..... Izadyar, Babaei, Efhamisisi: Effect of Natural Resin from Wild Pistachio Trees...

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# Effect of Natural Resin from Wild Pistachio Trees on Physical Properties and Durability of Beech Wood: Alone and in Combination with Boric Acid

# Utjecaj prirodne smole divljeg drva pistacije (same i u kombinaciji s bornom kiselinom) na fizička svojstva i trajnost bukovine

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ABSTRACT • This study was carried out to investigate the physical properties and decay resistance of beech wood treated with natural pistachio resin (PR) from Iranian wild pistachio trees (Pistacia atlantica), alone and in combination with boric acid (BA). Wood samples were impregnated with different concentration of PR dissolved in ethanol (3 to 20%) with vacuum-pressure technology. The combination of PR (20%) and BA (2%) was also conducted to evaluate any interaction or synergistic effects. The water absorption, volumetric swelling, and decay resistance against <u>Trametes versicolor</u> fungi, before and after a leaching test (EN 84), were measured on treated and untreated samples. The chemical compositions of PR were also identified by gas chromatography-mass spectrometry (GC-MS) techniques. The chemicals analysis identified more than 20 different compounds in the PR, monoterpenoids being the predominant fraction and  $\alpha$ -pinene the major component. The samples treated with a higher concentration of PR showed much higher weight gain percentage (WG%). The results showed that the increase in WG% reduced the average values of water absorption and volumetric swelling of treated samples even after long terms of soaking in water. The decay resistance of the treated samples increased against white rotting fungi as the values of WG% increased. Efficient protection was seen when a combined treatment of PR and BA was used. Even after the leaching process, the weight loss of the treated samples was less than 3 percent. The samples treated with BA alone largely lost their effectiveness against fungal attack after the leaching. The use of PR along with an environmental friendly co-biocide can also be recommended for wood preservation in places that require minimal toxicity.

Keywords: pistachio trees; natural resin; weight gain; durability; physical properties

**SAŽETAK** • *Cilj ovog rada bio je istražiti fizička svojstva i otpornost na propadanje bukovine tretirane prirodnom smolom pistacije (PR) dobivene iz divljeg drva pistacije koja uspijeva u Iranu (<u>Pistacia atlantica</u>) te kombinaci-*

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jom smole pistacije i borne kiseline (BA). Uzorci drva vakuumsko-tlačnim su postupkom impregnirani različitim koncentracijama PR-a otopljenoga u etanolu (3 do 20 %). Provedena je i impregnacija uzorka kombinacijom PR-a (20 %) i BA-a (2 %) kako bi se procijenili svi interakcijski i sinergijski učinci. Za tretirane i netretirane uzorke mjerena je upojnost vode, volumetrijsko bubrenje i otpornost na djelovanje gljive <u>Trametes versicolor</u> prije i nakon ispiranja (EN 84). Ujedno je uz pomoć plinske kromatografije s masenom spektrometrijom (GC-MS) utvrđen i kemijski sastav smole (PR). Kemijskom analizom u PR-u je identificirano više od 20 različitih spojeva; momoterpeni su bili dominantna frakcija, a a-pinen glavna komponenta. Uzorci tretirani većom koncentracijom PR-a rezultirali su većim dobitkom mase (WG%). Rezultati su pokazali da se s porastom WG% smanjuje prosječna vrijednost upojnosti vode i volumetrijsko bubrenje tretiranih uzoraka, čak i nakon dugotrajnog potapanja u vodi. Otpornost tretiranih uzoraka na djelovanje gljiva bijele truleži povećala se s povećanjem WG%. Učinkovita zaštita primijećena je pri primjeni kombiniranog tretmana PR-om i BA-om; čak je i nakon postupka ispiranja gubitak mase tretiranih uzoraka bio manji od 3 %. Uzorci tretirani samo BA-om nakon ispiranja su uglavnom izgubili otpornost može preporučiti upotreba PR-a zajedno s ekološki prihvatljivim biocidom.

Ključne riječi: drvo pistacije; prirodna smola; dobitak mase; trajnost; fizička svojstva

#### 1 INTRODUCTION 1. UVOD

While wood is a unique biomaterial that currently has many uses, it also has some disadvantages that limit its use for some applications. Some wood species are prone to be readily degraded by fungi, termites, and other organisms (Reinprecht, 2016). Wood protection is a process for reducing and/or preventing attack by wood deteriorating agents to increase its service life (Jones and Brischke, 2017). CCA (chromium (VI)copper-arsenic) formulations have been widely used for the treatment of wood (Freeman et al., 2003). However, CCA-treated lumber contains arsenic, which may pose serious health risks even after its service time ends and the CCA treated wood becomes waste. As a result, arsenic (and of course CCA) has been banned since 2004 from most applications for wood preservation in Europe and North America (Caldeira, 2010). Environmental performance and sensitivity play an increasing role in the development and use of wood preservatives (Shmulsky and Jones, 2011). [There are several arsenic-free alternatives for CCA, and although their main ingredients have lower mammalian toxicity than arsenic, these systems contain high levels of copper, which can be toxic to aquatic life (Lebow, 2004). Therefore, many studies are underway to replace metal oxides with more eco-friendly biocides.

In recent years, many studies have been conducted on the use of plant extracts for wood preservation. Singh and Singh (2012) have reviewed many of these studies, and concluded that progress in implementation of the technologies has been slow because of certain limitations. It was found that the essential oil from Lippia origanoides showed high fungicidal activity against two wood decay fungi. This activity was attributed to thymol, the major component of the essential oil. The U.S. Environment Protection Agency (EPA) has no significant incident reports involving thymol (De Medeiros et al., 2016). In another study, 16 plant essential oils were applied to Fagus orientalis and Pinus taeda wood samples by vacuum impregnation method (Bahmani and Schmidt, 2018). The treated samples were then infected with different kinds of rotting and molding fungus. Their results showed that lavender oil, lemon grass oil, and thyme oil had the greatest effect against mold and wood decay fungi. Yang and Clausen (2007) evaluated the ability of seven essential oils to inhibit the growth of some molding fungi on southern yellow pine that were either dip treated or exposed to vapors of the test oils. Thyme and Egyptian geranium oil inhibited the growth of all test fungi. The extract of cinnamon leaves has also proven to be highly effective against wood decay fungi and termites (Cheng et al., 2006). It should be noted, however, that breathing, eating, or touching the cinnamon products can trigger an allergic reaction in some people. The effect of cinnamon, clove, anise, lime, and tangerine oils on the control of mold fungi were also studied on rubber wood (Matan and Matan, 2007, 2008).

The impact of plant extracts and essential oils on wood growing molds have been extensively studied in recent years (Salem *et al.*, 2016). Virtually none of the oils have been commercialized, but they may be used especially for artistic or domestic uses.

A number of studies have also suggested that a combination of plant extracts with more environmentally friendly preservatives may achieve positive interactions or synergy effects. The modification of mimosa tannin with a copper-ammonia complex appeared to promote anti-decay properties of treated wood, while unmodified tannin had no preventive effect on fungal attack (Yamaguchi and Okuda, 1998; Yamaguchi and Yoshino, 2001). The association between tannins and boric acid could also be another remedy. Pizzi and Baecker (1996) used preservative solutions based on tannins and boron in which boric acid was used to induce hardening reactions of polyflavonoid tannins. Equally, boric acid can be partially fixed into the wood by being trapped in the tannin polymer (Efhamisisi *et al.*, 2017).

Boron compounds, such as boric acid, have been used for over 40 years as wood preservatives in Australia and Europe (Caldeira, 2010). Borates offer some of the most effective and versatile wood preservative systems available today, combining the properties of broad spectrum efficacy and low mammalian toxicity (Freeman *et al.*, 2003). Due to the favorable environmental characteristics of borates, researchers have re-

focused on boron-including compounds in the last two decades (Obanda et al., 2008). However, more recently (August, 2008), the European Commission decided to make an ATP - Adaptation to Technical Progress of Council Directive 67/548/EEC (the 30th ATP), and since then boric acid and sodium borate have been classified as reprotoxic. This means that these borate compounds are now classified as substances toxic for reproduction category 2 for both fertility and developmental effects. According to this restriction, the concentration limit for boric acid is  $\geq$  5.5 % for wood treatment. However, borates have been registered by the EPA as wood preservatives. Also, they are still in use in Europe, but the concentration is limited. High susceptibility of borates to leach is the main obstacle to their widespread use as a major component in the broad spectrum (Obanda et al., 2008).

*Pistacia* is a genus of flowering plants from the *Anacardiaceae* family that can be found in about twenty species (Bozorgi *et al.*, 2013). Extracts of *Pistacia atlantica* could be considered as a potential alternative to antifungal chemicals that have a detrimental effect on the environment and public health (Amri *et al.*, 2015). On the other hand, it was found that natural materials alone cannot provide full protection.

There are no exact statistics on the removing of resin from wild pistachio trees in Iran. These trees are found in Zagros, the forests located in all the western provinces of the country from north to south. Generally, about 7,000 tons of this resin is produced annually in Iran, with more than seventy percent being exported overseas without any processing (Jahanbazi et al., 2006). Zagros forests, with an area of about 6 million hectares (3.5 percent of Iran), are located in the west of the country (Sadeghi et al., 2017). Wild pistachio trees are considered the most important species in Zagros forests (Javanmiri Pour et al., 2013). In this study, the resin of pistachio trees, grown in the western forests of Iran, was used as wood preservative material. Since the natural materials cannot provide full protection alone, the pistachio resin was used both alone and in combination with boric acid. Although boric acid is easily leached from treated wood (Obanda et al., 2008), it seems that its combination with pistachio resin, as a water insoluble material, prevents its leaching.

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

### 2.1 Materials

#### 2.1. Materijali

The natural resin of wild pistachio (*Pistacia atlantica*) trees was obtained from an area located at  $45^{\circ}30'$  to  $46^{\circ}15'$  longitude and  $35^{\circ}45'$  to  $36^{\circ}15'$  altitude in the Kurdistan province, western Iran. The average elevation of the area stands 1400 m above sea level. The average annual precipitation is 300 to 800 mm/year and average annual temperature is between 12 to 18 °C. Boric acid of 99 % purity was purchased from the Sigma Aldrich Company and ethanol of 96 % purity was purchased from the Merck Company. The sapwood of beech (*Fagus orientalis*) was prepared from the Hezarjeribs forests of Mazandaran province in northern Iran. The climate of this region is mild and humid and wood specimens were harvested at the altitude of 1000 m. The chosen specimens were free from cracks, stain, decay, insect damage, and other defects. The samples were then prepared according to relevant standards (Table 1).

#### 2.2 Methods

2.2. Metode

## 2.2.1 Gas chromatography-mass spectrometry (GC-MS) of the resin

2.2.1. Plinska kromatografija s masenom spektrometrijom (GC-MS) za smolu

The ingredients of the resin were determined with a gas chromatography/mass selective detector (GC-MS). The PR was firstly dissolved in ethyl ether before injection into the GC apparatus. The analysis was performed on an Agilent 7890A gas chromatograph. The separation was achieved with a Rtx 5MS capillary column (30 m  $\times$  0.25 mm; 0.25 µm film thickness) with He as the carrier gas (1.3 ml/min). The oven temperature was programmed from 40 to 200 °C at 5 °C/min. The temperatures of the injector and quadrupole and ion sources were 250 °C, 150 °C, and 230 °C, respectively. The MS detector was run in electron impact mode with electron energy of 70 eV. Volatile organic compounds were identified by comparison of their retention indices, calculated by the use of a series of n-alkanes (C9–C16), with those reported in the literature.

### 2.2.2 Sample preparation

#### 2.2.2. Priprema uzoraka

Different treatment solutions were prepared by solving PR in ethanol with different concentrations of 3, 6, 9, 12, 15 and 20 %. One treatment solution contained 20 % PR and 2 % boric acid, and the other contained 2 % boric acid without any PR. The components of the treatment solutions and their nomenclature are shown in Table 2. Specimens were treated with the vacuum-pressure method (Dhamodaran and Gnanaharan, 2007). The samples were put inside the cylinder under 0.8 bar vacuums for 30 minutes and then 4 bar pressure was applied for 2 hours at 50 °C. Afterward, the treated samples were kept at lab ambience for 2 weeks to evaporate the solvent and then were oven dried at  $(103\pm2)$  °C.

Table 1	Standards	used in	different tests
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Tablica 1. Standardi	i primijenje	eni za različita	ispitivanja
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Test	Number of treatment	Dimensions (L×R×T), mm	Standard
Ispitivanje	Broj tretmana	<i>Dimenzije (L</i> × <i>R</i> × <i>T</i> ), mm	Stanuaru
Fungal attack test / napada gljiva	12	15×25×50	EN 113 (1996)
Physical test / fizičkih svojstava	10	20×20×20	ISO 13061 (2014)

 Table 2 Components of treatment solution and their nomenclature

 Tablia 2 Kamponenta u stanini za tratirania i niika

**Tablica 2.** Komponente u otopini za tretiranje i njihova nomenklatura

Samples ID Oznaka uzorka	Concentration in solution Koncentracija u otopini wt%	
02110110 0201110	Resin Smola	Boric acid Borna kiselina
Control (Solvent treated)		
kontrolni uzorak	0	0
(tretirano otapalom)		
PR3	3	0
PR6	6	0
PR9	9	0
PR12	12	0
PR15	15	0
PR20	20	0
PR20BA2	20	2
BA2	0	2

# **2.2.3 Measurement of weight gain and retention** 2.2.3. Mjerenje dobitka mase i retencije

Since some extractive content of wood is removed from the samples during the impregnation process, which causes a mistake in the calculation of WG, WG values were calculated by two methods. The first was the theoretical weight gain ( $WG_t$ ), which was calculated based on the wet weight after impregnation and concentration of materials in the solutions (Eq.n 1). The second was the actual or experimental weight gain ( $WG_e$ ), which was based on the oven dried samples after impregnation (Eq. 2).

$$WG_{t}(\%) = \frac{\left(M_{1} - M_{0}\right) \cdot C}{M_{0}} \cdot 100 \tag{1}$$

Where,  $M_1$  is the wet weight of the sample after impregnation (g);  $M_0$  is the oven dried weight before impregnation (g); and C is the solid percent content in solvent (%).

$$WG_{\rm e}(\%) = \frac{M_2 - M_0}{M_0} \cdot 100$$
 (2)

Where,  $M_2$  is the oven dried weight after impregnation (g) and  $M_0$  is the oven dried weight before impregnation (g).

Also, the retention  $(R_t)$  of materials as kilogram per cubic meter of treated wood sample was calculated based on Eq. 3:

$$R_{\rm t} \left( \rm kg \cdot m^{-3} \right) = \frac{\left( M_2 - M_0 \right) \cdot C}{V} \cdot 10^{-3}$$
 (3)

Where,  $M_2$  is the oven dried weight of the sample after impregnation (g);  $M_0$  is the oven dried weight before impregnation (g); C is the solid percent content in solvent (%); and V is the volume of the sample (m<sup>3</sup>).

# 2.2.4 Water absorption and volumetric swelling measurements

#### 2.2.4. Mjerenje upojnosti vode i volumetrijskog bubrenja

The treated and untreated specimens were placed in beakers, which were then filled with distilled water

and maintained at 23 °C for 8 days. During that time, the water was replaced by fresh distilled water at 2, 4, 6, 8, and 24 h and then replaced again at 24 h intervals. The weight and volume of the samples were measured at the end of the treatment. The water absorption (WA) of the samples was calculated according to Eq. 4.

$$WA(\%) = \frac{(W_1 - W_0)}{W_0} \cdot 100$$
 (4)

Where,  $W_1$  is the weight of the specimen after immersion in water;  $W_0$  is the oven dried weight before immersing in water.

The volumetric swelling (*S*) of the samples was calculated according to Eq. 5.

$$S(\%) = \frac{(V_1 - V_0)}{V_0} \cdot 100$$
 (5)

Where,  $V_1$  is the volume of the sample after immersion in water and  $V_0$  is the volume of the sample before immersion in water.

### **2.2.5** Leaching test 2.2.5. Test ispiranja

A leaching test for treated wood was carried out according to the EN 84 standard. In this way, deionized water fivefold the sample volume was added to the samples and exposed to 4 kPa vacuums for 20 minutes. The water was replaced with fresh water after two hours and thereafter at 24 h intervals for 14 days. Weight loss of the samples were then measured.

#### 2.2.6 Wood decay test

#### 2.2.6. Ispitivanje propadanja drva

The treated and untreated specimens were tested for resistance to biological attack according to the European EN 113 standard criteria, 1996, against Trametes versicolor (tropical white rot) grown on malt-agar medium. The Trametes versicolor fungi, strain CTB 863A were prepared from Tehran university fungi bank. The wood samples were dried at 105 °C for 24 h and the dry weight of sample was measured before decay testing. Petri dishes (145 mm diameter) with malt extract agar (50 ml per plate) were inoculated with a mycelium agar disc (5 mm diameter) taken from the sub-margin of 1-month-old cultures of T. versicolor. When the fungal mycelium reached the border of the plate, three untreated and three treated wood samples were added on separate metal grids to prevent moisture uptake by the wood sample. The plates were incubated at (22±2) °C and (70±5) % relative humidity for 16 weeks. Twelve wood samples for each treatment from four different plates were used to determine the mass loss of the wood samples. After incubation, the sample surfaces were cleaned gently and dried at 105 °C for 24 h to obtain the dry weight of sample after decay testing. The weight loss (WL) of the samples was calculated by Eq. 6.

$$WL(\%) = \frac{T_0 - T_1}{T_0} \cdot 100$$
 (6)

Where,  $T_0$  is the oven dried weight of sample before fungi test (g) and  $T_1$  is the oven dried weight after fungi test (g).

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

### **3.1 Pistachio resin (PR) analysis** 3.1. Analiza smole iz pistacije (PR)

The GC-MS analysis of the PR identified more

than 20 compounds. Total number of components and their retention times are shown in Table 3 and Figure 1.

In their study of *Pistacia atlantica* resin from the Kordestan province in Iran, Mahjoub *et al.* (2018) reported 82.64 % for  $\alpha$ -pinene as the main constituent and 3.04 % for  $\beta$ -pinene, while Barrero *et al.* (2005) obtained 42.9 % for  $\alpha$ -pinene and 13.2 % for  $\beta$ -pinene as the major components of Moroccan *Pistacia atlantica* oil. Benabderrahmane *et al.* (2016) reported 79.8, 65.3, and 25.4 % for  $\alpha$ -pinene content of *pistacia atlantica* growing wild in three different regions in the west and north-west of Algeria.

Comparison with previously studied essential oil of the resin from different species of *Pistacia* showed that monoterpenes are the predominate fraction and  $\alpha$ -pinene is the major component.

### **3.2 Weight gain and retention analyses** 3.2. Analiza dobitka mase i retencije

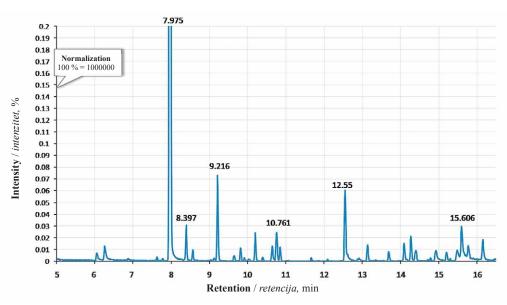
 $WG_{t}$  and  $WG_{e}$  of the treated samples are presented in Figure 2. As can be seen, the values of WG increased as the PR concentration increased from 3 to 20 %. The negative values of  $WG_{e}$  for the solvent treated samples may be due to the removal of wood extractives by the ethanol during the impregnation process.

The values of  $R_t$  increased from 11.86 to 78.34 kg/m<sup>3</sup> by increasing resin concentration from 3 to 20 %, respectively (Figure 3).

Lesar *et al.* (2009) indicated that boric acid retention of 0.4 kg/m<sup>3</sup> was enough to inhibit the growth of *A. vaillantii*, *S. lacrymans*, and *T. versicolor*, while the retention of 0.8 kg/m<sup>3</sup> of boric acid was needed to preserve wood against *P. ostreatus* and *H. fragiforme* 

Table 3	Components of PR
Tablica	3. Komponente u PR-u

Compounds	Retention time Vrijeme	<b>Area</b> Površina
Spojevi	retencije	%
	min	0.52
meta-Xylene	6.27	0.52
(-)-alpha-Pinene	7.975	85.61
Camphene	8.397	0.70
Bicyclo[2.1.1]hex-2-ene, 2-ethenyl	8.574	0.23
beta-Pinene	9.216	1.72
Cyclotetrasiloxane, octamethyl	9.824	0.24
3,7,7-Trimethylbicyclo[4.1.0] hept-3-ene	10.204	0.58
p-Cimene	10.651	0.36
L-Limonene	10.761	0.69
Eucalyptol	10.854	0.30
alpha-Terpinene	12.55	1.94
Verbenene	13.141	0.37
1,7,7-Trimethylbicyclo[2.2.1] hept-5-en-2-ol	13.699	0.22
Trans-Pinocarveol	14.104	0.45
Bicyclo[3.1.1]heptan-3-ol, 6,6-dimethyl-2-methylene	14.273	0.57
Cyclopentasiloxane, decamethyl	14.408	0.32
p-Mentha-1,5-dien-8-ol	14.931	0.45
4-Terpineol	15.21	0.19
Benzenemethanol, alpha,alpha,4- trimethyl	15.488	0.42
Alpha terpinolene	15.606	1.32
Myrtenol	15.775	0.49
Bicyclo[3.1.1]hept-2-en-6-one, 2,7,7-trimethyl	16.155	0.61
Isobornyl acetate	18.223	0.78
Nonadecane	28.117	0.42
Tetracosane, 2,6,10,15,19,23-hexa- methyl	28.227	0.45



**Figure 1** Chromatogram of PR **Slika 1.** Kromatogram PR-a

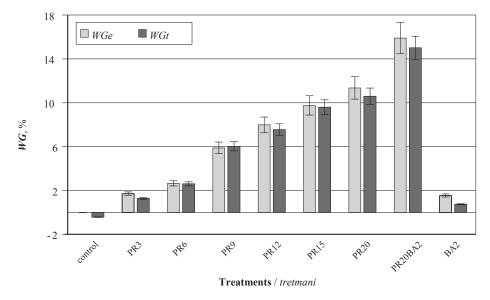


Figure 2 WG values of treated samples Slika 2. WG vrijednosti tretiranih uzoraka

fungi. However, Beachler and Roth (1956) reported that boric acid retentions between 0.52 and 2.88 kg/m<sup>3</sup> are required to protect wood against *G. trabeum* in laboratory conditions. In wood treated with creosote or other oil compounds, higher preservative levels (200 kg/m<sup>3</sup>) are necessary to prevent biological destruction (Lebow, 2010).

#### 3.3 Water absorption and volumetric swelling analyses

#### 3.3. Analiza upojnosti vode i volumetrijskog bubrenja

The water absorption of samples from different treatments is shown in Figure 4. At 0-8 h, the water absorption of the control and all treated samples was slow, and the water absorption for all samples was below the FSP. At 8-96 h, the water absorptions increased rapidly until 96-192 h, where they increased slowly. As shown in the figure, the water absorption decreased as the concentration of PR increased. This result is related to the water-insoluble  $\alpha$ - pinene in PR and its hydrophobic property (Lebrero, 2012). The water absorption of the 2 % boric acid treated sample is similar to that of

the control sample and confirms the leachability of boron in water.

The samples treated with 20 % PR and 20 % PR-2 % boric acid had the lowest water absorption. The water absorption in 20 % PR-2 % boric acid treated sample at 192 h was reduced by 18.69 % in comparison to the control sample.

The volume swelling of the samples is depicted in Figure 5. As can be seen, the volumetric swelling of the control and all treated samples slowly increased at 0-8 h. The volumetric swelling sharply increased at 8-48 h, and then slowly increased after 48 h. This result can be related to the water saturation point of the samples, which does not change very much.

The volumetric swelling of the PR treated samples decreased as the *WG* increased. The maximum volumetric swelling was observed for the untreated controls, and the minimum was related to the PR20 %-BA2 % sample. The decrease in volumetric swelling of the treated samples is probably due to the hydrophobic nature of PR, which may consequently reduce the contact of water with the cell walls (Lebrero, 2012).

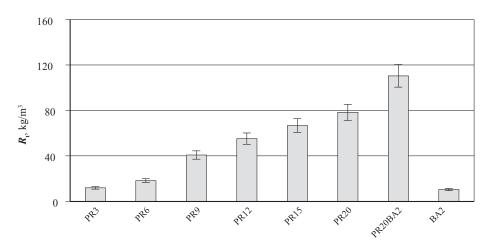


Figure 3 Theoretical retentions of treated samples Slika 3. Teorijska retencija tretiranih uzoraka

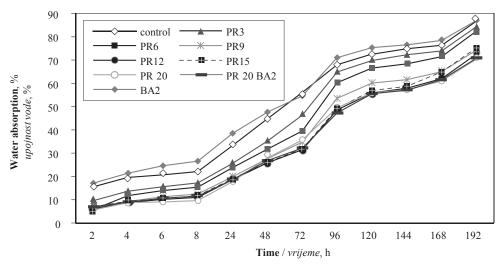


Figure 4 Water absorptions of samples with time Slika 4. Upojnost vode uzoraka tijekom vremena

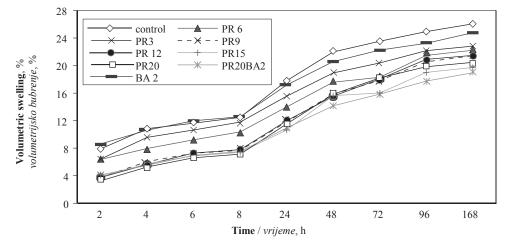


Figure 5 Volume swelling of samples with time Slika 5. Volumetrijsko bubrenje uzoraka tijekom vremena

It has been reported that the addition of PR into canola oil during the oil heat treatment of poplar wood caused lower volumetric swelling (Mahmoud kia *et al.*, 2017).

#### 3.4 Leaching analysis

#### 3.4. Analiza nakon ispiranja

Figure 6 shows the amount of material released from the treated specimens in a 14 day leaching period. In boric acid treated specimens, the weight loss was 1.86 %, which is almost equal to its weight gain (1.54) %). This result shows that almost all of the boric acid was easily leached from the wood. This agrees with the findings of other researchers (Lebow, 2007; Kartal, 2009). Both PR and dual 20 % PR-2 % boric acid treated specimens showed lesser weight loss as compared to the boric acid treated specimen. About 45 % of the total boric acid remained in the specimens treated with dual PR-boric acid compounds. Lower boric acid leachability in the dual PR-boric acid treated specimen can be related to two reasons: one, less space within the cell wall, which leads to reduction of water absorption, and two, the hydrophobic property of the resin components. The existence of free water in wood provides a suitable environment for fungi growth. Therefore, limiting the amount of free water in wood will reduce fungi attacks. The reduction of water percent gain and volumetric swelling (Figures 4 and 5) emphasizes that the treatment of wood with PR improved its water repellency. Another reason for the decline in leachability of boric acid can be related to the electrostatic interaction of  $\alpha$ -pinene and boric acid molecules.  $\alpha$ -pinene is an alkene with a carbon-carbon double bond. When it is mixed with boric acid solution, the pi bond between the two carbons is broken. When this pi bond breaks, the sigma bond between the two carbons is still intact, but one of them will have a negative charge and can attract the boron atom in the boric acid molecule. This electrostatic interaction keeps the boric acid in the wood and reduces its leachability in contact with water.

### 3.5 Decay resistance analysis

#### 3.5. Analiza otpornosti na propadanje

The results of the fungi test are given in Figure 7. The control samples had a weight loss higher than 20 %, when applying the EN 113 standard criteria. The weight loss of the samples with the 2 % boric acid

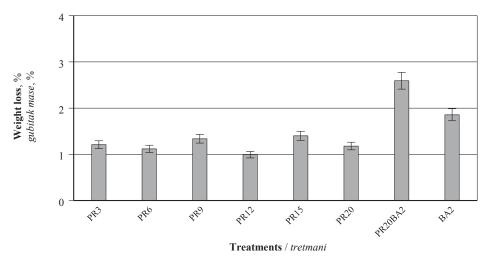


Figure 6 Weight loss of samples after leaching test Slika 6. Gubitak mase uzoraka nakon ispiranja

treatment was less than 1 % before leaching, but it was high after leaching and almost equal to the weight loss of the untreated samples. The weight loss of the samples saturated with only PR before and after leaching was in the range of 20-35 %, and there was not much difference between the weight loss of the leached and unleached samples. The results showed that, by increasing the PR concentration from 3 to 20 %, the weight loss of the samples against white rot fungi was reduced to less than half compared to the untreated sample, but this is not enough for effective protection of wood according to the EN 113 standard criteria. Previous works also demonstrated the inhibitory effect of the extract of *Pistacia atlantica* on mycelia growth of *Geotrichum candidum* (Talibi *et al.*, 2014).

It was expected that the efficacy of the PR would be related to the chemical composition of the resin. As shown in Table 3, the main components of the resin were  $\alpha$ -pinene (85.61 %),  $\alpha$ -terpinene (1.94 %),  $\beta$ -pinene (1.72 %), and  $\alpha$ -terpinolen (1.32 %). The antifungal property of the resin can be related to the  $\alpha$ -pinene, which is the major constituent of PR.  $\alpha$ -pinene is a monoterpene made of two structural units of terpenes with five carbon units  $(-(C_{5}H_{8})_{n})$  and a molecular formula of  $C_{10}H_{16}$ . Studies have shown that terpene compounds, including  $\alpha$ -pinene, have analgesic, antibacterial, and antifungal properties. Glisić *et al.* (2007) found that  $\alpha$ -pinene is effective against the growth of *Alternaria sp.*, *A. nidulans* and *A. niger*. Salem *et al.* (2016) showed that *P. rigida* oil can inhibit mold growth, which could be related to the major components such as L- $\alpha$ -pinene,  $\alpha$ -terpineol, borneol and fenchyl alcohol present in the oil. Powers (2018) outlined that  $\alpha$ -pinene-rich (46.1 %  $\alpha$ -pinene) commercial *Myrtus communis* essential oil showed a similar antifungal activity against *C. neoformans*.

As shown in Figure 7, the dual treatment of boric acid and PR gave a better effect than boric acid after leaching and better efficiency compared to the PR treatment alone. The weight loss of treated specimens with 20 % PR and 2 % boric acid after leaching was less than 3 %, which provides effective protection against *Trametes versicolor* according to EN 113 standard criteria. This result of the present study showed that boric acid can be successfully fixed in the wood by PR. Moreover, the combination of boric acid and PR improved the fungicide properties of PR.

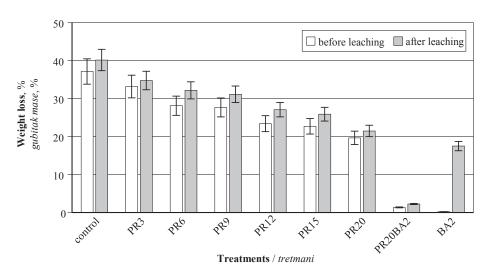


Figure 7 Weight loss of treated samples exposed to *Trametes versicolo* Slika 7. Gubitak mase tretiranih uzoraka izloženih gljivi *Trametes versicolo* 

#### 4 CONCLUSIONS 4. ZAKLJUČAK

This study was undertaken to investigate the decay resistance performance of beech wood treated with a PR and boric acid mixture against *Trametes versicolor* fungi. PR is an environmentally friendly material that has two fungicide and hydrophobic properties, which can prevent wood decay. Fungi test showed that PR could not fully protect the wood and must be combined with other preservatives. The 20 % PR-2 % boric acid treatment showed a suitable protection against fungi with 2.2 % weight loss. Also, the samples treated with 20 % PR-2 % boric acid showed a 26.9 and 18.69 % reduction in volumetric swelling and water absorption, respectively, in comparison with the untreated sample.

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