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Determination of Fire Resistance, Mechanical Property and Physical Stability of Boron Phosphate Containing Wood Polymer Composites

Određivanje vatrootpornosti, mehaničkih svojstava i fizičke stabilnosti drvno-plastičnih kompozita koji sadržavaju bor-fosfat

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ABSTRACT • *This study presents the improvement in flame retardancy of wood polymer composites (WPCs) by boron phosphate (BPO_4) additive. The WPCs were manufactured by phenol formaldehyde and wood flour of Oriental beech (Fagus orientalis L.) using compression molding. Polydiphenylmethane-4,4'-diisocyanate (PMDI) was also added to enhance the compatibility of hydrophilic wood flour and hydrophobic polymer resin. The strengthening of interfacial adhesion by PMDI incorporation resulted in better mechanical (flexural) and physical (water absorption, thickness swelling) properties. The BPO_4 flame-retardant additive in WPCs formulation was first reported and thermal behaviors of composites were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI) and UL-94 tests. The BPO_4 compound promoted the char formation of WPCs, and the LOI values of composites were increased from 28.7 to 35.6. The UL-94 tests also showed that the flame retardancy of composites were improved by changing the V-2 rating to V-0 with the addition of 5 wt.% BPO_4.*

KEYWORDS: *boron phosphate; wood polymer composite; flame-retardant; polydiphenylmethane- 4,4'-diisocyanate (PMDI) compatibilizer*

SAŽETAK • *Ovo istraživanje opisuje poboljšanje vatrootpornosti drvno-plastičnih kompozita (WPC) dodavanjem bor-fosfata (BPO_4). Drvno-plastični kompoziti proizvedeni su od fenol formaldehida i drvnog brašna bukovine (Fagus orientalis L.) kompresijskim lijevanjem. Usto, smjesi je dodan polidifenilmetan-4,4'-diizocijanat (PMDI) kako bi se poboljšala kompatibilnost hidrofilnoga drvnog brašna i hidrofobne polimerne smole. Jačanje međupovršinske adhezije dodavanjem PMDI-ja rezultiralo je boljim mehaničkim svojstvima (na savijanje) i boljim fizičkim svojstvima (upijanje vode, debljinsko bubrenje). Prvi je put u formulaciji WPC-a upotrijebljen BPO_4 kao usporivač gorenja, a toplinska su ponašanja kompozita ispitana termogravimetrijskom analizom (TGA), mjerenjem graničnog indeksa ki-*

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sika (LOI) i UL-94 testovima. Spoj BPO_4 pospješio je stvaranje pougljenjenih WPC-ova, a LOI vrijednosti kompozita povećane su s 28,7 na 35,6. Provedeni UL-94 testovi također su pokazali da je vatrootpornost kompozita poboljšana jer je nakon dodavanja 5 težinskih postotaka BPO_4 ocjena V-2 promijenjena u V-0.

KLJUČNE RIJEČI: *bor-fosfat; drvno-plastični kompozit; polidifenilmetan-4,4'-diizocijanat (PMDI) kompatibilizator*

1 INTRODUCTION
1. UVOD

Wood processing wastes have been considered as natural and renewable resources for fabrication of wood plastic composites (WPC). Woodworking wastes can be shifted to a new material for construction, furniture, garden products and also for automotive applications (Li, 2011; Schwarzkopf and Burnard, 2016; Clemons, 2008). WPCs have been classified as plywood, particleboard, oriented strand board (OSB), fiberboard (MDF, HDF), etc. These composites are commercial products obtained by mixing thermoplastic/thermoset polymer matrix wood flour. WPCs are designed to meet the needs of specific usage, and they are formulated for high mechanical, physical and thermal properties and long durability. Additives/fillers can be added into WPCs or different functionalities can be incorporated to improve their properties. Crosslinkers, coupling agents/compatibilizers, flame-retardants, dye pigments and fungicides are commonly used as admixtures.

Boron based additives can serve both as a wood preservative against fungi/insects and as a flame-retardant filler for fire resistance (Marney and Russell, 2008). Boric acid, borax, zinc borate and disodiumoctaborate tetrahydrate were mostly used due to the colorless, odorless, non-toxic and cheap additives (Mohareb *et al.,* 2011). Many researchers showed that, as a flame-retardant additive, boron compound has two effects on wood materials. First, it can form a glassy layer insulating the surface of wood and block the further diffusion of oxygen into the material. Second, it increases the char yield by acidic dehydration mechanism (Roth *et al.,* 2007; Yang, Y. *et al.,* 1999; Simsek *et al.,* 2010). Ammonium polyphosphate (APP) is another well-known flame-retardant additive and can be used alone or in synergy with boron compounds such as boric acid (BA), borax (BX), zinc borate, etc. When BA/BX mixture and APP were used together, the observed char acted first as an insulator to keep condensed phase at lower temperatures, and second as a barrier to prevent the volatile fuel from reaching the flame front (Kurt and Mengeloğlu, 2011). Similarly, with different contents of boron compounds, phosphate compounds were added to wood flour/polypropylene composites and results showed that 4/8 wt.% formulations of the flame-retardants have optimum physical, mechanical and fire resistance properties of composites (Ayrilmis *et al*., 2012). Synergistic effect of various boron compounds and APP has been revealed for improved flame retardancy of a polypropylene (PP) intumescent system. Cone calorimeter and TGA results demonstrated that the boron compounds showed their synergistic effect by reinforcing and increasing the barrier effect of the char (Doğan *et al*., 2010).

Based on the above studies, it can be concluded that the new flame-retardant to be designed should contain both boron and phosphate constituents. Hence, in this study boron phosphate (BPO_4) was synthesized by hydrothermal and microwave-assisted technique and then the effects of BPO_4 on physical, mechanical and thermal properties of WPCs were investigated. BPO_4 previously imparted flame retardancy to PET and Nylon fibers (Kilinc *et al*., 2015; Doğan *et al*., 2011), but boron phosphate was used for the first time as a flame-retardant in wood polymer composites made of phenol formaldehyde resin and Oriental beech (*Fagus orientalis* L.) flour. Many organic thermoplastic and thermoset polymers are of hydrophobic nature, and they are not compatible with hydrophilic wood. Hence, compatibilizers are used that can bond with the hydrophilic and hydrophobic parts at the interfaces. Organic based compatibilizers used in WPCs are generally maleic anhydride and isocyanate functional group compounds containing two or more functional groups. In the present study, polydiphenylmethane- 4,4'-diisocynate (PMDI) is used as compatibilizer in WPC composition. This study focuses on the effects of BPO_4 additive on flame retardancy, thermal stability, physical and mechanical properties of WPCs. It also provides scientific data for the utilization of BPO_4 in WPCs production. The secondary aim of this study is to investigate the effect of PMDI compatibilizer on the properties of WPCs together with BPO_4 flame-retardant.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

Phenol formaldehyde resin (ALFEN 74 resol, density 1.12 g/cm^3 at 20 °C, viscosity 350 cP at 20 °C) was purchased from GENTAŞ Chemical Co. The liquid phenol formaldehyde resin with 47 % solid content was used as polymer matrix and a gel time of 6 min at 130 °C. Oriental beech wood (*Fagus orientalis* L.)

flour was sieved (40 mesh) and dried in an oven, first at 80 °C for 24 hours and then dried at 35 °C until it reached a constant weight. The sieved and dried wood flour was kept in a desiccator at (23±2) °C and (50±5) % relative humidity for subsequent use. Boric acid (99.5 %, Merck), o-phosphoric acid (85 %, Merck) and poly-diphenylmethane- 4,4'-diisocynate (PMDI, Ravago Petrochemical Co.) were used as received.

2.2 BPO_4 synthesis
2.2. Sinteza bor-fosfata (BPO_4)

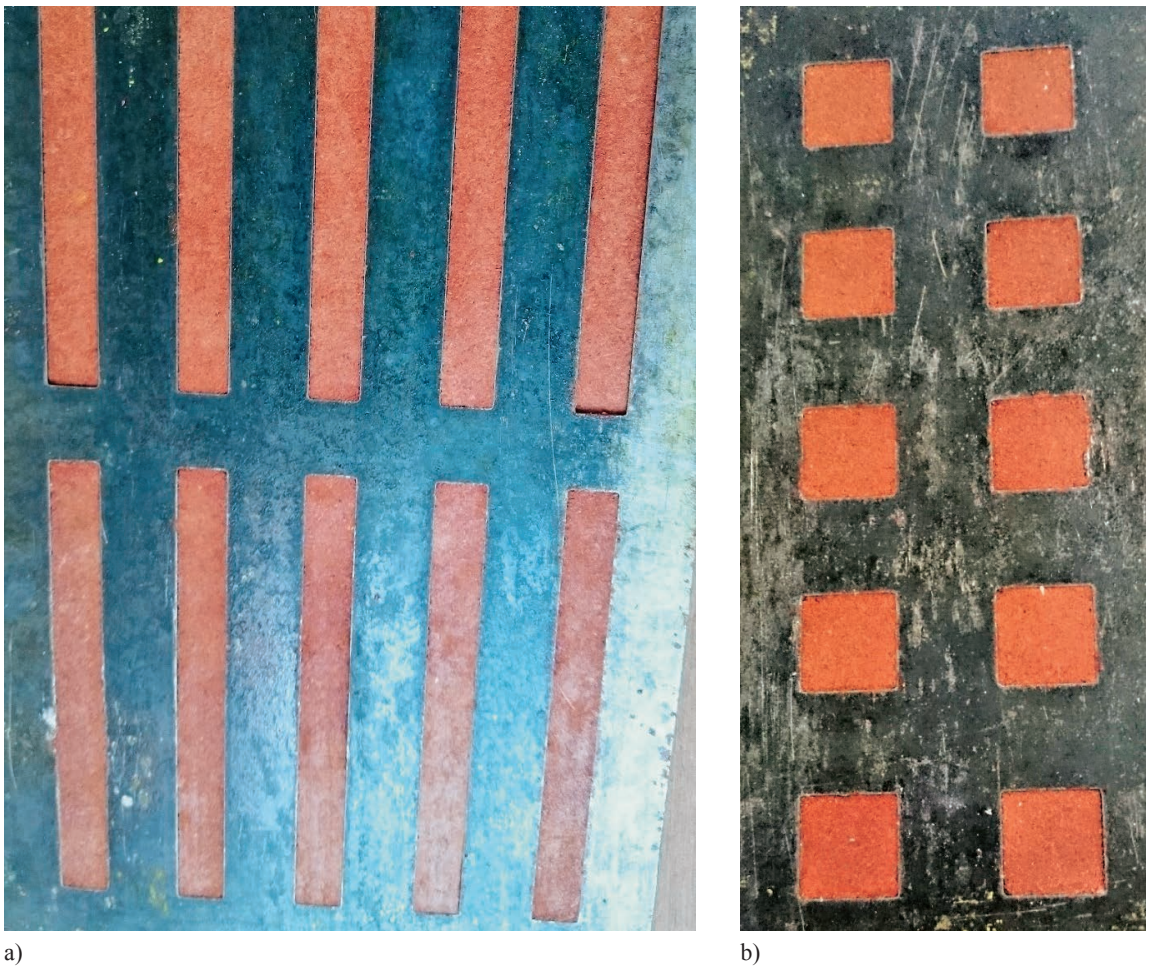
Boron phosphate (BPO_4) was synthesized by thermal and microwave-assisted methods (Hauf *et al.*, 1998). Equal molar of H_3BO_3 (0.03 mol) and H_3PO_4 were mixed in an ultrasonic bath for 30 minutes and then exposed to microwave irradiation at 800 watt for 10 minutes. The reaction mixture was then calcined at 600 °C for 5 hours. The reaction between boric acid and o-phophoric acid is given below as chemical equation.

$$H_3BO_3(s) + H_3PO_4(aq) \rightarrow BPO_4(s) + H_2O(g) \quad (1)$$

FT-IR spectroscopy and XRD analysis were performed for the characterization of the obtained product. The BPO_4 powder XRD patterns were recorded between $5°<2\theta<90°$, with 0.05° step and 1°/min rate on a Rigaku-Miniflex diffractometer. The measurements were made by using monochromatic CuKα (30 kV, 15 mA and λ=1.54051 Å) radiation at room temperature. The FTIR spectrum of BPO_4 was recorded using a Thermo Scientific Nicolet iS10 FTIR spectrometer to verify its chemical structure. The spectrum was obtained within the wavenumber range of 600-4000 cm^{-1}, using the ATR mode of operation.

2.3 Composite preparation
2.3. Priprema kompozita

WPCs were manufactured based on the recipe given in Table 1. Phenol-formaldehyde resin, beech flour, BPO_4 flame-retardant and PMDI compatibilizer were mixed homogeneously by mechanical stirrer. Compression molding was performed for curing the mixtures, and stainless-steel molds were filled with mixtures and then inserted into the hot press. The press temperature, pressure and time were 160 °C, 10 bar and 12 min, respectively. The mold was then removed from the hot press and cooled to ambient temperature. 10 specimens from each sample were prepared in-situ for physical, mechanical and thermal tests.



a) b)

Figure 1 Photos of experiment samples: a) for mechanical tests, b) for water absorption tests
Slika 1. Fotografije ispitnih uzoraka: a) za mehanička ispitivanja, b) za ispitivanja upijanja vode

Table 1 Composites components ratios (wt.%), codes and densities
Tablica 1. Omjeri komponenata u kompozitu (tež.%), oznake i gustoća

Sample codes *Oznake uzoraka*	**Resol, %**	**Wood flour, %** *Drvno brašno, %*	**PMDI, %**	**BPO_4, %**	**Density, g/cm³** *Gustoća,* g/cm³
PF (Control)	68.3	31.7	-	-	0.64
PFI	64.9	30.1	5	-	0.72
PFB	64.9	30.1	-	5	0.75
PFBI	61.5	28.5	5	5	0.71

Figure 1 shows the photos of the samples used in mechanical and water absorption tests. Figure 1a was used for mechanical tests, while Figure 1b was used for water absorption

2.4 Physical properties
2.4. Fizička svojstva

Densities of composites with standard deviations were determined by dry weight and volume, as shown in Table 1. To obtain the mean values of air-dry densities, five specimens of each group were prepared with dimensions 50 mm × 50 mm × 5 mm. The specimens were weighed with an accuracy of 0.0001 g on analytical balance and the volumes were measured by digital micrometer. Density values were calculated by the following equation.

Water absorptions of WPCs were examined, and ASTM D 1037 and standard procedure was followed for preparing the specimens and measurements. Samples with dimensions 50 mm × 50 mm × 5 mm were weighed on a 0.0001g precision analytical balance, and then the specimens were immersed in pure water for the duration of the experiment. The measurements were made periodically for 2, 24, 48, 72, 96, 120, 144, 168 hours, 2, 3, 4 weeks, 2, 3, 4, 5, 6 months. At the end of these periods, the surface water of the samples was wiped off with a cloth and then weighed again with the same precision. Ten replicates were tested for all test groups and the water uptakes were calculated by the equation below.

$$\%\ WA = (W_w - W_o) / (W_o) \times 100 \quad (g/cm^3) \qquad (2)$$

Where;
WA – water absorption (%)
W_o – dry weight (g)
W_w – wet weight given in the formula (g)

The thickness swelling tests were carried out according to EN 317 standard and samples conditioned at a relative humidity of (60±5) % and a temperature of 25 °C. Thicknesses of specimens prepared in 50×50×5 (mm) plate dimensions were measured with a micrometer sensitive to 0.01mm from the exact mid-point. The conditioned samples were entirely immersed for 2, 24, 48, 72, 96, 120, 144, 168 hours, 2, 3, 4 weeks, 2, 3, 4, 5, 6 months. Then, the excess water was removed with a clean dry cloth and their thickness was measured again from the first measured point. Ten replicates were tested for all test groups and the thickness swelling ratio was calculated according to Eq. 3.

$$TS\% = (T_w - T_c)/T_c \times 100 \qquad (3)$$

Where:
TS% – thickness swelling in percentage
T_w – thickness of the wet sample at certain time
T_c – initial thickness of the conditioned sample.

2.5 Mechanical properties
2.5. Mehanička svojstva

Since the components are used in different proportions in the production of wood polymer composites, three point bending tests were performed to examine the effect of the addition of PMDI compatibilizer and boron phosphate flame-retardant on the mechanical properties of the composites. 10 samples with dimenssions of 3.2 mm × 12.7 mm × 125 mm were prepared from each composition according to ASTM D790-92 standard and measured on Zwick Z250 with a crosshead speed of 2 mm/min. The modulus of elasticity (MOE) and modulus of rupture (MOR) of specimens were determined by three point bending test.

2.6 Thermal analysis
2.6. Toplinska analiza

Thermogravimetric analysis (TGA) has been carried out to determine the thermal stability, the decomposition temperature and degradation mechanism, which is the investigation of main degradation peaks and shoulders (Badji *et al*., 2016) of composites. Approximately 10 mg of the sample was heated in a thermogravimetric analyzer (Perkin Elmer TGA 4000 instrument) from room temperature to 750 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The temperature and corresponding mass loss (%) of the samples were monitored. The rate of weight loss as a function of time was derived from TG curve resulting in a derivative TG curve.

2.7 Fire resistance tests
2.7. Test vatrootpornosti

The flame retardancy of WPCs was determined by UL-94 vertical burning test and limiting oxygen index (LOI) tests according to ASTM D 3801 and ASTM D 2863 standards, respectively. The LOI test method is used to determine the minimum amount of oxygen needed to maintain a flammable condition under test conditions. According to the test, high-burning materials should have a low oxygen index, and low-burning materials should have a high oxygen index. 3 samples

with dimension of 3.2 mm × 12.7 mm × 125 mm were prepared for each composition and the samples were placed vertically into the glass chamber. The oxygen and nitrogen gas mixture were adjusted to flow into the chamber. The specimen was ignited at the top by flame like a candle. The minimum oxygen concentrations required to sustain combustion were measured as a percentage. UL-94 is used to determine the V-0, V-1 and V-2 flammability ratings of the specimens. The self-extinguishing time of the vertically positioned specimens were measured by this test. Three replications were performed for each group, and the specimen dimensions were the same as in LOI test (3.2 mm × 12.7 mm × 125 mm). The specimen was clamped at the top and the flame was applied to the bottom. The flame was brought into contact with the test specimen for 10 seconds and then removed. The combustion time, dripping of sample and burning state at fixing determines the class of the sample. In the UL-94 rating system, the material will be rated V0 if burning time ≤10 seconds and no dripping after removal of the burner. The V1 and V2 rating requires the burning time of each specimen ≤ 30 seconds. The V2 rating allows the dripping of burning specimen, but for V1 rating specimen must not drip.

2.8 Scanning electron microscope (SEM)
2.8. Pretražni elektronski mikroskop (SEM)

The effect of the addition of PMDI to the composite composition on the morphology of WPCs was determined by scanning electron microscopy (SEM). SEM images of the surfaces and cross-sections of the samples were obtained by a Quanta 400F Field Emission SEM (FEI Company, The Netherlands). Samples were gold-coated and viewed at an acceleration voltage of 20 kV with different magnifications.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 BPO_4 Synthesis
3.1. Sinteza bor-fosfata (BPO_4)

Hydrothermal and microwave synthesis methods were used together to obtain pure BPO_4 and it was characterized by FTIR spectroscopy and XRD analysis, respectively (Figure 2). The unit cell parameters a=4.3414(2), c=6.6427(4) Å are in good agreement with the literature (a = b = 4.342 Å and c = 6.642 Å) (Wang *et al.*, 2012). In literature, the XRD analysis of synthesized boron phosphate indicated the tetragonal structure and crystallographic parameters of a=4.3425Å

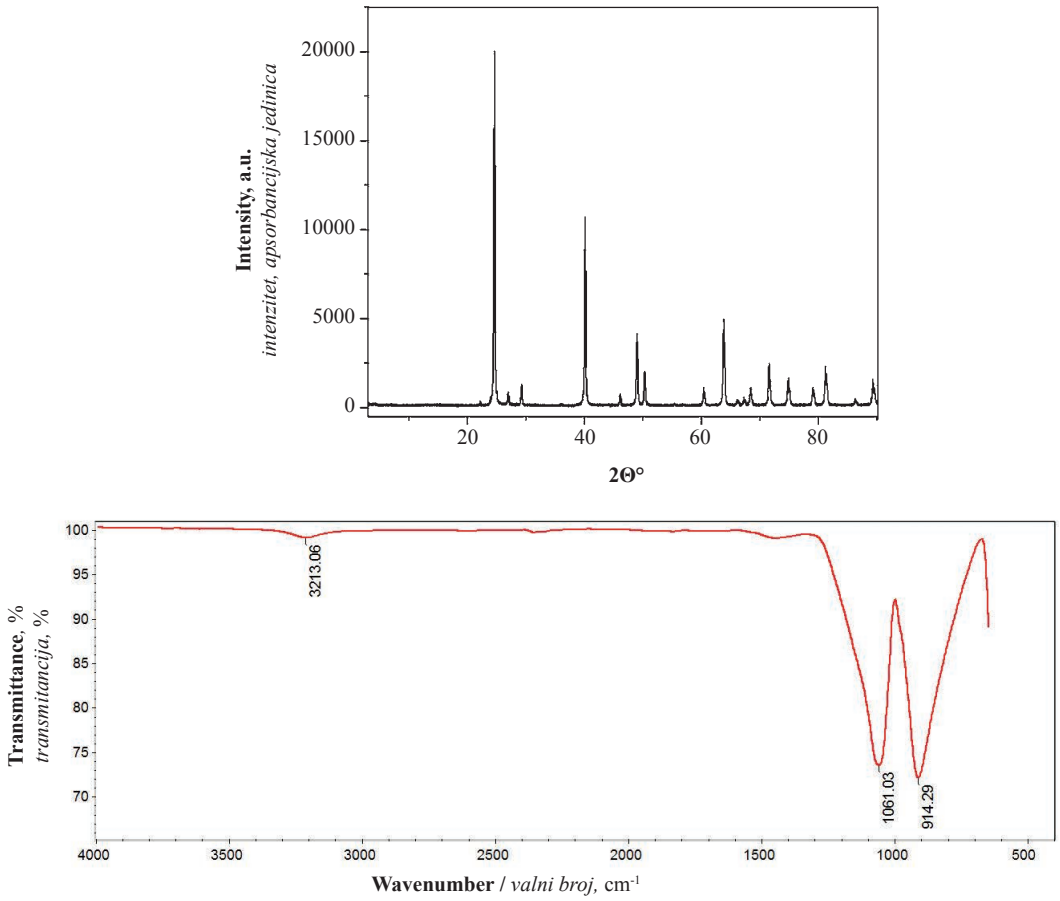


Figure 2 a) XRD pattern and b) FT-IR spectroscopy of BPO_4
Slika 2. a) Uzorak XRD, b) FT-IR spektroskopija spoja BPO_4

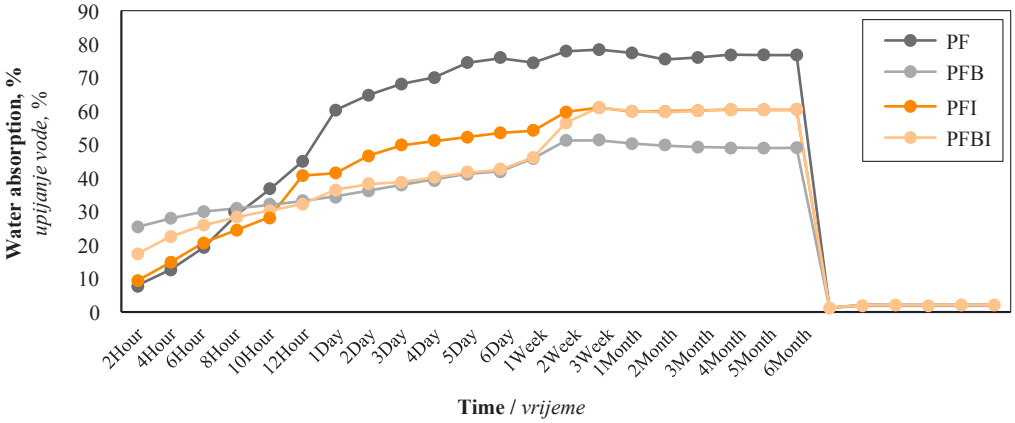


Figure 3 Water absorption (%) of WPCs in 6 months
Slika 3. Upijanje vode (%) WPC-a tijekom šest mjeseci

and *c*=6.6415Å (Mamlouk *et al.*, 2015). FTIR spectrum of BPO_4 also revealed the B-O stretching peak at 911 cm^{-1} and PO_4 asymmetric stretching peak at 1060 cm^{-1}. The peaks match with the previous studies in the literature, in which the broad band at 1100 cm^{-1} and the peak at 933 cm^{-1} was assigned to the asymmetric stretching vibrations of PO_4^{3-}, and B-O stretchings, respectively (Abd El-Ghaffar *et al*., 2018). Accordingly, it has been proved that BPO_4 was successfully synthesized.

3.2 Physical properties
3.2. Fizička svojstva

The densities of boards were found in the range of 0.64-0.75 g/cm^3 as shown in Table1. The PFB group (phenol-formaldehyde resin + wood flour + BPO_4) has the highest density within wood polymer composites. The introduction of BPO_4 flame-retardant additive has been found to increase density of composite. PMDI, which was introduced as a compatibilizer, showed the same effect. It was observed that the voids between the cells were filled with additive materials and the density was increased.

The rate of water uptake can vary depending on whether the materials forming the composites are water-attractive (hydrophilic) or water-repellent (hydrophobic). Figures 3 and 4 show the water absorption and thickness swelling tests results, respectively.

It was found that the control group (PF) was the group with the maximum absorption capacity of water, while the PFB group, which is a BPO_4 containing group, exhibited the minimum amount of water absorption. The PFB composite group showed about 50 % WA, while the PF group weight gained about 75 % within 6 months. The highest density can be seen in PFB (containing BPO_4) group, and the lowest density was found in control sample (PF) according to Table 1. Different densities led to different WA% of composites. The highest WA% was observed in the control group which has the lowest density. The presence of more empty pores in control sample made it easily accessible to water. As the other groups (PFI and PFBI) have close density values, the % WA values are close to each other. Baysal *et al*. (2007) investigated the water absorption rates of wood polymer composites impregnated with a mixture of boric acid and bo-

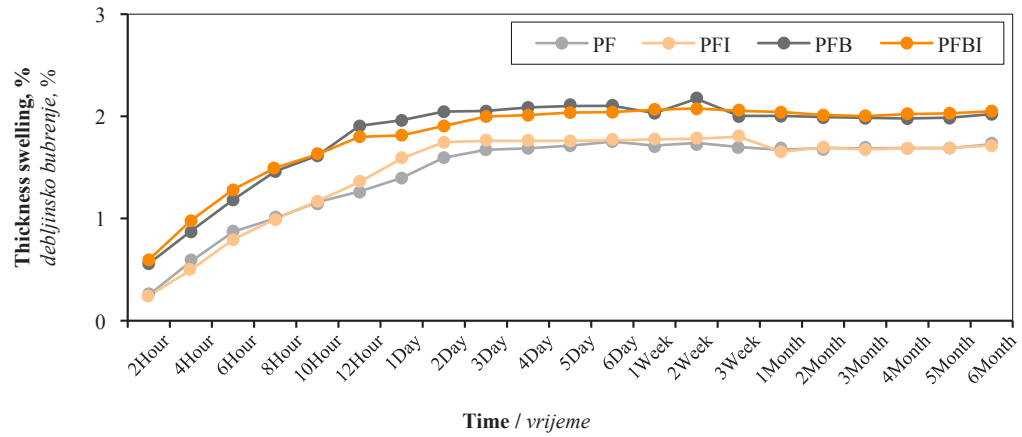


Figure 4 Thickness swelling (%) of WPCs in 6 months
Slika 4. Debljinsko bubrenje (%) WPC-a tijekom šest mjeseci

rax. They found that the boric acid and borax mixture impregnation resulted in less water absorption than the control groups.

The material can expand volumetrically as it receives water and, after a period of time, there may be deformation on the composite surfaces. The thickness swellings (*TS*) of the composite groups are given in Figure 4. The TS% of all groups increased over time and then remained almost fixed from the 3rd day. It can be seen that the composites having the highest *TS*% are groups containing BPO_4 and this group also showed the highest density values. The lowest *TS*% was found in the control group (PF) and this was expected because the control group has a low density and a more porous structure. While water diffuses into these empty spaces, there is no increment in volume. As the water filled the gaps in the composite structure, no volumetric expansion was seen.

3.3 Mechanical properties
3.3. Mehanička svojstva

Table 2 represents the flexural properties of WPCs with different formulations. The highest values of flexural modulus (*MOE*) were obtained from PMDI containing composites (PFI group). The lowest bending modulus was found in the control group (2.09 GPa). The *MOE* for PFI composite showed an increment of 37 % from 2.09 to 2.86 GPa. The modulus of rupture (MOR) of composites was also increased from 11.4 to 21.2 MPa by adding PMDI compatibilizer. Composites containing BPO_4 (PFB, PFBI) slightly decreased the *MOE* values when compared with PMDI added composites (PFI). The increase in bending strength and *MOE* of composites provided evidence of proper interfacial adhesion between wood flour and phenol formaldehyde resin in PMDI incorporated samples. The stress can be effectively transferred from resin to wood fibers by this strong adhesion and attraction. The significant improvements in both strength and modulus of PMDI compatibilizer added wood polymer composites were also reported by different research groups (Lu *et al*., 2000; Geng *et al*., 2005). Most polymers are hydrophobic and not compatible with hydrophilic wood. This structural difference resulted in a poor interfacial adhesion. The isocyanates functional groups of PMDI react with the hydroxyl groups of the wood and hydroxyl groups of phenol formaldehyde resin to form carbamate and urethane bonds. Hence, strong adhesion through covalent bonding between wood flour and polymer resin provides improved mechanical properties (Bodîrlău *et al*., 2012).

As seen in Table 3, according to the results of the statistical analysis applied for F_{max} loads, it was significant according to the $P = 0.000$ significance level for the ANOVA test. According to the LSD test results, it was found that the PFI composite group showed the best load carrying capacity compared to that of the other three composite groups. According to LSD test results, it can be seen that PFI test samples carried more load, such as 17.84 %, than PF test samples, 17.58 % more than PFB test samples and 17.58 % more than PFBI test samples. Additionally, PFBI samples were significant with a significance level of P = 0.048 and carried 1.23 % more load than PF test samples according to the LSD test (Table 4).

3.4 Morphology of WPCs
3.4. Morfologija WPC-a

The fracture surfaces of specimens tested in bending were characterized by SEM. Figures 5a and 5c show SEM images of control group (PF) and BPO_4 flame-retardant added WPCs group (PFB), respectively. There are voids and cracks around wood flour and these morphologies displayed a weak interfacial adhesion between wood particles and polymer resin. Besides, in the presence of PMDI compatibilizer the SEM images revealed fewer cavities (Figure 5b and 5d). It was also noticed that wood particles were surrounded by polymer and wood lumens were filled up with phe-

Table 2 Mechanical (flexural) properties of WPCs
Tablica 2. Mehanička (savojna) svojstva WPC-a

Sample codes *Oznake uzoraka*	***MOE*, GPa**	***MOR*, MPa**	**F_{max}, kg**	**S_o, mm²**
PF	2.09 ± 0.12	11.4 ± 1.5	0.93 ± 0.11	39.01 ± 1.33
PFI	2.86 ± 0.10	21.2 ± 1.9	1.65 ± 0.18	37.97 ± 0.53
PFB	2.28 ± 0.05	12.4 ± 0.5	0.94 ± 0.06	37.35 ± 1.37
PFBI	2.56 ± 0.09	14.6 ± 0.7	1.13 ± 0.02	38.00 ± 0.88

Table 3 Summary of ANOVA results for load carrying capacity (F_{max}) tests of experimental specimen
Tablica 3. Sažetak ANOVA rezultata za ispitivanje nosivosti (F_{max}) eksperimentalnog uzorka

Source *Izvor*	**DOF**	**Sum of squares** *Zbroj kvadrata*	**Mean square** *Srednji kvadrat*	***F* value** *F-vrijednost*	**Level of sig.** *Razina značajnosti*
Between groups / *između grupa*	1.035	3	0.345	28.676	0.000
Within groups / *unutar grupa*	0.096	8	0.012		
Total / *ukupno*	1.132	11			

Table 4 Comparison of averages of test samples for load carrying capacity (F_{max})
Tablica 4. Usporedba srednjih vrijednosti nosivosti (F_{max}) ispitnih uzoraka

	(I) **Sample code** *Oznaka uzorka*	(J) **Homogenous** group *Homogena grupa*	(I-J) **Mean difference** *Srednja razlika*	**Sig*.**	**95 % Confidence interval** 95 %-*tni interval pouzdanosti*	
					Lower bound *Donja granica*	**Upper bound** *Gornja granica*
LSD	PF = A	PFI B	-0.725000	0.000	-0.93157	-0.51843
		PFB C	-0.013333	0.885	-0.21990	0.19324
		PFBI D	-0.208333	0.048	-0.41490	-0.00176
	PFI = B	PF A	0.725000	0.000	0.51843	0.93157
		PFB C	0.711667	0.000	0.50510	0.91824
		PFBI D	0.516667	0.000	0.31010	0.72324
	PFB = C	PF A	0.013333	0.885	-0.19324	0.21990
		PFI B	-0.711667	0.000	-0.91824	-0.50510
		PFBI D	-0.195000	0.061	-0.40157	0.01157
	PFBI = D	PF A	0.208333	0.048	0.00176	0.41490
		PFI B	-0.516667	0.000	-0.72324	-0.31010
		PFB C	0.195000	0.061	-0.01157	0.40157

*The mean difference is significant at the 0.05 level. / *Srednja je razlika značajna na razini od 0,05.*

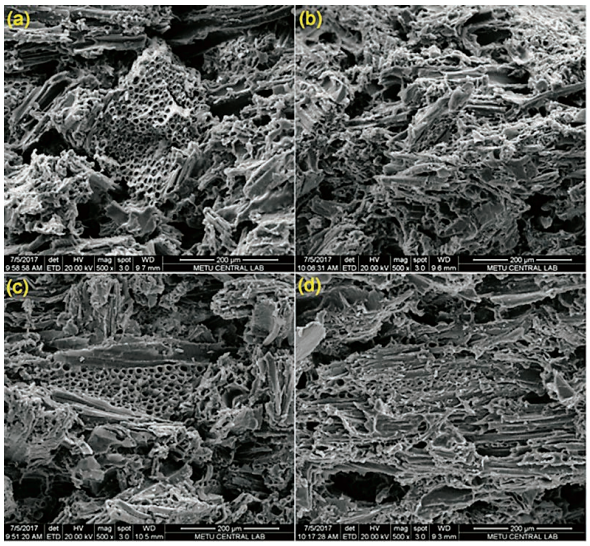


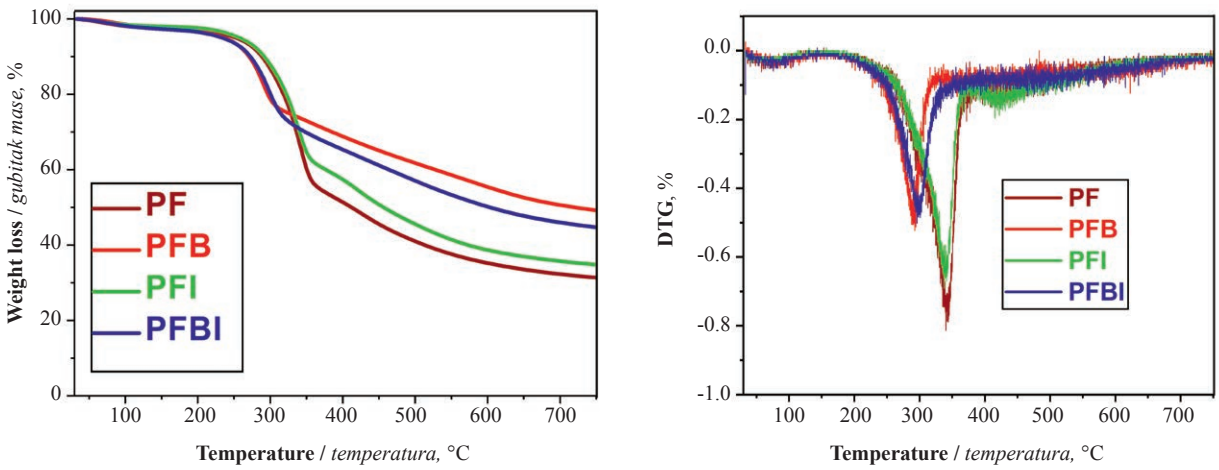
Figure 5 Morphology of fractured surfaces of WPCs: (a) PF (wood + polym), (b) PFI (wood + polym + compatibl), (c) PFB (wood + polym + BPO_4) and (d) PFBI (wood + polym + compatibl + BPO_4)
Slika 5. Morfologija lomnih površina WPC-a: (a) PF (drvo + polimer), (b) PFI (drvo + polimer + kompatibilizator), (c) PFB (drvo + polimer + BPO_4) i (d) PFBI (drvo + polimer + kompatibilizator + BPO_4)

nol formaldehyde resin (Figure 5d). The introduction of PMDI compatibilizer into the WPCs resulted in a good bonding between polymer matrix and wood flours. The well dispersed morphologies of PMDI added WPCs agreed well with the improved mechanical properties of PMDI added WPCs.

3.5 Thermogravimetric analysis
3.5. Termogravimetrijska analiza

Thermal degradation temperatures of the composite groups were compared by thermogravimetric analysis and the effects of BPO_4 addition to the composites on the thermal stabilities were investigated. The main decomposition temperatures and the char content at 750 °C of the composites are given in Table 5 and the TGA thermograms of composites is presented in Figure 6.

It is known that the wood components (hemicellulose, cellulose and lignin) start to degrade when they are subjected to heat. Initial degradation starts by hemicellulose hydrolysis at around 200 °C and the random cleavage of glycosidic linkages of cellulose, followed by the degradation of lignin at higher temperatures. To improve the thermal stability of wood, boron compounds were impregnated or added to the WPCs. Boron based compounds increased the degradation rate at lower temperatures, which causes the higher char yield. Boric acid, borax and their mixture were used with ammonium polyphosphate (APP) as a synergist for flame-retardants in WPCs (Kurt *et al*., 2012). APP and boron compounds retard flame by producing carbonaceous barrier which delays the heat transfer. Recently, five kinds of phosphorus-boron based transparent intumescent flame-retardants were synthesized by boric acid (BA) and cyclic phosphate ester acid (PEA). These flame-retardants were coated onto wood substrates and the results indicated that BA imparts excellent synergistic smoke suppression effect. Also, the residual masses of the coatings were noticeably increased with higher loading of BA. The reduction in the release of combustible gases resulted in less smoke production and heat release during burning (Xu *et al*., 2018). The effect of boron compounds on fire protection of epoxy system was studied by Unlu *et. al.* (2014) and three kinds of boron compounds namely boric acid (BA), zinc borate (ZB) and melamine borate (MB) were used with ammonium polyphosphate (APP). According to the fire test results, borates can promote ceramification and form strong residue among these additives (Unlu *et al*., 2017). Li *et*



a) b)

Figure 6 a) TGA, b) DTG curves of WPCs with different formulations
Slika 6. a) TGA, b) DTG krivulje WPC-a s različitim formulacijama

al. (2017) prepared boron phosphates through the reaction between boric acid and phosphoric acid for charring agent in epoxy resins. They increased the acid cites on the boron phosphate surface and it exerted a synergistic effect by catalyzing the carbonization of epoxy resin (Unlu *et al*., 2014).

TGA results revealed that the control (PF) group composite has the highest weight loss (69 %), while the BPO_4 containing (PFB) group composites has the lowest weight loss (51 %). The increase of residue is more obvious in the presence of BPO_4, and it promoted the charring (Table 3). It was also noticed that BPO_4 and PMDI addition decreased the main decomposition temperatures but increased the char yield of WPCs. Tomak *et al*. (2012) reported similar TGA results. When boron compounds were added to the composites, they observed that the main decomposition temperatures were reduced by 15-50 °C, while the char content was increased. Mengeloğlu and Karakus (Mengeloglu and Karakus, 2008) examined thermal degradation temperatures of composites obtained from high density polyethylene (HDPE) and wheat straw flour. They observed that by adding boric acid and borax additives to composites, decomposition temperature shifted to the lower value and increased the char residue. As a result, they have indicated that the boron compounds increase the thermal stability of the composites.

3.6 LOI and UL-94 tests
3.6. LOI i UL-94 testovi

The flammability and flame retardancy of WPCs were investigated by LOI and vertical UL-94 tests and the results are presented in Table 5. The LOI values of composites were found in the range of 28.7 and 35.6. When the flame-retardant BPO_4 was added for 5wt% in WPCs, the LOI value increased from 28.7 to 35.6. The PMDI compatibilizer and BPO_4 containing composites (PFBI) also exhibited a higher LOI value than that of the control group (PF). It is well known that boron compounds form a protective barrier and promote charring (Unlu *et al*., 2014). Obviously, BPO_4 improved the thermal stabilities of WPCs, and LOI values correlated very well with the char yield data (Table 3) in TGA. The UL-94 test results revealed that the BPO_4 containing composites achieved V-0 rating and the BPO_4 incorporation into composite formulation improved the fire performance of WPCs. Stark *et al*. (2010). evaluated the effect of five additive-type commercial fire retardants (decabromodiphenyl oxide/ antimony trioxide mixture, magnesium hydroxide, zinc borate, melamine phosphate, ammonium polyphosphate) on fire performance of wood flour-polyethylene composites. All of these fire-retardant systems were incorporated into the composites for 10 wt%. They found that the most effective was ammonium polyphos-

Table 5 Results of TGA, LOI test and vertical flame (UL-94) test
Tablica 5. Rezultati TGA, LOI testa i testa okomitog plamena (UL-94)

Sample codes *Oznake uzoraka*	$T_{main,}$ °C	**Char yield at 750 °C, %** *Prinos ugljena pri 750 °C, %*	**UL-94 classification** *UL-94 klasifikacija*	**LOI**
PF	342.9	31.4	V2	28.7
PFI	339.4	34.8	V2	28.3
PFB	290.2	49.2	V0	35.6
PFBI	300.3	44.7	V0	33.8

phate with 29 LOI value. Comparing our LOI results of composites with those of Stark et. al, it can be concluded that even a lower amount of BPO_4 incorporation (wt 5%) into our composites resulted in a higher LOI value.

4 CONCLUSIONS
4. ZAKLJUČAK

This study focused on the use of boron phosphate (BPO4) flame-retardant in WPCs for the first time and the effect of BPO4 on physical, mechanical and thermal performances of WPCs. The earlier investigations reported several flame-retardant chemicals, and the boron compounds together with ammonium polyphosphates additives have shown a synergistic effect in enhancing the flame retardancy of polymers. Hence, in this study, BPO4 was added as a flame-retardant compound in WPCs made of phenol formaldehyde resin and Oriental beech wood (Fagus orientalis Lipsky) flour. TGA results revealed that the char yield of composite was 31.4 % in the absence of BPO4 and this value was increased to 49.2 % by incorporation of 5 wt% BPO4 to the formulation. The LOI values were increased from 28.7 to 35.6. The UL-94 test results also demonstrated that the BPO4 added composites have good flame retardancy. PMDI compatibilizer also played an important role in interfacial adhesion between wood particles and polymer matrix. The improved flexural strength and well dispersed SEM morphologies of composites proved that the PMDI was a good compatibilizer in WPCs.

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