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# Effect of Boron and Phosphate Compounds on Thermal and Fire Properties of Wood/HDPE Composites

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Melting and non-isothermal crystallization behaviors, oxidative induction time, and fire performance of the injection-molded wood flour-high density polyethylene (HDPE) composites (WPCs) incorporated with different levels (4, 8, or 12 wt %) of boron compounds [borax/boric acid (BX/BA) (0.5:0.5 wt %), zinc borate (ZB)] and phosphorus compounds [mono- and di-ammonium phosphate] were investigated. The samples without the boron or phosphate had a HDPE content of 60%. The effect of the coupling agent loading (2, 4, or 6 wt %, maleic anhydride-grafted PE (MAPE)), on the above mentioned properties of the treated WPCs was also investigated. Heat release rate (HRR) measurements were conducted with a cone calorimeter. WPC samples including inorganic fire retardant particles generally exhibited higher degree of crystallinity values than control sample. Furthermore, degree of crystallinity increases with the increasing amount of FRs. the DAP and MAP with MAPE significantly increased the OIT values of the WPC compared to other FRs. The FR treatments produced modest improvements in fire performance as indicated by reductions in the heat release rates. Reducing both the wood fiber content and the polymer content equally to accommodate the addition of the FR chemicals likely reduced the net improvement provided by the FR treatment.

***Keywords:*** boron, phosphate, HDPE, fire retardants, thermal properties, wood plastic composite

## INTRODUCTION

Wood plastic composites (WPCs) represent an emerging class of materials that combinethe favorable performance and cost attributes of both wood and thermoplastics. In comparison to other fillers, the natural and wood fiber reinforced polymer composites are more environmentally friendly, and are used in transportation, residential construction industry, outdoor deck floors, etc. Mechanical and physical properties, such as dimensional stability, strength, stiffness, impact resistance, density, and color, are important considerations in many WPC applications. Although the WPCs have the mentioned advantages, one of the the main drawback in residential construction industry is their high flammability. As organic materials, i.e. both polymers and wood, are sensitive to fire, improvement of fire retardancy of the composite materials has become important in order to comply with the safety requirements of the WPC products.

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Boron compounds, such as zinc borates, are usually used in combination with other flame retardants substances and act as synergists for a variety of halogen flame retardants or of antimony oxide, as smoke suppressants (promoting and stabilising char formation). Boron compounds can also act by releasing water, in a heat absorbing reaction, and forming a protective glassy layer on the material's surface. One of the most widely used fire retardants is mono- and di-ammonium phosphates; which act by acceleration of char formation and inhibit the release of flammable volatile compounds (Grexa and Kosik 1992). Evidence of their fire retardant efficacy include more smoke and a greater CO:CO2 ratio in the smoke gases, which are both strong indicators of inefficient combustion. The inorganic fire retardants act simultaneously on the surface of the solid phase by cooling the substrate via endothermic breakdown process and reducing the formation of pyrolysis products. In addition, as in the case of inorganic boron compounds, a glassy protective layer can form

on the substrate, fending off the effects of oxygen and heat (Russell *et al.* 2007).

It is well known that the physical properties of a semi-crystalline polymer are governed by the supramolecular structure, which in turn is controlled by the crystallization. Many studies have been reported on the correlation of mechanical properties of WPC materials with their crystallization and melting properties (Sewda and Maiti 2010, Li and Yan 2007) which were conducted by differential scanning calorimetry (DSC) method. Thermal degradation behavior of thermoplastics composites under the oxidative conditions can also be studied qualitatively via DSC analysis. In this study, crystallization, melting and thermo-oxidative degradation behaviors of WPCs and were examined by various DSC procedures depending on the compositional parameters such as coupling agent amount, type and amount of fire retardants employed.

The cone calorimeter based on the oxygen consumption principle is widely used to evaluate the flammability characteristics of materials. Although the cone calorimeter is a small-scale test, the obtained results have been found to correlate well with those obtained from a large-scale fire test and are used to predict the combustion behavior of materials in a real fire. The heat release rate (HRR) measured by cone calorimeter is a very important parameter as it expresses the intensity of a fire. A highly flame retardant system normally shows a low average-HRR value. The peak HRR value is a measure of the intensity of a fire. The objectives of the present study were to determine effects of the boron and phosphate compounds on the thermal and fire properties of the injection molded HDPE WPCs with and without coupling agent.

## MATERIALS AND METHODS

### Materials

Wood particles were obtained from beech (*Fagus orientalis* Lipsky) lumbers by using laboratory type disc chipper with three knives. The moisture content of the wood particles, as determined by oven-dry weight, was found to be 40-50% prior to the treatment. The wood particles were ground in a laboratory *Willey* grinder. The wood flour (WF) passing through a U.S. 35-mesh screen was retained by a U.S. 80-mesh. The high density polyethlene (HDPE) ($q$ = 0.968 g/cm$^3$, MFI/190°C/2.16 kg = 5.5 g/10 min) produced by Petkim Petrochemical Co., Turkey, was used as the polymeric material. Maleic anhydride-grafted PE (MAPE-OPTIM E 156; $q$ = 0.954 g/cm$^3$, MFI/190°C/2.16 kg = 4.5 g/10 min) was supplied by Pluss Polymers Pvt. Ltd. in India.

Four FR systems (powder) were investigated:

1. A mixture of boric acid (BA) ($H_3BO_3$) (ρ = 1.7 g/cm$^3$) and borax (BX) ($Na_2B_4O_7.10H_2O$) (ρ = 1.4 g/cm$^3$) (BA/BX, 1:1 by weight)
2. Zinc borate (ZB) ($3ZnO.2B_2O_3$) (ρ = 2.8 g/cm$^3$)
3. Monoammonium phosphate (MAP) $NH_4H_2PO_4$ (ρ = 1.8 g/cm$^3$)
4. Diammonium phosphate (DAP) $(NH_4)_2HPO_4$ (ρ = 1.6 g/cm$^3$)

### Preparation of Injection Molded WPC Samples

The WF was dried in a laboratory oven at 102°C for 24-h to a moisture content of 0-1% based on the oven-dry WF weight and then stored in a polyethylene bags. The WF, HDPE and MAPE granulates, and the FR powder were processed in a 30-mm co-rotating twin-screw extruder with a length-to-diameter (L/D) ratio of 30:1. The raw materials were fed into the main feed throat using a gravimetric feed system. The barrel temperatures of the extruder were controlled at 170, 180, 185, and 190°C for zones 1, 2, 3, and 4, respectively. The temperature of the extruder die was held at 200°C. The extruded strand passed through a water bath and was subsequently pelletized. These pellets were stored in a sealed container and then dried to the moisture content of 1-2% before the injection molding. The temperature used for injection molded samples was 180-200°C from feed zone to die zone. The WPC samples were injected at injection pressure between 45 and 50 kg/m$^2$ with cooling time about 30 s. Finally, the samples were conditioned at a temperature of 23 °C and relative humidity (RH) of 50% according to ASTM D 618 (ASTM International 2008a). Air-dry density values of the samples varied from 1020 to 1090 kg/m$^3$. The raw material formulations used for the WPCs are presented in Table 1.

### Determination of Thermal Properties

Melting and crystallization behavior of the WPCs were studied in a heat-flux type differential scanning calorimeter (DSC, SII Nanotechnology, ExStar 6200) according to ASTM D3418 (ASTM International 2008b). Temperature and heat flow calibration of the instrument were performed with high purity indium (In), tin (Sn) and zinc (Zn) metals. The test samples weighing about 9-10 mg in an aluminum crucible were heated up to 200 °C with the heating rate of 10

**Table 1**
**Compositions of the Injection Molded WPC**

| *WPC type* | *WPC compositon* | | | |
|---|---|---|---|---|
| | *Fire retardant (FR) content* | *MAPE content* | *Wood flour (WF)* | *High density polyethlyene (HDPE)* |
| | *(wt %)* | *(wt %)* | *(wt %)* | *(wt %)* |
| Control | - | - | 40 | 60 |
| BX/BA | 4 | - | 38 | 58 |
| ZB | 4 | - | 38 | 58 |
| DAP | 4 | - | 38 | 58 |
| MAP | 4 | - | 38 | 58 |
| BX/BA | 8 | - | 36 | 56 |
| ZB | 8 | - | 36 | 56 |
| DAP | 8 | - | 36 | 56 |
| MAP | 8 | - | 36 | 56 |
| BX/BA | 12 | - | 34 | 54 |
| ZB | 12 | - | 34 | 54 |
| DAP | 12 | - | 34 | 54 |
| MAP | 12 | - | 34 | 54 |
| BX/BA | 4 | 2 | 37 | 57 |
| ZB | 4 | 2 | 37 | 57 |
| DAP | 4 | 2 | 37 | 57 |
| MAP | 4 | 2 | 37 | 57 |
| BX/BA | 8 | 4 | 34 | 54 |
| ZB | 8 | 4 | 34 | 54 |
| DAP | 8 | 4 | 34 | 54 |
| MAP | 8 | 4 | 34 | 54 |
| BX/BA | 12 | 6 | 31 | 51 |
| ZB | 12 | 6 | 31 | 51 |
| DAP | 12 | 6 | 31 | 51 |
| MAP | 12 | 6 | 31 | 51 |

BX/BA (1:1): borax/boric acid, ZB: zinc borate. MAP: Monoammonium phosphate. DAP: Diammonium phosphate. MAPE: Maleic anhydride-grafted PE.

°C/min and kept at this temperature for 2 min to remove thermal history. Then the samples were cooled down to 0°C with the cooling rate of 10 °C/min by an electrical cooling device, Thermo Scientific EK90C/SII intracooler, to allow the sample crystallize dynamically and kept at this temperature for 2 minutes. Subsequently, the non-isothermally crystallized samples were re-heated up to 200 °C with the heating rate of 10 °C/min. All heating-cooling runs in melting and crystallization studies were carried out under nitrogen ($N_2$) atmosphere at a flow rate of 50 ml/min to prevent oxidation of the samples. Degree of crystallinity ($X_c$%) was determined from the second melting enthalpy values using the following equation:

$$X_c = \frac{\Delta H_m}{(1-\alpha)\Delta H_m^o} x100$$

Where, $\Delta H_m$ is melting enthalpy of the samples (J/g), $\Delta H_m^o$ is the enthalpy value of melting of a 100% crystalline form of HDPE (293 J/g) and (1-a) is the weight fraction of polymer into the WPC material.

Oxidative induction time (OIT) test is a well-known thermal stability assessment method for thermoplastic formulations. The OIT test was performed in the DSC according to ASTM D3895 (ASTM International 2007) in order to indicate oxidation mechanism and effects of crystallinity and other compositional variations on the oxidative degradation performance of the samples. In the OIT run, the test sample was heated up to 210 °C in an open crucible under the nitrogen flow and isothermally kept at this temperature for three minutes. Then at this temperature, the gas was switched from inert purge to the $O_2$ (99.9%) and the time taken from the gas switching to the onset of exothermic oxidation reaction which is defined as the OIT value was recorded.

Beside the OIT test and isothermally following the thermo-oxidative degradation of the WPC samples as a function of time, dynamic oxidative-degradation tests were also performed under the non-isothermal conditions and the degradation behavior of the samples were evaluated as a function of the types and loading levels of FR by comparing the degradation onset temperatures ($T_{do}$). In this test, sample was heated up to 205 °C with the heating rate of 10 °C/min under the inert atmosphere and kept at this temperature for a minute. Then the test atmosphere was suddenly switched to pure $O_2$ and the heating rate was applied to 5 °C/min under the oxidative conditions. In this case, degradation onset temperatures of the samples could be compared depending on the sample compositions. Experimental conditions applied to the samples were very challenging in both dynamic and isothermal degradation tests due to the using of the pure oxygen.

## Fire Performance

Heat release rate is widely considered one of the most dominant material properties affecting the growth of a fire. Heat release measurements were conducted in accordance with ASTM E 1354 (ASTM International 2008c) at U.S. Forest Products Laboratory, Madison WI. Samples were 100 mm x 100 mm and sample thickness was 10 mm. The samples were conditioned at 23°C and 50% RH prior to the testing. The cone

calorimeter tests were conducted in the horizontal orientation with the conical radiant electric heater set at a heat flux level of 50 kW/m$^2$. The samples were tested in the optional retainer frame but without the wire grid over the test sample. Ignitability was determined by using a 4 seconds criteria for sustained ignition for observing the time for sustained ignition of the sample. Two replicate samples were tested for each type of sample. Regression analyses of the cone calorimeter results as function of the treatment levels were conducted to determine the statistical significance of the changes in results due to the FR treatments.

## RESULTS AND DISCUSSION

### Thermal Properties

A typical melting and crystallization thermogram of a WPC sample is illustrated in Fig. 1. It was found that the crystallization onset and peak temperatures of HDPE are 119.6 and 114.0 °C, respectively. On the other hand, $T_{co}$ and $T_{cp}$ values of the control WPC sample were found to be 120.2 and 114.6, respectively. All WPC samples showed similar $T_{co}$ and $T_{cp}$ values to the control sample, in the range of 119.4-121.2 for the $T_{co}$ and 114.2-119.0 for the $T_{cp}$. Characteristic peak temperatures for each sample are not given here. No significant change due to sample composition was observed in the crystallization behavior of the WPCs. Any effect of compositional change on the crystallization rate of polymer matrix was not observed because the HDPE is a very fast crystallizing polymer due to its chain structure. But, it was found that the second melting enthalpy and corresponding degree of crystallinity values of the WPC samples crystallized under the same cooling conditions varied depending on the composition. Second melting enthalpies and degree of crystallinity values of the samples are listed in Table 2. As seen in Table 2, the control WPC sample yielded lower degree of crystallinity than the HDPE which indicate that the wood fibers could not effectively nucleate polyethylene spherulites. On the other hand, WPC samples including inorganic fire retardant particles generally exhibited higher degree of crystallinity values than control WPC sample. Furthermore, degree of crystallinity increases with the increasing amount of FRs. This result implies that the crystallization of HDPE was enhanced with the FRs. It could be speculated that more crystalline structure into the polymer phase might lead better mechanical performance for the WPCs.

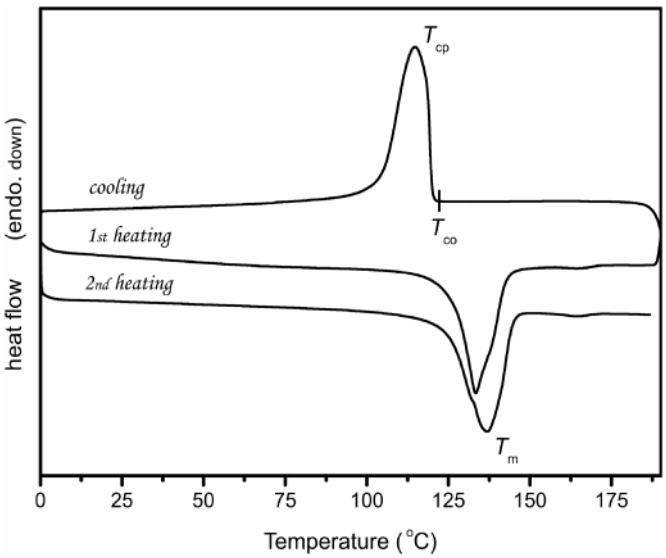


**Figure 1:** Typical Melting and Crystallization Thermograms of a WPC Sample. $T_m$, $T_{co}$ and $T_{cp}$ Indicate the Melting Peak, Crystallization Onset and Crystallization Peak Temperatures, Respectively

OIT is an accelerated test used as a qualitative evaluation of the oxidative stability of a material. Especially in polyolefin formulations, it is frequently used as criteria of the thermal stability of polyolefins in an oxidative atmosphere. It can also be used to compare the aging resistance of different plastics, to detect the impact of antioxidant concentration and to assess the effectiveness of antioxidants. In this study, isothermal and non-isothermal degradation behaviors of the samples were used to evaluate effects of different fire retardants on the thermo-oxidative degradation of WPC samples. The isothermal OIT curves for samples of the four FRs at the loading level of 12% and prepared with MAPE are illustrated in Figures 2 and 3 compares the OIT values of the WPC samples as a function of types of fire retardants loaded at a particular level (12 wt%). As seen in Fig. 3 (a), the MAP without MAPE cannot effectively protect the composite against thermo-oxidative conditions but introducing MAPE into the composition dramatically changed the OIT value of WPC including MAP. It was also found that the DAP and MAP with MAPE significantly increased the OIT values of the WPC compared to other FRs.

The onset temperatures of thermo-oxidative degradation ($T_{do}$) obtained from the non-isothermal DSC runs are listed in Figure 4. It was found that the WPC including DAP as the FR begins to degrade at relatively higher temperature than the other samples in the both case of with or without MAPE. This result implies that the DAP yielded the best results against

**Table 2**
**Second Melting Enthapy and Degree of Crystallinity Values of the WPC Samples**

| *Polymer* | *Sample composition (wt%)* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *HDPE* | *Fire retardants* | | | | *Coupling agent* | *Filler* | | |
| | *BX/BA* | *ZB* | *MAP* | *DAP* | *MAPE* | *Wood* | $DH_m$(J/g) | $X_c$ (%) |
| 100 | | | | | | | 184 | 62.8 |
| 60 | | | | | | 40 | 101 | 57.5 |
| 58 | 4 | | | | | 38 | 114 | 67.1 |
| 56 | 8 | | | | | 36 | 112 | 68.3 |
| 54 | 12 | | | | | 34 | 111 | 70.2 |
| 58 | | 4 | | | | 38 | 99 | 58.3 |
| 56 | | 8 | | | | 36 | 103 | 62.8 |
| 54 | | 12 | | | | 34 | 101 | 63.8 |
| 58 | | | 4 | | | 38 | 106 | 62.4 |
| 56 | | | 8 | | | 36 | 109 | 66.4 |
| 54 | | | 12 | | | 34 | 110 | 69.5 |
| 58 | | | | 4 | | 38 | 100 | 58.8 |
| 56 | | | | 8 | | 36 | 112 | 68.3 |
| 54 | | | | 12 | | 34 | 124 | 78.4 |
| 57 | 4 | | | | 2 | 37 | 118 | 68.3 |
| 54 | 8 | | | | 4 | 34 | 117 | 68.8 |
| 51 | 12 | | | | 6 | 31 | 124 | 74.2 |
| 57 | | 4 | | | 2 | 37 | 125 | 72.3 |
| 54 | | 8 | | | 4 | 34 | 103 | 60.6 |
| 51 | | 12 | | | 6 | 31 | 88 | 52.7 |
| 57 | | | 4 | | 2 | 37 | 92 | 53.2 |
| 54 | | | 8 | | 4 | 34 | 111 | 65.3 |
| 51 | | | 12 | | 6 | 31 | 114 | 68.3 |
| 57 | | | | 4 | 2 | 37 | 120 | 69.4 |
| 54 | | | | 8 | 4 | 34 | 102 | 60.0 |
| 51 | | | | 12 | 6 | 31 | 124 | 74.2 |

the thermo-oxidative degradation with and without a coupling agent. The ZB without MAPE also resulted in a significant increase in the onset temperature of thermo-oxidative degradation.

## Fire Properties

The main results from the cone calorimeter tests were the curves for heat release rate as a function of time (see Figure 5 for example curves). There is an initial peak followed by a reduction in the heat release rate. In the cone calorimeter tests; the other results measured as a function of time include the mass loss, and specific extinction area (i.e. visible smoke). The observed times for sustained ignition (TSI, s) was also recorded (Table 3). The specimens with the longest average TSI (28.2 s) were the ones treated with 12% ZB and 6% MAPE compared with 22.7 s for the untreated WPC control specimens.

From the curves of heat release rate, the recorded observations included the initial peak heat release rate (PHRR, kW/m$^2$), heat release rates averaged over 300 s (AHRR-300, kW/m$^2$) after sustained ignition, and total heat released (THR, MJ/m$^2$) (Table 3). The results presented in Table 3 are means and standard deviations for the two replicates. The treated samples demonstrated modest reductions in the heat release rate (Figure 5). Compared with the PHRR of 523 kW/m$^2$ for the untreated WPC controls, the lowest PHRR was 411 kW/m$^2$ for the specimens treated with 12% MAP and 6% MAPE. The same specimens also had the lowest AHRR-300 at 270 kW/m$^2$ compared with 408 kW/m$^2$ for the untreated WPC controls. An average mass loss rate (AMLR, g/m$^2$s) was calculated for the period from time for 10% of the ultimate mass loss to the time for 90% of the ultimate specimen mass loss (Table 3). Compared with 11.5 g/m$^2$s for the

**Tablo 3**
**Cone Calorimeter Results for the WPCs at Different Loading Levels of the Fire Retardant and Coupling Agent**

| | | | *Cone calorimeter results*[c] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *WPC type*[a] | *Fire retardant content wt%* | *MAPE content wt%* | *Time to sustained ignition* s | *Peak heat release rate* kW/m² | *Avg. heat release rate 300s* kW/m² | *Total heat released* MJ/m² | *Avg. mass loss rate (10%-90%)* g/m²s | *Avg. effective heat of combustion* MJ/kg | *Avg. specific extinction area* m²/kg |
| Control | - | - | 22.7 (1.0) | 523 (5) | 408 (7) | 335 (13) | 11.5 (0.4) | 33.2 (0.4) | 458 (78) |
| BX/BA | 4 | - | 25.9 (0.5) | 516 (11) | 399 (8) | 319 (10) | 10.4 (0.6) | 34.0 (0.5) | 459 (21) |
| ZB | | | 24.7 (0.5) | 477 (33) | 363 (25) | 273 (58) | 10.4 (1.3) | 33.2 (0.8) | 359 (94) |
| MAP | | | 20.9 (0.6) | 465 (13) | 369 (7) | 266 (64) | 10.7 (0.1) | 34.5 (0.4) | 410 (77) |
| DAP | | | 23.1 (2.8) | 486 (33) | 366 (6) | 311 (2) | 9.8 (0.4) | 33.0 (0.3) | 472 (19) |
| BX/BA | 8 | - | 23.0 (0.7) | 483 (16) | 361 (3) | 315 (6) | 9.9 (0.1) | 33.7 (0.4) | 371 (6) |
| ZB | | | 22.2 (1.3) | 448 (5) | 331 (13) | 317 (6) | 9.5 (0.7) | 33.5 (0.6) | 418 (27) |
| MAP | | | 22.6 (0.1) | 457 (8) | 322 (18) | 309 (9) | 8.7 (0.3) | 32.7 (1.4) | 554 (108) |
| DAP | | | 23.8 (0.4) | 479 (26) | 337 (38) | 307 (10) | 8.9 (1.3) | 32.2 (0.1) | 560 (4) |
| BX/BA | 12 | - | 26.5 (0.7) | 462 (1) | 359 (25) | 310 (4) | 9.5 (0.6) | 34.6 (0.9) | 448 (33) |
| ZB | | | 25.9 (1.6) | 461 (9) | 344 (13) | 305 (0) | 9.7 (0.5) | 33.3 (0.1) | 371 (58) |
| MAP | | | 20.7 (0.7) | 499 (31) | 334 (3) | 307 (4) | 9.0 (0.1) | 32.9 (0.2) | 570 (98) |
| DAP | | | 22.2 (0.1) | 444 (25) | 317 (49) | 300 (14) | 8.8 (0.8) | 32.3 (1.5) | 514 (98) |
| BX/BA | 4 | 2 | 25.2 (1.1) | 510 (24) | 382 (20) | 320 (6) | 10.1 (0.8) | 33.8 (0.4) | 379 (40) |
| ZB | | | 25.3 (2.1.) | 465 (25) | 358 (4) | 329 (2) | 10.1 (0.1) | 34.2 (0.1) | 375 (47) |
| MAP | | | 24.6 (2.2) | 459 (3) | 322 (0.3) | 325 (13) | 8.4 (0.3) | 33.5 (0.4) | 416 (55) |
| DAP | | | 22.3 (0.6) | 466 (11) | 325 (4) | 311 (6) | 8.9 (0.4) | 33.1 (0.6) | 472 (27) |
| BX/BA | 8 | 4 | 26.5 (2.3) | 494 (1) | 398 (31) | 310 (10) | 11.3 (0.1) | 32.6 (1.3) | 382 (23) |
| ZB | | | 25.7 (1.1) | 483 (2) | 380 (11) | 335 (3) | 9.8 (0.4) | 33.9 (0.8) | 446 (25) |
| MAP | | | 26.1 (2.1) | 448 (16) | 332 (15) | 314 (2) | 9.5 (0.4) | 33.9 (0.04) | 442 (39) |
| DAP | | | 25.6 (1.0) | 446 (17) | 315 (4) | 312 (5) | 8.5 (0.2) | 33.8 (0.1) | 542 (7) |
| BX/BA | 12 | 6 | 26.1 (2.7) | 458 (38) | 363 (16) | 311 (16) | 10.1 (0.5) | 33.7 (0.6) | 371 (27) |
| ZB | | | 28.2 (1.4) | 440 (10) | 345 (9) | 309 (8) | 9.6 (0.7) | 33,4 (0.05) | 344 (6) |
| MAP | | | 25.1 (0.1) | 411 (28) | 270 (10) | 298 (19) | 7.9 (0.1) | 32.7 (0.9) | 564 (57) |
| DAP | | | 25.0 (0.4) | 424.5 (5) | 301.5 (23) | 305 (16) | 8.0 (0.4) | 32.8 (0.9) | 583 (12) |

[a] WF: wood flour, BX/BA (1:1): borax/boric acid, ZB: zinc borate. [b] MAPE: maleic anhydride-grafted PE. [c] Values are means and standard deviations in parentheses.

untreated WPC controls, the AMLR for the specimens treated with 12% MAP and 6% MAPE was also the lowest at 7.9 g/m²s. The total heat release and the mass loss were used to calculate an effective heat of combustion (AEHOC, MJ/kg) (Table 3). The specimens with the lowest AEHOC values were the 8% DAP (no MAPE) specimens (32.2 MJ/kg) compared with 33.2 MJ/kg for the untreated WPC controls. The average AEHOC for the 12% MAP and 6% MAPE specimens was 32.7 MJ/kg. A laser beam in the exhaust provided a measure of the visible smoke being emitted. The results are reported as the average specific extinction area (ASEA, m²/kg) (Table 3). Compared with the ASEA of 458 m²/kg for the untreated WPC controls, the 12% ZB/6% MAPE specimens had the lowest ASEA at 344 m²/kg and the 12% DAP/6% MAPE specimens had the highest ASEA at 583 m²/kg.

The data were further analyzed by performing linear regression analysis of the results as a function of treatment levels (Tables 4-6). Results are presented for the PHRR (Table 4 and Fig. 6), THR (Table 5), and residual mass fraction (Table 6). The slope indicates the change in the results with each increase in percentage FR. The Pf>f indicates the statistical significance of the slope from zero and the R-square reflect the portion of the variations explained by the regression. The MAP treated samples with the MAPE coupling agent resulted in the greatest reductions (-8.78 kW/sq-m per % change in the FR) in the peak heat release rate while the MAP without the MAPE coupling agent had the least (-2.07) and statistically

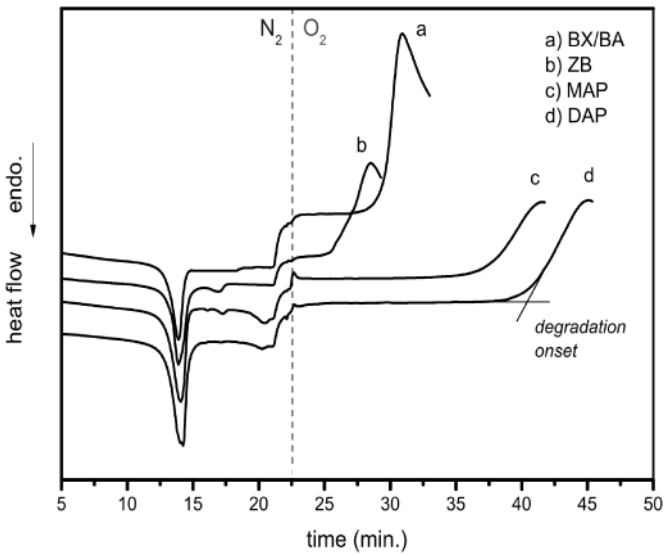


**Figure 2:** Comparing the Isothermal OIT Curves of the WPC Samples Including 12 wt% of BX/BA, ZB, MAP and DAP and Prepared with the 6 wt% of MAPE

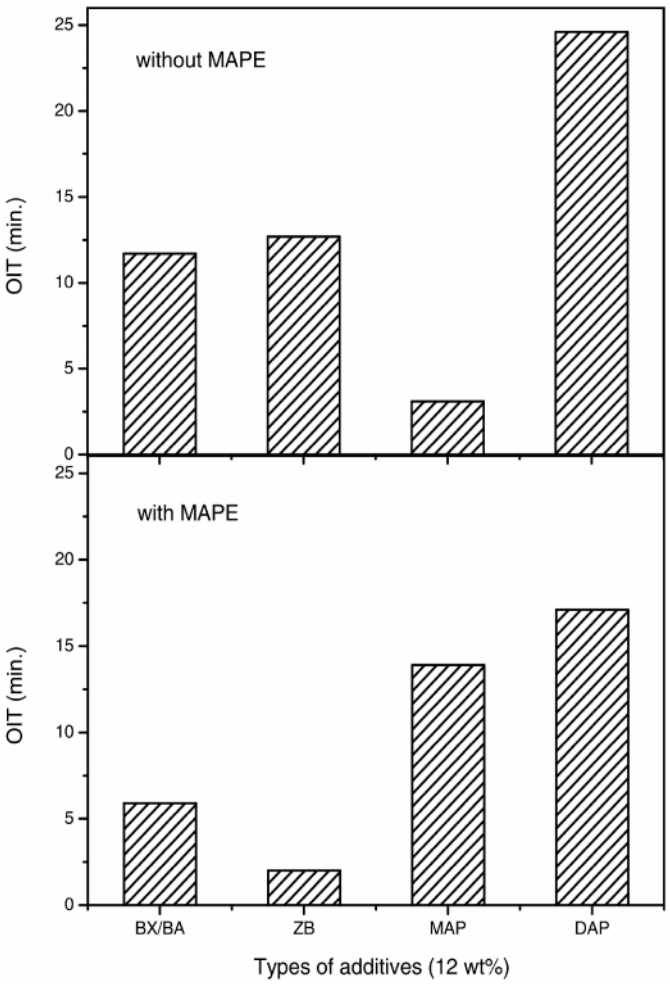


**Figure 3:** Comparing the OIT Values Obtained from the Isothermal DSC Test as a Function of Types of Fire Retardants Loaded at a Particular Level (12 wt%) for the WPC Samples Prepared

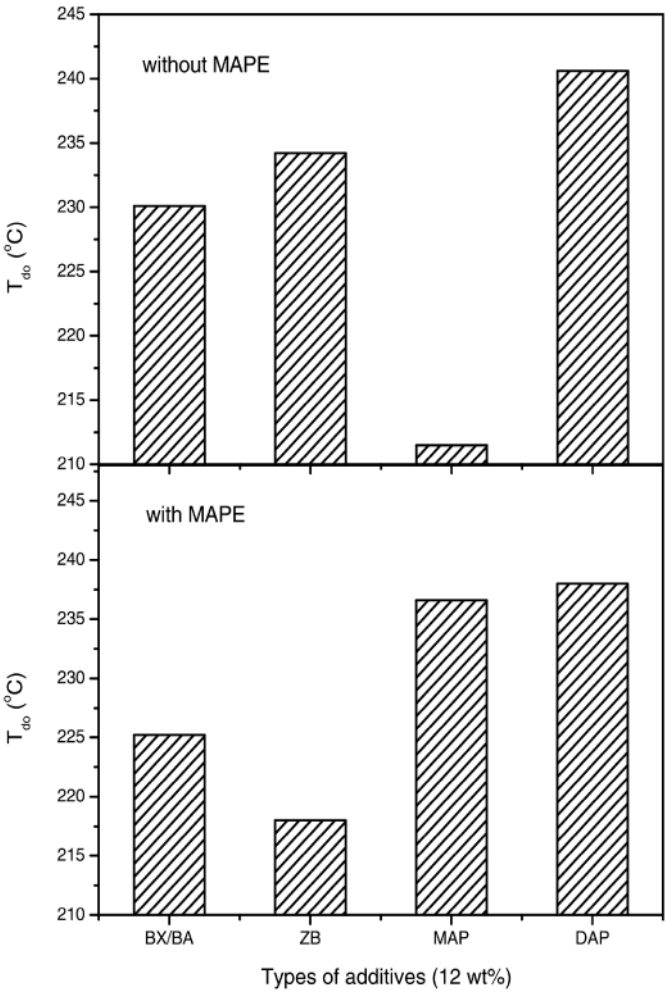


**Figure 4:** Comparing the Degradation Onset Temperatures ($T_{do}$) Obtained from the Non-isothermal DSC Test as a Function of Types of Fire Retardants Loaded at a Particular Level (12 wt%) for the WPC Samples Prepared

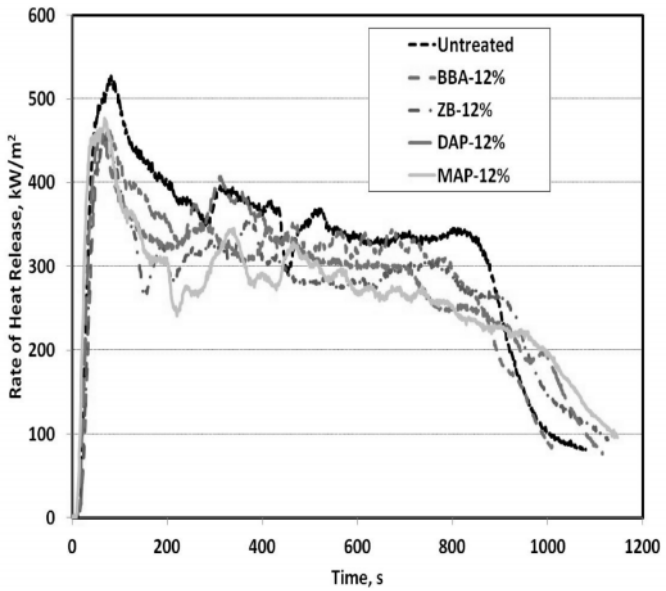


**Figure 5:** Rate of Heat Release of WPC as a Function of FR Type

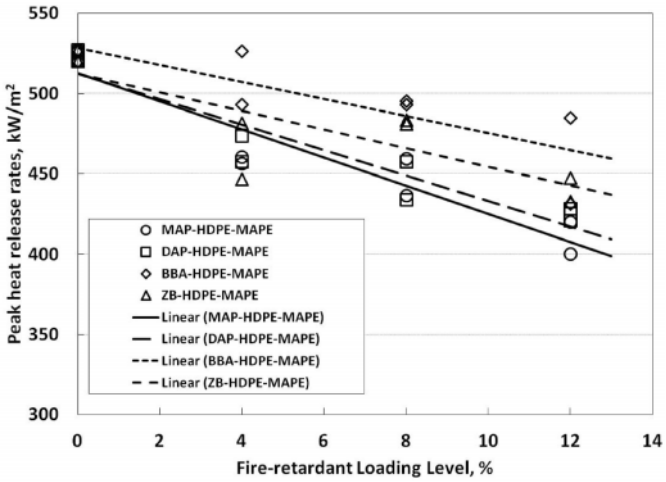


**Figure 6:** Peak Heat Release Rates for Four FR Treatments with Coupling agent Plotted against the FR Treatment Level

**Table 4**
**The Regressions of the Peak Heat Release Rate with the Percentage Fire Retardant Treatment Level**

| *FR treatment* | *Slope, kW m-2/% FR* | *Pr>f* | *R2* |
|---|---|---|---|
| BX/BA | -5.49 | 0.0006 | 0.88 |
| BX/BA-MAPE | -5.31 | 0.0141 | 0.66 |
| ZB | -5.46 | 0.0235 | 0.60 |
| ZB-MAPE | -5.81 | 0.0144 | 0.66 |
| MAP | -2.07 | 0.4504 | 0.10 |
| MAP-MAPE | -8.78 | 0.0004 | 0.89 |
| DAP | -6.10 | 0.0119 | 0.68 |
| DAP-MAPE | -7.94 | 0.0005 | 0.89 |

**Table 5**
**The Regressions of the Total Heat Release with the Percentage Fire Retardant Treatment Level**

| *FR treatment* | *Slope, MJ m-2/% FR* | *Pr>f* | *R2* |
|---|---|---|---|
| BX/BA | -2.02 | 0.0201 | 0.62 |
| BX/BA-MAPE | -2.11 | 0.0508 | 0.50 |
| ZB | -1.19 | 0.6860 | 0.03 |
| ZB-MAPE | -1.82 | 0.0674 | 0.45 |
| MAP | -1.01 | 0.7549 | 0.02 |
| MAP-MAPE | -3.02 | 0.0132 | 0.67 |
| DAP | -2.70 | 0.0186 | 0.63 |
| DAP-MAPE | -2.18 | 0.0463 | 0.51 |

**Table 6**
**The Regressions of the Residual Mass Fraction with the Percentage Fire Retardant Treatment Level**

| *FR treatment* | *Slope, kg kg-1/% FR* | *Pr>f* | *R2* |
|---|---|---|---|
| BX/BA | 0.0080 | 0.0014 | 0.84 |
| BX/BA-MAPE | 0.0052 | 0.0153 | 0.65 |
| ZB | 0.0089 | 0.0005 | 0.88 |
| ZB-MAPE | 0.0069 | 0.0180 | 0.63 |
| MAP | 0.0044 | 0.1116 | 0.37 |
| MAP-MAPE | 0.0080 | 0.0010 | 0.85 |
| DAP | 0.0061 | 0.0097 | 0.70 |
| DAP-MAPE | 0.0067 | 0.0131 | 0.67 |

insignificant reductions (Pr>f of 0.45 and $R^2$ of 0.10). The PHRR results for the four treatments with the coupling agent are illustrated in Figure 6. The reductions in peak heat release rate for the other treatments ranged from 5.3 to 7.9 kW/m² per percentage increase in FR level and had $P_r$>f less than 0.025 and R-sq higher than 0.60 (Table 4). The different results for the MAP treatments with and without the coupling agent largely reflected the different results for the 12% treatment level. There is no obvious effect of the coupling agent at the 4 and 8% treatment levels. The similar results for the total heat released during the tests are presented in the Table 5. The results are similar to the peak heat release rate results, except in this case, the results for the zinc borate also did not indicate a statistically significant reduction in the total heat released with the FR treatment. The mechanism of fire retardant treatment is often to increase the residual mass fraction and thereby reduce the production of flammable volatile gases. The zinc borate (ZB) without coupling agent resulted in the greatest increase in residual mass fraction while the MAP without coupling agent resulted in the smallest and statistically insignificant increase in residual mass fraction. The regressions of the residual mass fraction with the percentage fire retardant treatment level are presented in Table 6. Similar analysis for the average effective heat of combustion and average specific extinction area indicated regression results that were not statistically significant (high Pr>f and low $R^2$).

The improvements in fire performance with FR treatment in these tests were less than that shown in other studies (White et al. 2011). One likely contributing factor is that both the wood fiber content and the polypropylene contents were adjusted to accommodate the addition of the fire retardant. In other studies, only the polymer content was adjusted to accommodate the fire retardant. Reducing the polymer content by increasing the wood fiber content has been shown to improved fire performance in the cone calorimeter test. Other possible factors that require further investigation include the manner of adding the FR in the manufacture of the wood plastic composite.

## CONCLUSIONS

WPC samples including inorganic fire retardant particles generally exhibited higher degree of crystallinity values than control sample. Furthermore, degree of crystallinity increases with the increasing amount of FRs. the DAP and MAP with MAPE significantly increased the OIT values of the WPC

compared to other FRs. The FR treatments produced modest improvements in fire performance as indicated by reductions in the heat release rates. Reducing both the wood fiber content and the polymer content equally to accommodate the addition of the FR chemicals likely reduced the net improvement provided by the FR treatment.

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