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# INTUMESCENT POLYPROPYLENE: INTERACTIONS BETWEEN PHYSICAL AND CHEMICAL EXPANSION

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## ABSTRACT

To decrease the reaction to fire of a highly flammable plastic, polypropylene (PP), the concept of intumescence was applied. Two intumescent systems were designed, based on different mechanisms: physical expansion with expandable graphite (EG) and chemical expansion with modified ammonium polyphosphate (AP). Fire behavior of PP containing EG, AP or an AP/EG mixture with a total loading of 10wt% was evaluated by cone calorimetry at 35 kW.m<sup>-2</sup>. Thermocouples allowed measuring the temperature at the backside or inside samples over time and evaluating the thermal barrier of these intumescent materials. Two grades of AP (difference in composition) and several grades of EG (difference in expansion characteristics) were compared. Mixing AP and EG does not create a synergistic effect in studied conditions. Contrarily, the incorporation of small amount of EG in PP-AP modifies heat transfer in the coating, creating a strong anisotropy. Graphite worms are trapped vertically into the expanded AP, which increases the transverse heat conductivity (lower efficiency of the thermal barrier) and decreases the fire performance. This phenomenon disappears in thicker specimens. While a higher expansion volume of graphite worms improves fire performances of PP with only small amount of EG (1wt%), this effect is not noticeable with AP/EG mixtures.

## KEYWORDS

Intumescence; Expandable graphite; Modified ammonium polyphosphate; Polypropylene; Fire behavior

## INTRODUCTION

Plastics find more and more applications in many industrial sectors: building, transportation, electrical engineering, paper industry, etc. In particular, polypropylene (PP) is the fastest growing commodity plastic worldwide. However, organic polymer systems are flammable and lead to greater fire risks. The high carbon and hydrogen content of PP makes it combustible. To decrease its reaction to fire, flame-retardants (FRs), acting chemically or physically on the condensed or gaseous phase, can be incorporated in the bulk.<sup>1</sup>

Firstly, halogenated compounds were used as FRs because they interfere with free radicals in gas phase. However, their use is limited because of their oxidizing nature or potential toxicity. Inorganic hydroxide compounds are another kind of FRs. They undergo dehydration reactions under fire conditions. This endothermic dehydration decreases the temperature, the released water dilutes the fuel / oxygen mixture and a ceramic layer is formed in the condensed phase. However, large amounts of FRs are needed, which modify the mechanical properties of the polymer. Finally, intumescent compounds can also be considered as FRs for polymeric systems.<sup>2</sup> They lead to materials exhibiting high fire

performance<sup>3</sup>. Indeed, when heated beyond a critical temperature, an intumescent material begins to swell and then to expand. A charred layer is formed at the surface, protecting the underlying material from the action of the heat flux or the flame (thermal barrier) and limiting the transport of decomposition gases and of oxygen from the material and from the flame, respectively.<sup>4</sup>

Intumescence can be obtained from a series of chemical reactions occurring timely or using physical expansion phenomena. In the first case, typically, the combination of three main ingredients makes intumescence possible: an inorganic acid or a material yielding acidic species upon heating (e.g. phosphate), a char former (e.g. pentaerythritol) and a component that decomposes at the right temperature and at the right time to enable the blowing of the system (e.g. melamine).<sup>5</sup> Modified ammonium polyphosphate (AP) is a well-known example of this kind of FRs. More sophisticated FRs combining the three ingredients in one molecule were designed but they provide similar performance as the conventional formulation<sup>6,7</sup>. The second case (physical expansion) can be obtained by the rapid sublimation of a molecule (and/or the decomposition products) leading to the expansion of the top degraded layer of the polymer to make an intumescent coating. This mechanism occurs when using expandable graphite (EG), which acts both as a carbonization compound and a blowing agent<sup>8</sup>. EG is a synthesized intercalation compound of graphite that expands or exfoliates when heated. A wide variety of chemical species can be used to intercalate graphite materials (e.g. sulfate or nitrate)<sup>9</sup>. EG was incorporated in PP alone<sup>10</sup> or in combination with conventional intumescent ingredients<sup>11–13</sup>.

This paper examines interactions and possible synergies between these two modes of action of intumescence: physical expansion with EG and chemical expansion with AP. Indeed, synergistic effects between these two components were already demonstrated in different materials, such as polyurethane foams<sup>14</sup>, wood-PP composites<sup>15</sup>, jute-PP composites<sup>16</sup>, poly(butylene terephthalate)<sup>17</sup>, polylactide<sup>18</sup> or acrylonitrile–butadiene–styrene resin<sup>19</sup>. This work focuses on PP. Reaction to fire of PP containing EG and AP in different ratios (total loading of 10wt% FR) is evaluated by cone calorimetry and the efficiency of the intumescent barrier is measured quantitatively versus time during the same experiment. Influence of AP grade, sample thickness and graphite expansion volume is investigated. The aim is to better understand the physical and chemical intumescent mechanisms, and particularly to explain a phenomenon observed in a previous work with 9wt% AP / 1wt% EG in PP<sup>20</sup>.

## MATERIAL AND METHODS

### Materials

Two polypropylenes were used in this work: PPH 9060 supplied by Total petrochemicals (Belgium) and PP 089 Y1E supplied by Repsol (Spain). Cone calorimetry tests showed that both react to fire in the same way. Subsequently, they will not be differentiated and they will be indifferently named PP.

Several expandable graphites were tested: ES 350 F5 and ES 700 F5 supplied by Graphitwerk Kropfmühl (Germany), Nyagraph FP and Nyagraph KP251 supplied by Nyacol (USA) and FireCarb TEG 315 supplied by Minelco Ltd (Italy). Their expansion characteristics are presented in table 1.

Two modified ammonium polyphosphates supplied by Clariant (Germany) were also compared: Exolit AP760 and Exolit AP766. They are intrinsic intumescent systems containing phosphorus and nitrogen in different proportions (Table 2) acting in synergy. They are mainly based on ammonium polyphosphate as acid source.

## Processing

PP was blended with flame-retardants in a HAAKE Rheomix OS PTW 16 twin-screw extruder. The extruder is a co-rotating intermeshing twin screw with a barrel length of 400 mm and screw diameter of 16 mm ( $L/D = 25$ ) with 10 zones. PP and FRs were incorporated using two gravimetric side feeders into the extruder. Polymer flow rate was fixed to extrude about  $500 \text{ g}\cdot\text{h}^{-1}$  with a screw speed of 300 rpm. The temperature profile of the extruder from feeder to die was set at 200 / 200 / 200 / 200 / 200 / 170 / 185 / 180 / 200 / 200°C. The total loading of FRs in PP was 10wt%, with different AP/EG ratios.

## Cone Calorimetry

Measurements were carried out with a Fire Testing Technology (FTT) Mass Loss Calorimeter (MLC), following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain heat release rate (HRR) rather than employing the oxygen consumption principle. The samples were 100 mm x 100 mm plates exposed to the heat flux in horizontal orientation. They were 3 mm thick, except for the study of the influence of material thickness, for which 6 mm thick specimens were also used. External heat flux was set to  $35 \text{ kW}\cdot\text{m}^{-2}$ , corresponding to common heat flux in mild fire scenario<sup>21,22</sup>. HRR, peak of HRR (pHRR) and total heat release (THR) were measured with a reproducibility of  $\pm 10\%$ .

In addition, temperature gradient in samples and intumescent structures during a conventional cone experiment was monitored using thermocouples embedded vertically (K-type thermocouple of 0.5 mm diameter). For the 3 mm thick samples, only one thermocouple was put on the backside of materials. For the 6 mm thick samples, additional thermocouples were located at different heights, below and above the surface exposed to heat flux, as presented in figure 1. Studied heights are the surface of the sample, 2 mm, 4 mm and 6 mm (backside of the material) under the surface and 5 mm, 10 mm and 15 mm above the surface (in the structure after swelling only). In this experimental set-up, it is necessary to assume that additional conductive effects due to thermocouples are negligible.

Each experiment was replicated three times. Data reported in this paper correspond to the most representative of them: it is the experiment that presents the best fire behavior for neat PP and the worst fire behavior for PP with FRs. Average values are not used to avoid a potential loss of information on curves.

## RESULTS AND DISCUSSION

### Selection of the Expandable Graphite

Intumescence produced by expandable graphites is due to the decomposition into gaseous products of an intercalation compound present in the EG structure. These products blast off the graphite flakes and an entangled network of graphite worms is formed at the

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2  
3 surface of the material.<sup>23</sup> Nevertheless, the efficiency of this physical intumescence depends  
4 on expansion characteristics of EG, in particular the temperature at which the expansion  
5 begins. That is why the fire behavior of polypropylene blended with 10wt% EG was tested  
6 with five commercial EGs presenting different expansion temperatures (Table 1).  
7  
8

9 Figure 2 compares curves of heat release rate as a function of time for the different  
10 PP-EG mixtures and table 3 gathers values of peak of HRR, total heat release and time to  
11 ignition (TTI) during cone calorimeter experiment (with neat PP as a reference). The lowest  
12 pHRR is observed for ES 350 F5, ES 700 F5 and Nyagraph FP (91-92 kW.m<sup>-2</sup>, 76% lower  
13 than neat PP), whose HRR curves are similar. However, THR of Nyagraph FP (66 MJ.m<sup>-2</sup>,  
14 13% lower than neat PP) is higher than that of ES 350 F5 and ES 700 F5 (56 and 57 MJ.m<sup>-2</sup>,  
15 26% and 25% lower than neat PP, respectively). FireCarb TEG 315 also reduces HRR and  
16 THR compared to neat PP (reduction by 65% and 9%, respectively), but it is slightly less  
17 efficient than the previously cited EGs. Finally, Nyagraph KP251 barely improves the fire  
18 behavior of PP.  
19  
20

21 These results can be related to the temperature of expansion of the graphites. The best  
22 fire behavior is obtained for a temperature of expansion of 200-230°C (ES 350 F5 and  
23 ES 700 F5). Then, the lower the temperature of expansion, the worse the fire behavior. The  
24 optimal expansion temperature is related to the rheology of PP as a function of temperature. It  
25 is reasonable to assume that if this temperature is too low, PP is not enough molten and  
26 prevents or limits EG expansion.  
27  
28

29 The presence of EG also accelerates the ignition that occurs earlier than that of neat  
30 PP (reduction between 18% and 52% of TTI, depending on EG). This is due to the good heat  
31 conductivity of graphite worms: although it allows a better dissipation of heat through the  
32 material, it enhances the decomposition of PP<sup>24</sup>.  
33  
34

35 When used as the only flame retardant compound in PP, ES 350 F5 and ES 700 F5  
36 appear to provide similar fire protection. These are similar EG with a different expansion  
37 volume (twice as much for ES 700 F5), but the influence of this expansion volume is not  
38 noticeable here. Thereafter, ES 350 F5 was kept to study the interaction of EG with modified  
39 ammonium polyphosphate, providing a chemical-based intumescence. Then, the influence of  
40 the graphite expansion volume will be studied in more detail, especially in AP/EG mixtures.  
41  
42

### 43 **Interactions between Modified Ammonium Polyphosphate and Expandable Graphite**

44  
45 Contrary to EG, whose intumescence is due to physical expansion, the expansion  
46 induced by AP is chemical. An intumescent char is formed by a series of chemical reactions  
47 during burning. To study interactions between these two kinds of intumescence, experiments  
48 were carried out on PP blended with AP/EG mixtures in different ratios: 5/5, 9/1 and 9.5/0.5  
49 (wt% / wt%) and compared to only AP and only EG (10wt% in PP). Commercial grades  
50 Exolit AP766 as AP and ES 350 F5 as EG are used in this section.  
51  
52  
53

54 Figure 3 presents HRR curves of intumescent materials. Two successive peaks of  
55 HRR (67 kW.m<sup>-2</sup> and 145 kW.m<sup>-2</sup>) appear for PP containing 10% AP, corresponding to a  
56 respective decrease of 83% and 62% compared to neat PP. The first peak is due to ignition  
57 and the second peak corresponds to the degradation of the intumescent char<sup>25</sup>. This curve will  
58 be discussed in more details in the next section, in comparison with another AP. The HRR  
59 curve for the mixture 5% AP / 5% EG is close to that obtained for 10% EG. The mixture  
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2  
3 9.5% AP / 0.5% EG has an intermediate behavior between EG and AP (observation of a  
4 second peak). Its maximal peak of HRR appears later than for other materials, except for 10%  
5 AP. The mixture 9% AP / 1% EG has an unexpected behavior. Compared to neat PP, this  
6 mixture improves the fire behavior (reduction by 65% of pHRR) but its pHRR is higher than  
7 that of PP containing only EG and it appears at shorter times than that of PP containing only  
8 AP.  
9

10  
11 The temperature profiles at the backside of intumescent materials, presented in  
12 figure 4, allow quantifying the efficiency of the intumescent barrier and complete the  
13 previous observations. Compared to neat PP, whose curve was stopped when the  
14 thermocouple is no longer in the matter because of the complete decomposition of PP, the  
15 slope of the curve (the rate of the temperature rise) decreases faster with intumescent PPs  
16 containing 10% AP and 10% EG. For mixtures containing 5% AP / 5% EG and 9.5% AP /  
17 0.5% EG, the initial temperature rise is a little bit faster than PP but then, it is strongly  
18 reduced. By contrast, with PP containing 9% AP / 1% EG, the temperature rise is quite high  
19 at short time. Then, the temperature decreases and a stabilization occurs at the same level  
20 than for other blends.  
21  
22

23  
24 The nature of intumescent phenomena could explain these observations. Figure 5  
25 presents pictures of char residues obtained after the cone calorimetry experiments for the  
26 different samples. Degraded PP-AP presents a cohesive char, with a high expansion and a  
27 smooth surface (Figure 5.a), whereas non-cohesive worms of graphite can be observed in the  
28 PP-EG char (Figure 5.b). When AP and EG are mixed in the polymer (5% AP / 5% EG),  
29 visual observations suggest that the network of graphite worms is trapped in the intumescent  
30 char formed from AP (Figure 5.c). However, with only 1% EG, there are not enough worms  
31 to form an entangled network. Worms are trapped in vertical position (Figure 5.d). They may  
32 then disturb the action of AP and enhance heat conductivity through the material. This could  
33 explain the sudden increase in temperature. The sample with 9.5% AP / 0.5% EG does not  
34 present this particular behavior. Performance of this system is closer to that of PP with 10%  
35 AP. It can be assumed that, from a certain threshold, there is too little graphite to disturb the  
36 action of AP and to modify heat conductivity (Figure 5.e).  
37  
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39  
40 Interactions between AP and EG in PP are fully commented in a previous paper<sup>20</sup>, but  
41 this previous study was carried out with another grade of AP. The following section presents  
42 a comparison between the fire performances of the two APs, alone or in combination with  
43 EG.  
44

### 45 **Influence of Modified Ammonium Polyphosphate**

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48 The study of AP and AP/EG mixtures as FRs into PP was first carried out with the  
49 commercial grade of modified ammonium polyphosphate Exolit AP760<sup>20</sup>. Experiments were  
50 interrupted because of the discontinuation of the marketing of this AP and Exolit AP766  
51 was then used. AP760 and AP766 do not have the same composition (Table 2) and differences in  
52 fire properties can be observed.  
53

54  
55 Figure 6 presents HRR curves and temperature profiles of PP blended with AP760  
56 and with AP766. The maximal peak of HRR of these two materials is close (139 kW.m<sup>-2</sup> for  
57 AP760 and 145 kW.m<sup>-2</sup> for AP766) but it appears at very different times (61 s for AP760 and  
58 788 s for AP766) and HRR profiles are not similar. For PP with AP760, the first peak is high  
59 and is followed by a small peak (around 500 s). For PP containing AP766, there are a first  
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3 small peak followed by a stabilization and, then, an important second peak. As for  
4 temperature at the backside of materials, AP766 provides a better thermal barrier than  
5 AP760: a gap of more than 100°C between the two temperatures is observed from 80 s of  
6 test. Intumescent char of AP766 appears earlier but its structure is weaker than that of AP760.  
7 Visual observation indicates the formation of cracks at the surface of the intumescent coating.  
8 Therefore, AP766 offers a better fire protection at the beginning of the burning. Then, cracks  
9 allow a release of gases trapped between the material and the char, which leads to a  
10 resumption of ignition and to the high second peak of HRR. Nevertheless, no influence of  
11 this second ignition is noticeable on the temperature at the backside of the sample since the  
12 char still protects the material and limits heat transfer.  
13  
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15  
16 To see how these differences impact the interactions between AP and EG in PP,  
17 figure 7 compares HRR curves and temperature profiles of PP blended with AP/EG mixtures  
18 (ratios 5/5 and 9/1) for AP760 and AP766. With 5% AP / 5% EG, results are very close.  
19 There is no influence of the grade of AP, which suggests that fire performances are more  
20 related to EG than to AP for this ratio. This observation is confirmed by the similarity of  
21 HRR curves of 5% AP / 5% EG and of 10% EG materials (Figure 3). Regarding 9% AP / 1%  
22 EG mixtures, the unexpected behavior described in the previous section is noticeable with  
23 both APs. pHRR are higher than for other intumescent PPs and there is an important rise of  
24 temperature at the TTI. Nevertheless, AP was incorporated in a large amount and its  
25 influence on fire performances is obvious: with AP760, pHRR is higher and the temperature  
26 remains at its maximum value for a longer time than for AP766. The earlier decrease of  
27 temperature for AP766 may be related to the faster swelling of this AP. Indeed, for PP  
28 blended with 9% AP / 1% EG, graphite worms trapped in vertical position delay the blowing  
29 of AP because they prevent the formation of a smooth surface of char. The decrease of  
30 temperature only observed with these blends is due to the late expansion of the char<sup>20</sup>.  
31  
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34 The composition of AP used as FR has an influence on the fire behavior and on the  
35 intumescent barrier of PP. Nevertheless, trends observed when AP is mixed with EG are  
36 similar with AP760 and AP766. Therefore, it can be assumed that changing AP does not  
37 affect the study of the interactions between chemical intumescence of AP and physical  
38 intumescence of EG, which is the aim of this work.  
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40

### 41 **Influence of Material Thickness**

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43 All previous results were obtained during cone calorimetry experiments with material  
44 specimens measuring 100 mm x 100 mm x 3 mm. To study the influence of material  
45 thickness, a comparison with specimens of 6 mm thick (considered as thermally thick)  
46 instead of 3 mm (considered as thermally thin) was carried out. To get a better idea of what  
47 happens upon burning, a mapping of temperatures in intumescent materials during cone  
48 calorimetry experiments was made with several thermocouples (section Material and  
49 methods, Figure 1). This section focuses on PP blended with 9% AP / 1% EG in order to  
50 better understand the intumescent phenomenon in this mixture.  
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54 Figure 8 only compares temperature profiles at the backside of 3 mm thick and 6 mm  
55 thick PP blended with 9% AP / 1% EG. Then, figure 9 presents temperature profile as a  
56 function of time and as a function of the distance to the surface for 6 mm thick PP blended  
57 with 9% AP / 1% EG, and in comparison with PP blended with 10% AP. The entire mapping  
58 of temperatures for these two intumescent PPs is represented in figure 10, obtained by  
59 extrapolation from thermocouple measurements. Char expansion is also shown in figure 10  
60



(plain black line). Above it, measured temperatures are not relevant because thermocouples are not in solid structure. That is why temperature profiles at 15 mm above the surface of the material are not represented in figure 9.

At the backside of 6 mm thick PP blended with 9% AP / 1% EG, the temperature slowly increases and stabilizes around 1000 s (Figure 8). Despite the small amount of EG mixed with AP and the heat conductivity of worms of graphite, there is no significant rise of temperature at the start of burning. The greater thickness of sample could partially explain the change of temperature profile. Graphite worms conduct heat from the surface into the material but heat can be dispersed through PP in last millimeters. Indeed, the difference between 3 mm thick and 6 mm thick samples is already noticeable with neat PP. The increase in temperature appears later with thermally thick material. However, for PP blended with 9% AP / 1% EG, temperature profiles at -2, -4 and -6 mm are very close (Figure 9 and Figure 10). There is also no important increase in temperature around -3 mm, such as in the case of 3 mm thick sample. That supports the idea that the thickness of the material affects intumescent phenomena.

In 6 mm thick PP blended with 9% AP / 1% EG, expansion of graphite worms from the bottom of the sample is disturbed by phenomena at the surface. That may lead to different orientations of worms, not only normal to the surface. The different development of expansion may also change reactions in the material around -3 mm. That is why changes in temperature profile are observed between thermally thin and thermally thick materials. Results for 6 mm thick sample are more similar to those of PP blended with 10% AP, with a stabilization at a higher temperature. Nevertheless, these results must be considered cautiously since the presence of thermocouples can have an impact on swelling and heat conductivity.

Mapping offers an overall view of the evolution of temperature over time in the sample and in the intumescent structure. Two phases can be observed: a transient phase during which the temperature under the surface increases and the temperature above the surface strongly fluctuates because of char expansion process (thermocouples are covered by the intumescent structure one by one); a steady state during which the temperature becomes uniform and stabilizes. These two phases are observable in figure 9 and figure 10 for PP with 10% AP and with 9% AP / 1% EG, as well as for other AP/EG ratios (mappings not shown here).

### **Influence of Graphite Expansion Volume**

In 2001, Xie and Qu studied the influence of graphite expansion volume on fire performances of polyethylene. They found that a higher expansion volume allows reaching best results for LOI and thermal stability but a lower char yield.<sup>8</sup> This section aims at studying the influence of expansion volume on cone calorimetry and thermal barrier results when EG is used alone or in combination with AP in PP.

ES 700 F5 is an expandable graphite similar to ES 350 F5 with a double expansion volume (Table 1). Figure 2 showed that it also provides good fire performances to PP. A more detailed comparison between these two EGs is presented here. Dimensions of samples are 100 mm x 100 mm x 3 mm. Commercial grade Exolit AP766 is used as AP.

Figure 11 compares HRR curves for 1% EG and 10% EG in PP between ES 350 F5

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3 and ES 700 F5. The curve for the mixture 5% ES 350 F5 / 5% ES 700 F5 is also presented.  
4 With only 1% EG in PP, pHRR for ES 700 F5 ( $300 \text{ kW.m}^{-2}$ , 22% lower than neat PP) is  
5 lower than that of ES 350 F5 ( $345 \text{ kW.m}^{-2}$ , 10% lower than neat PP). The higher expansion of  
6 graphite allows a better fire behavior of the material. The same cannot be said for 10% EG in  
7 PP, for which the two HRR curves are superimposed. It can be assumed that the protection is  
8 optimal in these proportions (reduction by 76% of pHRR). Increasing the graphite expansion  
9 volume does not improve the protection. Mixing 5% ES 350 F5 and 5% ES 700 F5 does not  
10 modify HRR curve either.  
11  
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13  
14 Figure 12 compares ES 350 F5 and ES 700 F5 when they are mixed with AP in PP. It  
15 presents HRR curves and temperature profiles at the backside of the material for mixtures  
16 with 5% AP / 5% EG and with 9% AP / 1% EG. Table 4 gathers values of pHRR and THR  
17 for the same materials (with neat PP as a reference). For both ratios, the profiles of HRR are  
18 similar for both EGs, but fire behavior is better with ES 350 F5. Its pHRR and its THR are  
19 lower, especially for 9% AP / 1% EG mixture. With regard to the thermal barrier, for 5% AP  
20 / 5% EG, this trend is reversed: the rise of temperature is slower for ES 700 F5 than for ES  
21 350 F5, even if the stabilization is at the same level. For 9% AP / 1% EG mixtures, the large  
22 increase in temperature at the beginning of burning appears on both curves. The maximum of  
23 temperature is reached sooner with ES 350 F5 but the temperature rapidly decreases while it  
24 stabilizes with ES 700 F5.  
25  
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27  
28 The worse fire behavior observed with ES 700 F5 may be due to the higher expansion  
29 of this EG. With graphite worms maintained by the intumescent structure of AP, the surface  
30 of intumescent material is getting closer to the resistance of the cone calorimeter and,  
31 therefore, heat flux is greater. However, the faster growth of graphite worms can allow a  
32 faster dissipation of heat. That explains the slower rise of temperature for 5% AP / 5% EG  
33 mixture.  
34

## 35 CONCLUSION

36  
37 Modified ammonium polyphosphate and expandable graphite act as flame-retardants  
38 in polypropylene in two different ways. AP expands by chemical reactions leading to the  
39 formation of a cohesive intumescent barrier and decomposition gases are trapped under this  
40 barrier. EG physically expands and forms an entanglement network of worms at the surface  
41 of PP, which allows the dissipation of heat. When AP and EG are mixed, cone calorimetry  
42 experiments show that fire performances of PP are not improved compared to only AP or  
43 only EG. No synergistic effect is observed in studied ratios. Contrarily, when EG is added in  
44 small amount in a chemical intumescent system (9% AP / 1% EG), worms disturb the system,  
45 increase transverse heat conductivity and decrease fire performances.  
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49  
50 Several EGs were tested. Among them, ES 350 F5 and ES 700 F5 allow the best fire  
51 protection. They start to expand at  $200^{\circ}\text{C}$  and have an expansion volume of 350 and  
52  $700 \text{ cm}^3.\text{g}^{-1}$ , respectively. A higher expansion volume is useful when there is little EG (1%)  
53 in PP but no influence is observed with bigger amount of EG (10%). When EG is mixed with  
54 AP, ES 350 F5 seems to provide a better fire behavior but a higher graphite expansion brings  
55 the intumescent swelling closer to the resistance of the cone calorimeter. Conversely, the  
56 faster growth of worms with ES 700 F5 provides a better thermal barrier at the beginning of  
57 burning.  
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59  
60 Two different APs were compared. Experiments show that AP composition modifies

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3 the properties of intumescent protection and therefore fire behavior of PP. Nevertheless,  
4 adding EG modifies the system for both APs similarly. So, interactions between physical and  
5 chemical expansions are not dependent on the grade of AP.  
6  
7

8 Finally, the establishment of intumescent protection and thermal barrier depends on  
9 material thickness. Temperature mappings of samples allow seeing that, with a double  
10 thickness, the increase in transverse heat conductivity by graphite worms in 9% AP / 1% EG  
11 mixtures in PP is not noticeable. Temperature profile at the backside of the material is closer  
12 than that of PP with 10% AP.  
13

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21

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Table 1. Expansion characteristics of expandable graphites

	<b>ES 350 F5</b>	<b>ES 700 F5</b>	<b>Nyagraph FP</b>	<b>FireCarb TEG 315</b>	<b>Nyagraph KP251</b>
<b>Expansion volume (cm<sup>3</sup>.g<sup>-1</sup>)</b>	350	700	≥ 230	220	≥ 230
<b>Expansion start temperature (°C)</b>	200 - 230	200 - 230	170 - 190	170	135 - 155

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Table 2. Characteristics of modified ammonium polyphosphates

	<b>AP760</b>	<b>AP766</b>
<b>Phosphorus (wt%)</b>	19.0 - 21.0	23.0 - 25.0
<b>Nitrogen (wt%)</b>	≈ 14	14.4 - 16.4
<b>Decomposition temperature (°C)</b>	> 250	> 275

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Table 3. Peak of heat release rate, total heat release and time to ignition of PP with 10wt% of different EGs - Comparison with neat PP

	<b>PP</b>	<b>PP - ES 350 F5</b>	<b>PP - ES 700 F5</b>	<b>PP - Nyagraph FP</b>	<b>PP - TEG 315</b>	<b>PP - Nyagraph KP251</b>
<b>pHRR (kW.m<sup>-2</sup>)</b>	383	91	92	92	134	308
<b>Reduction of pHRR</b>		76%	76%	76%	65%	20%
<b>THR (MJ.m<sup>-2</sup>)</b>	76	56	57	66	69	69
<b>Reduction of THR</b>		26%	25%	13%	9%	9%
<b>TTI (s)</b>	66	32	35	44	53	54
<b>Reduction of TTI</b>		52%	47%	33%	20%	18%

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Table 4. Peak of heat release rate and total heat release of intumescent PPs (AP766 is used as AP) - Comparison with neat PP

	<b>PP</b>	<b>PP - 5% AP / 5% ES 350 F5</b>	<b>PP - 5% AP / 5% ES 700 F5</b>	<b>PP - 9% AP / 1% ES 350 F5</b>	<b>PP - 9% AP / 1% ES 700 F5</b>
<b>pHRR (kW.m<sup>-2</sup>)</b>	383	98	121	135	172
<b>Reduction of pHRR</b>		74%	68%	65%	55%
<b>THR (MJ.m<sup>-2</sup>)</b>	76	64	77	60	78
<b>Reduction of THR</b>		16%	1%	21%	3%

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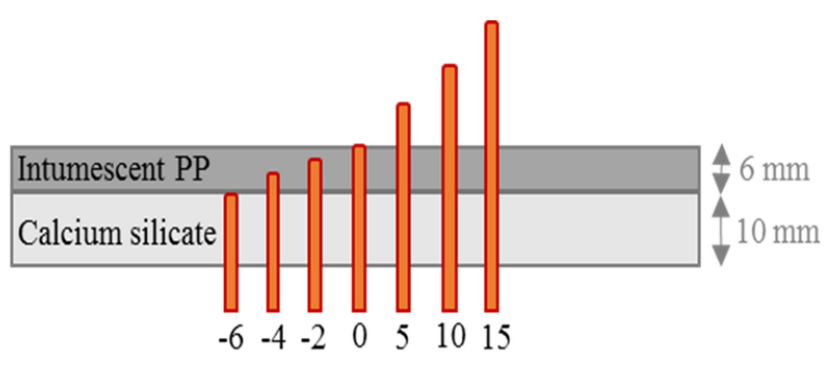


Figure 1. Arrangement of thermocouples (in orange) in 6 mm thick samples (sectional view) - Numbers are the height in mm of thermocouples compared to the surface exposed to heat flux (0 mm)

40x22mm (600 x 600 DPI)

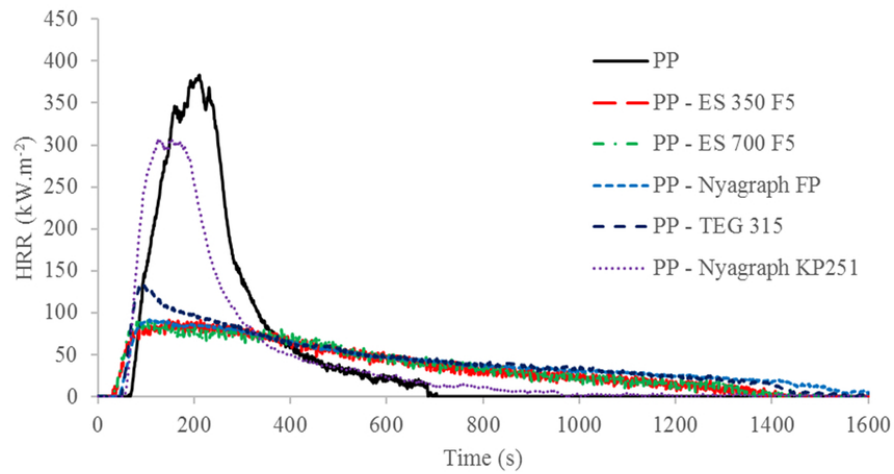


Figure 2. Heat release rate as a function of time of PP with 10wt% of different EGs during cone calorimetry experiment (external heat flux =  $35 \text{ kW.m}^{-2}$ )

40x22mm (600 x 600 DPI)

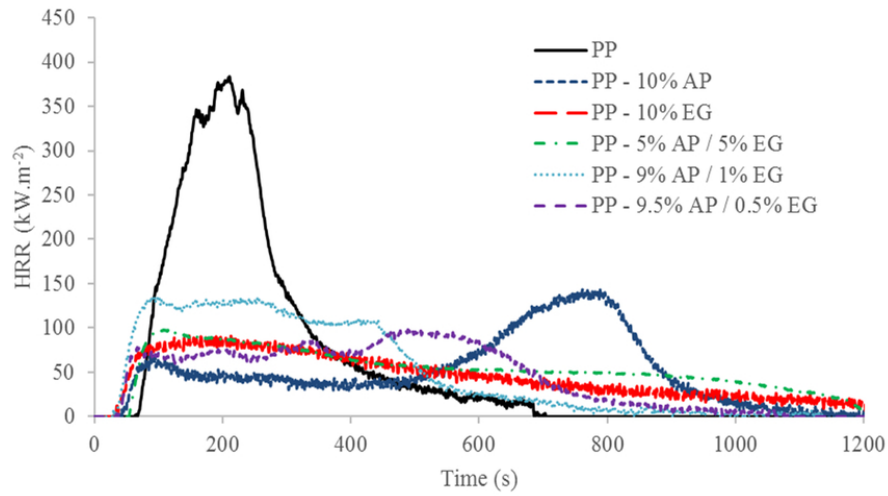


Figure 3. Heat release rate as a function of time of intumescent PPs during cone calorimetry experiment (external heat flux =  $35 \text{ kW.m}^{-2}$ ) – AP766 and ES 350 F5 are used as AP and EG, respectively

40x22mm (600 x 600 DPI)

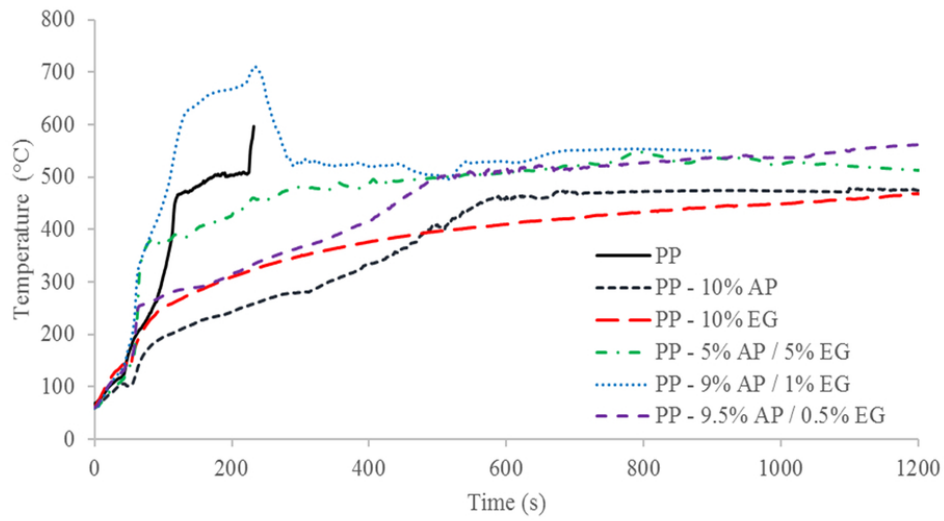


Figure 4. Temperature as a function of time at the backside of intumescent PPs during cone calorimetry experiment (external heat flux = 35 kW.m<sup>-2</sup>) – AP766 and ES 350 F5 are used as AP and EG, respectively

40x22mm (600 x 600 DPI)

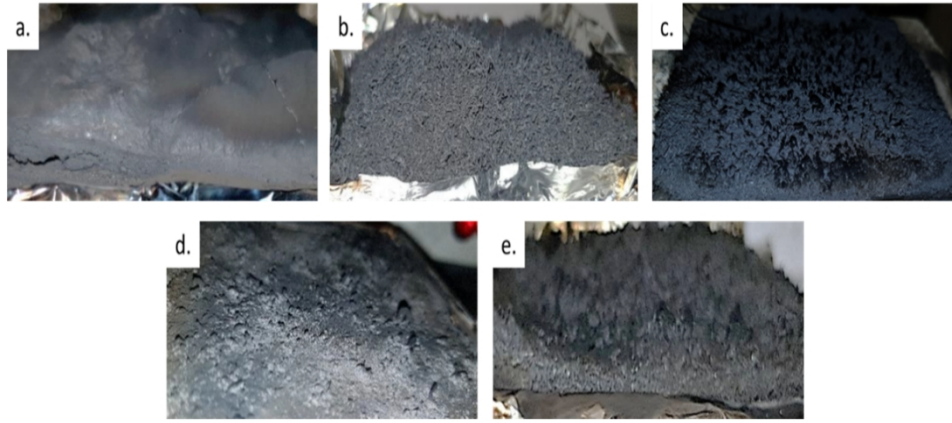


Figure 5. Char residues after cone calorimetry experiment for PP with AP766 / EG 350 F5 at different ratios (wt% / wt%): a. 10/0; b. 0/10; c. 5/5; d. 9/1; e. 9.5/0.5

108x60mm (300 x 300 DPI)

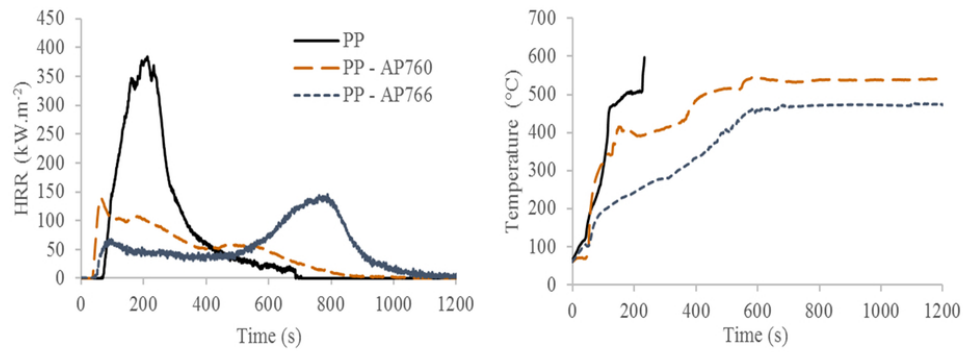


Figure 6. Heat release rate (left) and temperature at the backside (right) as a function of time of PP with 10wt% of different APs during cone calorimetry experiment (external heat flux = 35 kW.m<sup>-2</sup>)

40x22mm (600 x 600 DPI)

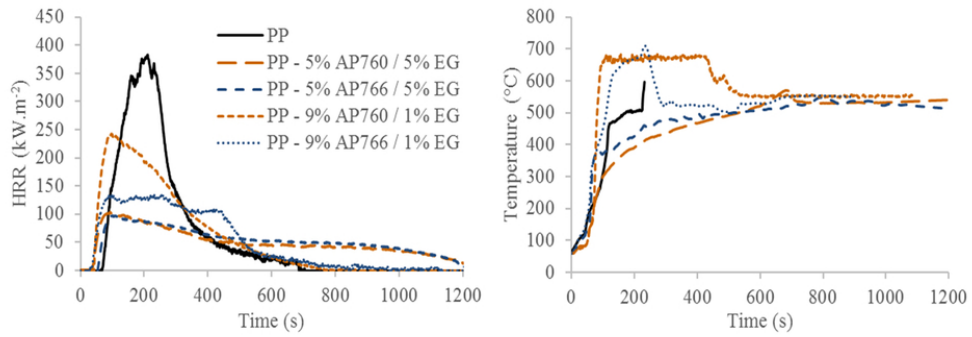


Figure 7. Heat release rate (left) and temperature at the backside (right) as a function of time of intumescent PPs during cone calorimetry experiment (external heat flux =  $35 \text{ kW}\cdot\text{m}^{-2}$ ) – ES 350 F5 is used as EG

40x22mm (600 x 600 DPI)

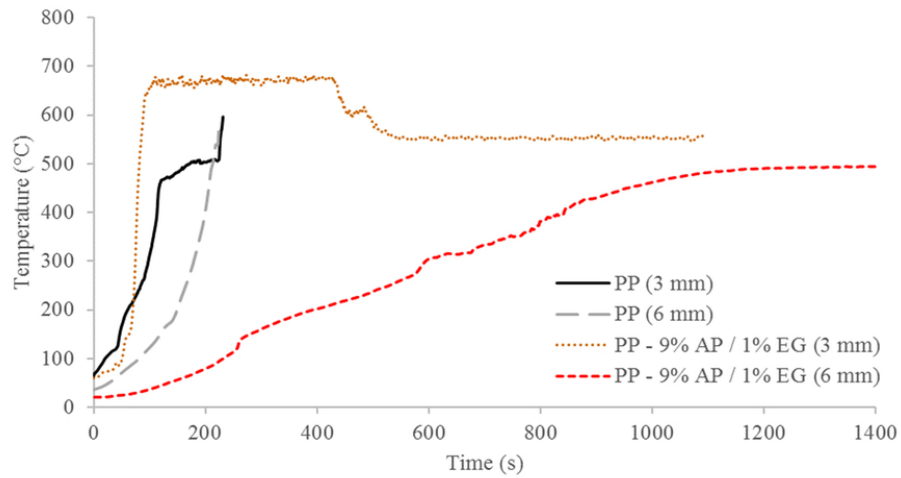


Figure 8. Temperature as a function of time at the backside of materials of different thicknesses during cone calorimetry experiment (external heat flux =  $35 \text{ kW}\cdot\text{m}^{-2}$ ) – AP760 and ES 350 F5 are used as AP and EG, respectively

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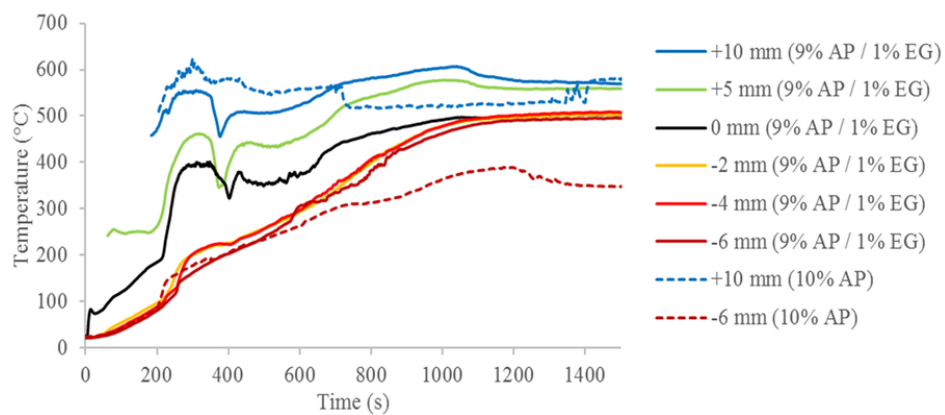


Figure 9. Temperature as a function of time inside and above 6 mm thick samples of intumescent PPs during cone calorimetry experiment (external heat flux =  $35 \text{ kW}\cdot\text{m}^{-2}$ ) – 0 mm is the height of the surface exposed to heat flux – AP760 and ES 350 F5 are used as AP and EG, respectively

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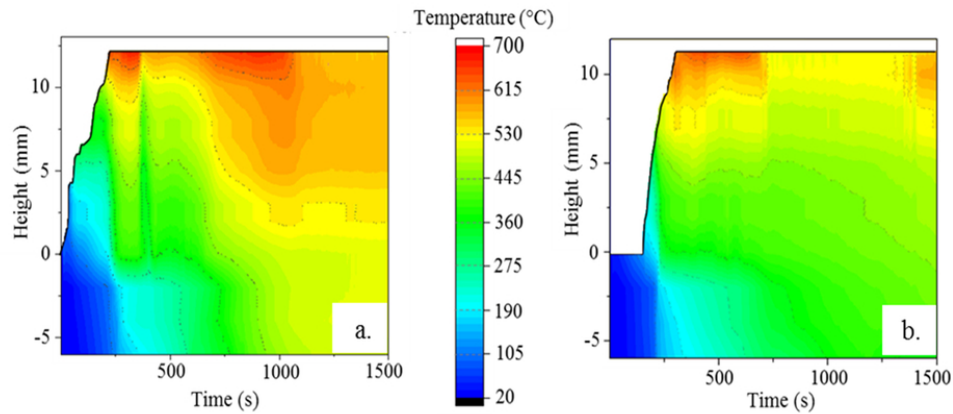


Figure 10. Mapping of temperature inside and above 6 mm thick samples of PP with AP760 / EG 350 F5 in ratios (wt% / wt%): a. 9/1; b. 10/0 during cone calorimetry experiment (external heat flux =  $35 \text{ kW}\cdot\text{m}^{-2}$ ) – 0 mm is the height of the surface exposed to heat flux – Plain black line represents char expansion

40x22mm (600 x 600 DPI)

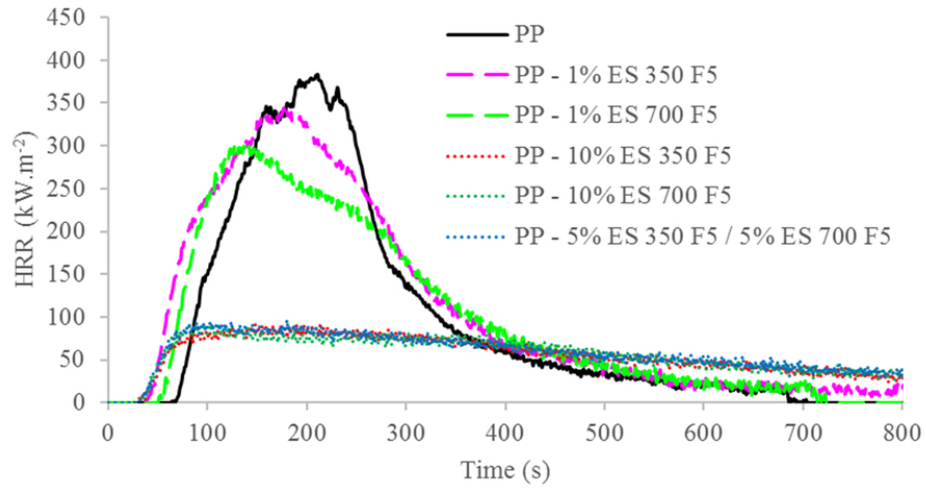


Figure 11. Heat release rate as a function of time of PP with different EGs during cone calorimetry experiment (external heat flux =  $35 \text{ kW.m}^{-2}$ )

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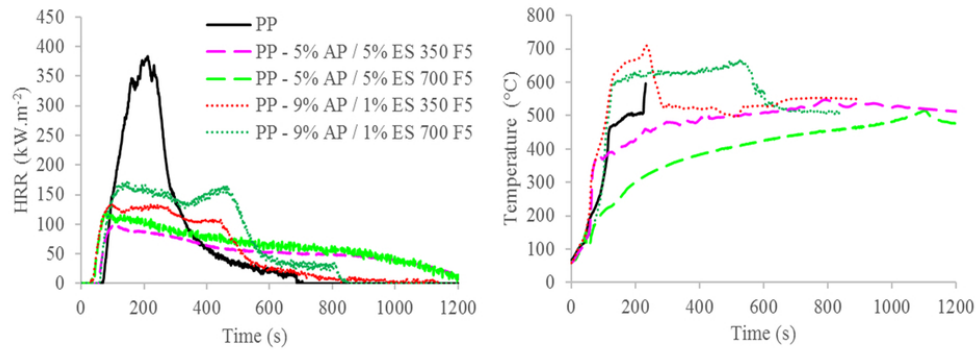


Figure 12. Heat release rate (left) and temperature at the backside (right) as a function of time of intumescent PPs during cone calorimetry experiment (external heat flux = 35 kW.m<sup>-2</sup>) – AP766 is used as AP

40x22mm (600 x 600 DPI)