

# Flammability and thermal degradation behavior of flame retardant treated wood flour containing intumescent LDPE composites

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**Abstract** In the current study, the flame retardant wood-plastic composites (WPC) were produced by reducing the flammability of both the wood flour (WF) and the matrix material. Accordingly, WF was treated either with bis[trakis (hydroxymethyl) phosphonium] sulfate (THPS) or with dicyandiamide-formaldehyde-phosphoric acid flame retardants (DFP). The synergistic mixture of ammonium polyphosphate (m-APP) was used to improve the flame retardancy of matrix material based on low density polyethylene (LDPE). The flame retardant properties of LDPE based composites were investigated using limiting oxygen index (LOI), UL-94 standard, thermogravimetric analysis (TGA), and cone calorimeter. The addition of 30 wt% m-APP increased the LOI value from 17.5 to 24.2 and still burned to a clamp (BC) in UL-94 test. The THPS and DFP treatments of WF did not have any remarkable effects on the flammability properties (LOI and UL-94 ratings) with respect to LDPE/WF/APP composite. According to cone calorimeter test results, the treatments of WF with THPS and DFP improved the fire performance with approximately 25 % reduction in total heat evolved (THE) with respect to LDPE/WF/APP. The high reduction in THE value demonstrated that there was an increase in the fire performance of the LDPE based composites when THPS or

DFP treated WF was used with m-APP due to the increase in the amount of foamed char providing barrier effect.

## 1 Introduction

Lignocellulosic fibers are mostly used as outstanding reinforcing agents in plastics due to their low-weight, low-cost and certain specific properties. However, some problems such as low thermal stability of lignocellulosics, poor interfacial adhesion between polar lignocellulosics and non-polar matrix material and moisture uptake restrict the use of lignocellulosics (George et al. 2001; Jawaid and Abdul Khalil 2011; Mohanty et al. 2005). One of the most widely used lignocellulosics in the applications of construction and building products is wood flour (WF). Wood polymer composites (WPC) must meet fire retardant specifications in these application areas. There is a limited number of studies with regard to the flame retardancy of WPC in literature (Chapple and Anandjiwala 2010; Kozłowski and Władysław-Przybylak 2008).

The flame retardant WPC can be produced by decreasing the flammability of the matrix or the fiber material or both of them (Chapple and Anandjiwala 2010; Kozłowski and Władysław-Przybylak 2008). The studies are mainly focused on increasing the flame retardant properties of the WPC by improving the flame retardant behavior of the matrix material with the addition of commercial flame retardants. Schartel et al. (2003) produced flame retardant polypropylene-flax fiber composites by addition of two different commercial flame retardant agents, namely ammonium polyphosphate (APP) and expandable graphite during extrusion process. According to cone calorimeter and LOI test results, the best fire performance was obtained when 25 wt % of expandable graphite was used. Sain et al.

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(2004) investigated the effect of zinc borate or boric acid in combination with magnesium hydroxide on the flame retardant and mechanical properties of saw dust and rice husk filled polypropylene composites. The study made by Suardana et al. (2011) could be given as the example of producing flame retardant composites by reducing the flammability of fiber material. They treated jute fabric and coconut filter fiber with diammonium phosphate and mixed it with poly(lactic acid) and polypropylene to produce flame retardant biocomposites. Seefeldt and Braun (2012) studied the flame retardant effect of ammonium phosphonate in wood-polypropylene composites and compared the fire performance with APP. They found that ammonium phosphonate showed its flame retardant behavior in the condensed phase by increasing the char yield. Ammonium phosphonate showed better fire performance than APP.

Flame retardant WPC can also be produced by reducing the flammability of both the lignocellulosics and the matrix material. In the literature, this strategy was only used in one study (Shumao et al. 2010). Shumao et al. (2010) investigated the effect of ammonium polyphosphate (APP) on the flame retardant and mechanical properties of ramie fiber reinforced polylactic acid (PLA) biocomposites. They produced biocomposites by using three different methods. In the first method, APP was directly mixed with the matrix material. In the second method, ramie fiber was impregnated with APP solution. In the third method, both PLA and ramie fiber were treated with APP solution. The best flame retardant performance was obtained using the third method with a LOI value of 35.6 %.

The main objective of the current study is to investigate the effect of flame retardant treatments of WF with bis[tetrakis (hydroxymethyl) phosphonium] sulfate (THPS) and dicyandiamide-formaldehyde-phosphoric acid flame retardants (DFP) on flammability and thermal properties of WF-LDPE composites containing APP. Thermal gravimetric analysis (TGA) was used for the characterization of pristine WF, the flame retardant treated WF and their composites. Limiting oxygen index (LOI), vertical UL-94 and cone calorimeter tests were also used for the characterization of composites.

## 2 Materials and methods

### 2.1 Materials

LDPE, under the trade name of LDPE F2-12, was obtained from PETKIM A.S. (Turkey). The density is  $0.92 \text{ g/cm}^3$  and the melt flow index is 2–3.5 g/10 min (2.16 kg, 190 °C) as provided by the supplier. WF from pine (under 20-mesh size) was obtained from local sources. AP 750, which is a synergistic mixture of APP,

was kindly provided by Clariant under the trade name of Exolit AP750. It is an intumescent based flame retardant and develops its effect through phosphorus/nitrogen synergism. Urea, ammonium dihydrogenphosphate, NaOH, formalin (37 %) and dicyandiamide were obtained from Merck and tetrakis(hydroxymethyl)phosphonium sulfate (THPS in 70–75 %  $\text{H}_2\text{O}$ ) from Sigma Aldrich. Phosphoric acid (85 %) was supplied by Fluka.

### 2.2 Flame retardant treatments

#### 2.2.1 Flame retardant treatment of WF with Dicyandiamide-Formaldehyde-Phosphoric Acid (DFP)

4.05 g (0.05 mol) of 37 % formaldehyde solution was placed in round bottom flask and its pH was adjusted to 8–8.5 with NaOH solution and heated in an oil bath to 120 °C. 4.2 g (0.05 mol) dicyandiamide was added to the mixture and stirred with a magnetic stirrer until dissolved. The mixture was refluxed for 10 min and then the heating was stopped and the reactants were allowed to cool at room temperature. Finally, 5.75 g (0.05 mol) 85 % phosphoric acid solution was added slowly to the cooled mixture (Pan et al. 2003).

The product was diluted with 15 ml of water and 10 g WF was added into the solution. The suspension was stirred with magnetic stirrer for 30 min at room temperature. The mixture was filtrated and the treated WF was cured at 160 °C for 10 min. After curing, WF was washed with water, filtrated and dried. Finally, 11.64 g of WF was obtained. WF took up 16.4 wt% DFP.

#### 2.2.2 Flame retardant treatment of WF with Tetrakis(hydroxymethyl)phosphonium sulfate (THPS)-Urea-Ammonium Dihydrogenphosphate

7.5 g THPS solution (75 %) was neutralized with NaOH solution to get a pH value of 6.5. 5.625 g of urea was dissolved in 25 ml of water to obtain 22.5 % urea solution. Urea solution was mixed with THPS solution and then the pH was again adjusted to 6.5. After mixing of two solutions, 0.375 g of ammonium dihydrogenphosphate (ADP) was added to the mixture. The resulting mixture was used for the treatment of WF (Bagga et al. 1990).

10 g of WF was added to the resulting solution. The suspension was stirred with a magnetic stirrer for 30 min at room temperature. The mixture was filtrated and the treated WF was cured at 160 °C for 10 min. After curing, WF was washed with water, filtrated and dried. Finally, 11.20 g WF was obtained. WF took up 12.0 wt% flame retardant agent.

## 2.3 Sample preparation

LDPE, APP and pristine or flame retardant treated WFs were mixed in a counter rotating twin screw microextruder (15 ml microcompounder<sup>®</sup>, DSM Xplore, Netherlands) at 100 rpm at 190 °C for 2.5 min. The extrudate was chopped into small pellets and then oven-dried for 48 h at 60 °C. It was stored in a desiccator for compression molding. The samples for thermal or flammability tests were produced by compression molding at 190 °C. A laboratory scale hot-press (Pneumo Hydraulic Press, Ats Faar, Italy) was used for compression molding. All compositions contained the same amount of LDPE (40 wt %) and WF (30 wt%). The amount of flame retardant material impregnated on WF was deducted from the amount of APP and the total amount of flame retardant additive was kept constant at 30 wt % by weight. The abbreviations PE, WF, APP, THPS and DFP, are used for polyethylene, wood flour, ammonium polyphosphate, dicyandiamide-formaldehyde-phosphoric acid treatment, tetrakis(hydroxymethyl)phosphonium sulfate - urea-ammonium dihydrogenphosphate treatment during sample coding, respectively. The formulations of composites are given in Table 1.

## 2.4 Characterization methods

LOI value was measured using Fire Testing Technology Limiting Oxygen Index Analyzer instrument on test bars of size  $130 \times 6.5 \times 3.2 \text{ mm}^3$ , according to the standard oxygen index test of ASTM D2863-13 (2013). UL-94 ratings of composites with dimensions of  $130 \times 13 \times 3.2 \text{ mm}^3$  were determined according to ASTM D3801-10 (2010). TGA was carried out on Perkin Elmer Pyris 1 TGA & Spectrum 1 FTIR Spectrometer at a heating rate of 10 °C/min up to 800 °C under nitrogen flow of 50 ml/min. The cone calorimeter test was carried out according to the procedures in ISO 13927 using Mass Loss Cone with thermopile attachment (Fire testing Technology, U.K). Square specimens ( $100 \times 100 \times 3 \text{ mm}^3$ ) were irradiated at a heat flux of  $35 \text{ kW/m}^2$ , corresponding to a mild fire scenario.

**Table 1** Formulations of composites, LOI values and UL-94 ratings

Sample	PE	WF	AP 750	THPS	DFP	LOI	UL-94
PE/WF	70	30	–	–	–	17.5	BC
PE/WF/APP	40	30	30	–	–	24.2	BC
PE/THPS-WF/APP	40	30	26	4	–	24.8	BC
PE/DFP-WF/APP	40	30	24	–	6	24.6	BC

BC burn to clamp

## 3 Results and discussion

### 3.1 Decomposition of LDPE-WF Composites

Decomposition characteristics of pristine WF, flame retardant treated WF and their relevant composites were studied by TGA. TGA graphs of pristine and flame retardant treated WFs are given in Fig. 1.

It is a well-known fact that wood thermally decomposes between 170 and 550 °C due to the degradation of hemicellulose (decomposes at 150–350 °C), cellulose (decomposes at 275–350 °C) and lignin (decomposes at 250–500 °C) constituents (Bodirlău et al. 2007). It was observed that untreated wood flour mainly decomposes at a maximum degradation temperature of 364 °C. DFP and THPS treated WF have low maximum decomposition temperature at about 295 and 304 °C, respectively. The treatments of DFP and THPS enhance the char yield of pristine WF from 10.6 to 29.6 % and 31.2 %, respectively. The reduction of maximum decomposition temperature and increase in char yield for both treatments arises from the presence of phosphorus species in both flame retardant treatments. The flame retardants containing phosphorous minimize the formation of levoglucosan (Gao et al. 2004a; Kandola et al. 1996). The minimization of levoglucosan is performed by reducing the decomposition temperature of cellulose and increasing the char formation by catalyzing dehydration and decomposition reactions (Blasi et al. 2008; Gao et al. 2004b; Jain et al. 1985; Joseph and Ebdon 2010).

Figure 2 and Table 2 show the TGA curves and data of all composites, respectively. All samples decompose in two degradation steps. First step arises from the degradation of WF and the second step arises from the decomposition of LDPE. The char yield of PE/WF was found as 5.1 % at 600 °C due to the decomposition products of WF remained in the condensed phase. The char yield decreases by about 43 % at 800 °C due to the degradation of low thermal stability decomposition products of WF. The addition of 30 wt% of APP (PE/WF/APP) decreases  $T_5 \%$  and  $T_{\text{max}}$  (first step) at about 40 and 50 °C, respectively. The main decomposition product of APP, polyphosphoric acid, causes the phosphorylation of cellulose resulting in the reduction of  $T_5 \%$  and  $T_{\text{max}}$  (first step) (Chen et al. 2011;

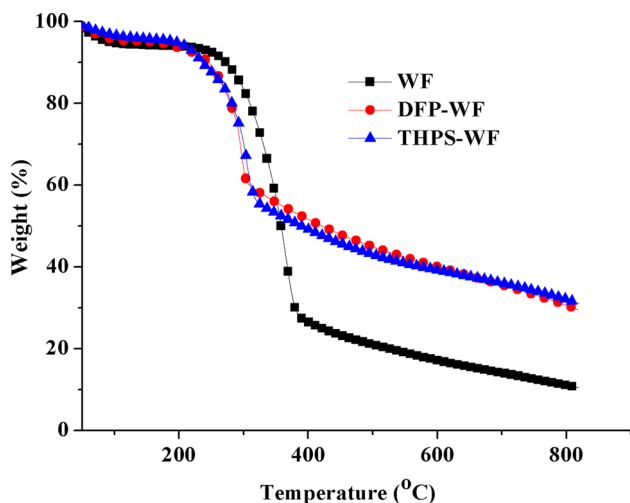


Fig. 1 TGA graphs of untreated WF and THPS or DFP treated WF

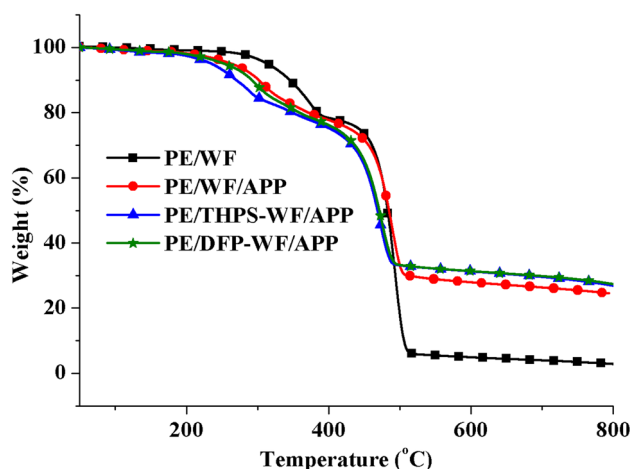


Fig. 2 TGA graphs of all composites

Shumao et al. 2010). The addition of 30 wt % APP enhances the char yield from 5.1 to 27.9 % at 600 °C due to the formation of thermally stable char arising from the carbonization reaction which occurs between the constituents of IFR system and favoring the char formation of

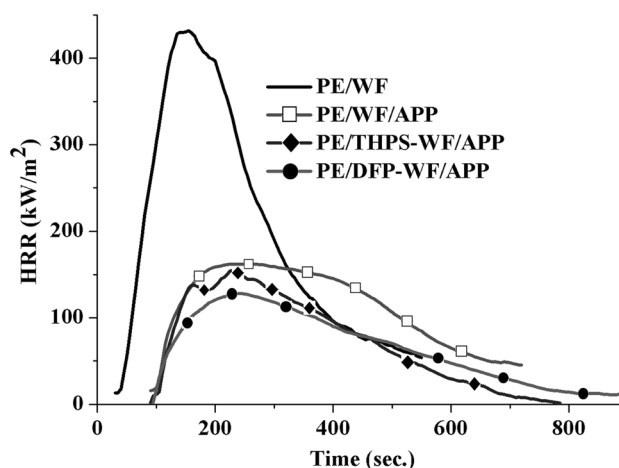


Fig. 3 HRR curves of composites

WF by catalyzing effect of polyphosphoric acid. The samples containing flame retardant treated WF (PE/THPS-WF/APP and PE/DFP-WF/APP) have lower  $T_5$  % and  $T_{max}$  than those of PE/WF/APP.

The char yield at 600 and 800 °C increases by about 3 % when m-APP and DFP-WF or THPS-WF is used together. As a result, the use of both WF treated with flame-retardant chemicals favor the char formation due to the formation of fewer flammable gases and more water which eventually cause dehydration and charring of cellulose (Hashim et al. 2009; Shumao et al. 2010). In addition, it is proposed that at temperatures above 400 °C, the matrix and the intumescent component start to fully develop a bonded char structure (Horrocks et al. 1996; Shumao et al. 2010).

### 3.2 Flammability properties

The flammability characteristics of composites are determined by LOI and UL-94 rating. According to Table 1, the LOI value and UL-94 rating of sample without flame retardant (PE/WF) are 17.5 % and burn to clamp (BC), respectively. The addition of 30 wt % m-APP (PE/WF/

Table 2 TGA data of all composites

Sample	$T_5$ % (°C) <sup>a</sup>	$T_{max}$ (°C) <sup>b</sup>		Char Yield (%) <sup>c</sup>	
		1st step	2nd step	600 °C	800 °C
PE/WF	314	361	488	5.1	2.9
PE/WF/APP	275	309	490	27.9	24.5
PE/THPS-WF/APP	235	298	478	31.3	26.9
PE/DFP-WF/APP	241	287	475	31.2	27.7

<sup>a</sup> Temperature at 5 % weight loss

<sup>b</sup> The maximum rate degradation temperature

<sup>c</sup> Char Yield at 600 and 800 °C

**Table 3** Mass loss calorimeter composites

Samples	TTI (s)	pHRR ( $\text{Kw m}^{-2}$ )	Av. HRR ( $\text{Kw m}^{-2}$ )	THE ( $\text{MJ m}^{-2}$ )	Char Yield (%)
PE/WF	37	432	225	98.1	6.3
PE/WF/APP	91	162	118	68.9	41.7
PE/THPS-WF/APP	99	155	75	51.2	43.6
PE/DFP-WF/APP	94	128	75	50.6	45.8

TTI time to ignition, pHRR peak Heat Release Rate, Av. HRR average HRR, THE total heat evolved, TML total mass loss

APP) increases LOI value to 24.2 % owing to the formation of foamed char structure which protects the underlying material (Camino et al. 1984a, b; Le Bras et al. 1996). However, the UL rating remained the same (BC). The flame retardant treatments of WF with THPS or DFP do not alter the LOI value and UL-94 rating with respect to PE/WF/APP. As a result, THPS and DFP treatments of WF do not have any effect on the flammability properties of LDPE-WF composites.

### 3.3 Cone calorimeter studies

Cone calorimeter is used to monitor heat release rate (HRR) during combustion. The HRR is recognized to be the most important parameter to evaluate the developing, spreading, and the intensity of fires (Niel et al. 2008). The low values of peak heat release rate (pHRR) and total heat release (THE) normally indicate improved fire performance. Figure 3 and Table 3 show the HRR curves and cone calorimeter data of all compositions at a heat flux of  $35 \text{ kWm}^{-2}$ .

According to Fig. 3, it is noteworthy that the sample without flame retardant (PE/WF) burns very fast after ignition, and the pHRR value appears at  $432 \text{ kWm}^{-2}$  with one sharp peak. When m-APP is added (PE/WF/APP), the HRR curves become more plateau like with extended burning time owing to barrier effect of foamed char structure. The addition of m-APP (PE/WF/APP) reduces the pHRR, average HRR and THE values by about 62.5, 47.6 and 29.7 % with respect to the sample without any flame retardant (PE/WF), respectively. The addition of THPS treated WF (PE/THPS-WF/APP) decreases the pHRR, average HRR and THE values more by about 4, 36, 17 % with respect to PE/WF/APP and 64, 67, 48 % with respect to PE/WF sample, respectively. The more decrease in pHRR, average HRR and THE values is observed when DFP treated WF (PE/THPS-WF/APP) is added. The pHRR, average HRR and THE values decrease by about 21, 36, 27 % with respect to PE/WF/APP and 70, 67, 48 % with respect to PE/WF, respectively. In the view of these results, the high reduction in pHRR values shows that the flame retardant treatments of WF with THPS or DFP

improves the fire performance of composites due to the increase in the amount of char providing barrier effect.

## 4 Conclusion

Thermal and fire retardant properties of the THPS and DFP treated WF containing intumescent LDPE composites were investigated and compared with pristine WF containing one. The addition of 30 wt% m-APP increased the LOI value from 17.5 to 24.2 and UL-94 rating remained as burn to clamp (BC). THPS and DFP treatments of WF did not have any effect on the LOI value and UL-94 ratings with respect to PE/WF/APP. The combined use of THPS or DFP treated WF with m-APP increased the fire performance of composites with approximately 25 % reduction in total heat evolved (THE) with respect to LDPE/WF/APP owing to the increase in the amount of foamed char providing barrier effect. In this study, since no V0 value is observed in all formulations and procedures tested, some other synergy agents have to be tried.

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