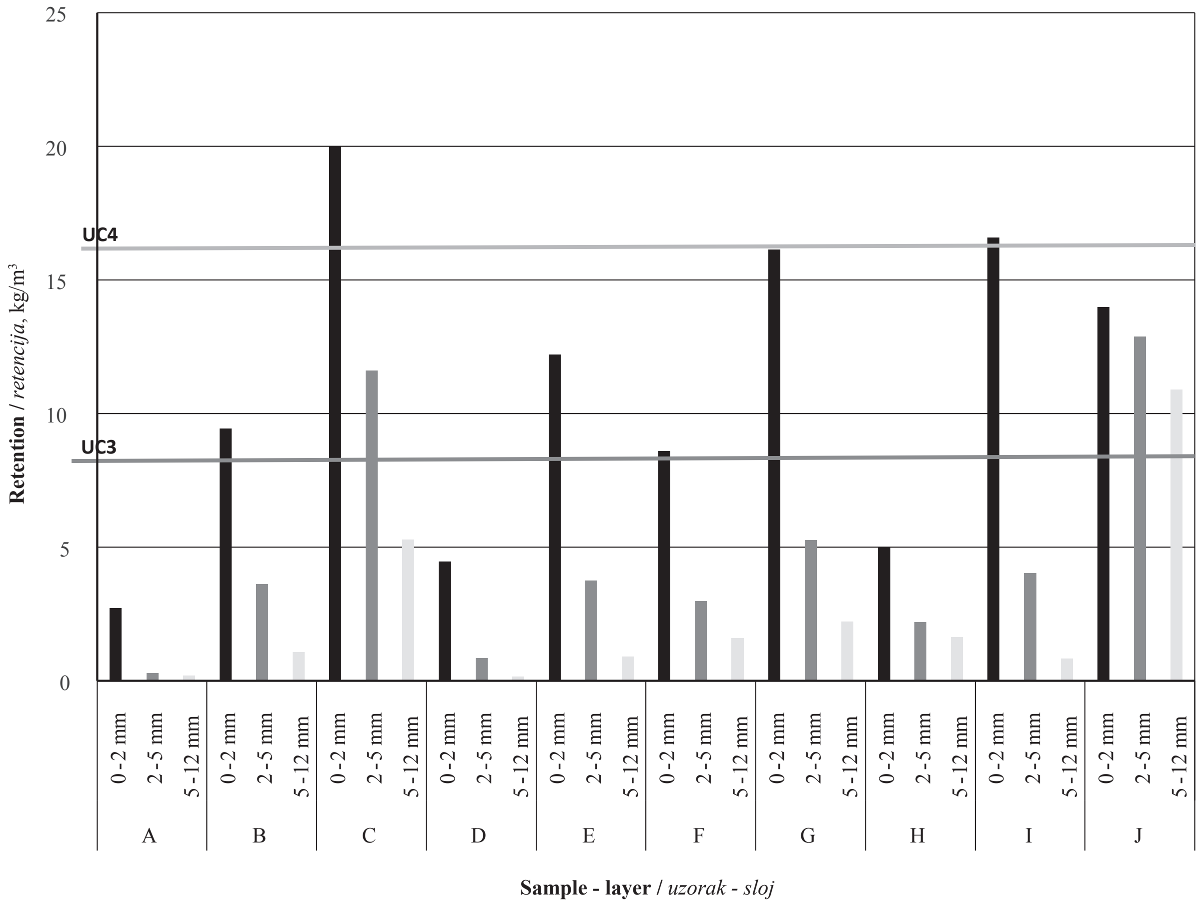

Figure 3 Retention of copper based wood preservatives in different layers of analysed impregnated wood. Grey lines indicate prescribed retention levels for use classes 3 and 4.
Slika 3. Retencija zaštitnog sredstva za drvo na bazi bakra u različitim slojevima analiziranoga impregniranog drva (sive linije pokazuje propisane razine retencije za klase primjene 3 i 4)

(Humar *et al.,* 2006). Its copper tolerance can be clearly seen in Table 3 Mass losses of the copper treated wood species after exposure to brown rot fungi. Bold values indicate mass losses that did not exceed the 3% limit. Standard deviations are given in parenthesis.. This copper tolerant strain was able to degrade all of the wood samples used in the tests. It should be noted that these samples had not been leached or weathered, so high mass losses clearly indicate poor performance of the tested wood. Mass losses of the copper treated samples ranged between 10.8 % (sample E) and 20.2 % (samples C and G). It should be born in mind that poor performance of copper treated wood is not only the result of high copper tolerance but also of poor penetration. Although we tried to prepare the samples from the impregnated part of the tested wood, this was not always pos-

Table 3 Mass losses of the copper treated wood species after exposure to brown rot fungi. Bold values indicate mass losses that did not exceed the 3% limit. Standard deviations are given in parenthesis.
Tablica 3. Gubitci mase uzoraka drva premazanoga zaštitnim sredstvom na bazi bakra nakon izlaganja gljivicama smeđe truleži (zadebljane vrijednosti pokazuju masene gubitke koji ne prelaze granicu od 3 %; standardna su odstupanja navedena u zagradama)

Abbreviation *Oznaka*	**Form** *Oblik*	**Wood species** *Vrsta drva*	**Mass loss, %** / *Gubitak mase, %*	
			F. vaillantii	***G. trabeum***
A	Batten / *letva*	Scots pine / *obični bor*	13.8 (2.4)	**0.6** (0.1)
B	Post / *stup*	Scots pine / *obični bor*	20.0 (4.1)	9.8 (0.4)
C	Post / *stup*	Scots pine / *obični bor*	20.2 (3.3)	**3.0** (0.3)
D	Post / *stup*	Norway spruce / *visoka smreka*	17.6 (2.7)	39.4 (3.1)
E	Post / *stup*	Scots pine / *obični bor*	10.8 (1.8)	**0.9** (0.1)
F	Batten / *letva*	Scots pine / *obični bor*	17.7 (1.5)	**1.3** (0.1)
G	Batten / *letva*	Norway spruce / *visoka smreka*	20.2 (2.6)	**1.0** (0.0)
H	Batten / *letva*	Scots pine / *obični bor*	16.2 (2.7)	11.2 (2.5)
I	Batten / *letva*	Norway spruce / *visoka smreka*	16.2 (1.5)	35.7 (4.9)
J	Post / *stup*	Norway spruce / *visoka smreka*	17.9 (4.1)	5.3 (0.3)
Control / *Kontrolni uzorak*		Norway spruce / *visoka smreka*	18.8 (2.1)	31.4 (4.1)
Control / *Kontrolni uzorak*		Scots pine / *obični bor*	25.1 (1.8)	33.2 (3.8)

sible due to poor penetration (Samples A, D, E, G, I; Table 2). On the other hand, *G. trabeum* exhibited higher differentiation of the analysed wood species. Mass losses of five samples (A, C, E, F and G) did not exceed 3.0 %. This low mass loss is not always associated with high copper retention and good penetration. For example, low mass loss of sample A was associated with the presence of heartwood, which is much more durable than sapwood. The highest mass losses were determined with post D (39.4 %) and batten I (35.7 %), made of Norway spruce, which clearly indicates the susceptibility of spruce wood to brown rot decay.

4 CONCLUSIONS
4. ZAKLJUČAK

Samples of impregnated wood from hardware stores were analysed to determine the penetration, retention and fungicidal properties of the treated wood. The results of the analysis clearly indicated that none of the impregnated wood samples fully met the relevant European standards. It can be expected that these treated products will not meet the expectations of the end users due to premature failures. However, novel EN 350 procedure enables even classification of impregnated wood to durability classes. Unfortunately, there is no procedure available for that. Reduced durability of impregnated wood could be the result of poor penetration and/ or insufficient retention. However, existing experimental procedure does not allow to classify impregnated wood to durability classes as defined by EN 350.

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Corresponding address:

Prof. Dr. MIHA HUMAR, Ph.D.

University of Ljubljana, Biotechnical Faculty
Jamnikarjeva
SI-1000, Ljubljana, SLOVENIA
e-mail: miha.humar@bf.uni-lj.si

Mojtaba Asadi[1], Behzad Bazyar[1], Amir Hooman Hemmasi[1], Ismail Ghsemi[2], Mohammad Talaeipoor[1]

Assessment of Mechanical and Morphological Properties of New Poly Lactic Acid (PLA) / Wood Fibers / Nanographene Composite

Procjena mehaničkih i morfoloških svojstava kompozita proizvedenih od polilaktičke kiseline i drvnih vlakana s dodatkom nanografena

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ABSTRACT • *The present study analyzed the effect of nanographene (NG) application at three rates (0.75, 1.5, and 3 %) on the production of PLA85/F15 and PLA70/F30 composites. The incorporation of NG into the PLA/wood fiber composites significantly improved the tensile and bending properties. The results indicated that composites made from PLA68.5/F30/NG1.5 had the highest tensile and bending properties. Furthermore, it was revealed that the addition of fibers to PLA decreased the composite impact strength in comparison with pure PLA, whereas the addition of NG improved its impact strength, but not as much as pure PLA. The highest impact strength was observed in the composites containing 15 % fibers and 1.5 % NG (PLA83.5/F15/NG1.5 composites). The composites made from 30 % wood fiber and 1.5 % (PLA68.5/F30/NG1.5 composites) NG had the best interfacial surface between the wood fiber and the matrix of composites.*

Keywords: *Polylactic acid, wood fiber, nanographene, mechanical properties*

SAŽETAK • *U radu je analiziran učinak nanografena (NG), dodanoga u različitim količinama (0,75, 1,5 i 3 %), na svojstva kompozita proizvedenih od polilaktične kiseline (PLA) i drvnih vlakana (F) (kompoziti PLA85/F15 i PLA70/F30). Ugradnjom NG-a u kompozite PLA/F znatno su poboljšana vlačna i savojna svojstva kompozita. Rezultati su pokazali da su kompoziti s dodatkom 1,5 % NG-a (PLA68.5/F30/NG1.5) imali najbolja vlačna i savojna svojstva. Nadalje, iz rezultata se može zaključiti da se dodavanjem drvnih vlakana u PLA smanjuje otpornost kompozita na udarce u usporedbi s čistim PLA, a dodavanjem NG-a poboljšava se otpornost kompozita na udar-*

[1] Authors are Ph.D. student, assistant professor, professor and associate professor at Department of Wood and Paper Science and Technology, College of Agriculture and Natural Resources, Science and Research Branch, Islamic Azad University, Tehran, Iran. [2]Author is professor at Department of Processing, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965.115, Tehran, Iran.

[1] Autori su doktorand, docent, profesor i izvanredni profesor Odjela za znanost i tehnologiju drva i papira, Fakultet za poljoprivredu i prirodne resurse, Islamsko sveučilište *Azad*, Teheran, Iran. [2]Autor je profesor Odjela za obradu, Iranski institut za polimere i petrokemiju, Teheran, Iran.

ce. Međutim, ta je otpornost i dalje manja od otpornosti kompozita od čistog PLA. Najveća otpornost na udarce zabilježena je za kompozite koji sadržavaju 15 % drvnih vlakana i 1,5 % NG-a (kompoziti PLA83.5/F15/NG1.5). Kompoziti proizvedeni od 30 % drvnih vlakana i 1,5 % NG-a (kompoziti PLA68.5/F30/NG1.5) imali su najbolju površinu između drvnih vlakana i matrice kompozita.

Ključne riječi: *polilaktična kiselina, drvna vlakna, nanografen, mehanička svojstva*

1 INTROUDUCTION
1. UVOD

As environmental issues are growingly addressed, the use of materials, which are helpful for sustainable development, increases worldwide. One of the most significant improvements in the recent years has been the use of biodegradable polymers instead of crude oil-based polymers such as polypropylene and polyethylene. Recently, one of the most important biodegradable polymers has been poly lactic acid (PLA).

PLA has some advantages, including relatively high mechanical strength and processing feasibility on most equipment, but it needs to be strengthened for practical uses owing to its inherent brittleness (Petinakis *et al*., 2009). The use of natural fibers can be a proper solution for strengthening its mechanical properties (Puglia *et al.,* 2004; Mohanty *et al.,* 2000) and reducing its production costs (Chaharmahali *et al.,* 2014). Lignocellulosic fibers are a suitable substitution for traditional synthetic fibers in the production of polymer composite, because they feature such advantages as low density, renewability, biodegradability, wide availability, and low cost (Kim *et al*., 2009).

In spite of the advantages of PLA for producing PLA/wood fiber composite, some problems have been reported during the processing, including low fibers/ matrix interphase adhesion for PLA/natural fibers composite (Bledzki *et al.,* 2010). The use of nanoparticles in trace quantities is a solution to improve these properties, so that it has been demonstrated to be highly effective. Good dispersion of lignocellulosic fibers is guaranteed in polymers by the use of nanoparticles because of their high surface area, low density and high Young`s modulus. Among a wide range of nanoparticles, the use of NG has been considerably increased because of their unique mechanical and physical properties. It has been reported that the mechanical and electrical properties of NG-based composites are much better than nanoclay- and other nanocarbon-based composites. It has been shown that polylactic acid (PLA)/ wood fiber /nanographene has better mechanical, thermal, gas penetration and electrical properties than pure polymer due to the extraordinary properties of graphene in comparison with polymer (Balandin *et al.,* 2008; Ansari and Giannelis, 2009). Moreover, it has been reported that the improvement of mechanical and electrical properties of polymer/graphene composites has been much higher than those of nanoclay and other carbon filler-based polymer composites (Kim *et al*., 2009). Despite relatively good graphene distribution in polyethylene matrix, a 20 % improvement is observed in tensile modulus and a 13 % improvement is observed in tensile strength (Lin *et al*., 2011).

The objective was to add NG to PLA/wood fiber composite and to improve mechanical and morphological properties.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

The present study used the natural fibers obtained from MDF factory as filler for PLA matrix. Then, NG was added to the material at the rates of 0.75, 1.5, and 3 %.

2.1 Materials
2.1. Materijali

The PLA, which was used as the matrix, was procured from Chinese Shanghai Freeman Chemical Co., Ltd. It had the density of 1.25 $g \cdot cm^{-3}$, the melting point of 150-170 °C, and the melting flow index (MFI) of 15-30 $g \cdot 10min^{-1}$. The fibers used in this study were a mixture of 70 % broad-leaves from northern Iran gardens and 30 % spruce fibers procured from Khazar (Caspian) MDF plant. Table 1 shows some details about fibers used in this study.

2.1.1 Properties of nanographene
2.1.1. Svojstva nanografena

The NG powder (grade AO-4) was procured from the Graphene Supermarket Co (USA). The average thickness and lateral size of NG was about 12 nm and 4.5 µm, respectively. The purity was 99.2 wt % and the specific surface area was less than 15 m^2/g.

Table 1 Details of fiber used in this study
Tablica 1. Podatci o upotrijebljenim vlaknima

Fiber properties *Svojstva vlakana*	**Value** / *Vrijednost*
Fiber type *izvor vlakana*	Seventy percent were derived from twigs of the pruned orange, tangerine and lemon trees in orchards in Northern Iran Thirty percent were derived from spruce twigs gathered from the forests in Northern Iran. *70 % vlakana dobiveno je od grančica preostalih nakon orezivanja naranača, mandarina i limuna u voćnjacima sjevernog Irana.* *30 % vlakana dobiveno je od smrekovih grančica prikupljenih u* šumama *sjevernog Irana.*
Density / *gustoća*	0.36 $g \cdot cm^3$
Fiber length / *duljina vlakana*	5-5.5 mm

2.2 Methods
2.2. Metode

2.2.1 Composite fabrication
2.2.1. Proizvodnja kompozita

According to Table 2, the materials composed of different rates of cellulosic fibers and NG and PLA were made by an inner mixer. Before the mixing process, the material was oven-dried for 24 hours at 75 °C to remove the moisture. The mixture process was carried out by a mixer at three thermal rates of 170, 175, and 180 °C at 30 rounds per minutes (rpm) for 11 minutes (Internal mixer, Brabender, 2002 element, the W50 model). Compression molding was used for fabricating the standard samples and doing various mechanical experiments. As pre-compression, the samples were heated to 180 °C for 5-6 minutes. Then, they were compressed to 30 MPa for 4-5 minutes. Afterwards, the pressure was slowly removed in 5-6 minutes and the temperature was decreased to ambient temperature (mini test press, Japan, 2002, theWCH model, pressure of 25-35 MPa).

Table 2 Composition of materials for the composites
Tablica 2. Oznaka i sastav proizvedenih kompozita

Code *Oznaka*	**PLA** wt %	**Fibers** wt %	**NG** wt %
PLA100	100	0	0
PLA85/F15	85	15	0
PLA84.25/F15/NG0.75	84.25	15	0.75
PLA83.5/F15/NG 1.5	83.5	15	1.5
PLA82/F15/NG3	82	15	3
PLA70/F30	70	30	0
PLA69.25/F30/NG0.75	69.25	30	0.75
PLA68.5/F30/NG 1.5	68.5	30	1.5
PLA67/F30/NG3	67	30	3

PLA – Poly Lactic Acid / *polilaktična kiselina*, NG – nanographene / *nanografen*, F – Fiber / *vlakna*

2.2.2 Mechanical experiments
2.2.2. Ispitivanje mehaničkih svojstava kompozita

Bending and tensile strengths were tested at loading rate of 5 mm·min^{-1} by INSTRON machine (model 4489) in accordance with D790 and D638 procedures of the ASTM standard, respectively. Notched impact strength was tested by INSTRON machine (model 5102, ZWICK Co.) in accordance with D256 procedure of the ASTM standard.

2.2.3 Scanning Electron Microscopy
2.2.3. Skeniranje elektronskim mikroskopom

Refraction sections of tensile samples were imaged by Scanning Electron Microscopy (SEM) (VEGA, ITESCAN Co., the Czech Republic). The microscope uses the voltage of 20 W. Before shooting, the samples were covered (encrusted) with a 15 nm gold layer for five minutes by Covering Machine (Emitech k450x Quorum Technologies, UK).

2.2.4 Statistical data analysis
2.2.4. Statistička obrada podataka

Data collected from mechanical tests were analyzed by SPSS Software Package on the basis of a one-way analysis of variance. The mean values were compared by Duncan's multiple range test at the 95 % confidence level.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

According to Figure 1, the addition of 15 % fibers to PLA increased the tensile modulus of PLA/natural fibers composites. The addition of more natural fibers (30 %) brought about higher stiffness of composites. As NG was applied, tensile modulus of composites kept its ascending trend. When NG level was increased from 0.75 % to 1.5 %, the highest tensile modulus was obtained among all composites, whilst further increases in NG up to 3 % resulted in the loss of tensile modulus as compared to the composites containing 1.5 % NG. The highest tensile modulus or stiffness was related to PLA composites with 30 % natural fibers and 1.5 % NG, which was 30 % higher than that of 67 %. PLA70/F30 composites resulted in tensile modulus higher by about 32 % than the PLA83.5/F15/NG1.5 composites. It can be claimed that NG had higher stiffness than matrix polymer, which was the reason for the higher stiffness of PLA/natural fibers composite (Puglia *et al*., 2004). Statistical surveys indicate significant changes in tensile modulus with the variations of fiber/NG ratio. Duncan classification shows that the addition of fibers and NG to pure PLA entailed significant differences among various groups. Duncan test classified pure PLA in a separate project, while the use of fibers at 15 % and three various levels of NG did not present much difference and all projects were almost placed in one class. However, the application of 30 % fibers and various rates of NG resulted in greater differences among classes.

The analysis of the tensile strength of fabricated composites and their comparison to each other and to pure PLA revealed that, when 15 % wood fibers were added to PLA composites, the tensile strength of composites was diminished. Even when NG was added to composite structures at the rates of 0.75, 1.5, and 3 %, their tensile strength was lower than that of pure PLA. The reduction in the tensile strength of polymer with the addition of natural fibers has been confirmed in several studies (Nourbakhsh and Ashori, 2009). The addition of 30 % wood fiber to PLA decreased the tensile strength as did the addition of 15 % wood fiber. The addition of 0.75 % NG to composites increased the tensile strength as compared to the pure PLA and graphene-free composites. A higher level of tensile strength was observed in PLA68.5/F30/NG1.5 composites. The tensile strength of these composites was 26 % higher than that of PLA composites containing 15 % wood fiber and 1.5 % NG (PLA83.5/F15/NG1.5 composites) and 46 % higher than that of PLA composites containing 30 % wood fiber (PLA68.5/F30/NG1.5 composites). According to statistical analysis, the changes in the tensile strength were significant. Sun *et al*. (2005) reported that the rate of fibers and interfacial adhesion affected the tensile strength. It can be said

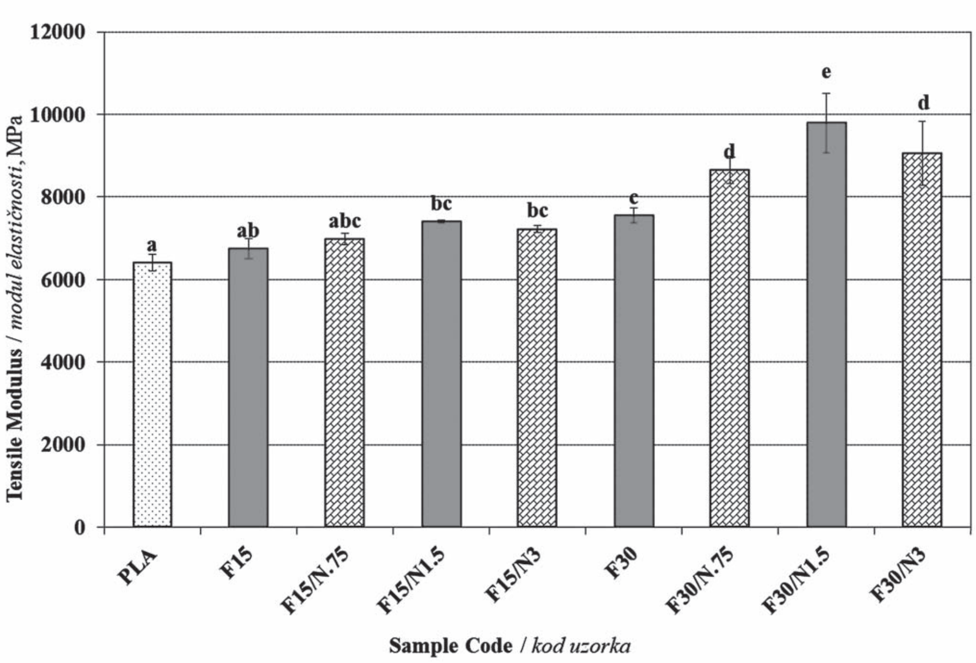

Figure 1 Tensile modulus of PLA/ wood fibers /NG composites. Letters above bars denote Duncan classification
Slika 1. Modul elastičnosti kompozita proizvedenih od PLA, drvnih vlakana i nanografena (slova iznad stupaca prikazuju Duncanovu klasifikaciju)

that, in addition to the application of NG to composite structures, the rate of wood fiber application can be a determinant of tensile strength. The enhancement of tensile properties among composites containing NG can be related to the higher apparent coefficient and high interfacial areas (Balandin *et al*., 2008).

The overuse of NG (i.e., 3 %) resulted in the accumulation of this particle in composite structures and decreased the composite properties as compared to composites containing 1.5 % NG. The proper distribution of NG in composite structures has been reported in several studies (Chang *et al*., 2005; Coleman *et al*., 2006).These results demonstrate the better interfacial behavior between fibers and PLA. The enhancement of tensile properties of composites containing nanoparticles is in agreement with previous studies (Li *et al.,* 2011; Hajian *et al.,* 2012; Mohamadi *et al.,* 2013). The significant difference in different groups can be clearly seen in Duncan classification.

Figure 3 shows the variation of bending modulus of the compositions used in the fabrication of PLA composites. The same as seen in tensile modulus in the study on the bending modulus of the fabricated composites and pure PLA, it was revealed that the bending

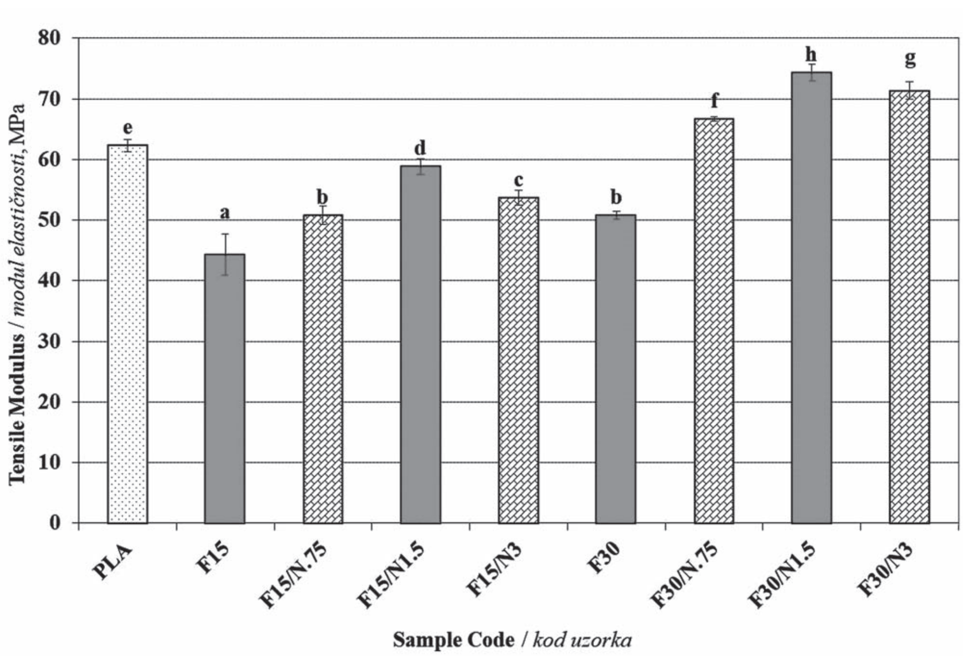

Figure 2 Tensile strength of PLA/wood fiber/NG composites. Letters above bars denote Duncan classification
Slika 2. Vlačna čvrstoća kompozita proizvedenih od PLA, drvnih vlakana i nanografena (slova iznad stupaca prikazuju Duncanovu klasifikaciju)

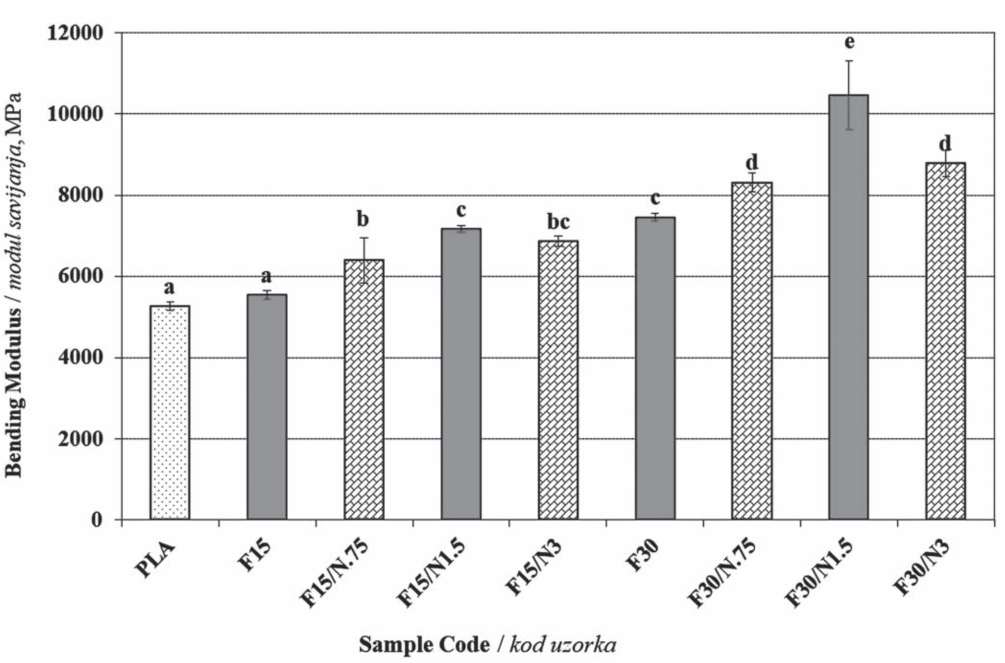

Figure 3 Bending modulus of PLA/wood fiber/NG composites. Letters above bars denote Duncan classification
Slika 3. Modul savijanja kompozita proizvedenih od PLA, drvnih vlakana i nanografena (slova iznad stupaca prikazuju Duncanovu klasifikaciju)

modulus was increased considerably as wood fiber was applied to PLA. By increasing wood fiber from 15% to 30% in composite compositions, the bending modulus was remarkably improved. Nevertheless, the addition of NG increased the significance of PLA composites (GhajeBeigloo *et al.,* 2017; Chaharmahali *et al.,* 2014). The composites containing 30 % wood fiber and 1.5 % NG indicated the highest bending modulus. Adding 1.5 % NG to PLA68.5/F30 composite into wood structure, fiber showed a 99 % increase as compared to pure PLA and a 46 % increase as compared to PLA83.5/F15/NG1.5 composites. Duncan classification showed no significant difference in stiffness between pure PLA and composites containing PLA percentages and 15 % fibers. These two structures were placed in one class, while the addition of NG and the application of 30 % fibers rendered the difference between classes significant, so that they were placed in separate classes.

Figure 4 indicates that the addition of 15 or 30 % wood fiber did not improve bending strength of PLA composites when compared with pure PLA. On the other hand, none of the studied rates of NG could increase bending strength to that of pure PLA. The application of NG at the rate of 30 % of fibers applied in

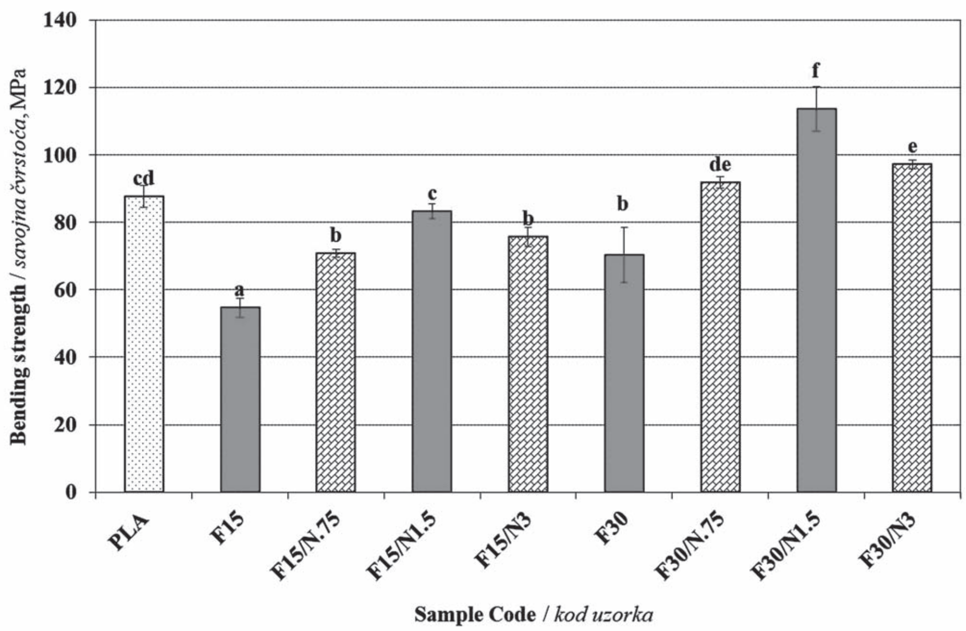

Figure 4 Bending strength of PLA/wood fiber/NG composites. Letters above bars denote Duncan classification
Slika 4. Čvrstoća savijanja kompozita proizvedenih od PLA, drvnih vlakana i nanografena (slova iznad stupaca prikazuju Duncanovu klasifikaciju)

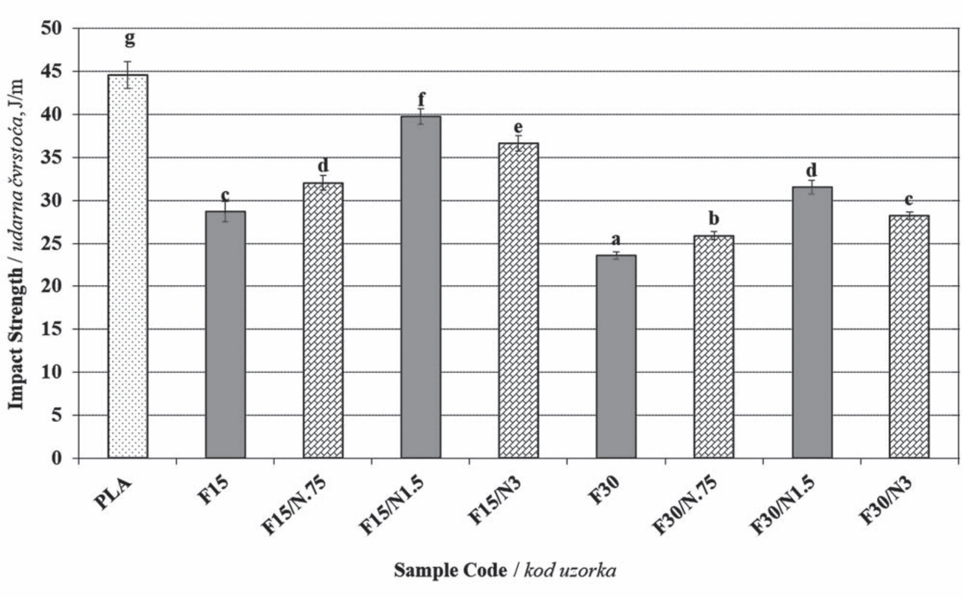

Figure 5 Impact strength of PLA/wood fiber/NG composites. Letters above bars denote Duncan classification
Slika 5. Udarna čvrstoća kompozita proizvedenih od PLA, drvnih vlakana i nanografena (slova iznad stupaca prikazuju Duncanovu klasifikaciju)

PLA composites resulted in a good improvement of PLA composites. One of the most important factors in composite fabrication with NG is the distribution of nanoparticles across the matrix. Improper distribution of nanoparticles can decrease the NG composite properties at high rates of NG application in NG composites (Sheshmani and Amini, 2013). Moreover, the higher bending properties in composites containing 1.5 % NG as compared to other compositions can be attributed to higher stiffness, higher apparent coefficient, and higher interfacial connections.

Amani and Seshmani (2013) reported that the application of high rates of NG did not improve the bending properties due to the accumulation of nanoparticles. Statistical surveys showed significant changes in bending properties (modulus and strength) with the variations of the level of fibers and NG. According to the Duncan classification, the use of 1.5 % NG and 15 % fibers could enhance the bending strength to as high as that of pure PLA and these two classes were nearly placed in one class and higher rates of fibers and nanoparticles application increased the bending strength as compared to pure PLA.

Figure 5 depicts the amounts and trend of impact strength of fabricated composites. The strength of material against breakage and the crack initiation and gap in weak spots reflects the impact strength of composites. These weak spots are mainly located at the interface of fibers and polymer. The application of wood fiber decreased PLA composite impact strength as compared to pure PLA. The enhancement of composite impact strength, achieved by increasing wood fiber, can be related to the accumulation of wood fiber in composite structures (Nourbakhshand Ashori, 2009). Nevertheless, the application of NG could not increase the impact strength to a level as high as that of pure PLA. However, it should be noted that the application of NG increased the impact strength to a greater extent in PLA composites than in PLA-free composites. Among fabricated composites, PLA83.5/F15/NG1.5 composites had the highest impact strength. When NG is increased by more than 1.5 %, the stress is concentrated and, consequently, some cracks are created in the composites. In a study on polymer/fibers/NG composites, Sheshmani *et al*. (2013) reported lower impact strength of composites at the presence of NG. Duncan classification shows significant differences between groups and classifies each one in a separate class.

3.1 Morphology
3.1. Morfologija

To better analyze the results and study the morphology of break level and interstitial area of polymer and wood fiber, electron imagery was prepared by SEM system from break sections of module in bending test.

Figure 6 shows the distension of fibers from the matrix and the porosity between the matrix and fibers. It presents a weak connection area between the two phases, where there was no proper adhesion between the polymer and the matrix, finally proving weaker composite properties than the other compositions.

In spite of the presence of 1.5 % NG in the composition of PLA and 15 % wood fiber, the fibers flow out the matrix with lower rate and less pores. Moreover, the images show that NG settled on matrix more than fibers, implying better union between NG and matrix than between NG and fibers. Also, NG did not accumulate.

Figure 6.C shows the PLA82/F15/NG3 composites with fracture surface. As can be seen, NG did not accumulate. The accumulation of NG results in the loss of adhesion between matrix and NG and the loss of proper distribution of NG on fibers and matrix. Finally, the connection does not emerge between the two phases leading to the fracture and distension of fibers from the matrix.

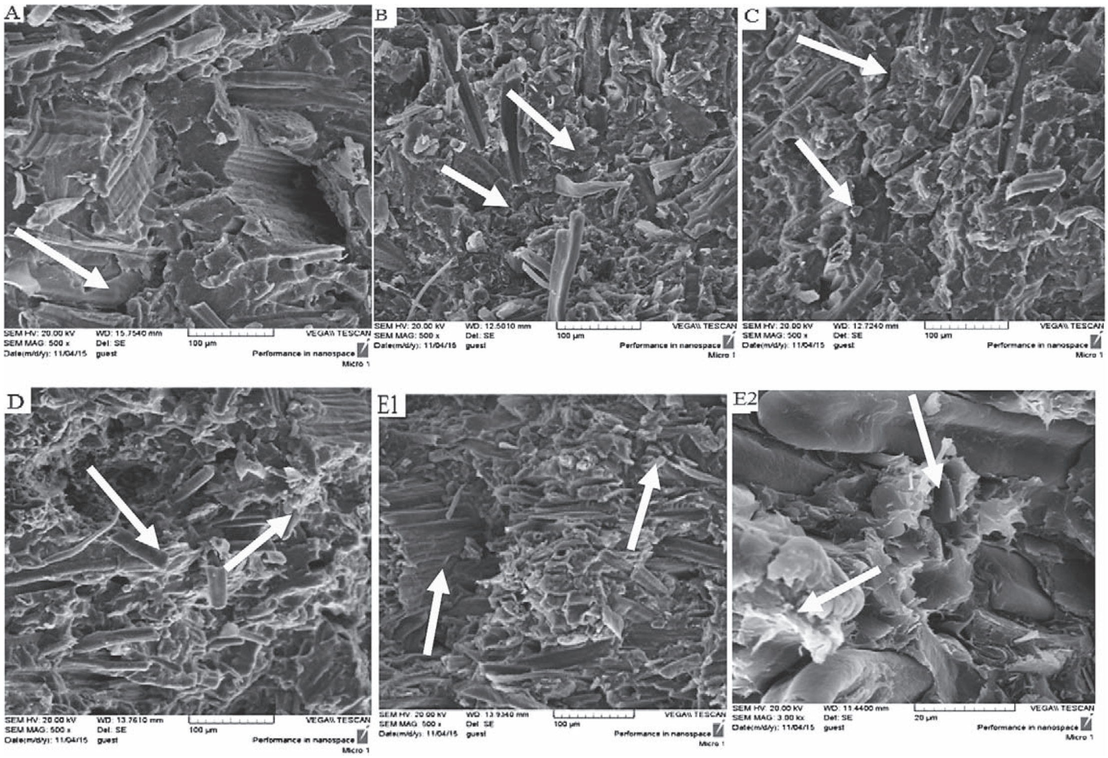

Figure 6 A: PLA85/F15 composites; B: PLA83.5/F15/NG1.5 composites; C: PLA82/F15/NG3 composites; D: PLA70/F30 composites; E1 and E2: PLA68.5/F30/NG 1.5 composites
Slika 6. Prikaz kompozita dobiven skenirajućim elektronskim mikroskopom: A – kompozit PLA85/F15; B – kompozit PLA83.5/F15/NG1.5; C – kompozit PLA82/F15/NG3; D – kompozit PLA70/F30 composites; E1 i E2 – kompozit PLA68.5/F30/NG 1.5

Figure 6.D presents the fracture surface of samples from PLA composites, which shows porosity like PLA70/F30 composites. Here, however, because of the presence of more fibers, the distension is lower, since the fibers are closer to each other. The fractures show a weak connection surface between the two phases.

Figures 6.E1 and E2 show a connection of good interface surface between two sample phases of PLA68.5/F30/NG1.5 composites. Figure 6E clearly shows that the use of 30 % wood fiber resulted in higher uptake of NG and that NG can settle on matrix and fibers, causing the adhesion of interface between fibers and matrix. Here, no accumulation of NG was observed. The good distribution of fibers among the matrix and NG among the fibers and matrix was the reason for this good interface connection between the two phases (it can clearly be seen in Figure 6E2). Finally, it results in more effective transfer of tension from the matrix to fibers. It is the effect of NG on fibers and matrix that caused the adhesion of interface surfaces. The highest mechanical properties were observed in these composites.

4 CONCLUSIONS
4. ZAKLJUČAK

The application of natural fiber in the PLA matrix increased the stiffness of PLA/natural fiber composites. The increase in fibers from 15 % to 30 % in composite structures improved the stiffness of the composites. The use of 30 % fibers and 1.5 % NG (PLA68.5/F30/NG1.5 composites) resulted in the highest stiffness among composites.

As fiber (15 %) was applied to PLA composites, its tensile and bending strength was decreased as compared to pure PLA, whilst further enhancements of fibers to 30 % improved the tensile and bending strength. PLA68.5/F30/NG1.5 composites exhibit the highest tensile and bending strength.

The results of impact strength tests revealed that the use of natural fibers at two rates of 15 and 30 % decreased the impact strength of PLA/natural fiber composites and even the use of NG could not improve the impact strength of PLA composites as compared to that of pure PLA.

The SEM images show that the application of 30 % fibers resulted in lower outflow of fibers from matrix and their better dispersion in matrix when compared with the application of 15 % fibers. Moreover, the application of NG at the rate of 1.5 % presented better dispersion of fibers in matrix than other rates of NG.

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Corresponding address:

Assist. Prof. BEHZAD BAZYAR, Ph.D.

Department of Wood and Paper Science and Technology
College of Agriculture and Natural Resources
Science and Research Branch
Islamic Azad University
Teheran, IRAN
e-mail: bazyar@srbiau.ac.ir

Konstantin Bahcevandziev, Nikola Mihajlovski[1]

Dimensional Stability and Water Absorption of Spruce Wood (*Picea Abies* Karst.) Impregnated and Coated with Polyurethane and Acrylic Coatings

Dimenzijska stabilnost i apsorpcija vode smrekovine (*Picea abies* Karst.) impregnirane i premazane poliuretanskim i akrilnim premazom

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ABSTRACT • *Impregnating materials may affect the stabilization of wood dimensions in two ways: blocking of free water movement paths and chemical connection with hydroxyl groups of wood. The degree of modification depends on the applied material, its penetration and fixation to the wood. The paper investigates the impact of impregnation and coating with polyurethane and acrylic coatings of spruce wood (Picea abies Karst.) on absorption of water and dimensional stability of wood (anti-shrinking efficiency) after being immersed in water for a specific time. Impregnated spruce wood absorbs two times less water than untreated wood and it is dimensionally more stable than coated spruce wood. The water absorption of coated spruce wood is low, but it is not dimensionally stable.*

Keywords: *impregnation, coatings, spruce wood, anti-shrinking efficiency*

SAŽETAK • *Impregnacijski materijali utječu na dimenzijsku stabilnost drva na dva načina: blokiranjem putova za slobodno kretanje vode i uspostavom kemijskih veza s hidroksilnim skupinama drvne tvari. Stupanj modifikacije ovisi o impregnacijskom sredstvu te o njegovoj penetraciji i fiksaciji u drvu. U radu je prikazano istraživanje utjecaja impregnacije drva i premazivanja smrekovine (Picea abies Karst.) poliuretanskim i akrilnim premazima na apsorpciju vode i dimenzijsku stabilnost drva (Anti shrinking efficiency*) *nakon određenog vremena natapanja u vodi. Impregnirana je smrekovina upila dva puta manje vode od neimpregniranog drva i dimenzijski je stabilnija od smrekovine zaštićene premazivanjem. Premazana smrekovina pokazala je sposobnost vrlo male apsorpcije vode, ali nije ostala dimenzionalno stabilna.*

Ključne riječi: *impregnacija, premazi, smrekovina, poboljšanje dimenzijske stabilnosti drva*

[1] Authors are full time professor and laboratory technician at Ss. Cyril and Methodius University in Skopje, Faculty of Design and Technologies of Furniture and Interior - Skopje, Republic of Macedonia.
[1] Autori su profesor i laboratorijski tehničar Sveučilišta *Sveti Ćiril i Metod* u Skoplju, Fakultet dizajna i tehnologije namještaja i interijera, Skoplje, Republika Makedonija.

1 INTRODUCTION
1. UVOD

Wood products in outdoor use are exposed to both short-term and long-term water damage. The dimension stability of wood depends on its properties, processing technology, surface treatment and used materials. In a humid environment, the wood absorbs water until the moisture equilibrium is reached. At the same time, wood dimensions are changed, which has a negative impact on wood products. Therefore, there is a need for surface treatments that would protect the products and keep their dimensional stability.

Coating is a traditional method of surface treatment of wood and it is applied to provide its dimensional stabilization (Rowell, 1981). It is known that the wood coating film is relatively porous, thereby absorbs water, causing resizing of the wood. This method is not sufficiently effective and transparent coatings are not recommended as a long-term protection of wood especially wood used in the exterior, where the coatings should be renewed periodically (TRADA, 1984). A possible solution to this problem is the wood modification method (Jirouš-Rajković *et al.*, 2007), which changes the natural properties of wood with the aim of improving its properties and extending the duration of its use. A type of wood modification is the impregnation with resins (Hill, 2006).

Impregnation is a capillary saturation of wood cavities with implanted viscous materials aimed at reducing its porosity. There are different types of wood modification: filling the lumens - lumen modification, penetrating in the cell wall - cell modification, and chemical reaction between the implanting material and the cellulose hydroxyl groups - chemical modification (Homan, 2004). Also the implanting materials can cause dimensional stabilization in two ways: by blocking the water paths in the wood and disabling the cellulose hydroxyl groups to connect with the water. The degree of modification depends on the applied material penetration and fixation in the wood (Archer and Lebow, 2006).

A possible solution that may address the problem of wood dimensional instability is the impregnation with coatings as a wood surface treatment. Using the vacuum method to implant these materials in the wood may result in the obstruction of the water movement paths or in a chemical modification of the cellulose material, which will increase the wood dimensional stability. Most commonly used wood coatings are those based on polyurethane and acryl resins (Bulian and Graystone, 2009). Both resins have the ability to react with the wood, forming covalent bonds with the cellulose molecule (Rowell and Banks, 1985), which results in a modification of wood surfaces.

The purpose of this investigation is to determine the influence of wood impregnation with polyurethane and acrylic coatings on water absorption and dimensional stability, after several days of immersion in water. It also aims to compare these properties between the untreated wood surfaces, impregnated wood surfaces and wood surfaces coated with those two coatings.

Understanding the complexity of this problem, the investigation should contribute to improving the dimensional stability of the wood used for making interior and exterior wood products.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Preparation of test pieces
2.1. Izrada ispitnih uzoraka

Test pieces were made of spruce wood (*Picea abies* Karst.) in dimensions 20x20x30 mm. The selected wood was without visible flaws, average growth in radial direction to eight annual rings of 10 mm. Test pieces were conditioned to equilibrium moisture content of the wood in accordance with ISO 554.

The moisture content and wood density were determined according to ISO 3130 and ISO 3131 standards. The average value of moisture content was W = 12 %, the average value of density in absolutely dry condition was ρ_o = 0.45 g/cm^3. Two impregnated groups and two coated groups with 32 test pieces were treated for each type of coating, as well as a control group of untreated pieces.

2.2 Coating properties
2.2. Svojstva premaza

The coatings were based on polyurethane and acrylic resins, standard products from the range of a reputable manufacturer (ICA LP152P and ICA LAC367). The preparation of the coatings was carried out according to the instructions given by the manufacturer; they were not additionally diluted. The viscosity was determined according to ISO 2431 standard, and the dry residue percentage according to ISO 1515 standard. The polyurethane coating viscosity was v_{pu} = 15 “F4/20 °C and the acrylic coating viscosity was v_{ak} =27 “ F4/ 20 °C. During the process, the viscosity was not changed. The dry residue of polyurethane coating was $N.V._{pu}$ = 49.3 %, and the one of acrylic coating was $N.V._{ak}$ = 54 %. Although the amount of the dry residue of the acrylic coating was slightly higher, the difference of 4.7 % was statistically negligible.

2.3 Impregnation procedure
2.3. Postupak impregnacije

Wood impregnation was performed according to “Double Vacuum Process” procedure (Videlov, 1980; Richardson, 2003). This treatment is applied to impermeable wood species, where the impregnation pressure has a minor impact on the penetration and retention of wood materials, while the increased time of action has a more significant impact (Richardson, 2003). The wood test pieces were completely immersed in the coating solution. The final operation of the vacuum procedure (Figure 1 point 6 and 7) was to remove the impregnating solution from the autoclave, in order to prevent the formation of the film on the wood surface. The ratio of pressure and time of the operation is shown in Figure 1.

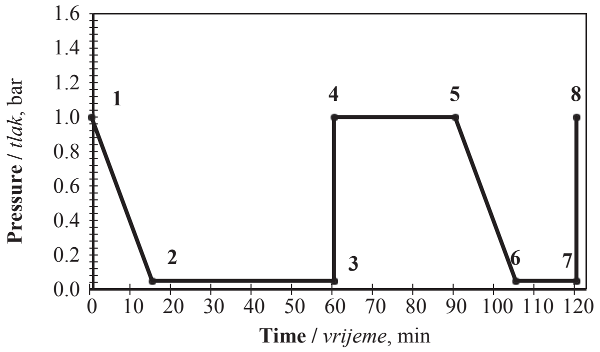

Figure 1 Mode treatment of samples
Slika 1. Postupak tretmana uzoraka

After the treatment, the poly-addition process was carried out until reaching the constant weight, under conditions of ISO 554 standard.

Following the impregnation and surface coating, the test pieces were immersed in water for a period of seven days. The dimensional stability was investigated throughout the mass increase as weight percentage gain, water absorption and anti- shrinking efficiency.

The weight percentage gain - WPG is defined by the formula (Hill, 2006):

$$WPG = \frac{m_m - m_u}{m_u} \cdot 100 \quad (1)$$

m_m – mass of treated sample / *masa tretiranog uzorka* (g)
m_u – mass of sample before treatment / *masa uzorka prije tretmana* (g)

Water absorption - W_a is expressed by the percentage of humidity of the sample before and after immersion, according to the formula:

$$W_a = \frac{m_2 - m_1}{m_1} \cdot 100 \quad (2)$$

m_1 – mass of sample before immersion / *masa uzorka prije uranjanja u vodu* (g)
m_2 – mass of sample with absorbed water / *masa uzorka s apsorbiranom vodom* (g)

The dimensional stability is expressed as anti-shrinking efficiency - ASE is defined by the formula (Stamm, 1964):

$$ASE = \frac{\beta_{vu} - \beta_{vm}}{\beta_{vu}} \cdot 100 \quad (3)$$

β_{vu} – volume swelling of control test piece / *volumno bubrenje kontrolnoga ispitnog uzorka* (%)
β_{vm} – volume swelling of treated test piece / *volumno bubrenje tretiranoga ispitnog uzorka* (%)

Statistical data processing - checking the differences between two related values; significance for statistical data sets with over 30 measurements is determined by:

$$T = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}} \quad (4)$$

The level of the test significance α = 0.01, or the degree of reliability of 99 %, whereby the critical values are outside of the threshold of ± 2.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Weight percentage gain - WPG
3.1. Postotno povećanje mase drva

The average value of the weight percentage gain of wood pieces impregnated with polyurethane coating is 20.3 % higher than the average value of wood pieces impregnated with acrylic coating, but according to the factor of significance ($T = 1.57$), the weight increase is not significant. The average WPG values of the samples are shown in Figure 2. Also, the average value of the weight percentage gain of wood coated with acrylic is 12.5 % higher than the weight percentage gain of wood coated with a polyurethane coating, but this difference is not statistically significant ($T = 1.5$).

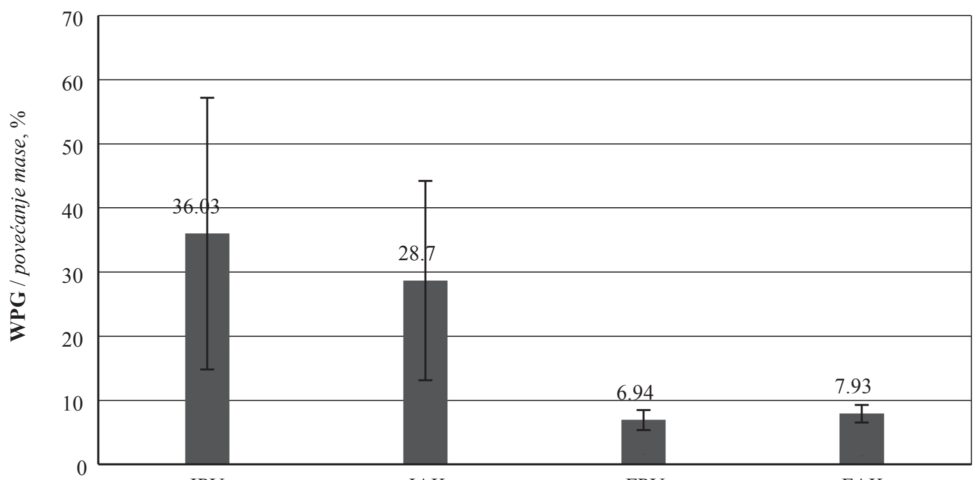

Figure 2 Weight percentage gain of test pieces (IPU - samples impregnated with polyurethane, IAK - samples impregnated with acrylic, FPU - samples coated with polyurethane, FAK - samples coated with acrylic)
Slika 2. Postotno povećanje mase ispitnih uzoraka (IPU - uzorci impregnirani poliuretanom, IAK - uzorci impregnirani akrilom, FPU - uzorci s poliuretanskim premazom, FAK - uzorcimi s akrilnim premazom)

The differences in WPG of the impregnated wood are followed by high coefficients of variation. This is confirmed by the fact that spruce wood is not permeable and it is processed with difficulties due to impregnation (Militz, 1993; Mamonova, 2000). It is the result of closed pore structure of spruce wood, created during the wood drying process. It is also the result of low permeability of the cell lumens (Gindl *et al.*, 2006), and this is the reason for low penetration of the impregnating materials in the wood.

3.2 Water absorption
3.2. Upijanje vode

Water absorption was gradually increased in all tested groups during a seven-day immersion. By the fourth day it was intense, and with low dynamics it increased until the last day. Water absorption is shown in Figure 3.

Untreated wood absorbed water during all seven days and it increased by 41.9 %.

After a seven-day treatment, water absorption also increased in wood impregnated with polyurethane coating by 27.4 %, and in wood impregnated with acrylic by 21.6 %. Related to absorption of untreated wood, it was almost twice lower. The water absorption of wood impregnated with polyurethane coating was significantly higher than the absorption of wood impregnated with acrylic coating. The difference was 5.8 %, and it started to be significant on the fourth day, continuing to be significant until the seventh day. The increase of water absorption in wood treated with polyurethane coating can be explained by the presence of polyester component in the coating, which makes it inconsistent with hydrolysis (Daniliuc *et al.*, 2012).

Until the seventh day, water absorption of wood coated with polyurethane coating increased by 11.9 % and of wood coated with acrylic by 12.5 %. This is about two times less than water absorption of impregnated wood and about three times less than the untreated wood.

3.3 Anti-shrinking efficiency - ASE
3.3. Poboljšanje stabilnosti dimenzija drva

The values of anti-shrinking efficiency of impregnated and coated spruce wood are shown in Figure 4.

The anti-shrinking efficiency of the impregnated wood and coated wood was improved, but during the seven-day immersion it decreased.

The improvement of ASE of wood impregnated with polyurethane and wood impregnated with an acrylic resin is almost equal (T = 0.67). On the first day of immersion, ASE improved by 35.7 %, and on the second day it decreased to 24.5 %. Until the seventh day of immersion, there was no change. On the seventh day of immersion, the ASE of the impregnated wood was 24.2 %. The correlation coefficients of the impregnated wood shows (R = 0.26 and R = 0.34) that there was a weak correlative dependence between the percentage of improved ASE and the duration of immersion. The duration of treatment has a negligible impact on ASE, actually a negligible impact on the stability of wood dimensions.

The improvement of ASE of wood coated with acrylic was higher than that of wood coated with polyurethane coatings (T = 3.89). However, in a period of six-day immersion, the ASE was equaled. On the first day of immersion, ASE of the coated wood was improved by 74.1 %. Then the stability of the coated wood was constantly decreasing and on the fifth day of immersion it was equal with the dimensional stability of the impregnated wood.

In the coated wood, ASE decreased. On the seventh day, it was 17 % and was less than ASE of the

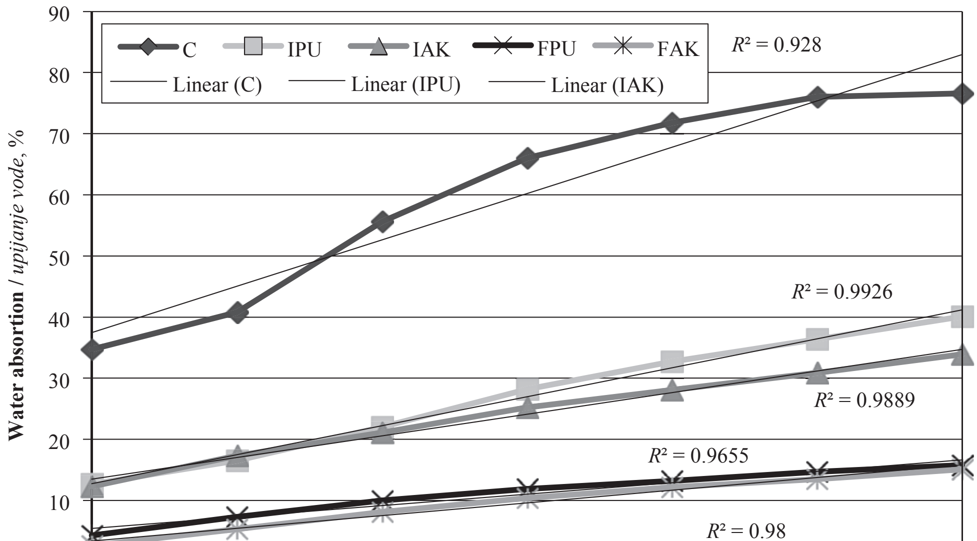

Figure 3 Wood water absorption (C – control samples , IPU - samples impregnated with polyurethane, IAK - samples impregnated with acrylic, FPU - samples coated with polyurethane, FAK - samples coated with acrylic)
Slika 3. Upijanje vode (C – kontrolni uzorci, IPU - uzorci impregnirani poliuretanom, IAK - uzorci impregnirani akrilom, FPU - uzorci s poliuretanskim premazom, FAK - uzorcimi s akrilnim premazom)

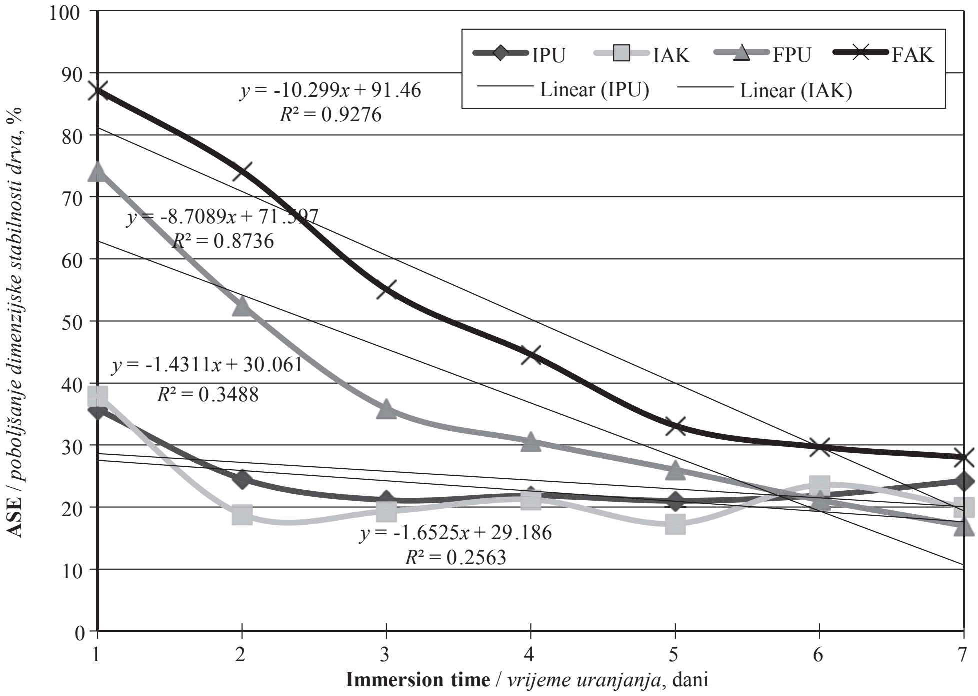

Figure 4 Anti-shrinking efficiency (IPU - samples impregnated with polyurethane, IAK - samples impregnated with acrylic, FPU - samples coated with polyurethane, FAK - samples coated with acrylic)
Slika 4. Poboljšanje stabilnosti dimenzija drva (IPU - uzorci impregnirani poliuretanom, IAK - uzorci impregnirani akrilom, FPU - uzorci s poliuretanskim premazom, FAK - uzorcimi s akrilnim premazom)

impregnated wood (T = 2.76). The high correlation coefficient (R = 0.92 and R = 0.87) shows that there is a strong correlation dependence between the percentage of improvement in ASE and the duration of immersion of the coated wood, i.e. with the increase of immersion time, the dimensions changed. These ASE results coincide with the literature (Reinprecht, 2010; Hazarika *et al.*, 2014; Can and Sivrikaya, 2016; Giridhar *et al.*, 2017) on wood impregnation with resins.

As well known, when the water leaks through the coated film, the wood starts swelling, causing cracks in the film and weakening the film adhesion. After a few such cycles, parts of the film are removed from the wood surface and the water freely diffuses in, causing unhindered dimensional changes. So, it can be said that the coating is not a proper procedure to stabilize the wood exposed to conditions of increased humidity and action of water.

According to the results obtained from the two applied wood surface treatments, the best wood stability would be certainly achieved by a combination of both treatments. The surface treatment with impregnating modification and film coating on the wood can achieve connection of the surface film with the inner part beneath the surface, where the cellular and intercellular cavities of the wood are filled with the same film material and are able to make a chemical connection with wood.

4. CONCLUSIONS
4. ZAKLJUČCI

Based on the obtained results of water absorption and dimensional stability of spruce wood impregnated and coated with polyurethane and acrylic coatings, the following can be concluded:

- The water absorption of wood impregnated with polyurethane coating was 27.4 %, with acrylic coating 21.6 % and related to untreated wood, it was almost twice lower.
- The water absorption of wood coated with polyurethane coating was 11.9 % and with acrylic coating 12.5 %; it was about twice less than that of impregnated wood and about three times less than that of untreated wood.
- The impregnation with polyurethane and acrylic coatings improved the dimensional stability of spruce wood - anti-shrinking efficiency of 24.2 %.
- On the first day of immersion, anti-shrinking efficiency of impregnated spruce wood decreased to 32.2 %, about 1.5 times less, and till the seventh day it remained unchanged.
- Anti-shrinking efficiency of spruce wood coated with polyurethane and acrylic coatings, constantly decreased during the seven-day period until reaching 77 % or 4.3 times.
- Improvement of dimensional stability - anti-shrinking efficiency of the impregnated spruce wood compared to the coated wood is 29.7 % higher.
- The impregnated spruce wood absorbed water two times less the untreated. It was dimensionally stable. By absorbing water, the coated spruce wood was permanently altering the dimensions.
- This research contributes to the development of a wood treatment method that will improve permeability of surfaces and dimensional stability of the wood immersed or exposed to water.

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Corresponding address:

MIHAJLOVSKI NIKOLA, MSc, laboratory technician

Ss. Cyril and Methodius University in Skopje
Faculty of Design and Technologies of furniture and interior – Skopje
16-ta Makedonska brigada 3
1130 Skopje, MACEDONIA
e-mail: mihajlovski@fdtme.ukim.edu.mk

Gökhan Gündüz, Nejla Aşık[1]

Production and Characterization of Bacterial Cellulose with Different Nutrient Source and Surface–Volume Ratios

Proizvodnja i karakterizacija bakterijske celuloze pri različitim izvorima hranjivih tvari i različitim omjerima površine i volumena

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ABSTRACT • *In this research, commercially available, carrot juice was explored as alternative feedstock for production of bacterial cellulose (BC) by Gluconacetobacter hansenii (ATCC® 23769™). Two types of culture media were used: Hestrin–Schramm (HS) and the carrot juice medium and these culture media were incubated statically for 10 days. The effect of different volumes of media on the microbial process and the utilization of substrates by the bacteria, were also examined. The produced BC was analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FT-IR). The water holding capacity (WHC) did not vary greatly with 210 mL (38.6 %), 310 mL (35.4 %), 360 mL (36.4 %) and 410 mL (37.3 %) of carrot juice media, however the WHC of 310 mL HS media (77.1 %), actually achieved a greater WHC, compared to 410 mL of HS media (55.8 %). BC produced in the carrot juice media showed higher yields than cellulose produced in HS media, with values of 1.19 g, 1.35 g, 1.33 g and 1.21 g for media with 210 mL, 310 mL, 360 mL and 410 mL, respectively. According to XRD and TGA results, there were no significant differences in the crystallinity and thermal stability of cellulose produced between HS and the carrot juice medium. FT-IR of BC from HS and carrot juice medium also demonstrated a similar spectrum to alpha cellulose and microcrystalline cellulose.*

Keywords: *Bacterial cellulose, crystallinity, morphology, carrot, production*

SAŽETAK • *U radu je predstavljeno istraživanje komercijalno dostupnog soka mrkve kao alternativne sirovine za proizvodnju bakterijske celuloze (BC) uz pomoć bakterije Gluconacetobacter hansenii (ATCC 23769 ™). Primijenjene su dvije vrste medija za kulturu: Histrin-Schramm (HS) i medij od mrkvina soka te su ti mediji statički inkubirani deset dana. Istraživani su utjecaji različitih obujama medija na mikrobni proces i iskorištenje supstrata od bakterija. Dobiveni je BC analiziran s pomoću rendgenske difrakcije (XRD), skenirajuće elektronske mikroskopije (SEM), termogravimetrijske analize (TGA) i Fourierove transformirane infracrvene spektroskopije*

[1] Authors are associate professor and MSc Engineer at Department of Forest Products Engineering, Faculty of Forestry Bartin University, Bartin, Turkey.
[1] Autori su izvanredni profesor i magistar inženjer, zaposlenici Odjela za drvnu tehnologiju, Šumarski fakultet Sveučilišta u Bartinu, Bartin, Turska.

(FT-IR). Kapacitet zadržavanja vode (WHC) nije se znatnije mijenjao pri različitom obujmu medija od mrkvina soka: pri 210 mL (38,6 %), 310 mL (35,4 %), 360 mL (36,4 %) i 410 mL (37,3 %). Međutim, medij HS pri obujmu 310 mL (77,1 %) ostvario je veći WHC u usporedbi s obujmom od 410 mL (55,8 %). Proizvodnja BC-a u mediju od mrkvina soka pokazala je veće prinose od proizvodnje celuloze u mediju HS, s vrijednostima 1,19 g, 1,35 g, 1,33 g i 1,21 g za obujam medija 210 mL, 310 mL, 360 mL i 410 mL. Prema rezultatima XRD i TGA, nije bilo značajnih razlika u kristaliničnosti i toplinskoj stabilnosti proizvedene celuloze između medija HS i mrkvina soka. FT-IR analiza BC-a proizvedenoga u mediju HS i mediju od mrkvina soka također je pokazala sličan spektar alfa-celuloze i mikrokristalne celuloze.

Ključne riječi: *bakterijska celuloza, kristaliničnost, morfologija, mrkva, proizvodnja*

1 INTRODUCTION
1. UVOD

Bacterial cellulose (BC) is a bio-nanomaterial with unique properties. This material is produced by several species of bacteria. The most notable of this group is *Acetobacter xylinum*, renamed nowadays as *Gluconacetobacter xylinus* and it is found wherever the fermentation of sugars and plant carbohydrates occur (Gama *et al.,* 2013). BC is similar to plant cellulose. However, it is purer and does not contain hemicelluloses and lignin. On the other hand, BC has higher crystallinity, degree of polymerization, water absorbing and holding capacity, mechanical strength in the wet state and stronger biological adaptability (Castro *et al.,* 2011; Wan *et al.,* 2007). BC has a wide application in medicine (artificial blood vessels, skin tissue repair), cosmetics, food industry (Nata de Coco) and in the production of magnetic aerogels and magnetic nano papers (Klemm *et al.*, 2001; Olsson *et al.,* 2010; Halib *et al.,* 2012; Fu and Yang, 2013). Many studies were carried out to decrease the high production costs of bacterial cellulose, which is the main problem for industrial scale production. Alternative carbon sources, such as olive oil residues, molass, corn steep liquor and fruits, were used and evaluated (El-Saied *et al.,* 2008; Gomes *et al.,* 2013; Castro *et al.,* 2011).

The aim of this study was to determine the ability of carrot juice media as a nutrient source in different surface-volume ratios; 15 x 20 cm - 210 ml (A), 15 x 20 cm - 310 ml (B), 15 x 20 cm - 360 ml (C) and 15 x 20 cm - 410 (D) ml compared to standard Hestrin-Schramm (HS) media (KA), (KB), (KC) and (KD), respectively.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

Gluconacetobacter hansenii strain used in this research was obtained from the American Type Culture Collection (ATCC® 23769™). The seed culture was prepared according to the ATCC procedure. The main culture was started by inoculating 10 % (v/v) of the seed culture with the standard Hestrin–Schramm culture medium (Hestrin and Schramm, 1954). It was incubated at 30 °C for 7 days under stable conditions in 250 ml Erlenmeyer flasks. Two types of culture media were used for the experiments: Carrot juice (Carrot) media; squeezed juice of 1.5 kg planed fresh carrots in 1/1.5 ratio with deionized water and Hestrin–Schramm (HS) media for control.

2.2 Methods
2.2. Metode

The culture media used were sterilized at 121 °C in an autoclave for 20 min and poured into Erlenmeyer flasks. Experiments were prepared by adding 10 % (v/v) inoculums to the Carrot and HS media in different surface-volume ratios, namely 17.5 x 11.5 x 1.5 cm = 210 ml (A), 17.5 x 11.5 x 2.0 cm = 310 ml (B), 17.5 x 11.5 x 2.2 cm = 360 ml (C), 17,5 x 11,5 x 2,5 cm = 410 ml (D) and (KA), (KB), (KC) and (KD), respectively, and they were statically incubated at 30 °C for 14 days. The collected pellicles were boiled in water for 1h and treated for 12 h in a 0.5 M NaOH solution, rinsed overnight with tap water and followed by washing with deionized water to neutral pH and weighed (wet weight). Freeze dried samples were prepared after a pre-treatment for 15 °C (48 h) under 0.454 mBar and -55 °C conditions and weighted (dry weight).

The water holding capacity (*WHC*) and yield (*Y*) were calculated as follows (Shezad *et al*. 2010);

$$WHC = \frac{\textit{Mass of water removed during drying (g)}}{\textit{Dry weight of BC sample (g)}} \times 100 \quad (1)$$

$$Y = \frac{\textit{Dry weight of BC sample (g)}}{\textit{Volume of each nutrient source (ml)}} \times 100 \quad (2)$$

2.2.1 Scanning electron microscopy (SEM)
2.2.1. Skenirajuća elektronska mikroskopija (SEM)

The freeze-dried samples were coated with gold (Quorum, UK). Analysis of the BC structure was performed by using a SEM (Quanta FEG 450, Netherlands) at 5 kV. Images were taken with 50000 x SEM micrograph magnifications.

2.2.2 X-Ray diffraction (XRD)
2.2.2. Rendgenska difrakcija (XRD)

XRD was performed with a high resolution X-ray diffractometer (Model Rigaku Smartlab, Made in Japan) with a Ni-filtered Cu Kα (2 kW, kα: 1.54 Å) radiation source operated at voltage of 40 kV and 30 mA. The samples were scanned from 10°-40° 2θ range with a step of 10 °/min. Crystallinity index (*C.I.*) of BC samples were calculated from the reflected intensity data using Segal method (Keshk, 2014; Terinte *et al.,* 2011):

$$CI = 100 \cdot \frac{I_{020} - I_{non-cr}}{I_{020}} \ (\%) \qquad (3)$$

Where; I_{020} is the maximum intensity of lattice diffraction (2θ of 16º to 17º) and $I_{non\text{-}cr}$ is that of the amorphous material between 2θ of 14º to 15º where the intensity is minimum.

2.2.3 FT-IR spectroscopy
2.2.3. FT-IR spektroskopija

Fourier-Transform InfraRed (ATR-FTIR) spectroscopy analysis of the BC sample was carried out on a Shimadzu IRAffinity- One FTIR spectrometer (Japan), equipped with a Universal ATR accessory, using 200 scans and a resolution of 4 cm^{-1}, over the range 4000–800 cm^{-1}.

2.2.4 Thermogravimetric analysis (TGA)
2.2.4. Termogravimetrijska analiza (TGA)

TGA analysis was evaluated with an SII Model TG/DTA 7200 EXSTAR (Made in Japan) analyser. Each sample (5 mg) was scanned from 30° to 450 °C at a heating rate of 10 °C/min in the presence of nitrogen with a flow rate of 20 ml/min to avoid sample oxidation.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Some data such as the yield, wet-dry weight values, and water holding capacity (WHC) of BC are given in Table 1, 2 and 3.

The composition of the nutrient medium, pH, temperature and the interaction of the surface area to the volume of substrate, as well as strain activity, are the fundamental factors affecting BC production and the profitability of the biotechnological process (Krystynowicz *et al.,* 2002; Poyrazoglu and Biyik, 2011; Ruka *et al.,* 2012). The yield increased in Carrot-BC (1.27 g/L) compared to HS-BC (0.60 g/l). The water holding capacity (WHC) is considered one of the most important physical characteristics of BC, which is directly involved in the biomedical applications of BC as wound dressing material (Ul-Islam *et al.,* 2012; Tsouko *et al.,* 2015). The variations between the WHC are related to the porosity and surface area of each BC and it is also known that the greater the surface area and the larger the pore size, the greater will be the WHC of the BC sample (Tsouko *et al.,* 2015). The results showed that the HS-BC absorbed 68 times its dry weight of water. The WHC decreased to 37 in Carrot-BC medium compared to HS-BC.

Scanning electron micrographs (SEM) of freeze-dried Carrot-BC pellicle and of the reference medium HS-BC were evaluated. The fracture surface morphology of the Carrot-BC pellicles exhibits a slightly smaller and narrower diameter distribution in comparison with HS-BC. The SEM micrographs indicate that most of the fibers are in the range of 60 to 70 nm for Carrot-BC and 80-100 nm for HS-BC pellicles. The Carrot-BC pellicles showed much thinner and better network structure than the HS-BC pellicles (Figure 1).

Table 1 Bacterial cellulose yield (dry-basis)
Tablica 1. Prinos bakterijske celuloze (suha tvar)

Volume *Obujam* mL	**Bacterial cellulose yield, g/l** *Prinos bakterijske celuloze, g/l*		**Difference** *Razlika* %
	Carrot-BC *BC - medij od mrkvina soka*	HS-BC *BC - medij HS*	
210	1.19	0.61	95
310	1.35	0.51	164
360	1.33	0.63	111
410	1.21	0.65	86
Average *Prosječna vrijednost*	1.27	0.60	112

Table 2 BC wet - dry weight values
Tablica 2. Vrijednosti mase suhe i vlažne bakterijske celuloze

Volume *Obujam* mL	**Carrot-BC** *BC - medij od mrkvina soka*		**HS-BC** *BC - medij HS*	
	Wet *Vlažna* g	**Dry** *Suha* g	**Wet** *Vlažna* g	**Dry** *Suha* g
210	9.90	0.25	9.11	0.13
310	15.28	0.42	12.56	0.16
360	17.93	0.48	16.06	0.23
410	19.14	0.50	15.33	0.27

Table 3 BC water holding capacity
Tablica 3. Kapacitet zadržavanja vode BC-a

Volume *Obujam* mL	**Water holding capacity** *Kapacitet zadržavanja vode, %*	
	Carrot-BC *BC - medij od mrkvina soka*	**HS-BC** *BC - medij HS*
210	39.60	69.07
310	35.38	77.05
360	36.35	71.17
410	37.28	55.77
Average *Prosječna vrijednost*	37.20	68.27

Thermal stabilities of BCs obtained from different nutrition resources and surface–volume ratios were investigated by thermogravimetric analysis (TGA). According to TGA curves in Figure 2, it was observed that Carrot-BC showed lower thermal stability compared to HS-BC.

For TGA curves of the carrot-BC and HS-BC, low weight loss was detected over the temperature range of 50-200 ℃ because of evaporation of water bounded in the BCs, and the T_{onsets} were generally found to be 265-290 °C for all BCs. According to TGA curves, all TGA results are summarized in Table 4.

As seen in Table 4, the best stability of the BCs was determined as KA. $T_{10\%}$ and $T_{50\%}$ of KA were found

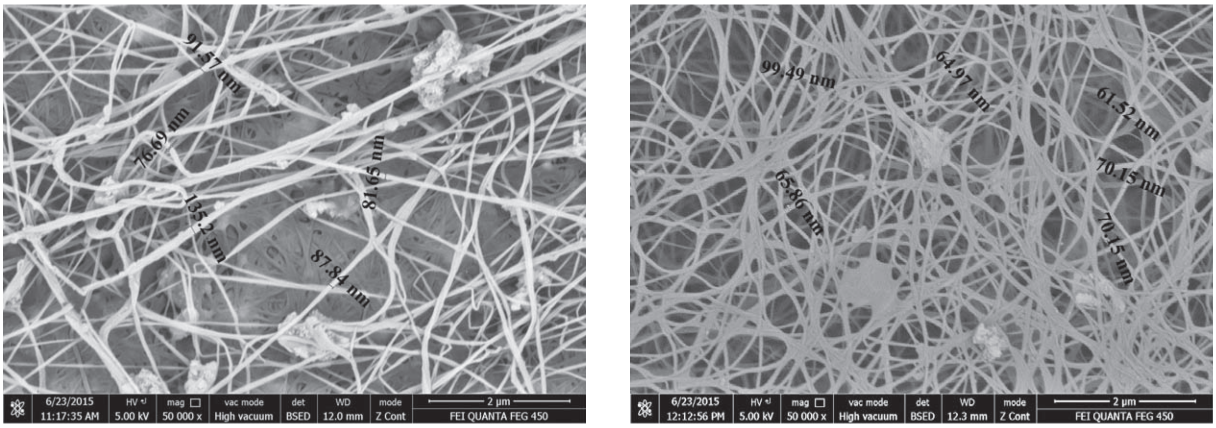

Figure 1 SEM micrographs of Carrot-BC (left) and HS-BC pellicles (right)
Slika 1. SEM mikrografije bakterijske celuloze proizvedene u mediju od mrkvina soka (lijevo) i u mediju HS (desno)

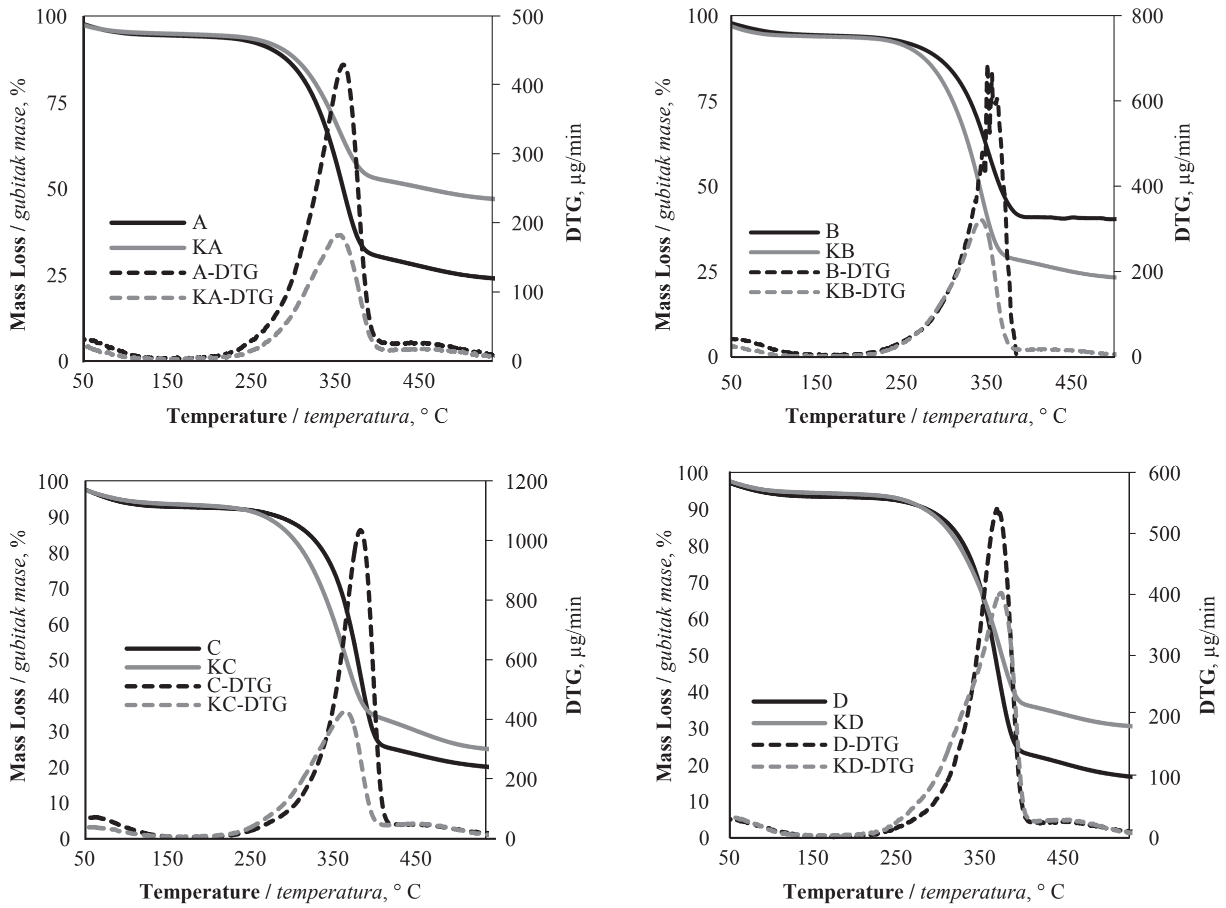

Figure 2 TGA and derivate TGA (DTG) of cellulose produced by G. *hansenii* from Carrot-BC (A, B, C and D) and HS-BC (KA, KB, KC and KD).
Slika 2. TGA i DTG krivulje celuloze proizvedene bakterijom *G. hansenii* u mediju od mrkvina soka (A, B, C i D) i u kontrolnom HS mediju (KA, KB, KC i KD)

as 273.2 °C and 427.9 °C, respectively. $T_{10\%}$ and $T_{50\%}$ of the others were found to be lower than KA except for D in $T_{10\%}$. According to the weight loss, the maximum degradation was found as 83.4 % for H, and the minimum degradation was measured as 52.6 % for KA. DTG curves showed maximum degradation at 354.2 °C for F. As seen in TGA-DTG curves of the BCs, they exhibited three different degradation stages: (1) in the range of 50–200 °C with weight loss of small percentage (%). This mass loss may be attributed to vaporization of water; the free water is evaporated below 100 °C, while linked water that forms physical bounds with polymers is only evaporated above 100 °C. (2) in the range of 200-370 °C as a result of thermal degradation of cellulose main chains, and (3) at 370-500 °C due to thermal degradation of BCs.

The FT-IR spectra demonstrated a similar spectrum to cellulose (alpha cellulose and microcrystalline cellulose), which proved that the material produced by *G. hansenii* was cellulose (HS-BC). The band at 1045

Table 4 Summarized results of TGA curves of BCs
Tablica 4. Sažeti prikaz rezultata dobivenih TGA i DTG analizom BC-a

BC Source *Izvor BC-a*	$T_{\%10}$ ºC	$T_{\%50}$ ºC	DTG_{max} ºC	**Weight loss** / *Gubitak mase* %
A	259.5	335.7	335.3	75.9
KA	273.2	427.9	328.3	52.6
D	278.6	366.2	348.2	64
KE	260.8	330.3	336.2	77.2
F	267.2	355.7	354.2	80.2
KG	250.5	341.8	336.5	75.5
H	271.5	348.6	344.3	83.4
KH	266.9	353.9	347.8	69.8

to 1065 cm^{-1} is related to C-O-C and C-O-H stretching vibration and at 1430 and 1660 cm^{-1} for carboxylate groups and carboxylic acid (Moosavi-Nasab and Yousefi, 2010). The bands at 2900 and 3300 to 3400 cm^{-1} are attributed to the CH_2 stretching and the intramolecular hydrogen bonding, respectively, and the band at 3300 to 3400 cm^{-1} is important for elucidating hydrogen-bonding patterns (Sturcova *et al*., 2004). There is no significant difference between HS-BC and Carrot-BC and the results confirmed that both BC samples exhibited similar chemical binding (Table 5, 6 and Figure 3).

XRD analysis of BC from Carrot-BC and HS-BC medium showed three major characteristic peaks around 2θ = 14º, 16º and 25º, indicating the typical cellulose I structure. The only difference between the samples is a slight intensity change in the peaks. The crystalline indices (CI) of Carrot-BC (83 %) were also

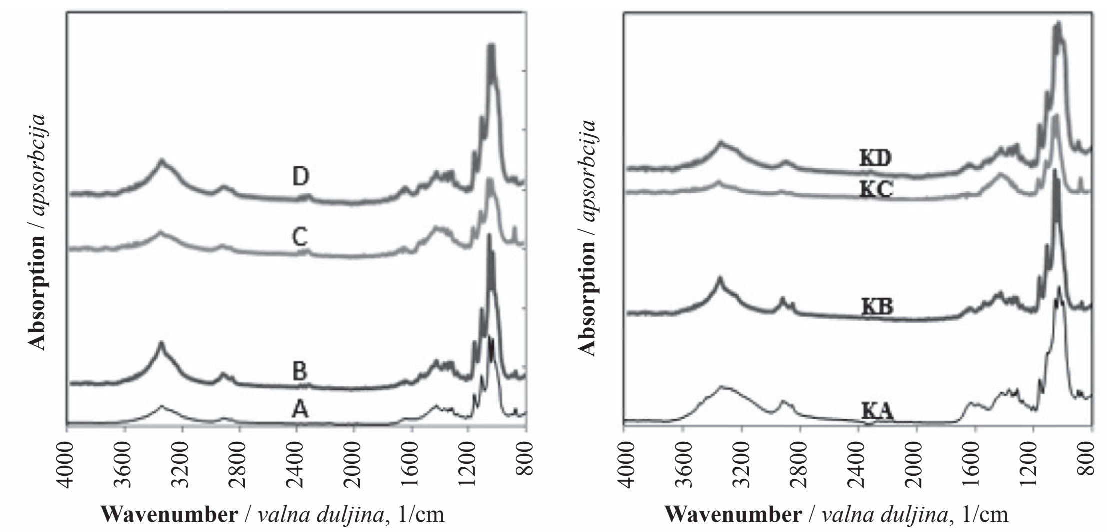

Figure 3 FT-IR spectra of cellulose produced by G. *hansenii* from Carrot-BC (A, B, C and D) and HS-BC (KA, KB, KC and KD)
Slika 3. FT-IR spektar celuloze proizvedene bakterijom *G. hansenii* u mediju od mrkvina soka (A, B, C i D) i u kontrolnom HS mediju (KA, KB, KC i KD)

Table 5 FT-IR Spectra of Carrot-BC (cm^{-1})
Tablica 5. FT-IR spektar bakterijske celuloze proizvedene u mediju od mrkvina soka

Analysis / *Analiza*	**Wave Number, cm^{-1}** / *Broj valova, cm^{-1}*				
A (210 ml)	1031, 1056	1107, 1163	1315, 1336, 1369, 1425	2919	3342
B (310 ml)	1056, 1033	1107, 1163	1427, 1336, 1315, 1371	2916	3346
C (360 ml)	1053, 1029	1109, 1161	1315, 1342, 1375, 1421	2914	3346
D (410 ml)	1056, 1031	1109, 1161	1315, 1338, 1369, 1427	2918	3340

Table 6 FT-IR Spectra of HS-BC (cm^{-1})
Tablica 6. FT-IR spektar bakterijske celuloze proizvedene u mediju HS

Analysis / *Analiza*	**Wave Number, cm^{-1}** / *Broj valova, cm^{-1}*				
KA (210 ml)	1028, 1055	1107, 1159	1315, 1336, 1371, 1421	2916	3336
KB (310 ml)	1056, 1033	1110, 1161	1425, 1336, 1317, 1361	2918	3350
KC (360 ml)	1056, 1033	1109, 1163	1317, 1340, 1369, 1423	2920	3336
KD (410 ml)	1055, 1031	1109, 1161	1315, 1336, 1369, 1425	2895	3334

Table 7 Crystalline indices values (%) of different cellulose sources
Tablica 7. Vrijednosti indeksa kristaliničnosti (%) BC-a iz različitih izvora

Sample / *Uzorak*	**Crystalline indices, %** *Indeks kristaliničnosti, %*	**Reference** *Izvor literature*
Bacterial Cellulose (Carrot_BC)	83	Study Results
Bacterial Cellulose (HS-BC)	84	Study Results
Bacterial Cellulose	82	(Keshk, 2014)
Bacterial Cellulose	75	(Grande *et al.* 2009)
Bacterial Cellulose	79	(Carreira *et al.* 2011)
Bacterial Cellulose	78	(Shezad *et al.* 2010)
Bacterial Cellulose	85-93	(Cheng *et al.* 2009)
Bacterial Cellulose	84-89	(Czaja *et al.* 2004)
Bacterial Cellulose	63-81	(Sheykhnazari *et al.* 2011)
Bacterial Cellulose	74-85	(Amin *et al.* 2014)
Bacterial Cellulose	80	(Gomes *et al.* 2013)
Microcrystalline Cellulose	77	(Keshk, 2014)
Microcrystalline Cellulose	79	(Amin *et al.* 2014)
Cotton	78	(Terinte *et al.* 2011)

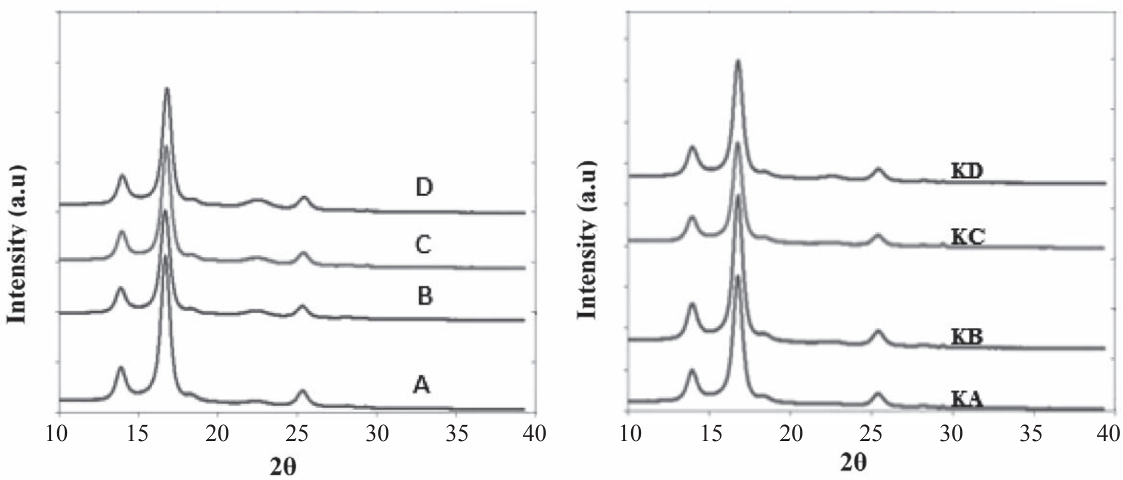

Figure 4 X-ray pattern of cellulose produced by G. *hansenii* from Carrot-BC (A, B, C and D) and HS-BC (KA, KB, KC and KD).
Slika 4. Rezultati rendgenske difrakcije celuloze proizvedene bakterijom *G. hansenii* u mediju od mrkvina soka (A, B, C i D) i u kontrolnom HS mediju (KA, KB, KC i KD)

slightly lower than those of HS-BC (84 %) (Figure 4). Similar results were also found for the utilization of dry olive mill residues for the production of BC (Gomes *et al*., 2013). Comparison of XRD results of different cellulose structures are given in Table 7.

4 CONCLUSIONS
4. ZAKLJUČAK

It is generally accepted that fruits containing sufficient glucose can be used as a nutrient source for BC production. The results of this research demonstrated the possibility to produce BC in carrot juice instead from Hestrin-Schramm as a nutrient source. The fracture surface morphology of the carrot-BC medium pellicles provided a smaller cellulose fibril diameter and a better network in comparison with the BC pellicle from the Hestrin–Schramm medium (HS-BC). The HS-BC absorbed 68 times its dry weight of water. The WHC decreased to 37 in Carrot-BC medium compared to HS-BC. The average yield of Carrot-BC was found to be 112 % higher than that of control samples (HS-BC). The yield also increased in both media with volume ratio. The crystalline indices (CI) of Carrot-BC (83 %) were similar to those of HS-BC (84 %). The FT-IR spectra showed no significant difference between Carrot-BC and HS-BC. The results confirmed that BC samples exhibited similar chemical binding. Carrot-BC showed lower thermal stability compared to HS-BC.

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Corresponding address:

Assoc. Prof. GÖKHAN GÜNDÜZ, Ph.D.

Department of Forest Products Engineering
Faculty of Forestry Bartin University
Bartin, TURKEY
e-mail: ggunduz@bartin.edu.tr

Robert Kalbarczyk, Monika Ziemiańska, Aleksandra Machowska-Molik[1]

Dendroclimatological Analysis of Radial Growth of Old-Growth Oak (*Quercus Robur* L.) on the Oder River Floodbank in the City of Wrocław, South-Western Poland

Dendroklimatološka analiza radijalnog rasta stabala starih hrastova (*Quercus robur* L.) na naplavnoj obali rijeke Oder u gradu Wrocławu, u jugozapadnoj Poljskoj

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ABSTRACT • *The goal of this work was to study the temporal stability of the climate/growth relationship of 15 pedunculate oak trees in Wrocław, SW Poland. Furthermore, pointer years were defined and the span of their meteorological conditions was assessed. The tree-ring widths were measured with an accuracy of 0.01 mm using LINTAB™ 6 and the TSAP-Win software. The site chronology covered 128 years from 1887 to 2014. The tree rings were on average 3.56 mm wide and ranged from 2.10 to 5.43 mm. Their variation was significantly influenced by temperature and precipitation. Tree-ring widths from 1965 to 2014 were most influenced (positively) by June precipitation in the year previous to the formation of the rings. From 1915 to 1964, the tree-ring widths were most strongly and negatively influenced by November precipitation recorded in the previous year. Ten pointer years were identified, three of which were positive and seven negative. Both in the group of positive pointer years (1917, 1966 and 1982) as well negative years (1923, 1951, 1953, 1960, 1981, 1989 and 2009), we were unable to determine variation patterns of temperature and precipitation. Research on the TRW series of pedunculate oaks on flood protection embankments should be continued to better understand the effect of climate conditions on annual tree growth.*

Keywords: *dendrochronology, pedunculate oak, pointer years, temperature, precipitation, urban area*

[1] Authors are professor and PhD students at Faculty of Environmental Engineering and Geodesy, Institute of Landscape Architecture at Wrocław University of Environmental and Life Sciences, Wrocław, Poland.
[1] Autori su profesor i doktorandice Fakulteta zaštite okoliša i geodezije, Institut za krajobraznu arhitekturu Sveučilišta bioloških znanosti i zaštite okoliša u Wrocławu, Wrocław, Poljska.

SAŽETAK • *Cilj rada bio je proučiti vremensku stabilnost odnosa klime i rasta 15 stabala hrasta lužnjaka u Wrocławu, u jugozapadnoj Poljskoj. Nadalje, određene su pokazne godine i procijenjen raspon meteoroloških uvjeta među njima. Širine godova mjerene su s točnošću od 0,01 mm primjenom softvera LINTAB™ 6 i TSAP-Win. Kronologija staništa obuhvatila je 128 godina, od 1887. do 2014. Godovi stabala imali su prosječnu širinu 3,56 mm, a ona se kretala u rasponu od 2,10 do 5,43 mm. Na varijacije širine godova znatno su utjecale temperature i količine oborina tijekom promatranog razdoblja. Na širinu godova od 1965. do 2014. najviše su utjecale (pozitivno) oborine u lipnju u godini koja je prethodila formiranju goda. Od 1915. do 1964. na širine godova najviše su utjecale, i to negativno, oborine zabilježene u mjesecu studenome prethodne godine. Utvrđeno je deset pokaznih godina, tri pozitivne i sedam negativnih. U skupini pozitivnih godina (1917., 1966. i 1982.), kao i negativnih (1923., 1951., 1953., 1960., 1981., 1989. i 2009.), nije bilo moguće odrediti model promjene temperature i količine oborina. Radi boljeg razumijevanja učinka klimatskih uvjeta na godišnji rast stabala, potrebno je nastaviti istraživanje o nizovima širine godova stabala hrasta lužnjaka koja rastu na nasipima uz rijeku.*

Ključne riječi: *dendrokronologija, hrast lužnjak, pokazna godina, temperatura, količina oborina, urbana područja*

1 INTRODUCTION
1. UVOD

Pedunculate oak (*Quercus robur* L.) is a long-lived tree species of the *Fagaceae* family. It grows in forests throughout most of Europe except in northern areas and in areas situated around the Mediterranean and in Asia Minor (Eaton *et al*., 2016; Helama *et al.*, 2016). It prospers best in moderately moist, fertile loamy soil or sandy-loamy soil (Jagodziński *et al.,* 2016), and even tolerates periodic flooding (Rasheed-Depardieu *et al.,* 2015, Stojanović *et al.,* 2015). Studies in Poland point to a spontaneous expansion of native oaks (*Q. pedunculate* and *Q. sessile*) to poor habitats previously dominated by artificially planted Scots pine (Gniot, 2007). The volume increment of oak stands in mixed coniferous/deciduous forests exceeds the average value in single-species stands by about 30 % (Bielak *et al.,* 2015). Young oak trees tolerate lateral shading (Seneta and Dolatowski, 2012; Annighöfer *et al.,* 2015) and prefer full sun in later growth phases. A delay has been shown in the increase of height in shaded oaks growing in the bottom layer of pine stands in the early stages of development – usually for about 20-30 years, after which a marked rise in the growth rate occurs (Paluch, 2013). Pedunculate oak is sensitive to the late spring ground frost, which in some parts of Poland may occur as late as after the 25th of May (Kalbarczyk, 2010b; Seneta and Dolatowski, 2012). For proper growth and development, pedunculate oak requires higher temperatures than sessile oak.

Pedunculate oaks planted in cities are most commonly placed in estates and parks, but less frequently along roads because of their slow growth and difficulties with transplantation (Ziemiańska and Suchocka, 2013). In parks, the health of this tree species is mainly impacted by three factors: distance from the city center, proximity to thoroughfares, and emissions from the combustion of fossil fuels (Krzyżaniak *et al.,* 2013; Krutul *et al.,* 2014). The correct primary and secondary growth of oak trees in an urban space is also influenced by underground technical installations, typology of residential architecture, salinity associated with road maintenance in winter (Čermák *et al.,* 2013; Ziemiańska and Suchocka, 2013), as well as the altered course of meteorological conditions under the influence of the "urban heat island" in relation to non-anthropogenic ecosystems (Szymanowski and Kryza, 2012; Majewski *et al.,* 2014; Kalbarczyk *et al.,* 2016).

In this paper, we assessed the variability in tree-ring widths (TRWs) in oak trees, exemplified by pedunculate oaks growing on the embankments of the Oder River in an urban setting in Wrocław, and also determined the dependence of the ring widths on air temperature and precipitation. Moreover, we identified pointer years in which most oaks developed rings clearly deviating from those from adjacent years.

2 MATERIAL AND METHODS
2. MATERIJAL I METODE

The studied trees grew on the flood-protection embankment of the Oder River along Osobowicka street within the north-western part of the city (latitude 51°08'53"N, longitude 16°58'57"E, altitude 112 m a.s.l.), on the outskirts of Wrocław's Osobowice neighborhood (Figure 1). The levee on which the oaks grew was created in 1859. In addition to its protective function, it was also used as a strolling area. Up until 1903, several rows of oaks had been planted on the levee, but after a flood event in 1903, the height of the bank was raised. It is still used as part of the flood-protection sys-

Figure 1 Location of the study site (●) in south-west Poland
Slika 1. Lokacija mjesta istraživanja (●) u jugozapadnoj Poljskoj

tem. Wrocław is located in the middle of the Silesian Lowland, with the warmest climate in Poland (Szymanowski and Kryza, 2012; Kalbarczyk, 2010a). The stem discs were collected in the summer of 2015 following a planned felling action for the modernization of the Wrocław Floodway System, implemented by the Regional Water Management Authorities.

Fifteen solitary trees at least 100 years old, denoted WO1 to WO15, were selected according to the ECO strategy described by Zielski and Krąpiec (2004), which partially limits the influence of non-meteorological factors on TRWs (Bronisz *et al.,* 2012). After drying and planing, the stem discs were used to measure ring widths along two paths, each from bark to pith, by means of LINTAB™ 6 and TSAP-Win software, to an accuracy of 0.01 mm, as was done for example by Sohar *et al.* (2014), Génova *et al.* (2015), Jansons *et al.* (2015), and Kalbarczyk and Ziemiańska (2016). The two tree-ring paths were cross-dated and averaged so that one tree-ring series was available for each of the 15 study trees (WO1 to WO15). One sequence out of 15 (WO12) did not meet the similarity criteria and was excluded from further analysis to avoid additional variance due to individual growth patterns.

Synchronization of TRWs against the mean for all the sequences was performed by means of COFECHA software (Holmes, 1983; Krąpiec and Szychowska-Krąpiec, 2004). The similarity between the individual sequences was measured by the *t* value – TVBT (Baillie and Pichler, 1973), TVH (Hollstein, 1980), and GLK convergence coefficient (Eckstein and Bauch, 1969). Sequences were considered similar when $t > 3.5$ and $GLK > 65$ % (Rybníček *et al*., 2010; Kraler *et al*., 2012; Sohar *et al*., 2012).

The quality of individual sequences was also measured by the cross-dating indicator (CDI), which included the results of both the *t*-test and the GLK (Kraler *et al*., 2012; Rinn, 2012). All indicators describing the quality of individual sequences were calculated using the TSAP-Win software, and confirmed the correctness of dating and their similarity. Mean TVBP and TVH for the sequences of the pedunculate oaks was 9.7 and 9.6, respectively, while the mean GLK and CDI was 75 % and 72.9 %, respectively.

The tree-ring sequences were described by basic statistical parameters: average TRW ($\bar{x}$), standard deviation (SD), minimums (min) and maximums (max), and their frequency, determined on the basis of raw data, and transformed, i.e. narrower and wider growths, calculated with respect to the year preceding the formation of rings. The frequency was examined in adopted one-millimeter intervals and across three long time periods: 1887-2014, 1915-1964 and 1965-2014.

From the 14 dendrochronological sequences, we developed site chronology of pedunculate oak, denoted with the WO signature. Experience shows that chronologies composed of tree-ring series from at least 10 trees are sufficiently replicated to be used in dendroclimatological research (Matisons *et al.,* 2013). According to professors Zielski and Krąpiec (2004), and also Mäkinen and Vanninen (1999), a sample should range from 10 to 20 trees and should be harvested in duplicate. The representativeness of the tested series was measured using the expressed population signal (EPS), a measure of the similarity between a given tree-ring chronology and a hypothetical chronology that has been infinitely replicated from the individual radii included for a specific common time interval (Wigley *et al.,* 1984).

The site chronology (raw data, indexed, and residual chronology) was characterized, among others, by coefficients of linear trend correlation (*rt*) and first order autocorrelation (*ra*).

The effects of temperature and precipitation on the TRWs were calculated by correlation analysis, in which the dependent variable TRW was expressed in residual form, i.e. converted by procedures adopted in dendrochronology (Schweingruber, 1989; Ważny, 1990; Cedro, 2007; Stojanović *et al.,* 2015). The analysis was conducted for a 15-month period – from June of the previous year to September of the selected year through three time periods (1887-2014, 1915-1964, and 1965-2014).

The 2015 tree-ring (the year of stem disc collection) was not included in the site chronology, because at the time of the field work the cambium activity had not finished. For the weather/TRW association, we used monthly air temperatures (temp, °C) and the monthly sum of precipitation (prec, mm). These values came from the recently reconstructed 217-year series of homogeneous meteorological data describing the weather conditions in urban Wrocław (Bryś and Bryś, 2010).

The span of the meteorological conditions (temperature, precipitation) in individual months was described using means from the period 1915-2014, as well as temperature and precipitation deviations in the periods 1915-1964 and 1965-2015 relative to the period 1915-2014, as well as by means of linear trend correlation coefficients.

In this study, the term 'pointer years' refers to the years during which an unidirectional change in TRW occurred in 100 % of the studied tree-ring sequences (Zielski and Krąpiec, 2004; Danek *et al.,* 2007). Positive pointer years (wide rings) and negative pointer years (narrow rings) were described by average raw data and residual chronology values, as well as average raw data TRW calculated in relation to the previous year. In addition, each designated pointer year described the temperature and precipitation during the four seasons: autumn (September to November – 9p-11p, where p represents the year preceding the formation of tree-rings), winter (from December to February – 12p-2), spring (from March to May – 3-5) and summer (from June to August – 6-8). Air temperature was evaluated by two statistical parameters – mean ($\bar{x}$) and standard deviation (SD), designated for the 1915-2014 period, and the mean in the designated pointer year (δ). A given season was considered normal (average), when the air temperature in a given pointer year met the following conditions $\bar{x} - 1.0\ SD \leq \delta \leq \bar{x} + 1.0\ SD$; warm $\bar{x} + 1.0\ SD < \delta \leq \bar{x} + 1.5\ SD$; hot $\delta > \bar{x} + 1.5\ SD$; cool $\bar{x}$ - 1.5

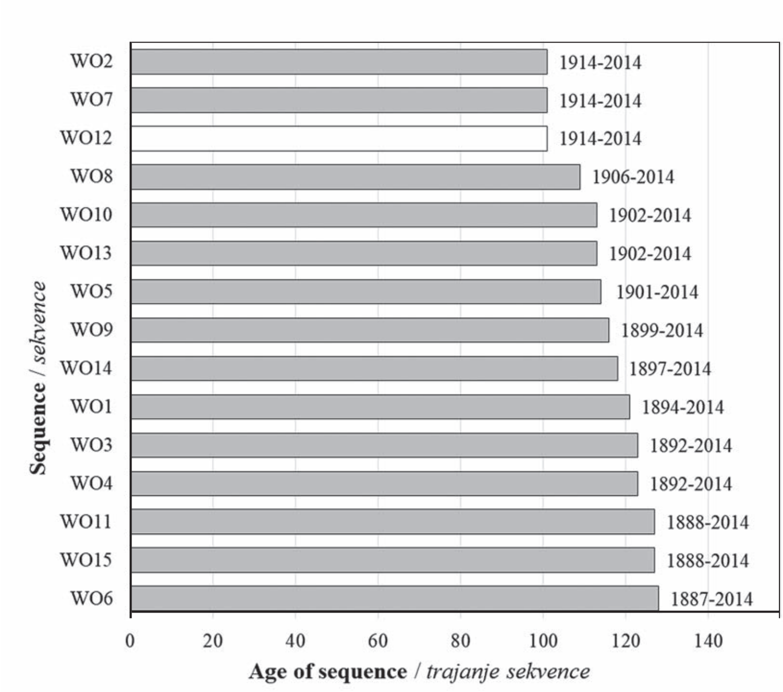


Figure 2 Dating of individual tree-ring sequences of pedunculate oaks from 1887-2014
Slika 2. Pojedinačne sekvence širine godova hrasta lužnjaka od 1887. do 2014. godine

SD ≤ $\delta < \bar{x}$ - 1.0 *SD*; and cold $\delta < \bar{x}$ - 1.50 *SD*. A season was considered normal in terms of precipitation when, in a given pointer year, precipitation was 76 % to 125 % of long-term mean; dry – from 50 % to 75 %; very dry < 50 %; humid from 126 % to 150 %; and very humid > 150 % of the long-term precipitation mean.

3 RESULTS
3. REZULTATI

3.1 Individual tree-ring width series
3.1. Pojedinačni nizovi širina godova

The average number of years of all the analyzed individual sequences (*N*sy) of pedunculate oak was 116 years and ranged from 101 years (1914-2014) in the case of trees marked with signatures WO2, WO7, and WO12, to 128 years in the case of the tree WO6 that grew from 1887-2014 (Figure 2). Six of the fifteen considered sequences were over 120 years. One sequence designated by the WO12 code, due to a low similarity to others (t < 3.5, *GLK* < 65 %), was excluded from further analysis.

The highest average TRW was designated for trees WO8 ($\bar{x}$ = 4.83 mm, *N*sy = 109 years) and WO2 ($\bar{x}$ = 4.79 mm, *N*sy = 101 years) (Figure 3). These trees (WO8 and WO2) also had the widest tree-rings, 11.30 mm and 11.71 mm, respectively. The lowest average TRW was measured for trees WO6 ($\bar{x}$ = 2.19 mm, *N*sy = 128 years), and WO9 ($\bar{x}$ = 2.82 mm, *N*sy = 116 years).

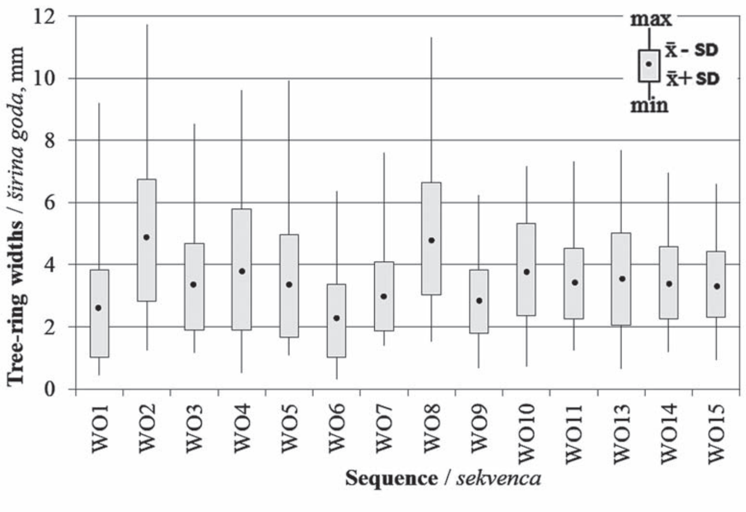
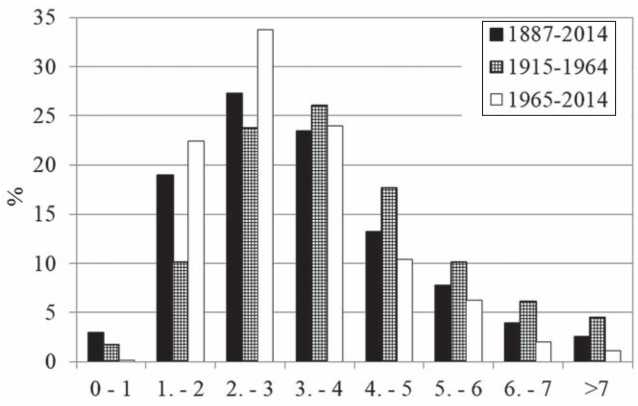
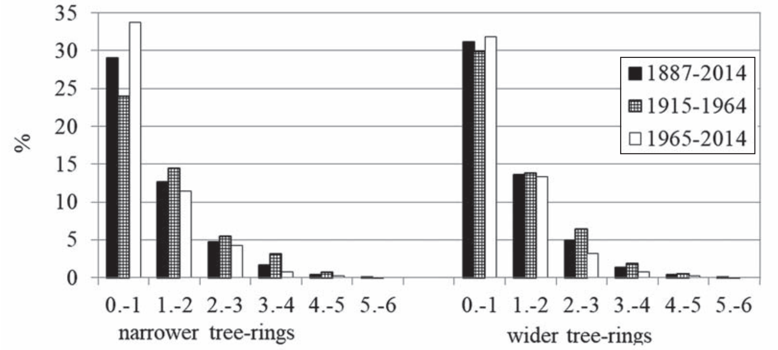


Figure 3 Statistical characteristics of individual sequences describing the variations of tree-ring width of pedunculate oak from 1887-2014. Symbols as in Table 1
Slika 3. Statistička obilježja pojedinačnih sekvenci koje opisuju varijacije širine godova stabala hrasta lužnjaka od 1887. do 2014. godine (značenje oznaka dano je uz tablicu 1.)



a)



b)

Figure 4 Frequency (%) of TRWs in individual sequences of pedunculate oaks in one-millimeter intervals. a) actual ring size, b) size of the rings in relation to the previous year.
Slika 4. Frekvencija (%) širina godova u pojedinim sekvencama hrasta lužnjaka u intervalima od jednog milimetra: a) stvarna širina goda, b) širina goda s obzirom na prethodnu godinu

The minimum sizes of TRWs in the individual trees ranged from 0.34 mm in WO6 (*N*sy = 128 years) to 1.53 mm in WO8 (*N*sy = 109 years). The standard deviation in assessing the variability of TRWs in the analyzed individual sequences ranged from 1.01 mm in WO9 (*N*sy = 116 years) to 1.95 mm in WO2 (*N*sy = 101 years) and WO4 (*N*sy = 123 years).

In the period 1887-2014, the most common pedunculate oak TRW was 2 to 3 mm (27.3 % of all measured rings), followed by 3 to 4 mm (23.4 %) and 1 to 2 mm (19 %). Only 2.4 % of all measured TRWs were greater than 7 mm (Figure 4a).

The frequency distribution of individual TRW sequences differed between the two half century periods 1915-1964 and 1965-2014 from the period 1887-2014. TRWs from 3 to 4 mm and > 7mm were most common in the earlier 1915-1964 period (26 %), and 2-3 mm TRWs in the later 1965-2014 period (about 34 %).

Frequency analysis, showing TRWs in relation to the preceding year, indicated that most often (in approx. 30 % of cases) the year-to-year difference did not exceed 1 mm (Figure 4b). The negative difference in TRW was about 10 % more frequent in the second 50-year period (1965-2014). A year-to-year difference for the remaining TRW intervals, i.e. 1-2, 2-3, 3-4, 4-5 and 5-6 (both positive and negative), was observed more frequently in the earlier 50-year period (1915-1964).

3.2 Site chronology
3.2. Kronologija staništa

The course of the considered dendrochronological curves of individual pedunculate oak sequences, along with the determined site chronology, is shown in Figure 5. In the period 1915-2014, which covers all the study samples, the average raw data TRW of pedunculate oak site chronology was 3.56 mm. In the earlier part of that period (1915-1964), the average was higher, at 3.96 mm (Table 1 and Figure 5). The standard deviation (SD) of TRW from 1915-2014 was 0.87 mm, wherein SD in the earlier half of that period was higher at 0.90 mm and was 0.26 mm more than in the later half of that period. TRW in the site chronology ranged from 0.20 to 5.43 mm. A higher difference between maximum and minimum TRW (3.02 mm) was found in the earlier half of that period (1915-1964).

The researched 100-year period of pedunculate oak chronology is characterized by a negative trend ($rt = -0.44$, $\alpha < 0.01$), which shows the presence of an age related trend. The smaller year-to-year TRWs were statistically proven ($rt = -0.24$, $\alpha < 0.1$) in the later half of the analyzed long-term period (1965-2014). The I^o autocorrelation coefficient was clearly visible during the 1915-2014 period ($ra = 0.38$, $\alpha < 0.01$), and slightly lower from 1915-1964 ($ra = 0.22$, $\alpha < 0.1$). After the transformation of raw data TRW data into residual, we

Table 1 Statistical indicators describing chronology in various long-term periods
Tablica 1. Statistički pokazatelji koji opisuju kronologiju u različitim dugoročnim razdobljima

Indicator *Pokazatelj*	**Period** *Razdoblje*	**Chronology** / *Kronologija*		
		Raw-data *Neobrađeni podatci*	**Indexed** *Indeksirani podatci*	**Residual** *Ostatak*
x̄±SD (mm)	1	3.56±0.87	0.99±0.21	0.73±0.25
	2	3.96±0.90	1.02±0.23	0.74±0.29
	3	3.16±0.64	0.97±0.19	0.72±0.21
min (mm)	1	2.10	0.59	0.09
	2	2.41	0.59	0.09
	3	2.10	0.63	0.24
max (mm)	1	5.43	1.48	1.43
	2	5.43	1.48	1.43
	3	4.45	1.46	1.22
rt	1	-0.441	-0.01^{ns}	-0.01^{ns}
	2	0.01^{ns}	0.22^{ns}	-0.16^{ns}
	3	-0.243	0.07^{ns}	0.02^{ns}
ra	1	0.38^{1}	0.212	-0.05^{ns}
	2	0.223	0.243	0.07^{ns}
	3	0.19^{ns}	0.10^{ns}	-0.12^{ns}

Explanation: $\bar{x}$ – average / *prosječna vrijednost*, *SD* – standard deviation / *standardna devijacija*, *min* – lowest value / *najniža vrijednost*, *max* – highest value / *najviša vrijednost*, *rt* – linear trend correlation coefficient / *koeficijent korelacije linearnog trenda*, *ra* – I^{o} autocorrelation coefficient, long-term period / *koeficijent autokorelacije, dugoročno razdoblje*: 1 – 1915 – 2014, 2 – 1915 – 1964, 3 – 1965 – 2014, $^{1}\alpha \leq 0.01$, $^{2}\alpha \leq 0.05$, $^{3}\alpha \leq 0.1$, ns – not statistically significant at least at $\alpha \leq 0.1$ / *nije statistički značajno pri α ≤ 0,1*

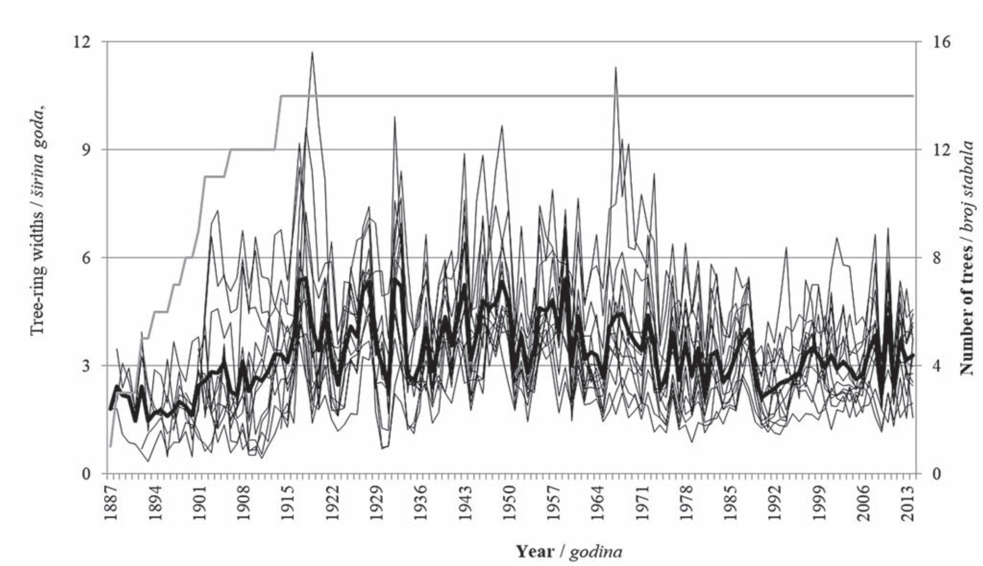
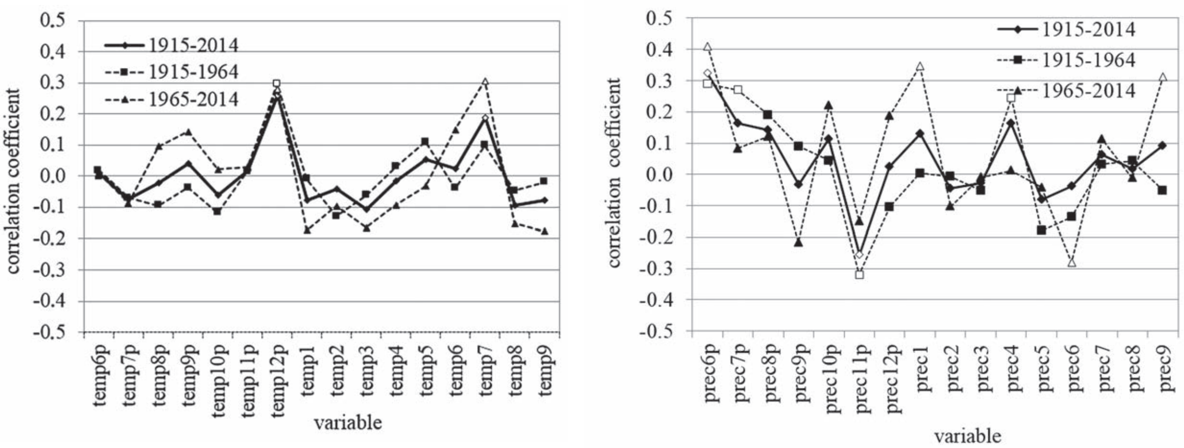


Figure 5 Dendrochronological curves of individual sequences of pedunculate oak comprising the WO site chronology (▬) from 1887-2014 against the background of the size of the research sample (number of trees) in subsequent years in the considered long-term period 1915-2014
Slika 5. Dendrokronološke krivulje pojedinih sekvenci hrasta lužnjaka koje obuhvaćaju kronologiju WO mjesta (▬) od 1887. do 2014. u odnosu prema veličini istraživačkog uzorka (broj stabala) u kasnijim godinama razmatranoga dugoročnog razdoblja od 1915. do 2014.

managed to eliminate both the age-related trend and the impact of the growth from the preceding year in the 3 considered long-term periods.

3.3 Temperature and precipitation, and site chronology relations
3.3. Temperatura i oborine te odnosi među kronologijama staništa

Correlation analysis was carried out for the three periods of research (1915-2014, 1915-1964, 1965-2014) between TRW and air temperature (temp), and precipitation (prec) and indicated that each of the examined meteorological elements interacted with different strengths and directions – positive or negative (Figure 6ab). The strongest positive impact of temp on TRW, in all studied periods, was evident in December of the year preceding the tree-ring formation. In the first half of the full long-term period study, i.e. from 1915-2014, the air temperature of the year preceding the formation of the tree-ring – from July to October, as well as the observed year – from January to March and



a) b)

Figure 6 Effect of air temperature (a) and precipitation (b), from June of the year preceding the formation of rings (temp6p, prec6p) till September of the current year (temp9, prec9), on the size of annual tree-rings of pedunculate oak in various long-term periods (p – year preceding the formation of annual growth, temp – air temperature, prec – precipitation, 1, 2… … 12 – consecutive month of the year, marker with no fill – relationship significant at α ≤ 0.1)

Slika 6. Utjecaj temperature zraka (a) i oborina (b) od lipnja godine prije nastanka goda (temp6p, prec6p) do rujna tekuće godine (temp9, pre-9) na širinu goda hrasta lužnjaka u tekućoj godini za različita dugoročna razdoblja (p – godina koja prethodi formiranju godišnjeg rasta, temp – temperatura zraka, prec – oborine, 1, 2 …12 – uzastopni mjesec u godini, prazne oznake – korelacija je značajna pri α ≤ 0,1)

in June, and from August to September, contributed to a reduction of TRW in the pedunculate oaks.

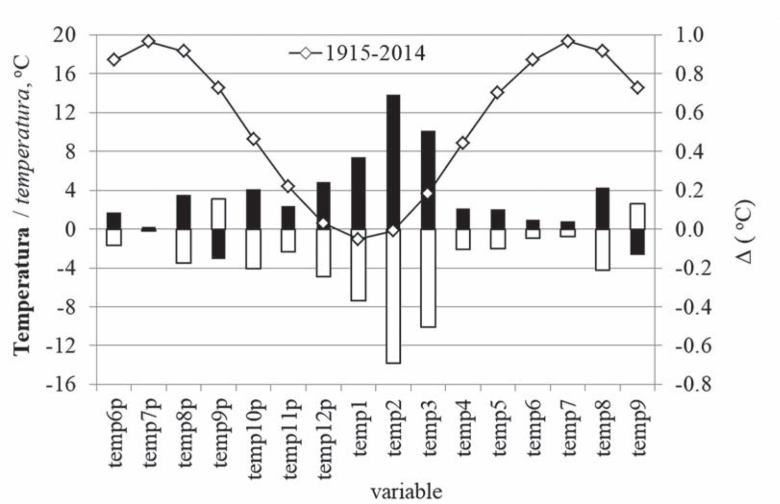
In the second half of the studied long-term period from 1965-2014, the effect on TRW was slightly different. TRW was favorably influenced by air temperature in the previous year from August to October as well as in the observed year in June, and differently, negatively, in the current year – from April to May. In all three studied long-term periods, TRW correlated positively with precipitation in the previous year from June to August and October, and the current year in January, April and July, while negatively with precipitation in the previous year in November, as well as in the current year in February, March, May and June. The strongest positive impact of precipitation on TRW was evident for June precipitation in the year preceding the formation of the tree-rings (r varied from 0.29 in 1915-1964 to 0.41 in 1965-2014) and in January (r = 0.35, $\alpha \leq 0.01$) and in September (r = 0.31, $\alpha \leq 0.01$) in the current year, but only from 1965-2014. TRW was significantly negatively influenced by precipitation in November in the preceding year, especially from 1915-1964 (r = -0.32, $\alpha \leq 0.01$) and in June in the current year (r = -0.28, $\alpha \leq 0.01$), but only from 1965-2014.

3.4 Variability of meteorological conditions
3.4. Varijabilnost meteoroloških uvjeta

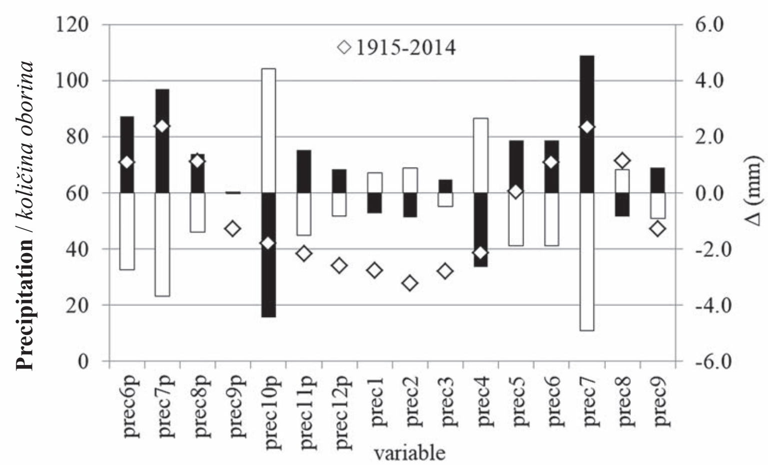
In the period 1915-2014, the air temperatures ranged, on average, from -1.4 °C in January to 19.3 °C in July (Figure 7a). The average annual air temperature in the earlier 50-year period (1915-1964) was 8.9 °C, 0.3 °C less than for the whole long-term period (1915-2014). This was determined by lower air temperatures recorded in winter, especially in January (0.4 °C lower in comparison to the 1915-2014 period) and in February (0.7 °C lower in comparison to the 1915-2014 period), and early spring, i.e. in March (0.5 °C lower in comparison to the 1915-2014 period). On the other hand, in the second half of the long-term period, the average air temperature was higher than the norm (1915-2014) in nearly all months of the year.

The largest temperature deviations, ranging from 0.2 °C to 0.7 °C, in the 1965-2014 period compared to the 1915-2014 period were evident from January to March, and in August and December. A positive indicator trend in the two 50-year periods calculated in relation to the 1915-2014 long-term period confirms the correlation analysis of the significance of the linear trend of monthly temperature values (Table 2).

A significant positive air temperature trend was evident in several months from 1915-2014. The value of the correlation coefficient for significant relationships between air temperature and TRW ranged from 0.17 for air temperature in June and November in the year preceding the forming of the tree-rings, to 0.32 in August of the current year. At the same time, the significant increase in air temperature from April to August throughout the long-term period was primarily determined by above-average temperature values in the later half of the long-term period (1965-2014). The average annual amount of precipitation during the whole research period was 578 mm (Figure 7b). Precipitation in the two analyzed 50–year periods differed by only 6 mm. A slightly higher precipitation was recorded in the later 50 year period (1965-2014, generally from May to July). The biggest differences in total precipitation between the earlier and later halves of the considered period (1915-2014) were reported in July (almost 10 mm), being wetter in the later half. In contrast to air temperature, precipitation was marked by a mostly negative trend, e.g. in January from 1915-1964 (r = -0.47, $\alpha \leq 0.01$) and in April from 1915-2014 (r = -0.23, $\alpha \leq 0.05$).



a)



b)

Figure 7 Air temperature (a) and precipitation variation (b) as well as their monthly deviations in 1915-1964 (□) and 1965-2014 (■) in relation to the 1915-2014 period. Explanation as in Figure 6.
Slika 7. Promjene temperature zraka (a) i količine oborina (b) te njihova mjesečna odstupanja u razdoblju 1915. – 1964. (□) i 1965. – 2014. (■) u odnosu prema razdoblju 1915. – 2014.

Table 2 Temperature and precipitation linear trend in consecutive analyzed months
Tablica 2. Linearni trend temperature i oborina u uzastopnim analiziranim mjesecima

Month *Mjesec*		**1915-2014**		**1915-1964**		**1965-2015**	
		temp °C	**prec** mm	**temp** °C	**prec** mm	**temp** °C	**prec** mm
previous year *prethodna godina*	6	0.17^3		0.24^3			
	7					0.40^1	
	8	0.30^1				0.57^1	
	9						
	10		-0.23^2		-0.24^3		
	11	0.17^3		0.25^3			-0.28^2
	12						
current year *tekuća godina*	1			-0.26^3	-0.47^1		
	2						
	3						0.24^3
	4	0.19^3	-0.23^2			0.59^1	
	5					0.38^1	
	6					0.27^3	
	7	0.18^3		0.27^3		0.46^1	
	8	0.32^1				0.52^1	
	9						

Explanation: temp – air temperature / *temperature zraka*; prec – precipitation / *količina oborina*; $^1\alpha \leq 0.01$; $^2\alpha \leq 0.05$; $^3\alpha \leq 0.1$; 1, 2… … 12 – months of the year / *mjeseci u godini*

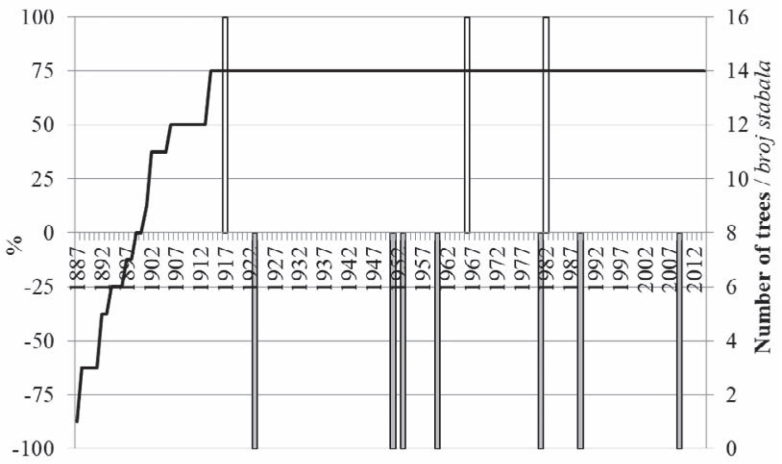


Figure 8 Distribution of identified positive and negative pointer years of pedunculate oak in the 1915-2014 long-term period and the size of the research sample (number of trees) in the respective years of the considered long-term period (▬)
Slika 8. Raspodjela identificiranih pozitivnih i negativnih pokaznih godina hrasta lužnjaka u dugoročnom razdoblju 1915. – 2014. i veličine istraživačkih uzoraka (broj stabala) u pojedinim godinama razmatranoga dugoročnog razdoblja (▬)

Table 3 Characteristics of pointer years of pedunculate oak and assessment of temperature and precipitation in further seasons
Tablica 3. Obilježja pokaznih godina hrasta lužnjaka i procjena temperature i količine oborina u sljedećim godišnjim dobima

Pointer years *Pokazne godine*	**Type of pointer year** *Obilježje pokazne godine*	**Chronology value** *Kronološka vrijednost* mm		**Measured average tree-ring width relative to the previous year** *Prosječna vrijednost izmjerenih širina godova u odnosu prema prethodnoj godini*	**Conditions** / *Uvjeti*							
					thermal *temperatura* (temp, °C)				precipitation *količina oborina* (prec, mm)			
		raw-data *neobrađeni podatci*	residual *ostatak*		A	W	Sp	S	A	W	Sp	S
1917	positive	5.39	1.16	1.56								
1923	negative	2.46	0.42	-0.76								
1951	negative	2.96	0.19	-1.79								
1953	negative	2.80	0.53	-1.04								
1960	negative	3.01	0.21	-2.38								
1966	positive	4.06	1.04	1.39								
1981	negative	2.12	0.40	-1.36								
1982	positive	3.29	0.92	1.17								
1989	negative	2.67	0.34	-1.32								
2009	negative	2.24	0.24	-1.62								

Explanation: A - autumn (season from September to November, taking place in the year previous to the formation of tree-rings), W - winter (season from December of the year preceding the formation of tree-rings to February of the current year), Sp - spring (season from March till May), S - summer (season from June till August)
Objašnjenje: A – jesen (sezona od rujna do studenoga; odnosi se na godinu koja je prethodila formiranju stabla), W – zima (sezona od prosinca godine koja prethodi formiranju stabla do veljače tekuće godine), Sp – proljeće (sezona od ožujka do svibnja), S – ljeto (sezona od lipnja do kolovoza)

3.5. Pointer years
3.5. Pokazne godine

We distinguished 10 pointer years in the 100 year long-term period, identified by pedunculate oak TRW. Seven were negative and three positive (Figure 8). The 3 positive pointer years were 1917, 1966 and 1982, and the 7 negative years were 1923, 1951, 1953, 1960, 1981, 1989 and 2009. The greatest annual growth occurred in 1917 at 5.39 mm, and the smallest in 1981 at 2.12 mm (Table 3, Table 4).

In positive pointer years, TRW in residual form ranged from 0.92 to 1.16mm, and average raw-data TRW in relation to the previous year ranged from 1.17 mm in 1982 to 1.56 mm in 1917. In the year in which the widest tree-ring of the pedunculate oak developed, air temperatures were normal in the period from September of the year preceding the formation of the rings to February of the current year, i.e. autumn and winter. The following season, spring (March-May) was cold, and the summer (June-August) was warm. Precipita-

Table 4 Explanation of marks in Table 3
Tablica 4. Objašnjenje oznaka u tablici 3.

Conditions *Uvjeti*	**Thermal** *Temperatura zraka* (temp, °C)	**Precipitation** *Količina oborina* (prec, mm)
	season / *godišnje doba*	
	hot / *vruće*	very dry / *vrlo suho*
	warm / *toplo*	dry / *suho*
	normal / *normalno*	normal / *normalno*
	cool / *hladno*	humid / *vlažno*
	cold / *vrlo hladno*	very humid / *vrlo vlažno*

tion in 1917 also varied significantly: autumn and summer – dry, spring – wet, and winter – average (normal). Two subsequent positive pointer years were also characterized by an individual pattern of temperature and precipitation. In 1966, autumn was cold and dry, winter – average (normal) and humid, and spring and summer did not deviate from the norm in terms of both these categories. There was another distribution of temperature and precipitation in 1982, where the autumn was average and humid, winter and spring average in terms of variations of temperature and precipitation, and summer warm and dry. In the group of negative pointer years, we were also unable to determine typical weather patterns, this time favorable to the formation of narrow TRW. For example, in 1923 and 1953, in which the average TRWs were only 2.46 mm and 2.80 mm, autumn was cold and damp, and spring and summer – average or cool and dry. By contrast, 1981 and 2009 were dry in autumn and cool in the summer, but with normal temperatures in autumn, winter and summer.

4 DISCUSSION
4. RASPRAVA

Slightly different statistical characteristics compared to the results obtained in Wrocław for the constructed TRW chronology of pedunculate oak were obtained by Rybníček *et al.* (2016) in Liteň Obora (about 10 km from Prague), as well as Čufar *et al.* (2014) in Croatia. Indicators calculated for both Czech and Croatian chronologies differed from those for Wrocław, e.g. $\bar{x}$ and *SD* were on average 1.55 and 0.16 mm lower, while the I^{o} autocorrelation coefficient was higher, on average by 0.29. The larger TRWs of pedunculate oak in Wrocław were most likely the result of the trees growing in urban conditions and not in semi-natural plant groups. In this way, the studied trees lacked neighboring tree interactions and also had greater access to solar radiation. The site from which the samples were taken, i.e. the Oder flood protection embankments, is not without significance. Even with long-lasting droughts, the root systems of the studied trees could always draw from ground water resources (in principle without limit). Besides that, Wrocław has milder winters than other Polish regions (Lorenc, 2005).

The significant positive relationship between TRW and temperature in the December of the previous year proven in this study, partially confirms the research carried out in northern Poland by Pritzkow *et al.* (2016), where they proved a positive correlation between the indicator describing the average surface area of vessel in the early wood of pedunculate oak and the minimum air temperature in the period 1951-2010 between the 29th of November and the 20th of January. According to Pritzkow *et al.* (2016), during the low temperatures in winter, damage may be caused to the tree root system, which often leads to the emergence of smaller vessels in the early wood and thus narrower TRW. Negative winter air temperatures adversely affect the cambium area and often cause variations in the development of spring wood (Khasanov, 2013). The percentage of winter damage to the tree-rings depends on the age of the tree, and decreases from approx. 76 % in young specimens (> 41 years during harsh winters) to approx. less than 4 % in older trees (> 81 years). According to Tulik (2014), the formation of narrow TRW and small diameter vessels in the early wood increases the susceptibility to degradation. The reduced diameter of the vessels negatively affects the hydraulic conductivity of oak tree trunks, resulting in deteriorated water transport. Matisons *et al.* (2013) obtained other results based on TRW, calculated only for the pointer years in Latvia and temperature and precipitation. In western Latvia, the strongest positive impact on TRW was from temperature in March and June, which is different than in Wrocław, where TRW was significantly positively influenced by temperature in July. On the other hand, in eastern Latvia, temp in December of the preceding year had a strong negative influence, similar to our study. In southeastern Estonia, from 1945-2008, pedunculate oak TRW depended significantly and favorably on temp in July (Sohar *et al.,* 2014), i.e. the same as in the Wrocław chronology from 1965-2014. Research aimed to establish a relationship between annual pedunculate oak tree growth and temperature, precipitation and other agrometeorological elements was also carried out by (among others): Helama *et al.* (2016) and González-González *et al.* (2015), who, in their analyses, considered both early as well as late wood separately. Such research was also carried out by Bronisz *et al.* (2012), Čufar *et al.* (2014), Cedro and Nowaka (2015), Rybníček *et al.* (2016) and Tulik and Bijak (2016). According to Cedro and Nowak (2015) TRW variability in north-western Poland can be explained by temperature and precipitation variability even in approx. 54 % of cases. According to Hughes (2002), the weather/TRW relations are stronger, the closer the studied trees grow to the natural range of the species.

In determining the pointer years, various values of unidirectional changes in tree-ring sequences are accepted, usually from 70 % to 90 % (Bronisz *et al.,* 2012; Okoński *et al.,* 2014). Due to the small sample in this study, pointer years were determined in the case of unidirectional change occurrences in tree-rings in 100 % of the studied sequences. Sohar *et al.* (2014) determined 38 pointer years throughout Estonia from 1769-2008, including 19 positive and 19 negative, which means that wide or narrow tree-rings of pedunculate oak formed every 6-7 years. In the Wrocław chronology, pointer years were noted every 10 years, and only three of them (1923, 1966, and 1981) coincided with the pointer years designated by Sohar *et al.* (2014). Certainly, the designated pointer years based on the Wrocław chronology corresponded to the local edaphic-climate conditions. Cedro and Nowak (2015) designated as many as 40 pointer years (13 positive and 27 negative) in a 111 year period, and among them only one, 1989, was consistent with our observations. In contrast, Stopa-Boryczka *et al.* (2007) determined a similar number of pointer years to our research. For example, pointer years occurred every 11 years in their Gdańsk chronology (1800-1982), and every 8 years for Toruń (1781-1984). According to Stopa-Boryczka *et al.* (2007), pointer years for oaks were 1923 (negative year), 1960 (negative), 1981 (negative) and 1982 (positive). The same pointer years were observed in Wrocław chronology in the period 1914-2014. The pointer years determined in this paper were also noted by other researchers examining *Quercus,* e.g: two pointer years – 1966 and 1982 by Stajić *et al.* (2015), one positive year – 1982 by Bronisz *et al*. (2012), four positive years – 1923, 1953, 1960, and 1989 by Kędziora *et al*. (2012). The pointer years were also analyzed by (among others): Cedro (2007) in north-western Poland, Bronisz *et al.* (2012) in central Poland, and Lebourgeois *et al.* (2004) in northern France. Those researchers, similar to this paper, noted the following pointer years: 1917, 1981, and 1989. Also Romanian and Wrocław studies partly confirmed the formation of narrow tree-ring widths in the years 1953 and 1981 (Nechita 2013).

5 CONCLUSIONS
5. ZAKLJUČAK

In our study, in the period 1887-2014, tree-ring widths (TRWs) of pedunculate oak growing on the embankment of the Oder River in Wrocław, south western Poland, were generally (ca 51 %) 2 to 4 mm wide. Tree-rings wider than > 7 mm grew very seldom, comprising only 2.4 % of all measured rings. The widest ring was 11.71 mm and the narrowest only 0.46 mm.

The created site chronology covered 128 years from 1887 to 2014. The average tree-ring width in 1915-2014 was 3.56 mm; ranging from 2.41 mm to 5.44 mm in the early half of the study period (1915-1964), and from 2.10 mm to 4.45 mm in the later half (1965-2014). Higher variability, described by TRW standard deviation, was observed in the earlier half (1915-1964).

TRW was significantly positively influenced by air temperature in December of the previous year and in July of the current year, but only in the later half of the analyzed period. In the same period (1965-2014), precipitation in June of the previous year and in January and September of the current year also had a positive effect on TRW, while precipitation in July of the current year had a negative effect on TRW.

Ten pointer years were determined, in which narrow or wide tree-rings developed. Both in the group of positive pointer years (1917, 1966 and 1982) as well negative years (1923, 1951, 1953, 1960, 1981, 1989 and 2009), we were unable to determine similar variation patterns of temperature and precipitation.

Research on the TRW series of pedunculate oaks on flood protection embankments should be continued. By analyzing numerous sites in the Oder valley, it will be possible to better understand the dendrometry of the created chronology and determine the effect of climate conditions on TRW.

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Corresponding address:

MONIKA ZIEMIAŃSKA

Wrocław University of Environmental and Life Sciences
Faculty of Environmental Engineering and Geodesy
Institute of Landscape Architecture
Grunwaldzka Street 55
50-357 Wrocław, POLAND
e-mail: monika.ziemianska@upwr.edu.pl

Maria Rosienkiewicz[1], Arkadiusz Kowalski, Joanna Helman, Marcin Zbieć[2]

Development of Lean Hybrid Furniture Production Control System based on Glenday Sieve, Artificial Neural Networks and Simulation Modeling

Razvoj sustava kontrole proizvodnje namještaja *Lean Hybrid* na temelju metode *Glenday sieve*, umjetnih neuronskih mreža i simulacijskog modeliranja

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ABSTRACT • *In the paper, by way of background, the role of Polish furniture industry in the world and in Europe is discussed and current trends in the field of furniture manufacturing management are presented. Further, an analysis of the technological process in a furniture company is performed and the research questions are identified. Based on this, the main aim of the research is provided – a concept of a new lean production control system based on Glenday sieve, artificial neural networks and simulation modeling. The aim of the present approach is to plan and execute the production program effectively and maximize the use of workstations at variable and hardly predictable demand for sets of furniture. The paper presents the methodological approach, results and discussion on the suggested solution.*

Key words: *production planning system, Glenday sieve, artificial neural networks, simulation modeling, furniture industry, industry 4.0*

SAŽETAK • *U radu je predstavljena uloga poljske industrije namještaja u svijetu i Europi te trendovi u području upravljanja proizvodnjom namještaja. Nadalje, provedena je analiza tehnološkog procesa u poduzeću za proizvodnju namještaja i identificirane teme istraživanja. Na temelju toga definiran je osnovni cilj istraživanja – koncept novog sustava lean kontrole proizvodnje koji se temelji na metodi Glenday sieve, umjetnim neuronskim mrežama i simulacijskome modeliranju. Cilj opisanog pristupa jest učinkovito planiranje i izvršavanje proizvodnog programa te maksimalna iskorištenost proizvodnih kapaciteta pri promjenjivoj i teško predvidivoj potražnji namještaja. Rad prikazuje metodološki pristup, rezultate i raspravu o predloženom rješenju.*

Ključne riječi: *sustav planiranja proizvodnje, metoda Glenday sieve, umjetne neuronske mreže, simulacijsko modeliranje, industrija namještaja, industrija 4.0*

[1] Authors are assistant professors at Faculty of Mechanical Engineering, Wrocław University of Science and Technology, Wrocław, Poland. [2]Author is professor at Faculty of Wood Technology, Warsaw University of Life Sciences,Warsaw, Poland.

[1] Autori su docenti Strojarskog fakulteta, Sveučilište znanosti i tehnologije u Wroclawu, Wrocław, Poljska. [2]Autor je profesor Fakulteta drvne tehnologije, Sveučilište bioloških znanosti u Varšavi, Varšava, Poljska.

1 INTRODUCTION
1. UVOD

In the contemporary global market, furniture manufacturers are facing strong competition (Zadnik Stirn *et al*. 2016). In order to maintain their market share, they have to improve their manufacturing and management processes and introduce innovations both in products and processes, as well as to be familiar with the consumer's needs (Fabisiak 2017, Oblak *et al*. 2017).

The main objective of every furniture company is an efficient business (Hrovatin *et al*. 2015). To achieve this goal, companies are forced not only to produce their furniture using high-quality and precise machinery and equipment but also to manage and control their process in an effective way. To do that properly in the floating environment and bearing in mind lumpy and intermittent customer's demand, companies have to plan their production in a very efficient, yet agile and flexible manner. Effective demand forecasting is essential for the companies, where ensuring the continuous and fault-free operation is required (Rosienkiewicz *et al*., 2017). The well-calculated demand forecasting is crucial to reduce purchase volumes and to optimize stocks (Santin *et al*., 2015). In his paper, Kolassa (2016) discusses about the big data trend in terms of retail sales forecasting. According to his research, operational forecasting in retail should be conducted not only at highly aggregated levels, but possibly at a most fine-grained level, i.e. for count data and intermittent demands.

According to the EU report on the furniture market (Centre for European Policy Studies, 2014), Poland is one of 10 top countries of world furniture production (2 % of world production). Although economic recession has strongly influenced the operation of the companies focused on wood processing and furniture manufacturing during the last several years (Jelačić *et al*., 2012), it can be noticed that furniture production in the EU is slowly recovering from the period of weakness. Italy, Germany, and Poland – Europe's three largest furniture producing countries – "all raised their output in 2014 and early 2015. Furniture production in Poland increased particularly sharply last year and in the first quarter of 2015" (ITTO, 2015). This situation encourages Polish furniture producers to invest in their factories, to enlarge them and to implement innovative solutions enhancing management processes, especially now – in the era of Industry 4.0. The term "Industry 4.0" comes from the name of the project, started by the German government for their high-tech-strategy, which has been developed to take advantage of recently emerged disruptive technologies including i.a.: Cyber-Physical Systems, Artificial Intelligence, Internet of Things and Services (IoTS), Big data, Augmented Reality. It is considered as the beginning of the fourth industrial revolution, which mainly refers to the digitization of industry. It is expected that it will fundamentally change the production methods and business models presently used in industrialized countries. Recently, certain producers, who have started implementing technology of IoTS, focused their sales on the Internet channel. The online sales market in the furniture industry is not very developed in Poland. Even IKEA started selling furniture via Internet only in February 2017 and this service is still in a pilot phase. However, this sales channel will be developing in the years to come. It is expected that IoTS, one of the pillars of Industry 4.0, will play a major role in the furniture industry in the near future.

As Perić *et al*. noticed, it is important to underline that wood industry is a resource-intensive industry, and as such does not have a high added value, yet is important to the national economy (Perić *et al*., 2017). Therefore, in cases of furniture companies, especially the SMEs, it is crucial to invest in knowledge, knowledge management and technology in order to be competitive on the market. It is a rather well-known trend that a lot of solutions, methods and tools are first developed in the automotive industry and other high-tech branches, and then they are implemented into less-automated sectors, like the mining or wood industry (Chlebus *et al*., 2015).

The Authors performed a literature review to analyze which aspects of production management in the furniture industry have been recently researched. Previous research studies of production management in the furniture industry indicate that Computer Aided Design (CAD) software is nowadays conventionally used in furniture companies (Hrovatin *et al*., 2015). Usage of the MRP or ERP systems is almost a standard, yet for companies that want to be more agile and flexible, this is not enough. These companies have to implement more advanced solutions (based e.g. on artificial intelligence). Santin *et al*. (2015) suggest an approach of minimizing the difference between production and demand based on ABC analysis and forecasting sales volumes on a quarterly basis implemented in the MRP system. According to Perić *et al*. (2017), the ERP systems are mainly used for the financial module, human resources, management, and production processes, purchasing and sales management. The issue of the supply chain management was discussed by many researchers. Zhang and Zhang (2007) investigated the implementation of the simulation approach to quantify the benefit of the demand information sharing in a three-tier supply chain model, whereas Robb *et al*. (2008) developed a model exploring relationships between supply chain/operations practice and operational/financial performance in a Chinese furniture manufacturer. In their research, Caridi *et al*. (2012) discussed whether supply chain choices depend on product modularity and innovativeness, and how supply chain choices can be aligned to these product features to maximize performance. Optimization of furniture production was analyzed in a technological aspect by Oliveira *et al*. (2016) and in a managerial aspect by Alem and Morabito (2012). Oliveira *et al*. (2016) presented an information system for the furniture industry to optimize the cutting process and the generated waste, while other mentioned authors were focused on the application of a robust optimization to production planning in furniture manufacture under data uncertainty.

Further, the literature review shows a promising research carried-out by Yao and Carlson (2003) on an agile furniture production concept based on MRP, JIT and TQM. In the paper of Massote and Santi (2013), an implementation of a cleaner production program in a Brazilian wooden furniture factory is described, showing that the trends for eco-friendly production can be observed not only in automotive industry. Rosa and Beloborodko (2015) suggested a decision support for the development of industrial synergies based on case studies of Latvian brewery and wood-processing industries. Guimarães *et al*. (2016) presented the results of their research on Brazilian furniture industry considering product innovation and organizational performance. These papers prove that a lot has been done to enhance and support furniture production from the research point of view.

Literature review presented by the Authors shows that there are many solutions implemented from automotive sector to wood or furniture industry, yet there is a lack of a comprehensive approach that would begin with an analysis of the demand and finish on production planning and control. In any manufacturing company, importance of furniture production management and control can not be overemphasized. An efficient control system based on accurate production plan influences agile production and realization of production orders. Therefore, the main aim of the paper is to develop a concept of a dedicated lean production control system, which would make it possible for a company to plan and execute its production program effectively, maximizing the use of workstations at variable and hardly predictable demand for furniture sets. The proposed solution is based on lean management, Artificial Neural Networks (ANNs), and simulation modeling. ANNs, being mathematical models for representing the biological processes of the human brain (Segall, 1995), for some time now have been advocated as an alternative to traditional statistical forecasting methods.

1.1 Development of a new production control system
1.1. Razvoj novog sustava kontrole proizvodnje

This paper is a summary of the research carried out for a company (described in section 2.5) from the furniture industry. In the company, whose key marketing channel is the online marketing channel, it was decided to develop a new production system that would result in increased effectiveness and production volume, delivery time reduced to 48 hours (in the online sales channel) and more precise sales forecasts, which, in turn, would result in improved production planning. All those features require implementation of Industry 4.0 technologies. Development of such a manufacturing system is a complex and multi-stage process. During the works on developing a dedicated system, several research questions appeared:

- In what way the sales level can be forecasted, when the company has no sufficient available base of reliably acquired statistic data?
- In these circumstances, how a set of explanatory variables should be constructed?
- In what way, at diversified demand (series production and individual, customized orders), the manufacturing process should be controlled?
- In what way the production strategy for various product types should be elaborated?
- How to verify whether the designed system will be immune to disturbances?

1.2 Demand forecasting problem
1.2. Problem predviđanja potražnje

Demand forecasting is an issue of large uncertainty and characterized by fluctuations. In order to solve this problem in the abovementioned company, future demand values were exactly analyzed, so that real demand could be characterized. According to the approach proposed by the Authors, the examination began from demand analysis and trial forecasts in daily terms. Preliminary results showed that the furniture demand is of a lumpy, intermittent nature and often takes the zero value. Demand forecasts in daily terms, both obtained by traditional methods and based on Artificial Neural Networks (ANNs) executing regressive relationships, were burdened with very high errors (see Appendix). For this reason, it was decided to perform the calculations in aggregated, monthly terms, which is a common practice in data science. The next problem hindering determination of effective forecasts was that the data required to build the ANNs executing regressive relationships, based on explanatory variables, were unavailable in the company. For this reason, the Authors decided to apply a hybrid approach in which the forecasts obtained by traditional methods (moving average (MA), exponential smoothing (SES) and naïve method) would play the role of some explanatory variables.

1.3 Pull system
1.3. Sustav povlačenja

Mass production of furniture with use of pressboards in the conditions of strong competition enforces low price and short delivery time. Large numbers of coloristic variants of the offered furniture, combined with large numbers of dimensions of individual cabinets, make storage of finished products impossible. Therefore, satisfying the customers' demand by collecting goods from the stock of finished products is impossible, even if these products are stored in packages to be individually assembled by the customers themselves. At the above-mentioned boundary conditions, the best solution would be basing the production system on the Lean Manufacturing concept and, in particular, on the sequential pull system and the replenishment pull system as suggested by Smalley (2009).

In the replenishment pull system, stocks of finished products from each group (after segmentation of products) are maintained, and manufacture is initiated only after shipment of individual products from the warehouse to the customer (necessity to replenish the stock). In this system, finished products can be shipped immediately after receiving the order. In the sequential pull system, manufacture is initiated upon a specific customer's order, at the moment of its receipt only. The production order is directed to the first manufacturing operation. However, this type of pull system is difficult to be implemented in the case of long takt time, unstable production processes and small availability of machines (Fulczyk, 2017).

Determination of inventory in the replenishment pull system will be based on the results of forecasts coming from the ANNs. In turn, all errors of the forecasts will be currently corrected by starting the sequential pull system.

1.4 Glenday sieve
1.4. Metoda *Glenday sieve*

Another problem to be solved is determining which product should be qualified to manufacture in the sequential pull system, and which to manufacture in the replenishment pull system. In this case, the Authors decided to use the Glenday Sieve. The Glenday sieve is a "method for identifying high-volume production processes upon which to focus process improvement initiatives. The Glenday sieve approach states that a small percentage of procedures, processes, units or activities account for a large portion of sales, and includes a color-coding system for labeling processes by output volume" (WebFinance, 2017). The Glenday sieve classifies products in four categories (Kerber, 2007): green – high volume items that are probably already produced frequently, yellow – encounter real barriers against introducing manufacture of each product in each cycle; blue –include materials and procedures introducing the additional complexity, adding no value for the customer; red – a question should be asked about rationality of manufacture and sales of these products. It was assumed that another production line should be built and added to the sequential pull system for unpredictable, individual and customized orders.

1.5 Simulation modeling
1.5. Simulacijsko modeliranje

As Zhang and Zhang (2007) state, implementation of a simulation enables the decision makers to examine changes in a part of the chain and subsequent consequences with less expense than would be required for a field experiment, which is usually difficult to be carried out. Therefore, in the present approach, the simulation was implemented. Within the solution of the issue that is connected with the possibility to verify whether the designed system will be resistant to disturbances, it was decided to build a simulation model of the manufacturing system of kitchen and bathroom furniture for the observed company. In this model, among others, it is possible to verify loads of machines and workers, to optimize the workshop layout, to introduce random failures and disturbances, as well as to evaluate a response of the designed control system to these occurrences.

1.6 Analysis of technological process
1.6. Analiza tehnološkog procesa

The analyzed company deals with the production of kitchen and bathroom furniture. It is located in the Wielkopolska region, the center of Polish cabinet furniture industry. The company has a wide range of models and patterns of manufactured products. This results in a large number of furniture variants to be made for a customer's order. The number of furniture variants $V_{\text{furniture}}$ is obtained by multiplying numbers of variants of bodies V_B, fronts V_F, handles V_{Ha}, hinges V_{Hi} and muntins V_M:

$$V_{\text{furniture}} = V_B \cdot V_F \cdot V_{Ha} \cdot V_{Hi} \cdot V_M. \tag{1}$$

Even with limited variant numbers of bodies and fronts or handles, hinges and muntins, the number of furniture variants – determined by the formula (1) – soon exceeds 20 000 pieces. There is no physical possibility to maintain stocks of furniture in this size; it is hard to imagine dimensions of such a warehouse and its maintenance costs. The storage space is also often restricted by the area of industrial plot at the company disposal. In addition, the number of variants should be enlarged by in-stock level for each variant.

It can be observed that, to preserve low manufacturing costs, furniture cannot be manufactured for stock because of too large number of variants. On the other hand, customers cannot accept a long time of waiting for the ordered furniture; waiting times in the furniture industry often reach 5 or 6 weeks. So, the furniture delivery time is an important competitiveness factor and customers often decide to buy from the manufacturer who delivers the products faster.

In the analyzed company, manufacturing of cabinet furniture proceeds according to the schedule of production and set order of technological operations. A diagram of the manufacturing process, written in the IDEF0 notation is shown in Fig. 1, where individual technological operations are represented in consecutively numbered A1- A6 boxes.

To satisfy the opposing requirements (unpredictable demand, production time longer than the order execution time, etc.), the company manufactures and stores bodies and face panels of the cabinets separately. Most often, the bodies appear in several colors and sizes, and face panels. In the warehouse, after receiving an order for a specific furniture set, bodies are combined with proper face panels in selling sets. At this stage, the order is completed with handles to the doors and drawers, hinges and other shopping items.

2 METHODS
2. METODE

The methodology of building a complex, lean hybrid production system that would increase production effectiveness and volume, as well as provide more precise production planning based on the Glenday sieve, ANNs and simulation modeling, is composed of several stages, as shown in Fig. 2.

The first stage is an analysis of a vast range of products using the Glenday Sieve (Glenday 2007). The manufactured wooden furniture was subjected to detailed analysis on the basis of historical data concerning production volume and frequency of customers orders. Based on that, four groups of products were created and three paths were selected: green stream (50

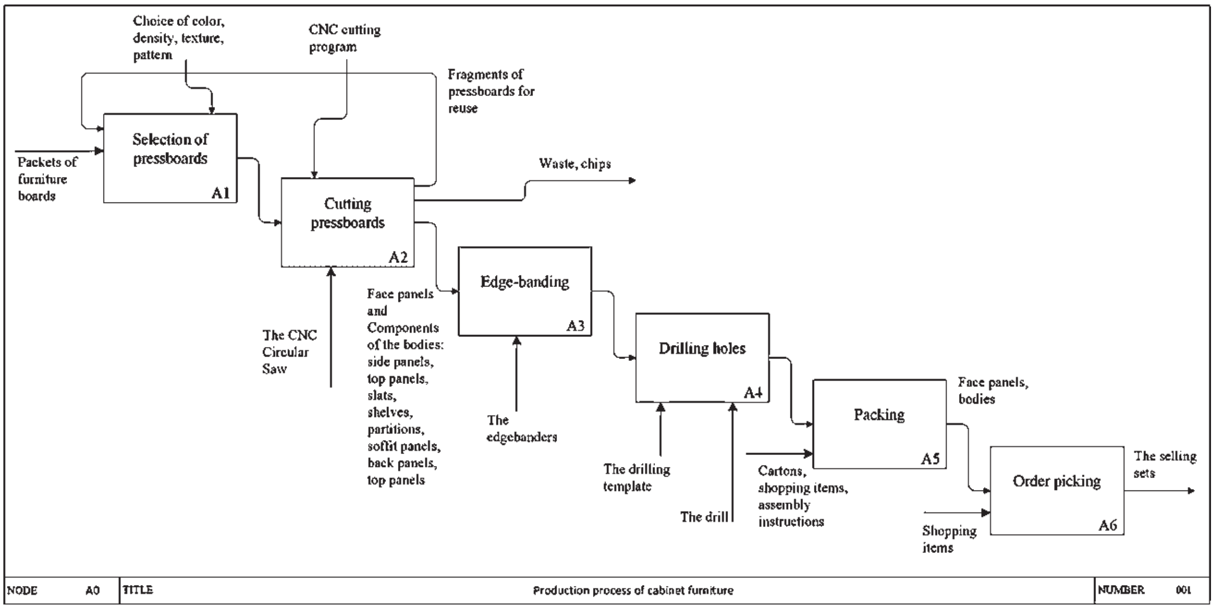

Figure 1 Diagram of cabinet furniture manufacturing process, created in IDEF0[1]
Slika 1. Dijagram procesa proizvodnje korpusnog namještaja, izrađeno u IDEF0

% of sales volume – mass production) – production forecast based on the ANN approach; blue and yellow streams (respectively up to 40 % and 10 % of sales volume – single order production) – production based on compensation of forecast errors; red stream (less than 1 % of sales volume) – shutdown of production.

On the basis of the forecast results, the required number of machines i_0 is calculated based on i_0 rate:

$$i_0 = \frac{\sum_{i=1}^{n} \left(setup\,time + n \cdot run\,time \right)}{\Psi_d \cdot D \cdot I \cdot h}, \quad (2)$$

Where is n – No. of pieces, Ψ_d – factor of day utilization, D – No. of days, I – No. of shifts, and h – No. of hours/shift.

According to the determined number of necessary machines, the simulation model should be built.

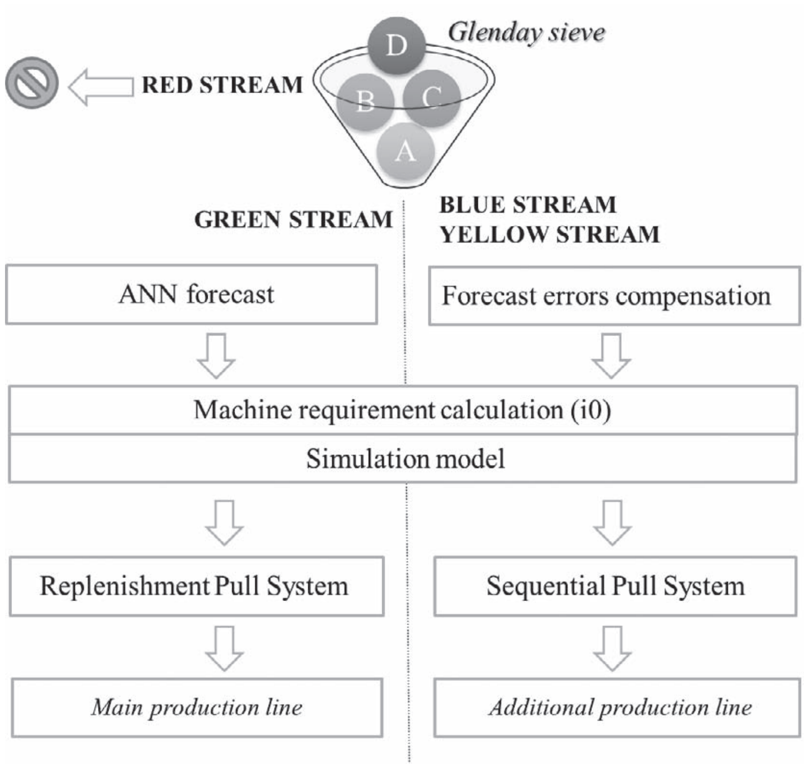

Figure 2 The concept of Lean Hybrid Furniture Production Control System
Slika 2. Koncept sustava kontrole proizvodnje namještaja *Lean Hybrid*

[1] *IDEF refers to a family of modeling language, where IDEF0 is Integration DEFinition for Function Modeling.*

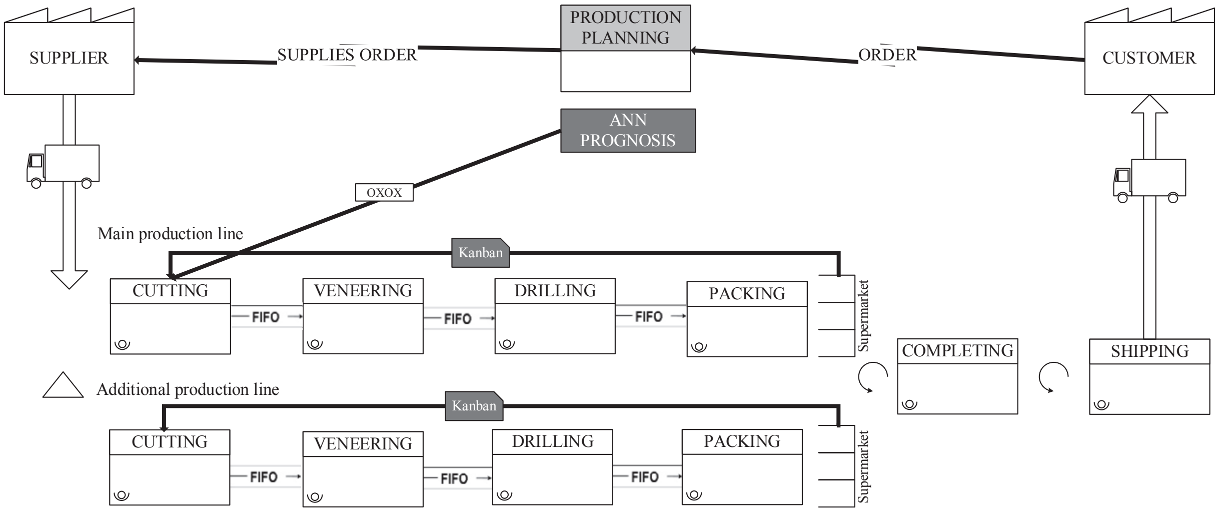

Figure 3 Current State Value Stream Map
Slika 3. Trenutačno stanje karte toka vrijednosti

Based on results of the simulation model (loads of machines and workers, optimization of the workshop layout, introduction of random failures and disturbances, as well as evaluation of a response of the designed control system to these occurrences), two paths should be used for the production systems:

1. for green products stream – Replenishment Pull System used in the main production line;
2. for blue and yellow products stream – Sequential Pull System used in the additional production line.

The main production line will use highly efficient machines for wood cutting, veneering, drilling and packing, while the additional production line will consist of smaller and less expensive machines. Both lines should have a Supermarket after the packing workstation, where all the elements, ready for completing, will be stored. When the products are completed from the supermarket, a production Kanban card will be moved to the first workstation in the line, giving a signal to start production of the taken element. The Current State Value Stream Map (Fig. 3) of wooden furniture production and Future State Map (Fig. 4) with the suggested changes are presented below.

According to the above-presented concept of production control system, forecasts for the green parts to be considered during production planning by means of a simulation model will be determined on the ground of the ANN. A diagram of building an ANN is shown in Fig. 5 below (MA stands for moving average, k is number of periods, SES stands for single exponential smoothing, α is a smoothing constant, x is an explanatory variable).

As mentioned above, because of unsatisfactory calculated forecasts of daily demand for selected types of furniture (caused by a shortage of available historical data), the analysis was carried-out in aggregated, monthly terms. From statistical point of view, a disadvantage of this approach (aggregation) is a significant reduction of the sample size (at daily forecasting it should be at least several hundred (n>400) and at monthly forecasting – because of missing data from previous periods – it should range between 17 and 23 observations). Usually, the more observations, the more precise are the forecasts, because the prediction models can better identify periodicity, seasonal relationships, and data trends. For the research and development purpose, a simulation model of the analyzed production system was developed, taking into account the following components of the system: workstations, components and parts of the products, transportation paths, production resources – workers and means of transport, manufacturing processes, and production plans.

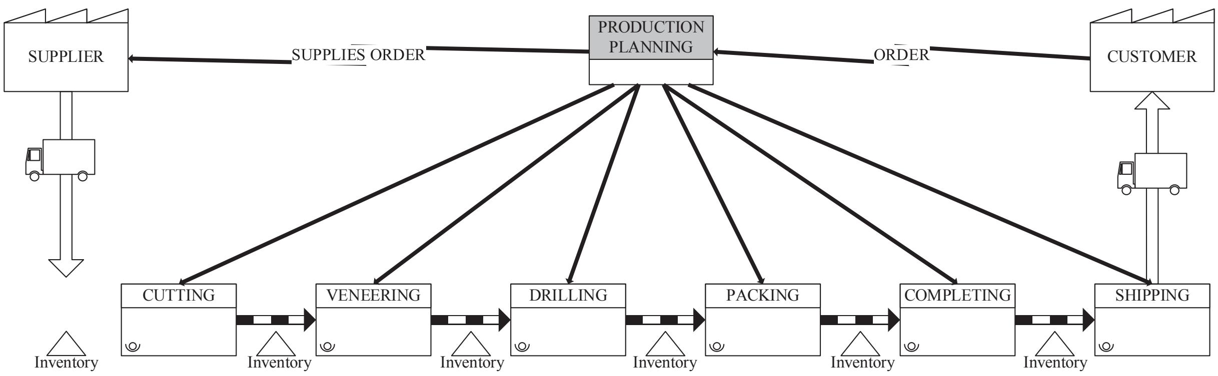

Figure 4 Future State Value Stream Map
Slika 4. Buduće stanje karte toka vrijednosti

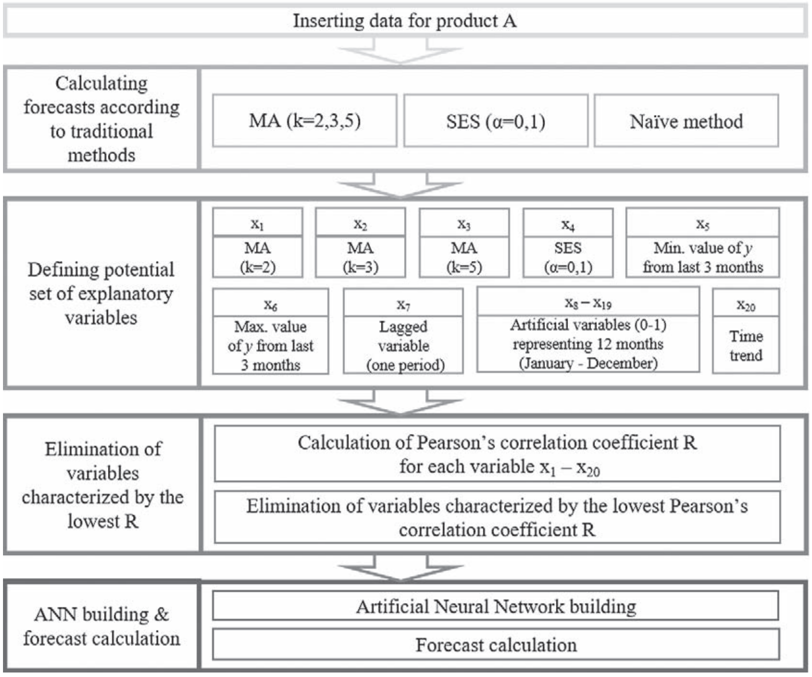

Figure 5 Hybrid algorithm for forecast calculation
Slika 5. Hibridni algoritam za proračun predviđenih vrijednosti

Next, the simulation model was subjected to numerous simulation examinations in order to validate it, comparing the effectiveness of the model – at specifically limited production resources – with its existing equivalent.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

In the analyzed company, 76 types of cabinet furniture are manufactured (without color differentiation). After analysis of the product line by the use of the Glenday Sieve, the products were assigned to the following groups: green stream – 15 products, yellow stream – 23 products, blue stream – 16 products, red stream – 22 products. On this ground, the furniture types were selected: the types that should be removed from the offer (red stream) and the types that should be applied for the two kinds of manufacturing approach. For the green-stream products – manufacture should be started in the main production line on the basis of the ANN forecasts, for the yellow- and blue-stream products – manufacture should be started in the additional production line based on real customer's demand. For further analysis, the green-stream products are designated by the characters from A to O so as not to disclose the company's data.

For each analyzed type of furniture (A-O), an ANN network was constructed in the Statistica 12.0 program. Characteristics of individual networks: sample size, variables being inputs to the ANN (x_1-x_{20}), the network structure: multilayer perceptron (MLP) and supervised learning algorithm (Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm), quality of learning, testing and validation are presented in Table 1 below. The table also shows the determined relative forecast errors ex-post for each type of furniture. To compare the effectiveness of the forecasts coming from the ANN, the forecasts were also calculated by traditional methods: moving average (MA) for k = 2, 3 and 5, exponential smoothing (SES) and naïve method.

The obtained effectiveness values for all the examined furniture types indicate that the most effective method of monthly sales forecasting for 13 out of 15 types are artificial neural networks. The ANNs appeared less effective in sales forecasts of the products A and B only (error >= 40 %). However, it should be emphasized that sample size in these cases was n=17 observations only, so the results are hardly reliable. The analysis of effectiveness levels of the forecasts also shows that values of the relative forecast error ex-post did not exceed 40 % for over 85 % of the furniture types. This result is much better than that obtained for the daily sales forecasting. The ANN forecast error values ranged between 15 % (min.) and 55 % (max.), with the average value for 15 furniture types equal to 31 % (median 27 %). Even if significant, these errors can be found acceptable, considering the modest number of observations.

On the grounds of the forecasts calculated with use of ANNs, a production schedule was prepared and then numbers of machines required for the execution of the assumed plan were calculated according to the formula (2). The results are given in Table 2.

This way a determined number of production machines was verified by the simulation model. This is an important part of the present method since the expression for i_0 does not consider i.a. the time of waiting for the machine operator (resulting from his moving between machines) or the time for transporting the elements between machines. The simulation model also makes it possible to observe the dynamics of load changes of the analyzed workstation, see Fig. 6.

Table 1 ANN characteristics and Relative Forecast Error ex-post for each analyzed method
Tablica 1. ANN karakteristike i relativna pogreška predviđanja *ex-post* za svaku analiziranu metodu

Product / *Proizvod*		Sample size (n) / *Veličina uzorka*	ANN characteristics / *ANN karakteristike*						Relative Forecast Error ex-post / *Relativna pogreška predviđanja* ex-post					
			Variables / *Varijable*	ANN structure / *Struktura ANN-a*	Quality (training)	Quality (testing)	Quality (validation)	Learning algorithm / *Algoritam učenja*	ANN	MA (2)	MA (3)	MA (5)	SES	Naïve method
1	A	17	*x*1-*x*3; *x*5-*x*7; *x*17; *x*19	MLP 8-5-1	0.999	0.397	0.72	BFGS 17	40 %	36 %	41 %	48 %	**33 %**	**33 %**
2	B	17	*x*1; *x*5; *x*7; *x*11; *x*20	MLP 5-3-1	0.818	0.885	0.129	BFGS 5	52 %	**44 %**	46 %	48 %	47 %	47 %
3	C	20	*x*1-*x*4; *x*6; *x*7; *x*10; *x*20	MLP 8-11-1	0.781	0.663	0.862	BFGS 21	**37 %**	56 %	51 %	54 %	65 %	65 %
4	D	20	*x*1-*x*7; *x*16; *x*20	MLP 9-5-1	0.814	0.808	0.999	BFGS 6	**36 %**	50 %	56 %	59 %	48 %	48 %
5	E	20	*x*2-*x*7; *x*19; *x*20	MLP 8-12-1	0.638	0.951	0.994	BFGS 3	**55 %**	83 %	69 %	67 %	81 %	81 %
6	F	20	*x*1-*x*7; *x*10; *x*20	MLP 9-10-1	0.98	0.905	1	BFGS 51	**20 %**	48 %	46 %	48 %	51 %	51 %
7	G	23	*x*1-*x*20	MLP 20-9-1	0.996	-0.55	0.838	BFGS 0	**24 %**	32 %	34 %	38 %	36 %	36 %
8	H	23	*x*1-*x*20	MLP 20-8-1	0.762	0.862	0.995	BFGS 3	**27 %**	42 %	43 %	47 %	51 %	51 %
9	I	23	*x*1-*x*20	MLP 20-15-1	0.942	1	1	BFGS 6	**23 %**	30 %	38 %	50 %	36 %	36 %
10	J	23	*x*1-*x*20	MLP 20-14-1	0.99	0.471	0.744	BFGS 0	**39 %**	45 %	42 %	47 %	47 %	47 %
11	K	23	*x*1-*x*20	MLP 20-13-1	0.676	0.962	0.522	BFGS 3	**34 %**	42 %	38 %	40 %	42 %	42 %
12	L	23	*x*1-*x*7; *x*20	MLP 8-6-1	0.949	0.823	1	BFGS 28	**23 %**	46 %	42 %	49 %	51 %	51 %
13	M	20	*x*1-*x*7; *x*11; *x*19; *x*20	MLP 10-6-1	0.912	0.973	0.658	BFGS 34	**22 %**	74 %	71 %	65 %	84 %	84 %
14	N	23	*x*1-*x*20	MLP 20-8-1	0.985	0.945	0.958	BFGS 17	**22 %**	52 %	54 %	53 %	61 %	61 %
15	O	21	*x*1-*x*7; *x*13; *x*20	MLP 9-4-1	0.968	0.445	0.9	BFGS 37	**15 %**	50 %	45 %	45 %	60 %	60 %

Table 2 Required number of machines i_0 calculation
Tablica 2. Broj strojeva potreban za izračun i_0

Machine type / *Vrsta stroja*	i_0	Number of machines / *Broj strojeva*
Saw / *stroj za piljenje*	3.29	4
one-sided edge banding machine / *stroj za jednostrano oblaganje rubova*	2.47	3
four-sided edge banding machine / *stroj za četverostrano oblaganje rubova*	0.46	1
drilling machine / *bušilica*	2.09	3
drilling machine for small elements / *bušilica za male elemente*	0.59	1
packing station / *stroj za pakiranje*	1.33	2

Loads of the machines result from their covering with technological operations (and numbers of the manufactured parts) and retooling when the manufactured product is to be changed. Comparison of verified loads of the machines and facilities is shown in Fig. 7.

Apart from percentage loads of the machines, Fig. 7 shows waiting time for a resource (e.g. for the operator; the machine can not start working without his execution of some initiating actions). Another element, not included in loads of the machines and facilities, according to the formula for i_0, is waiting time for removing the machine in the case when there is no place to put it aside (the buffer behind the machine is 100 % filled and the parts are not conveyed to another workstation because they are waiting for a transport means or for a free place in the buffer). In this condition, the machine is counted as blocked.

In the analyzed case, a verified load of the machines never exceeds 100 %, so it can be acknowledged that the forecast production plan is realizable and the customer's order should be executed within 48 hours.

4 CONCLUSIONS
4. ZAKLJUČAK

The main aim of the present research was to develop a dedicated lean production control system for a furniture company operating in the Internet environment, which would enable the production program to be planned and executed effectively, with maximum use of wood-processing workstations at variable and hardly predictable demand for furniture. Implementation of such a system makes it possible to obtain significant benefits, fitting the needs of Industry 4.0. According to the presented methodology, application of the Glenday sieve permits the wooden products to be classified into two groups. One group of products will be manufactured according to the forecasts obtained by

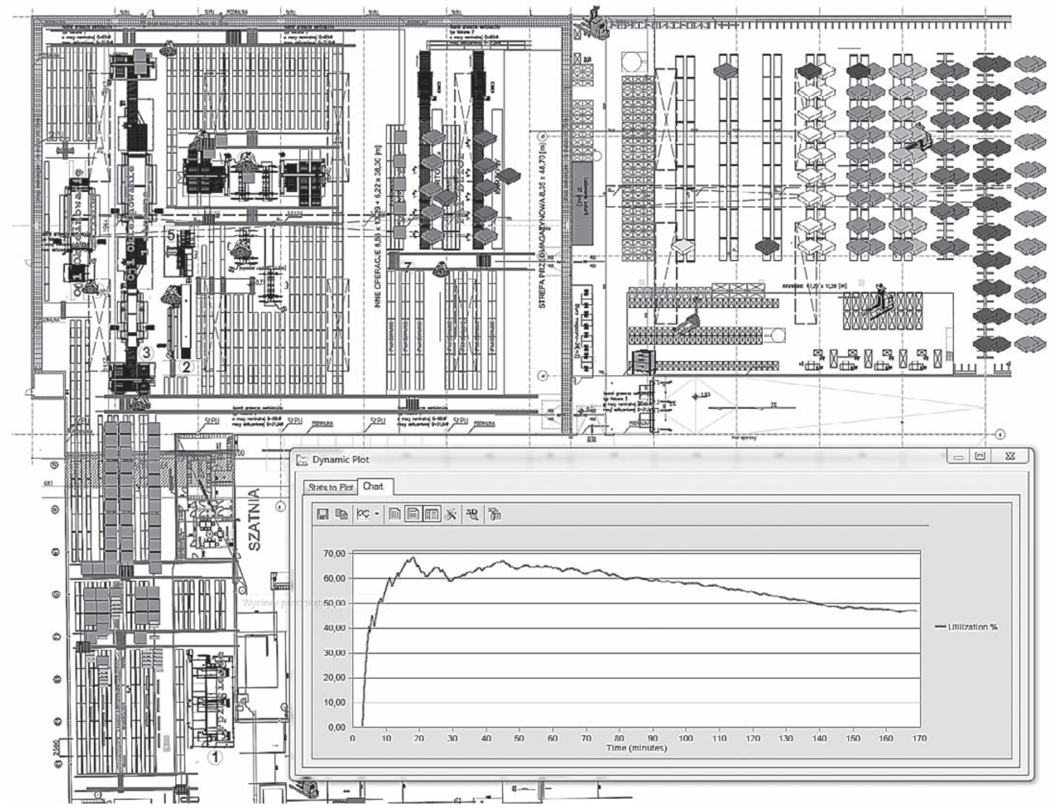

Figure 6 Load changes of the analyzed workstation during simulation examinations
Slika 6. Promjene opterećenja analiziranih radnih postaja tijekom simulacijskih pregleda

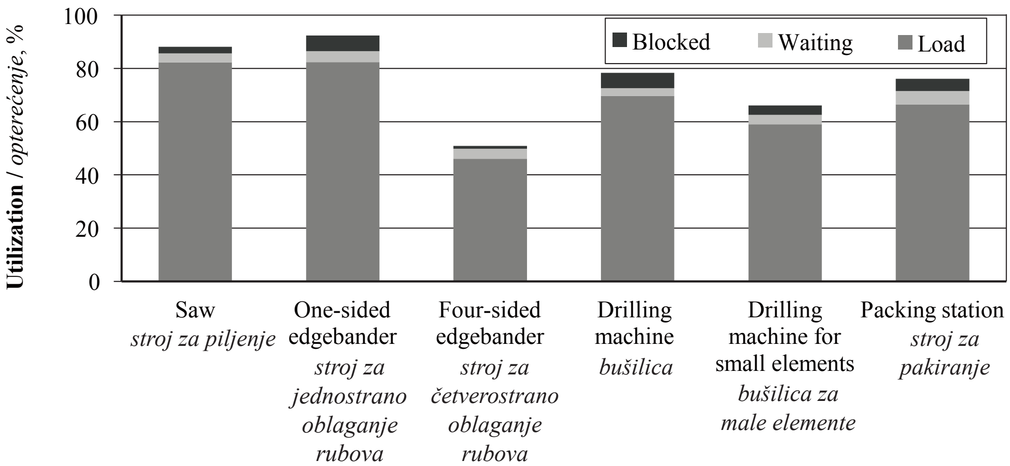

Figure 7 Loads of machines and facilities
Slika 7. Opterećenost strojeva i opreme

the use of ANN and manufacture of the other group will be based on a sequential pull system. The presented results confirm the rightness of the suggested approach to demand forecasting on the basis of ANNs executing regressive relationships, where the forecast values calculated in traditional ways are included in the set of explanatory variables (hybrid approach). Effective forecasts based on ANNs (in comparison to those determined by traditional methods) make a basis for designing a replenishment pull system. Inventories of furniture parts planned according to the pull system principles, located in proper places in the manufacturing system and in proper quantity, not only speed-up the response for the customer's needs but also significantly increase productivity. Thanks to the implemented pull system, excessive stock levels resulting, among others, from wrong forecasts, are eliminated. This compensation is realized by the additional production line introduced for unpredictable and customized orders, working on the basis of a sequential pull system. Moreover, implementation of the simulation model makes it possible to verify the number of wood-processing machines and to execute the assumed furniture production plan on the grounds of the i_0 value. Such a complex approach to planning and controlling production systems in furniture companies will provide them with an opportunity to become more efficient, agiler and flexible on the market.

Appendix – Dodatak

Table 3 Initial research results
Tablica 3. Inicijalni rezultati istraživanja

Product *Proizvod*	A			B			C			D			E			F			N		
Forecasting method / *Metoda predviđanja*	SES	MA	ANN	SES	MA	ANN	SES	MA	ANN	SES	MA	ANN	SES	MA	ANN	SES	MA	ANN	SES	MA	ANN
Relative Forecast Error ex-post, % *Relativna pogreška predviđanja, %*	128	114	60	136	105	101	131	108	95	130	113	86	135	124	111	125	108	95	140	117	100
Correlation coefficient *Koeficijent korelacije*	0.06	-0.05	0.77	0.00	-0.01	0.02	0.08	-0.03	0.35	0.08	0.01	0.47	0.07	-0.01	-0.02	0.13	0.11	0.30	-0.03	-0.04	0.20

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Corresponding address:

Assist. Prof. MARIA ROSIENKIEWICZ, Ph.D.

Faculty of Mechanical Engineering
Wrocław University of Science and Technology
27 Wybrzeże Wyspiańskiego
50-370 Wrocław, POLAND
e-mail: maria.rosienkiewicz@pwr.edu.pl

Haroon A. M. Saeed[1,2], Yu Liu[1], Lucian A. Lucia[1,3], Honglei Chen[1]

Sudanese Dicots as Alternative Fiber Sources for Pulp and Papermaking

Sudanske dvosupnice kao alternativni izvor vlakana za proizvodnju celuloze i papira

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ABSTRACT • *The suitability of the stems from two Sudanese dicotyledonous annual plants, namely castor bean (Ricinus communis) and Leptadenia pyrotechnica (L. pyrotechnica) were investigated for pulp and papermaking. Chemical compositions, elemental analysis, fiber dimensions, paper physical properties and morphology revealed a relatively high α-cellulose content (46.2 and 44.3 %) and low lignin (19.7 and 21.7 %) in the stems of castor bean and L. pyrotechnica, respectively. The average fiber length of castor bean and L. pyrotechnica is 0.80 and 0.70 mm with fiber width of 16.30 μm and 18.20 μm, respectively, which makes them acceptable candidates. Soda-AQ pulping of castor bean stem led to a higher pulp yield of 43.2 % at kappa number 18.2 compared to 40.3 % at kappa 20.3 for L. pyrotechnica. This yield is less than that obtained for wood plants and similar to that observed for annual plants. Paper handsheets produced from castor bean showed better mechanical properties than L. pyrotechnica. SEM images indicated that the produced papers were quite homogeneous, compact, closely packed, and well assembled.*

Key words: *Sudanese annual plants, castor bean, Leptadenia pyrotechnica, pulp and paper*

SAŽETAK • *U radu je opisano istraživanje prikladnosti stabljika dviju sudanskih jednogodišnjih biljaka dvosupnica, ricinusa (Ricinus communis) i Leptadenia pirotechnica za dobivanje celulozu i proizvodnju papira. Kemijski sastav, elementarna analiza, dimenzije vlakana, fizikalna svojstva papira i morfologija pokazali su da je u stabljikama ricinusa i L. pyrotechnica relativno visok sadržaj α-celuloze (46,2 i 44,3 %) i nizak sadržaj lignina (19,7 i 21,7 %). Prosječna duljina vlakana ricinusa i L. pirotechnice iznosi 0,80 i 0,70 mm, a širina vlakana im je od 16,30 μm i 18,20 μm, što ih čini prihvatljivima za proizvodnju celuloze i papira. Sulfatnim je postupkom od stabljika ricinusa dobiven veći prinos celuloze (43,2 %) pri kappa broju 18,2 u usporedbi s prinosom celuloze (40,3 %) pri kappa broju 20,3, koji je dobiven pri proizvodnji celuloze od stabljika L. pyrotechnice. Dobiveni prinos manji je od prinosa koji se postiže proizvodnjom celuloze od drvenastih biljaka i jednak je prinosu koji se ostvaruje proizvodnjom celuloze od jednogodišnjih biljaka. Listovi papira proizvedeni od ricinusa pokazali su bolja mehanička svojstva od papira proizvedenoga od stabljika L. pyrotechnice. Slike dobivene skenirajućim elektronskim mikroskopom (SEM) pokazuju da su proizvedeni papiri bili posve homogeni, kompaktni, zbijeni i dobro sastavljeni.*

Ključne riječi: *sudanske jednogodišnje biljke, ricinus, Leptadenia pirotechnica, celuloza i papir*

[1] Authors are scientists at Key Lab of Pulp and Paper Science and Technology of Ministry of Education (Shandong Province) Qilu University of Technology, Jinan, 250353, Shandong, P.R. China. [2]Author is assistant professor at Center of Fibers, Papers and Recycling, Faculty of Textiles, University of Gezira, Box 20, Wad Medani, Sudan. [3]Author is professor at Department of Forest Biomaterials, North Carolina State University, Raleigh, USA.

[1] Autori su znanstvenici Ključnog laboratorija za znanost i tehnologiju celuloze i papira Ministarstva obrazovanja (provincija Shandong), Tehničko sveučilište Qilu, Jinan, Shandong, Kina. [2]Autor je profesor Centra za vlakna, papir i recikliranje, Tekstilni fakultet Sveučilišta u Geziru, Wad Medani, Sudan. [3]Autor je profesor Odsjeka za šumske biomaterijale, Državno sveučilište North Carolina, Raleigh, SAD.

1 INTRODUCTION
1. UVOD

The annual world consumption of paper and paperboard is growing 2.1 % and it will reach an estimated 490 million tonnes by 2020 (Dutt *et al.*, 2008). However, ~ 4 billion trees are cut across the globe for pulp and paper manufacturing often raising ecological and climatic issues (Kamoga *et al.*, 2016) and leading to a demand for alternative pulp and papermaking raw materials. In some countries, pulp and paper industries have been facing some challenges due to the shortages of forest resources (Ferhi *et al.*, 2014b). However, non-wood species or annual plants and agriculture residues are likely the best candidates as alternative sources of cellulosic fibers (Kamoga *et al.*, 2016). Furthermore, as these cellulosic fiber materials have identical properties, they could be used as wood fibers for pulp and papermaking (Mechi *et al.*, 2016), textile, boards, and green composite materials (Mansouri *et al.*, 2012).

Many studies have been carried out to find new alternative lignocellulosic materials. Some of these studies have used tobacco (Shakhes *et al.*, 2011a), rice straw, sugarcane bagasse and cotton stalk (Adel *et al.*, 2016), pineapple (Wutisatwongkul *et al.*, 2016) millet stalks and date palm leaves (Saeed *et al.*, 2017b), *J. procera* (Nasser *et al.*, 2015), sunflower stalk (Barbash *et al.*, 2016) *gracilaria* and *eucheuma* (Machmud *et al.*, 2013), bitter orange (Tutuş *et al.*, 2016), *ipomea carnea* and *cannabis sativa* (Dutt *et al.*, 2008), *c. orientalis* and *c. tataria* (Tutus *et al., 2010),* wheat straws (Espinosa *et al.*, 2016) and broad bean, bell pepper and asparagus (Gonzalo *et al.*, 2017). However, there is no previous study on the application of castor bean (*Ricinus communis*) and *Leptadenia pyrotechnica* (*L. pyrotechnica*) stems for pulp and paper production.

Castor bean (*Ricinus communis*) is a tropical annual and fast-growing plant. It belongs to the Euphorbiaceae family that is grown across the world (de Assis Junior *et al.*, 2011; Udoh and Abu, 2016). Vasconcelos *et al.* (2014) investigated the physical and chemical properties of fibrous residues of castor bean, and they found that castor bean stems consist of 50.46 % of cellulose, 29.64 % of hemicelluloses, 17.34 % of lignin and 1.48 % of ash.

Leptadenia pyrotechnica (*L. pyrotechnica*) is an important multipurpose non-wood species of tropical and sub-tropical arid regions. Mojumder *et al.* (2001) investigated the chemical composition of *L. pyrotechnica,* and determined that it consists of 4.93 % of lignin, 75.26 % of α-cellulose and 2.77 % of ash. However, the results reveal that castor and *L. pyrotechnica* residues are a good alternative for the pulp and paper industries since they are plants of high cellulose content. This work investigated the chemical components and fiber properties of castor bean (*Ricinus communis*) and *L. pyrotechnica* stems after soda-AQ pulping.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

Castor bean (*Ricinus communis*) and *L. pyrotechnica* stems were collected from North Kordofan State, west of Sudan (latitudes 12° 30 North and longitudes 29° 30 East) in March 2017. Materials were randomly selected according to TAPPI standard methods. A part of the material was chipped to 1.5×1.5×2 cm and ground to powder with a mesh size of 40-60 in a laboratory by using a Wiley mill grinder for determining their chemical components. Hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), sodium oxide (Na_2O), acetic acid and anthraquinone (AQ) were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2 Methods
2.2. Metode

2.2.1 Chemical composition
2.2.1. Kemijski sastav

Materials were tested for extractive substances in different liquids according to common TAPPI standards: cold and hot water T207 cm-99, 1 % sodium hydroxide solution T212 om-98 and alcohol-toluene T204 cm-97 (López *et al.*, 2011). The amounts of lignin and ash contents were assessed according to T222 cm-99 and T211 om-02 (Yuan *et al.*, 2016), while, holocellulose contents were determined according to Wise method (Wise, 1946).

2.2.2 Morphological characteristics
2.2.2. Morfološka obilježja

For the measurements of fiber dimensions, samples were macerated in a mixture of 30 % hydrogen peroxide and acetic acid (1:1). Fiber length, width and kinked and curled index were measured with FQA device (OpTest, Canada), model LDA-02 according to T271 om-07. Lumen diameter and wall thickness were measured by Leica DMLB (Leica Microsystems GmbH, Wetzlar, Germany) connected to a video camera Leica DFC490 (Leica Microsystems GmbH, Wetzlar, Germany) at 400× magnifications. Fibers morphology and elemental composition (Carbon (C), Oxygen (O), Aluminium (Al), Nitrogen (N), silicon (Si), magnesium (Mg), and Calcium (Ca)) were determined using a scanning electron microscope (SEM-EDS) by (OCTANE 9.88/1114658 AMETEK® (USA)). Before the test, the paper specimens were coated with gold-palladium in a Sputtergerät SCD 005 sputter coater (England). A sputter current of 60 mA, sputter time 90 s, and film thickness of 20 nm to 25 nm were chosen as the coating conditions**.**

2.2.3 Pulping processing and testing
2.2.3. Proizvodnja i ispitivanje celuloze

Soda-AQ pulping was carried out in a rotary digester with electrical heating with four individual 2 L vessels. The charge was 100 g of oven dried (o.d.) material. The active alkali (NaOH) was constant 20 % on oven dried (o.d.), while AQ was 0.1 %. The cooking was continued for 120 min at the maximum temperature of 170 °C. At the end of pulping, pressure was relieved to atmospheric pressure; pulp was taken out from the digester, disintegrated and washed by continuous water flow. Pulp was screened on a 0.15 mm laboratory slot vibratory screener and the yield was determined gravimetrically. Pulp yield was determined as dry matter obtained on the basis of o.d. raw material. The pulp was subjected to mechanical beating using the PFI mill according to T248 sp-00, kappa number was determined according to T 236 cm-85 (Sarker *et al.*, 2017), while pulp viscosity was determined according to T 230 om-04 (Feria *et al.*, 2012). Moreover, a totally chlorine-free bleaching was carried out. According to Moral *et al.* (2016) 10 % pulp concentration is bleached in two stages by 4 % hydrogen peroxide (H_2O_2) in 0.2 % sodium hydroxide (NaOH) at 80 °C for 2 h of each stage. The pulp was washed properly until neutralization in every stage.

2.2.4 Papermaking and testing
2.2.4. Proizvodnja i ispitivanje papira

All pulps were beaten to 5000 revolution at 35°SR in a PFI mill T248 sp-00, and papers of 60 grams were made according to the T205sp -95 in a laboratory handsheet machine (PTI laboratory Equipment, Vorchdorf, Austria). The physical properties of the samples were determined according to common standards: burst index T403 om-10, tear index T414 om- 04 and tensile index T494 om-06 (Rudi *et al.*, 2016). The brightness and opacity were determined according to T525 om-92 and T425 om-96 (Tutuş *et al.*, 2016), respectively.

2.2.5 Calculations
2.2.5. Proračuni

The following parameters were calculated using the following formulas (Albert *et al.*, 2011; Pirralho *et al.*, 2014).

Slenderness ratio = fiber length ÷ fiber diameter (1)

Flexibility coefficient = (fiber lumen diameter ÷ fiber diameter)×100 (2)

Runkel ratio = (2×*fiber cell wall thickness*) ÷ *lumen diameter* (3)

Rigidity coefficient = (*cell wall thickness*×100) ÷ *fiber diameter* (4)

Felting power = fiber length ÷ fiber width (5)

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Chemical composition and extractives of castor bean and *L. pyrotechnica* in comparison with some common representatives of lignocellulosic annual plants are shown in Table 1. Castor bean and *L. pyrotechnica* show a relatively high cellulose content of 46.20 % and 44.30 %, respectively, compared to *prunus amygdalus* (Mechi *et al.*, 2017), *A. armatus* (Ferhi *et al.*, 2014a) vine stems (Mansouri *et al.*, 2012) and bagasse (Saeed *et al.*, 2017a), but lower than that of *I. tinctoria* (Comlekcioglu *et al.*, 2016), *cactus* (Mannai *et al.*, 2017) and similar to that of palm leaves (Saeed *et al.*, 2017b). On the other hand, *L. pyrotechnica* show a higher amount of hemicellulose (22.15 %) compared to castor bean value of 20.50 %. This result may explain the higher solubility of *L. pyrotechnica* in alkali solution (1 % NaOH), because it is adequate to dissolve the fragile branched components of the cellulosic chain, such as hemicelluloses (Mattos *et al.*, 2016). However, these results are not in line with vine stems (Mansouri *et al.*, 2012) and *A. armatus* (Ferhi *et al.*, 2014a). Lignin content was found to be higher in *L. pyrotechnica* (21.70 %), while it was 19.70 % in castor bean. However, these results are comparable with those of the listed annual plants and hardwoods (17-26 %) and lower than those of softwoods (25-32 %) (Ates *et al.*, 2008). Castor bean and *L. pyrotechnica* showed almost the same ash contents, 2.60 and 2.40 %, respectively, which is the range (1-3 %) for hardwoods and less than those of the materials listed in Table 1. However, high ash content is undesirable, as trace elements interfere with bleaching chemicals and alkali earth metals in the pulp will cause problems in chemical recovery. Moreover, high ash content may lead to damage in wood during processing (Dutt *et al.*, 2009, López *et al.*, 2012).

Table 1 Chemical composition of castor bean, *L. pyrotechnica* and some other annual plants
Tablica 1. Kemijski sastav ricinusa, *L. pyrotechnica* i nekoliko drugih jednogodišnjih biljaka

Annual plants *Jednogodišnje biljke*	**Chemical compositions** *Kemijski sastav*				**Solubility** / *Topljivost*				**Literature** *Literatura*
	Cellulose, % *Celuloza, %*	**Hemicellulose, %** *Hemiceluloza, %*	**Lignin, %** *Lignin, %*	**Ash, %** *Pepeo, %*	**Hot water, %** *Vruća voda, %*	**Cold water, %** *Hladna voda, %*	**Alcohol-toluene, %** *Alkohol-toluen, %*	**%1 NaOH, %**	
Castor bean / *ricinus*	46.2	20.5	19.7	2.6	10.5	9.4	4.8	18.6	Current Study
L. pyrotechnica	44.3	22.1	21.7	2.4	12.1	11.5	5.6	20.9	Current Study
Prunus amygdalus	40.7	20.0	19.2	3.6	12.3	11.3	5.0	28.7	Mechi *et al.* (2016),
I. tinctoria	48.5	18.6	23.9	4.9	17.2	13.6	4.4	43.8	Comlekcioglu *et al.* (2016)
A. armatus	41.5	29.3	19.0	2.8	15.6	12.2	4.0	39.0	Ferhi *et al.* (2014)
Vine stems / *stabljike vinove loze*	35.0	30.4	28.1	3.9	13.9	8.2	11.3	37.8	Mansouri *et al.* (2012)

The extractives also contain extraneous ingredients, such as inorganic compounds, tannins, gums, sugars and coloring in the lignocellulosic plants (Dutt *et al.*, 2009). The amount of extractives of castor bean and *L. pyrotechnica* in hot and cold water is relatively high compared to hardwood (2-8 %) (Ferhi *et al.*, 2014b), but less than that of several annual plants such as *I. Tinctoria* (Comlekcioglu *et al.*, 2016) and *A. armatus* (Mechi *et al.*, 2016). However, it is comparable to other annual plants such as *Prunus amygdalus* (Mechi *et al.*, 2016). The extractives in 1% NaOH are 18.60 % and 20.90 % for castor bean and *L. pyrotechnica*, respectively, lower than those for annual plants listed in Table 1. Castor bean showed similar alcohol-toluene extractives to *I. tinctoria* (Comlekcioglu *et al.*, 2016) and *A. armatus* (Ferhi *et al.*, 2014a). Among the listed data, castor bean showed the least hot and cold water and 1% NaOH extractives. However, the lower solubility resulted in high pulp yield and less chemical consumption in pulping and bleaching processing (Comlekcioglu *et al.*, 2016). The large cellulose contents and lower lignin content enhance the investigation of such annual plants as they have a high potential for use as fibers for pulp and paper production.

The basic parameters that affected the physical properties of the paper are fiber dimensions including fiber length, fiber width and fiber cell wall thickness (Albert *et al.*, 2011). The average fiber length of castor bean and *L. pyrotechnica* are 0.80 and 0.70 mm, respectively. They are less than that of softwood (2.7-4.6 mm) and in the range of hardwood (0.7-1.6 mm) (Comlekcioglu *et al.*, 2016) and they are considered as short fiber species (Jahan *et al.*, 2008). These fibers were similar to *A. armatus* (Ferhi *et al.*, 2014a) and longer than vine stems (Mansouri *et al.*, 2012) and *prunus amygdalus* (Mechi *et al.*, 2017). It is expected that paper handsheets produced from *L. pyrotechnica* pulp with relatively short fibers may give a smoother paper than that of castor bean because short fibers will fill the voids in the paper sheet, while the paper handsheet formed from castor bean pulps would result in higher strength properties and less fine sheet structure (Nasser *et al.*, 2015). Moreover, the higher the fiber length, the better will be the tearing resistance of paper (Agnihotri *et al.*, 2010). Therefore, paper made from these materials showed good mechanical strength and can be suitable for producing writing and printing papers as well as wrapping and packaging paperboard. On the other hand, *L. pyrotechnica* showed a thicker fiber with the width of 18.20 μm compared to the 16.30 μm of castor bean. However, the observed fibers are thinner than those of *A. armatus* (Ferhi *et al.*, 2014a), and those of *Prunus amygdalus* (Mechi *et al.*, 2017) are thicker than those of *I. tinctoria* (Comlekcioglu *et al.*, 2016). Cell wall thickness of castor bean (6.40 μm) is lower compared to that of *L. pyrotechnica* (7.00 μm) and *I. tinctoria* (Comlekcioglu *et al.*, 2016), However, longer fiber with lower cell wall thickness showed significant advantages in physical properties of the produced paper (Tutus *et al.*, 2010).

Values derived from the fiber dimensions, important for determining the suitability of the material for paper production, are listed in Table 2. Castor bean showed a relatively high felting power of 49 compared to 38.46 for *L. pyrotechnica*. However, these values are similar to those of hardwood (40-55) and lower than those of softwood (60-80) (Comlekcioglu *et al.*, 2016). If the felting power of a fibrous material is lower than 70, it is suitable for the pulp and paper industry (Tutus *et al.*, 2010). The values of the rigidity coefficient negatively influence tensile, tear, burst and double fold resistance of the paper (Anoop *et al.*, 2014). Both castor bean and *L. pyrotechnica* fibers showed higher rigidity coefficients of 38.04 and 38.46, respectively, compared to 30.44 of *cymodocea serrulata* (Syed *et al.*, 2016) and 26.40 of *I. tinctoria* (Comlekcioglu *et al.*, 2016). Moreover, it was reported that, if the slenderness ratio of fibrous material is less than 70 and higher than 33, the lignocellulosic material is considered to be good for pulp and paper production (Shakhes *et al.*, 2011a; Syed *et al.*, 2016). Both castor bean and *L. pyrotechnica* showed slenderness ratios of 49.00 and 38.46, respectively. Castor bean had a relatively high flexibility coefficient of 63.19 compared to 62.64 and 47.2 of *L. pyrotechnica* and *I. tinctoria*, respectively. Previous

Table 2 Fiber properties of castor bean, *L. pyrotechnica* and some annual plants
Tablica 2. Obilježja vlakanaca ricinusa, *L. pyrotechnica* i nekoliko drugih jednogodišnjih biljaka

Material *Materijal*	**Castor Bean** *Ricinus*	***L. pyrotechnica***	***Prunus amygdalus***	***I. tinctoria***	***A. armatus***	**Vine stems** *Stabljike vinove loze*
Fiber length, mm / *Duljina vlakana,* mm	0.80±0.05	0.70±0.06	0.48	0.60	0.81	0.59
Fiber width, μm / Širina *vlakana,* μm	16.30±1.4	18.20±2.2	21.00	15.70	20.60	24.60
Lumen diameter, μm / *Promjer lumena,* μm	10.30±1.5	11.40±1.3	N/A	8.80	N/A	N/A
Cell wall thickness, μm *Debljina stanične stijenke,* μm	6.20±1.1	7.00±2.1	N/A	8.60	N/A	N/A
Felting power / *Snaga filcanja*	49.00	38.46	N/A	39.7	N/A	N/A
Rigidity coefficient / *Koeficijent krutosti*	38.04	38.46	N/A	26.4	N/A	N/A
Slenderness ratio / *Vitkost*	49.00	38.46	N/A	N/A	N/A	N/A
Flexibility coefficient / *Omjer fleksibilnosti*	63.19	62.64	N/A	47.2	N/A	N/A
Runkel ratio / *Runkelov omjer*	1.20	1.23	N/A	1.1	N/A	N/A
Literature / *Literatura*	Current Study	Current Study	1	2	3	4

1) Mechi *et al.* (2016), 2) Comlekcioglu *et al.* (2016), 3) Ferhi *et al.* (2014), 4) Mansouri *et al.* (2012), N/A: Not available

Table 3 Properties of pulp from castor bean, *L. pyrotechnica* and some annual plants
Tablica 3. Svojstva celuloze proizvedene od ricinusa, *L. pyrotechnica* i nekoliko drugih jednogodišnjih biljaka

Material *Materijal*	**Total yield** *Ukupni prinos* %	**Screened yield** *Prinos prosijavanja* %	**Kappa number** *Kapa broj*	**Viscosity** *Viskoznost* mPa·s	**Literature** *Literatura*
Castor bean / *ricinus*	43.20	42.10	18.20	6.46	Current study
L. pyrotechnica	40.30	38.80	20.30	5.12	Current study
Prunus amygdalus	45.2	42.94	N/A	5.28	1
I. tinctoria	26.09	25.37	N/A	N/A	2
A. armatus	32.00	N/A	15.20	N/A	3
Vine stems / *stabljike vinove loze*	45.00	N/A	25.50	8.50	4

1) Mechi *et al.* (2016), 2) Comlekcioglu *et al.* (2016), 3) Ferhi *et al.* (2014), 4) Mansouri *et al.* (2012), N/A: Not available

studies stated that higher Runkel ratio fibers are stiffer, less flexible, and form bulkier paper of lower fiber to fiber bond than lower Runkel ratio fibers. High average fiber length and low Runkel ratio result in good pulp strength properties (Shakhes *et al.*, 2011b). Both castor bean and *L. pyrotechnica* showed high Runkel ratio of 1.20 and 1.23 compared to that of 1.1 of *I. tinctoria*.

The physical properties of the pulp obtained from the studied materials are summarized in Table 3. The results reveal that castor bean shows higher total pulp yield of 43.20 % with an acceptable kappa number of 18.20 compared to that of 40.30 % with kappa number of 20.30 of *L. pyrotechnica*. The low pulp yield of *L. pyrotechnica* is attributed to a relatively high content of extractives, especially in hot and cold water compared to that of castor bean (Ferhi *et al.*, 2014a) as well as low cellulose content (Gonzalo *et al.*, 2017). These values are higher than those of *A. armatus* (Ferhi *et al.*, 2014a) and *I. tinctoria* (Comlekcioglu *et al.*, 2016) and lower than those of vine stems (Mansouri *et al.*, 2012) and *A. armatus* (Ferhi *et al.*, 2014a). However, the differences in kappa number could be attributed to differences in lignin content in the materials. The value of viscosity is an indicator of fiber length and degree of polymerization (Kamoga *et al.*, 2016). However, caster bean showed higher viscosity (6.46 mP·s) compared to that of *L. pyrotechnica* (5.12 mP·s) and *prunus amygdalus* (5.28 mP·s) (Mechi *et al.*, 2017) but lower than that of vine stems (8.50 m mP·s) (Mansouri *et al.*, 2012).

3.1 Handsheet physical properties
3.1. Fizikalna svojstva listova papira

The physical and optical properties of handmade paper sheets produced from soda-AQ pulps of the studied annual plants are listed in Table 4. The paper handsheets produced from these species had good formation with basis weights of 63 and 65 g/m^2 and thicknesses of 115 and 117 μm for castor bean and *L. pyrotechnica*, respectively. Hand sheet formed from castor bean showed higher values of tensile, tear and burst index compared to those of paper produced from *L. pyrotechnica* and *Prunus amygdalus* (Mechi *et al.*, 2016). Castor bean and *L. pyrotechnica* papers showed a lower tearing index than that of *A. armatus* (Ferhi *et al.*, 2014a) and vine stems (Mansouri *et al.*, 2012). Remarkably high brightness of 75.20 and 69.20 % was achieved for caster bean and *L. pyrotechnica* with a preliminary bleaching sequence. This high brightness predicts good bleachability of the pulps from these two annual plants, meaning that lower chemical charges are required.

3.2 Morphological analysis of papers obtained from castor bean and *L. pyrotechnica*
3.2. Morfološka analiza papira proizvedenoga od stabljika ricinusa i *L. pyrotechnica*

Paper handsheets were observed by SEM and SEM-EDS analysis, as presented in Fig. 1. Handsheets were magnified at 500 x. SEM images indicated that the produced papers are quite homogeneous, compact,

Table 4 Physical properties of papers from castor bean, *L. pyrotechnica* and several annual plants
Tablica 4. Fizikalna svojstva papira proizvedenoga od ricinusa, *L. pyrotechnica* i nekoliko drugih jednogodišnjih biljaka

Properties *Svojstvo*	**Castor bean** *Ricinus*	***L. pyrotechnica***	***Prunus amygdalus***	***I. tinctoria***	***A. armatus***	**Vine stems** *Stabljike vinove loze*
Thickness, μm / *debljina,* μm	115±4	117±5	110±8	N/A	144	N/A
Basis weight, g/m^2 *osnovna jedinična masa,* g/m^2	63±0.5	65±0.2	64±0.8	N/A	65.20	69.50
Tensile index, N·m/g *vlačni indeks,* N·m/g	4.5±0.15	3.10±0.20	4.08±0.16	3.33	3.37	N/A
Tearing Index, mN·m^2/g *indeks cijepanja,* mN·m^2/g	2.24±0.26	2.01±0.54	2.19±0.27	1.03	3.57	5.74
Bursting Index, kPa·m^2/g *Indeks pucanja, kPa·m^2/g*	1.84±0.03	1.45±0.02	1.38±0.05	2.17	1.62	1.72
Opacity, % / *neprozirnost,* %	99.20±5.2	98.00±15	99.84±8.5	99.65	N/A	
Brightness, % / *sjajnost,* %	75.20±3.1	69.20±2.4	N/A	25.22	N/A	70.00
Literature / *literatura*	Current Study	Current Study	1	2	3	4

1) Mechi *et al.* (2016), 2) Comlekcioglu *et al.* (2016), 3) Ferhi *et al.* (2014), 4) Mansouri *et al.* (2012), N/A: Not available

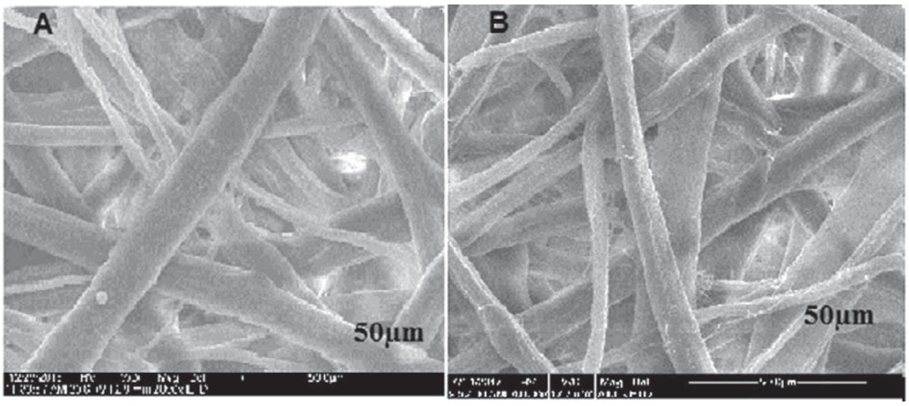

Figure 1 Scanning electron microscopy of (A) *L. pyrotechnica*, (B) castor bean
Slika 1. Slike dobivene skenirajućim elektronskim mikroskopom (A) *L. pyrotechnica*, (B) ricinus

Table 5 Elemental analysis of castor bean and *L. pyrotechnica*
Tablica 5. Elementarna analiza ricinusa i *L. pyrotechnica*

Material / *Materijal*	C (%)	O (%)	N (%)	Mg (%)	Al (%)	Si (%)	Ca (%)
Castor bean / *ricinus*	49.49	43.17	0.90	0.02	0.12	0.07	0.13
L. pyrotechnica	49.93	42.24	1.19	0.05	0.04	0.10	0.08

with a closely packed arrangement and good assembling. Well-arranged and compact fibers will lead to smooth surface and good structure of the produced paper, and thus higher mechanical properties could be obtained (Saeed *et al.*, 2017a).

3.3 Elemental analysis of castor bean and *L. pyrotechnica*
3.3. Elementarna analiza ricinusa i *L. pyrotechnica*

The detailed elemental analysis of castor bean and *L. pyrotechnica* is listed in Table 5. It clearly shows that ash is mainly composed of O, C, Mg, N, Al, Ca and Si atoms. Silicon is negligible in both castor bean and *L. pyrotechnica* (0.07 % and 0.10 %). Similar results were observed for *gracilaria* and *eucheuma* (Machmud *et al.*, 2013). High silicon-containing lignocellulosic materials are generally not preferable for pulping because they contribute to system issues in cooking and washing (Ferhi *et al.*, 2014a).

4 CONCLUSIONS
4. ZAKLJUČAK

The chemical composition of castor bean and *L. pyrotechnica* stems revealed a sufficient level of polysaccharides and reduced lignin contents compared to other annual plants, which explains their suitability as new lignocellulosic candidates for pulp and paper making. The pulp and paper of castor bean were identified with acceptable yield, medium viscosity, high bleachability, long and narrow fibers compared to *L. pyrotechnica.* Values derived from fiber dimensions, such as felting power, rigidity coefficient and slenderness ratio, determined the suitability of the material for paper production. SEM images indicated that the produced papers are quite homogeneous, compact, with a closely packed arrangement and good assembling, thus providing good mechanical properties of the produced papers.

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Corresponding address:

Professor, YU LIU
Dr. HAROON A. M. SAEED

Key Lab of Pulp and Paper Science and Technology
Ministry of Education (Shandong Province)
Qilu University of Technology
Jinan, 250353, Shandong, P.R. CHINA
e-mail: leoliuyu@163.com, haroonsaeed75@gmail.com

Hrvoje Turkulin, Vjekoslav Živković[1]

Microtensile Testing of Wood – Influence of Material Properties, Exposure and Testing Conditions on Analysis of Photodegradation

Ispitivanje mikrovlačne čvrstoće drva – utjecaj svojstava materijala, izlaganja i uvjeta ispitivanja na fotodegradaciju

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ABSTRACT • *This paper presents the effects of properties of tested material and exposure conditions on the final result of testing. These include density, uniformity of ring width, number of rings and latewood portions, as well as light source, presence of water and duration of exposure. Influences of these parameters in testing of several softwood species after exposure to different natural and artificial photodegradation regimes were monitored by means of changes in microtensile properties. The main findings indicate that comparisons between various species should be made taking into account average material properties, predominantly latewood portion. The fact that strength loss changes follow the same pattern during different exposure conditions indicates that there is no difference in the nature of degradation process in various weathering machines. This forms a basis for the sound comparison between the artificial and natural weathering regimes.*

Keywords: *softwoods, microtensile testing, thin strips, density, photodegradation*

SAŽETAK • *U radu se opisuje istraživanje utjecaja svojstava ispitivanog materijala i uvjeta izlaganja drva na konačni rezultat ispitivanja fotodegradacije njegova površinskog sloja. Ispitivana svojstva materijala obuhvaćaju gustoću drva, ujednačenost širine goda, broj godova i udio kasnog drva, utjecaj izvora zračenja, postojanje vode i duljinu izlaganja vremenskim utjecajima. Mjerenje mikrovlačne čvrstoće u smjeru drvnih vlakana ispitano je na više vrsta drva nakon prirodnoga i ubrzanih umjetnih izlaganja vremenskim utjecajima. Rezultati pokazuju kako je za valjanu usporedbu različitih vrsta drva potrebno odabrati materijal prosječne gustoće, posebno pazeći na udio kasnog drva. Činjenica da je gubitak čvrstoće tijekom različitih vrsta izlaganja podjednak upućuje na zaključak kako nema bitne razlike u prirodi procesa površinske degradacije ovisno o vrsti izvora zračenja. To je osnova za valjanu usporedbu rezultata dobivenih izlaganjem u različitim prirodnim i umjetnim uvjetima.*

Ključne riječi: *četinjače, mikrovlačno ispitivanje, tanki listići, gustoća, fotodegradacija*

[1] Authors are professor and assistant professor at Department for Furniture and Wood Products, Faculty of Forestry, University of Zagreb, Zagreb, Croatia.
[1] Autori su profesor i docent Zavoda za namještaj i drvne proizvode, Šumarski fakultet, Sveučilište u Zagrebu, Zagreb, Hrvatska.

1 INTRODUCTION
1. UVOD

Properties of tested material as well as weathering conditions strongly affect the reliability of microtensile testing and its final result. Derbyshire *et al.* (1995, 1996) demonstrated that the measurement of loss of microtensile strength of thin wood strips exposed to solar radiation offers a consistent, reliable and precise means of determining photodegradation rates for wood. It was shown that artificial weathering regimes could provide good simulation of the effects of natural weathering, and mathematical analysis procedures were developed to characterize the strength changes observed during weathering. In the third paper in a series, Derbyshire *et al.* (1997) further showed that photodegradation rates of a number of different softwood species during artificial weathering were temperature dependent, increasing with rising temperature. In an additional paper in that series (Part 4: Turkulin and Sell, 2002), the strength changes were shown to be consistent with fractographic evidence of the structural changes in wood, namely with cell delamination, development of brittleness and loss in cell wall integrity. In the last paper in that series (Turkulin *et al.*, 2004), the thin strip technique was used to investigate the effect of moisture on photodegradation rates. Moisture is a significant factor in accelerating photodegradation of wood by means of increasing the rates of strength loss.

Another interesting finding demonstrated that the exposure of the strips at high levels of relative humidity could result in an initial increase in tensile strength, evident in the form of a shoulder or small initial positive peak in the strength loss curves. This strength increase appeared to be associated with cellulose changes, since it is regularly recorded in testing over zero initial span of clamps of the testing instrument, and is believed that it reflects some form of cellulose crosslinking at shorter exposure times, followed by the general strength loss that develops at prolonged exposure to elements (Derbyshire *et al.*, 1996; Turkulin and Sell, 2002). Differences in photoresistance between the different wood species, and between heartwood and sapwood, were most notably visible under dry exposure conditions. These differences progressively diminished as the pronounced effect of water was introduced in subsequent weathering regimes.

The thin strip method was also successfully applied in studies of weathering of acetylated and thermally modified wood surfaces (Evans *et al.*, 2000; Altgen and Militz, 2016), determination of the depth profile of weathering effects on unprotected and protected softwoods (Jirouš-Rajković *et al.*, 2004; Kataoka *et al.*, 2005), effects of chemical modifications on its mechanical properties (Bischof Vukušić *et al.*, 2006; Xie *et al.*, 2007), the degradation effects of wood destroying fungi (Lehringer *et al.*, 2011), effects of seawater wetting on the weathering of wood (Klüppel and Mai, 2017) as well as spectral sensitivity and depth profiling during photodegradation of fir wood surfaces (Živković *et al.*, 2014 and 2016).

This paper presents the effects of selected properties of tested material on the final result of testing. Variables included the specific anatomical and physical properties of several wood species, namely the density, ring width, number of rings and latewood portions. Other parameters that varied in a series of experiments involved weathering conditions - particularly the light source, presence of water and duration of exposure. Results presented here demonstrate specific aspects of the thin strip method as a useful tool in the analysis of photodegradation of wood surfaces and its applicability to other studies on wood surfaces.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Material characteristics
2.1. Svojstva materijala

Radial strips of nominal thickness of 80 μm were microtomed from Scots pine sapwood – SPS (*Pinus sylvestris* L.); European spruce (*Picea abies* Karst.), in further text Norway spruce – NS and Croatian spruce – CS, according to the place of origin; and European Silver Fir (*Abies alba* Mill.) marked as Croatian fir – CF that was selected as fast grown – FG and slow grown – SG. An overview of the basic physical and mechanical properties of the tested material is given in Table 1. The testing material has been deliberately selected from the commercial stock so that the recorded changes could be associated with the standard processed wood products. Optimal thickness for the investigation of the wood surface photodegradation is the depth to which light and elements will cause the greatest effect, which was shown to be ca 70 – 80 μm for temperate softwoods. This thickness is also practical from the experimental point of view - resulting in no slipping of the samples and achieving the optimal range of ultimate load values when tested with short span tensile tester. Detailed elaboration on the issue of specimen geometry is presented by Živković and Turkulin (2014).

The basic physical and mechanical properties of tested species are given in Table 1. The procedures for the preparation and testing of the radial and tangential thin strips were fully reported and analyzed earlier (Derbyshire *et al.*, 1995, 1996; Živković and Turkulin, 2014) and only a brief description is given here.

The strips were stored in the dark prior to and after exposure, and handled in controlled and constant atmospheric conditions of 20 ± 2 °C and 60 ± 5 % relative humidity.

Codes in the first column of Table 1 are used throughout the text as acronyms for wood species. The conditions and codes for weathering regimes are given in Table 2.

2.2 Exposure conditions and specimen handling
2.2. Uvjeti izlaganja i rukovanje uzorcima

Strips were mounted on frames made of 1.2 mm thick aluminum sheets with two rectangular openings. A batch of five strips was attached over each of these open-

Table 1 Basic physical and mechanical properties of the testing material
Tablica 1. Osnovna fizikalna i mehanička svojstva ispitivanog materijala

Species code *Oznaka vrste drva*	**Average density at 12 % m.c.** *Prosječna gustoća pri 12 % s.v.*	**Strip thickness range** *Raspon debljine listića*	**Growth rings** *Godovi*		**Latewood** *Kasno drvo*		**Initial tensile strength at chosen testing span*** *Početna čvrstoća na vlak na izabranom rasponu čeljusti**			
		Min - **Avg** - Max	**Width** *Širina*	**Nr per 10 mm** *Broj na 10 mm*	**Width** *Širina*	**Proportion** *Udio*	0 mm **Span** *Razmak*	C.V.**	10 mm **Span** *Razmak*	C.V.**
	kg/m^3	μm	mm		mm	%	N/mm^2	%	N/mm^2	%
SPS1	440±10	70 - **78.6** - 90	2.56	4	0.95	38	89	7.2	50	9.1
SPS2	540±10	67 - **68.7** - 73	2.45	4	0.88	36	90	8.1	66	9.6
NS	369±10	70 - **81.5** - 90	3.33	3 - 4	1.58	48	82	11.3	58	12.5
CS	483±10	65 - **72.3** - 75	2.60	4	1.01	38	85	8.5	67	11.3
CFSG	510±20	70 - **79.4** - 90	1.36	6 - 7	0.48	35	138	5.7	102	11.7
CFFG	545±20	70 - **81.5** - 90	2.45	3 - 4	1.12	46	125	9.1	103	14.16

*initial strength was calculated for initial testing only on the basis of the geometrical cross-section of the strips. Further on, only the retained percentage of initial load to failure was used as indicator of strength changes that form the strength-loss curves./ *Početna čvrstoća izračunana je na početku istraživanja samo na temelju geometrijskoga poprečnog presjeka listića. Nadalje, samo je zadržani postotak početnog opterećenja do loma korišten kao pokazatelj promjena čvrstoće koji čine krivulje gubitka čvrstoće* ** C.V. is abbreviation for the Coeficient of variation. / *C.V. kratica je za koeficijent varijacije.*

ings using double-sided adhesive tape. Aluminum frames were generally backed with aluminum backing panels in close contact with the strips in order to keep the control of the chamber conditions, since the space behind the panels was ventilated by room air to activate condensation on the strips in cycle QUV 2. The strips exposed to high humidity (QUV3 cycle and natural exposure) were mounted on aluminum frames using 3 mm thick double-sided adhesive tape spacer to avoid any formation of liquid (droplets or accumulation at the bottoms) on the material. Metal backing plates were used consistently throughout the experiment to reflect the light to the back of the strips and seal the chamber and ensure that the desired conditions are met.

Specimens of wood species listed in Table 1 were either exposed to some of artificial weathering regimes (UV-fluorescent light, further denoted as "QUV") or boron-glass filtered xenon-arc light (in further text "XT") or to natural weathering (NE). The overview of specific weathering conditions is given in Table 2. Batches of strips (usually 9 batches of five strips) were withdrawn at intervals adjusted to the expected development of degradation in particular exposure regime. Intervals were shorter in initial phases and gradually longer with development of exposure duration until the strips were degraded beyond the point of physical coherence. At the end of natural exposure and exposure to wet conditions, the earlywood bands of the strips were fully disintegrated. The effect of selected conditions on photodegradation rates was readily monitored after each withdrawal.

Strips for natural weathering were backed with white filter paper and exposed horizontally on the exposure site at the Building Research Establishment (BRE,

Table 2 Conditions and technical details used in artificial weathering regimes
Tablica 2. Uvjeti i tehnički detalji ubrzanog izlaganja uzoraka vremenskim utjecajima

Weathering code *Oznaka izlaganja*	**Weathered wood species** *Vrsta drva*	**General conditions** *Opći uvjeti*	**Light source** *Izvor svjetlosti*	**Conditions in exposure regimes** *Uvjeti tijekom izlaganja*			**Sample mounting details** *Pozicioniranje uzoraka*	
				Chamber Temp. *Temperatura komore* °C	Relative Humidity in chamber *Relativna vlažnost zraka u komori* %	Black Panel Temp. *Temperature crne ploče* °C	Exposure setting *Vrsta izlaganja*	Backing *Oslonac*
QUV-1	CFSG, CFFG	Constant dry	UVA 340	57 - 65	26 - 30	56 - 59	Single-sided	Al panel in contact
QUV-2	CS, NS, CFSG, CFFG, SPS	High humidity	UVA 340	57 - 59	80 - 100*	57 - 60	Single-sided	Al panel no contact
QUV-3	CS, SPS	High humidity	UVA 340	57 - 59	80 - 100*	57 - 60	On both sides	No backing
XT	CFSG, CFFG, SPS	Moderate humidity	Xenon (4.5 kW)	55 - 59	> 90	78	On both sides	No backing

*These conditions were achieved and continuously maintained during exposure. / *Ti su uvjeti postignuti i tijekom izlaganja održavani stalnima.*

Watford, England 52° N and 70 m above sea level) for a period of 3 months during summer (warm continental climate with incidental rain spells).

After withdrawal, the strips were allowed to recondition in room conditions on the frame, and stored in the dark. They were removed from the frame by rocking action of the oval scalpel immediately before tensile testing, and were cut in minimum 10 specimens for each testing span (0 mm and 10 mm).

2.3 Testing and presentation of results
2.3. Ispitivanje i prikaz rezultata

Tensile tests were carried out on dry samples, after conditioning in the dark at 20±1°C and 60±5 % RH using a short span tensile tester. The exception to this procedure was with Croatian spruce, which was tested both dry and wet (Živković and Turkulin, 2014). Tests were carried out at 0 mm span and 10 mm span (details presented by Živković and Turkulin, 2014). Graphs showing the loss in zero and 10 mm span strength for all species presented in this paper are plotted according to the following expression:

$$S = S_0\{1 + C(1 - \exp(-bD))\} \times \{(1 - f)\exp(-k_1 D) + f\exp(-k_2 D)\}$$

Where S is the tensile strength at radiation dose D, S_0 is the initial value of tensile strength prior to exposure. The constant b is the rate of strength increase and the constant C is the limiting value of strength, k_1 is the rate of degradation of the photochemically more susceptible component and k_2 that of the photochemically more resistant component. Constant f is a weighing factor presenting the quantity of the photochemically resistant material as a fraction of the total wood substance. This equation generally enables the interpretation of three distinct, yet combined processes involved in photo-induced wood decomposition: there are two different rates of degradation (the first, more intensive, associated with delignification, and the later, slower rate associated with carbohydrate decomposition). Additionally, there may appear a short-lived initial antagonistic process of strength increase. A detailed formulation of this mathematical model is described by Derbyshire *et al.* (1996).

In all of the plots, the correlation factors between the curves plotted on the basis of measured and calculated values exceeded 0.96, and in vast majority of cases were higher than 0.98.

3 RESULTS
3. REZULTATI

3.1 Dry / Wet testing
3.1. Ispitivanje u suhim i mokrim uvjetima

Wet testing gives the same initial value of the zero span ultimate load, but 30 % smaller values in 10 mm span test. This indicates the effect of the penetration of water into the intercell regions and probably onto the fibre interfaces.

The character of tensile changes over the time of exposure and results in dry and wet conditions, i.e. after full aspiration of the specimens for at least half an hour prior to tensile testing, are presented in Figure 1. The dry testing shows very typical strength changes: in zero span testing, the strength initially rises forming a shoulder, then gradually drops. The finite span dry testing shows a slight delay of the strength loss rate in the second phase, then fairly stable strength loss.

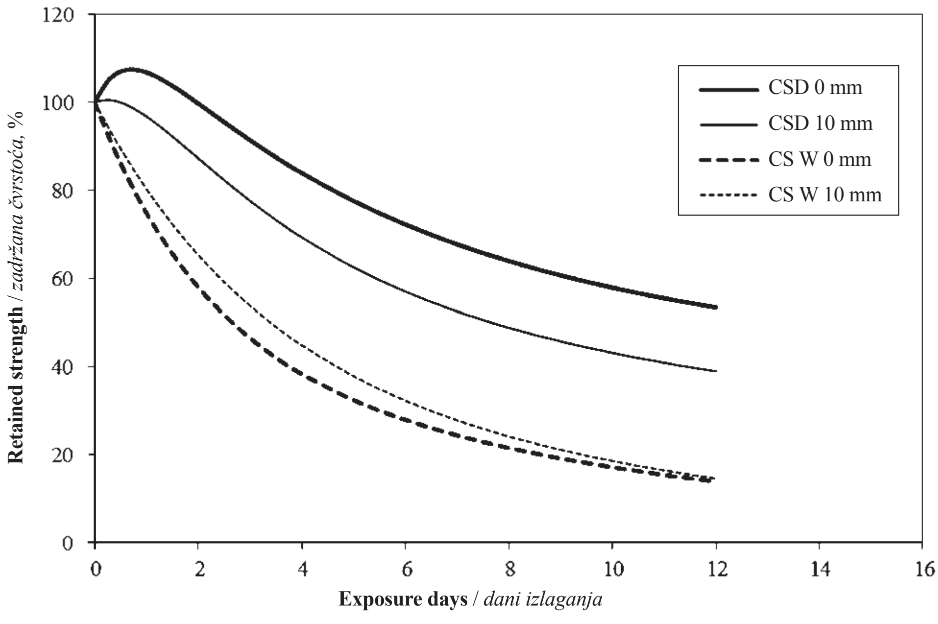

Figure 1 The effect of wet testing of Croatian spruce (CS) on the character of tensile changes during exposure to high humidity conditions (QUV-3). Specimens were tested in dry (D) conditions (at 20±1 °C and 60±5 % RH) and wet (W), i.e. after full aspiration of water

Slika 1. Učinak mokrog ispitivanja smrekovine (CS) na karakter vlačnih promjena tijekom izlaganja u uvjetima visoke vlažnosti (QUV-3). Probni su uzorci kidani u suhom stanju (pri 20±1 °C i 60±5 % r.v.z.) ili u mokrom stanju, tj. nakon potapanja u vodi

Table 3 Dry to wet strength ratio of the Croatian spruce radial strips during weathering in QUV-3 cycle
Tablica 3. Odnos čvrstoće suhih i mokrih radijalnih listića jelovine tijekom izlaganja uvjetima u QUV-3

Span / *Raspon* mm	**Dry / wet strength after exposure (days)** / *Čvrstoća suhih /čvrstoća mokrih listića nakon izlaganja (dani)*								
	0	0.5	1	1.5	2	2.5	3	4	7
0	~1	1.3	1.5	1.5	1.6	1.7	2	2	3.2
10	1.4	1.6	1.7	1.6	2	1.9	2.1	2.5	3.4

Wet testing strength loss curves show different characteristics of strength changes than the dry tensile changes:

a) no initial effect on strength increase (shoulder) or delayed strength drop can be seen;
b) strength loss rates are much higher than in dry testing in both span tests;
c) dry to wet strength ratio progressively grows during exposure (Table 3) and the trend is similar in both span tests. As the wood deteriorates, its strength becomes more sensitive to the effect of water.

Increase of the dry/wet ratio with photodegradation conforms to Ifju's (1964) conclusion that the material of shorter cellulose chains or shorter crystalline portions is more affected by water than the material of longer chain structure. The fact that the dry to wet ratio in both spans increases during 7 days of weathering indicates that it is not delignification, but the effect of water on cellulose structures, which is the primary consequence of samples wetting. Furthermore, based on FT-Raman spectra of wood heat treated at low temperatures, Yamauchi *et al.* (2005) concluded that water has little or no contribution to chemical reactions of lignin. However, while dry/wet ratio (Table 3) changes gradually for spruce, pine retains almost constant ratio, while lime was shown to exhibit very intensive changes in this ratio (Derbyshire and Miller, 1981). These differences may be due to the amount and distribution of lignin (Derbyshire and Miller, 1981; Agarwal, 2006; Lehringer *et al.*, 2008), the length and crystallinity of cellulose (Ifju, 1964; Newman and Hemmingson, 1990; Andersson *et al*., 2004), variations in the physical properties and anatomical organization of wood tissue (Wardrop, 1951; Wellwood, 1962; Kennedy, 1966; Nordman and Quickstrom, 1969), or by combinations of these parameters, as proposed by Evans (1984). These aspects should be, however, further addressed in further research.

3.2 Effect of density and latewood portion
3.2. Utjecaj gustoće i udjela kasnog drva

Wood density was shown to greatly determine the degradation rates. This is in accordance with the findings by Feist and Mraz (1978) and Arnold *et al.* (1991), who determined that erosion rates during full natural exposure can be significantly changed with only 10 % variations in wood density. Density affects the measured strength inasmuch as the level of recorded strength is significantly different (vertical shift of the curves in Figure 2), and the initial increase in strength noticeably differs for specimens of different density.

However, the density does not seem to affect the rates of strength loss, since the curves of strength changes remain parallel throughout a longer exposure. The wood of higher density shall weather slower, but the deterioration generally develops at the same rate as with woods of

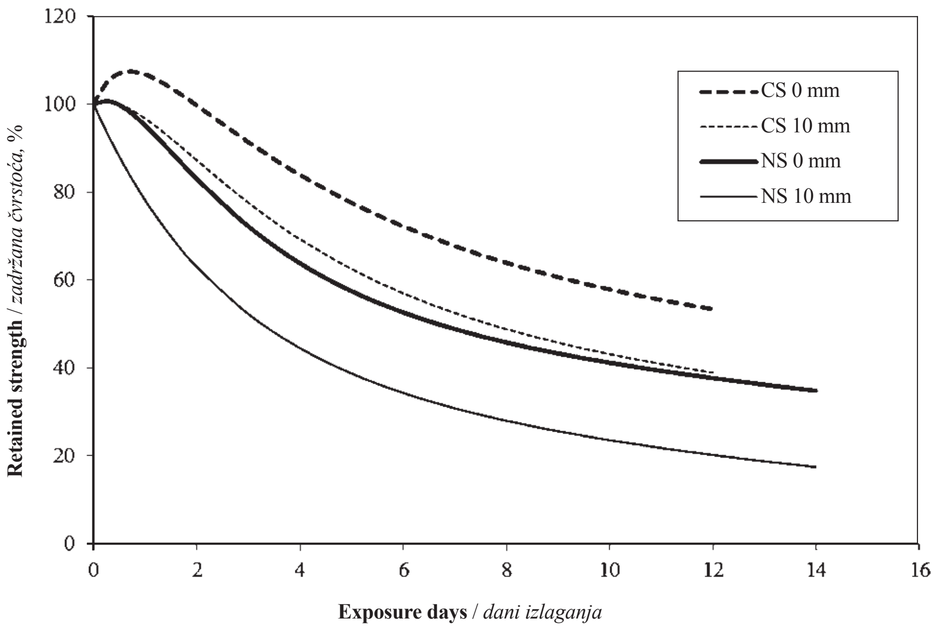

Figure 2 Strength changes of spruce coded as Croatian spruce (CS, density 480 g/cm³) and Norway spruce (NS, density 370 g/cm³) during artificial weathering in humid conditions in QUV-2 regime
Slika 2. Promjene čvrstoće hrvatske smrekovine (CS, gustoća 480 g/cm³) i norveške smrekovine (NS, gustoća 370 g/cm³) tijekom laboratorijskog izlaganja u uvjetima visoke vlažnosti QUV-2

lower density, except in initial stage of weathering. After prolonged weathering exposures, wood of different density could reach the same level of degradation.

Interestingly enough, there were cases recorded in this experiment when the density was not a sufficient parameter for the estimation of the tensile properties of the wood material. The aberrations in linearity of the density - tensile strength relationship, which Biblis (1970) defined for tangential earlywood and latewood microtensile specimens, were too small to explain the irregularities recorded in our experiment. Table 1 shows that the ranking of the blocks for sectioning regarding the initial strength of their strips was not directly related to their density, but rather to the proportion of the latewood in the growth rings. That leads to the conclusion that it is earlywood that degrades at faster rate, while denser material will degrade at a slower pace. The reflection of the degradation on tensile properties, however, will depend more on latewood proportion than on density, since latewood controls the recorded changes in tensile strength.

3.3 Effect of growth rate
3.3. Utjecaj brzine rasta

The effect of the rate of growth has been tested using fir specimens of two distinct growth rates designated here as "slow grown" (SG in further text) and "fast grown" (FG) wood.

The visual difference in the growth rate of the two sets of fir blocks was very pronounced, but the

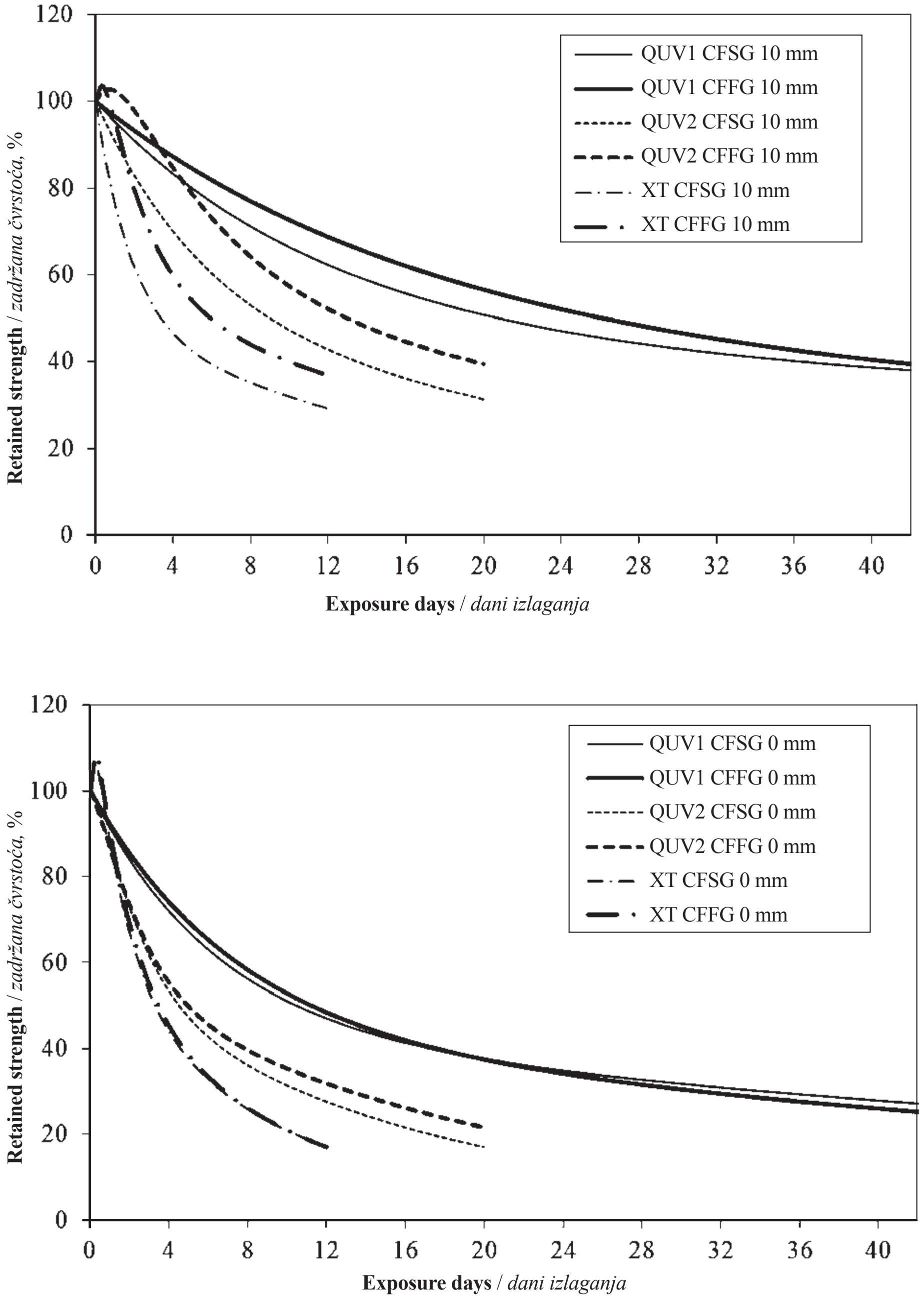

Figure 3 Strength changes of slow grown (CFSG) and fast grown (CFFG) Croatian fir in different levels of humidity effect in QUV-1, QUV-2 and XT regime
Slika 3. Promjene čvrstoće jelovine sporog rasta (CFSG) i brzog rasta (CFFG) tijekom izlaganja različitim uvjetima vlažnosti u režimu QUV-1, QUV-2 i XT

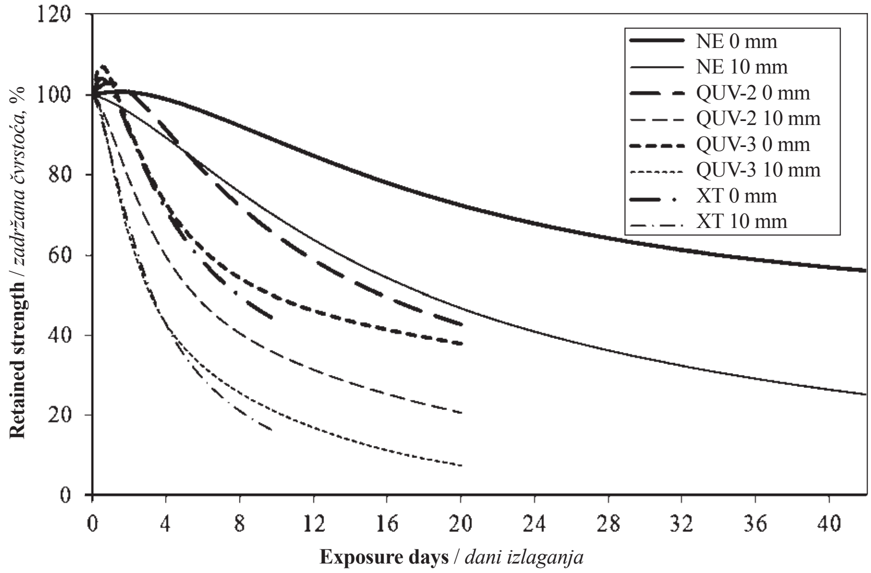

Figure 4 Strength changes of Scots pine sapwood (SPS) in natural exposure and in artificial weathering regimes of high humidity
Slika 4. Promjene čvrstoće bjeljike bijele borovine (SPS) tijekom prirodnoga i laboratorijskih izlaganja pri visokoj relativnoj vlažnosti zraka

density and latewood portions were shown to exhibit certain anomaly. Slow grown material consisted of lower latewood proportion and lower density than "fast grown" strips. Initial strength values did not differ much, especially not in the finite span testing (Table 1). Figure 3 shows that in the finite span testing, the curves of fast and slow grown material show almost perfect match. On the contrary, in zero span testing, the curves never match; the fast grown material degrades at somewhat lower rate. In humid exposure conditions, the fast grown specimens exhibit a shoulder, and this seems to "shift" the curve to the up and right. This never happened with the slow grown material. Even in dry conditions (QUV-1), the fast grown material shows a tendency to strength retention in the initial phase. It is important to notice that the same positioning of the strength loss curves was observed in all regimes.

It seems that the characteristic structural behavior in tension - as seen in finite span testing - is dominated by the species' anatomical features and does not differ significantly for the given range of density and latewood portion. This is valid for the absolute values of the ultimate load as well as for the rate of its changes with the time of exposure. However, the cellulosic microfibrilar strength – as seen in zero span results – greatly depends on the organization of the cellulosic structural elements in the latewood bands. Zero span testing can depict very fine cellulose changes, but caution must be taken so as not to misjudge the strength changes – e.g. appearance or absence of the shoulder - by mechanical aspects of the testing process.

The reduction in ring width generally leads to the increase in density and consequently to higher mechanical properties. The growth rate should nevertheless be combined with density and latewood proportion to form a set of parameters, which determine the strength level and strength loss rates of particular wood material. This is in accordance with the findings by Feist and Mraz (1978), who found that fast grown latewood erodes more slowly than slow grown latewood, due to thinner and more fragile cell walls of the slow grown latewood. It must be emphasized that caution must be taken about the density and growth rates not only because of their influence on weathering behavior but also because of the sensitivity and dependence of the tensile testing procedure on these parameters.

3.4 Effect of weathering conditions
3.4. Utjecaj uvjeta izlaganja

When strips were exposed to UV light using the same mounting system as for those exposed to Xenon source (QUV-3 and XT curves in Figure 4), there were virtually no differences in the degradation rates between the two machines. Surprisingly enough, the XT curve presents the strength loss of the material of the density (440 kg/m^3 - SPS1, Table 1) lower than the one used in the QUV-3 test (540 kg/m^3– SPS2, Table 1). This would mean that the degradation effect in the UV is relatively more intensive, for it had caused similar degradation rates of significantly denser material.

The output of the Xenon source with window glass filter in the spectral range 295 - 540 nm is 567 W/m^2 and that of the UVA-340 lamps is 37 W/m^2, which makes the ratio of 15.3. If consideration of the radiation output is restricted to the wavelength range 295 - 400 nm, i.e. to UV output only, then the output of the Xenon source is 133 W/m^2 and that of the UV remains 37 W/m^2. Thus the ratio of the UV outputs of the two machines is 3.6, still considerably higher than the acceleration factors recorded from the strength loss curves. As can be seen in Fig. 4, exposure conditions like relative humidity, fluctuations of climatic conditions, thermal effects, etc. can significantly influence the strength changes at the same levels of radiation in a weathering machine. Additionally, Figure 4 reflects the relationship between the effects of different levels of radiation on the same time basis. The results from natural weathering with its unpredictable and stochastic variations in exposure conditions, is presented only for a better insight into the relationship between various exposure regimes and recorded tensile properties.

It would, therefore, seem that the precise nature of the spectral distribution of the radiation source does not significantly affect the nature of the photodegradation process of wood strips. The degradation rates are enhanced by a high UV content in the radiation spectrum. Since no great differences in the degradation rates were observed in the machines of different intensities even in a narrow 300-400 nm range, it may be postulated that the lower portion of the UV spectrum is responsible for the initiation of photodegradation.

4 CONCLUSION
4. ZAKLJUČAK

The microtensile testing proved to be a sensitive and precise tool in monitoring the alterations of wood composition (due to degradation by light or elements). However, the results clearly showed that specific physical and structural properties of material may have detrimental effect on consistency and coherence of results. Latewood proportion and its tensile strength were shown to dominate the tensile testing process.

The comparisons between various species should be made on the material of average density and latewood proportion for each species, so as not to mix the effect of variations in physical and structural properties with the effects caused by main experimental variable, such as weathering resistance of particular timber species.

Generally, higher density results in greater strength and lower degradation rates of wood material. Based on the experiment shown here, it can be seen that such general conclusion must be taken with caution. Its latewood proportion and its mechanical properties affect both the degradation rates and tensile testing reliability.

The exposures in both artificial devices (Xenon and UV source) were shown to offer a satisfactory range of conditions to enable the testing of weathering degradation rates of wood. Despite the great differences in the spectral distribution of the radiation sources, the results differed only in the rate of degradation. The fact that strength loss changes followed the same pattern indicates that there is no difference in the nature of degradation process in various weathering machines, but the speed and rates of degradation may be different. Careful choice of material and artificial weathering conditions forms a basis for the sound comparison between the artificial and natural weathering regimes.

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Corresponding address:

Assist. Prof. VJEKOSLAV ŽIVKOVIĆ, Ph.D.

Department for Furniture and Wood Products
Faculty of Forestry
University of Zagreb
Svetošimunska 25
10002 Zagreb, CROATIA
e-mail: zivkovic@sumfak.hr

Aydin Demir[1], Ismail Aydin[1], Hasan Ozturk[2]

Formaldehyde Release from Plywood Manufactured with Two Types of Urea Formaldehyde Resins after Fire Retardant Treatment of Veneers

Oslobađanje formaldehida iz uslojene drvene ploče proizvedene od furnira obrađenih usporivačima gorenja i lijepljenih dvama tipovima urea-formaldehidnih ljepila

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ABSTRACT • *In the present study, it was aimed to investigate the formaldehyde release of plywood panels manufactured from beech, poplar, alder and scots pine veneers treated with 5 % aqueous solutions of commonly used fire retardants: zinc borate, boric acid, monoammonium phosphate and ammonium sulfate. Two types of urea formaldehyde (UF) resin with different free formaldehyde ratios (0.16 % and 0.20 %) in adhesive were used as adhesive. Formaldehyde release of plywood panels was determined according to flask method described in EN 717-3 standard. As a result of this study, it was found that formaldehyde release from panels produced by beech, poplar, alder and scots pine veneers treated with zinc borate and boric acid were higher than those of control panels, while lower formaldehyde release was obtained for panels treated with monoammonium phosphate and ammonium sulfate. This is valid for all four wood species. Treatment of monoammonium phosphate and ammonium sulfate caused considerable reduction in formaldehyde emission from manufactured plywood panels. In some usage areas, where high strength properties are not expected, plywood panels manufactured from veneers treated with monoammonium phosphate and ammonium sulfate may be used for reducing formaldehyde release.*

Key words: *formaldehyde release, plywood, veneer, fire retardant, urea formaldehyde*

SAŽETAK • *U radu je predstavljeno istraživanje oslobađanja formaldehida iz uslojenih drvenih ploča proizvedenih od furnira bukve, topole, johe i običnog bora tretiranih s 5 %-tnim vodenim otopinama najčešće upotrebljavanih usporivača gorenja: cinkova borata, borne kiseline, monoamonijeva fosfata i amonijeva sulfata. Za lijepljenje furnira upotrijebljene su dvije vrste urea-formaldehidnog ljepila (UF) različitog omjera slobodnih formaldehida*

[1] Authors are research assistant and professor at Karadeniz Technical University, Faculty of Forestry, Department of Forest Industry Engineering, Trabzon, Turkey. [2]Author is lecturer at Arsin Vocational School, Materials and Material Processing Technologies, Karadeniz Technical University, Trabzon, Turkey.
[1] Autori su znanstveni asistent i profesor Tehničkog sveučilišta u Karadenizu, Šumarski fakultet, Odjel za industrije na bazi šuma, Trabzon, Turska.[2] Autor je predavač Visoke škole Arsin, Materijali i tehnologije obrade materijala, Tehničko sveučilište Karadeniz, Trabzon, Turska.

(0,16 i 0,20 %) u njemu. Oslobađanje formaldehida iz uslojenih drvenih ploča određeno je perforatorskom metodom opisanom u standardu EN 717-3. Istraživanja su pokazala da je oslobađanje formaldehida iz uzoraka ploča proizvedenih od furnira bukve, topole, johe i običnog bora i tretiranih cinkovim boratom i bornom kiselinom veće nego iz kontrolnih uzoraka ploča, dok je za ploče tretirane monoamonijevim fosfatom i amonijevim sulfatom ustanovljena manja količina oslobođenog formaldehida. To vrijedi za sve četiri vrste drva. Tretiranje ploča monoamonijevim fosfatom i amonijevim sulfatom rezultirala je znatnim smanjenjem emisije formaldehida iz proizvedenih uslojenih drvenih ploča. Stoga se u nekim područjima uporabe u kojima se ne zahtijeva velika čvrstoća ploča mogu upotrebljavati ploče od uslojenog drva izrađene od furnira tretiranih monoamonijevim fosfatom i amonijevim sulfatom jer se iz njih oslobađaju manje količine formaldehida.

Ključne riječi: *oslobađanje formaldehida, ploča od uslojenog drva, furnir, usporivač gorenja, urea-formaldehid*

1 INTRODUCTION
1. UVOD

Plywood is preferred as constructional material and has conventionally played an important role in light frame construction. Plywood and other wood-based materials are extensively used in the production of furniture, engineered flooring, housing, and other industrial materials (Bohm *et al.,* 2012). However, the usage and application areas of plywood are limited since the plywood is a flammable material. Therefore, there has been much interest in the fire-retardant-treatment of wood-based panels (Cheng and Wang, 2011). The plywood panels treated with fire retardant chemicals are extensively used. Especially, they are generally preferred in furniture industry and construction applications (Tanritanir and Akbulut, 1999; Winandy, 2001; Ayrilmis *et al.*, 2006).

The wooden materials treated with fire retardant chemicals enable an applicable alternative to conventional non-combustible products, where a higher level of fire safety is necessary or desirable (White and Mitchell, 1992). Boron compounds are known as one of the best fire retardant chemicals due to their beneficial effects like neutral pH, protective efficiency, and less effect on mechanical strength than the others (Levan and Tran, 1990). Also, phosphorus-containing compounds like mono- and di-ammonium phosphates are considered very effective fire retardant chemicals, so they have been preferred for wooden and wood-based products for quite a long time (Grexa *et al.,* 1999).

Formaldehyde has a high risk level and it is a potential human carcinogen, so it is categorized more distinctly than most other pollutants (Salem *et al.,* 2013). Also, this chemical has adverse health effects such as eye and respiratory irritation, irritability, inability to concentrate and sleepiness (Milota, 2000; Colak and Colakoglu, 2004). The formaldehyde, one of the most significant sources, is made by people, e.g. releases from automotive exhaust not fitted with catalytic converters. The formaldehyde is also released industrially in large quantities and utilized in many processes. The products containing formaldehyde like resins, glues, insulating materials, oriented strand board (OSB), plywood, and fabrics are the major anthropogenic sources with a serious impact on people in the indoor environment (Uchiyama *et al.,* 2007). During recent years, many studies have evaluated the effects of press conditions like press temperature and time, mat moisture content, lower-molecular-weight UF resins, and formaldehyde scavengers for formaldehyde release, because wood-based panels are one of the sources of the possible formaldehyde release, and investigated the production of various wood-based panels bonding with low-formaldehyde and non-formaldehyde resins (Minemura, 1976; Hao and Liu, 1993; Grigoriou, 2000; Wiglusz *et al.,* 2002; Wang *et al.,* 2003; Aydin *et al.,* 2006; Wang *et al.,* 2007, 2008). Moreover, it was stated that plywood manufactured by adding borax ($Na_2B_4O_7 10- H_2O$) (Colak and Colakoglu, 2004) and polyvinyl acetate (Kim and Kim, 2005) to the glue mixture caused the reduction of formaldehyde release. It was also determined that formaldehyde release decreased by laminating wood-based composite panel surfaces with decorative vinyl film and melamine-impregnated paper (*Groah et al.,* 1984; Nemli and Colakoglu, 2005). Also, studies have been made with tannin extracted from the bark of wattle (Vazquez *et al.,* 2000; Kim *et al.,* 2003; Santana *et al.,* 1995; Pizzi and Scharfetter, 1978), acacia (Pizzi, 2000; Jahanshahee *et al.,* 2010; Jahanshahee *et al.,* 2012) and starch (Farag, 1995; Yoshida *et al.,* 2005; Turunen *et al.,* 2003; Basta *et al.,* 2006), mangrove (Sowunmi, 2000) in co-condensed resins with phenol and formaldehyde.

The cost was a significant issue in evaluating a wood adhesive in specific implementations, its technical properties and gluing behaviour in the past. However, the environmental and health aspects of the adhesive itself have gained more significance during recent years (Aydin *et al.,* 2006). However, few published papers describing techniques for reducing formaldehyde release as an environmental pollutant from wood-based panels, such as plywood, are available. In this study, the effect of fire retardant chemicals on reducing formaldehyde release from plywood was investigated.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

In this experimental study, 2 mm-thick rotary cut veneers with the dimensions of 500 mm by 500 mm were obtained from beech *(Fagus orientalis Lipsky)*, poplar (*Populus deltoides* I-77/51 clone), alder *(Alnus glutinosa* subsp. *barbata)* and scots pine *(Pinus sylvestris L.)* logs. A laboratory scale rotary type peeler (Valette&Garreau - Vichy, France), with a maximum horizontal holding capacity of 800 mm, was used for manufacturing veneer. While the alder and poplar veneers were manufactured from freshly cut logs, beech and spruce logs were steamed for 12 h before veneer production. The main function of steam heating is to soften the veneer log temporarily, making it more plastic, pliable, more readily peeled, and improving the quality and quantity of the material recovered from the log (Baldwin, 1995). Therefore, beech and spruce logs were steamed to make easier the rotary cutting, whereas alder and poplar veneers were manufactured from freshly cut logs because alder and poplar logs can be peeled freshly. The horizontal opening between knife and nosebar was 85 % of the veneer thickness, and the vertical opening was 0.5 mm in rotary cutting process. The veneers were then dried to 6-8 % moisture content in a veneer dryer. After drying, veneer sheets were treated with some fire retardant chemicals. For this aim, 5 % aqueous solutions of zinc borate, boric acid, monoammonium phosphate (MAP) and ammonium sulfate were used. The veneers were subjected to re-drying process at 110 °C after they being immersed in the fire retardant solution for 20 min. The retention level for each treatment solution was calculated with the following equation, and they are presented in Table 1.

$$R = \frac{G \cdot C}{V} \cdot 10, \text{ kg/m}^3 \qquad (1)$$

Where
R – Retention level, kg/m^3;
G – grams of treatment solution absorbed by the sample;
C – grams of preservative or preservative solution in 100 g treatment solution;
V – volume of sample in cm^3.

Three-ply-plywood panels, 6 mm thick, were manufactured by using two types of urea formaldehyde resin with different free formaldehyde ratios. The formulations of adhesive mixtures used for plywood manufacturing are given in Table 2. Veneer sheets were conditioned to approximately 5-7 % moisture content in a climatization chamber before gluing. The glue mixture was applied at a rate of 160 g/m^2 to the single surface of veneer by using a four-roller glue spreader. Hot press pressure was 12 kg/cm^2 for alder and beech and 8 kg/cm^2 for scots pine and poplar panels, while hot pressing time and temperature were 6 min and 110 ºC, respectively. Two replicate panels were manufactured for each test group.

Formaldehyde release of plywood panels was determined according to flask method described in EN 717-3 standard. This is a simple and inexpensive method for testing formaldehyde release and suitable for testing of uncoated boards (Aydin *et al.,* 2006). In this method, test pieces of known mass are suspended over water in a closed container at constant temperature (40 °C). The formaldehyde released from the test pieces is absorbed by the water and determined photometrically (Sundman *et al.,* 2007). The temperature and time were 40 °C and 3 h, respectively, in determining the formaldehyde release. The test apparatus shown in Figure 1 was used for the determination of formaldehyde release from plywood panels (in milligrams per 100 gram of oven-dry panel).

Table 1 Retention levels of fire retardant chemicals at 5 % solution
Tablica 1. Razine retencije kemikalija za usporavanje gorenja pri uporabi 5 %-tne otopine

Wood species *Vrsta drva*	**Fire retardant chemicals** *Kemikalija za usporavanje gorenja*	**Average retention** *Prosječna retencija* kg/m^3		**Wood species** *Vrsta drva*	**Fire retardant chemicals** *Kemikalija za usporavanje gorenja*	**Average retention** *Prosječna retencija* kg/m^3
Beech *bukva*	Zinc borate / *cinkov borat*	12.58		**Alder** *joha*	Zinc borate / *cinkov borat*	15.80
	Boric acid / *borna kiselina*	13.28			Boric acid / *borna kiselina*	13.75
	MAP / *monoamonijev fosfat*	8.71			MAP / *monoamonijev fosfat*	10.60
	Ammonium sulfate *amonijev sulfat*	9.10			Ammonium sulfate *amonijev sulfat*	10.74
Poplar *topola*	Zinc borate / *cinkov borat*	13.49		**Scots pine** *obični bor*	Zinc borate / *cinkov borat*	18.22
	Boric acid / *borna kiselina*	10.51			Boric acid / *borna kiselina*	15.97
	MAP / *monoamonijev fosfat*	10.76			MAP / *monoamonijev fosfat*	9.06
	Ammonium sulfate *amonijev sulfat*	11.03			Ammonium sulfate *amonijev sulfat*	17.94

Table 2 Formulations of UF1 and UF2 glue mixtures used for manufacturing plywood panels
Tablica 2. Formulacije ljepila UF1 i UF2 upotrijebljenih za proizvodnju ploča od uslojenog drva

Glue type / *Vrsta ljepila*	**Ingredients of glue mixture** / *Sastojci smjese ljepila*	**Parts by weight** *Težinski udjel*
UF1 Free formaldehyde max. 0.16 % *slobodni formaldehid, najviše 0,16 %*	UF resin (with 55 % solid content) / *UF smola (55 % suhe tvari)*	100
	Wheat flour / *pšenično brašno*	30
	Hardener - NH_4Cl (with 15 % concentration) *otvrdnjivač - NH_4Cl (koncentracija 15 %)*	10
UF2 Free formaldehyde max. 0.20 % *slobodni formaldehid, najviše 0,20 %*	UF resin (with 65% solid content) / *UF smola (65 % suhe tvari)*	100
	Wheat flour / *pšenično brašno*	30
	Hardener - NH_4Cl (with 15 % concentration) *otvrdnjivač - NH_4Cl (koncentracija 15 %)*	10

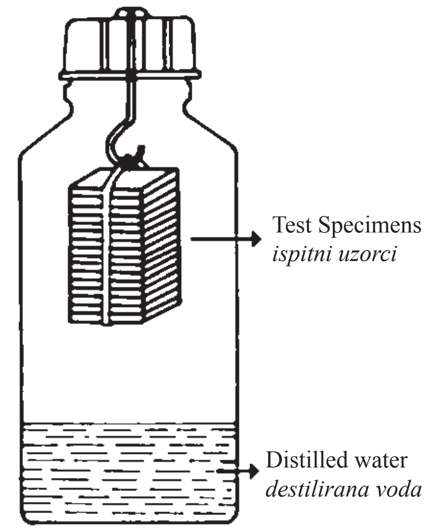

Figure 1 Test apparatus used for the determination of formaldehyde release of plywood panels (Aydin *et al.,* 2006)
Slika 1. Uređaj za određivanje formaldehida oslobođenog iz ploče od uslojenog drva (Aydin *et al*., 2006.)

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Formaldehyde release test results are presented in Fig. 2 and Fig. 3. As can be seen, the poplar plywood panels had the highest formaldehyde release for both UF types. The highest formaldehyde release of poplar plywood panels may be due to high permeability of veneers. The lowest formaldehyde release was found with alder for UF1 and beech for UF2. Also, the formaldehyde release results obtained from UF2 were higher than those obtained from UF1. In literature, it was stated that formaldehyde release increased with increasing free formaldehyde ratio in adhesive (Roffael, 1982).

The treatment processes with fire retardant chemicals evidently affected the formaldehyde release of the panels. Monoammonium phosphate and ammonium sulfate showed a decreasing effect on the formaldehyde release, whereas zinc borate and boric acid showed an increasing effect for both UF types. The lowest formaldehyde release values were obtained for plywood treated with ammonium sulfate. Treatment with ammonium sulfate decreased the formaldehyde release values of the panels produced from treated veneers by 69.53 % and 71.65 % for beech, 18.41 %, and 74.43 % for poplar, 55.94 % and 74.74 % for alder, 19.61 % and 68.70 % for Scots pine panels bonded with UF1 and UF2, respectively.

During the hot pressing, ammonium sulfate and monoammonium phosphate were partially decomposed and produced ammonium in gas. Gao *et al.,* (2015) stated that the released ammonium gas would react with free formaldehyde to produce hexamethylenetetramine, which would be stable in cured glue line and was probably related to the reduction of formaldehyde release levels. In their study, they observed that ammonium pentaborate caused decreasing of free formaldehyde content and formaldehyde release levels, which were mostly reduced by 79.0 % and 81.4 %, respectively (Gao *et al.,* 2015). In literature, it is also stated that the released ammonium could produce N-H functional groups on the surface of the veneer sheets, which contributes to reducing the formaldehyde release (Zhang *et al.,* 2013; Schroder *et al.,* 2001; Wen *et al.,* 2006). Also, Zhang *et al.,* (2013) found for plywood panels that formaldehyde release values decreased with cold-ammonia plasma pretreated veneer sheets and stated that this could result from some etching effect and a large number of free radicals generated after the cold-ammonia plasma treatment, which could develop the wetting and interfacial contact between the

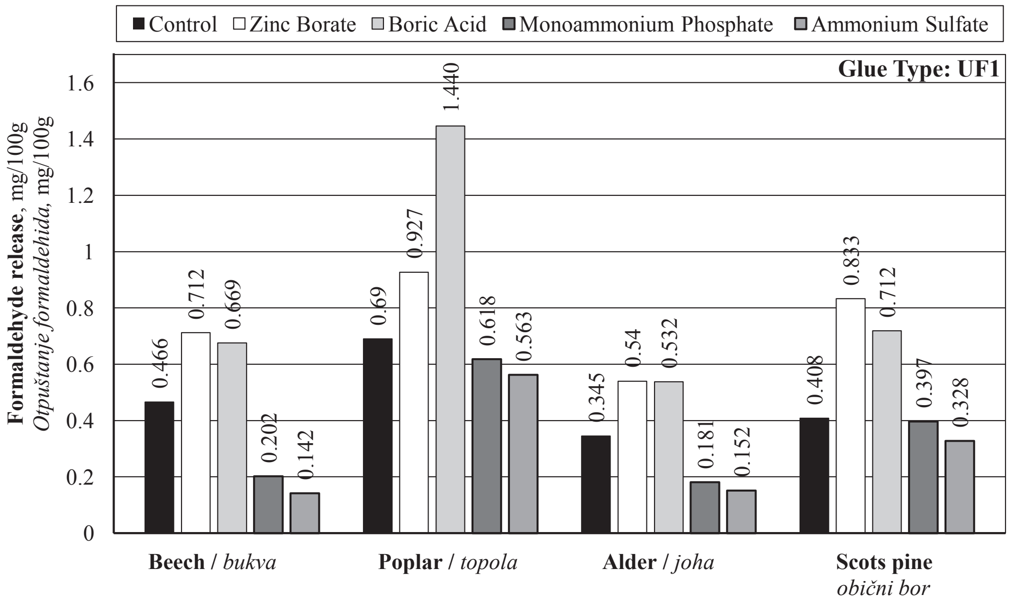

Figure 2 Effect of fire retardant chemicals on formaldehyde release of plywood panels manufactured with UF1 glue
Slika 2. Utjecaj kemikalija za usporavanje gorenja na oslobađanje formaldehida iz ploča od uslojenog drva proizvedenih uz uporabu UF1 ljepila

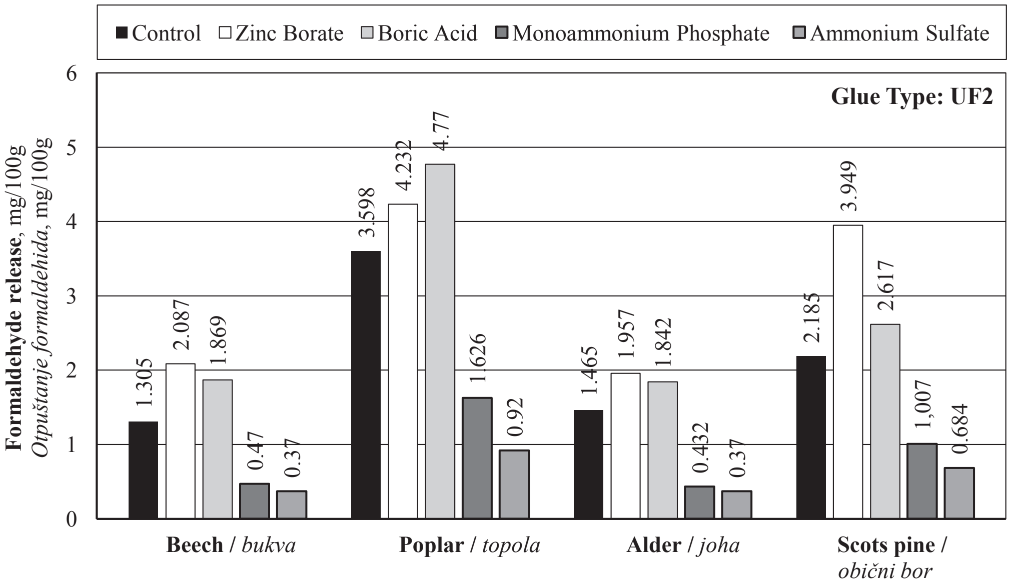

Figure 3 Effect of fire retardant chemicals on formaldehyde release of plywood panels manufactured with UF2 glue
Slika 3. Utjecaj kemikalija za usporavanje gorenja na oslobađanje formaldehida iz ploča od uslojenog drva proizvedenih uz uporabu UF2 ljepila

UF resin and the veneer sheets (Rehn *et al.,* 2003; Wolkenhauer *et al.,* 2008; Blanchard *et al.,* 2009). The development of the wetting and contact increased the shear strength and obstructed the channels preventing the release of formaldehyde (Zhang *et al.,* 2013).

Some studies have also indicated that, when wood was treated with ammonium acetate solution, the formaldehyde release from the wood composites was reduced (Colak *et al.,* 2002; Myers, 1986). Aydin (2004) stated that the ammonium acetate behaves as a formaldehyde scavenger especially when urea-formaldehyde glue was used as adhesive in the manufacturing of wood composites. In addition, Junyou and Shengyou (2010) found that the formaldehyde release from poplar plywood was significantly decreased with the addition of ammonia (Junyou and Shengyou, 2010). Wang *et al.,* (2010) stated that combinations of ammonia and sodium sulfite as formaldehyde scavengers had positive effects on the formaldehyde release of plywood panels.

The boron compounds used in this study increased the formaldehyde release of all wood species for both UF types. Colak and Colakoglu (2004) found that the boric acid increased the formaldehyde release of the panels and explained it by the fact that acetic acid arisen from boric acid reacted with free formaldehyde in the resin. Due to the increase of pH values of veneers, the ability of UF resins to undergo hydrolyses in acidic environment may have decreased (Colak and Colakoglu, 2004; Pizzi, 1989). Also, Demir *et al.,* (2014) found that the zinc borate increased the formaldehyde release of the panels.

4 CONCLUSIONS
4. ZAKLJUČAK

This study investigated the effect of fire retardant chemicals on the formaldehyde release of plywood panels. As a result of this study, for both UF types, formaldehyde release contents of the panels produced from veneers treated with zinc borate and boric acid were higher than those of the control panels, while lower formaldehyde release values were obtained for the panels treated with monoammonium phosphate and ammonium sulfate when compared to the control panels. UF2 type resin, which had a high free formaldehyde ratio, gave higher release values than UF1 type resin. Treatment of monoammonium phosphate and ammonium sulfate caused considerable reduction in formaldehyde release from manufactured plywood panels. In some usage areas, where high strength properties are not expected, plywood panels manufactured from veneers treated with monoammonium phosphate and ammonium sulfate may be used for reducing formaldehyde release.

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Corresponding address:

Prof. ISMAIL AYDIN, Ph.D.

Karadeniz Technical University
Faculty of Forestry
Department of Forest Industry Engineering
61080 Trabzon, TURKEY
e-mail: iaydin@ktu.edu.tr

Nesogordonia papaverifera (A. Chev.) R. Capuron

NAZIVI

Nothofagus procera Oerst. naziv je drva botaničke vrste iz porodice *Fagaceae*. Trgovački su nazivi te vrste rauli (Argentina, Čile, Francuska, Italija, Nizozemska, Njemačka, SAD, Velika Britanija), chilean beech, south american beech (SAD), roble pellin, ruili (Čile).

NALAZIŠTE

Stabla *Nothofagus procera* Oerst. rastu u Južnoj Americi; u Čileu ih ima zapadno od Anda, između 35 i 39° južne širine, istočno od Anda samo mjestimično, na sjeveru se rasprostiru uz rijeku Mauli, a na jugu od Valdivije i njezina pritoka San Pedra. Drveću te botaničke vrste pogoduje vlažna i topla klima. Uglavnom ga nalazimo na nižim visinama umjereno toplih kišnih šuma, katkad i na većim visinama toplijih kišnih šuma, na zaštićenim lokacijama do tisuću metara nadmorske visine. Gotovo uvijek raste zajedno s vrstom coigue (*Nothofagus dombeyii* Bl.).

STABLO

Drvo naraste od 30 do 40 (50) metara, duljina debla mu je do 20 m, prsnog promjera 0,8 do 1,2 m. Deblo je pravilnoga, cilindričnog oblika. Vanjska mu je kora ispucana, smeđkasta ili siva. Debljina kore je od 1 do 2,5 cm.

DRVO

Makroskopska obilježja

Drvo je rastresito porozno. Bjeljika i srževina međusobno se razlikuju bojom. Srževina je svjetlocrvena do crvenkastosmeđa, a bjeljika je uska i sivoružičasta. Tekstura drva je fina, jednolična i dekorativna. Žica drva je ravna ili usukana. Granica goda dobro je uočljiva. Pore i drvni traci vidljivi su povećalom.

Mikroskopska obilježja

Raspored traheja je pojedinačan, u paru i radijalan. Promjer traheja iznosi 25...95...180 mikrometara, gustoća im je 70...85...95 po milimetru četvornom poprečnog presjeka. Volumni udio traheja je oko 36 %. Traheje srži ispunjene su tilama. Aksijalni je parenhim apotrahealano raspoređen. Volumni je udio aksijalnog parenhima vrlo malen. Staničje drvnih trakova je heterogeno, visine 250...300...450 mikrometara, a širine 13...29...39 mikrometara, odnosno 1 – 2 stanice. Gustoća drvnih trakova je 8...12...18 po milimetru poprečnog presjeka. Volumni je udio drvnih trakova oko 14 %. Drvna su vlakanca libriformska, a dugačka su 800...1150...1500 mikrometara. Debljina staničnih stijenki vlakanaca je 2,4...5,6...8,8 mikrometara, a promjer lumena 4,8...11,2...19,6 mikrometara. Volumni je udio vlakanaca oko 50 %.

Fizička svojstva

Gustoća standardno suhog drva, ρ_o	460...510...530 kg/m^3
Gustoća prosušenog drva, ρ_{12-15}	500...550...580 kg/m^3
Gustoća sirovog drva, ρ_s	800...1000 kg/m^3
Poroznost	oko 66 %
Radijalno utezanje, β_r	oko 4,1 %
Tangentno utezanje, β_t	oko 8,6 %
Volumno utezanje, β_v	oko 13,0 %

Mehanička svojstva

Čvrstoća na tlak	37,3...40...47 MPa
Čvrstoća na vlak, paralelno s vlakancima	73...111...131 MPa
Čvrstoća na savijanje	79...87...95 MPa
Tvrdoća prema Brinelu, paralelno s vlakancima	34...41...46 MPa
Tvrdoća prema Brinelu, okomito na vlakanca	13...15...18 MPa
Modul elastičnosti	10,7...12,6 GPa

TEHNOLOŠKA SVOJSTVA

Obradivost

U usporedbi s europskom bukovinom, drvo rauli ima znatno manju gustoću i čvrstoću. Dobro se ručno i strojno obrađuje. Lako se ljušti, pili, blanja, brusi, buši i politira. Prije bušenja drvo je potrebno predbušiti.

Sušenje

Drvo se dobro i polako suši. Za vrijeme sušenja rijetko se pojavljuje vitoperenje ili kolaps.

Trajnost i zaštita

Prema normi HRN-EN 350, 2016, srž drva slabo je otporna na gljive truležnice (razred otpornosti 4) i također je slabo otporna na napad termita (razred otpornosti S). Srž je slabo permeabilna (razred 4). Prema normama, može se upotrebljavati u uvjetima razreda opasnosti 2 (u unutarnjim prostorima i na otvorenome, ali natkrivenom prostoru).

Uporaba

U Čileu se drvo rauli rabi za slične namjene kao i bukovina u Europi.

Upotrebljava se za izradu namještaja, parketa i stolarije te za proizvodnju bačava i drvenih ploča.

Sirovina

Drvo *Nothofagus procera* Oerst. na tržište dolazi u obliku trupaca i piljenica različitih dimenzija.

Napomena

Vrsti *Nothofagus procera* Oerst. za sada ne prijeti nestanak i nije na popisu ugroženih vrsta CITES – Convention on International Trade in Endangered Species. Drvo sličnih svojstava imaju i vrste *Nothofagus cunninghamii* Oerst., *N. Dombeyi* Bl., N. *Menziesii* Oerst., *N. Obliqua* Mirb., *N- spp*. Poznato je oko 16 porodica vrste *Nothofagus* .

Drvo ostalih južnoameričkih vrsta *Nothofagus* izgledom je slično drvu rauli, ali gustoća i čvrstoća mu variraju i slabije je kvalitete.

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prof. dr. sc. Jelena Trajković
izv. prof. dr. sc. Bogoslav Šefc

Upute autorima

Opće odredbe

Časopis *Drvna industrija* objavljuje znanstvene radove (izvorne znanstvene radove, pregledne radove, prethodna priopćenja), stručne radove, izlaganja sa savjetovanja, stručne obavijesti, bibliografske radove, preglede te ostale priloge s područja biologije, kemije, fizike i tehnologije drva, pulpe i papira te drvnih proizvoda, uključujući i proizvodnu, upravljačku i tržišnu problematiku u drvnoj industriji.

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Upute

Predani radovi smiju sadržavati najviše 15 jednostrano pisanih A4 listova 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 *doc formatu*, u potpunosti napisan fontom *Times New Roman* (tekst, grafikoni i slike), normalnim stilom, bez dodatnog uređenja teksta.

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Znanstveni i stručni 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. Obvezatna 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 (programom za pisanje formula 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.

Broj slika mora biti ograničen 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 koloru moguće je na zahtjev autora i uz posebno plaćanje), 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, uz plaćanje). 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 (*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 : 1".

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. (Bađun, 1965). 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).

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Primjer

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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/node00.html. First published 1997 (pristupljeno 27. siječnja 2010).

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