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Synthesis of Phenolic Resin Reinforced with TiO_2 Nanoparticles and its Effect on Combustion Performance of Laminated Veneer Lumber (LVL)

Sinteza fenolne smole ojačane nanočesticama TiO_2 i njezin utjecaj na gorivost lamelirane drvne građe (LVL)

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ABSTRACT • *In this study, phenol-formaldehyde (PF) resin has been modified with titanium dioxide nanoparticles (nano-TiO_2) at a varying ratio from 0.05 wt.% to 1.5 wt.% to enhance the thermal properties and combustion performance of the resins. The effect of the nano-TiO_2 modification on the properties (chemical or thermal) of the resins was determined by Fourier to transform infrared (FT-IR) and thermal analysis (TGA) techniques. In addition, the combustion performance of laminated veneer lumber (LVL) samples bonded with the PF resin modified with nano-TiO_2 was tested. The result of the FT-IR analysis indicated that the modified PF resins had match peaks to the reference PF resin. These similarities of the peaks supported that the modified PF resins were successfully synthesise with phenol, formaldehyde, and nano-TiO_2. The PF resins modified by nano-TiO_2 demonstrated better thermal stability than the reference resin. The nano-TiO_2 modified PF resin exhibited a favourable influence on the combustion characteristics of LVL. In consequence, PF resin modified with nano-TiO_2 could be used as a combustion retardant adhesive in the wood industry.*

KEYWORDS: *adhesive; combustion; FT-IR; nano-chemicals; TiO_2 nanoparticles*

SAŽETAK • *U ovom je istraživanju fenol-formaldehidna smola (PF) modificirana nanočesticama titanijeva dioksida (nano-TiO_2) u različitim omjerima, od 0,05 tež.% do 1,5 tež.% kako bi se poboljšala njezina toplinska svojstva i svojstva gorivosti. Utjecaj modifikacije nanočesticama TiO_2 na svojstva smola (kemijska i toplinska) određen je Fourierovom transformiranom infracrvenom spektroskopijom (FT-IR) i termogravimetrijskom analizom (TGA). Osim toga, ispitana je gorivost uzoraka lamelirane drvne građe (LVL) lijepljene PF smolom modificiranom nano-*

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česticama TiO_2. Rezultati FT-IR analize pokazali su da modificirane PF smole imaju jednake vrhove kao referentna PF smola. Te sličnosti vrhova potvrđuju da su modificirane PF smole uspješno sintetizirane s fenolom, formaldehidom i nanočesticama TiO_2. PF smole modificirane nanočesticama TiO_2 pokazale su bolju toplinsku stabilnost od referentne smole i povoljno su utjecale na gorivost LVL-a. Stoga zaključujemo da bi se PF smola modificirana nanočesticama TiO_2 mogla upotrebljavati kao ljepilo za usporavanje gorenja u drvnoj industriji.

KLJUČNE RIJEČI: *ljepilo; gorenje; FT-IR; nanokemikalije; nanočestice TiO_2*

1 INTRODUCTION
1. UVOD

Adhesive plays a fundamental role in the strength and durability of wooden structures. Recently, adhesives reinforced by different types of chemicals have become a very significant area of research since they can be provided to improve dimensional stability and fire retardancy of wood constructions. In that case, phenolic resins are generally used as wood adhesives for outdoor applications. They are classified into two main types: novolac and resol. Novolac resins are synthesise by reacting to a molar excess of phenol and formaldehyde under acidic conditions. Resol resins are prepared by an alkaline reaction of phenol and formaldehyde. PF resol resin is generally preferred for the production of wood and wood-based composites (laminated veneer lumber (LVL), laminated strand lumber (LSL), oriented strand board (OSB), plywood, etc.), due to its faultless durability, strong bonding quality, water resistance, and mechanical strength. However, the resin has two main disadvantages. First, it is more expensive than other amino resins such as melamine-formaldehyde (MF) and urea-formaldehyde (UF) as the price and availability depend on petroleum. Secondly, the application of PF resin at high temperatures has poor thermal stability (Turunen *et al.,* 2003; Pizzi, 1993; Kokten *et al.,* 2020; Hassan *et al.,* 2009; Farhaninejad *et al.*, 2021; Park *et al.*, 2002; Cheng *et al.,* 2012; Lima García *et al.,* 2018). Several studies around the world have shown that there are several methods to improve the combustion and thermal properties of the composites, such as reinforcing adhesive with micro and nano chemicals (Prasad *et al.,* 2018; Hanumantharaya *et al.,* 2021; Ozbay *et al.,* 2021; Guerra *et al.,* 2019). Kumar and co-workers studied the influence of nano-TiO_2 in enhancing the mechanical and thermal properties of the flax fibre reinforced epoxy composites. They reported that the nanofillers have specific characteristics that can improve the mechanical and thermal properties of the composite system (Kumar *et al*., 2016).

Nano-chemicals such as nano-SiO_2, nano-TiO_2, nano-AlO_3, and nano-ZnO have gained increasing interest due to their comprehensive industrial applications. In particular, these chemicals are widely used in different types of polymers synthesis for improving the desired properties (Mu et *al.,* 2011; Yuen *et al.,* 2009; Kavitha *et al.,* 2013; Zhang *et al.,* 2018; Prabhu *et al.,* 2021). There are many reports on adhesive modification with nano-chemicals including nano-SiO_2, nano-$CaCO_3$, nano-Al_2O_3, nano-TiO_2, and others to enhance the mechanical, physical, and chemical properties of adhesives in the literature (Zhai et *al.,* 2008; Zhang *et al.,* 2013; Ghosh *et al.,* 2016; Li *et al.,* 2016; Raghavendra *et al*., 2021). However, there is less information about the effect of nano-chemicals on the thermal properties of adhesives (Pang *et al.,* 2018; Ataberk *et al.,* 2020; Gultekin *et al.,* 2021).

The purpose of this experimental study was to examine the effect of the addition of nano-TiO_2 on some properties of PF resins such as chemical, physical and thermal. The combustion behaviour of LVL bonded with modified PF resins was also identified by considering ASTM-E 160-50 Standard.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

The chemicals applied in resin synthesis are analytical grades of NaOH (pellets) and nano-TiO_2, all purchased from Sigma Aldrich. The diameter of the nano-TiO_2 particle size was 50 nm. Phenol (liquid) and paraformaldehyde were supplied by GENTAŞ chemical industries (Turkey).

2.2 Preparation of test samples
2.2. Priprema ispitnih uzoraka

Laminated veneer lumbers (LVL) were produced from beech wood (*Fagus Orientalis* Lipsky) with a density of 0.58 g/cm^3. Wood planks were purchased from a local supplier. Initially, LVL samples with the dimension of 25 mm x 25 mm x 500 mm were cut from planks and acclimatise at a temperature of (20 ± 2) °C and (65 ± 5) % relative humidity until they reached an equilibrium in moisture content. Then the resin was applied on one surface (200 g/m^2) of the lamella using a hand brush. The pressure, temperature and duration were 0.2 N/mm^2, 130 ºC, and 15 min, respectively. LVL samples were conditioned for 10 days in the climate room at (20 ± 2) °C and (65 ± 5) % relative humidity. Combustion test samples (Figure 1) dimensions of 13 mm x 13 mm x 76 mm were cut from the laminated lumbers according to ASTM E 160.

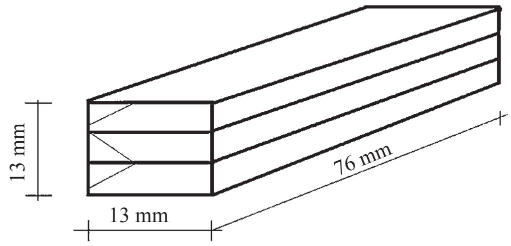

Figure 1 Combustion test samples
Slika 1. Uzorci za ispitivanje gorivosti

2.3 PF resin synthesis procedure
2.3. Postupak sinteze PF smole

The PF resin was prepared in a glass-made reactor endowed with a mechanical stirrer, cooling condenser and a water bath. Control PF (unmodified) was synthesise in the reactor according to the following procedure: the reactor was charged with phenol (90 %), paraformaldehyde (46 %), and pure water. After heating the mixture to 40 °C, the first part of the NaOH solution (50 wt%) was added slowly. The temperature was slowly increased to 60 °C. The temperature of the components was increased to 90 °C and maintained at this temperature for 60 min. After that, the second proportion of NaOH solution (50 wt%) was put into the reactor to regulate the pH value of about 11 at 60 °C. When the reaction was completed, the temperature of the PF resin was cooled to near room temperature. Similar procedures as described above were carried out for the synthesis of the PF resin as the control PF resin and other nano-PF resins with varying nano-TiO_2 ratios (0.05 wt.%, 0.10 wt.%, and wt.% 0. 15). Before the synthesis process, various amounts of nano-TiO_2 were mixed with phenol, paraformaldehyde, and pure water using a mechanical stirrer at about 600 rpm until a homogeneous appearance was achieved at room temperature.

2.4 Resin characterisation methods
2.4. Metode karakterizacije smole

The effect of nano-TiO_2 addition on the physical properties such as pH value, gel time, dynamic viscosity, and the solid content of the resin was examined. The pH value was measured using a previously calibrated digital pH meter (TES-1380 pH meter). The viscosity was measured by Brookfield digital viscometer (model: Dv-I Prime), number spindle 1 at 2.09 rad/s (20 rpm) at 25 °C. This test method is described in ASTM D1084-08 standard. The solid content of resins was calculated according to ASTM D3529M-97. The liquid PF resin characterisation was subjected to Infrared spectrometry (FT-IR, model- Alpha) by direct transmittance using KBr pellet technique. Infrared spectra were scanned in a range wavenumber between 4000-400 cm^{-1}. The thermal stability of the liquid PF resins was analysed by thermo-gravimetric technique on a TGA (HITACHI STA 7300). Appx. 10 mg of the sample was used with a heating rate of 10 °C /min under nitrogen atmospheres flow rate of 30 ml/min. The curves were recorded by heating from 20 °C to 700 °C. Three replicates were used for each resin.

2.5 Combustion test
2.5. Test gorivosti

A combustion test was performed in a combustion test stand based on ASTM E 160-50 standards. In accordance with this standard, laminated samples were conditioned until they reached a moisture content of 7 % before the combustion test. In the combustion test, 24 pcs test samples were aligned as a rectangular prism and burned. 3 different tests were made for each combustion test and 72 pcs test samples were used for each of them (Figure 2).

Combustion tests were performed in three steps: combustion from the flame, self-combustion, and com-

Figure 2 Test samples and combustion test
Slika 2. Ispitni uzorci i test gorivosti

bustion as an ember. Each sample batch was weighed before the test was put on a wire stand. The samples on the stand were placed vertically to the below and above stands. The fire distance from the lower maker type outlet was set as (25 ± 1.3) cm when the device was empty, and the gas pressure was set as 0.5 kg/cm^2 in the manometer. When the gas was burned, the temperature in the thermocouple funnel was tried to be fixed at (200 ± 8) °C. The flame source was centred at the bottom of the sample pile, and then the burning of the flame source was maintained for 3 minutes. The temperature change of combustion was also measured with a thermometer (ASTM E 160-50, 1975).

2.6 Evaluation of data
2.6. Evaluacija podataka

Multiple variance analysis was utilised to identify both the combustion properties and the effects of rate TiO_2 on combustion with flame sourced (FSc), flameless: self-burning (FLs) and combustion period within the context of fire test. Furthermore, the Duncan test was applied between groups at the end of the analysis in case the differences were recognised to test the homogeneity of the groups.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Resin properties
3.1. Svojstva smole

The basic physical properties of modified resins and control PF resin are given in Table 1. The solid content ranges from 43.14 % to 44.51 %. The solid content of the PF resin-modified with nano-TiO_2 varied depending on the additive ratio of nano-TiO_2. The pH value of PF resins ranged from 11.50 to 10.90. The viscosity of PF resins ranged from 294 to 334 cPs. The viscosity of PF resins modified with nano-TiO_2 was more viscous than that of the control PF resin, so it can be said that the addition of nano-TiO_2 up to 0.15 % did not reveal any significant trend in the fundamental physical properties of the PF resin.

PF resin modified with nano-TiO_2 was characterised by FT-IR spectral analysis to determine the effect of adding nano-TiO_2 on the chemical properties of the PF resin. The FT-IR spectra of the resins reveal that the functional groups observed were similar to each other, indicating structural similarity between PF and modified PF resins. (Fig. 3). Mainly, the bonds that appeared in the spectrum of PF were also observed in the spectra of modified PF resins. IR spectrum of all samples had a strong wideband between 3400 and 3200 cm^{-1}, assigned to OH stretching vibrations (1). The absorption peak between 2950 cm^{-1} and 2800 cm^{-1} was assigned to C–H stretching frequencies from methyl and methylene groups (2). The band at 1750-1700 cm^{-1} showed the aromatic ring C=C stretching vibrations (3). The peaks at about 1600 and 1480 cm^{-1} corresponded to aromatic ring stretching bands (4), and the peak at 1250 - 1200 cm^{-1} was assigned to the C-O stretching in the aromatic ring for all samples (5). The peak was observed in the range of 800-750 cm^{-1} presenting C–H out-of-plane bending vibrations of the aromatics (6). (Cui *et al.,* 2017; Poljansek and Krajnc, 2005; Ibrahim *et al.,* 2011; Horikawa *et al.,* 2003; Wang *et al.,* 2009; Wang *et al.,* 2011). It was confirmed that the synthesis of nano-TiO_2 PF resin followed a reaction pathway similar to that of the control PF resin.

Thermal degradation and stability of the PF and PF resin modified with nano-TiO_2 were studied by TGA analysis. Figure 4 shows the TGA graphs of the PF resin and modified PF resins. The control PF resin was stable up to 250 °C. The maximum rate loss in control PF resins occurs at the temperature range of 300 - 450 °C. The PF resins modified with nano-TiO_2 were more thermally stable than the control PF resin in the range of 200 - 600 °C. The thermal stability of PF resin modified with nano-TiO_2 showed a rising trend with adding nano-TiO_2. TGA analysis results were consistent with previous studies on the thermal stability of adhesives modified with nano-chemicals (Yuan *et al.,* 2008; Lin *et al.,* 2009; Ekrem *et al.,* 2018; Sahoo *et al.,* 2017; Zheng *et al.,* 2021).

3.2 Combustion properties
3.2. Gorivost

The results of multiple variance analysis regarding the effect of combustion type and content of nano-TiO_2 on combustion temperature (°C) are given in Table 2.

The effects of combustion type and amount of TiO_2 on combustion temperature were statistically sig-

Table 1 Basic physical properties of PF resins modified with nano-TiO_2
Tablica 1. Osnovna fizička svojstva PF smola modificiranih nanočesticama TiO_2

Resin *Smola*	Solid content, % *Sadržaj suhe tvari, %*	pH at 20 °C *pH pri 20 °C*	Viscosity, cPs at 25 °C *Viskoznost,* cPs *pri 25 °C*
Control PF	43.14	11.90	294
0.05 % nano-TiO_2- PF	43.75	11.78	319
0.10 % nano-TiO_2- PF	44.16	11.71	325
0.15 % nano-TiO_2- PF	44.51	11.50	334

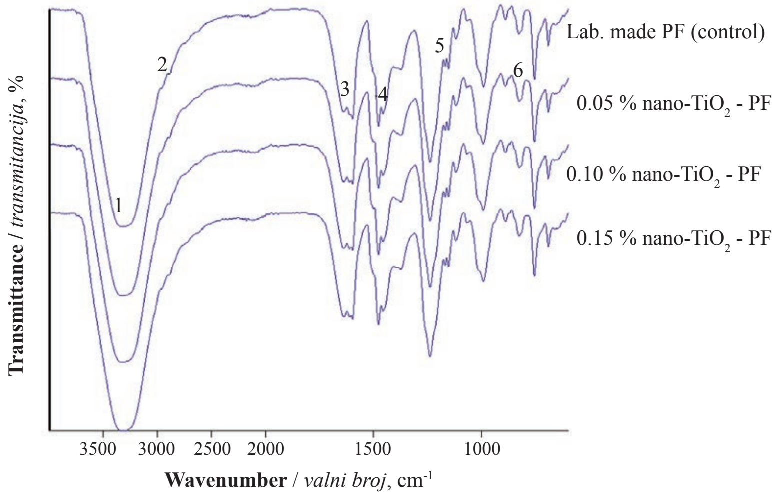

Figure 3 FT-IR spectra of resins (control PF and modified PF)
Slika 3. FT-IR spektar kontrolne i modificirane PF smole

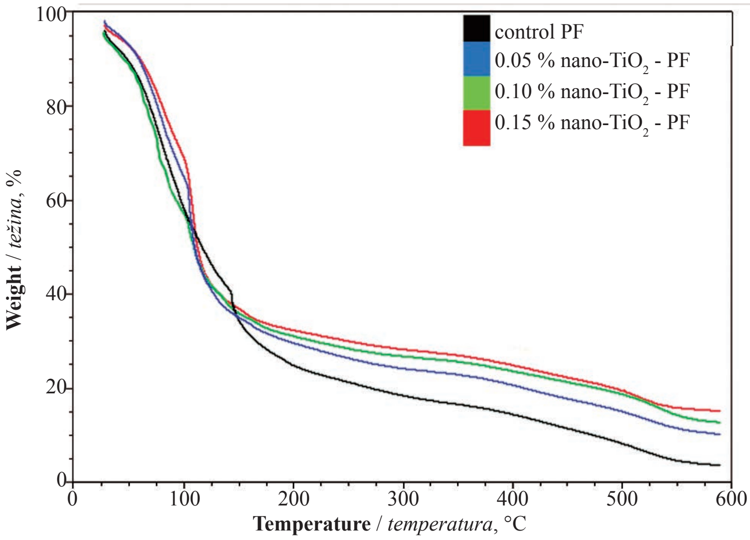

Figure 4 TGA curves of PF resins
Slika 4. TGA krivulje PF smola

nificant (α=0.05). Duncan test was applied to evaluate the differences between the groups. The results of the Duncan test are presented in Table 3.

It may be seen in Table 3 that the highest temperature depending on the combustion type in flame sourced combustion was 536 °C, and the lowest in Cb was 260.5 °C; on the other hand, as for the amount of nano-TiO_2, the highest value was measured in 0.01 nano-TiO_2 – 389.1 °C, the lowest in 0.05 nano-TiO_2 - 389.1 °C. Lin and co-workers reported that nano-PF resins were thermally stable up to a temperature of about 300 °C. This thermal stabilisation may be explained by new structures, which can be formed during resin synthesis (Lin *et al.*, 2006). With respect to combustion type and content of nano-TiO_2, the highest temperature value was measured in flameless+0.15 - 560.3 °C, and the lowest in charcoal burning+0.15 - 245 °C. According to these results, when the % amount of nano-TiO_2 was increased, the combustion temperature decreased.

Table 2 Multiple variance analysis results
Tablica 2. Rezultati analize višestruke varijance

Source *Izvor*	**Degrees of freedom** *Stupnjevi slobode*	**Sum of squares** *Zbroj kvadrata*	**Mean square** *Srednji kvadrat*	**F value** *F-vrijednost*	**Prob.**
Factor A	460898.604	460898.604	230449.302	749.0285	0.0000
Factor B	12328.539	12328.539	4109.513	13.3571	0.0000
AB	24913.756	24913.756	4152.293	13.4962	0.0000
Error	7383.943	7383.943	307.664		
Total	505524.842	505524.842			

Factor A – combustion type, Factor B – nano-TiO2+control, coefficient of variation: 4.50 % / *faktor A – vrsta izgaranja; faktor B – nano-TiO_2 + kontrola; koeficijent varijance: 4,50 %*

Table 3 Duncan test results
Tablica 3. Rezultati Duncanova testa

Combustion type* / *Vrsta izgaranja**	***X*, °C**	**HG**
Flame sourced / *s izvorom plamena* (FSc)	536.0	A
Flameless / *bez plamena* (FLs)	372.2	B
Charcoal burning / *pougljenje* (Cb)	260.5	C
Nano chemical ** / *Nanokemikalije***		
Control / *kontrolni uzorci* (C)	419.3	A
0.10% TiO_2	389.1	B
0.15% TiO_2	380.2	BC
0.05% TiO_2	369.7	C
Type of process *** / *Vrsta procesa ****		
Flameless + 0.15 % TiO_2 *bez plamena* + 0,15 % TiO_2	560.3	A
Flameless + 0.10 % TiO_2 *bez plamena* 0,10 % TiO_2	538.3	AB
Flameless + C / *bez plamena + C*	527.7	B
Flameless + 0.05% TiO_2 *bez plamena* + 0,05 % TiO_2	517.7	B
Flame sourced + C / *s izvorom plamena + C*	449.0	C
Flame sourced + 0.05 % TiO_2 *s izvorom plamena* + 0,05 % TiO_2	371.3	D
Flame sourced + 0.10 % TiO_2 *s izvorom plamena* + 0,10 % TiO_2	364.8	D
Flame sourced + 0.15 % TiO_2 *s izvorom plamena* + 0,15 % TiO_2	303.7	E
Charcoal burning + C / *pougljenje + C*	281.3	EF
Charcoal burning + 0.10 % TiO_2 *pougljenje* + 0,10 % TiO_2	264.0	FG
Charcoal burning + 0.05 % TiO_2 *pougljenje* + 0,05 % TiO_2	251.7	FG
Charcoal burning + 0.15 % TiO_2 *pougljenje* + 0,15 % TiO_2	245.0	G

*LSD value = 14.54, ** LSD value = 16.79, *** LSD value = 29.07, X – Average, HG – Homogeneous group
LSD vrijednost = 14,54, ** LSD vrijednost = 16,79, * LSD vrijednost = 29,07, X – srednja vrijednost, HG – homogene grupe*

Multivariance analysis (Table 4) was applied to determine the effect of both the amount of nano-TiO_2 and combustion type on the length of burning time or combustion duration. Considering the significance of the Duncan test, each test group was compared with each other and with themselves (in Table 5).

The multivariance analysis was carried out to test the results obtained from the combustion tests. In accordance with the multivariance analysis, the effects of nano-TiO_2 and combustion type on combustion duration were statistically significant. The interactions between nano-TiO_2 and combustion type were statistically important ($P \leq 0.05$). The means of variation sources that were found to be significant were compared using Duncan's test and the average values are summarised in Table 5.

According to total combustion duration, in terms of the effect of combustion type on the combustion duration, the highest value was 40.58 min in charcoal burning, the lowest was 3.87 min. in Flameless. As for the amount of nano-TiO_2 (%), the highest value was 61.61 in 0.01 TiO_2, the lowest was 3.76 min in 0.05 TiO_2. The interaction of combustion type and the amount of nano-TiO_2, total combustion duration +0.05 TiO_2 showed the longest combustion duration as 99.10 min, the shortest duration was obtained in flameless +0.15 nano-TiO_2 - 3.867 min. The duration of combustion was reduced by the amount of nano-TiO_2. The nano-chemical was quite effective in flame sourced combustion, extinguishing the flame and decreasing the risk of fire enhancement. This situation positively affected especially the charcoal duration at the end of the combustion. Similar to other reported results, nano-chemicals improved the thermal stability of phenolic resin (Zheng *et al.,* 2003; Ma *et al.,* 2005; Wang *et al.,* 2011; Özbay *et al.,* 2021).

4 CONCLUSIONS
4. ZAKLJUČAK

The purpose of this study was to evaluate the influence of adding nano-TiO_2 on the chemical, physical and thermal characteristics of PF resins. Additionally, combustion properties of laminated veneer lumber (LVL) bonded with the PF resins modified with different content of nano-TiO_2 were determined. The following can be concluded:

The addition of nano-TiO_2 up to 0.15 % did not reveal any significant trend in the fundamental physical properties such as solid content, pH value and viscosity of the PF resin.

The synthesis of nano-TiO_2 PF resin followed a reaction pathway similar to that of the control PF resin as confirmed by FT-IR spectroscopy analysis.

TGA analysis indicated that the increase of nano-TiO_2 content in the resin formula enhanced the thermal stability of the PF resin.

Table 4 Results of multivariance analysis
Tablica 4. Rezultati analize višestruke varijance

Source *Izvor*	**Degrees of freedom** *Stupnjevi slobode*	**Sum of squares** *Zbroj kvadrata*	**Mean square** *Srednji kvadrat*	**F value** *F-vrijednost*	**Prob.**
Factor A	2	15476.264	7738.132	521.0473	0.0000
Factor B	3	10437.310	3479.103	234.2655	0.0000
AB	6	5347.205	891.201	60.0090	0.0000
Error	24	356.427	14.851		
Total	35	31617.206			

Factor A – combustion type, Factor B – nano-TiO_2 + control, coefficient of variation: 4.40 % / *faktor A – vrsta izgaranja; faktor B – nano-TiO_2 + kontrola; koeficijent varijance: 4,40 %*

Table 5 Effects of nano-TiO_2 content (%) and combustion type on length of burning time, or combustion duration (min)
Tablica 5. Utjecaj sadržaja nano-TiO_2 (%) i vrste izgaranja na duljinu gorenja odnosno na trajanje izgaranja (min)

Combustion type* / ***Vrsta izgaranja****	***X***	**HG**
Flameless / *bez plamena*	3.875	C
Charcoal burning / *pougljenje*	40.58	B
Total combustion duration *ukupno trajanje izgaranja*	52.63	A
Nano-chemical /** ***Nanokemikalije*****		
Control / *kontrolni uzorci* (C)	21.44	C
0.10% TiO_2	61.62	A
0.15% TiO_2	26.02	B
0.05% TiO_2	20.36	C
Type of process* /** ***Vrsta procesa******		
Total combustion duration + 0.15 TiO_2 *ukupno vrijeme izgaranja* + 0,15 TiO_2	99.10	A
Charcoal burning + 0.05 TiO_2 / *pougljenje* + 0,05 TiO_2	82.00	B
Total combustion duration + 0.10 TiO_2 *ukupno vrijeme izgaranja* + 0,10 TiO_2	44.20	C
Total combustion duration / *ukupno vrijeme izgaranja*	35.00	D
Total combustion duration + 0.15 TiO_2 *ukupno vrijeme izgaranja* + 0,15 TiO_2	32.20	D
Charcoal burning + 0.10 TiO_2 *pougljenje* + 0,10 TiO_2	30.00	DE
Charcoal burning / *pougljenje*	25.33	E
Charcoal burning + 0.15 TiO_2 *pougljenje* + 0,15 TiO_2	25.00	E
Flameless – control / *bez plamena – kontrola*	4.000	F
Flameless + 0.15 TiO_2 *bez plamena* + 0,15 TiO_2	3.867	F
Flameless + 0.10 TiO_2 *bez plamena* + 0,10 TiO_2	3.865	F
Flameless + 0.05 TiO_2 *bez plamena* + 0,05 TiO_2	3.767	F

*LSD value = 3.069, ** LSD value = 3.688, *** LSD value= 6.388, X – Average, HG – Homogeneous group
LSD vrijednost = 3,069, ** LSD vrijednost = 3,688, * LSD vrijednost = 6,388, X – srednja vrijednost, HG – homogene grupe*

LVL samples bonded with nano-TiO_2 modified PF resin exhibited better fire resistance as compared to LVL bonded with PF resin (control). The PF resin modified with nano-TiO_2 can be used as a combustion resistance adhesive in the wood industry.

Nano-TiO_2, due to its availability and remarkable thermal properties, can be used as reinforcement in phenolic resin production.

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