

## POLYPROPYLENE COMPOUNDS FOR HALOGEN-FREE LOW SMOKE (HFLS) CONDUITS

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**Main message:** The target herein is to develop flame retardant polypropylene (FR-PP) formulations for manufacture of conduits. The latter are completely halogen free or have a halogen content below 1500 ppm. The formulations were developed by melt compounding and their flammability behavior was studied by UL94V test. Additional thermal characterization *via* TGA, DSC and rheological behavior by melt flow rate measurements (MFR) were performed in order to assess the effect of the FR additives onto the PP matrix.

**Keywords:** polypropylene, flame retardants, intumescence, ammonium polyphosphate.

### Introduction

PP is widely used as commodity polymer, showing mechanical durability, chemical resistance, electrical insulation, and processability [1]. Nevertheless, due to its flammability, flame retardance is required in the field of conduits, so as to comply with the stringent EU safety regulations [2]. Herein, 2 FR systems were developed by the incorporation of commercial FRs into PP; one based on intumescence tested for PE [2,3] and a second based on radical chain mechanism in the gas phase [1,4].

### Experimental

An extrusion-grade PP (ISPLEN PB131N5E) was used. Ammonium polyphosphate was supplied by Clariant, a triazine-morpholine-piperazine derivative by MCA Technologies GmbH and a low halogen grade consisting of aluminum hypophosphite (AHP) and a phosphorous-bromine salt by Italmatch Chemicals. 3 formulations were prepared (FR1-FR3) with total loading at 25wt% for FR1 and FR2 and 2wt% for FR3. Each formulation was prepared by melt compounding in a twin-screw extruder (HAAKE Thermo-Fisher PTW16, L/D = 25) at a speed of 80 rpm, and the temperatures of the respective zones from feeder to die were 190–220 °C. The flammability was assessed according to UL 94V tests (ASTM D3801) on rectangular bars (125x13x1.6mm) derived by compression molding (210 °C, 15 min, 200 bar). 2 sets of 5 bars per formulation were tested. Thermal properties were determined by DSC analysis (Mettler Toledo DSC 700) with a heating-cooling-heating cycle at a rate of 10 °C/min between 30 and 210°C, and TGA analysis (Mettler Toledo TGA/DSC1 HT) from 30 to 800 °C at the same heating rate. MFR was measured at 230 °C and 2.16 kg in a KAYENESS Dynisco 4004 Melt Indexer.

### Results and Discussion

FR1 and FR2 (Table 1) consist of ammonium polyphosphate (APP) and a triazine compound, at a total load of 25 wt%. The ratio between triazine and APP is 1:3 in FR1, while FR2 is richer in APP and the ratio becomes 1:4. Both FR1 and FR2 reached V0 classification in the UL94V test, proving that they are very promising candidates for the manufacture of HFLS conduits (Table 1). The FR mechanism is based on intumescence, where a swollen char is formed on the surface of the polymer (condensed phase) that acts as a heat insulator and physical barrier to the transport of oxygen and pyrolysis products [1,2]. In particular, APP upon heating decomposes to polyphosphoric acid (HPO<sub>3</sub>)<sub>n</sub> meanwhile releasing ammonia (NH<sub>3</sub>). Subsequently, a thermally more stable ester is formed by the esterification between the (HPO<sub>3</sub>)<sub>n</sub> and the triazine derivative, which is further swollen by the formed NH<sub>3</sub> [1-3]. The release of NH<sub>3</sub> is responsible for reducing the onset of degradation ( $T_{d5\%}$ ) in TGA analysis by ca. 20-31 °C compared to the neat PP (Table 1). On the other hand, the increase in the maximum decomposition

temperature ( $T_d$ ) by 11-14 °C is due to the formation of the protective char layer (Table 1). Turning to the DSC analysis, it seems that the melting point values ( $T_m$ ) of the 2<sup>nd</sup> heating are slightly increased (ca. 3 °C), but the crystallinity is decreased only for FR1 (Table 1). Finally, MFR was decreased by ca. 29% in both FR1 and FR2, as a consequence of relatively high loading i.e., 25wt%, of infusible FR additives.

FR3 aimed both at a lower formulation cost and lower FR performance. The used additive comprises AHP and a phosphorous-bromine salt. The loading level was limited to 2wt%, so as to follow the EN 50642(2018) standard, which dictates maximum bromine content below 1500 ppm. In this case the FR mechanism is the generation of bromine radicals (Br $\cdot$ ) in the gas phase, which dilute the concentration of O $\cdot$ , H $\cdot$  and OH $\cdot$ , which in turn promote the fire [4]. In addition, AHP upon heating decomposes, releasing phosphine gas (PH $_3$ ) and water (H $_2$ O) [5]. FR3 reached V2 class in the UL94 test,  $T_{d5\%}$  was reduced by ca. 44 °C, and MFR was increased to 3.63 g/10 min (Table 1).

**TABLE 1.** Selected properties of flame retarded polymeric samples

Sample	FR content [wt%]	UL94 Class [V0, V1, V2, NC]	$T_m$ [°C]	$X_c^*$ [%]	$T_{d5\%}$ [°C]	$T_d$ [°C]	MFR [g/10min]
Neat PP	0	NC	167.0	27.8	391.7	433.5	1.31
FR1	25	V0	170.5	21.5	371.8	447.3	0.95
FR2	25	V0	170.0	28.3	360.4	444.6	0.93
FR3	2	V2	172.0	25.7	348.2	413.7	3.63

\* $\Delta H_0 = 209 \text{ J}\cdot\text{g}^{-1}$

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## References:

- Weil E.D., Levchik S.V.: Flame Retardants in Commercial Use or Development for Polyolefins. *Journal of Fire Sciences*, **26**, 5-43 (2008). <https://doi.org/10.1177%2F0734904107083309>
- Luyt A.S., Malik S.S., Gasmi S.A., Porfyrus A., Andronopoulou A., Korres D., Vouyiouka S., Grosshauser M., Pfaendner R., Brüll R., Papaspyrides C.: Halogen-Free Flame-Retardant Compounds. Thermal Decomposition and Flammability Behavior for Alternative Polyethylene Grades. *Polymers*, **11**, 1479 (2019). <https://doi.org/10.3390/polym11091479>
- Porfyrus A.D., Vouyiouka S.N., Luyt A.S., Korres D.M, Malik S.S., Gasmi S., Grosshauser M., Pfaendner R., Papaspyrides C.: Development of value-added polyethylene grades with extended service lifetime: Weathering resistant flame retarded materials for outdoor applications. *Journal of Applied Polymer Science*, **138(19)**, 50370 (2021). <https://doi.org/10.1002/app.50370>
- Marney D.C.O., Russell L.J, Soegeng T.M., Dowling V.P.: Mechanistic Analysis of the Fire Performance of a Fire-Retardant System, *Journal of Fire Sciences*, **25**, 491-497 (2007). <https://doi.org/10.1177%2F0734904107081106>
- Zhao P., Guo C., Li L.: Flame retardancy and thermal degradation properties of polypropylene/wood flour composite modified with aluminum hypophosphite/melamine cyanurate, *Journal of Thermal Analysis and Calorimetry*, **135**, 3085-3093 (2019). <https://doi.org/10.1007/s10973-018-7544-9>