Thermal Degradation of Particleboards Incorporated with Colemanite and Common Boron-based Fire Retardants

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Fire-resistance and thermal degradation were evaluated for particleboards incorporated with colemanite and common boron-based fire retardants (zinc borate and boric acid:borax mixture). The main purpose of this study was to suggest an alternative fire retardant to be used in particleboards with low cost and considerably lower environmental impact compared to common boron-based fire retardants. For this purpose, the colemanite mineral was chosen as a raw boron mineral because of its good fire performance demonstrated previously in wood-plastic composites. The test compounds were incorporated into the furnish during the particleboard manufacturing process. Fire performance tests and thermal degradation analysis were then performed in the treated particleboard specimens. Mass loss calorimeter tests were applied to determine the oxidative thermal degradation properties of the produced particleboards, whilst thermogravimetric analyses were used to evaluate the non-oxidative thermal behavior of the particleboards. The lowest peak heat release rate and the highest activation energy values were recorded for the boric acid:borax mixture-incorporated particleboards at a loading level of 10%. Overall the results showed that colemanite had a lower fire-retardant property in the particleboards compared to the common boron-based compounds tested in the study.

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INTRODUCTION

The use of boron-based preservatives has increased in recent years because these protective compounds are considerably effective against both biodegradation by fungi, termites, insects, and thermal degradation. Terzi *et al.* (2017) stated that boron compounds available in various forms, such as pure compounds, minerals, or their combinations, are likely to continue to be among the most promising biocides for wood protection for future generations. They have numerous advantages, such as low toxicity and cost, ease of use for solid wood and wood-based composites, high transparency, non-volatility, and non-corrosiveness, when compared to conventional wood preservatives (Bhatia 2002; Kartal 2009).

Magnesium hydroxide, aluminum hydroxide, boric acid, ammonium phosphate, ammonium borate, ammonium sulphate, ammonium chloride, zinc chloride, zinc borate, phosphoric acid, dicyanodiamide, sodium borate, and antimony oxide are among the common fire retardants used in wood-based composites. Boron-based fire retardants from boron minerals have long been used in the wood and wood-based composite industry. One

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of the most common boron minerals found in large deposits in Turkey is colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$), with a boron trioxide (B_2O_3) content of 50.8 wt%, and it is generally used to produce boric acid (Kistler and Helvaci 1994; Birsoy and Özbaş 2012; Özdemir *et al*. 2014; Terzi 2015).

Wood-based composites have received increased attention in recent years due to improvements in building designs and protection methods (Morrell 2002; Terzi *et al.* 2017). Besides increased performance against biodegradation, proper protection technologies against fire are also needed for these materials to perform more reliably under conditions suitable for thermal degradation (Morrell 2002) as well as to expand into new markets. A number of studies have suggested that boron compounds can be effectively used to increase the resistance of wood-based composites against fire (Tsunoda 2001; Baysal *et al.* 2007; Yalinkiliç *et al.* 2007; Wang *et al.* 2008; Kurt *et al.* 2012; Pedieu *et al.* 2012; Tondi *et. al.* 2012; Özdemir and Tutus 2013; Tondi *et al.* 2014). Because wood-based composites have a heterogeneous structure consisting of wood fillers, adhesives, and additives, the use of raw boron minerals as additional additives is not expected to cause difficulties during processing. Thus, the use of raw boron minerals, such as colemanite in various applications without the use of advanced technologies for purification, could be sustainable and cost-effective as well. In the authors' previous study, it was shown that colemanite can be considered to be a reasonable fire retardant in wood-plastic composites based on its proper fire-retardant properties, relatively low cost, and considerably low environmental concerns. Colemanite showed the best cone calorimetry test performance, according to the peak heat release rate (PHRR) values, without any flexural property loss when compared with zinc borate, borax, ulexite, and tincalconite in wood-plastic composites. When colemanite-incorporated composites were exposed to heat, they showed the same thermal behaviors as magnesium hydroxide-incorporated composites. It was also stated that colemanite could be combined with a smoke suppressant additive for a better fire-retardant performance in wood-plastic composites (Terzi *et al.* 2018). In previous studies on various products without wood particles, such as polystyrene-based composites, low-density polyethylene, epoxy composites, ethylene vinyl acetate/ethylene methyl acrylate copolymers, colemanite has been considered as a successful candidate due to its high fire-retardant properties. Colemanite has also showed synergistic effects with common metal hydroxides to increase the fire performance of such materials (Kaynak and Işitman 2011; Işitman and Kaynak 2012; Guzel *et al.* 2016; Cavodeau *et al.* 2017).

The objective of the current study is to evaluate the potential of colemanite in particleboard manufacturing by comparing its fire and thermal performance to that of commercial boron compounds (zinc borate and boric acid:borax mixture) as common fire retardants. In the study, all chemicals were incorporated into the furnish during the particleboard manufacturing process, and fire performance tests and thermal degradation analyses were then performed in the produced particleboard specimens.

EXPERIMENTAL

Materials

The materials used were colemanite (C; $Ca_2B_6O_{11} \cdot 5H_2O$; Eti Boron Corp., Balıkesir, Turkey) as a raw boron mineral, and boric acid (BA; $B(OH)_3$; Eti Boron Corp., Balıkesir, Turkey), borax (BX; $Na_2B_4O_7 \cdot 10H_2O$; Eti Boron Corp., Balıkesir, Turkey), and zinc borate (ZnB; $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$; Melos Corp., Sakarya, Turkey) as the commercial

fire retardants. All of the compounds were used as received without any purification or further processing.

Methods

Manufacturing of particleboard panels

Single layer particleboard test panels with a target density of 600 kg/m^3 were manufactured at the Medium-Density Fiberboard (MDF) and Particleboard Facility of Kastamonu Integrated Wood Industry and Trade Company in Gebze, Turkey. Urea-formaldehyde (UF) resin at a 10% level was employed based on the oven-dry weight of the wood furnish that consisted of 65% softwood (pine – *Pinus* spp.) and 35% hardwood (oak- *Quercus* spp. and beech- *Fagus* spp.) particles by weight. The particles were placed in a drum blender and sprayed with UF resin with 1% ammonium chloride as a hardener for 5 min to obtain a homogenized mixture. No wax or water-repellent chemicals were used in the manufacturing process.

For the treated test panels, either zinc borate, or boric acid: borax mixture (1:1 w/w), or colemanite at loading levels of 2% or 10% by weight were well-mixed in the drum blender for 5 min to thoroughly disperse them. Experimental particleboard panels (550 mm × 550 mm × 10 mm) were pressed at 2.5 N/mm^2 pressure and 180 °C for 3 min. The panels were conditioned at 20 °C ± 2 °C and 65% ± 5% relative humidity (RH) to a moisture content (MC) of approximately 12%. The edges of the boards were trimmed to a final dimension of 500 mm × 500 mm × 10 mm. For the tests, three panels were manufactured for each particleboard type.

Fire performance test

The values of time to ignition (TTI), peak heat release rate (PHRR), average heat release rate (av-HRR) for 180 s and 300 s, and mass loss percentage (MLP) of the treated and untreated particleboard test specimens were determined by a mass loss calorimeter (with thermopile and chimney) (Fire Testing Technology Ltd., London, UK) in accordance with the ISO 13927 (2015) standard.

Prior to testing, the test specimens (100 mm × 100 mm × 10 mm) were conditioned at 23 °C and 50% RH. Then, they were tested in the horizontal orientation with the conical radiant electric heater located above the specimen based on the ISO 13927 (2015) standard. The temperature of the conical heater was adjusted to generate an external heat flux of 50 kW/m^2 on the exposed test specimens to simulate a real room fire (Mouritz and Gibson 2007).

Thermal analysis and kinetics

Freeze-milling (SPEX SamplePrep 6770, SPEX SamplePrep LLC., Metuchen, NJ, USA) was applied for all of the particleboards to obtain homogeneous specimens before thermogravimetric analyses (TGA). The panels were divided into small pieces with the correct amount of sample (up to 1/3 of the vial volume) and the sample was placed into the vial at room temperature. The vial was then placed into the mill filled with liquid nitrogen, and the freezer mill was gently closed. After milling, it was necessary to wait for the cooling of the vial to room temperature. The specimens were then taken out from the vial and placed into a sealed polyethylene-based container. Thermogravimetric analyses were performed by using a TGA analyzer (Perkin Elmer Ltd., Pyris Diamond Model, Beaconsfield, UK). Before the analyses, the TGA analyzer was calibrated using the melting points of indium (Tm = 156.6 °C) and tin (Tm = 231.9 °C) under the same conditions as

the specimens. For each experiment, the same procedure was followed, and Pyris 7 Software (Perkin Elmer Ltd., Beaconsfield, UK) was used for data evaluation. In this study, kinetic analysis of the thermal analyses data of the dehydration reaction was performed by using the Coats-Redfern non-isothermal method and the reaction order was assumed equal to one.

In the present study, the degradation reaction of the samples can be defined as in Eq. 1:

$$\text{Particular board (s)} \; \rightarrow \; \text{Volatiles (g) + solid residue (s)} \tag{1}$$
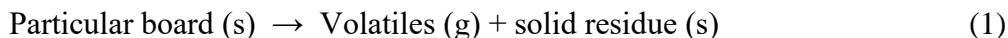
Kinetic analysis of reactions was investigated by using mathematical equations (Eq. 2) of Coats-Redfern non-isothermal kinetic model. According to the Coats-Redfern method, values of $[\log (-\log(1-\alpha)/T_2)]$ versus $1/T$ were plotted. The slope of the line was used to calculate E_A, and also k_0 was determined from the intercept of the line. To calculate the kinetic parameters, thermal dehydration reaction mechanism was assumed to be first order ($n=1$). The decomposition faction (α) was calculated (Eq. 3), and in the decomposition fraction (α) range from 0.1 to 0.9 it was used for activation energies calculation.

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{k_0 R}{\beta E_a}\left[1-\frac{2RT}{E}\right] - \frac{E_A}{2.303RT} \tag{2}$$

$$\alpha = \frac{(W_0 - W)}{(W_0 - W_f)} \tag{3}$$

In Eqs. 2 and 3, E is the activation energy (kJ/mol), α is the decomposition fraction, T is the temperature (K), β is the heating rate (K/min), R is the gas constant, A is the Arrhenius constant, W_0 is the initial weight of the specimen at the beginning of the main thermal degradation reactions, W is the weight of specimen in the specific temperature, and W_f is the final weight of the specimen at the end of the main thermal degradation reactions.

The thermogravimetric analyses test conditions are summarized in Table 1.

Table 1. Thermogravimetric Analyses Test Conditions

| TGA Test Conditions	
Temperature Range	30 °C to 600 °C
Atmosphere/Pure Gas	Nitrogen, 99.999% pure
Pure Gas Rate	100 mL/min
Heating Rate	10 °C/min
Crucible Type	Platinum
Sample Size	~ 10 mg

RESULTS AND DISCUSSION

Mass Loss Calorimeter Test Results

The HRR, broadly defined as the rate at which heat is generated from a fire, is the most important parameter for the assessment of the fire hazard of a given material during a fire. The HRR can be decreased with the addition of fire retardants (FRs) to the materials (Babrauskas and Peacock 1992; Grexa and Lübke 2001; Mouritz and Gibson 2007). The

initial peak HRR values were recorded as PHRR. The peaks and averages derived from the heat release and the mass loss (ML) curves are reported in Figs. 1 and 2 as well as in Tables 2 and 3.
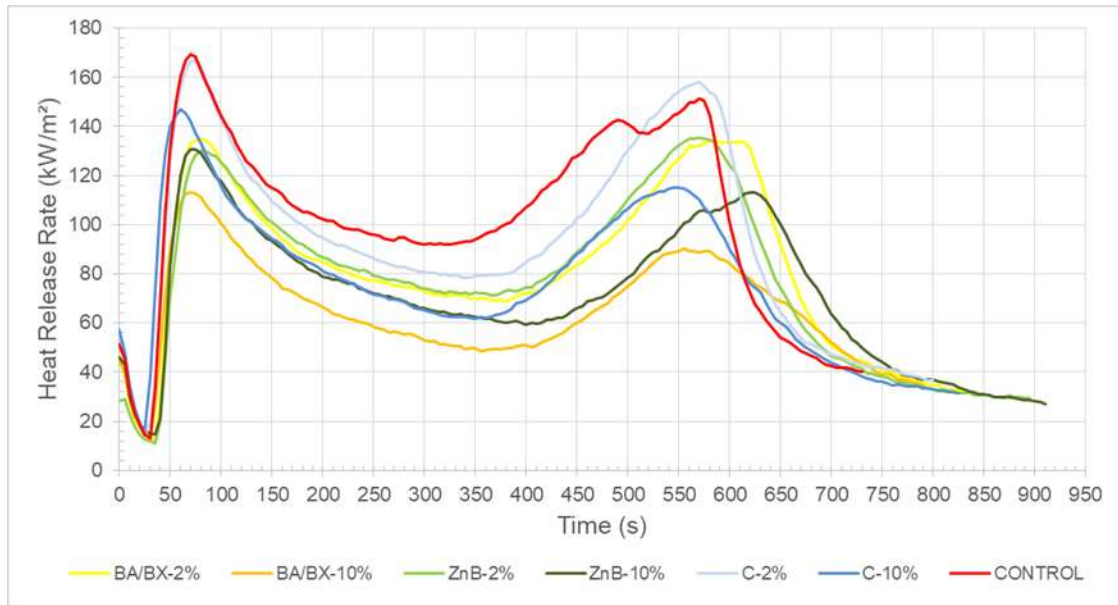
Fig. 1. HRR curves for the control particleboard (PB) and FR-incorporated particleboards (PBs) at loading levels of 2% and 10% (w/w) (BA = Boric acid, BX = Borax, ZnB = Zinc borate, and C = Colemanite)
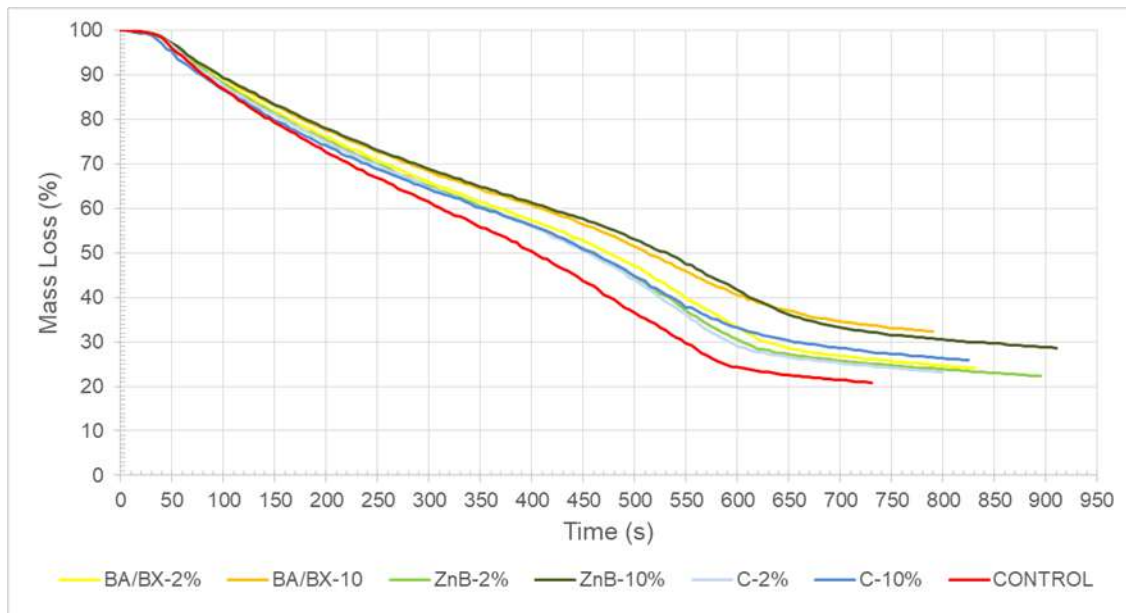
Fig. 2. ML curves for the control PB and FR-incorporated PBs at loading levels of 2% and 10% (w/w) (BA = Boric acid, BX = Borax, ZnB = Zinc borate, and C = Colemanite)

The TTI and HRR values relate important information about the first stage of fire development within the first 3 min after ignition (Babrauskas and Peacock 1992; Arao *et al*. 2014). In this study, the TTI of the FR-incorporated particleboards were longer than

that for control particleboard specimens except for the colemanite-added particleboard specimens. The highest TTI was recorded for zinc borate-incorporated particleboard specimens at a loading level of 10% (Table 2).

The MLP values decreased nearly 14% in the boric acid:borax mixture-incorporated particleboards at a loading level 10% when compared with the control particleboard specimens. The second highest decrease (nearly 10%) in the MLP occurred when zinc borate was incorporated at a loading level of 10% (Table 2).

As expected, the increased amount of fire retardants decreased the PHRR values (Table 3). The results showed that the most important reduction in the initial PHRR values was recorded in the boric acid:borax mixture- and the zinc borate-added particleboards at a loading level of 10%. The amount of reduction in the PHRR values of the particleboards incorporated with boric acid:borax mixture and zinc borate at a loading level of 10% was approximately 31% and 23%, respectively, when compared with the control particleboard specimens. In contrast, the lowest reduction rates in the PHRR values were obtained as 1.5% and 13.5% in the colemanite-added particleboard specimens at loading levels of 2% and 10%, respectively.

The av-HRRs (Table 3) of the FR-incorporated particleboards were considerably lower than those for the control particleboard specimens, except for the colemanite-added particleboard specimens. The lowest av-HRR recorded for boric acid:borax mixture-incorporated particleboards with a loading level of 10% occurred during the first 180 s to 300 s. The second lowest av-HRR in the same time period was recorded in zinc borate-incorporated particleboard specimens at the same loading level. In contrast, no notable change in the av-HRRs values could be obtained after adding 2% colemanite to particleboards. At loading level of 10%, the smallest reduction in the av-HRR value (nearly 15%) was determined in the colemanite-added particleboard specimens.

The fire growth index (FGI) is used to define the flashover potential of specimens as a fire hazard. The FGI was defined as the PHRR/TTI and a higher ratio of PHRR/TTI indicated a higher propensity for flashover (Babrauskas 1984; Petrella 1994; Işitman 2012). The highest FGI was calculated for the control particleboard specimens and the lowest FGI value was determined for the zinc borate-incorporated particleboard specimens at a loading level of 10%. The second lowest FGI was recorded with the boric acid:borax mixture-incorporated-particleboard specimens at a loading level of 10%. Among the additives used, colemanite had the least effect on decreasing the FGI value. Furthermore, the FGI values were lower in the control particleboard specimens than in the 2% colemanite-added specimens (Table 3).

Table 2. Mass Loss Calorimetry Test Results of the Fire Retardant-treated and Untreated Particleboards at Loading Levels of 2% and 10%

Particleboard Specimens	TTI (s)		Mass Loss (%)	
	Average	SD	Average	SD
Control Particleboard	32.33	4.16	79.22	2.31
Boric acid:borax-2%	37.33	3.51	75.90	1.57
Boric acid:borax-10%	34.33	6.51	67.64	1.61
Zinc Borate-2%	37.67	3.51	77.72	0.37
Zinc Borate-10%	39.00	3.61	71.42	1.11
Colemanite-2%	31.67	8.50	76.76	1.66
Colemanite-10%	28.00	3.46	74.16	1.47

Note: SD is the standard deviation

Table 3. Calculated PHRR, av-HRR, and FGI for Control Particleboard and the FR-incorporated Particleboards at Loading Levels of 2% and 10%

Specimens	PHRR (kW/m²)		av-HRR kW/m²				Fire Growth Index (FGI)
	Average	SD	Average at 180 s	SD	Average at 300 s	SD	
Control Particleboard	170.60	9.47	124.80	1.58	112.70	1.35	5.28
Boric acid:borax-2%	138.86	22.09	103.23	12.58	91.90	10.27	3.72
Boric acid:borax-10%	117.66	6.93	83.33	0.48	73.53	4.91	3.43
Zinc Borate-2%	130.25	0.66	101.55	0.73	91.77	0.82	3.46
Zinc Borate-10%	131.76	13.86	98.22	6.76	86.43	5.64	3.38
Colemanite-2%	168.20	8.33	119.77	4.12	105.47	2.48	5.31
Colemanite-10%	147.32	12.97	106.47	6.21	91.67	4.69	5.26

Note: SD is the standard deviation

Thermal Analysis Results and Activation Energy Calculation

The thermal-nonoxidative degradation behaviors of particleboard were investigated based on thermogravimetric analysis (TGA). The corresponding thermogravimetric (TG) and derivative thermogravimetric (DTG) curves are presented in Fig. 3. The DTG curves of the control-PBs, the FR-treated particleboards at loading levels of 2% and 10% exhibited three reaction stages during the heating of the composites between 30 °C to 600 °C at 10 °C/min heating rate. Thermal degradation stages could be classified and explained according to common knowledge in the literature. The first stage of the degradation was clearly separated from the other stages due to the release of water up to about 150 °C. The second stage data were obtained in the range from about 150 °C to 400 °C and named as the "main thermal degradation stage". This stage could also be named as the "charring phase" (Yunchu *et al.* 2000). In this stage, most of hemicellulose, cellulose, and a part of lignin in wooden particles decompose. Hemicellulose starts to decompose at lower temperatures than cellulose and causes a "shoulder peak" at about 325 °C. The decomposition of cellulose gives a distinct exothermal peak at about 350 °C, and this temperature is denoted as the "peak thermal degradation temperature". The peak thermal degradation temperature is the point of maximum rate of the wood pyrolysis. In the third stage, a slow and long decomposition of lignin proceeds until the end of the thermal analysis without any shoulder or peak (Beall and Eickner 1970; Cozzani *et. al.* 1997; Orfao *et al.* 1999; Wang *et al.* 2004; Prins *et al.* 2006; Gao *et al.* 2006; Di Blasi 2008; Shen *et al.* 2009; Gašparovič *et al.* 2010; Tomak *et al.* 2012).

As expected, increasing the amount of additives from 2% to 10% led to an increased residual amount compared with the control specimen as shown in Fig. 3. The thermal and kinetic results demonstrated that from the various chemicals used, the boric acid:borax mixture appeared to have the most positive effect and the addition of the boric acid:borax mixture increased the overall resistance of the particleboard specimens to thermal degradation. The highest residue increase was observed with the boric acid:borax mixture-added particleboards at a loading level 10% based on the control particleboard specimens. In contrast, the lowest residue amount was obtained after thermal degradation of the particleboard specimens incorporated with colemanite at 2% loading level. According to

the initial degradation temperature recorded during the main thermal degradation (second) stage, the boric acid:borax treatment groups showed the highest initial degradation temperature values at approximately 165 °C. The highest initial degradation temperature value may be related to the fact that boric acid: borax mixture with the lowest dehydration temperatures in the fire retardants used in this study. The boric acid: borax mixture could have a cooling effect at the beginning of the main degradation stage by water released and the heat energy required for hemicellulose degradation can be created later. Because the initial degradation temperature is mainly the temperature at which hemicellulose begins to decompose, an increase at the initial degradation temperature could be a reason the fire retardancy effect of boric acid:borax mixture.

At the thermal degradation stage, a distinct thermal decomposition peak, determined form the DTG curve, appeared at 343.4 °C and 337.5 °C for boric acid:borax (2% loading level) and boric acid:borax (10% loading level), respectively. With the addition of boric acid:borax mixture into the particleboard composition, the main thermal degradation stage is shifted to the left relative to the control group (T_m = 352.1 °C), based on the peak thermal decomposition temperature caused by the cellulose decomposition. Cellulose is the main component of wood responsible for the proceeding of thermal degradation. When the peak thermal decomposition caused by the cellulose reactions occurs at a lower temperature, this situation causes less flammable volatile products and higher amount of char. A char layer acts a thermal barrier on wood surface and saves the wood component especially cellulose against a severe thermal degradation. Some types of fire retardants have a similar mechanism of action (Karastergiou and Philippou 2000; Wang 2004; Gao 2006; Tomak *et al.* 2012).

Activation energies (E_a) for between initial and final thermal degradation temperatures of all particleboard specimens were determined by the Coats-Redfern non-isothermal method and, as the table shows, higher activation energies were found for the treated samples than for the control specimens. It was calculated that E_a increased from 62 kJ/mol to 69 kJ/mol with the addition of the boric acid:borax mixture. It seemed that boric acid:borax mixture in the particleboards influenced the thermal degradation reaction mechanism towards production of more char. Higher E_a values showed that higher energy was required to activate the molecules and start a degradation reaction (Fig. 3; Table 4). The inverse ratio between the amounts of residue and activation energies indicates the correspondence between the values.

Even though the colemanite mineral showed apparently good fire-retardant properties in different sorts of composites and polymers, it was not effective in particleboards without any polymer matrix such as polyethylene, polystyrene, epoxy, or acetate-acrylate-based copolymers (Kaynak and Işitman 2011; Işitman and Kaynak 2012; Guzel *et al.* 2016; Cavodeau *et al.* 2017; Terzi *et al.* 2018). When such polymers and copolymers are exposed to external heat flow, they emit high enough energy to activate the dehydration of the colemanite mineral due to the cleavage of bonds in their structures. While the peak heat release rates were between 800 kW/m^2 and 1600 kW/m^2 in these kinds of materials (Stark *et al.* 2010; Kaynak and Işitman 2011; Guzel *et al.* 2016; Cavodeau *et al.* 2017), in the untreated particleboards tested in this study the peak heat release rates were found as low as 170 kW/m^2.

According to thermal analysis studies, dehydration reactions begin at approximately 80 °C, 130 °C, and 315 °C for borax, boric acid, and zinc borate, respectively. However, significant release of water in colemanite begins at a relatively high temperature at about 390 °C (Waclawska *et al.* 1988; Işitman and Kaynak 2012; Motor

2017; Kizilca and Copur 2017). Kizilca and Copur (2017) discussed that the decomposition of colemanite mineral starts with the removal of water molecules in a two-step reaction mechanism. While only 1.2% of total water content of colemanite is released at 100 °C, dramatic decreases are seen at 320 °C. As temperature increases up to 386 °C, the strong hydrogen bonds associated with borate rings are broken and this rapid water release continues slowly up to 550 °C. Thus, the thermal decomposition of colemanite mineral proceeds within 386 and 550 °C. In this temperature range, considerable amount of the water (nearly 95% of total water content) is released.

Differences in peak heat release rate values of the materials and the dehydration reaction temperatures of various boron-based fire retardants may explain why colemanite was not effective in the particleboard specimens when compared to the zinc borate and boric acid/mixture.

(a)

(b)
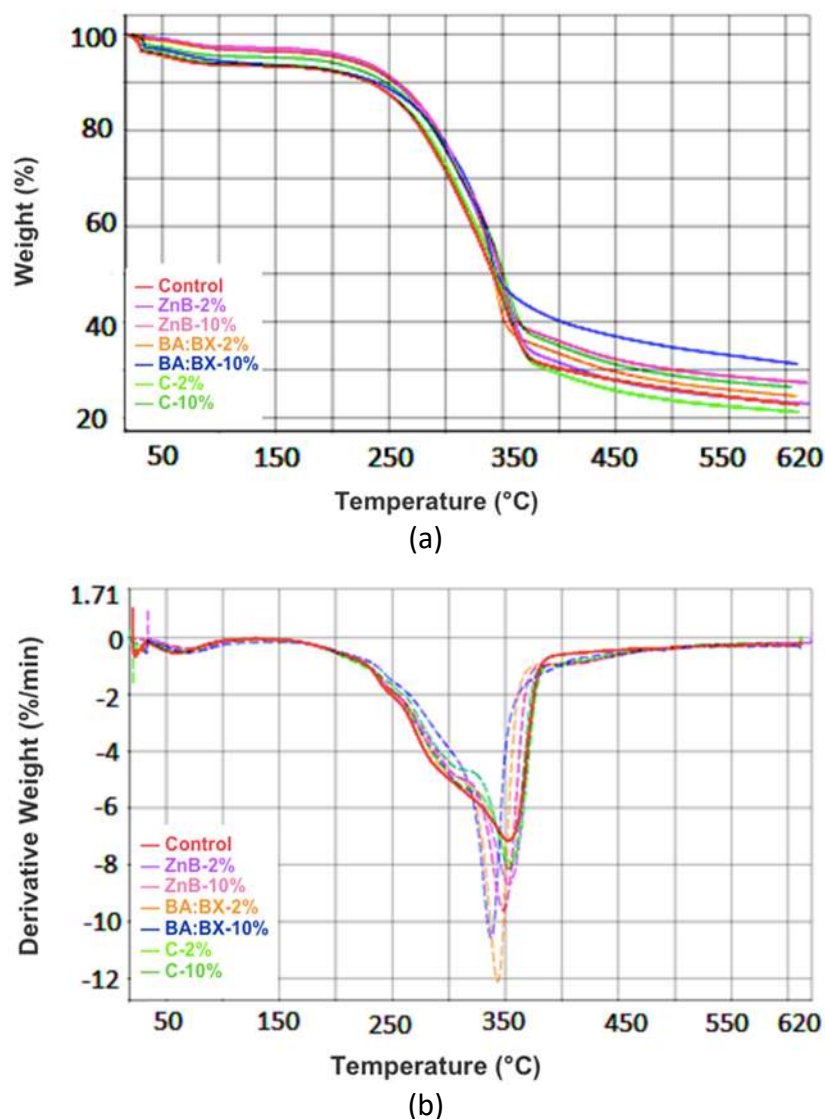
Fig. 3. TG and DTG curves of control particleboards, FR-incorporated particleboards at loading levels of 2% and 10 % during heating of the composites between 30 ℃ to 600 ℃ at 10 ℃/min heating rate under non-oxidative atmosphere: (a) TG, (b) DTG (BA = Boric acid, BX = Borax, ZnB = Zinc borate, and C = Colemanite)

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Table 4. Thermal and Kinetic Analysis Results

Particleboard Specimens	Residual Amount [a] (%)	Initial Degradation Temperature [a] (°C)	Peak Degradation Temperature [b] (°C)	Final Degradation Temperature [a] (°C)	E_a [c] (kJ/mol)
Control Particleboard	22.03	154.99	352.13	395.52	61.75
Boric acid:borax-2%	29.39	165.66	343.42	379.31	69.31
Boric acid:borax-10%	36.05	164.75	337.46	359.08	68.25
Zinc Borate-2%	26.00	163.21	353.40	391.53	64.67
Zinc Borate-10%	33.40	160.11	348.62	384.86	64.92
Colemanite-2%	23.56	157.83	355.93	389.23	63.06
Colemanite-10%	30.77	156.85	354.53	395.40	63.47
a: determined from TG curve, b: determined from DTG curve, and c: calculated from Coats-Redfern non-isothermal method (n = 1)					

CONCLUSION

1. According to the peak heat release rate (PHRR) values obtained from the mass loss calorimeter (MLC) tests, the lowest PHRR recorded for the boric acid:borax-incorporated particleboards was at a loading level of 10%.

2. Based on the thermal analysis results, the boric acid:borax mixture incorporation to particleboards led to the start of the decomposition of cellulose in wooden material of particleboards at a lower temperature than the control particleboard specimens, which accelerated the char formation, and thermal degradation reaction paths during main thermal degradation stage needed more energy than the control specimens. The boric acid:borax mixture have also a cooling effect during the beginning of the main thermal degradation stage.

3. Zinc borate as a common boron-based fire retardant generally showed better performance against thermal degradation than colemanite but worse than the boric acid:borax mixture.

4. It can be stated that colemanite should not be suggested as a good alternative to common boron-based fire retardants for particleboards due to thermal behavior and fire performance test results of colemanite-incorporated particleboards.

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