MECHANICAL AND FIRE PROPERTIES OF ORIENTAL BEECH IMPREGNATED WITH FIRE-RETARDANTS AND COATED WITH POLYUREA/POLYURETHANE HYBRID AND EPOXY RESINS

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ABSTRACT

This study was performed to investigate some mechanical properties such as modulus of rupture and compression strength parallel to grain and some fire properties such as weight loss and temperature values of Oriental beech (\textit{Fagus orientalis}) treated with fire-retardants 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 method was applied by using fire-retardants which are boron chemicals and ammonium sulfate 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 primed with epoxy resin by using Sikafloor\textsuperscript{®}-156, and then coated with Sikalastic\textsuperscript{®}-851, a polyurethane/polyurea hybrid resin. Results showed that modulus of rupture and compression strength parallel to grain values of polyurethane/polyurea and epoxy resin coated Oriental beech wood were higher than that of un-treated and non-coated (control) group. Fire-retardants treatment before polyurethane/polyurea and epoxy resin coatings caused to decrease modulus of rupture and compression strength parallel to grain values of Oriental beech in some extent. Weight loss and temprature values of polyurethane/polyurea and epoxy resin coated Oriental beech were higher than that of un-treated and non-coated (control) group. However, fire-retardants treatment before polyurethane/polyurea and epoxy resin coatings improved fire properties of Oriental beech wood.

Keywords: Boron compounds, epoxy resin, fire retardants, 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).

The fire retardant effectiveness of boron compounds is a physical mechanism achieved by the formation of a coating or protective layer on the wood surface at high temperature, and 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 have found many application areas in the wood preservation industry in order to get the benefit 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 little effect on flame spread (LeVan and Tran 1990).

Many of the effective chemicals, which are used for wood protection, are questionable because they are poisonous chemicals. Boron compounds have become up-to-date due to their high activity against biological pests, their ability to be easily applied by dissolving with water, their diffusion ability to wood, being cheap and easy to supply, negligibly low toxicity effects 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 indoors as they are easily washed from wood due to rain (Yalınkılıç 2000, Hafızoğlu et al. 1994). Yalınkılıç et al. (1998) investigated fire properties of Cryptomeria japonica wood impregnated with boric acid prior to vinyl monomers treatment. Styren and methylmethacrylate were used as vinyl monomers. They found that wood samples pre-impregnated with boric acid 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 Calabrian pine wood borate pre-impregnated and then water repellent chemicals treatment were lower than un-impregnated and only water repellent chemicals treated wood after fire test. Yalınkılıç et al. (1996) determined that Douglas wood treated with a boric acid (BA) + borax (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 added to a urea formaldehyde adhesive during chipboard production from waste tea leaves. The fire test results showed that BA shortened the flash time while BX extended it, and the mixture of these borates increased the overall fire retardant effectiveness. Baysal et al. (2007) investigated weight loss of Scots pine impregnated with BA and BX mixture (5: 1; w/w) before vinyl monomers such as styrene, methylmethacrylate, and their mixture (50: 50; volume:volume) after fire test. They found that monomer treatment caused higher weight loss when compared to untreated wood. However, BA and BX mixture pre-impregnation caused to reduce mass loss of wood. Moreover, weight loss of BA and BX mixture impregnated and styrene coated wood were lower than those of monomer only treated wood clarifying the protective effect of boron in combustion.

Baysal (2002) studied fire retardancy of Scots pine wood impregnated with melamine formaldehyde (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.

Wood strength is affected when wood is treated with preservatives or fire retardant chemicals (Winandy et al. 1988). The relative impact of various waterborne preservative systems is directly related to the system’s chemistry and the severity of its fixation/precipitation reaction. Şimşek et al. (2013) investigated some mechanical properties such as compression strength parallel to grain (CSPG), modulus of rupture (MOR), and modulus of elasticity (MOE) of wood treated with some borates preservatives. Their results showed that CSPG, MOR, and 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 MOE of both wood
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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 resistance greatly improved as well as dimensional stability (Meyer 1981). Yalınkılıç et al. (1999) found that addition of boron to low formaldehyde reagents greatly increased both biological resistance and dimensional stability. Fruno (1992) and Fruno et al. (1993) found that the application of boron compounds such as boric acid, borax, boron trioxide, ammonium borate, and potassium borate were investigated to produce insoluble organic substances in wood by reacting with water glass by the acid treatment. As a result, it was recognized that the utilization of the water glass-boron compound system made wood into a composite material feasible having dimensional stability with less hygroscopicity as well as having fire resistance.

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

MATERIALS AND METHODS

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 longitudinal) dimensions for MOR, CSPG, and fire tests, respectively.

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-e1 (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 (Equation 1 and Equation 2):

\[ Retention (kg / m^3) = \frac{GC \times 10}{V} \]  
\[ G = T_2 - T_1 \]

Where;

\[ T_2 = \text{Wood mass after impregnation (kg)} \]
\[ T_1 = \text{Wood mass before impregnation (kg)} \]
\[ V = \text{Wood volume (m}^3\text{)} \]

\[ C = \text{Solution concentration (\%)} \]

**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 (AS) are given in Figure 1a, Figure 1b and Figure 1c.

![Figure 1](image)

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

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).

During the study, epoxy coated specimens are labelled as EPR and polyurethane/polyurea coated specimens are labelled as PUU, as well.

**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](image)

**Figure 2:** EPR coated wood.

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 attacked 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).

[Image: Possible curing reaction between epoxy part (A) and hardener part (B) for EPR coatings.]

**PUU coatings**

Sikalastic®-851 R resin was used for PUU coatings. Sikalastic®-851 R is also obtained from Sika company in Turkey. PUU coated by using Sikalastic®-851 R resin were made after test specimens were primed with epoxy resin (Sikafloor®-156). Before primed with epoxy, an 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 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 maximum 6 hours after the first layer application.

[Image: PUU coated wood.]

Sikalastic®-851 R is known as a two component hybrid resin. Component A consists of isocyanate derivatite 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.

[Image: The reaction between isocyanate and a mixture of polyols and polyamines.]
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 occurred (Figure 6). Polyurea/polyurethane and epoxy moieties are formed an epoxy-urea bond (Attard et al. 2019).

![Chemical Reaction](image)

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

**Modulus of rupture (MOR)**

The modulus of rupture (MOR) of wood specimens was determined according to TSE 2474 (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 (Equation 3).

\[
MOR(MPa) = \frac{3Pl}{2bh^2} \quad (3)
\]

Where;
- \(P\) is the maximum load (N)
- \(l\) is span (mm)
- \(b\) is width of specimen (mm)
- \(h\) is thickness of specimen (mm).

**Compression strength parallel to grain (CSPG)**

The compression strength parallel to grain test was determined according to the TSE 2595 (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 conditioned at 20 °C and 60 % RH for 6 weeks.

**Fire test**

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

\[
Mass \ losses = \frac{Mbf - Maf}{Wbf} \times 100 \quad (4)
\]
Where:

$M_{bf}$ is the mass (g) of a wood specimen before fire test

$M_{af}$ is the mass (g) of a wood specimen after fire test

**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.

**RESULTS AND DISCUSSION**

**MOR and CSPG of oriental beech**

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/mm$^2$ for PUU coated Oriental beech wood. MOR values of PUU coated Oriental beech were higher than that 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. 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 resin of an isocyanate and a polyol/amine derivatives.

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

| FRs and coating materials | Retention (kg/m³) | MOR (MPa) | Standard deviation | Homogeneity group | Percentage change compare to control |
|---------------------------|-------------------|-----------|--------------------|------------------|-------------------------------------|
| Control (un-treated and non-coated) | - | 116,29 | 10,30 | BCD | - |
| PUU | 12,16 | 131,48 | 17,05 | A | (+)13,06 |
| BA+PUU | 11,37 | 121,96 | 17,69 | AB | (+)4,87 |
| BX+PUU | 8,19 | 124,39 | 13,33 | AB | (+)3,96 |
| AS+PUU | 15,02 | 124,49 | 16,22 | AB | (+)7,05 |
| (BA+BX)+PUU | 120,75 | 123,82 | 13,51 | AB | (+)6,47 |
| EPR | 16,84 | 116,45 | 4,05 | BCD | (+)0,13 |
| BA+EPR | 16,88 | 117,85 | 2,32 | BCD | (+)1,34 |
| BX+EPR | 11,33 | 116,39 | 11,03 | BCD | (+)0,08 |
| AS+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 values of Orien-
tal beech than those of only PUU and EPR coated Oriental beech. For example, MOR of only PUU and EPR coated Oriental beech were 131.48 MPa and 120.75 MPa, respectively, they were decreased from 118.41 MPa to 124.49 MPa and 116.33 MPa to 117.85 MPa for FRs impregnated and PUU and EPR coated Oriental beech, respectively. As, treatments with boron derivatives before PUU and EPR coatings increase the rate of hydrolysis 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-treated and non-coated (control) group. However, no statistically significant difference in MOR values between only PUU coated Oriental beech and FRs impregnated and PUU coated Oriental beech. Yalınkılıç et al. (1999) investigated MOR values of borate impregnated and vinyl monomers coated wood. They used boric acid, borax, and theirs mixture as borates. Styrene which is derivative of benzene (ST), methylmetacrylate which is methyl ester of methacrylic acid (MMA) and theirs mixture were used as a vinyl monomers. They were found that styrene and methylemethacrylate mixture was the most effective monomer followed by ST and MMA in increasing MOR levels of wood. It was found that wood specimens pre-treated with BA and BX mixture (boron derivatives) generated lesser MOR levels than that of without BA and BX mixture pre-treatment. Baysal et al. (2007) investigated MOR of Scots pine pre-treated with boric acid (BA) and borax (BX) mixture prior to vinyl monomer coating. Styrene, methylmethacrylate, and their mixture (50: 50; volume: volume) were used as vinyl monomers. It was found that vinyl monomers considerably improved MOR of Scots pine than that of un-treated control specimens. MOR of only vinyl monomers coated Scots pine were higher than pre-treated with BA and BX mixture and then coated vinyl monomers coated Scots pine. Geçer et al. (2015) investigated MOR levels of wood polymer composites (WPCs) were prepared by styrene (ST) and different boron compounds impregnated sapwood of Oriental beech (Fagus orientalis) Boric acid (BA), Borax (BX) and their mixture (1:1; w/w) aqueous solutions at 0.25 %, 1.00 %, and 4.70 % concentrations were prepared and then impregnated into wood prior to styrene treatment. The MOR levels of WPCs pre-impregnated with borates were decreased to some extent. It can be said that boric acid and borax mixture pretreatment increased the rate of hydrolysis in the wood, thereby causing loss in strength (Toker et al. 2008). Our results are compatible with these researchers’ findings.

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

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

| FRs and coating materials | Retention (kg/m³) | CSPG (MPa) | Standard deviation | Homogeneity group | Percentage change compare to control |
|--------------------------|-------------------|------------|--------------------|-------------------|--------------------------------------|
| Control (untreated and non-coated) | - | 61.71 | 7.64 | C | - |
| PUU | - | 79.63 | 2.93 | A | (+)29.03 |
| BA+ PUU | 13.36 | 68.19 | 4.44 | CDEF | (+)10.50 |
| BX+PUU | 15.54 | 67.99 | 3.20 | B | (+)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 | C | (+)0.43 |
| AS+EPR | 13.60 | 61.82 | 3.96 | C | (+)0.17 |
| (BA+BX)+EPR | 14.23 | 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 wood. There were statistically significant difference in CSPG values between un-treated and 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 values of PUU and EPR coated Oriental beech were higher than that of un-treated and non-coated (control) group. Results showed that FRs treatment before PUU and EPR coating 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 65.97 MPa, respectively, they were changed from 61.82 MPa to 68.19 MPa for FRs 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 hydrolytic reduction upon contact with wood sugars. This process, known as fixation, oxidizes the wood cell wall components and may reduce wood strength (Winandy et al. 1988). There was a statistically significant difference in CSPG values between PUU coated Oriental beech 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 impregnated and PUU coated Oriental beech. Also, there was a statistically significant difference in CSPG values between EPR coated Oriental beech and FRs impregnated and EPR coated Oriental beech. Geçer et al. (2015) investigated CSPG values of Oriental beech wood 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-impregnated and styrene coated Oriental beech (814 kg·cm⁻² - 860 kg·cm⁻²). Also, there is a statistical difference between styrene only impregnated wood specimens and borates pre-impregnated and styrene coated oriental beech. Our results are in good agreement with data Geçer et al. (2015). Winandy (1995) determined that there appears to be a little relative difference in their effect on strength when retention levels of chemicals were between 4.0 kg/m³ and 9.6 kg/m³. Mourant et al. (2008) reported that wood samples with salts retention values ranging from 24 kg/m³ to 40 kg/m³ had a significantly lower than the untreated control samples. According to our results, retention values of MOR wood specimens were changed from 8.19 kg/m³ to 16.88 kg/m³ and while FRs treatment decreased from 5.31 % to 7.24 % MOR of FRs treated and PUU coated Oriental beech, it decreased 2.40 % to 3.66 % (Table 3).

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 materials | MOR (MPa) | Percentage change compared to only PUU 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.

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 1993) recommends that the allowable stresses for fire-retardant treated wood for design purposes be reduced by 10 % as compared to untreated wood; the allowable loads for fasteners are also reduced by 10 %. Also, it requires a 10 % to 20 % reduction in allowable design stress, depending on mechanical property under consideration (NFPA 2017). Generally, our results met the NFPA requirements.
Table 4: Percentage CSPG changes of FRs impregnated and PU/EPR coated Oriental beech wood compared to only PUU or EPR coating.

| FRs and coating materials | CSPG (MPa) | Percentage change compared to PUU/EPR 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.

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.

Weight loss and temperature values of PUU coated Oriental beech were higher than that of EPR coated Oriental beech wood. The highest weight loss and temperature values were obtained for PUU coated Oriental beech wood. Polyurethane resins are known as highly cellular polymers, are easily ignitable and highly flammable. This knowledge explains why PUU coated woods have higher weight loss during fire tests. The flammability of polyurethanes has long been a factor that limits their greater uses. FRs impregnation before PUU and EPR coatings caused to lower weight loss and temperature values than those of only PUU and EPR coated Oriental beech wood. PUU and EPR coatings caused higher weight loss when compared to un-treated 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 temperature values of FRs impregnated and PU/EPR coated Oriental beech after fire test.

| FRs and coating materials | Retention (kg/m³) | Weight loss (%) | Standard deviation | Homogeneity group | Percentage change compared to control | Temperature values (°C) | Standard deviation | Homogeneity group | Percentage change compared to control |
|---------------------------|-------------------|-----------------|--------------------|-------------------|---------------------------------------|--------------------------|-------------------|-------------------|---------------------------------------|
| Control (un-treated and non-coated) | -                 | 83.26           | 2.66               | A                 | -                                    | 292.55                  | 77.95             | A                 | -                                    |
| PUU                       | -                 | 86.24           | 2.44               | A                 | (+3.57)                               | 308.28                  | 126.33            | A                 | (+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             | A                 | (+2.12)                               |
| BA+ EPR                   | 15.12             | 71.05           | 0.95               | C                 | (+14.66)                              | 199.00                  | 87.02             | B                 | (+31.97)                              |
| BX+ EPR                   | 13.85             | 73.83           | 1.24               | C                 | (+11.32)                              | 250.15                  | 115.02            | A                 | (+14.49)                              |
| AS+EPR                    | 15.28             | 73.57           | 4.93               | C                 | (+11.63)                              | 260.49                  | 98.67             | A                 | (+10.95)                              |
| (BA+BX)+EPR               | 15.02             | 69.89           | 2.05               | C                 | (+16.05)                              | 164.76                  | 21.25             | C                 | (+43.68)                              |

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.
Moreover, boron compounds ($H_3BO_3$ (BA) and $Na_2B_4O_7\cdot10H_2O$ (BX); Figure 1a, Figure 1b) used as fire retardant chemicals in this study dehydrates above 75 °C to metaboric acid ($HBO_2$) and finally boric oxide occurs, thereby generating water, which acts as a heat sink and dilutes oxygen and flammable gases (Wang 2016). There was no statistically significant difference in weight loss values and temperature values between PUU and EPR coated Oriental beech and 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.

Baysal et al. (2003) found that the weight loss of Ailanthus altissima wood pre-impregnated with boric acid before styrene coating was reduced approximately 5 % - 6 % levels compare to only styrene coated Ailanthus altissima wood. Another study, Yalınkılıç et al. (1997b) determined the fire properties of particleboard made from waste tea leaves which boric acid and borax added to ureaformaldehyde adhesive. Fire test results showed that boron–monomer combination treatment may be of advantage in fire-resistance. Baysal et al. (2007) studied fire properties of wood polymer composite (WPC) was obtained by vinyl monomers such as styrene (ST), methlmethacrylate (MMA), and their mixture (50:50; volume: volume) of treated sapwood of Scots pine ($Pinus sylvestris$). Boric acid (BA) and borax (BX) mixture 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 Keskin (2007) investigated the combustion properties of Uludağ fir wood, which was varnished after being impregnated with boron compounds. For this purpose, test samples prepared from Uludağ fir wood were impregnated with boric acid and borax. After impregnation, the surfaces are covered with cellulosic, synthetic, polyurethane, water-based, acrylic and acid hardening varnishes. As a result, they determined that the process of impregnation with boron compounds before varnishing reduces the burning temperature of wood. Atar (2008) investigated the combustion properties of oak wood impregnated with boron compounds and then varnished. The impregnated test samples were prepared from oak wood ($Quercus petreae$) with boric acid and borax. After the impregnation process, it was coated with cellulosic, synthetic, polyurethane, water-based, acrylic and acid hardening varnishes. As a result, it has been determined that impregnation of wood material with boron compounds before varnishing reduces the burning temperature. Our results were compatible with these researchers findings.

**CONCLUSIONS**

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

Results showed that while coating 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 impregnation before PUU and EPR coatings of wood will provide improvements fire properties of the wood.

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