Combustion properties of medium-density fiberboards coated by a mixture of calcite and various fire retardants

Abdullah İSTEK*, Deniz AYDEMİR, Hüdaverdi EROĞLU
Department of Forest Industrial Engineering, Faculty of Forestry, Bartın University, Bartın, Turkey

Received: 19.06.2012  Accepted: 23.02.2013  Published Online: 28.08.2013  Printed: 25.09.2013

Abstract: In this study, we investigated the effect of fire retardants (FRs) on the combustion performance of medium-density fiber boards (MDFs) that were coated with mixtures of water, binder, calcite, and various FRs (FR coatings). We used MDF panels, calcite as the coating pigment, melamine formaldehyde as the binder, and FRs, including borax (BX), boric acid (BA), and zinc borate (ZB), to investigate the effects on the properties of the test boards. According to the results of combustion properties of coated MDFs with FR coatings, BA presented the highest stability, followed by BX and ZB, respectively. It was also found that the fire resistance of coated MDFs was better than that of uncoated MDF panels. For samples coated with FR coatings, the lowest burning temperature of 3% BA coatings was about 216 °C, and the highest burning temperature of 1% BX coatings was found as approximately 271 °C. The lowest mass losses were 35.5% for BA and 36% for BX. As a result, both surfaces of MDF panel can be coated with a mixture of calcite and FR, thereby improving the combustion properties of the MDFs. BA coatings showed to be have better thermal properties than both BX and ZB coatings.

Key words: Burning performance, coated medium-density fiber board, combustion properties, fire retardants, pigment coating, wood-based composites

1. Introduction
The properties of wood and wood-based panels may be affected by many factors, such as fungi, insects, humidity, and fire. For reducing these influences, wood and wood-based panels can be treated with various chemicals, including a PVC-based layer and various dyes, or coated with wood veneers or foils, depending on the structure of the material and its intended use. Generally, the panels are coated in order to increase the areas in which they can be used, improve their strength characteristics, and enhance their aesthetic appeal (Thoemen et al. 2010; İstek et al. 2010).

The coating process is a technique in which various materials can be applied to the surfaces of paper, paperboard, wood, and wood panels. The materials used for coating may include clay, calcite, some other pigments, an adhesive mixture, or some other suitable materials. Thus, the coatings that are used improve the properties of the coated materials, such as their aesthetic appeal, smoothness, opacity, quality of the applied colors, or other surface properties. The term ‘coating process’ is also used with reference to lacquered and varnished wood and wood panels (Lavigne 1986). Currently, clay and calcite are commonly used as coating materials for many applications because they increase the strength and the physical and surface properties of the materials to which they are applied. Fire retardants (FRs), such as borax (BX), boric acid (BA), and zinc borate (ZB), can be added to the coating mixture to increase the desirable combustion properties of materials, depending on their intended uses (Casey 1961). Generally, chemicals used as FRs may affect many properties of materials. It was found that FRs combined with boron reduced the mechanical properties and surface quality of wood panels (Baysal et al. 2006; Ustaömer 2008). Generally, FRs do not prevent the burning of wood and wood panels. Some of them do increase the temperature at which combustion can occur. Thus, the rate at which a fire will propagate is decreased due to the increased ignition temperature and the time required to reach that temperature (Örs et al. 1999). Some FRs, when in wood, reduce the temperature, resulting in thermal degradation of the wood. The result is pyrolysis gases that are less combustible (and more char), which then results in less flaming combustion to propagate the flames. Therefore, for increasing the combustion performance of wood and wood panels, they must be coated with various

* Correspondence: aistek@bartin.edu.tr
When investigating the mechanism of FRs during fire tests, it was determined that the FRs melted completely during high-temperature tests, and they flowed and covered the whole panel like a lamella. Thus, FRs can improve the fire performance of panels in this way (Ishihara 1981).

Usta and Ustaömer (2008) researched the physical properties and fire performance of medium-density fiber boards (MDFs) treated with boron compounds. FR containing boron was found to decrease the physical properties of treated MDFs while improving their fire performance. In another study, wood samples treated by various compounds that contained nitrogen, phosphorus, halogens, and boron were assessed by thermogravimetric analysis, differential thermogravimetric analysis, and differential thermal analysis to determine their fire performance. The results indicated that the fire performance of the wood samples improved from 10.2% to 30.2% (Gao et al. 2006).

The effect of liquid and solid FRs on the fire performance of wood panels was investigated. The results showed that both types of FR had essentially the same performance, with no statistically significant differences between them (Murphy et al. 1993). The effects of FR on the fire performance of MDFs and plywood were determined, and the results indicated that the fire performance of MDFs and plywood increased about 6.4% and 1.6%, respectively. When the ratio of FR in wood panels was increased, it was found that their fire performances improved even more (Tsunoda 2001). In another study, beech wood was impregnated with monoammonium phosphate, diammonium phosphate, ammonium sulfate, and monoammonium phosphate-borax as FRs to investigate the effect of these FRs on the fire performance of the wood. The best results were obtained from panels impregnated with diammonium phosphate (Akhtari et al. 2006).

The fire performance of wood and wood panels was investigated by using ZB as a fire retardant. The results showed that ZB had an important FR effect when used in the vapor phase and in the condensed phase (Garba 1999). In another study, fire properties of pine plywood, oriented strand boards, MDF, hardboard, and particleboard coated with FR paint were researched. There were significant differences in mass loss and carbonization index for all the boards with FR compared with the boards without protection (Garay and Henriquez 2009).

The objective of this study was to investigate the combustion performance of MDF panels coated by a coating material that comprised a mixture of water, binder, calcite, and various FRs, including BA, BX, and ZB.

### 2. Materials and methods

The MDF panels and the binder (melamine formaldehyde) used in this study were obtained from Kastamonu Integrated Forest Industry, Inc., in Turkey. The dimensions of the MDF samples were 250 × 400 × 12 mm. The surfaces of all of the samples were sanded with abrasive paper of 120 grit until they were smooth to ensure good bonding with the FR materials. Three samples were prepared for each surface coating parameter. Chemicals used were obtained from FarmaLab, Inc. The ratios of chemicals used in the preparation of the coating materials were determined according to the dry mass of calcite. The coating materials were prepared by using a blender to mix the components of the FR, i.e. calcite, water, binder, and FRs including BA, ZB, and BX. The components were mixed until the mixture was homogeneous. The viscosity and pH values of the coating material were adjusted to a range of 50–100 cP and 8–11, respectively. A ruler was used to apply the coating materials to the surfaces of the panels. Preparation conditions of the coating materials and the ratios of coating materials used in the tests are provided in the Table.

FR was added to the coating material at 1%, 2%, and 3%, and the coating layer was applied until the thickness of the layer was 0.25 mm. The coated samples and the combustion equipment are shown in Figures 1a and 1b, respectively.

Combustion tests were conducted according to ASTM E69 standard methods and 6 replicates were tested in each group. A digital balance (±0.01% sensitivity) was added to the test mechanism to measure the mass that the samples lost during testing. Butane gas was used as the flame source.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Rate</th>
<th>Materials</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>100%</td>
<td>Sodium hexametaphosphate</td>
<td>1%</td>
</tr>
<tr>
<td>Melamine formaldehyde</td>
<td>22%</td>
<td>Brightner</td>
<td>0.3%</td>
</tr>
<tr>
<td>Boric acid</td>
<td>1, 2, 3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Borax</td>
<td>1, 2, 3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc borate</td>
<td>1, 2, 3%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
source, and the height of the flame was 25 cm at a test temperature of 1000 °C. The samples were put vertically into a burning cabinet. Mass loss, change of temperature, and ratios of O₂, CO, and NO were measured every 30 s during combustion. To initiate combustion, the flame source was used for 4 min and then turned off, and then the test continued for 6 min. The total time of the test was 10 min (Indrea 1987; Lee 1989; Örs et al. 1999; Yapıcı 2011). Gas analyzers were used to determine the concentrations of the released gases, and temperatures were measured throughout the test period. The temperature probe was inserted into the first hole from the top of the fire tube. Given temperatures are for the top of tube and reflect the intensity of the flames, depletion of O₂ reflects the amount of combustion and thus the amount of heat released, CO reflects incomplete combustion, and NO reflects burning of the melamine formaldehyde.

3. Results
Temperature changes, mass loss, and ratio of O₂, CO, and NO of coated samples and control samples (uncoated MDFs) were investigated. The results obtained are presented in Figure 2.

According to the results given in Figure 2a, the coated surfaces and FRs burned slower than the uncoated surfaces. Thus, the coated MDFs had better thermal stability properties than the uncoated MDFs. The maximum burning temperature was determined to be 306 °C for the uncoated samples and 279 °C for the coated samples without FR. The high temperatures showed that the samples reached higher burning temperatures in the same duration. The burning temperature of the uncoated samples was approximately 10% greater than that of the coated samples. Thus, it is apparent that the coating process had a positive effect on the FR properties of the MDFs. The maximum burning temperatures for 1%, 2%, and 3% BA were approximately 236 °C, 228 °C, and 216 °C, respectively. When the ratio of BA that was added increased, the rate of burning decreased, as did the maximum temperature measured. When 1%, 2%, and 3% ZB was added to the coatings for the test samples, the maximum temperatures obtained were 266 °C, 264 °C, and 240 °C, respectively. During the addition of ZB with concentrations increasing from 1% to 3%, the ignition temperature decreased. Burning temperatures in samples with BX were reduced as the amount of BX was increased from 1% to 3%.

In Figure 2b, the minimum value of O₂ for the uncoated MDFs was 17%, whereas the minimum value of O₂ for the coated MDFs was 18%. Decreasing the ratio of O₂ in the fire environment proved that the test samples burned quickly. The amounts of O₂ for BA and ZB were determined as 18.2% (1% and 2%), 19% (3%), 17.9% (1%) and 18.1% (2%), respectively, when the concentrations increased from 1% to 3%. In samples with BX, the O₂ values during the burning test were 17.7% (1% and 2%) and 18.1 (3%).

According to Figure 2c, while the concentration of CO produced from burning the uncoated MDFs was 1064 ppm, it was only 639 ppm for the coated MDFs. Thus, coating the MDFs had a positive effect during the burning process. While 639 ppm of CO were produced during the burning test for coated samples without FR, the values for the MDF samples treated with 1%, 2%, and 3% BA were 597 ppm, 585 ppm, and 410 ppm, respectively. In samples with ZB and BX, the CO values were 700 ppm, 640 ppm, and 600 ppm. 
The changes showed that adding FR had a positive effect on thermal stability. As the ratio of ZB was increased, the amount of CO decreased by 3%. However, the amounts of CO produced by MDFs with 1% and 2% ZB were greater than the amount produced by coated MDFs without FR. MDFs coated with ZB presented an incomplete burning process compared to other FRs.

As seen in Figure 2d, the concentration of NO produced during the burning process increased during the first stage, after which it decreased for the rest of the test. The amount of NO gas produced was less for the coated MDFs. At first, the NO value of all samples increased, after which it decreased gradually. The maximum values of NO for BA, ZB, and BX were 142 ppm, 138 ppm, and 134 ppm; 190 ppm, 181 ppm, and 173 ppm; and 187 ppm, 183 ppm, and 172 ppm for 1%, 2%, and 3%, respectively. ZB as a FR had a positive effect on the fire performance of the coated MDFs when compared with the control samples. The mass losses of uncoated samples, coated samples, and coated samples with FRs are shown in Figure 3.

While total mass loss that occurred after burning of uncoated MDFs, as shown in Figure 3a, was 58.3%, this value was 48.4% for coated MDFs. When the decreasing amount of these values was measured as percentage, mass loss difference was calculated as 16.8% between coated samples and uncoated samples. As seen in the results, the coating process improved the fire performance of MDFs. After the effect of coating on fire performance was determined, the effect of the FR used was investigated. In Figure 3b, the mass losses for the samples with coatings that contained 1%, 2%, and 3% BA are shown as 44%, 41%, and 36%, respectively. Mass loss thus decreased as the concentration of BA in the coating material increased.

Figure 2. Results of temperature received (a) and amounts of O<sub>2</sub> (b), CO (c), and NO (d) for uncoated, coated, and coated MDFs with FR.
Figure 3c illustrates that the mass losses in ZB during the burning tests were 49%, 44%, and 42% for 1%, 2%, and 3%, respectively. Mass loss decreased as the amount of ZB increased. As shown in Figure 3d, the minimum burning temperatures for BX were 271 °C, 269 °C, and 246 °C for 1%, 2%, and 3%, respectively. The mass losses of the MDFs coated with BX in the coating material decreased. The maximum values were 45%, 43%, and 36% for 1%, 2%, and 3% BX addition, respectively. The combustion properties of the MDFs coated by calcite and various FRs were investigated. All of the FRs had a significant effect on fire performance. The effect of boric acid was greater than that of either zinc borate or borax. When the amounts of all of the FRs were increased, the combustion properties of all of the samples were improved. The amount of O₂ obtained during the burning test decreased when the FRs were used.

4. Discussion
The results of this study demonstrated that the thermal stability of coated MDFs was better than that of uncoated MDF panels. Thermal stability of coated panels also improved with the addition of FRs (BA, ZB, and BX). The burning temperature was decreased with the increase of the addition ratio of FRs. BA has better thermal stability on coated MDFs than the others. According to the results, the lowest burning temperature of coated MDFs with 3% boric acid was 216 °C, and the highest burning temperature of coated MDFs with 1% borax was 271 °C (Figure 2a). The amounts of O₂ for BA, ZB, and BX were generally increased as the ratio of FR increased (Figure 2b). Figure 2c shows that the amount of CO was generally increased with the addition of FR, except for samples with ZB. As seen in Figure 2d, the concentration of NO
produced during the burning process increased during the first stage, after which it decreased for the rest of the test. In previous research, the effects of surface-coating materials on the thermal conductivity and combustion properties of particleboards were studied. It was found that the surface-coating materials increased the thermal conductivity and that coated panels were more combustible than uncoated particleboard (Nemli and Kalaycıoğlu 2001). Another study evaluated FR chemicals, including sodium aluminate, ZB, and aluminum trihydrate, which were incorporated with rubber wood fibers into manufacture experimental MDF. ZB-treated boards had the highest value of mass loss. Boards treated with ZB seemed to be less efficient in reducing flame propagation in comparison to boards treated with sodium aluminate and aluminum trihydrate. Aluminum trihydrate functioned most efficiently as a FR. According to thermogravimetric analysis, untreated control samples showed a significant mass loss of 74% in comparison to the samples treated with FR. This information was used as a relative measure of the effectiveness of a given FR (Hashim et al. 2009). According to Figure 3, coated panels and coated panels with FR were more stable than uncoated panels. The adding of FR led to decreased ratio of mass loss. The lowest mass loss for a FR was for 3% BA, at 35.5%. The highest ratio of mass loss was for 1% ZB. In a study done on laminated veneer lumber, the mean weight loss rate after the combustion test for laminated veneer lumbers and host woods was 85.74% and 95.21%, respectively. Mean weight loss values of laminated veneer lumber were considerably less than those of host woods. This was explained by effects of densification and manufacturing factors similar to those in the mechanical properties’ increase (Kurt et al. 2012). A study was done on radiata pine structural plywood, oriented strand board, MDF, hard board, and particleboard treated with FR paint. The results obtained were compared with those for nontreated boards. Radiata pine wood with and without FR paint was included in the study. The statistical analysis showed significant differences in mass loss and carbonization index for all the boards with FR as compared to the boards without protection. Among the structural boards, i.e. plywood and oriented strand board, the plywood with FR presented the best fire performance, while hard board presented the worst. It was demonstrated that the FR paint was effective for the protection of the boards studied when compared to boards without protection. The implementation of this standard test was a good indicator of fire performance and contributed significant information about the boards, so its utilization is advised as a complement to the fire resistance tests that are conducted at a real scale (Garay and Henriquez 2009). In a similar study, the fire performances of veneers treated with BA, disodium octaborate tetrahydrate (DOT), alumina trihydrate, and a mixture of BA and DOT were examined. Although the treated samples performed better than the untreated control samples, the improvement was considerably less than expected for a wood product that was fully treated with a FR. Tests to determine heat release rate indicated significant reductions in the predicted flame spread rate. However, these improvements fell short of the levels required for typical Class I FR-treated materials. The improvements were limited by the relatively thin veneer of the dip-treated wood exposed during the fire testing. Specifically, more thorough treatment of the veneers could be achieved with pressure treatment and another level of fire performance could be achieved through treatment of the core (Laufenberg et al. 2006).

In conclusion, the results showed that the maximum burning temperatures of uncoated MDFs (control samples) measured during the burning process were greater than those for coated MDFs. Thus, the uncoated MDFs burned more easily than the coated MDFs. The burning temperature was decreased by increasing the ratio of FR added. It was also found that the boron-containing compound delayed the burning temperature. While BA showed the best fire performance, the combustion properties of BX were the lowest. The lowest burning temperature of coated MDFs with 3% BA was 216 °C, and the highest burning temperature of coated MDFs with 1% BX was 271 °C. It was found that BA is a better fire retardant than either BX or ZB. According to Figure 2b, one can see that the 3% BA and coating delayed the initial combustion and that 3% BA reduced the depletion of O₂ (i.e. heat-released). Meanwhile, 3% ZB and BX immediately showed evidence of combustion like in the uncoated wood, but the depletion of O₂ was less, particularly once the burner was extinguished. The plot of temperature provides more convincing support that the BA was more effective.

These research results indicate that MDF panel surfaces that are coated with a mixture of coating materials comprising water, binder, calcite, and a FR have improved combustion properties.

**Acknowledgments**

This study was funded by project number 2008-Ç0197 from the National Boron Research Institute (BOREN). The authors thank Dr Sezgin Koray Gülsay for the sample preparation and his help with some tests.
References


