Maderas-Cienc Tecnol 24(2022):23, 1-26
Ahead of Print: Accepted Authors Version

DOI:10.4067/S0718-221X2022005XXXXXX

2 MECHANICAL AND FIRE PROPERTIES OF ORIENTAL BEECH IMPREGNATED

3 WITH FIRE-RETARDANTS AND COATED WITH POLYUREA/POLYURETHANE

4 HYBRID AND EPOXY RESINS

- 5 Çağlar Altay^{1*} <u>https://orcid.org/0000-0003-1286-8600</u>
- 6 Hilmi Toker² <u>https://orcid.org/0000-0002-1900-9887</u>
- 7 Ergün Baysal² <u>https://orcid.org/0000-0002-6299-2725</u>
- 8 İlknur Babahan³ <u>https://orcid.org/0000-0001-6081-4899</u>
- 9 Halil Kılıç² <u>https://orcid.org/0000-0002-7164-6840</u>
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- ¹ Aydın Adnan Menderes University, Aydın Vocational School, Department of Interior Design, Aydın,
 Turkey.
- ¹³ ² Muğla Sıtkı Koçman University, Faculty of Technology, Department of Wood Science and
- 14 Technology, Mugla, Turkey.
- ³ Aydın Adnan Menderes University, Faculty of Arts and Sciences, Department of Chemistry, Aydın,
- 16 Turkey.
- 17 *Corresponding author: caglar.altay@adu.edu.tr
- 18 **Received:** April 08, 2021
- 19 Accepted: January 23, 2022
- 20 **Posted online:** January 24, 2022
- 21

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ABSTRACT

23 This study was performed to investigate some mechanical properties such as modulus 24 of rupture and compression strength parallel to grain and some fire properties such as weight 25 loss and temperature values of Oriental beech (Fagus orientalis) treated with fire-retardants 26 and coated with polyurethane/polyurea hybrid resin and epoxy resin were investigated. The coatings are based on epoxy and polyurethane\polyurea hybrid resins. Firstly, an impregnation 27 28 method was applied by using fire-retardants which are boron chemicals and ammonium sulfate 29 before coating process. Oriental beech was impregnated with 3 % aqueous solution of boric acid, borax, boric acid and borax mixture (1:1), and ammonium sulfate. Oriental beech was 30 primed with epoxy resin by using Sikafloor[®]-156, and then coated with Sikalastic[®]-851, a 31 32 polyurethane/polyurea hybrid resin. Results showed that modulus of rupture and compression 33 strength parallel to grain values of polyurethane/polyurea and epoxy resin coated Oriental beech 34 wood were higher than that of un-treated and non-coated (control) group. Fire-retardants 35 treatment before polyurethane/polyurea and epoxy resin coatings caused to decrease modulus 36 of rupture and compression strength parallel to grain values of Oriental beech in some extent. 37 Weight loss and temprature values of polyurethane/polyurea and epoxy resin coated Oriental 38 beech were higher than that of un-treated and non-coated (control) group. Hovewer, fire-39 retardants treatment before polyurethane/polyurea and epoxy resin coatings improved fire 40 properties of Oriental beech wood. 41

- 42 Keywords: Boron compounds, epoxy resin, fire retardats, Oriental beech, polyurethane resin.
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INTRODUCTION

Since wood consists of organic based materials containing carbon and hydrogen, is flammable. The temperature for wood must be increased to 275 °C for it to burn itself. However, in the presence of any ignition flame source, it can ignite at much lower temperatures. In the absence of oxygen, heat source, and combustible material, there is no ignition (Kollman and Cote 1968). Although it has superior aspects compared to most structural materials during fire, treatment with impregnation materials that increase resistance to fire is necessary in terms of ensuring safety and preventing burning (LeVan and Winandy 1990, Yalınkılıç *et al.* 1996).

The most commonly used fire-retardant chemicals in the wood industry are inorganic salts and include ammonium and ammonium phosphate, ammonium chloride, ammonium sulfate, borax, boric acid, phosphoric acid, and zinc chloride (Woo and Schniewind 1987). These fire-retardant chemicals drastically reduce the rate of flame spread across the wood surface, thereby reducing the capacity of the wood to contribute to a fire (LeVan and Tran 1990, LeVan and Winandy 1990).

59 The fire retardant effectiveness of boron compounds is a physical mechanism achieved 60 by the formation of a coating or protective layer on the wood surface at high temperature, and 61 by forming glassy films that may inhibit mass transfer of combustible gases (LeVan and Tran 1990; Wang et al. 2004). Boric acid and borax are the most common boron compounds which 62 63 have found many application areas in the wood preservation industry in order to get the benefit 64 of their biological effectiveness and fire retardancy.Borax tends to reduce flame spread but can promote smoldering or glowing. On the other hand, boric acid suppresses smoldering but has 65 66 little effect on flame spread (LeVan and Tran 1990).

67 Many of the effective chemicals, which are used for wood protection, are questionable 68 because they are poisonous chemicals. Boron compounds have become up-to-date due to their 69 high activity against biological pests, their ability to be easily applied by dissolving with water, 70 their diffusion ability to wood, being cheap and easy to supply, negligibly low toxicity effects 71 against mammals, and significantly increase the resistance of wood against burning (Thevenon et al. 1997, Williams 1980, Arthur and Quill 1992). However, their use has been limited only 72 73 indoors as they are easily washed from wood due to rain (Yalınkılıç 2000, Hafizoğlu et al. 74 1994). Yalınkılıç et al. (1998) investigated fire properties of Cryptomeria japonica wood impregnated with boric acid prior to vinyl monomers treatment. Styren and methylmethacrylate 75 were used as vinyl monomers. They found that wood samples pre-impregnated with boric acid 76 77 generated remarkably lesser smoke, and bad smell almost disappeared during burning in comparison to wood treated with monomer only. Baysal (1994) reported that weight loss of 78 79 Calabrian pine wood borate pre-impregnated and then water repellent chemicals treatment were 80 lower than un-impregnated and only water repellent chemicals treated wood after fire test. 81 Yalınkılıc *et al.* (1996) determined that Douglas wood treated with a boric acid (BA) + borax 82 (BX) mixture (7: 3; weight: weight) had higher fire retardant properties than wood treated with BA or BX. Yalınkılıç (2000) investigated BA, BX and their mixtures (BA+BX, 5: 1, w/w) were 83 84 added to a urea formaldehyde adhesive during chipboard production from waste tea leaves. The 85 fire test results showed that BA shortened the flash time while BX extended it, and the mixture 86 of these borates increased the overall fire retardant effectiveness. Baysal et al. (2007) 87 investigated weight loss of Scots pine impregnated with BA and BX mixture (5: 1;w/w) before 88 vinyl monomers such as styrene, methylmethacrylate, and their mixture (50: 50; 89 volume:volume) after fire test. They found that monomer treatment caused higher weight loss 90 when compared to untreated wood. However, BA and BX mixture pre-impregnation caused to 91 reduce mass loss of wood. Moreover, weight loss of BA and BX mixture impregnated and 92 styrene coated wood were lower than those of monomer only treated wood clarifying the 93 protective effect of boron in combustion.

Baysal (2002) studied fire retardancy of Scots pine wood impregnated with melamine formaldeyde (MF) and boron combinations. Oxygen index (OI), thermal gravimetric analysis (TGA), and differential thermal analysis (DTA) of Scots pine were investigated as fire tests. Results showed that Almost all MF–boron combinations reduced the decomposition temperature to lower levels than untreated wood and limited the exothermic reactions. GA residues increased linearly with the amount of boron addition.

100 Wood strength is affected when wood is treated with preservatives or fire retardant 101 chemicals (Winandy et al. 1988). The relative impact of various waterborne preservative 102 systems is directly related to the system's chemistry and the severity of its fixation/precipitation 103 reaction. Şimşek et al. (2013) investigated some mechanical properties such as compression 104 strength parallel to grain (CSPG), modulus of rupture (MOR), and modulus of elasticity (MOE) 105 of wood treated with some borates preservatives. Their results showed that CSPG, MOR, and 106 MOE of wood specimens treated with chemicals were lower than that of untreated control specimens. Preservative treatments caused the most decrease in MOR followed by CSPG and 107 108 MOE of both wood specimens, respectively. Winandy et al. (1988) noted that the effects of fire 109 retardant treatments on mechanical properties of Douglas-fir and aspen plywood. They found 110 that FR treatment did not affect modulus of elasticity (MOE) of both species, whereas it reduced the other mechanical properties. 111

Water repellent polymers or hydrophobic reagents and phenolic resins have been tried to reduce boron leachability and increase dimensional stability as well as providing high biological and fire resistance (Ryu *et al.* 1992, Peylo and Willeitner 1999, Su *et al.* 1997, Murphy *et al.* 1995, Yalınkılıç *et al.* 1996, Yalınkılıç *et al.* 1997a). It is well known that vinyl monomers contribute to dimensional stability and strength properties of wood and they are expected to provide a delayed leaching of boron from wood (Lutomski 1975). By adding bulk vinyl monomers to the void spaces in wood; compression strength, hardness, and abrasion

119 resistance greatly improved as well as dimensional stability (Meyer 1981). Yalınkılıç et al. 120 (1999) found that addition of boron to low formaldehyde reagents greatly increased both 121 biological resistance and dimensional stability. Fruno (1992) and Fruno et al. (1993) found that 122 the application of boron compounds such as boric acid, borax, boron trioxide, ammonium 123 borate, and potassium borate were investigated to produce insoluble organic substances in wood 124 by reacting with water glass by the acid treatment. As a result, it was recognized that the 125 utilization of the water glass-boron compound system made wood into a composite material 126 feasible having dimensional stability with less hygroscopicity as well as having fire resistance.

127 In this study, it was aimed to determine the strength properties of Oriental beech wood 128 coated with PUU (primed with epoxy resin and then coated with a polyurethane/polyurea hybrid 129 resin) and EPR (primed with epoxy resin) coated wood, and influence of FRs (boric acid, 130 borax, and ammonium sulfate) for increasing the fire resistance of wood. As well as PUU and 131 EPR coated wood have high mechanical properties, they are the materials having the low fire 132 properties. Thus, a dual treatment of wood with fire-retardands (FRs) impregnation and 133 followed by PUU and EPR coating may be of advantage in fire properties as well as mechanical 134 properties. Therefore, some mechanical properties such as MOR and CSPG and fire properties 135 such as weight loss and temprerature values of Oriental beech impregnated with FRs, and 136 PUU and EPR coated Oriental beech wood were studied.

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2. MATERIALS AND METHODS

139 **Preparation of test specimens**

Oriental beech (*Fagus orientalis* L.) wood was prepared in 20 mm x 20 mm x 360 mm,
20 mm x 20 mm x 30 mm, and 9 mm x 19 mm x 1016 mm (radial, tangential, and longitudional)
dimensions for MOR, CSPG, and fire tests, respectively.

144 *Impregnation procedure*

3 % aqueous solutions of boric acid (BA), borax (BX), boric acid and borax mixture (50
%; BA+BX), and ammonium sulfate were prepared to impregnate the Oriental beech wood
specimens. Oriental beech wood was impregnated according to ASTM D 1413-07 (ASTM 2007). Test specimens were left to diffuse in the solution at atmospheric pressure for 30 minutes
after a pre-vacuum of 760 mm Hg was applied for 30 minutes in the impregnation process. The
FRs retention of Oriental beech was calculated by the following equations (Eq.1-2):

151
$$R = \frac{G.C}{V} 10^3 \text{ (kg/m^3)}$$

- 152 Where;
- 153 $G=T_2 T_1$
- 154 Where;
- 155 $T_2 = Wood mass after impregnation (g)$
- 156 $T_1 =$ Wood mass before impregnation (g)
- 157 V = Wood volume (cm³)
- 158 C = Solution concentration (%)
- 159 *Coating procedure*

In this study, epoxy and polyurethane\polyurea hybrid resins were used for the coatings.
Firstly, an impregnation method was applied by using FRs which are boron chemicals and
ammonium sulfate before coating process. The structures of BA, BX and ammonium sulfate

- 163 (AS) are given in Figure 1a, 1b and 1c.
- 164

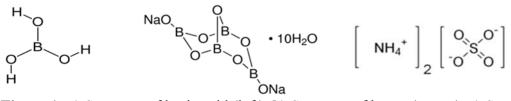


Figure 1: a) Structure of boric acid (left), b) Structure of borax (center), c) Structure of
 ammonium sulfate (right).

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(1)

(2)

While the impregnated test specimens were primed with epoxy resin (Sikafloor®-156) for the
EPR coatings, they were coated with polyurethane/polyurea hybrid resin (Sikalastic®-851 R)
to obtain the PUU coatings. PUU coatings were primed with epoxy resin (Sikafloor®-156)
before coating with polyurethane/polyurea hybrid resin (Sikalastic®-851 R).

172During the study, epoxy coated specimens are labelled as EPR and173polyurethane\polyurea coated specimens are labelled as PUU, as well.

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175 EPR Coatings

Sikafloor®-156 resin obtained from Sika company in Turkey was used as an epoxy resin for EPR coatings. Sikafloor®-156 is well-known as an epoxy primer with two ingredients, which is consists of an epoxy part (A) and a hardener part (B), low-viscosity and solvent-free. The mixtures were obtained from the epoxy and hardener with a 3:1 ratio of epoxy to hardener as follows the manufacturer's instruction. Then they were applied to the wood specimens which are impregnated with FRs (boron chemicals and ammonium sulfate). The coating procedure for EPR is illustrated in Figure 2.

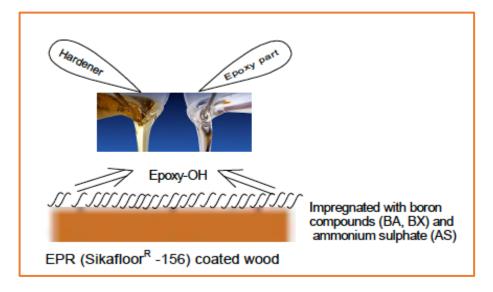


Figure 2: EPR coated wood.

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The possible cure reaction between an epoxy part and a hardener part is given in Figure 3. The hardeners are known the chemicals which are converted epoxy resin to thermosets, have usually bear active hydrogen attacted to an electronegative atom such as, N, O or S. The curing reaction is a ring opening reaction between the oxirane ring and a nucleophile (Figure 2b). The ring opening reaction occurs via nucleophilic attack by the hardener to the oxirane ring, then a second reaction follows until the remaining active hydrogens attached to the hardeners are fully reacted (Babahan *et al.* 2020).

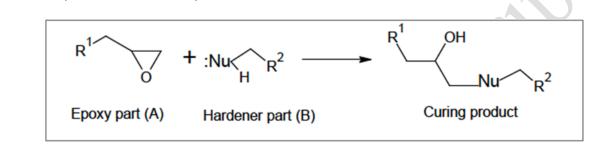


Figure 3: Possible curing reaction between epoxy part (A) and hardener part (B) for EPR
 coatings.

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197 PUU Coatings

Sikalastic[®]-851 R resin was used for PUU coatings. Sikalastic[®]-851 R is also obtained 198 199 from Sika company in Turkey. PUU coated by using Sikalastic[®]-851 R resin were made after 200 test specimens were primed with epoxy resin (Sikafloor[®]-156). Before primed with epoxy, an 201 impregnation process with boron chemicals and ammonium sulfate was applied to the wood specimens (Figure 4). The coating was done professionally by the manufacturer. Two layers 202 203 were applied to the floor using special polyurea coating machines (GAMA G-30 H) at a consumption of 1,7 kg - 2,2 kg per m² and the second layer application was started within 204 205 maximum 6 hours after the first layer application.

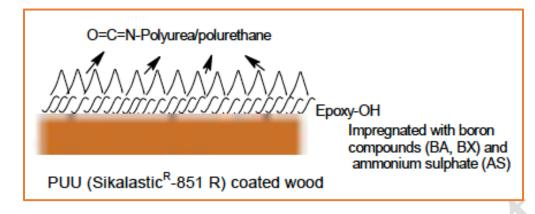
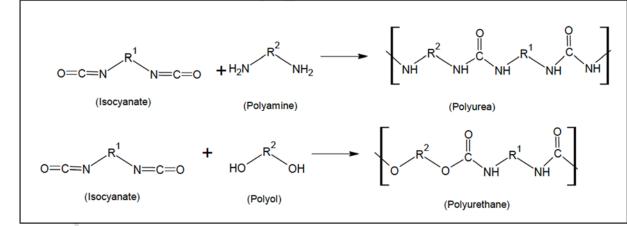


Figure 4: PUU coated wood.

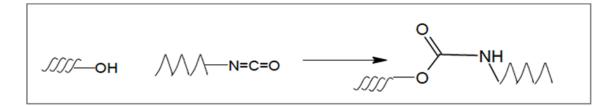
Sikalastic[®]-851 R is known as a two component hybrid resin. Component A consists of isocyanate deritavite and component B consists of polyol/amine derivatives. The reaction between isocyanate and a mixture of polyols and polyamines is given Figure 5. A polyurethane is occured by the reaction of an isocyanate and a polyol. A polyurea is occured by the reaction between an isocyanate and an amine. PUU coating is a hybrid coating, a mixture of polyurethanes and polyureas. Hybrids are unique options for the largest range of applications, as they have superior performance, moisture insensitivity, and low cost.



216 217

- Figure 5: The reaction between isocyanate and a mixture of polyols and polyamines.
- 218

The new interfacial chemical reaction between Sikafloor®-156 and Sikalastic®-851 R on the surface of PUU coatings based on an epoxy-urea bond is occured (Figure 6). Polyurea/polyurethane and epoxy moieties are formed an epoxy-urea bond (Attard *et al.* 2019).



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Figure 6: Reaction between epoxy and polyurea/polyurethane moieties.

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226 Modulus of rupture (MOR)

The modulus of rupture (MOR) of wood specimens was determined according to TS 2474 (TS 1976). A total of 110 wooden materials were prepared, 10 from each specimen group, with dimensions of 20 mm x 20 mm x 360 mm. Wood specimens had been conditioned at 20°C and 60% RH for 6 weeks prior to testing. The MOR of wood specimens was calculated using the following formula (Eq. 3);

232

233 MOR=
$$\frac{3XPX1}{2XhXh2}$$
 (MPa)

Where;

- 235 **P** is the maximum load (N)
- 236 *I* is span (mm),
- 237 **b** is width of specimen (mm),
- 238 *h* is thickness of specimen (mm).
- 239

240 Compression strength parallel to grain (CSPG)

The compression strength parallel to grain test was determined according to the TS 2595 (TS 1977) standard by using a 4000-kp capacity universal test machine, and applying 6 mm/min loading time. A total of 110 wooden materials were prepared, 10 from each specimen group, with dimensions of 20 mm x 20 mm x 30 mm. Before tests, wood specimens had been condi-

tioned at 20 $^{\circ}$ C and 60 $^{\circ}$ RH for 6 weeks.

(3)

246 Fire test

247 The fire test was performed according to ASTM E 69 (ASTM 1975). A total of 55 248 wooden materials were prepared, 5 from each specimen group, with dimensions of 9 mm x 19 249 mm x 1016 mm. Butane gas was used to make the ignition flame. The gas flow was kept 250 standard with the flame 25 cm high, and the temperature was held at 100 °C. Before the fire 251 test, wood specimens had been conditioned at 20 °C and 60 percent relative humidity (RH) for 252 6 weeks. During the test, mass loss and temperature values were measured every 30 seconds. 253 Average mass loss and temperature readings were obtained 10 minutes after the flame source 254 was taken away. The mass losses of test specimens after fire test were calculated from the following equation (4): 255

256

257 Mass losses =
$$\frac{Mbf - Maf}{Wbf} x100$$
 (4)

258 Where;

259 *Mbf* is the mass (g) of a wood specimen before fire test,

260 *Maf* is the mass (g) of a wood specimen after fire test.

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262 Statistical evaluation

Test results were analysed by a computerized SPSS statistical program (Statistics 2019) include analysis of variance and Duncan test applied at 95 % confidence level. Statistical evaluations were made on homogeneity groups (HG) where different letters reflected statistical significance.

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RESULTS AND DISCUSSION

272 MOR and CSPG of Oriental beech

273 The MOR values of Oriental beech wood impregnated with FRs and coated with PUU and EPR are given in Table 1. The highest MOR value was obtained as 131,48 N/mm² for PUU 274 275 coated Oriental beech wood. MOR values of PUU coated Oriental beech were higher than that 276 of EPR coated Oriental beech wood. Moreover, MOR values of PUU and EPR coated Oriental beech were higher than that of un-treated and non-coated (control) Oriental beech wood. 277 278 Results showed significant improvements in the modulus of rupture with using the coated polymer consist of polyurethane and polyurea (PUU). PUU (Sikalastic[®]-851 R) is a mixture 279 280 resin of an isocyanate and a polyol/amine derivatives.

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Table 1: MOR values of Oriental beech wood impregnated with FRs and coated with PUU
 and EPR.

and Er K.									
FRs and coating Retention		MOR	Standard	Homogeneity	Percentage				
materials	(kg/m^3)	(MPa)	deviation	group	change compare				
			X		to control				
			1						
Control	-	116,29	10,30	BCD	-				
(un-treated and	X								
non-coated)									
PUU		131,48	17,05	А	(+)13,06				
BA+ PUU	12,16	121,96	17,69	AB	(+)4,87				
BX+ PUU	11,37	124,39	13,33	AB	(+)6,96				
AS+ PUU	8,19	124,49	16,22	AB	(+)7,05				
(BA+BX)+PUU	15,02	123,82	13,51	AB	(+)6,47				
EPR	-	120,75	3,08	AB	(+)3,83				
BA+ EPR	16,84	116,45	4,05	BCD	(+)0,13				
BX+ EPR	16,88	117,85	2,32	BCD	(+)1,34				
AS+EPR	11,33	116,39	11,03 BCD		(+)0,08				
(BA+BX)+EPR	11,23	116,33	11,69	BCD	(+)0,03				
Note: PUU: Polyurethane/Polyurea hybrid resin (Sikalastic®-851 R), EPR: Epoxy resin (Sikafloor®-156), BA:									
Boric acid, BX: Borax, AS: Ammonium sulfate.									
Ten replicates were made for each group. Homogeneity group was realized at 95 % confidence level.									

The isocyanates are particularly reactive and the urethanes can form bonds with the hydroxyls in the wood surface. Polyols and amines also can make H bonding with the wood surface. Changes can be produced in the wood, with the biodegradable cellulose hydroxyls being replaced by isocyanates. That a small quantity of isocyanates can react with the cellulose hydroxyls to give covalent bonds (Pommier and Elbez 2006) increases the modulus of rupture (MOR).

Results showed that FRs treatment before PUU and EPR coatings decreased the MOR 291 292 values of Oriental beech than those of only PUU and EPR coated Oriental beech. For examle, 293 MOR of only PUU and EPR coated Oriental beech were 131,48 MPa and 120,75 MPa, 294 respectively, they were decreased from 118,41 MPa to 124,49 MPa and 116,33 MPa to 117,85 295 MPa for FRs impregnated and PUU and EPR coated Oriental beech, respectively. As, 296 treatments with boron derivatives before PUU and EPR coatings increase the rate of hydrolysis 297 in the wood, MOR levels of PUU and EPR coatings are lower (Toker et al. 2008). There was a statistically significant difference in MOR values between PUU coated Oriental beech and un-298 299 treated and non-coated (control) group. However, no statistically significant difference in MOR 300 values between only PUU coated Oriental beech and FRs impregnated and PUU coated 301 Orientral beech. Yalınkılıç et al. (1999) investigated MOR values of borate impregnated and 302 vinyl monomers coated wood. They used boric acid, borax, and theirs mixture as borates. 303 Styrene which is derivative of benzene (ST), methylmetacrylate which is methyl ester of 304 methacrylic acid (MMA) and theirs mixture were used as a vinyl monomers. They were found 305 that styrene and methylmethacrylate mixture was the most effective monomer followed by ST 306 and MMA in increasing MOR levels of wood. It was found that wood specimens pre-treated 307 with BA and BX mixture (boron derivatives) generated lesser MOR levels than that of without 308 BA and BX mixture pre-treament. Baysal et al. (2007) investigated MOR of Scots pine pre-309 treated with boric acid (BA) and borax (BX) mixture prior to vinyl monomer coating. Styrene,

310	methylmethacrylate, and their mixture (50: 50; volume: volume) were used as vinyl monomers.
311	It was found that vinyl monomers considerably improved MOR of Scots pine than that of un-
312	treated control specimens. MOR of only vinyl monomers coated Scots pine were higher tan
313	pre-treated with BA and BX mixture and then coated vinyl monomers coated Scots pine. Geçer
314	et al. (2015) investigated MOR levels of wood polymer composites (WPCs) were prepared by
315	styrene (ST) and different boron compounds impregnated sapwood of Oriental beech (Fagus
316	orientalis) Boric acid (BA), Borax (BX) and their mixture (1:1; w/w) aqueous solutions at 0,25
317	%, 1,00 %, and 4,70 % concentrations were prepared and then impregnated into wood prior to
318	styrene treatment. The MOR levels of WPCs pre-impregnated with borates were decreased to
319	some extent. It can be said that boric acid and borax mixture pretreatment increased the rate of
320	hydrolysis in the wood, thereby causing loss in strength (Toker et al. 2008). Our results are
321	compatible with these researchers' findings.

322The CSPG values of Oriental beech wood impregnated with FRs and coated with323PUU and EPR are given in Table 2.

325	Table 2: CSPG values of	Oriental beech wood impregnated with FRs and coated with PUU
326	and EPR.	

FRs and coating	Retention	CSPG	Standard	Homogeneity	Percentage					
materials	(kg/m^3)	(MPa)	deviation	group	change compare					
					to control					
Control (un-		61,71	7,64	С	-					
treated and non-										
coated)										
PUU	-	79,63	2,93	А	(+)29,03					
BA+ PUU	13,36	68,19	4,44	CDEF	(+)10,50					
BX+PUU	15,54	67,99	3,20	В	(+)10,17					
AS+PUU	12,11	66,41	5,79	FG	(+)7,61					
(BA+BX)+PUU	10,56	66,15	4,19	FG	(+)7,19					
EPR	-	65,97	6,22	FG	(+)6,90					
BA+ EPR	11,53	62,13	6,40	CD	(+)0,68					
BX+ EPR	15,50	61,98	9,09	С	(+)0,43					
AS+EPR	13,60	61,82	3,96	С	(+)0,17					
(BA+BX)+EPR	62,49	1,92	CD	(+)1,26						
Note: PUU: Polyurethane/Polyurea hybrid resin (Sikalastic [®] -851 R), EPR: Epoxy resin (Sikafloor [®] -156), BA: Boric acid, BX: Borax, AS: Ammonium sulfate. Ten replicates were made for each group. Homogeneity group was realized at 95 % confidence level.										

The highest CSPG value was obtained as 79,63 MPa for PUU coated Oriental beech 328 329 wood. There were statistically significant difference in CSPG values between un-treated and 330 non-coated (control) group and PUU coated Oriental beech. CSPG values of PUU coated Oriental beech were also higher than that of EPR coated Oriental beech wood. Moreover, CSPG 331 332 values of PUU and EPR coated Oriental beech were higher than that of un-treated and non-333 coated (control) group. Results showed that FRs treatment before PUU and EPR coating 334 decreased the CSPG values of Oriental beech than those of only PUU and EPR coated Oriental beech. For example, CSPG of only PUU and EPR coated Oriental beech were 79,63 MPa and 335 336 65,97 MPa, respectively, they were changed from 61,82 MPa to 68,19 MPa for FRs 337 impregnated and PUU and EPR coated Oriental beech, respectively. It may be due to the fact that waterborne preservative formulations do react with the cell wall components by undergoing 338 339 hydrolytic reduction upon contact with wood sugars. This process, known as fixation, oxidizes 340 the wood cell wall components and may reduce wood strength (Winandy et al. 1988). There 341 was a statistically significant difference in CSPG values between PUU coated Oriental beech 342 and un-treated and non-coated (control) group. Our results showed that there was a statistically significant difference in CSPG values between PUU coated Oriental beech and FRs 343 344 impregnated and PUU coated Oriental beech. Also, there was a statistically significant 345 difference in CSPG values between EPR coated Oriental beech and FRs impregnated and EPR 346 coated Oriental beech. Gecer et al. (2015) investigated CSPG values of Oriantal beech wood 347 impregnated with borates and than coated with styrene. Results showed that wood specimens only styrene impregnated generated higher CSPG level (887 kg·cm⁻²) than that of borates pre-348 impregnated and styrene coated Oriental beech (814 kg·cm⁻² - 860 kg·cm⁻²). Also, there is a 349 350 statistical difference between styrene only impregnated wood specimens and borates pre-351 impregnated and styrene coated oriental beech. Our results are in good agreement with data 352 Geçer et al. (2015). Winandy (1995) determined that there appears to be a little relative

353	difference in their effect on strength when retention levels of chemicals were between 4.0 kg/m^3
354	and 9,6 kg/m ³ . Mourant et al. (2008) reported that wood samples with salts retention values
355	ranging from 24 kg/m ³ to 40 kg/m ³ had a significantly lower than the untreated control samples.
356	According to our results, retention values of MOR wood specimens were changed from 8,19
357	kg/m ³ to 16,88 kg/m ³ and while FRs treatment decreased from 5,31 % to 7,24 % MOR of FRs
358	treated and PUU coated Oriental beech, it decreased 2,40 % to 3,66 % (Table 3).
359	

Table 3: Percentage MOR changes of FRs impregnated and PU/EPR coated Oriental beech
 wood compared to only PUU or EPR coating.

FRs and coating	MOR	Percentage change compare to only PUU				
materials	(MPa)	or EPR coating				
PUU	131,48					
BA+ PUU	121,96	(-)7,24				
BX+ PUU	124,39	(-)5,39				
AS+ PUU	124,49	(-)5,31				
(BA+BX)+PUU	123,82	(-)5,82				
EPR	120,75	-				
BA+ EPR	116,45	(-)3,56				
BX+ EPR	117,85	(-)2,40				
AS+EPR	116,39	(-)3,61				
(BA+BX)+EPR	116,33	(-)3,66				
Note: PUU: Polyurethane/Polyurea hybrid resin (Sikalastic [®] -851 R), EPR: Epoxy resin (Sikafloor [®] -156), BA: Boric acid, BX: Borax, AS: Ammonium sulfate.						

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Retention values of CSPG wood specimens were changed from 10,56 kg/m³ to 15,54 kg/m³ and while FRs treatment decreased from 14,36 % to 16,92 % CSPG of FRs treated and PUU coated Oriental beech, it decreased from 5,27 % to 6,29 % CSPG of Oriental beech impregnated with FRs and EPR coated Oriental beech (Table 4). The National Forest Products Association (NFPA) (1973) recommends that the allowable stresses for fire-retardant treated wood for design purposes be reduced by 10 % as

369 compared to untreated wood; the allowable loads for fasteners are also reduced by 10 %. Also,

- 370 it requires a 10 % to 20 % reduction in allowable design stress, depending on mechanical
- 371 property under consideration (NFPA 1986). Generally, our results met the NFPA requirements.
- 372
- Table 4: Percentage CSPG changes of FRs impregnated and PU/EPR coated Oriental beech
 wood compared to only PUU or EPR coating.

1 ,	0					
FRs and coating	CSPG	Percentage change compare to PUU/EPR				
materials	(MPa)	coating				
PUU	79,63	_				
BA+ PUU	68,19	(-)14,36				
BX+PUU	67,99	(-)14,61				
AS+PUU	66,41	(-)16,60				
(BA+BX)+PUU	66,15	(-)16,92				
EPR	65,97					
BA+ EPR	62,13	(-)5,82				
BX+ EPR	61,98	(-)6,04				
AS+EPR	61,82	(-)6,29				
(BA+BX)+EPR	62,49	(-)5,27				
Note: PUU: Polyurethane/Polyurea hybrid resin (Sikalastic [®] -851 R), EPR: Epoxy resin (Sikafloor [®] -156), BA: Boric acid, BX: Borax, AS: Ammonium sulfate.						

376 Fire properties of Oriental beech

Weight loss and temperature values of Oriental beech impregnated with FRs and coated with PUU and EPR after fire test are given in Table 5.

379 Weight loss and temperature values of PUU coated Oriental beech were higher than that of EPR

380 coated Oriental beech wood. The highest weight loss and temperature values were obtained for

381 PUU coated Oriental beech wood. Polyurethane resins are known as highly cellular polymers,

382 are easily ignitable and highly flammable. This knowledge explains why PUU coated woods

383 have higher weight loss during fire tests. The flammability of polyurethanes has long been a

- 384 factor that limits their greater uses. FRs impregnation before PUU and EPR coatings caused to
- 385 lower weight loss and temperature values than those of only PUU and EPR coated Oriental
- 386 beech wood. PUU and EPR coatings caused higher weight loss when compared to un-treated
- 387 and non-coated (control) group. However, FRs impregnation before PUU and EPR coatings

played an important role in reducing weight loss of wood. Moreover, weight loss of Oriental beech FRs impregnated before PUU and EPR coating were lower than those of only PUU and EPR coated Oriental beech wood clarifying the protective effect of FRs in combustion. These findings are consistent with earlier reports on the weight loss of un-treated and boron–vinyl monomer combination-treated wood (Ayrılmış *et al.* 2005). In other words, wood became more difficult to ignite and more oxygen was needed to burn the treated materials as consistent to the effect of boron reported earlier (Wen-Yu 1997).

Table 5: Weight loss and tempreture values of FRs impregnated and PU/EPR coated Oriental
 beech after fire test.

FRs and caoting materials	Retention (kg/m ³)	Weight loss	Standard deviation	Homogeneity group	Percentage change compare	Temperature values (°C)	Standard deviation	Homogeneity group	Percentage change compare
		(%)			to control		>		to control
Control (un- treated and non- coated)	-	83,26	2,66	AB		292,55	77,95	А	-
PUU	-	86,24	2,41	А	(+)3,57	308,28	126,33	А	(+)5,37
BA+ PUU	15,75	82,69	0,66	AB	(-)0,68	152,15	60,30	CD	(-)47,99
BX+ PUU	13,66	84,97	0,41	A	(+)2,05	155,46	20,52	CD	(-)46,86
AS+ PUU	15,51	84,13	1,39	AB	(+)1,04	175,04	32,46	BC	(-)40,16
(BA+BX)+PUU	15,33	83,80	0,94	AB	(+)0,64	129,76	23,82	D	(-)55,64
EPR	-	85,62	2,10	A	(+)2,83	298,78	72,32	А	(+)2,12
BA+ EPR	15,12	71,05	0,95	С	(-)14,66	199,00	87,02	В	(-)31,97
BX+ EPR	13,85	73,83	1,24	С	(-)11,32	250,15	115,02	А	(-)14,49
AS+EPR	15,28	73,57	4,93	С	(-)11,63	260,49	98,67	А	(-)10,95
(BA+BX)+EPR	15,02	69,89	2,05	С	(-)16,05	164,76	21,25	С	(-)43,68
Note: PUU: Polyurethane/Polyurea hybrid resin (Sikalastic [®] -851 R), EPR: Epoxy resin (Sikafloor [®] -156), BA: Boric acid, BX: Borax, AS:									

Note: PUU: Polyurethane/Polyurea hybrid resin (Sikalastic[®]-851 R), EPR: Epoxy resin (Sikafloor[®]-156), BA: Boric acid, BX: Borax, Al Ammonium sulfate. Ten replicates were made for each group. Homogeneity group was realized at 95 % confidence level.

397

398 Moreover, boron compounds (H₃BO₃ (BA) and Na₂B₄O₇.10H₂O (BX); Figures 1a,b)

399 used as fire retardant chemicals in this study dehydrates above 75 °C to metaboric acid (HBO₂) 400 and finally boric oxide occurs, thereby generating water, which acts as a heat sink and dilutes 401 oxygen and flammable gases (Wang 2016). There was no statistically significant difference in 402 weight loss values and temperature values between PUU and EPR coated Oriental beech and 403 un-treated and non-coated (control) group. While, there was a statistically significant difference in weight loss values between EPR coated Oriental beech and FRs impregnated and EPR coated
Oriental beech, there was no statistically significant difference in weight loss between PUU
coated Oriental beech and un-treated and non-coated (control) group.

407 Baysal et al. (2003) found that the weight loss of Ailanthus altissima wood pre-408 impregnated with boric acid before styrene coating was reduced approximately 5% - 6% levels 409 compare to only styrene coated Ailanthus altissima wood. Another study, Yalınkılıc et al. 410 (1997b) determined the fire properties of particleboard made from waste tea leaves which boric 411 acid and borax added to ureaformaldehyde adhesive. Fire test results showed that boron-412 monomer combination treatment may be of advantage in fire-resistance. Baysal et al. (2007) 413 studied fire properties of wood polymer composite (WPC) was obtained by vinyl monomers 414 such as styrene (ST), methlmethacrylate (MMA), and their mixture (50:50; volume: volume) 415 of treated sapwood of Scots pine (Pinus sylvestris.). Boric acid (BA) and borax (BX) mixture 416 was impregnated into wood at 1% concentration prior to monomer treatment. They found that borate impregnation before monomer treatment improved fire properties of WPC. Atar and 417 418 Keskin (2007) investigated the combustion properties of Uludağ fir wood, which was varnished 419 after being impregnated with boron compounds. For this purpose, test samples prepared from 420 Uludağ fir wood were impregnated with boric acid and borax. After impregnation, the surfaces 421 are covered with cellulosic, synthetic, polyurethane, water-based, acrylic and acid hardening 422 varnishes. As a result, they determined that the process of impregnation with boron compounds 423 before varnishing reduces the burning temperature of wood. Atar (2008) investigated the 424 combustion properties of oak wood impregnated with boron compounds and then varnished. 425 The impregnated test samples were prepared from oak wood (Quercus petreae) with boric acid 426 and borax. After the impregnation process, it was coated with cellulosic, synthetic, 427 polyurethane, water-based, acrylic and acid hardening varnishes. As a result, it has been

428 determined that impregnation of wood material with boron compounds before varnishing429 reduces the burning temperature. Our results were compatible with these researchers findings.

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- 431

CONCLUSIONS

432 Some mechanical, and fire properties of Oriental beech impregnated with FRs and PUU433 and EPR coated Oriental beech were studied.

Results showed that while caoting with PUU and EPR improved MOR and CSPG values of Oriental beech than that of un-treated and non-coated (control) group, it showed negative effect on fire properties of Oriental beech. MOR and CSPG values of PUU coated Oriental beech were higher than that of EPR coated Oriental beech. FRs treatment before PUU and EPR coatings resulted in to decrease MOR and CSPG values of Oriental beech. Results showed that FRs pre-treatment was combined with PUU and EPR coatings to enhance fire properties of Oriental beech.

In conclusion, Oriental beech impregnated with FRs before PUU and EPR coatings enhanced fire properties. They caused lower weight loss and temperature values of FRs impregnated and PUU and EPR coated Oriental beech than un-treated and non-coated (control) group. However, they caused to lower MOR and CSPG of Oriental beech. PUU and EPR coated wood is an alternative structural material for exterior use, where high mechanical properties required. But, these products have low fire properties. Thus, FRs impregnataion before PUU and EPR coatings of wood will provide improvements fire properties of the wood.

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ACKNOWLEDGEMENTS

450 This manuscript was prepared from some results of the Phd thesis of Çağlar ALTAY,
451 who is studying for a doctorate in Woodworking Industrial Engineering at Muğla Sıtkı Koçman

- 452 University Institute of Science. This study is supported by the Scientific Research Project BAP-
- 453 20/099/01/2.
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