



# Evaluations of the effects of different flame retardants combinations on particleboards produced using urea–formaldehyde resin

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## Abstract

Nowadays, using flame-retardant chemicals is gaining importance in chipboard production. Melamine resins to produce chipboard are preferred to provide flame retardancy properties with a cost of approximately 2.5 times the urea–formaldehyde (UF) resin. In this study, the UF resin to produce the chipboard was preferred due to its economical availability. To improve the flame retardancy properties of the chipboard, phosphate-based and inorganic flame retardants were used in the chipboards. In chipboard production, oak, pine, poplar, sawdust, urea–formaldehyde resin as adhesive, flame retardant chemicals like triphenyl phosphate (TPP), ammonium polyphosphate (APP), and calcium gluconate (CaG) were used. Flame retardant chemicals were added to chipboards in single and double compositions and prepared by pressing method. Mechanical (tensile, bending, and surface strength), physical (humidity, density, formaldehyde emission), and fire (limiting oxygen index (LOI), cone calorimeter, and UL-94 vertical) tests were performed on wooden boards. It has been observed that the use of different types of flame retardant and their combinations in chipboard does not significantly change the mechanical properties. It was seen that the free formaldehyde emission rate decreased by using flame retardant added compared to the control sample. The chipboard samples with added flame-retardant chemicals have entered the V-0 rating in the UL-94. LOI values of the chipboard samples containing 50% CaG–50% APP and 50% TPP—50% CaG were observed as 29.7% and 29.8%, respectively. Besides, the highest heat release rate (HRR) reduction was obtained in the chipboard sample containing 50% CaG—50% APP.

## 1 Introduction

In search of sustainable material resources that will be renewable and economically competitive, the wood sector covers a significant percentage of human use. As a renewable natural resource, wood has been the most versatile material for building, construction, decoration, or furniture, due to its aesthetically pleasing, superior properties such as high strength/mass ratio, low thermal conductivity, and low economic cost. One of its major disadvantages is probably due to its combustibility, which limits its wide use for residential and non-residential buildings (Sharma et al. 2015;

Yan et al. 2015; Rowell and Dietenberger 2012). Wood has a complicated burning behavior. However, the processes of pyrolysis, ignition, combustion, and extinction are largely well known with good agreement in the fire science literature for key parameters such as critical heat flux for ignition and heat of combustion over a wide variety of experimental settings. When natural polymers in wood are heated, they decompose, creating inert and combustible gases (the type and composition of which depends on the char yield), liquid tars, solid carbonaceous char (usually 20% the density of the wood), and inorganic ash. Additionally, as temperatures within a wood member approach 100 °C, free water begins to evaporate before the commencement of pyrolysis. Water vapour will travel further into the sample in some cases (away from the source of heat) (Bartlett et al. 2019; Drysdale 2011; Friquin 2011). Increased coal formation reduces flammable gas formation and helps insulate wood against further thermal degradation. Thermal degradation of wood results in the formation of a charred layer on the surfaces and a reduction in the affected cross-sectional area (Buchanan 2000; Janković and Dodevski 2018; Wong et al. 2014; Yue

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et al. 2017). The charred layer protects the underlying wood from heat exposure due to its low thermal conductivity. Wood has found use in many application areas, such as railway wooden bridges, due to its poor thermal conductivity and protection against the carbonization of structural wood (Rowell and Dietsberger 2012). Therefore, the development and improvement of the non-flammability of wood materials have become an important issue due to safety requirements (Schmid et al. 2015; Lowden and Hull 2013; ISO 5660-1 2015). Although various flame retardants (FRs) are used for synthetic polymer materials, ideal flame retardants for wood materials are still in development and new studies are urgently needed. With these FRs to be developed, it will be possible to increase the use of wood-based materials by preventing or delaying ignition and flame spread on wooden surfaces (Gu et al. 2007; Ozciftci and Okcu 2008). FRs are used to interfere, and suppress the combustion process at certain stages such as warming, decomposition, and ignition (Garlotta 2001; Grover et al. 2014). The most common flame retardants used for wood materials are inorganic salts, boron compounds, phosphoric acid, mono ammonium phosphate, diammonium phosphate, ammonium sulfate, nitrogen, and zinc chloride. The application of natural minerals, which is a new approach to high-tech flame retardants in the wood industry, creates an important potential (Candan et al. 2011; Taghiyari et al. 2013).

Halogen-based flame retardants (such as those based on bromine or chlorine) have several disadvantages such as the propensity tendency for bioaccumulation, the potential of corroding metal components, and the ability to generate toxic and corrosive hydrogen halides during combustion. Furthermore, halogenated flame retardants need often toxicologically critical antimony oxides as synergists. With growing environmental concerns, the usage of halogen-based flame retardants that are effective has been curtailed in both the plastics and wood industries. Although halogenated flame retardants are highly effective, it has been established that halogen-free flame retardants are safer for both people and the environment. Phosphorus, inorganic, and nitrogen (PIN) flame retardants are non-halogenated. PIN flame retardants reduce gas emissions by reducing burning intensity during the initial phase of a fire, tend to ensure lower-smoke density, and do not contribute to possible gas corrosivity and smoke toxicity. As a result, several international rules that expressly mandate the use of halogen-free flame retardants in items made of wood have been implemented in a wide range of sectors. Nitrogen and phosphorus compounds, which can lead to carbon-yielding reactions instead of carbon monoxide in degradation events, have received more attention in both academic and industrial areas. Phosphorus is found in several flame retardant compounds used in wood products (Janssens 2005; Levchik and Weil 2008; Tirri et al. 2012; Ekpe et al. 2020; Jiang et al.

2010). Therefore, in this study, non-halogen flame retardants containing especially phosphorus were used together with calcium gluconate.

In the chipboard production industry, three different production technologies are generally used horizontal, vertical, and molded chipboards. Although the methods follow the same phases, there are some changes in the stamping techniques, laying processes, and binder types used (Jiang et al. 2010). In the 1930s, urea–formaldehyde (UF) resin was developed as a chipboard binder, and today, ninety percent of the particleboard in the world is produced by using UF resin. Following that, melamine–formaldehyde (MF) resins, which are more water-resistant, have been widely used in areas where the product may encounter water, such as exterior-grade panel items and kitchen furnishings. The only disadvantage is that MF resin is more expensive than UF resin. Other resin types used are phenol–formaldehyde resins (Colakoglu 2001; Guler 2001; Bicer 2014; Uysal and Seref 2005).

This research aims to improve flame resistance and mechanical properties of chipboards with a high burning tendency by adding flame retardants in single and double combinations. The physical, mechanical, and flame performances such as the UL-94 vertical burning test, limiting oxygen index test (LOI), and cone calorimeter test on prepared particleboards by adding flame retardant at different rates were investigated. It is aimed to reduce the amount of free formaldehyde in the added chemicals by improving the mechanical properties of the produced chipboards. This study is also aimed to create different application areas, increase the usage areas, and thus provide both economic and ecological benefits by giving flame retardant behavior to the particleboard. It is also aimed to investigate the use of these compounds, which improve the fire performance of chipboard, in wood industries such as medium density fiberboard and impregnation.

## 2 Materials and methods

### 2.1 Materials

One of the main raw materials used in this study, fine and coarse wood chips were provided by Gebze Kastamonu Integrated Wood Industry company in Turkey. Urea–formaldehyde resins used as binders in the sheet were also provided by the resin department of Kastamonu Entegre Ağaç Sanayi in Turkey. The properties of UF resin are also given in Table 1. Ammonium polyphosphate (APP), triphenyl phosphate (TPP), and calcium gluconate (CaG) were used as flame retardant chemicals and were purchased from Clariant company and Merck, respectively.

**Table 1** Features of UF resin types used in the chipboard production stage

Features	UF %65 resin type (middle layer)
Solid content (%)	64.55
Density (g/cm <sup>3</sup> ) (20 °C) (limit: 1.270–1.295 g/cm <sup>3</sup> )	1.277
pH (20 °C) (limit: 7.80–9.00)	8.53
Viscosity (cps) (20 °C) (limit: 150–400 cps)	203
Gel time (s) (35–50 s)	39
Expiry time (day)	30
Features	UF %50 resin (bottom and top layer)
Solid content (%)	50.52
Density (g/cm <sup>3</sup> ) (20 °C) (limit: 1.200–1.215 g/cm <sup>3</sup> )	1.211
pH (20 °C) (limit: 7.80–9.00)	8.65
Viscosity (cps) (20 °C) (limit: 20–50 cps)	32
Gel time (s) (35–60 s)	49
Expiry time (day)	30

**Table 2** Chemical composition of the produced chipboards

Board group	Component	Compound (%) <sup>a</sup>
1	Pressed normal particle-board (control)	No FR
2	APP	100
3	TPP	100
4	CaG	100
5	APP/TPP	50–50
6	CaG/APP	50–50
7	TPP/CaG	50–50

<sup>a</sup>The ratios of flame retardants added to the UF resin to each other

## 2.2 Preparation of chipboards produced by adding flame retardant chemicals

Firstly, the fine and coarse wood chips taken from the Kastamonu Entegre (Kocaeli, Turkey) were dried in a laboratory oven for 2–4 h at 105 °C. Before gluing the chipboard, the moisture of the chips was reduced to 0.5–3%. The chemical composition and proportions added to the produced chipboards are shown in Table 2.

Then, the resin required to produce the test plates in 400×400×8 mm dimensions has been weighed. The types of resin used were: UF %65 is for the middle layer and UF %50 is for the lower and upper layers. Calculations have been made so that the density of the chipboards to be produced is 0.78 g/cm<sup>3</sup>. UF resin was used at the rate of 10% in

the surface layers and 8% in the middle layer compared to the full dry chip weight. 1% ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>) relative to its full dry weight was used as a hardener in the resin. Similarly, chemical agents that retard the flame in proportion to the full dry chip weight were sprayed on the resin chips with a pulverizer after the resin process in powder form at 20% to the middle layer and 10% to the bottom and top layers. The spraying process was carried out in a rotary drum gluing machine and homogeneous mixing was achieved. The resin was sprayed onto the chips with a pressure of 5–6 bars using a spray nozzle from the center of the drum rotating at 20 rpm. The resin was added to the chips by mixing so that the gluing process was completed in approximately 5–6 min. The gluing process was done separately for the middle layer, the lower and upper layer. After the gluing process, flame retardant chemicals were prepared and added to the drum in powder form at a rate to be used at this stage. After the chemicals were added, it was mixed homogeneously for a certain period.

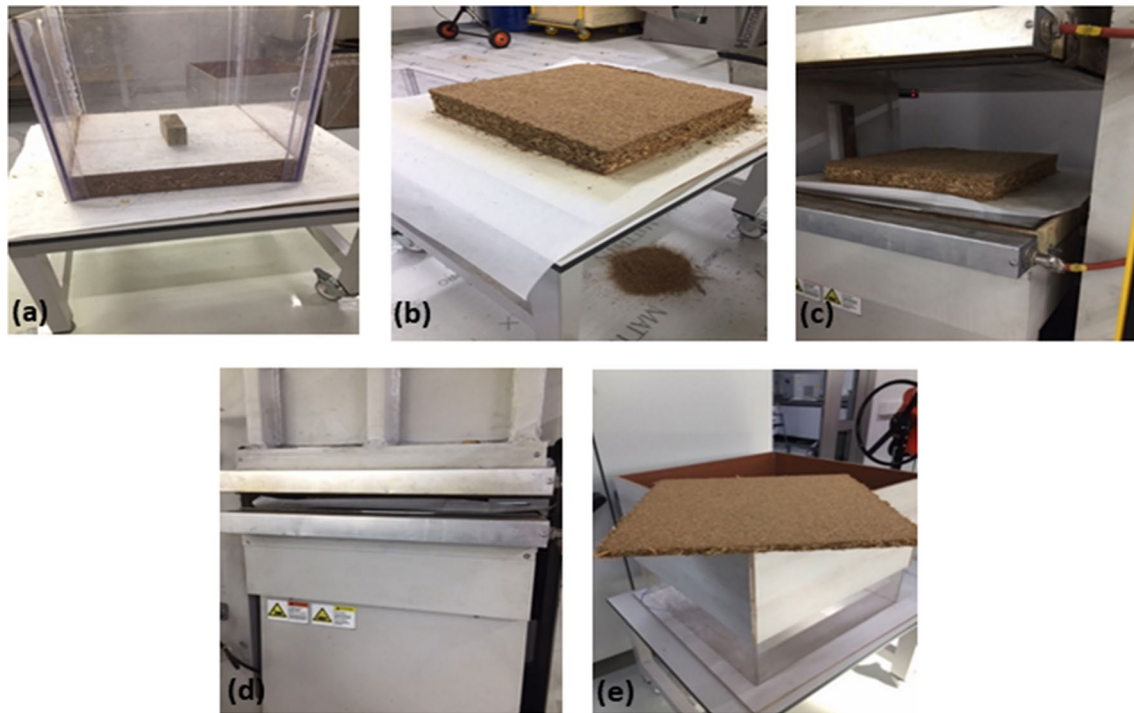
## 2.3 Preparation of the board

The thin chips taken for the substrate were laid manually in the cold press mould of 400×400 mm, as shown in Fig. 1a. After this process, the middle layer chips were glued and chemically added and finally, the top sheet chips were laid. After the laying process, the chips were pressed and compacted with a tray in mould size. Then, the frame was lifted by the edges, on the condition that it does not move the draft slowly (Fig. 1b). The laboratory type single-story hydraulic press was used for pressing the prepared plate draft. Figure 1c, d show the view of the plate placed in the press device in the press machine and the execution of pressing, respectively. The image of the chipboard removed after the press is given in Fig. 1e. The features of the press conditions of the chipboards in the stamping stage are given in Table 3. Then, the plate surfaces were sanded to improve the surface smoothness of the plates and to make the thickness of the plates more homogeneous.

## 2.4 Characterization

### 2.4.1 Physical properties of produced chipboards

Moisture measurements of the produced chipboards were taken according to the principles determined in TS EN 322 (1999) and by cutting them in 50×50 mm dimensions. The determination of the density of the produced chipboard samples was made according to TS EN 323 (1999). The dimensions of the samples to be cut according to TS EN 325 (1999) were examined and the cut of the chipboard sample in 50×50 mm dimensions was realized.



**Fig. 1** **a** Compressing the chipboard with a table, **b** de-moulding process and paste ready to stamp, **c** placement of the plate draft between the press plates, **d** the step of performing pressing, and **e** particleboard coming out after pressing

**Table 3** Conditions of the press machine during the production of chipboards

Width (mm)	8 and 14
Board dimension (mmxmm)	400×400
Press pressure (bar)	0–70
Press temperature (°C)	200
Press time (s)	141
Number of press step	9

#### 2.4.2 Mechanical properties of produced chipboards

Bending strength tests have been done according to TS EN 310 (1999). TS EN 326-1 (1999) served as information about how to take the sample and how to cut the dimensions. The particleboard parts are rectangular, 50 mm wide and the length is adjusted to be 20 times the thickness of the particleboard  $\pm 50$  mm, maximum 1050 mm. The chipboard samples produced were made using a universally used test device according to TS EN 319 (1999) for internal bond strength tests. Taking the chipboard samples and cutting the test pieces were made following TS EN 326-1 (1999), and the edges were cut in a square shape with  $50 \pm 1$  mm side length, with vertical edges with straight edges. Surface strength tests were made according to TS EN 311 (2005) Wood-based plates—surface strength test

method. Taking the sample and cutting the test pieces was done according to TS EN 326-1 (1999). The test pieces were prepared in the form of a square with a width and length of  $50 \pm 1$  mm.

#### 2.4.3 Formaldehyde emission

Formaldehyde emission measurement was made by the perforator method according to TS 4894 EN 120 (1999). In this method, a certain amount of sample was boiled in toluene to allow the free formaldehyde in the plate to pass into the water by extraction. For this test, chipboard samples of  $25 \times 25$  mm were used.

#### 2.4.4 UL-94 vertical burning test

UL-94 vertical burning test was performed on chipboard samples following ASTM D 3801-0 (2003) Standard. The sample size was cut to  $100 \times 10 \times 6$  mm as specified in the standard.

#### 2.4.5 Limit (limiting) oxygen index (LOI)

To measure the flame resistance of the flame retardant chemicals added during the production of the chipboard samples, analyses were made on the wood samples using the LOI test device following the ISO 4589-2 (2018) Standard. The wood

samples were cut in  $80 \times 10 \times 4$  mm dimensions and placed vertically with the holding mold inside a transparent glass chimney, through which a mixture of oxygen and nitrogen passes upwards.

#### 2.4.6 Cone calorimeter

Four of the chipboards produced were analyzed with a cone calorimeter device following with ISO 5660-1 (2015). The time to ignition, heat release rate, smoke generation, and oxygen consumption of the samples were obtained with the cone calorimeter analysis. The size of the standard sample is  $100 \times 100$  mm<sup>2</sup>. The sample thickness is also 14 mm. At least 3 tests were performed for each sample in the measurements made with the cone calorimeter.

### 3 Results and discussion

#### 3.1 Physical features

The average density, humidity, and thickness values of the produced chipboards are given according to the standard deviation in Table 4. When the results of the thickness and density data of the chipboard samples are examined, values close to each other were determined. According to TS EN 312 (2005) Standard, the tolerance for the average density in chipboards should be  $\pm 10\%$ . Average density values varied between 0.78 and 0.83 g/cm<sup>3</sup>, and when these values are compared with the 0.78 g/cm<sup>3</sup> targeted at the beginning of the study, it is seen that the deviation difference is by the standards. When the table is examined, it is seen that the chipboard sample moisture values vary between 4.82 and 5.05%. It was determined that these values are within the 5–13% range specified in the TS EN 312 standard for the average chipboard humidity.

#### 3.2 Mechanical properties

Table 5 shows the results of the mechanical (bending strength, internal bond strength, surface strength) tests of the chipboard samples produced by adding flame retardant

chemicals. It was observed that the sample with the highest bending strength 50% CaG—50% APP has a value of 17.03 MPa, while the lowest value is the chipboard sample with 100% APP chemical composition with a value of 15.03 MPa. Besides, it was found 0.88 MPa in the 100% CaG sample with the highest internal bond strength, and the internal bond strength was found as 0.68 MPa for the control sample. While the chipboard sample with the highest surface strength has a value of 1.04 MPa in the 50% APP—50% TPP sample, the lowest surface resistant value of 0.90 MPa in the chipboard with APP chemical added at a rate of 100% was found.

As can be clearly seen in Table 5, the surface durability of chipboards with added flame retardant chemicals was not significantly affected compared to the control sample. According to these results, the added chemicals do not have any negative effect on the surface strength values. Considering the surface strength values for all plates in general, it can be seen that TS EN 311 is suitable for min. 0.80 MPa value for plates with  $6 < t < 13$  mm interval.

The bending strength values of the produced samples are given in Fig. 2. The bending strength results of the chipboards produced with the flame-resistant chemical added at different rates showed similar results compared to the control sample. This means that the different amounts of added chemicals did not harm the flexural strength of the sheet. In general, when the bending strength values of all plates are examined, it is seen that the bending strength of the plates was higher than the value of min.11 MPa required by TS EN 312 (2005).

The internal strength values of the produced samples are given in Fig. 3. It is seen that there is an increase of about 30% in tensile values vertical to the surface when we compare the particleboard produced with the addition of flame-resistant chemicals with the normal non-added form. Therefore, it was observed that the added flame retardant chemicals do not reduce the internal tensile values of the chipboard, on the contrary, it increases the mechanical properties of the board. In general, when the values of internal bond strength of all plates are examined, it is seen that the internal bond strength is higher than the value of min. 0.40 MPa for the plates in the range of  $6 < t < 13$  mm

**Table 4** Physical properties of chipboards produced

Composition	Length (mm)	Width (mm)	Thickness (mm)	Density (g/cm <sup>3</sup> )	Moisture (%)
Control	49.94 ± 0.01	50.16 ± 0.31	8.10 ± 0.25	0.79 ± 0.01	4.85 ± 0.14
100% APP	49.89 ± 0.01	50.16 ± 0.19	7.95 ± 0.30	0.78 ± 0.01	4.82 ± 0.14
100% TPP	49.85 ± 0.05	50.02 ± 0.34	8.13 ± 0.21	0.80 ± 0.01	4.90 ± 0.10
100% CaG	49.83 ± 0.01	49.82 ± 0.10	7.89 ± 0.11	0.81 ± 0.01	5.05 ± 0.04
50% APP—50% TPP	50.00 ± 0.19	50.13 ± 0.27	7.92 ± 0.09	0.82 ± 0.02	4.96 ± 0.08
50% CaG—50% APP	50.04 ± 0.01	50.10 ± 0.17	8.11 ± 0.42	0.80 ± 0.01	4.87 ± 0.06
50% TPP—50% CaG	50.19 ± 0.20	50.25 ± 0.03	7.92 ± 0.32	0.82 ± 0.02	4.79 ± 0.05

**Table 5** Physical properties of produced chipboards

Composition	Bending strength (MPa)	Internal bond strength (MPa)	Surface strength (MPa)
Control	15.27 ± 0.95	0.68 ± 0.01	0.92 ± 0.02
100% APP	15.03 ± 0.68	0.79 ± 0.04	0.90 ± 0.08
100% TPP	15.92 ± 0.12	0.85 ± 0.06	0.99 ± 0.01
100% CaG	16.10 ± 0.92	0.88 ± 0.01	1.03 ± 0.05
50% APP—50% TPP	15.83 ± 0.40	0.72 ± 0.07	1.04 ± 0.14
50% CaG—50% APP	17.03 ± 0.50	0.82 ± 0.06	0.99 ± 0.08
50% TPP—50% CaG	16.92 ± 0.33	0.76 ± 0.04	1.01 ± 0.08

required by TS EN 312 (2005). Consistent with the literature, it has been observed that the added flame retardant chemicals increase the internal adhesion strength of chipboards above the minimum value and generally increase the mechanical properties of the board (Yue et al. 2017, 2020).

### 3.3 Formaldehyde emission results

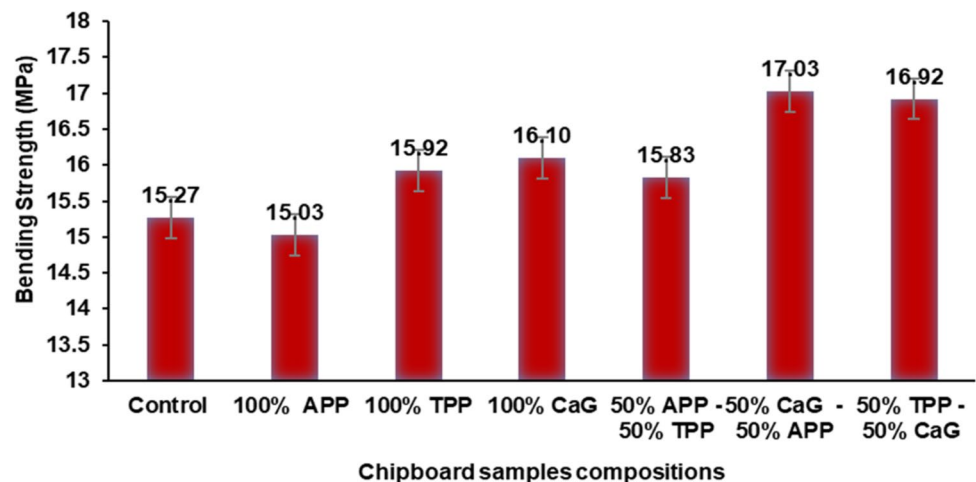
For formaldehyde emission, samples of the plates are extracted with boiling toluene and transferred into distilled or deionized water after this event. The formaldehyde of the solution containing water was analyzed photometrically by the acetyl acetone method TS 4894 EN 120 (1999). The free formaldehyde emission results analyzed by the perforator method of the chipboard samples produced by adding flame retardant chemicals in different proportions are given in Table 6. When the formaldehyde emission results were evaluated, it was seen that the free formaldehyde emission rate decreased in all chipboard samples with flame retardant added compared to the control sample. This indicates that the rate of free formaldehyde emitted into the environment is decreasing. The lowest formaldehyde emission was obtained for 100% APP, and 50% CaG—50% APP samples. In addition, this case is the desired result for the chipboard producers. The free formaldehyde emission rate specified

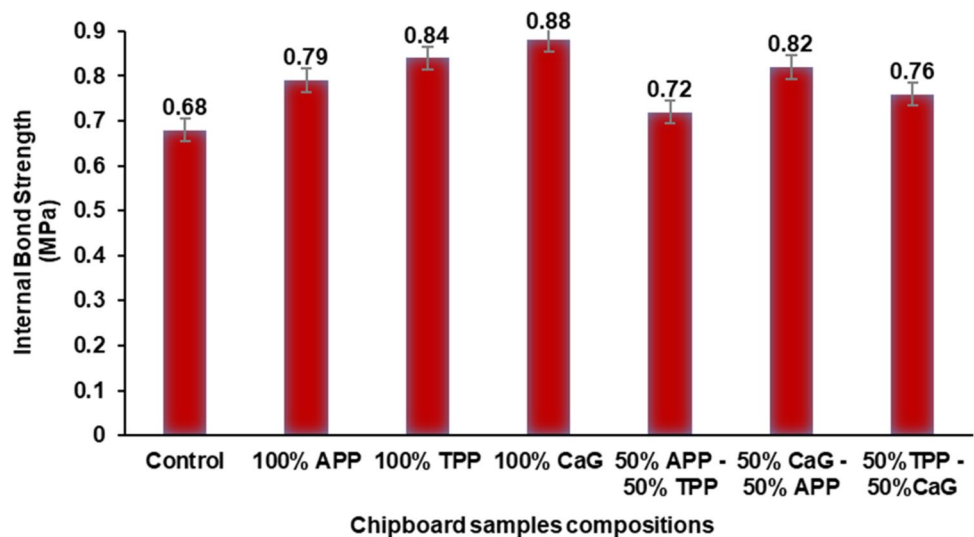
in the TS EN ISO 12460-5 (2015) Standard was determined as < 8 (mg/100 g), and all chipboards produced are below this value.

### 3.4 UL-94 vertical burning test and limit (limiting) oxygen index (LOI)

UL-94 vertical combustion test was applied to analyze the combustion behavior of vertically positioned samples in contact with the ignition source (burner flame) (Tuzcu 2010). In the UL-94 vertical combustion test, the samples are classified in three ways ( $V_0$ ,  $V_1$ ,  $V_2$ ) regarding the flammability of the material, the individual burning time of all samples, the total burning time of all samples, and the amount of falling droplets, accompanied by the recorded times and observations after being exposed to the flame ASTM D 3801-0 (2003). The chemical structures of the polymers significantly affect the LOI values. LOI values can be determined by the number of oxidizable atomic or molecular groups of polymers. The higher the ratio of hydrogen and carbon, which affects its flammability, the higher the flammability of the materials. The high LOI value of any material indicates that it is difficult to be flammable in the atmospheric environment. For this reason, materials with an LOI value of less than

**Fig. 2** The average bending strength values of chipboard samples



**Fig. 3** Average internal bond strength of chipboard samples**Table 6** Average free formaldehyde emission results for the chipboard samples

Samples	Composition	Free formaldehyde emission (mg/100 g)
1	Control	5.41 ± 0.34
2	100% APP	1.42 ± 0.10
3	100% TPP	1.58 ± 0.05
4	100% CaG	1.80 ± 0.15
5	50% APP—50% TPP	1.62 ± 0.18
6	50% CaG—50% APP	1.49 ± 0.13
7	50% TPP—50% CaG	2.17 ± 0.26

25% can burn very easily in the air, while those with an LOI value of more than 25% are self-extinguishing in the air (Kayan 2004).

LOI measurements and UL-94 vertical burning tests are widely used to evaluate the flame-resistant properties of wood materials added with flame retardant chemicals. Table 7 shows the LOI values in O<sub>2</sub>% of all samples and the results of the UL-94 tests, respectively. According to these test results, the LOI value of the control sample was 24.6% and the burning time was 39 s. The LOI test performed with the 50% TPP—50% CaG chipboard sample gave an improved result of 29.8%. In addition, the burning time has decreased compared to the control sample. In addition, it has been determined that the LOI performance of chipboards produced by adding 100% APP is lower than the chipboards added with CaG or TPP.

UL-94 vertical burning test was applied to determine the combustibility of the flame retardant added chipboard samples in the vertical position and the combustibility when exposed to a low amount of flame. While it was

observed that the chipboard sample without flame retardant chemical burned for more than 5 min and fell into the flammable substance category, the chipboard samples with flame retardant chemicals added were seen to enter the V-0 grade. It is thought that APP, TPP, and CaG flame retardant chemicals slow down the ignition and prevent contact with oxygen on the surfaces of the samples in contact with the flame, creating a protective carbonized layer.

### 3.5 Cone calorimeter

The cone calorimeter is recognized as one of the most important bench-scale devices for determining the effects of the addition of flame retardants (Wang et al. 2010). Four of the chipboards produced were analyzed with a cone calorimeter device by ISO 5660-1 (2015). The basic principle to determine the heat release rate is to measure the decreasing oxygen concentration in the combustion gases of a standard sample subjected to a given heat flux. With cone calorimetry analysis, it provides comprehensive insight not only into the fire risks of samples such as total heat release, heat release rate, and ignition time but also into fire hazards such as smoke emission, CO production, and oxygen consumption. These test data easily contribute to the scientific understanding of the combustion and fire reaction properties of samples.

Tables 8 and 9 show the average results of the ignition time, heat dissipation rate, total heat release, specific extinction area, effective heat of combustion, and smoke production rate values determined by the cone calorimeter analyses. Cone calorimeter smoke data is usually presented in terms of a 'specific extinction area' which is a measure of the smoke production of a material (Yang and Zhang 2019). The effective heat of combustion (EHC) is the ratio of heat release (HRR) rate to mass loss rate measured in a small-scale

calorimeter (Janssens 2005). In other words, EHC is the amount of energy produced per unit mass lost in the cone calorimeter test. The mass-loss rate is determined by measurement of the specimen mass and is derived numerically ISO 17554 (2014). Ignition time is defined as the time when ignition occurs on the sample surfaces for the first time. Ignition time is important for evaluating the flame performance of plate (Li 2000). Compared to the control sample, it was observed that the chipboard sample containing 100% CaG showed a 45% increase at the ignition time. Chipboard samples with 50% CaG—50% APP and 50% TPP—50% CaG chemical content showed an increase of 29.5% and 26.1%,

respectively, compared to the control sample. Since the ignition time of the 100% CaG applied sample is higher, it provides a longer ignition start and higher flame retardancy than the others.

Ignition time, heat release rate, total heat release, and smoke production rate are important parameters used to evaluate the flame retardancy and combustibility of interior materials (Li 2003). Table 8 and Fig. 4 show the heat release rate of the samples. The primary result from the cone calorimeter test is the rate of heat release relative to the time curve. Heat release is defined as the heat emanating from the sample per unit of time and is determined by the oxygen

**Table 7** LOI and UL-94 test results for particleboard with FR chemicals

Sample	LOI (% O <sub>2</sub> )	Burning duration (s)	Burning length <sup>a</sup>	UL-94 rating	Dripping
Control	24.6	39	No	Flammable material	No
100% APP	26.8	16	No	V <sub>0</sub>	No
100% TPP	29.1	16	No	V <sub>0</sub>	No
100% CaG	29.1	16	No	V <sub>0</sub>	No
50% APP—50% TPP	28.6	18	No	V <sub>0</sub>	No
50% CaG—50% APP	29.7	20	No	V <sub>0</sub>	No
50% TPP—50% CaG	29.8	16	No	V <sub>0</sub>	No

<sup>a</sup>Whether the burning length passes the 50 mm limit or not

**Table 8** Average results of combustion parameters of cone calorimeter analysis

Component %	Ignition time (s)	Heat release rate (1st peak) (kW/m <sup>2</sup> )	Heat release rate (2nd peak) (kW/m <sup>2</sup> )	Total heat release (MJ/m <sup>2</sup> )	
Control	31.0	165.7	128.0	0–300 s	34.6
				0–600 s	63.4
				0–1200 s	112.4
100% CaG	56.5	159.7	158.6	0–300 s	29.8
				0–600 s	53.2
				0–1200 s	106.6
50% CaG—50% APP	44.0	109.3	109.2	0–300 s	21.9
				0–600 s	39.8
				0–1200 s	81.4
50% TPP—50% CaG	42.0	156.7	123.0	0–300 s	32.9
				0–600 s	61.0
				0–1200 s	109.1

**Table 9** Average results of combustion parameters obtained from cone calorimeter device

Component %	Specific extinction area (m <sup>2</sup> /kg)	Effective heat of combustion (MJ/kg)	Smoke production rate (m <sup>2</sup> /s)	Total smoke production (m <sup>2</sup> )	Mass loss rate (g/s m <sup>2</sup> )
Control	37.90	13.89	0.013	3.5	5.47
100% CaG	27.44	12.77	0.008	2.9	5.28
50% CaG—50% APP	9.03	11.19	0.006	0.9	4.88
50% TPP—50% CaG	150.70	12.75	0.027	6.3	5.39



consumed during combustion (ASTM E 1354 2008). As can be seen in Fig. 4, when the samples are ignited, the rate of heat release firstly increased, then decreased, and then increased again. Two exothermic peaks were observed with time in heat release rates in all samples (Grexa and Lübke 2001; Chung 2010; Lee et al. 2011). Two peaks are commonly mentioned in the literature on wood-burning tests. These peaks are reported as a peak during the first phase of combustion and a second peak before the flame is extinguished (Grexa and Lübke 2001; Chung 2010). The surface of the wooden samples was first exposed to heat radiation to decompose the flammable material. The burning reaction of the sample continued under high-temperature conditions and the first exothermic peak occurred. The first exothermic peak is due to the formation of the charred layer on the surface. After the formation of this layer, the tendency to decrease in the rate of heat release is the effect of the outer charred layer, which reduces the amount of heat and gas emission to the inner combustion area. It was observed that the chipboard samples shrank and bent after the first peak in the heat release, while the coal layer formed on the chipboard surface expanded significantly in volume on the surface. It has been observed that the burning of the shrinking and bending chipboard takes place from the bottom and the edges. The carbonized layer increased the distance between the flame and the underlying materials, reducing the combustion intensity and combustion temperature of the sample. The second exothermic peak formed was initiated due to the heat accumulated behind the sample at high temperatures (Li et al. 2015). The heat is gradually transferred to the interior area. The interior of the wood specimens is then exposed to heat, decomposed, and burned under high-temperature conditions. The second exothermic peak occurred as flammable

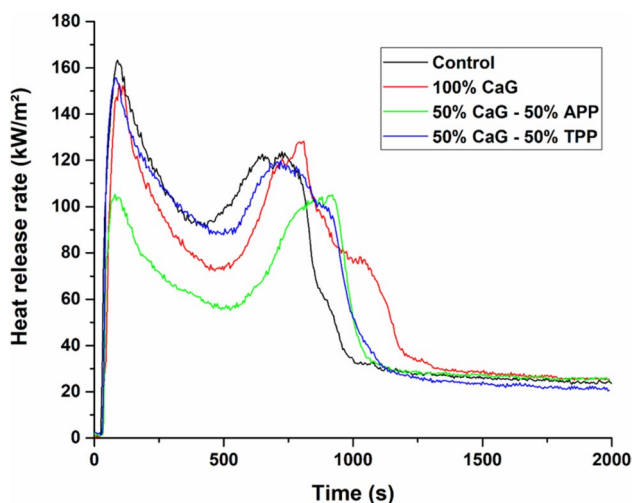


Fig. 4 Comparative graph of heat release rates of chipboard samples

materials increased, and the rate of heat release increased (Xu et al. 2015). While evaluating, the rates with the highest heat emission rate were used. When the 1st exothermic peak values are examined, the sample showing the highest decrease is the chipboard sample containing 50% CaG—50% APP flame retardant. The chipboard sample containing 50% CaG—50% APP flame retardant showed a 34% decrease in the rate of heat release compared to the control sample. The heat release rate of chipboard samples containing 100% CaG and 50% CaG—50% TPP flame retardant chemical decreased by 3.6% and 5.4%, respectively.

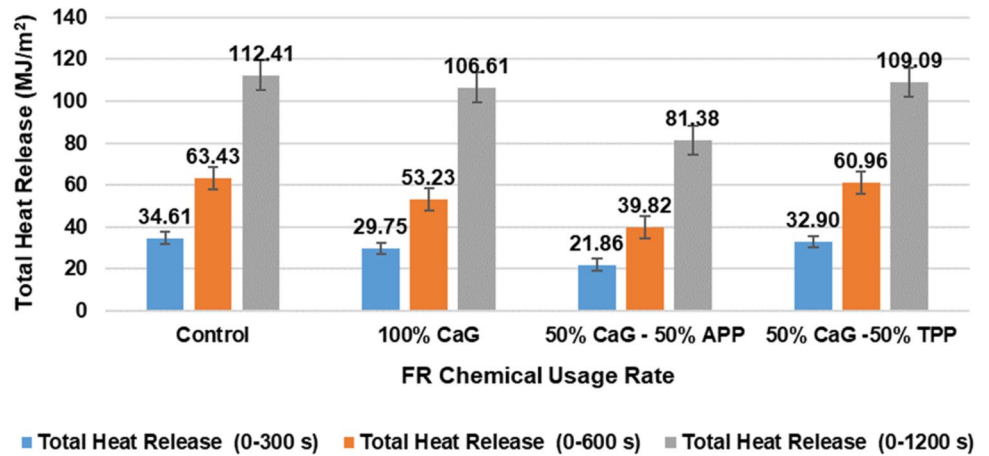
The total heat release rate values of the chipboard samples are given in Fig. 5 and Table 8. The chipboard samples containing 100% CaG, 50% CaG—50% APP, and 50% CaG—50% TPP showed a decrease of 14%, 36.8%, and 4.9% in turn compared to the control sample. The highest reduction was obtained in the chipboard sample containing 50% CaG—50% APP.

The smoke production rate refers to the amount of intensive smoke released per unit time, which can be calculated by dividing a given extinguishing area by the ratio of mass loss. Total smoke production is defined as the total amount of smoke released by the material during the combustion and pyrolysis process. Table 9 and Fig. 6 show the comparison of the smoke production rates of the chipboard samples. If the smoke production rates are evaluated, the chipboard samples containing 100% CaG, 50% CaG—50% APP decreased by 38.5%, and 53.8%, respectively, compared to the control sample. An increase of 107% was observed for the 50% CaG-50% TPP sample compared to the control sample. In the results of total smoke production, the chipboard samples containing 100% CaG, 50% CaG—50% APP decreased by 17.1% and 74.3%, respectively, compared to the control sample, while the sample containing 50% CaG—50% TPP was an increase of 44.4%. As a result of both smoke production rate and total smoke production values, it was determined that the combination of APP and CaG flame retardant for flame retardant chipboards had a synergistic smoke suppression effect.

Another index of smoke emission is the specific extinction area. It is a measure of smoke efficiency, and the higher this value, the greater the amount of smoke emitted per kilogram of sample (Angelini et al. 2019). The quenching areas of the samples containing 100% CaG, 50% CaG—50% APP flame retardant compared to the control sample showed a decrease of 27.6% and 76.2%. The sample containing 50% CaG—50% TPP showed an increase of approximately five times when compared to the control sample.

The effective heat of combustion is the energy released per mass lost by combustion. There was a decrease in the effective heat of combustion values in all samples compared to the control sample (Table 9). Effective heat values of particleboard samples containing 100% CaG, 50% CaG—50%

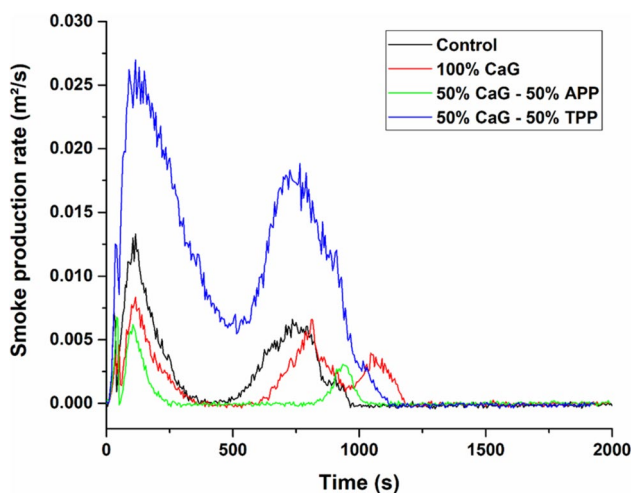
**Fig. 5** Total heat release values of chipboard samples at certain times



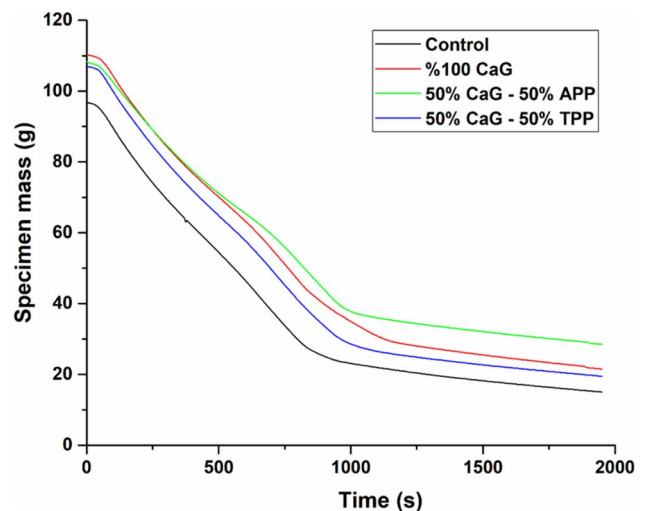
APP, and 50% CaG—50% TPP were obtained at the values of 12.77 MJ/kg, 11.19 MJ/kg, and 12.75 MJ/kg, respectively. According to the results obtained, it has been observed that the volatile gases formed as a result of combustion reduce the possibility of combustion. The mass-loss rate is one of the other parameters measured by the cone calorimeter. The lower the mass loss values and the higher the coal residue during the combustion, the higher the flame retardant ability of the chipboard material. According to the results of the mass-loss rate values of the samples, the lowest value belongs to the sample containing 50% CaG—50% APP chemical. The results of the samples containing 100% CaG and 50% CaG—50% TPP chemicals are very close to the control sample. The change in masses of chipboard samples with time is given in Fig. 7.

The images obtained as a result of the cone calorimeter analysis of chipboard samples are given in Fig. 8. It was

observed that the coal layer expanded significantly in volume, forming a worm-like and white structure dispersed on the surface of the material, and increasing the distance between the heat flux and the underlying materials for the sample of 50% CaG—50% APP. This case reduces the burning intensity and combustion temperature of the sample (Han et al. 2007; Bai et al. 2014). The sample containing 50% CaG—50% APP appears to have a more compact coal structure as the polyphosphates formed by the decomposition of APP form a cross-linked carbonaceous structure (Stark et al. 2010; Zhang et al. 2012). Besides, the control sample and particleboard including 100% CaG flame retardant created residual images with a similar structure. When all combustion analysis results were evaluated, it was seen consistent with the literature that the addition of flame retardants to chipboard samples clearly improved the fire resistance performance (Yue et al. 2017, 2020).

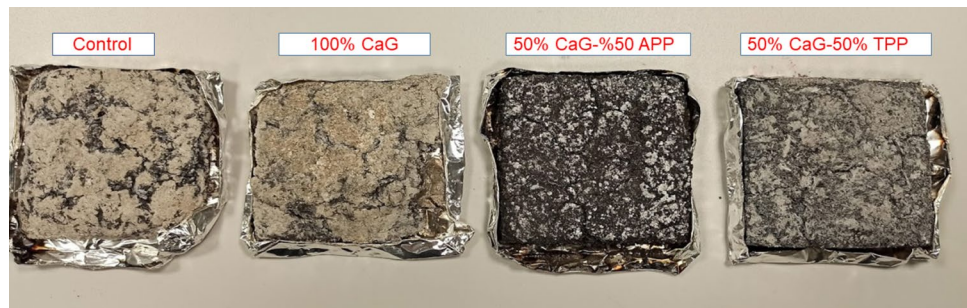


**Fig. 6** Comparative graph of smoke production rates of chipboard samples



**Fig. 7** Change in masses of chipboard samples with time

**Fig. 8** Image of residual samples as a result of conical calorimeter analysis



## 4 Conclusion

This research aims to improve the flame resistance and mechanical properties of chipboards, which have a high tendency to burn, by adding flame retardants in single and double hybrid combinations, and to make the use of UF resin more economical than the use of melamine resin. While the chipboard sample with the highest bending strength was 50% CaG—50% APP, the chipboard sample with the highest surface strength was seen in the 50% APP—50% TPP sample. In the UL-94 vertical burning test results, while the control chipboard sample entered the flammable substance category, chipboard samples with added flame retardant chemicals entered the V-0 rating. LOI values of the chipboard samples containing 50% CaG-50% APP and 50% TPP—50% CaG determined 29.7% and 29.8%, respectively. In the cone calorimetry test, when compared to the control sample, the ignition time of the sample containing 100% CaG increased by 45%, which is the highest value, compared to other samples. It was observed that the heat release rate and total heat release rate of the sample containing 50% CaG—50% APP decreased by 34% and 36.8%, respectively, which are the lowest values. Considering both the smoke production rate and the total smoke production values, a decrease was observed in the chipboard samples containing 100% CaG, 50% CaG—50% APP compared to the control sample, while an increase was observed in the 50% CaG-50% TPP sample. At the same time, it was determined that the 50% CaG—50% APP sample had more coal layer after burning than the other samples.

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**Data availability** The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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## References

- Angelini S, Barrio A, Cerruti P, Scarinzi G, Garcia-Jaca J, Savy D, Piccolo A, Malinconico M (2019) Lignosulfonates as fire retardants in wood flour-based particleboards. *Int J Polym Sci*. <https://doi.org/10.1155/2019/6178163>
- ASTM D 3801-0 (2003) Standard test method for measuring the comparative burning characteristics of solid plastics in a vertical position ASTM. American Society for Testing Materials
- ASTM E 1354 (2008) Annual Book of ASTM standards, vol 4.07. American Society for Testing and Materials, Conshohocken
- Bai G, Guo C, Li L (2014) Synergistic effect of intumescent flame retardant and expandable graphite on mechanical and flame-retardant properties of wood flour-polypropylene composites. *Constr Build Mater* 50:148–153. <https://doi.org/10.1016/j.conbuildmat.2013.09.028>
- Bartlett AI, Hadden RM, Bisby LA (2019) A review of factors affecting the burning behaviour of wood for application to tall timber construction. *Fire Technol* 55(1):1–49. <https://doi.org/10.1007/s10694-018-0787-y>
- Bicer A (2014) Sodium carboxymethylcellulose (Na-CMC) modified particleboard production. Forest Industrial Engineering, Bartın University, Bartın
- Buchanan AH (2000) Fire performance of timber construction. *Prog Struct Eng Mater* 2(3):278–289. [https://doi.org/10.1002/1528-2716\(200007/09\)2:3%3c278::AID-PSE33%3e3.0.CO;2-P](https://doi.org/10.1002/1528-2716(200007/09)2:3%3c278::AID-PSE33%3e3.0.CO;2-P)

- Candan Z, Ayrimlis N, Akbulut T (2011) Dimensional stability performance of fire retardant treated veneer-oriented strandboard composites. *BioResources* 6(1):308–316
- Chung Y-J (2010) Comparison of combustion properties of native wood species used for fire pots in Korea. *J Ind Eng Chem* 16(1):15–19. <https://doi.org/10.1016/j.jiec.2010.01.031>
- Colakoglu G (2001) Stratified wood material, vol 223. K.T.Ü. Faculty of Forestry Publications, Trabzon
- Drysdale D (2011) An introduction to fire dynamics. In: Rowell RM, Dietsberger MA (eds) *Thermal properties, combustion, and fire retardancy of wood. Handbook of wood chemistry and wood composites*. Wiley, pp 127–150
- Ekpe OD, Choo G, Barceló D, Oh J-E (2020) Introduction of emerging halogenated flame retardants in the environment. In: *Comprehensive analytical chemistry*, vol 88. Elsevier, pp 1–39
- Friquin KL (2011) Material properties and external factors influencing the charring rate of solid wood and glue-laminated timber. *Fire Mater* 35(5):303–327. <https://doi.org/10.1002/fam.1055>
- Garlotta D (2001) A literature review of poly (lactic acid). *J Polym Environ* 9(2):63–84
- Grexa O, Lübke H (2001) Flammability parameters of wood tested on a cone calorimeter. *Polym Degrad Stab* 74(3):427–432. [https://doi.org/10.1016/S0141-3910\(01\)00181-1](https://doi.org/10.1016/S0141-3910(01)00181-1)
- Grover T, Khandual A, Chatterjee K, Jamdagni R (2014) Flame retardants: an overview. *Colourage* 61:28–36
- Gu J-W, Zhang G-C, Dong S-I, Zhang Q-Y, Kong J (2007) Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. *Surf Coat Technol* 201(18):7835–7841. <https://doi.org/10.1016/j.surfcoat.2007.03.020>
- Guler C (2001) Research on the production possibilities of the particle board from cotton (*Gossypium hirsutum* L.) stalks. Forestry and Forest Engineering, Karaelmas University, Zonguldak
- Han Z, Dong L, Li Y, Zhao H (2007) A comparative study on the synergistic effect of expandable graphite with APP and IFR in polyethylene. *J Fire Sci* 25(1):79–91. <https://doi.org/10.1177/0734904107066308>
- ISO 17554 (2014) Reaction to fire tests—mass loss measurement. International Standards Organization, Geneva
- ISO 5660-1 TI (2015) Reaction-to-fire tests—heat release, smoke production and mass loss rate—part 1: heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement). International Organization for Standardization, Geneva
- Janković B, Dodevski V (2018) The combustion performances and thermo-oxidative degradation kinetics of plane tree seeds (PTS) (*Platanus orientalis* L.). *Energy* 154:308–318. <https://doi.org/10.1016/j.energy.2018.04.149>
- Janssens ML (2005) Material flammability. In: *Handbook of environmental degradation of materials*. Elsevier, pp 207–225
- Jiang J, Li J, Hu J, Fan D (2010) Effect of nitrogen phosphorus flame retardants on thermal degradation of wood. *Constr Build Mater* 24(12):2633–2637. <https://doi.org/10.1016/j.conbuildmat.2010.04.064>
- Kayan S (2004) Combustion mechanism of textile materials and limit oxygen index values. Marmara University Institute of Science and Technology, Textile Education Department Instrumental Analysis Course, Istanbul
- Lee B-H, Kim H-S, Kim S, Kim H-J, Lee B, Deng Y, Feng Q, Luo J (2011) Evaluating the flammability of wood-based panels and gypsum particleboard using a cone calorimeter. *Constr Build Mater* 25(7):3044–3050. <https://doi.org/10.1016/j.conbuildmat.2011.01.004>
- Levchik S, Weil E (2008) Developments in phosphorus flame retardants. In: *Advances in fire retardant materials*. Elsevier, pp 41–66.
- Li B (2000) Smoke suppression and fire-retardant of poly(vinyl chloride). Northeast Forestry University Press, Harbin, pp 85–204
- Li B (2003) Influence of polymer additives on thermal decomposition and smoke emission of poly(vinyl chloride). *Polym Degrad Stab* 82(3):467–476. [https://doi.org/10.1016/S0141-3910\(03\)00201-5](https://doi.org/10.1016/S0141-3910(03)00201-5)
- Li K, Pau DS, Wang J, Ji J (2015) Modelling pyrolysis of charring materials: determining flame heat flux using bench-scale experiments of medium density fibreboard (MDF). *Chem Eng Sci* 123:39–48. <https://doi.org/10.1016/j.ces.2014.10.043>
- Lowden LA, Hull TR (2013) Flammability behaviour of wood and a review of the methods for its reduction. *Fire Sci Rev* 2(1):1–19
- Ozcifci A, Okcu O (2008) Impacts of some chemicals on combustion properties of impregnated laminated veneer lumber (LVL). *J Mater Process Technol* 199(1–3):1–9. <https://doi.org/10.1016/j.jmatprotec.2007.10.003>
- Schmid J, Just A, Klippel M, Fragiaco M (2015) The reduced cross-section method for evaluation of the fire resistance of timber members: discussion and determination of the zero-strength layer. *Fire Technol* 51(6):1285–1309. <https://doi.org/10.1007/s10694-014-0421-6>
- Sharma NK, Verma C, Chariar VM, Prasad R (2015) Eco-friendly flame-retardant treatments for cellulosic green building materials. *Indoor Built Environ* 24(3):422–432. <https://doi.org/10.1177/1420326X13516655>
- Stark NM, White RH, Mueller SA, Osswald TA (2010) Evaluation of various fire retardants for use in wood flour–polyethylene composites. *Polym Degrad Stab* 95(9):1903–1910. <https://doi.org/10.1016/j.polymdegradstab.2010.04.014>
- Taghiyari HR, Rangavar H, Nouri P (2013) Fire-retarding properties of nanowollastonite in MDF. *Eur J Wood Prod* 71(5):573–581. <https://doi.org/10.1007/s00107-013-0711-6>
- Tirri T, Aubert M, Wilén C-E, Pfaendner R, Hoppe H (2012) Novel tetrapotassium azo diphosphonate (INAZO) as flame retardant for polyurethane adhesives. *Eur J Wood Prod* 97(3):375–382. <https://doi.org/10.1016/j.polymdegradstab.2011.12.005>
- TS EN 310 (1999) Wood Based Boards-Determination of Flexural Strength and Flexural Modulus of Elasticity. Turkish Standards Institute, Ankara
- TS EN 311 (2005) Wood Based Panels-Surface Soundness-Test Method. Turkish Standards Institute, Ankara
- TS EN 312 (2005) This standard specifies the requirements for resin-bonded unfaced particleboards. Turkish Standards Institute, Ankara
- TS EN 319 (1999) Particle boards and fiberboards—determination of tensile strength perpendicular to the board surface. Turkish Standards Institute, Ankara
- TS EN 322 (1999) Wood based boards—determination of moisture amount. Turkish Standards Institute, Ankara
- TS EN 323 (1999) Wood-based panels—determination of density. Turkish Standards Institute, Ankara
- TS EN 325 (1999) Wood-Based panels—determination of dimensions of test pieces. Turkish Standards Institute, Ankara
- TS EN 326-1 (1999) Wood-based panels—sampling, cutting and inspection—part 1: sampling test pieces and expression of test results. Turkish Standards Institute, Ankara
- TS EN ISO 12460-5 (2015) Wood-based panels-determination of formaldehyde release-part 5: extraction method (called the perforator method). CEN, European Committee for Standardization: Bruxelles
- Tuzcu H (2010) Experimental investigation of flammability and combustion characteristics of fire resistant polyurethane based materials used in thermal insulation and automotive industries. Pamukkale University Institute of Science and Technology
- Uysal B, Seref K (2005) Dimensional stability of laminated veneer lumbers manufactured By using different adhesives after the steam test. *Gazi Univ J Sci* 18(4):681–691

- Wang L, He X, Wilkie CA (2010) The utility of nanocomposites in fire retardancy. *Materials* 3(9):4580–4606. <https://doi.org/10.3390/ma3094580>
- Wong KK, Gamage N, Setunge S, Pannirselvam M (2014) Thermal behaviour of hardwood and softwood composites. *Advanced Materials Research. Trans Tech Publ, Zurich*, pp 220–225
- Xu Q, Chen L, Harries KA, Zhang F, Liu Q, Feng J (2015) Combustion and charring properties of five common constructional wood species from cone calorimeter tests. *Constr Build Mater* 96:416–427. <https://doi.org/10.1016/j.conbuildmat.2015.08.062>
- Yan Y, Dong Y, Li J, Zhang S, Xia C, Shi SQ, Cai L (2015) Enhancement of mechanical and thermal properties of Poplar through the treatment of glyoxal-urea/nano-SiO<sub>2</sub>. *RSC Adv* 5(67):54148–54155. <https://doi.org/10.1039/C5RA07294H>
- Yang X, Zhang W (2019) Flame retardancy of wood-polymeric composites. In: *Polymer-based multifunctional nanocomposites and their applications*. Elsevier, pp 285–317.
- Yue K, Chen Z, Lu W, Liu W, Li M, Shao Y, Tang L, Wan L (2017) Evaluating the mechanical and fire-resistance properties of modified fast-growing Chinese fir timber with boric-phenol-formaldehyde resin. *Constr Build Mater* 154:956–962. <https://doi.org/10.1016/j.conbuildmat.2017.08.035>
- Yue K, Wu J, Xu L, Tang Z, Chen Z, Liu W, Wang L (2020) Use impregnation and densification to improve mechanical properties and combustion performance of Chinese fir. *Constr Build Mater* 241:118101–118108. <https://doi.org/10.1016/j.conbuildmat.2020.118101>
- Zhang ZX, Zhang J, Lu B-X, Xin ZX, Kang CK, Kim JK (2012) Effect of flame retardants on mechanical properties, flammability and foamability of PP/wood–fiber composites. *Compos B Eng* 43(2):150–158. <https://doi.org/10.1016/j.polymdegradstab.2010.04.014>

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