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Influence of Urea-Formaldehyde Resin Modification with Liquefied Wood on Particleboard Properties

Utjecaj modifikacije karbamid-formaldehidne smole s utekućenim drvom na svojstva ploča iverica

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ABSTRACT • *In the group of wood composite materials from fragmented wood, "valueless" biomass and residues are converted to valuable material. The problem of application of other necessary synthetic chemical components, particularly adhesives, which are essential non-wooden components in wood composite production (mainly oil derivatives), has been the subject of many scientific researches that gave positive results. Further to the above, many researches are focused on wood liquefaction and liquefied wood (LW) application as potential adhesives, related to gluing solid particles with liquid wood. Based on previous studies, maximum attention was given to LW applications in modification of phenol-formaldehyde (PF) resins, polyurethanes, saturated and unsaturated polyesters, isocyanates and epoxy resins, and their further application in novel material types. It is evident that because of their "inferior" properties, researches on urea-formaldehyde (UF) resins failed, as well as researches on preparations of UF base adhesives modified with LW. Therefore, the subject of this study was to research the influence of specific experimental parameters on liquefied wood compatibility with UF resins, its influence on polymer structure and adhesion-cohesion properties of modified UF adhesives, and particleboard physical mechanical properties and formaldehyde emission. The results showed that in all cases of UF resin replacement with LW, there was a significant reduction of formaldehyde emission in particleboards, which is one of the aims of this study. Furthermore, it was shown that LW does not show any polymer or adhesion properties, and in this regard laboratory synthesis was conducted of designed liquefied wood-formaldehyde (LWF) resin and LW was synthesized with formalin. With the LWF resin modification of particleboards, results showed increased mechanical properties and free formaldehyde emission as a direct influence of added formalin. To reduce the increased free formaldehyde emission, LWF resin was synthesized analogously to the production of PF resin novolak type, and prepared based on the percentage of lignin content (because of polyphenol properties) in investigated wood species (black poplar), which was applied in further researches.*

Key words: *liquefied wood (LW), composite materials, urea-formaldehyde (UF) resin modification, liquefied wood-formaldehyde (LWF) resin*

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SAŽETAK • *U drvnim kompozitnim materijalima od usitnjenog drva „bezvrijedna“ se biomasa i ostaci nakon uporabe pretvaraju u vrijedan materijal. Problem primjene ostalih nužnih sintetičkih kemijskih komponenenata, osobito ljepila koja su esencijalne nedrvne komponente u proizvodnji drvnih kompozita (uglavnom naftni derivati), već je odavno predmetom znanstvenih istraživanja koja daju pozitivne rezultate. Vezano za navedenu problematiku, brojna su istraživanja usmjerena na utekućenje drva i primjenu utekućenog drva kao ljepila, odnosno na lijepljenje krutih drvnih čestica tekućim drvom. Na temelju dosadašnjih istraživanja, najviše je pozornosti pridano primjeni utekućenog drva u modifikaciji fenol-formaldehidnih (FF) smola, poliuretana, zasićenih i nezasićenih poliestera, izocijanata i epoksidnih smola te njihovoj daljnjoj primjeni u novim vrstama materijala. Evidentno je da su zbog njihovih „lošijih“ svojstava, istraživanja karbamid-formaldehidnih (KF) smola modificiranih utekućenim drvom izostala. Stoga je predmet istraživanja ovog rada utjecaj eksperimentalnih parametara na kompatibilnost utekućenog drva s KF smolama, utjecaj na polimernu strukturu i adhezijsko-kohezijska svojstva modificiranih KF ljepila te na fizikalno-mehanička svojstva i emisiju formaldehida ploča iverica. Rezultati su pokazali da je u svim primjerima zamjene KF smole UD-om znatno smanjena emisija formaldehida u pločama ivericama, što je i jedan od ciljeva ovog rada. Nadalje, pokazalo se da UD ne pokazuje polimerna ni vezivna svojstva, te je u tom smislu provedena laboratorijska sinteza projektirane utekućeno drvo-formaldehidne (UDF) smole, odnosno UD je sintetiziran formalinom. Modifikacijom ploča iverica UDF smolom, rezultati su pokazali povećana mehanička svojstva i emisiju slobodnog formaldehida kao izravan utjecaj dodanog formalina. Da bi se smanjila povećana emisija slobodnog formaldehida, UDF smola sintetizirana je analogno proizvodnji FF smola novolačnog tipa, te je pripravljena na temelju postotka sadržaja lignina (zbog polifenolnih svojstava) u istraživanoj vrsti drva (topolovini), te je upotrijebljena u daljnjim istraživanjima.*

Ključne riječi: *utekućeno drvo (UD), kompozitni materijali, modifikacija karbamid-formaldehidne (KF) smole, utekućeno drvo-formaldehidna (UDF) smola*

1 INTRODUCTION
1. UVOD

Wood is one of the most abundant and accessible renewable resources available to men. With growing emphasis on sustainable development, new methods involving alternative wood use are being explored. Particularly interesting is the application of wood as a feedstock for producing polymers that could replace a part of the conventional fossil oil based plastics.

The global use of polymers has experienced decades of consistent growth and is showing no signs of reduction, especially as developing countries are poised to increase their per capita consumption. The growth in polymer consumption is in principle limited by finite oil reserves. However, polymer waste and its incompatibility with nature is often a more visible and in some cases dangerous problem. The solution to both problems could be increasing the use of renewable resources used for polymer production. By improving properties of polymers such as biodegradation, polymers would remain in the natural carbon cycle.

Panels based on fragmented wood and wood composite materials, respectively (particleboards, fiberboards, OSB, MDF, WPC and other panels), are materials of the future. With their wide spectra of potential applications these materials occupy almost all fields of use. Their technological flexibility is not just following modern trends, but is primal impulse and pathway for acquisition of new trends. The quality of wood composite materials does not exclusively depend on wood species and their properties applied in production, and with the application of sophisticated technologies, composite quality is designed according to utilization demands (Jambreković *et al.*, 2005).

In the group of wood composite materials from fragmented wood, “valueless” biomass and residues are converted to valuable material. Uncompetitive wood species without technical values are converted to materials competitive in construction industry (OSB boards), plus novel wood materials (WPC) enable recycling of wood and waste plastic mass. The main advantage of composites from fragmented wood is the application of forest assortments without technical values (industrial wood, fuel wood, small-sized technical wood, waste like stem residues, branches, stumps), appliance of industrial residues (wood residues from primary and secondary sawmill, wood residues from veneers and panels production), and recycling possibility of wood and wood residues after use (Jambreković *et al.*, 2006).

The problem with the application of other necessary synthetic chemical components (particularly adhesives), mainly oil derivatives, which according to oil shortage and price growth in the world market can endanger that production, has been the subject of many scientific researches that gave positive results (Dunky, 2000). Adhesives for panels based on fragmented wood are essential non-wooden components in wood composite production. Nowadays, these adhesives are formaldehyde based, like PF and UF resins, and are dominant in the market of adhesives for wood composite materials. Raw materials for these formaldehyde based adhesives are from non-renewable oil and natural gas. Although, in this moment, there are no problems with the supply of these raw materials, development of these adhesives from renewable natural sources will ensure long term success in wood composite industry. It will reduce potential negative influence of oil price and ultimately restricted oil and natural gas delivering (Jambreković *et al.*, 2006).

Further to the above, many researches are focused on wood liquefaction and liquefied wood application as potential adhesives, related to gluing solid particles with liquid wood (Antonović *et al.*, 2006). With the application of natural adhesives, the problem with formaldehyde emission present in composites produced with the application of synthetic formaldehyde adhesives will be eliminated. This would cause higher ecological purity of wood-based panels, and further expansion of use of integral wood components.

From the chemical point of view, wood consists of 50-55 % cellulose, 15-25 % hemicellulose and 20-30 % lignin, along with minor content of ash (mineral substances) and accessory materials. All the main wood components are high-weight-molecular polymers and form an interwoven network in the wood cell wall; consequently we can say that the wood is a natural polymer with polyphenolic character (Fengel and Wegener, 1989). Wood liquefaction is novel method, and its aim is to convert wood material in biodegradable polymer materials and increase percentage of wood utilization. In previous years, scientists liquefied chemical components of wood like cellulose, hemicellulose (wood polyoses) and lignin in bioactive liquid materials (Kurimoto *et al.*, 1999).

As mentioned before, great efforts are directed to new technology development for achieving effective wood or biomass utilization, and obtaining ecologically acceptable materials on their base. Maximum attention attracted wood (biomass) liquefaction in presence of some organic reagents and their application in preparation of polymer materials. The most interesting are two wood liquefaction methods. The first one is the preparation in presence of phenol, which resulted in liquefaction products rich with phenol units, so it could be applied in the preparation of phenol adhesives (similar to conventional phenol resins), mouldings and other. The second liquefaction method was achieved in presence of alcohols, especially polyhydric alcohols, and the gained products can be used as polyols for the preparation of polyurethane and epoxy products (Shiraishi and Yoshioka, 1997; Tišler, 2002; Grbac *et al.*, 2003).

In previous researches, maximum attention was given to LW applications in modification of PF resins, polyurethanes, saturated and unsaturated polyesters, isocyanates and epoxy resins, and their further application in novel material types. It is evident that because of their "inferior" properties, researches on UF resins failed, as well as researches on preparations of adhesives on UF base modified with LW. Therefore, the subject of this paper is the influence of modification of UF resin (the most characteristic resin in wood-based panel production) with LW on particleboard properties by changing specific experimental parameters. Furthermore, the aim of this research was the analysis of liquefied wood compatibility with UF resins, its influence on polymer structure and adhesion-cohesion properties of modified UF adhesives, and particleboards physicalmechanical properties and formaldehyde emission. The main aim of this study was to determine optimal experimental parameters of particleboards, based on their physicalmechanical properties and formaldehyde emission.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

A total of 14 series of experimental particleboards (42 panels) were manufactured in this study in order to assess the influence of specific experimental parameters on the properties of particleboards, whose particles were glued with UF resin modified with LW. The above researches could be divided based on testing the influence of:

- pressing pressure:
  - with pre pressing where pressure was gradually increased,
  - with pre pressing where pressure was currently increased,
  - without pre pressing,
- pre pressing open time of 60, 75 and 90 s,
- UF resin replacement with LW alkalized with different NaOH concentrations:
  - 10 % LW addition – alkalized with 1N NaOH,
  - 10 % LW addition – alkalized with 2N NaOH,
- UF resin replacement with LW alkalized with different NaOH concentrations and increased addition of paraffin emulsion of 25 %:
  - 10 % LW addition – alkalized with 1N NaOH,
  - 10 % LW addition – alkalized with 2N NaOH,
- UF resin replacement with LW in different ratio only in middle layer (ML):
  - 10 % LW addition – alkalized with 2N NaOH,
  - 20 % LW addition – alkalized with 2N NaOH,
- UF resin replacement with LWF alkalized with 1N NaOH.

2.1 Liquefied wood (LW) preparation
2.1. Priprema utekućenog drva (UD)

Liquefied wood was prepared based on previous studies (Antonović *et al.*, 2006; Antonović, 2008). Wood meal of black poplar (*Populus nigra* L.) was liquefied with a mixture of glycerol and sulfuric acid (H_2SO_4) by acid catalyst method for 120 min at 150 °C. Undissolved residue percentage and wood liquefaction percentage, as well as hydroxyl number (OH-number) were determined as values that describe polymer properties of LW, for the purpose of selecting optimal liquefaction parameters.

Of all mixture types with polyhydric alcohols and glycerol used in previous studies (polyethylene glycol PEG 400, diethylene glycol DEG, dipropylene glycol DPG, ethylene glycol EG and glycerol), based on hydroxyl number (557-562 mg KOH/g), undissolved residue percentage (1.65 %) and wood liquefaction percentage (98.35 %), glycerol/H_2SO_4 (100/3) proved to be the best mixture, and therefore it was used in wood liquefaction method. According to that, the best polymer properties of LW were defined as further raw material in synthesis of modified UF resins, with respect to UF adhesives for experimental particleboard production.

2.2 Preparation of liquefied wood-formaldehyde (LWF) resin
2.2. Priprema utekućeno drvo-formaldehidne (UDF) smole

LWF resin was prepared as PF resin novolak type, because of polyphenol properties of lignin in LW. Novolak type of PF resin is the result of polycondensation reaction in acid medium (pH-value of liquefied wood was smaller than 1), and in stehiometric phenol excess compared to formaldehyde.

The amount of 36 % formaldehyde solution was added to liquefied wood, which is usually designed for commercial PF resin novolak type. Furthermore, the addition of formaldehyde was determined based on lignin percentage as polyphenol in liquefied wood species (Sertić, 2000). Formaldehyde/phenol ratio was defined in mole ratio 0.75/1, in reactor at 90 °C, during 120 min measured from the moment the above mentioned temperature was achieved. It was empirically established that the formaldehyde/phenol ratio can not be higher than 0.75/1, because polymerization reaction could be to rapid, and concentration of free formaldehyde in LWF system could become too high. To prevent rapid resin polymerization, after specific polycondensation degree, the entire mixture was alkalized with 1N sodium hydroxide (NaOH) until the mixture reached pH-value of 7-8, which conforms to pH-value of UF resin used in modification with LWF resin.

2.3 Technical parameters for particleboard pressing
2.3. Tehnološki parametri prešanja ploča iverica

Technical parameters (Tab. 1) for particleboard pressing and ratio of UF/LWF resins in the modification of adhesives were designed based on knowledge from previous studies (Jambreković, 1996; Jambreković, 2000; Antonović, 2008).

Commercial UF resin was used in this study, and it was sampled in particleboard factory. Sampling of representative UF resin was carried out according to standard HRN EN ISO 15605:2005 Adhesives – Sampling and standard HRN EN 1067:2007 Adhesives – Examination and preparation of samples for testing (EN 1067:2005).

The hardener based on ammonium chloride (NH_4Cl), which was prepared as 20 % water solution, was used in experimental particleboard production, based on previous researches (Jambreković, 2000). Paraffin emulsion, manufactured in petrochemical industry, was used for reduction of swelling in thickness.

2.4 Experimental particleboard testing
2.4. Ispitivanje eksperimentalnih ploča iverica

For sampling, cutting and presentation of test results, the following standard was used: HRN EN 326-1:1999: Wood-based panels – Sampling, cutting and inspection – Part 1: Sampling and cutting of test pieces and expression of test results (EN 326-1:1994).

Swelling in thickness (q-2) was tested as a physical property on experimental particleboards. This testing was provided according to standard HRN EN 317:2000: Particleboards and fiberboards – Determination of swelling in thickness after immersion in water (EN 317:1993) for samples with dimensions 50x50xpanel thickness (mm) and HRN D.C8.104: Particleboards – Water immersion and swelling for samples with dimensions 25x25xpanel thickness (mm).

Bending strength was tested according to standard HRN EN 310:1999: Wood based panels – Determination of modulus of elasticity in bending and bending strength (EN 310:1993) and tensile strength perpendicular to the plane of the board (delaminating strength) according to HRN EN 319:1999: Particleboards and fiberboards – Determination of tensile strength perpendicular to the plane of the board (EN 319:1993) were tested as mechanical properties.

Free formaldehyde content in experimental samples was determined according to standard HRN EN 120:2000: Wood based panels – Determination of formaldehyde content – Extraction method also called the perforator method (EN 120:1991).

3 RESULTS AND DISCUSSION
3. REZULTATI I DISKUSIJA

Maximum allowed deviation of thickness for all types of particleboards for general purpose and con-

Table 1 Technical parameters
Tablica 1. Tehnološki parametri

Resin addition / *Dodatak smole*		OL[1] / *VS*: 11.0 %	ML[2] / *SS*: 8.5 %
Ammonium chloride addition / *Dodatak amonijeva klorida*		OL / *VS: 0.2 %*	ML / *SS*: 3.0 %
Paraffin emulsion addition / *Dodatak parafinske emulzije*		OL / *VS*: 0.6 %	ML / *SS*: 0.6 %
Board dimensions (*h* x *l* x *t*) / *Dimenzije ploče (v x š x d)*		600 mm x 800 mm x 16 mm	
Board density / *Gustoća ploče*		0.750 g/cm^3	
Moisture content / *Sadržaj vode*		9 %	
Coating time and air pressure / *Vrijeme obljepljivanja i tlak zraka*	OL	8 min; 3.5 MPa	
	ML	12 min; 4.0 MPa	
Pressing temperature / *Temperatura prešanja*		180 °C	
Maximum pressing pressure / *Maksimalni tlak prešanja*		3.2 N/mm^2	
Pressing time / *Vrijeme prešanja*		300 s	

[1] OL - Outer layer / *VS - vanjski sloj*, [2] ML - Middle layer / *SS - srednji sloj*

Table 2 Phases, time and pressure for single pressing regime
Tablica 2. Faze, vrijeme i tlak prešanja za pojedini režim prešanja

Pressing phases *Faze prešanja*	**Regime 1** / *Režim 1.*		**Regime 2** / *Režim 2.*		**Regime 3** / *Režim 3.*	
	PT / *VP*[3] s	PP / *TP*[4] kPa	PT / *VP* s	PP / *TP* kPa	PT / *VP* s	PP / *TP* kPa
1. Press loading *1. punjenje preše*	0 - 15	-	0 - 15	-	0 - 15	-
2. Press closing *2. zatvaranje preše*	15 - 20	-	15 - 20	-	15 - 20	-
3. Light pressure *3. lagani tlak*	20 - 75	10	20 - 80	60	-	-
4. Maximum pressure – pressure fall *4. maksimalni tlak – pad tlaka*	75 - 85	20	80 - 90	180	20 - 30	180
5. Maximum pressure – pressure fall *5. maksimalni tlak – pad tlaka*	85 - 95	50	-	-	-	-
6. Maximum pressure – pressure fall *6. maksimalni tlak – pad tlaka*	95 - 105	100	-	-	-	-
7. Maximum pressure – pressure fall *7. maksimalni tlak – pad tlaka*	105 - 115	150	-	-	-	-
8. Maximum pressure – no pressure fall *8. maksimalni tlak – nema pada tlaka*	115 - 125	180	-	-	-	-
9. Press opening *9. otvaranje preše*	125 - 300	-	90 - 300	-	30 - 300	-
10. Press discharging *10. pražnjenje preše*	300 - 310	-	300 - 310	-	300 - 310	-

[3]PT – pressing time / *VP – vrijeme prešanja*, [4]PP – pressing pressure / *TP – tlak prešanja*

struction is ± 0.3 mm (according to HRN EN 312-1). Maximum allowed free formaldehyde concentration according to perforator method for E1 emission class is 8 mg HCHO/100 g of absolutely dry sample (according to HRN EN 312-1).

3.1 Influence of pressing pressure on particleboard properties
3.1. Utjecaj tlaka prešanja na svojstva ploča iverica

For the optimal determination of pressing regime based on tested properties, preliminary researches of pressing influence on particleboard properties were made without UF modification with LW. Previous experiences (Jambreković, 1996; Jambreković, 2000) gained in researches with commercial UF resins (also used in this research) were used in determining the pressing time and temperature. Total pressing time was 300 s, without press discharging time, and it was identical for all particleboards. For testing the influence of pressing pressure on particleboard properties, three pressing regimes were selected (Tab. 2):

- regime 1 – with pre pressing where pressure was gradually increased,
- regime 2 – with pre pressing where pressure was currently increased,
- regime 3 – without pre pressing.

When speaking about the influence of pressing pressure, with respect to pressing regime on particleboard properties, the following can be concluded from Tab. 3:

- it is evident that regime 2 is the most favorable, minimum swelling in thickness and significantly higher bending strength were achieved compared with other two regimes, with high tensile strength,

Table 3 Arithmetic means of testing results for influence of pressing pressure on particleboard properties
Tablica 3. Aritmetičke sredine rezultata ispitivanja utjecaja tlaka prešanja na svojstva ploča iverica

Testing properties *Ispitivana svojstva*	**Regime 1** *Režim 1.*	**Regime 2** *Režim 2.*	**Regime 3** *Režim 3.*
Thickness, mm / *debljina, mm*	15.94	15.79	15.64
Density, g/cm^3 / *gustoća, g/cm^3*	0.726	0.762	0.701
Moisture content, % / *sadržaj vode, %*	5.88	5.64	6.78
Swelling in thickness q-2, % / *bubrenje u debljinu q-2, %*	19.43	10.73	15.02
Bending strength, N/mm^2 / *savojna čvrstoća, N/mm^2*	15.117	21.395	12.887
Tensile strength, N/mm^2 / *čvrstoća raslojavanja, N/mm^2*	0.625	0.772	0.883

Table 4 Arithmetic means of testing results for influence of pressing open time on particleboard properties
Tablica 4. Aritmetičke sredine rezultata ispitivanja utjecaja otvorenog vremena prešanja na svojstva ploča iverica

Testing properties / *Ispitivana svojstva*	**60 s**	**75 s**	**90 s**
Thickness, mm / *debljina, mm*	15.78	15.88	16.37
Density, g/cm^3 / *gustoća, g/cm*^{3}	0.757	0.740	0.719
Moisture content, % / *sadržaj vode, %*	6.22	6.13	6.70
Swelling in thickness q-2, % / *bubrenje u debljinu q-2, %*	18.38	21.32	23.41
Bending strength, N/mm^2 / *savojna čvrstoća, N/mm*^{2}	18.429	16.730	16.174
Tensile strength, N/mm^2 / *čvrstoća raslojavanja, N/mm*^{2}	0.644	0.793	0.679

- tensile strength is slightly higher in regime 3, but it should be noted that values are very high in all regimes,
- the pressing pressure has the most unfavorable impact on swelling in thickness, where a high amount of 19.43 % was recorded in the first regime,
- if the obtained values are compared with standardized values, according to HRN EN 312-2:2000 and HRN EN 312-3:2000, it can be said that the values were exceptionally good for all three tested regimes, except for the increased swelling in thickness in regime 1, and extreme swelling in regime 3.

3.2 Influence of pre pressing open time on particleboard properties
3.2. Utjecaj otvorenog vremena pretprešanja na svojstva ploča iverica

The selected pressing regime had pre pressing, where pressure was currently increased (regime 2). Total pressing time was 300 s, without press discharging time, and it was identical for all particleboards. For testing the influence of pressing open time (pre pressing time) on particleboard properties, three different times were selected (60, 75, and 90 s), and the results are shown in Tab. 4.

When speaking about the influence of pressing open time, with respect to pre pressing time on particleboard properties, the following can be concluded:

- the property of swelling in thickness increases with the extension of the pressing open time, while the bending strength decreases,
- tensile strength is very high in all cases, and somewhat higher at the pressing open time of 75 s, when compared with the other two,
- comparing the obtained values with standardized ones, according to HRN EN 312-2:2000 and HRN EN 312-3:2000, it can be said that the properties of bending strength and tensile strength are exceptionally good, while the value of swelling in thickness is minimally or significantly increased.

3.3 Influence of LW concentration alkalized with NaOH on particleboard properties
3.3. Utjecaj koncentracije UD-a zaluženoga s NaOH na svojstva ploča iverica

For experimental particleboards, made with modified UF resin (UF resin was replaced with LW in the amount of 10 % with respect to UF resin dry matter weight), due to its pronounced acidity (pH is lower than 1) LW was alkalized to pH-value of about 8 (pH-value of commercial UF resin is also within these limits). The used alkali is sodium hydroxide, and it is applied in two concentrations - 1N NaOH and 2N NaOH.

During manufacturing of particleboards with modified UF resin replaced by LW alkalized with 1N NaOH, because of its high viscosity during particles coating, a significant decrease of coating time was recorded, which resulted in inferior particles coating. So, the possibility of LW alkalization with 2N NaOH was tested, in order to reduce resin viscosity before particles coating, and consequently also the effect of different concentrations on particleboard properties.

According to good results of particleboard properties with the tested regime, the pressing regime with pre pressing was applied, where pressure was currently increased (regime 2). Total pressing time was 300 s, without press discharging time, and it was identical for all particleboards. The obtained results are shown in Tab. 5.

Table 5 Arithmetic means of testing results for influence of UF resin replacement with LW alkalized with different NaOH concentrations
Tablica 5. Aritmetičke sredine rezultata ispitivanja utjecaja zamjene KF smole UD-om zaluženim različitim koncentracijama NaOH

Testing properties / *Ispitivana svojstva*	**1N NaOH**	**2N NaOH**
Thickness, mm / *debljina, mm*	15.97	15.87
Density, g/cm^3/ *gustoća, g/cm*^{3}	0.623	0.720
Moisture content, % / *sadržaj vode, %*	6.53	6.69
Swelling in thickness q-2, % / *bubrenje u debljinu q-2, %*	17.56	27.40
Bending strength, N/mm^2 / *savojna čvrstoća, N/mm*^{2}	8.674	12.788
Tensile strength, N/mm^2 / *čvrstoća raslojavanja, N/mm*^{2}	0.178	0.474
Formaldehyde emission, mg HCHO/100 g / *emisija formaldehida, mg HCHO/100 g*	3.56	3.72

Concerning the influence of UF resin replacement with LW alkalized with different NaOH concentrations on particleboard properties, when comparing the results presented in Tab. 5, it can be concluded that physical properties (swelling in thickness) are positive during LW alkalization with 1N NaOH (higher viscosity), and mechanical properties (bending and tensile strength) are positive during LW alkalization with 2N NaOH (lower viscosity). Regardless of that, comparing the obtained values with the values in valid standards for particleboards (HRN EN 312-2:2000 and HRN EN 312-3:2000), both particleboard series show inferior quality.

3.4 Influence of addition of paraffin emulsion on particleboard properties

3.4. Utjecaj dodatka parafinske emulzije na svojstva ploča iverica

UF resin was modified by replacement with LW in the amount of 10 % with respect to UF resin dry matter weight, and addition of paraffin emulsion of 25 % for testing the impact of increased addition of paraffin emulsion on particleboard properties. Two concentrations were applied for this test, as well as two viscosities of LW alkalized with 1N NaOH and 2N NaOH, as in previous testing.

The pressing regime with pre pressing was applied, where pressure was currently increased (regime 2). Total pressing time was 300 s, without press discharging time, and it was identical for all particleboards. The obtained results are shown in Tab. 6, for comparison with results from previous tests (also with the addition of paraffin emulsion of 25 %).

Regarding the influence of increased addition of paraffin emulsion of 25 % in adhesive recipe on particleboard properties without UF resin replacement with LW, it can be concluded that bending and tensile strength were reduced, as is well known from previous researches of impact of increased amount of addition of paraffin emulsion on particleboard quality.

Furthermore, too large addition of paraffin emulsion has the opposite effect on particleboard properties. The increased amount of addition of paraffin emulsion makes too inert the particles surface, so during the application of adhesive, particle coatings are reduced. This thereby prevents adhesion efficiency with particles, and consequently increases swelling in thickness and reduction of mechanical values. Regardless of the decreasing of mechanical properties, their values are still optimal, but the swelling in thickness is markedly increased.

When speaking about the influence of UF resin replacement with LW alkalized with different NaOH concentrations and increased addition of paraffin emulsion on particleboard properties, Tab. 6 shows that there are no significant differences between the particleboard physical and mechanical properties. Furthermore, so designed particleboards show similar properties as those without the increased addition of paraffin emulsion, as shown in the above Table. Similarly as in the previous example, when comparing the obtained values with values in valid standards for particleboards (HRN EN 312-2:2000 and HRN EN 312-3:2000), both particleboard series show inferior quality.

3.5 Influence of UF resin replacement with LW in middle layer (ML) on particleboard properties

3.5. Utjecaj zamjene KF smole UD-om u srednjem sloju (SS) na svojstva ploča iverica

This test was made with two recipes of UF resin replaced with different LW percentages (alkalized with 2N NaOH), and the modified resin was added only in the particleboard middle layer ML. Pressing regime with pre pressing was selected, where pressure was currently increased (regime 2). Total pressing time was 300 s, without press discharging time, and it was identical for all particleboards. The obtained results are shown in Tab. 7.

When speaking about the influence of UF resin replacement with LW only in middle layer ML on particleboard properties, Tab. 7 shows that there are no significant differences between the particleboard physical and mechanical properties. In addition to favorable tensile strength, bending strength is somewhat lower

Table 6 Arithmetic means of testing results for influence of increased addition of paraffin emulsion (25 %) without or with UF resin replacement with LW alkalized with different NaOH concentrations
Tablica 6. Aritmetičke sredine rezultata ispitivanja utjecaja povećanog dodatka parafinske emulzije (za 25 %) sa zamjenom KF smole UD-om zaluženim različitim koncentracijama NaOH i bez zamjene na svojstva ploča iverica

Testing properties *Ispitivana svojstva*	**Without LW addition** *Bez dodatka UD-a*	**10 % LW addition 1N NaOH** *Dodatak 10 % UD-a 1N NaOH*	**10 % LW addition 2N NaOH** *Dodatak 10 % UD-a 2N NaOH*
Thickness, mm / *debljina, mm*	15.82	15.88	16.04
Density, g/cm^3 / *gustoća, g/cm^3*	0.753	0.740	0.722
Moisture content, % / *sadržaj vode, %*	5.84	5.47	6.07
Swelling in thickness q-2, % / *bubrenje u debljinu q-2, %*	17.42	26.20	27.48
Bending strength, N/mm^2 / *savojna čvrstoća, N/mm^2*	17.840	13.826	13.365
Tensile strength, N/mm^2 / *čvrstoća raslojavanja, N/mm^2*	0.659	0.365	0.434
Formaldehyde emission, mg HCHO/100 g *emisija formaldehida, mg HCHO/100 g*	-	4.08	3.96

Table 7 Arithmetic means of testing results for influence of UF resin replacement with LW in particleboard middle layer (ML)
Tablica 7. Aritmetičke sredine rezultata ispitivanja utjecaja zamjene KF smole UD-om u srednjem sloju SS ploče iverice

Testing properties *Ispitivana svojstva*	**10 % LW addition** *Dodatak 10 % UD-a*	**20 % LW addition** *Dodatak 20 % UD-a*
Thickness, mm / *debljina, mm*	15.93	16.15
Density, g/cm^3 / *gustoća, g/cm^3*	0.720	0.714
Moisture content, % / *sadržaj vode, %*	6.72	6.61
Swelling in thickness q-2, % / *bubrenje u debljinu q-2, %*	29.68	33.84
Bending strength, N/mm^2 / *savojna čvrstoća, N/mm^2*	12.220	11.767
Tensile strength, N/mm^2 / *čvrstoća raslojavanja, N/mm^2*	0.483	0.422
Formaldehyde emission, mg HCHO/100 g *emisija formaldehida, mg HCHO/100 g*	4.22	3.85

than the standardized (according to HRN EN 312-2:2000 and HRN EN 312-3:2000), and swelling in thickness is extremely high in both cases.

3.6 Influence of UF resin replacement with LWF resin on particleboard properties
3.6. Utjecaj zamjene KF smole UDF smolom na svojstva ploča iverica

Based on previous tests, the results showed that the direct UF replacement with LW (in quantity of 10 or 20 %) caused considerably weaker mechanical properties of obtained particleboards, while the formaldehyde emission was significantly lower.

The following researches were based on the design of liquefied wood-formaldehyde system. Liquefied wood-formaldehyde (LWF) resin was prepared as PF resin novolak type, because of polyphenol properties of lignin in liquefied wood, explained in the above mentioned method of preparing LWF resin.

Based on the above, the originally conceived polycondensation was achieved with 100:75 ratio of liquefied wood/formaldehyde. This means that 100 g of LW was placed in the reactor and 75 g of 36 % formaldehyde (formaline) was added. Polycondensation reaction of this mixture was carried out at a temperature of 90 °C for 120 min, measured from the moment when the mentioned temperature was reached. To prevent rapid resin polymerisation, after specific polycondensation degree, the entire mixture was alkalized with 1N NaOH until the mixture reached pH-value of 7-8, which conforms to pH-value of UF resin used in modification with LWF resin.

Pressing regime with pre pressing was selected, where pressure was currently increased (regime 2). Total pressing time was 300 s, without press discharging time, and it was identical for all particleboards. The obtained results are shown in Tab. 8, with listed results of particleboard tests obtained by conventional method.

It can be seen from the above results for conventional particleboards and particleboards made through UF replacement with 15 % LWF resin that both have exceptionally good physical and mechanical properties, as compared with prescribed standards (HRN EN 312-2:2000 and HRN EN 312-3:2000) for particleboards. Unlike conventional particleboards, free formaldehyde emission recorded in the test particleboards is extremely high, which can be explained by an excessive amount of added formaldehyde in LW. It is noticeable that the tensile strength is also increased as a direct result of added formaldehyde, because formaldehyde causes better adhesion networking in particleboards.

After all these researches, the hypothesis was set that LWF resin should be prepared on the basis of lignin percentage content in investigated wood species (in this example, it is black poplar). The lignin content in black poplar is 21.25 % (Sertić, 2000). Dry matter of liquefied black poplar is 57.21 %, which means that the lignin content in dry matter of liquefied wood is 12.16 %. As mentioned before, the formaldehyde/phenol ratio

Table 8 Arithmetic means of testing results for influence of UF resin replacement with LWF resin
Tablica 8. Aritmetičke sredine rezultata ispitivanja utjecaja zamjene KF smole UDF smolom

Testing properties *Ispitivana svojstva*	**Without LWF addition** *Bez dodatka UDF-a*	**15 % LWF addition** *Dodatak 15 % UDF-a*
Thickness, mm / *debljina, mm*	15.79	15.78
Density, g/cm^3 / *gustoća, g/cm^3*	0.762	0.704
Moisture content, % / *sadržaj vode, %*	5.64	6.41
Swelling in thickness q-2, % / *bubrenje u debljinu q-2, %*	10.73	15.17
Bending strength, N/mm^2 / *savojna čvrstoća, N/mm^2*	21.395	13.580
Tensile strength, N/mm^2 / *čvrstoća raslojavanja, N/mm^2*	0.772	0.896
Formaldehyde emission, mg HCHO/100 g *emisija formaldehida, mg HCHO/100 g*	5.63	30.34

does not exceed 0.75/1. Accordingly, the amount of added formaldehyde is 75 % of dry matter of LW (12.16 %), which corresponds to the 9.12 %. LWF resin prepared in this way was applied in further researches.

4 CONCLUSIONS
4. ZAKLJUČAK

The aim of this research was to design optimal experimental parameters (pressing pressure, pre pressing open time, and modification only in particleboard middle layer) and recipe of modified UF resin with LW (NaOH alkalization with different concentrations, addition of paraffin emulsion, and modification with new synthesized LWF) to obtain standardized particleboard properties (swelling in thickness, bending and tensile strength, formaldehyde emission).

According to natural wood component functional groups, obtained during joining glycol and organic acid, which was activated through liquefaction reaction, liquefaction products were obtained and they were a source useful for further synthesis into various polymers like adhesives on UF resin base for wood based panel production.

The conducted researches of new formaldehyde resin systems indicated that LW designed with formaldehyde synthesis (LWF resin) form favorable system for UF resin modification, cause effective polymerization reaction, and create more stable compounds. Due to polyphenol properties of lignin in LW, LWF resin was synthesized analogously to the production of PF resin novolak type, and prepared based on the percentage of lignin content in investigated wood species (black poplar), which was applied in further researches.

This paper showed the research validity for LW application in "wood with wood" adhesive systems, and implied unforeseen opportunities for scientific and developing researches focused on specialization of adhesion-cohesion potential of resins obtained from LW. Consequently, this study opened new challenges in research area of natural and ecologically perfect materials with unlimited raw material potential.

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