Determination of the Properties of Medium-Density Fiberboards Produced Using Urea-Formaldehyde Resins Modified with Boron Compounds

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Effects of adding different boron compounds to the urea-formaldehyde resin were evaluated relative to the physical, mechanical, and other properties of medium-density fiberboard (MDF). While the chemical addition of boric acid to the urea-formaldehyde resin increased the modulus of rupture and modulus of elasticity values of MDF boards, the physical and chemical additions of other boron compounds decreased those values. While there were no significant decreases in internal bond values, the chemical addition of boric acid and borax decahydrate to urea-formaldehyde resin increased the internal bond values of MDF boards. It was observed that in both types of addition, borax pentahydrate reduced the formaldehyde emission values of MDF boards the most and also reduced the burnt area by up to 30%. When the type of addition of boron compounds to urea-formaldehyde was compared, the addition of boron compounds at the resin formation stage showed better results in the properties of MDF boards than physical addition.

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INTRODUCTION

Wood-based boards are materials obtained by pressing wood particles (fiber, chip, or particle) under certain temperatures and pressures *via* adding resin (Yıldırım 2019). Today, there are many types of wood-based boards with different properties that are produced industrially. Wood-based boards, wood composite boards, wood boards, veneer boards, particle boards, fiber boards, medium- and high-density boards (MDF and HDF), plywood, *etc*., are all well known. When MDF boards are compared with alternative materials, they have various advantages, such as economy, ease of use, homogeneous fiber distribution, smooth and uniform surface properties, and their production is increasing continually (Eroğlu and Usta 2000; Çöpür *et al.* 2008). In addition to their superior features, these boards also have disadvantages, such as fire hazards and formaldehyde gas emissions, which are harmful to health, and changes in size due to moisture intake (Roffael 2006; Özalp 2010).

Formaldehyde-based synthetic resins (urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde, melamine-urea formaldehyde, and isocyanate resin) are the most widely used binders in wood-based boards (Beram *et al.* 2021). Urea-formaldehyde resin, produced by the condensation of urea and formaldehyde, is one of the most used resins in wood-based board production in the world today (Pizzi 1994). Due to different preparation methods and reaction conditions, various urea-formaldehyde resins can be formed in liquid and solid form. Urea-formaldehyde resin has thermosetting properties and constitutes the most important group of amino-plastic resins (Dunky 1998). Urea-formaldehyde resin, which has excellent adhesion with lignocellulosic materials, has some advantages, such as being odorless, non-flammable, low cost, easy to prepare and apply, adjustable as an aqueous solution, compatible with various hardening conditions, and is transparent in the hardened state (Demirkır 2006). In addition, it has low resistance to water and moisture; however a key disadvantage is that it emits formaldehyde (Pizzi 1994; Dunky 1998).

Recently, studies on reducing formaldehyde emissions in board products, delaying combustion, and preventing swelling due to moisture have gained importance. It is known that different chemicals and/or nano-sized materials are physically incorporated into the glue and accordingly affect the properties of the sheet. In addition to modification studies on the glues used in the production of wood-based boards, it has been reported that materials with low formaldehyde emissions, high resistance, and resistance to water and fire can be produced by using the advantages offered by nanomaterials (Yıldırım *et al.* 2022). On the other hand, studies are being carried out to strengthen the material by treating it with various fire-retardant chemicals in order to affect its burning characteristics and increase its durability (Kozlowski *et al.* 1999; Gu *et al.* 2007). For these purposes, all over the world, fire-retardant chemicals are being applied to materials that require fire resistance using various methods. These chemicals used for fire retardant purposes also affect the physical, mechanical, and some other properties of the materials to which they are applied (Sweet and Winandy 1999). Studies in which different chemical materials are used with chemical bonding during the synthesis stage of glue and new-generation glues are produced are quite limited. In this study, boron compounds (BA, BPH, and BDH), which are known to have fire-retardant properties, are used in urea-formaldehyde resin by chemical bonding during the synthesis stage. When boron compounds are chemically bonded to the structure of the glue, a new generation of boron-modified glue is produced, and it was envisaged that the advantages offered by boron compounds could be used more effectively than the physical addition method.

Boron compounds are odorless and colorless and offer advantages such as protective properties, flame retardant effects, low volatility, and toxicity (Akgül and Çamlıbel 2021). There are many studies in which boron compounds are used as fire retardant by adding them to urea formaldehyde resin in macro-sized wood-based boards. Akbulut *et al.* (2004) stated that the physical and mechanical properties decreased with the increasing chemical substance ratio in the fiberboards made from urea-formaldehyde with different inclusion ratios of borax, boric acid, and N'-N-(1,8-naphthalyl) hydroxylamine (NHA-Na). The best performance in mechanical properties was seen in borax-group boards, and boric acid boards showed more swelling and water absorption than borax-based boards. In contrast, it has been stated that boric acid, like borax, absorbs moisture at lower relative humidities (Şensöğüt *et al.* 2009). Borax added to corn starch and tannin resin at different rates was tested in the production of two-layer wood composites, and it was observed that increasing borax concentration in the resin reduced the adhesive strength of the boards (Moubarik *et al.* 2009). Çolakoğlu *et al.* (2003) determined that the chemical treatment positively affected the mechanical properties of the boards in the laminated layer materials they made with UF resin from beech peeling veneers, which they treated by dipping them in aqueous solutions of borax and boric acid. In another study, it was stated that phenol formaldehyde (PF) resin modified with boric acid has higher thermal oxidation resistance and thermal stability than unmodified resin (Gao *et al.* 1999). Zinc borate can also be used as a flame retardant in accordance with the polymers used and the desired standards (Abalı and Gümüş 2010). Arsenault (1964) detected a decrease in bending strength in strip chip boards made from chips treated with different usage rates of zinc borate, because of which the boron compound caused an increase in the brittleness of the chips due to the chemical behavior. At the same time, he stated that the chemicals on the chip surface caused the chips to become less flexible, and accordingly, the bending resistance of the plate decreased with increasing usage rates. Han *et al.* (2012) produced structural boards using straw and tried to determine the rot and termite resistance characteristics of the boards produced by adding various amounts of zinc borate to pMDI (isocyanate) resin. The results obtained showed that the addition of zinc borate increased the biological strength of the plate. In contrast, Jinxue *et al.* (2011) reinforced UF resin with zinc borate, which has fire-retardant properties, and examined the thermal curing behavior of the resulting modified resin. The results obtained revealed that the use of zinc borate did not adversely affect the curing behavior of the resin.

In wood resin applications, the number of studies using boron compounds in the synthesis stage of resin is limited. It is not known how boron compounds will affect the molecular structure and curing behavior of the resin (Chai *et al.* 2016). It is thought that when boron compounds are added to the molecular structure, a much more effective boron effect can be observed, as it will now become a boron resin. Chai *et al.* (2016) examined the curing behavior, bonding performance, and effects on wood of phenol formaldehyde (PF) resin, which they modified with three different boron compounds (boric acid, borax, and zinc borate) and an alkali catalyst. The amount of boron compounds used in resin synthesis was 2% w/w. It has been reported that PF resins modified with boron compounds have a lower degree of polymerization and a longer gel time than the control PF resin. Boron modification reduced the curing temperature by affecting the curing kinetics. While boric acid and borax modification delayed the curing process, zinc borate modification slightly accelerated the curing process. The thermal stability of the cured modified PF resins was slightly lower than that of the control sample. In lap shear tests, wood impregnated with modified resins showed good dimensional stability, mechanical properties, and improved fire resistance comparable to the control sample, regardless of the type of boron compound. According to Kawamoto *et al.* (2010), a composite material with silicon fibers was obtained from a boron-modified phenolic resin (BPR) using salicylic alcohol and boric acid. Shear strength and shear stress values showed values close to those of the unmodified phenol-formaldehyde resin. In another study, it was stated that BPR synthesis was not possible from the reaction of resols with boric acid. In the study, quantitative amounts of boric acid (96%) were isolated in the resol/boric acid system at the end of the reaction period (Abdalla *et al.* 2003). Jiamei *et al.* (2019) reported that the fireproof fiberboard they made with boron-modified urea-formaldehyde resin had density and water absorption resistance close to commercially available medium-density wood fiberboards, but higher strength, lower formaldehyde emission, and better flame retardancy (high oxygen index), and stated that it has a sound insulation effect.

In this study, three different boron compounds (boric acid (BA), borax pentahydrate (BPH), and borax decahydrate (BDH)) were used as physical and chemical additives in urea-formaldehyde resin. Physical, mechanical, and other tests of MDF boards produced from boron-modified resins were performed. Boron compounds are intended to reduce formaldehyde emissions in the boards and delay combustion while not reducing the physical and mechanical properties of the boards.

EXPERIMENTAL

Materials

Wood fibers (a mixture of 70% beech, 20% pine, and 10% poplar) used in the production of medium-density fiber boards were supplied from Divapan Entegre Ağaç Panel San. Tic. A. Ş, Turkey. These fibers had a moisture content of approximately 30%. Ammonium chloride (NH_4Cl) used as a hardener and solid urea (CH_4N_2O), formaldehyde (CH_2O, 37%), formic acid (CH_2O_2, 98%), and sodium hydroxide (NaOH) used in UF resin production were supplied from Sigma Aldrich (Taufkirchen, Germany). Boric acid (H_3BO_3), borax pentahydrate ($Na_2B_4O_7.5H_2O$), and borax decahydrate ($Na_2B_4O_7.10H_2O$) were supplied from the Eti Maden Operations General Directorate, Turkey.

Methods

Preparation UF resins

The UF resin was synthesized by adding urea twice following the alkaline-acid-alkaline process. According to this process, the urea:formaldehyde initial mole ratio was 1:2.2, and the urea:formaldehyde final mole ratio was 1:1.8. The UF resin synthesis was performed in a glass reactor equipped with heating and mechanical stirring. To adjust the solution pH, 20% NaOH and 40% formic acid solutions were used. The reaction was carried out at 90 to 100 °C in an alkali medium and at 70 to 90 °C in an acidic medium. In the chemical addition process, boron compounds were added at a level of 5% compared to urea. The prepared resins were coded as UFBA-c, UFBPH-c, and UFBDH-c for BA, BPH, and BDH, respectively. In the physical addition process, boron compounds were added at 5% compared to resin. The prepared resins were coded as UFBA-p, UFBPH-p, and UFBDH-p for BA, BPH, and BDH, respectively. Unmodified UF resin was coded as control. The properties of all resins were determined on the production day, and the resins were used in MDF production on the following day. All resins were stored at room temperature in a dark environment.

Determination of properties of boron-modified UF resin

Solid content, pH, specific density, flow time, gel time, and free formaldehyde content in the synthesized resins were determined. The solids content of the resin was determined according to the BSI 5350-B2 (1976) standard. The pH of the resin was measured at 25 ± 1 °C using a pH meter. The specific density of the resin was measured at 25 ± 1 °C using a pycnometer according to the BSI 5350-B1 (1978) standard. The flow time of the resin was measured with a Ford cup (No. 4) at 25 °C. The gel time of the resin was determined according to the study by Dazmiri *et al.* (2019). About 5 g of resin solution (dry weight) was taken into a test tube and 10% NH_4Cl solution (20% aqueous) was added and mixed. It was then immersed in a water bath at 100 °C, and the time when the resin turned into a high-viscosity gel was determined. The amount of free formaldehyde in the resin was determined following the DIN EN ISO 9397 (1997) method. For this, 1.0 to 2 g of resin was mixed in 50 mL of methanol solution until it was completely dissolved, and the temperature was 23 ± 1 °C. The pH was fixed at 3.5 using 0.1 M HCl solution, and 25 mL of hydroxylamine hydrochloride solution was added and mixed for 10 min. It was then titrated with a 0.1 M NaOH solution until pH 3.5, and the amount of free formaldehyde was measured from the amount of NaOH consumed.

Production of MDF and determination of board properties

The wood fibers were dried in the oven at 70 °C for 7 days, up to an approximate 3% moisture level. The approximate moisture content of wood fibers was 4 to 5% during the production of MDF. Boron-modified urea formaldehyde resins with 65% solid content and NH_4Cl as a hardener with 20% solid content were used in the production of MDF. Resin and hardener were mixed homogeneously with a mechanical mixer. This mixture was applied to the fibers using a laboratory-type adhesive machine with a drum. Production of MDF boards was completed on a heated press (Cemil Usta SP 125; CemilUsta Wood Working Machinery Ind. Inc., Istanbul, Turkey) in the laboratory of Duzce University. The MDF board production parameters are summarized in Table 1.

Test samples were prepared according to standard EN 326-1 (1999) and were conditioned at a temperature of 20 ± 2 °C and a relative humidity of 65 ± 5%. The produced MDF boards were evaluated for mechanical, physical, flaming behavior, and formaldehyde emission properties. The thickness swelling (TS) and water absorption (WA) of MDF boards were determined according to EN 317 (1999) and ASTM D1037 (2020) methods, respectively. The modulus of rupture (MOR) and modulus of elasticity (MOE) of the MDF boards were determined according to EN 310 (1999) and the internal bond strength perpendicular to the plane of the board (IB) was determined according to EN 319 (1999). The formaldehyde emission of MDF boards was determined following TS 4894 EN 120 (1999) and flaming behavior using TS EN ISO 11925-2 (2011). Each test piece used in the flaming behavior test was prepared with dimensions of 250 x 90 x 14 mm. The ambient temperature where the experiment was carried out was (23 ± 5) °C, and the relative humidity was (50 ± 20%). The air speed measured at the central axis in the chimney of the combustion chamber was 0.7 ± 0.1 m/s. The ignition source was at an angle of 45° with the vertical axis. Two flame application times of 15 s or 30 s were used. All obtained results were statistically analyzed using the Duncan mean separation tests and analysis of variance (ANOVA).

Table 1. Production Parameters of MDF Boards

Parameter	Value
Pressing time (min)	12
Press pressure (N/mm^2)	5
Press temperature (°C)	150
Target density (kg/m^3)	750
Dimensions (mm)	500*500
Thickness (mm)	14
Number of MDF boards for each type	3
Resin content (%) [relative to the dry weight of the fibers]	10
Hardener content (%) [relative to the dry weight of the fibers]	1

RESULTS AND DISCUSSION

Resin Properties

The properties of UF resins, in which different boron derivatives were physically and chemically incorporated into the resin, are summarized in Table 2. The solid content of all resin samples ranged between 64.4% and 69.8% and density values between 1.277 and 1.300 g/cm^3. The physical and chemical addition of boron derivatives to the resin increased the density values. While the physical addition of BA to UF resin decreased the pH value, the additions of BPH and BDH increased the pH value. Due to the acidic or basic character of boron derivatives, these changes in pH values after physical addition were an expected result. In the study by Üner and Olgun (2017), when BA was physically added at different rates to urea-formaldehyde, which has a pH value of 8.4, results with pH values varying between 5.8 and 6.9 were obtained. In the same study, the physical addition of borax increased the pH value. As a result of the chemical bonding of boron derivatives to urea-formaldehyde, pH values increased for all samples. In a study where 2% boric acid (BA), borax (BX), and zinc borate (ZB) modified PF resin were used, BA and ZB slightly reduced the pH value, while BX increased the pH value (Chai *et al.* 2016). Physically adding boron derivatives to UF resin increased the flowing time. As a result of the chemical bonding of boron derivatives to urea-formaldehyde, BA and BPH increased the flowing time, while BDH decreased the flowing time. In the study conducted by Chai *et al.* (2016), 2% boric acid additives reduced the viscosity, while 2% borax and zinc borate additives increased the viscosity. The gel time of the control synthesized with a urea:formaldehyde molar ratio of 1:1.8 was found to be 50.7 s. This result is compatible with the study in which the expected gel times were determined according to the urea: formaldehyde molar ratio (Eroğlu and Usta 2000). The physical addition of BA, BPH, and BDH to UF resin increased the gel time to 75.3, 137.7, and 158.7 s, respectively. In the study where boric acid and borax were added to urea-formaldehyde, it was indicated that gel times increased (Yıldırım *et al.* 2022).

Table 2. Properties of UF Resins

Sample	Solids Content (%)	Density (g/cm^3)	pH	Flowing Point (s)	Gel Time (s)	Free HCHO Content (%)
Control	66.2 ± 0.10	1.277 ± 0.003	8.50 ± 0.04	140.7 ± 5.69	50.7 ± 3.06	1.859 ± 0.03
UFBA-p	69.4 ± 0.63	1.280 ± 0.003	5.80 ± 0.01	550.3 ± 11.7	75.3 ± 4.51	1.809 ± 0.06
UFBPH-p	69.8 ± 0.95	1.290 ± 0.002	9.41 ± 0.01	448.0 ± 9.00	137.7 ± 3.51	*
UFBDH-p	67.7 ± 0.50	1.279 ± 0.002	9.48 ± 0.04	374.3 ± 7.51	158.7 ± 3.21	*
UFBA-c	64.6 ± 0.56	1.280 ± 0.002	8.58 ± 0.01	171.7 ± 7.64	107.7 ± 2.08	1.789 ± 0.05
UFBPH-c	64.4 ± 0.08	1.300 ± 0.003	8.65 ± 0.03	563.0 ± 12.1	188.7 ± 4.62	1.129 ± 0.11
UFBDH-c	65.3 ± 0.30	1.296 ± 0.003	8.71 ± 0.03	107.7 ± 7.02	159.0 ± 2.65	1.299 ± 0.03

*Reliable results were not measured

The chemical binding of BA, BPH, and BDH to UF resin increased the gel time to 107.7, 188.7, and 159.0 s, respectively. The BPH in the chemical bonding of boron derivatives to UF resin and BDH in their physical addition increased the gel time the most. In a similar study, it was stated that boric acid increased the gel time of phenol-formaldehyde resin 36.8% (Chai *et al.* 2016). Chemical addition of boron compounds to urea-formaldehyde reduced the amount of free formaldehyde in the resin. In particular, it appears that borax pentahydrate has a greater effect on reducing free formaldehyde than other boron compounds.

Physical Properties of Produced MDF Boards

Density

The average densities of the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 1. There is no significant difference in the average density ($p > 0.05$) values of all boards produced under the same conditions. It is seen that the average density values of all boards were similar to each other, and the values ranged between 722.0 and 742.5 kg/m^3.

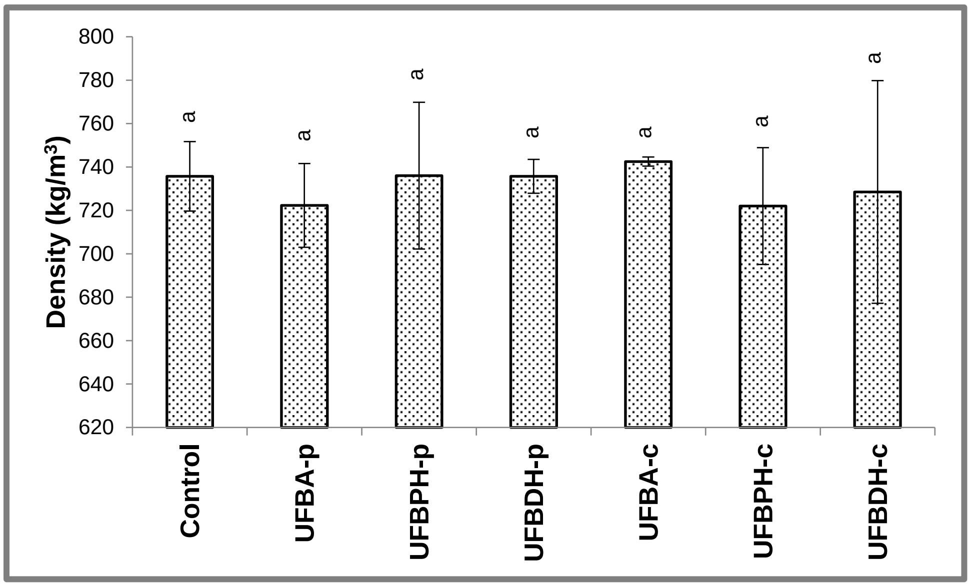

Fig. 1. ANOVA and Duncan test results regarding the density values of the produced boards. Values having the same letter are not significantly different (Duncan test at $p > 0.05$).

Thickness swelling and water absorption

The results of the average thickness swelling and water absorption of the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 2. The average thickness swelling ($p < 0.001$) and water absorption ($p < 0.05$) values of all boards produced under different conditions were different from each other at the 99.9% and 95% confidence levels, respectively.

According to the results in Fig. 2, it was observed that when the soaking time of MDF boards was increased from 2 to 24 h, the TS and WA rates increased for all boards produced. When the soaking time was increased from 2 to 24 h, the average increases in the TS and WA values of all board types were determined in the range of 1.1% and 2.7% and 10% and 14.6%, respectively. During 2 and 24 h of soaking, the highest TS and WA values were observed in the UFBA-p board, and the lowest TS and WA values were observed in the UFBDH-p board. At the end of 24 h of soaking in water, it was observed that values decreased in MDF boards produced from UFBPH-p, UFBDH-p, and UFBA-c resins, while it increased in the boards produced from other resins.

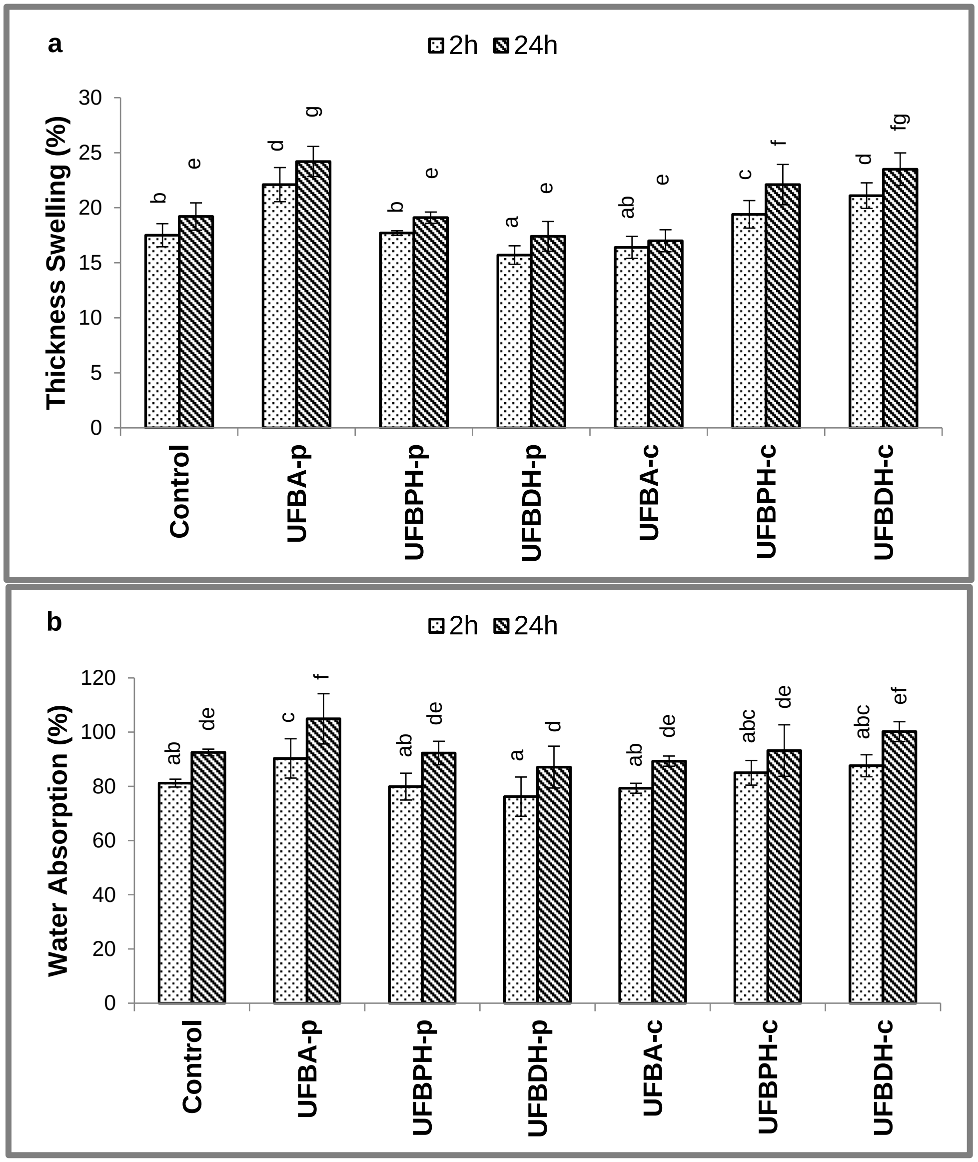

Fig. 2. ANOVA and Duncan test results regarding the (a) thickness swelling and (b) water absorption values of the produced boards. Values having the same letter are not significantly different (Duncan test at (a) $p < 0.001$, (b) $p < 0.05$).

Mechanical Properties of Produced MDF Boards

Modulus of rupture (MOR)

The results of the average MOR values in the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 3. The average MOR ($p < 0.001$) values of all boards produced under the same conditions were different from each other within the 99.9% confidence interval.

According to the results in Fig. 3, it is seen that the average MOR of all boards varies between 10.5 and 19.8 N/mm^2. The physical addition of 5% of BA, BPH, and BDH compounds to the UF resin decreased the MOR of MDF boards compared to the control. Akbulut *et al.* (2004) stated that when borax, boric acid, and N'-N-(1,8-naphthalyl)-hydroxylamine are the physical additions to urea-formaldehyde at different rates, the MOR of fiberboards is decreased. In another study, it was determined that when 5% boric acid, borax, and zinc borate were physically added to the resin, the MOR values of MDF boards decreased an average of 10% (Ustaomer and Usta 2012). In a similar study, when BPH was physically added to urea-formaldehyde at levels of 3%, 6%, and 9%, it was observed that the mechanical properties of MDF boards decreased compared to the control group, and with the addition of 9% BPH, the MOR decreased 24.3% (Akgül and Çamlıbel 2021). When boron compounds were chemically added to UF resin (5% to urea), BA increased the MOR of MDF board. In contrast, the additions of BPH and BDH decreased the MOR values. When the physical and chemical additions of boron compounds are compared, it is seen that chemical addition shows higher modulus of rupture values than physical addition. When boron compounds are compared, the highest average MOR value is seen in the BDH compound in the physical addition method and in the BA compound in the chemical addition method.

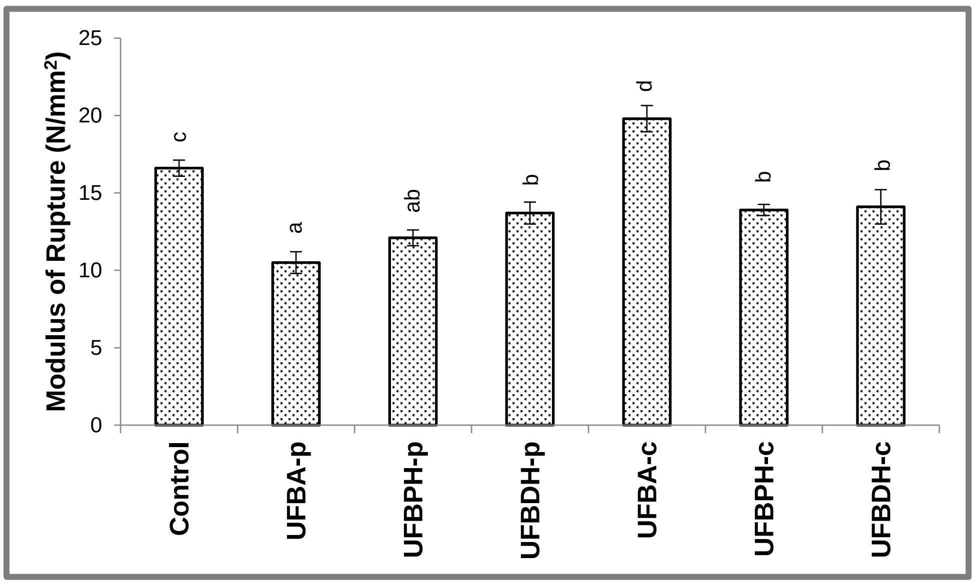

Fig. 3. ANOVA and Duncan test results regarding the modulus of rupture values of the produced boards. Values having the same letter are not significantly different (Duncan test at $p < 0.001$).

Modulus of elasticity (MOE)

The results of the average MOE in the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 4. The average MOE ($p < 0.01$) values of all boards produced under the same conditions were different from each other within the 99.0% confidence interval.

According to the results in Fig. 4, it is apparent that the average MOE of all boards ranged between 1530 and 2600 N/mm^2. The physical addition of 5% of BA, BPH, and BDH compounds to the UF resin decreased the MOE of MDF boards compared to the control. In the study where zinc borate was added to the resin at different levels, it was determined that there was a decrease in the elastic modulus of the strip particle boards. This result is explained by the fact that the boron compound causes an increase in the brittleness of the chips due to its chemical behavior (Arsenault 1964). The chemical addition of BA, BPH, and BDH compounds to the UF resin (5% to urea) decreased the MOE of MDF boards compared to the control. When the physical and chemical additions of boron compounds were compared, it was apparent that chemical addition showed higher modulus of elasticity values than physical addition. This result shows that chemical addition reduces brittleness more than physical addition for the boron compounds used in the study. When boron compounds were compared, the highest average MOE value was seen in the BDH compound in the physical addition method and in the BA compound in the chemical addition method.

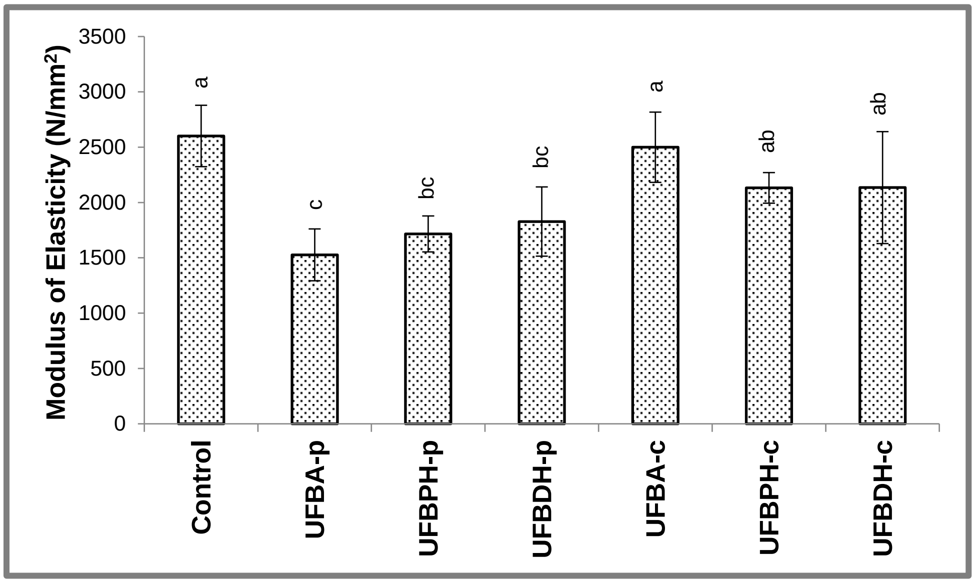

Fig. 4. ANOVA and Duncan test results regarding the modulus of elasticity values of the produced boards. Values having the same letter are not significantly different (Duncan test at $p < 0.01$).

Internal bond (IB)

The results of the average internal bond in the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 5. The average IB ($p < 0.001$) values of all boards produced under the same conditions were different from each other within the 99.9% confidence interval.

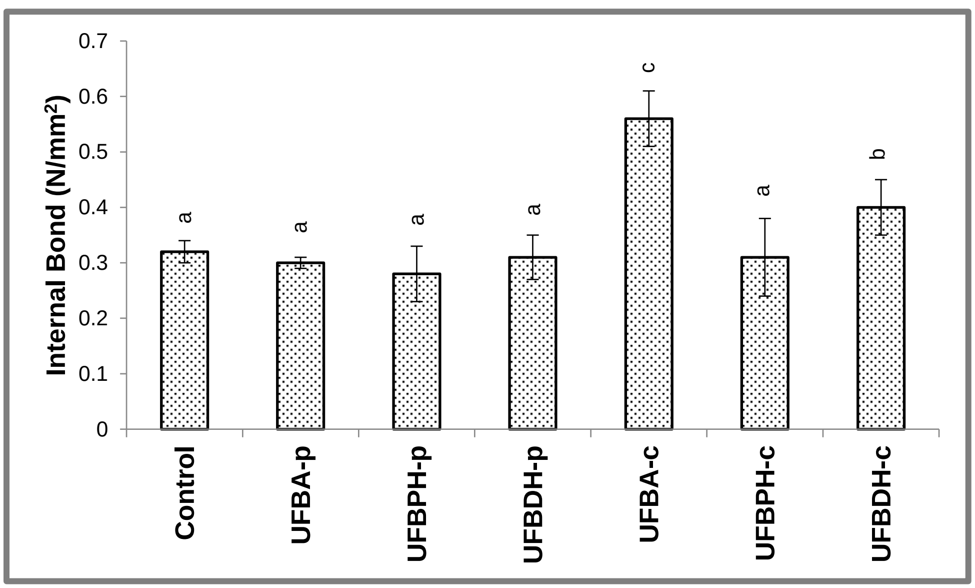

Fig. 5. ANOVA and Duncan test results regarding the internal bond values of the produced boards. Values having the same letter are not significantly different (Duncan test at $p < 0.001$).

According to the results in Fig. 5, the average IB of all boards ranged between 0.28 and 0.56 N/mm^2. The physical addition of 5% of BA, BPH, and BDH compounds to the UF resin decreased the internal bond of MDF boards compared to the control. In a study conducted by Moubarik *et al.* (2009), it was stated that borax added to corn starch and tannin resin at different rates reduced the adhesion resistance of wood composite boards. In another study, physical addition of boric acid, borax, and zinc borate to melamine-urea formaldehyde resin at different rates reduced the adhesion resistance of MDF boards (Ustaömer and Usta 2012). When boron compounds were chemically added to the UF resin (5% to urea), BPH decreased the IB values of MDF board. However, the addition of BA and BDH increased the IB values of MDF boards. When the physical and chemical additions of boron compounds were compared, it was apparent that chemical addition showed higher internal bond values than physical addition. When boron compounds were compared, the highest average IB value was seen in the BDH compound in the physical addition method and in the BA compound in the chemical addition method. A similar effect was also seen in the MOR and MOE results.

Other Properties of Produced MDF Boards

Formaldehyde emission

The results of the average formaldehyde emission values in the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 6. The average formaldehyde emission ($p < 0.001$) values of all boards produced under the same conditions were different from each other within the 99.9% confidence interval.

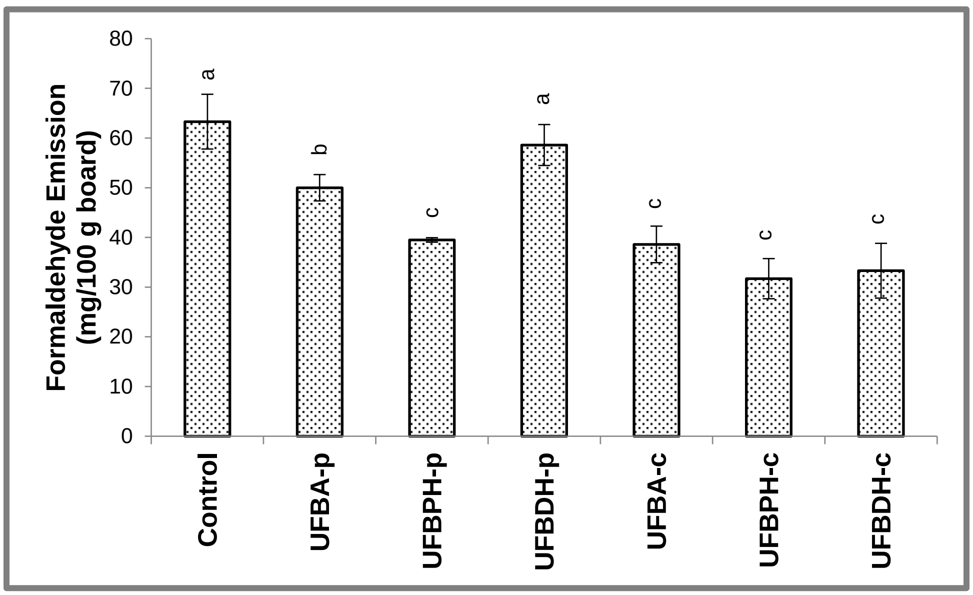

Fig. 6. ANOVA and Duncan test results regarding the formaldehyde emission values of the produced boards. Values having the same letter are not significantly different (Duncan test at $p < 0.001$).

According to the results in Fig. 6, the average formaldehyde emission values of all boards ranged between 31.7 and 63.3 mg/100 g board. The physical addition of 5% of BA, BPH, and BDH compounds to the UF resin decreased the formaldehyde emission of MDF boards compared to the control. Çolakoğlu and Demirkır (2006) produced plywood boards with borax-added UF resin and reported that formaldehyde emission values decreased 23% compared to control samples. Reductions in formaldehyde emissions were reported in a similar study by Şensöğüt *et al.* (2009). Authors indicated that the physical addition of 5%, 10%, and 20% borax significantly reduced the formaldehyde emission of MDF. The chemical addition of BA, BPH, and BDH compounds to the UF resin (5% to urea) decreased the formaldehyde emission of MDF boards compared to the control. Jiamei *et al.* (2019) reported that the boron-modified urea-formaldehyde added fiberboards had lower formaldehyde emissions than commercially available medium-density fiberboard. When the physical and chemical additions of boron compounds are compared, it is seen that chemical addition reduces the formaldehyde emission values in the boards more than physical addition. When boron compounds are compared, the lowest average formaldehyde emission values in the boards were seen in the BPH compound in both physical and chemical additions.

Flaming behavior

The results of the average width and length of the burnt area values in the single-source flame test on the produced MDF boards according to ANOVA and Duncan separation are given in Fig. 7. There was no significant difference in the average width ($p > 0.05$) of burnt area of all boards produced under the same conditions. The average length ($p < 0.05$) of burnt area values of all boards produced under the same conditions were different from each other within the 95% confidence interval.

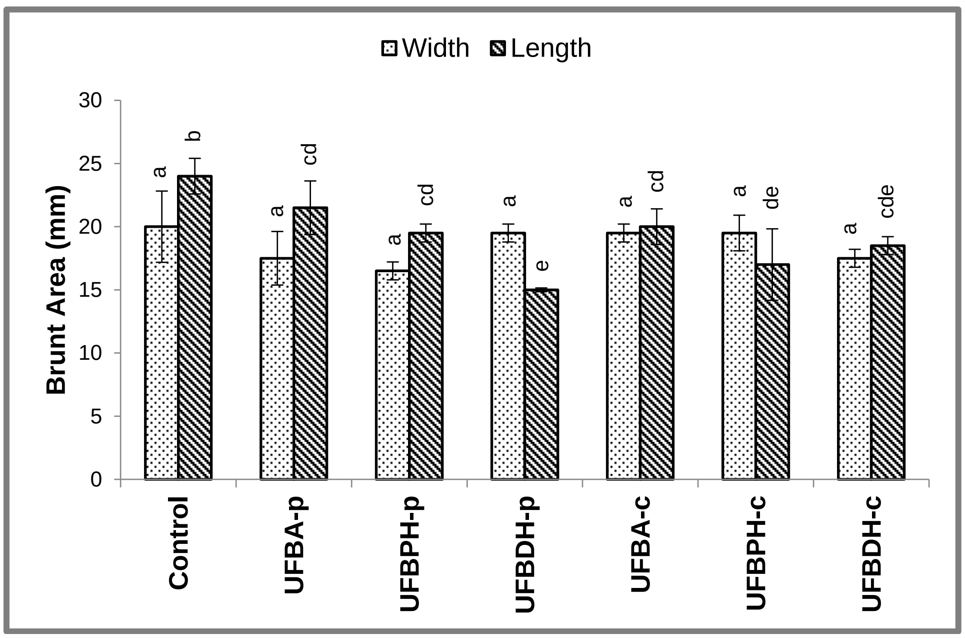

Fig. 7. ANOVA and Duncan test results regarding the burnt area values of the produced boards. Values having the same letter are not significantly different (Duncan test at $p > 0.05$ for width, $p < 0.05$ for length).

In the flaming behavior test of MDF boards, it was observed that there was no ignition and no intense smoke at 15 and 30 seconds. Accordingly, it was observed that the flame did not spread 150 mm, and no burning occurred on the filter paper. The difference between the boards involved the flame destruction dimensions.

According to the results in Fig. 7, it is apparent that the average width and length of burning area values of all boards ranged between 16 and 22 mm, and 15 and 25 mm, respectively. The physical addition of 5% of BA, BPH, and BDH compounds to the UF resin decreased the width and length burning area values of MDF boards compared to the control. While BPH provided the greatest decrease in the width burning area, BDH provided the highest decrease in the length burning area. Var (2000) stated that the fire-retardant effect of borax was more effective than that of boric acid in the flame-induced burning test. In contrast, Abdul Rashid (1987) added boric acid to the chips at rates of 10%, 15%, and 20% and observed that the lowest flame spread index was in the addition of 20% boric acid. Jiang *et al.* (2011) reinforced UF resin with zinc borate and examined the thermal curing behavior of the resulting modified resin and concluded that the use of zinc borate did not affect the curing behavior of the resin. El-Sayed *et al.* (2021) applied a mixture of diammonium phosphate and boric acid as a flame retardant onto the upper and lower layers of the particle board at levels of 0%, 5%, 10%, 15%, and 20%. It has been reported that fire retardant properties increase *via* addition of 15%, and after this rate, fire retardant properties decrease. Esmailpour *et al.* (2019) stated that the addition of 5% nano-wollastonite did not have any effect on the ignition time of the MDF board, but the addition of 10% nano-wollastonite increased the ignition time approximately 15%. The chemical addition of BA, BPH, and BDH compounds to the UF resin (5% to urea) decreased the width and length burning area values of MDF boards compared to the control. While BDH provided the highest decrease in the width burning area, the highest decrease in the length burning area was observed in BPH. Jiamei *et al.* (2019) stated that boron-modified urea-formaldehyde resin added medium-density fiber boards had higher flame-retardancy (high oxygen index). In another study, phenol formaldehyde (PF) resin was modified with three different boron compounds (boric acid, borax, and zinc borate) and an alkali catalyst and impregnated to the timbers. As a result, impregnated timbers showed higher fire resistance compared to the control sample, regardless of the type of boron compound (Chai *et al.* 2016).

CONCLUSIONS

1. The physical and chemical addition processes of boron compounds to UF resin increased the density, flow time, and gel time of the resin while reducing the amount of free formaldehyde.
2. Because of the fire-retardant properties of boron compounds, the burning area (length) of all medium density fiberboard (MDF) boards decreased.
3. Modification with boron compounds generally decreased the modulus of rupture (MOR) and modulus of elasticity (MOE) values of MDF boards. The chemical addition of boric acid to urea-formaldehyde (UF) resin increased the MOR and MOE values. While there were no significant decreases in the internal bond strength (IB) values of MDF boards, the chemical addition of boric acid (BA) and borax decahydrate (BDH) to UF resin significantly increased the IB values of MDF boards.
4. The physical and chemical addition of boron compounds to UF resin reduced the formaldehyde emission values of MDF boards. As a result of the chemical addition of boron compounds reduced approximately 50% rate formaldehyde emission values.
5. It has been observed that BA is more effective in improving the mechanical properties of MDF boards by the chemical addition of boron compounds to UF resin, and BPH is more effective in reducing formaldehyde emission.

6. It can be concluded that the use of boron compounds in the synthesis stage of UF resin provided better results in the properties of MDF boards than the physical addition by providing stabilization in the resin.

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