Journal of Physics: Conference Series

**PAPER** • **OPEN ACCESS**

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To cite this article: Serge Bourbigot *et al* 2018 *J. Phys.: Conf. Ser.* **1107** 032001

IOP Conf. Series: Journal of Physics: Conf. Series **1107** (2018) 032001 doi:10.1088/1742-6596/1107/3/032001

# Maze running into intumescence: mechanistic aspects in polypropylene

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## ABSTRACT

The concept of intumescence was applied to make flame retarded polypropylene (PP). This paper examines two types of intumescence in PP) based on expandable graphite (EG, physical expansion) and on modified ammonium polyphosphate (AP760, chemical expansion). Reaction to fire of PP containing EG and AP760 was first evaluated by cone calorimetry. The incorporation of intumescent additives at relatively low loading (10 wt%) in PP permits the reduction by 70% of pHRR. The mode of action occurs via the formation of an expanded carbonaceous layer in all cases. The protective coating acts mainly as heat barrier in the case of the formulations containing AP760 or as heat dissipater with EG. The incorporation of small amount of EG in PP-AP760 modifies heat transfer in the coating creating a strong anisotropy. Upon expansion graphite worms align normal to the surface increasing the transverse heat conductivity (lower efficiency of the heat barrier) and hence, decreasing the fire performance (decrease by only 30% of pHRR). Kinetic analysis was then performed to quantify the thermal stability of the intumescent systems. It reveals that the intumescent additives do not modify the reactional scheme of the PP thermal decomposition but they increase slightly the thermal stability of the intumescent systems.

## KEYWORDS:

*Intumescence; polypropylene; fire chemistry; kinetic analysis; heat transfer*

## NOMENCLATURE LISTING

| | |
|---|---|
| $A$ | frequency factor (1/s) |
| $E$ | activation energy (kJ/mol) |
| $t$ | time (s) |
| $k$ | kinetic constant (1/s) |
| f(α) | reaction model |

*Greek symbols*

| | |
|---|---|
| α | degree of conversion (kg/kg) |

## INTRODUCTION

The word "intumescence" comes from Latin 'intumescere', which means 'to swell up'. From the dictionary, intumescence is defined as the act or process of swelling or enlarging. Some definition also mentions the action of heat to expand the body. French Writers like Jules Verne or François-René de Chateaubriand used the word 'intumescence' with different meanings: a hilly area on volcano (J. Verne in The Mysterious Island, 1874) or the waves' swell (F.R. de Chateaubriand in Mémoires d'Outre-Tombe, 1848). Taken 'as is', those definitions are not directly linked to the flame retardancy of polymeric materials or to the fire protection. Nevertheless, the above definitions describe well the behavior of an intumescent material used for fire retardancy. When heating beyond a critical temperature, an intumescent material begins to swell and then to expand. The result of this process is a foamed cellular charred layer on the surface, which protects the underlying material from the action of the heat flux or the flame. Visually, the swelling and the expansion looks like 'black waves' swollen at the surface of the material and the final char exhibits hemispheric shape with a roughed or smooth surface. The paper focuses on intumescence and its application in polymeric materials.

The concept of intumescence enables to make flame retarded polymeric materials exhibiting high performance [1] but there is a lack of data (qualitative and quantitative) able to fully describe its mechanism. It is one of the goal of this paper to bring new insights on the mechanism of intumescent systems. This paper examines two types of intumescence in polypropylene (PP) based on expandable graphite (EG, physical expansion) and on modified ammonium polyphosphate (AP760, chemical expansion). Some examples of using ammonium polyphosphate and expandable can be found elsewhere [2-4]. Reaction to fire of PP containing EG and AP760 is first evaluated by cone calorimetry and the efficiency of the intumescent barrier is measured at the same time. Kinetic analysis is then performed to quantify the thermal stability of the intumescent systems.

## EXPERIMENTAL

### Materials and processing

Commercial grade of isotactic polypropylene (PP) was used in this study: PP (PPH9060) was supplied by Total petrochemicals (Feluy, Belgium). PPH9060 has a melt flow rate (MFR) for a load of 2.16 g at 230°C of 25 g/10 min. Expandable graphite (EG) is the commercial grade ES350F5 from Graphitwerk Kropfmühl (Germany) with an average grain size of 300 µm. 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, nitrate, various organic acids …) [5]. Sulfate was used in this grade to make graphite bisulfate. Modified ammonium polyphosphate (AP760) is the commercial grade of Clariant (Germany) with the brand name Exolit AP760. It is an intrinsic intumescent system containing 20 wt% phosphorus and 14 wt% nitrogen acting in synergy. It is mainly based on ammonium polyphosphate as acid source and tris(hydroxyethyl) isocyanurate (THEIC) as char former.

The strategy was to blend PP with flame-retardants (FRs) in a twin-screw extruder. The total loading of FRs in PP was 10 wt% varying the ratio AP760/EG (wt/wt) at 10:0; 5:5; 9:1 and 0:10. This loading was selected because it provides an acceptable performance according to cone calorimetry. Compounding was performed using 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 is fixed to extrude about 500 g/h 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.

### Cone calorimetry

FTT (Fire Testing Technology) Mass Loss Calorimeter (MLC) was used to carry out measurements on samples 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. Our procedure involved exposing specimens measuring 100 mm x 100 mm x 3 mm in horizontal orientation. External heat flux of 35 kW/m² was used for running the experiments. This flux corresponds to common heat flux in mild fire scenario. MLC was used to determine heat release rate (HRR). When measured at 35 kW/m², HRR is reproducible to within ±10%. The cone data reported in this paper are the average of three replicated experiments. In addition to those measurements, thermocouples were embedded on the backside of the materials in horizontal position. They measured temperature as a function of time during a regular cone experiment.

### Kinetic analysis

ThermoGravimetric Analysis (TGA) was carried out using a Netzsch TG 209 F1 Libra at five heating rates (1, 2, 5, 10, 20 and 50°C/min) from 30°C to 800 °C in nitrogen flow (50 $cm^3$/min). Samples of exactly 10 mg (±0.3 mg) were put in open alumina pans. Typically, two replicates were run for each sample, and the average was reported. Both the onset (5% mass fraction loss) and peak mass loss rate have an uncertainty of 0.9°C (2σ). We corrected for each heating rate the buoyancy force (calibration with empty pan). Kinetic analysis and modeling of the degradation of the samples was made using an advanced thermokinetic software package developed by Netzsch Company [6]. For kinetic analysis, it is assumed that the material decomposes according to the Eq. (1):

$$A_{solid} \rightarrow B_{solid\ or\ liquid} + C_{gas} \quad (1)$$

The rate expression dα/dt, where α is the degree of conversion is assumed to be defined by Eq. (2):

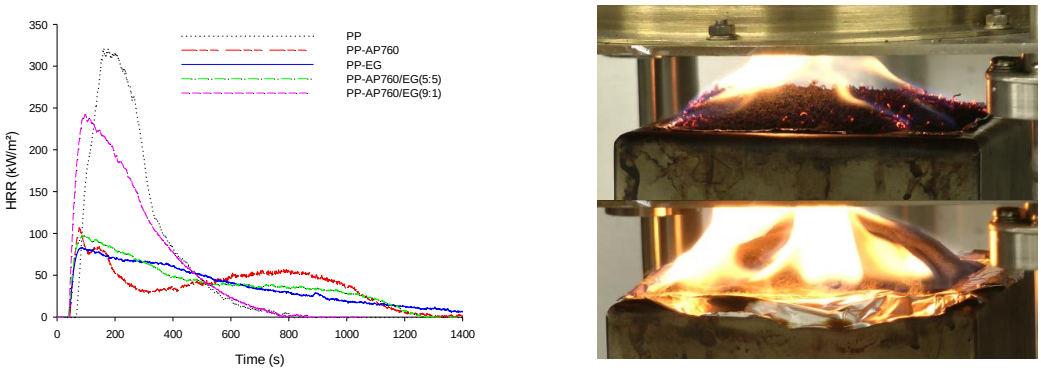
$$d\alpha/dt = k(T).f(\alpha) \quad (2)$$

where k is the kinetic constant, k = A.exp(-E/RT) according to the Arrhenius law, A is the frequency factor, E is the activation energy and f(α) is the so-called "reaction model". All reactions are assumed to be irreversible. In the case of decomposition and since the evolved gases were continuously removed by the fluid flow in the TGA chamber, this is a reasonable assumption. It is also assumed that the overall reaction (Eq. (1)) is the sum of individual reaction steps (formal or true step) with constant activation energy, as generally accepted in chemistry. The model can then include competitive, independent and successive reactions. The equations were solved with multivariate kinetic analysis (determination of the parameter via an hybrid regularized Gauss-Newton method or Marquardt method).

## RESULTS AND DISCUSSION

### Reaction to fire

EG and AP760 and some of their combinations (AP760/EG at 5:5 (wt/wt) and 9:1 (wt/wt)) were incorporated in PP at 10 wt% total loading. The four formulations were evaluated by cone calorimetry at an external heat flux of 35 kW/m² and compared to neat PP (Fig. 1-a).



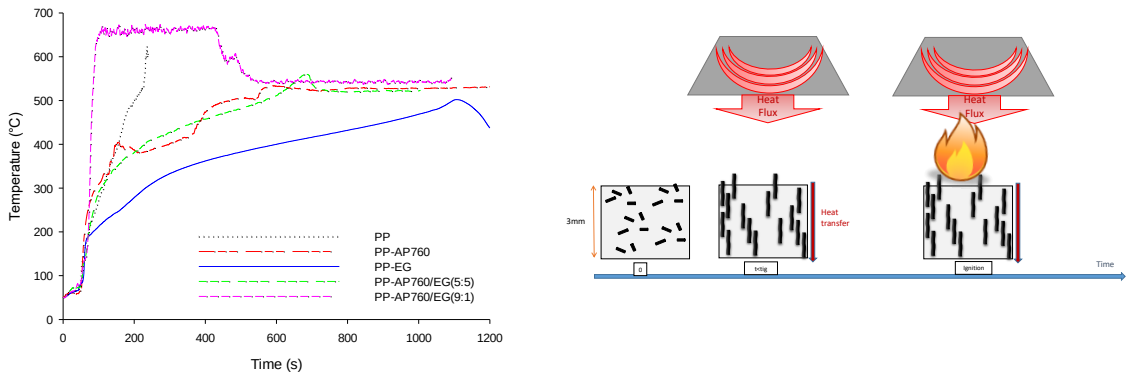

**(a)** **(b)**

Fig. 1. (a) HRR curves as a function of time of intumescent PP (external heat flux = 35 kW/m²); (b) Intumescent coatings formed from PP-EG (up) and PP-AP760 (bottom).

Except for the formulation containing 1 wt% EG, the intumescent PPs exhibit peaks of heat release rate (pHRR), which are decreased by about 70%. The formation of an expanded charred layer is observed at the surface of the materials evidencing an intumescent phenomenon. The formulation containing 1 wt% EG exhibits a pHRR only decreased by 30%. An intumescent phenomenon is also observed but its efficiency is not as high as the other intumescent PPs. It is noteworthy the formulations containing EG behave differently compared to PP-AP760 (Fig. 1-b). The intercalation compounds decompose rapidly into gaseous products, which blast off the graphite flakes. Those flakes make then worms forming an entangled network at the surface of the material. On the contrary, the intumescent char formed from PP-AP760 exhibits high expansion (higher than those with EG)

and a smooth surface. It evidences therefore two distinct mechanisms: (i) the physical expansion of graphite flakes forming a protective entangled network and (ii) the formation of an intumescent char by a series of chemical reactions. Those two types of protective coating provide the same level of protection according to the cone scenario.

During the cone calorimetry experiments, thermocouples were placed on the backside of the materials to measure the temperature as a function of time and to quantify the efficiency of the intumescent barrier (thermocouple embedded in the material in horizontal position). Fig. 2-a shows temperature changes as a function of time. Up to 50s, the slopes of the curves are similar. At higher times (t>50s for PP-EG and t>80s for PP-AP760 and PP-AP760/EG(5:5)), the slopes of the intumescent PPs (except PP-AP760/EG(9:1)) are smaller than that of neat PP (curve of PP was stopped when the thermocouple is no longer in the matter because of the complete decomposition of PP). It corresponds to the formation of an intumescent layer reducing heat transfer from the flame to the backside of the substrate and so, it limits the temperature rise on the backside. Note the network formed from PP-EG is the most efficient compared to the char layers formed by PP-AP760 and PP-AP760/EG(5:5). The final temperatures are close (525°C vs. 490°C at 1100s) but the temperature rise of PP-EG is much smaller than the others at the beginning of the experiment (50s<t<225s). PP-AP760/EG(9:1) exhibits an unexpected behavior because its backside temperature increases extremely rapidly to 650°C. Its backside temperature reaches a pseudo steady state at 670°C for 350s (50s<t<400s) and then decreases to 525°C. This temperature drop occurs when the combustion stops: it removes the additional heat feedback of the flame and hence it decreases the total heat flux affecting the material.




**(a)** **(b)**

Fig. 2. (a) Backside temperature as a function of time of intumescent PPs during cone calorimetry experiment (external heat flux = 35 kW/m²); (b) Schematic description of the effects of graphite worms in PP-AP760/EG(9:1) on heat transfer through the charred network.

The results suggest the involvement of different mechanisms. PP-A760 forms an expanded char at the surface, which reduces the heat transfer from the flame to the material. The incorporation of small amount of EG in a conventional intumescent system (PP-AP760) strongly affects its performance. Visual observation shows graphite worms grows up at the surface but there is no entanglement of the worms. The worms exhibit an alignment normal to the surface (Fig. 2-b) and hence, they might enhance heat conductivity (transverse heat conductivity) through the material as shown by temperature measurement. In the other cases, EG can form an entangled network, which flattens because of the expansion. Hence, in-plane heat conductivity is enhanced (parallel to the surface) and the worms play the role of heat dissipater (this effect is limited when EG is combined with AP760). Even if the cone heater irradiates the whole surface, it is reasonable to assume heat dissipation occurs on side surfaces of the samples. Those two types of behaviour leads to huge difference in terms of performance and it evidences the anisotropic character of EG when used as FR.

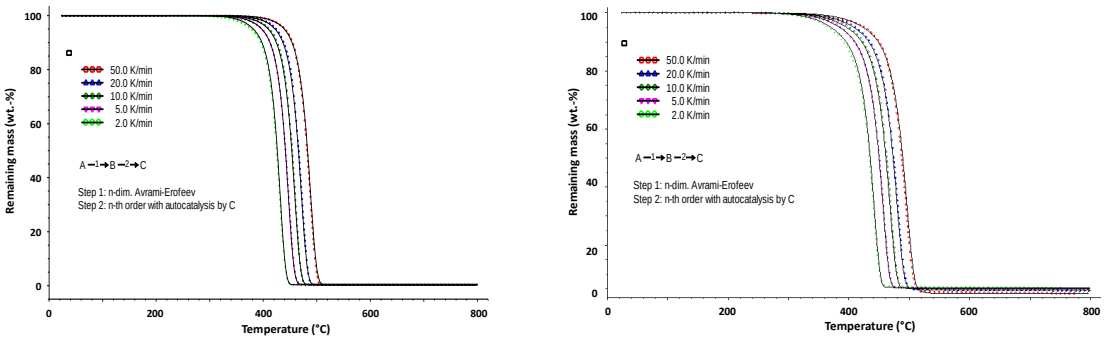
## Kinetic analysis

The previous section has shown the fire performance of PP was strongly enhanced incorporating AP760 and EG. The goal of this section is to examine whether the thermal stability of the intumescent PPs could be modified. The approach was to perform kinetic analysis on the thermal decomposition of the neat PP and of the 4 intumescent formulations. Before starting any fitting procedure, it is necessary to define a model (combination

of reactions) and to preset starting values for the kinetic parameters. A convenient approach is to use model-free analysis as a preliminary step of the kinetic analysis. A model-free analysis provides the plot of the activation energy versus the fractional weight loss. For the 5 materials, it reveals that the plot of activation energy exhibits a plateau at conversion degree higher than 0.2 of about 250 k/mol and a more complicated shape at low conversion degree (plots not shown). This indicates that the decomposition does not take place as a one-step reaction but as multi-step reactions.

TG curves of neat PP (Fig. 3-a) suggest a single step of decomposition but the simulation of the curves including only one single step does not give satisfactory results. The combination of two successive reactions considering an Avrami-Erofeev function followed by an auto-catalyzed order function gives an excellent fit (Fig. 3-a). The number of steps and the resulting calculated kinetic parameters (Table 1) are consistent with the conclusions of the Friedman analysis. The thermal decomposition of PP is a typical radical chain mechanism where initiation, H-abstraction, β-scission and radical recombination reactions are the relevant classes [7]. The first reaction described by an Avrami-Erofeev function (small contribution on the whole decomposition) is attributed to chain initiation reactions, which produce radicals and require lower activation energy. The second reaction is attributed to β-scission reactions, which are known to be the main decomposition reactions of PP. The autocatalysis is justified by the formation of allyl radicals and allyl H atoms during the decomposition of PP [8], which can enhance the decomposition of PP. Our reactional scheme makes then sense with the decomposition pathway of PP.

Intumescence occurs mainly in the condensed phase and it involves numerous chemical reactions. So, kinetic analysis of the reaction in the physical-chemical sense is not possible. That is why we have considered that the overall process of the intumescence could be described by multi-step processes. For the 4 intumescent PPs, TG curves were simulated using the same reactional scheme as the neat PP suggesting the decomposition of the intumescent PPs is mainly governed by the thermal decomposition of the neat PP. All the fits are excellent (Fig. 3-b shows the simulated curves of PP-AP760/EG(9:1) as typical example; the other simulations are not shown) and the calculated kinetic parameters are shown in Table 1. The activation energies of the intumescent PPs are slightly higher than that of the neat PP indicating some enhancement of the thermal stability of the intumescent PPs.




**(a)** **(b)**

Fig. 3. Experimental (dots) and simulated (line) TG curves at different heating rates in $N_2$ flow of neat PP (a) and PP-AP760/EG(9:1) (b).

Table 1. Computed kinetic parameters of the decomposition of neat PP and of the 4 intumescent PPs

| Reaction N° | log(A) (A: $s^{-1}$) | E (kJ/mol) | Reaction order or Dimension |
|---|---|---|---|
| | | ***PP*** | |
| 1 | 11.9 ± 0.3 | 182 ± 5 | 0.87 ± 0.07 |
| 2 | 15.3 ± 0.3 | 245 ± 3 | 0.91 ± 0.11 |
| | | ***PP-AP760*** | |
| 1 | 13.5 ± 0.3 | 204 ± 4 | 0.53 ± 0.02 |
| 2 | 16.9 ± 0.1 | 270 ± 2 | 0.90 ± 0.05 |
| | | ***PP-EG*** | |
| 1 | 20.4 ± 1.9 | 250 ± 15 | 0.20 ± 0.06 |

| Reaction N° | log(A) (A: $s^{-1}$) | E (kJ/mol) | Reaction order or Dimension |
|---|---|---|---|
| 2 | 17.2 ± 0.1 | 276 ± 2 | 1.10 ± 0.05 |
| ***PP-AP760/EG(5:5)*** | | | |
| 1 | 14.9 ± 0.6 | 219 ± 9 | 0.58 ± 0.02 |
| 2 | 16.1 ± 0.1 | 259 ± 2 | 0.90 ± 0.03 |
| ***PP-AP760/EG(9:1)*** | | | |
| 1 | 13.3 ± 0.4 | 205 ± 5 | 0.53 ± 0.02 |
| 2 | 16.5 ± 0.1 | 264 ± 2 | 0.77 ± 0.05 |

## CONCLUSION

The incorporation of intumescent additives at relatively low loading (10 wt%) in PP permits the reduction by 70% of pHRR. The mode of action occurs via the formation of an expanded carbonaceous layer in all cases. The protective coating acts mainly as heat barrier in the case of the formulations containing AP760 or as heat dissipater with EG. The incorporation of small amount of EG in PP-AP760 modifies heat transfer in the coating creating a strong anisotropy. Upon expansion graphite worms align normal to the surface increasing the transverse heat conductivity (lower efficiency of the heat barrier) and hence, decreasing the fire performance (decrease by only 30% of pHRR). Kinetic analysis on the intumescent PPs reveals that the intumescent additives do not modify the reactional scheme of the PP thermal decomposition but they increase slightly the thermal stability of the intumescent systems.

## ACKNOWLEDGEMENT

This work has received funding from the European Research Council (ERC) under the European Union's H2020 – the Framework programme for Research and Innovation (2014-2020) / ERC Grant Agreement n°670747 – ERC 2014 AdG/FireBar-Concept.

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