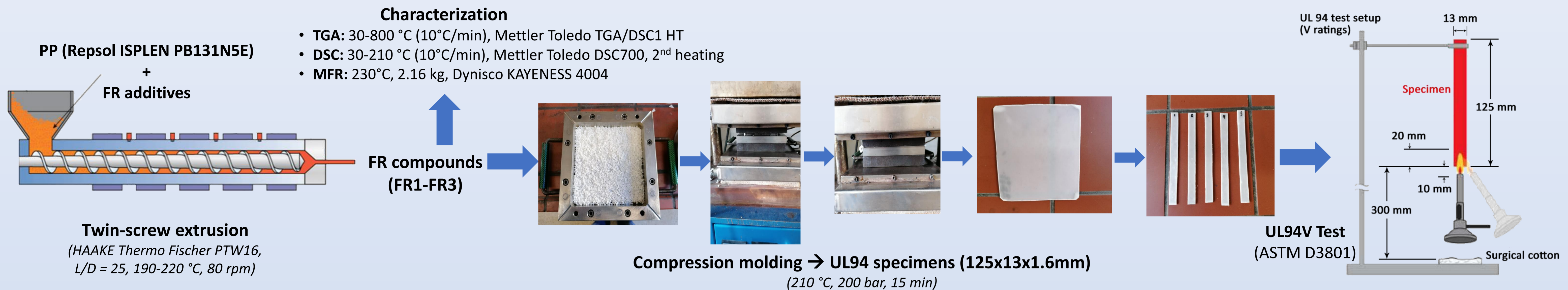


PP is widely used as commodity polymer, showing mechanical durability, chemical resistance, electrical insulation, and processability [1]. Recently, PP is rising as an alternative polymer for the manufacture of conduits and cable protection systems, replacing traditional PVC pipes. However, PP needs to be flame retarded in order to comply with the current stringent EU safety regulations regarding halogen content, smoke density and corrosiveness of

released gases (EN50642, EN61034-2, EN60754-2) [2]. The need for HFLS plastics becomes mandatory in the construction sector, so that in the event of fire, the release of toxic gases and smoke is inhibited and along with self-extinguishing behavior, human life is protected. Two FR systems were herein developed for PP. The first one involves two halogen-free formulations (FR1, FR2) based on intumescence (condensed phase FR mechanism). A swollen char is formed on the

surface of the polymer that acts as a heat insulator and physical barrier to the transport of oxygen and pyrolysis products [2,3]. The second system involves one low-halogen formulation (FR3) based on gas phase FR mechanism; bromine radicals (Br[•]) trap free radical species (O[•], H[•] and OH[•]) that preserve or promote the fire [1,4]. The halogen content was kept below 1500 ppm, thus complying with the current European Standard EN50642.



RESULTS AND DISCUSSION

Regarding the **halogen-free intumescent FR system**, two ratios between the char forming agent (triazine) and the acid source (APP) were examined: 1:3 (FR1) and 1:4 (FR2). Both FR1 and FR2 reached **V0 classification** by forming the protective char layer, as evidenced by SEM images (Fig. 1). FR1 exhibited lower total burning time vs. FR2, showing that the **1:3 ratio** performed better (Fig.2): the higher content of the char forming agent (CFA, triazine) leads to a char of higher quality. The latter can be observed also in the TGA curves (Fig. 3), where the **T_d value of FR1 was increased** by ca. 14 °C compared to neat PP. On the other hand, the **T_{d5%} values were found reduced** by ca. 20-31 °C, as a consequence of APP decomposition. Turning to the DSC analysis, the melting point values (T_m, 2nd heating) were slightly increased (ca. 3 °C), but the crystallinity was decreased only for FR1 (Table 1). **MFR was decreased** to ca. 0.9 g/10 min (by ca. 30%) in both FR1 and FR2 implying the need of processing aid additives.

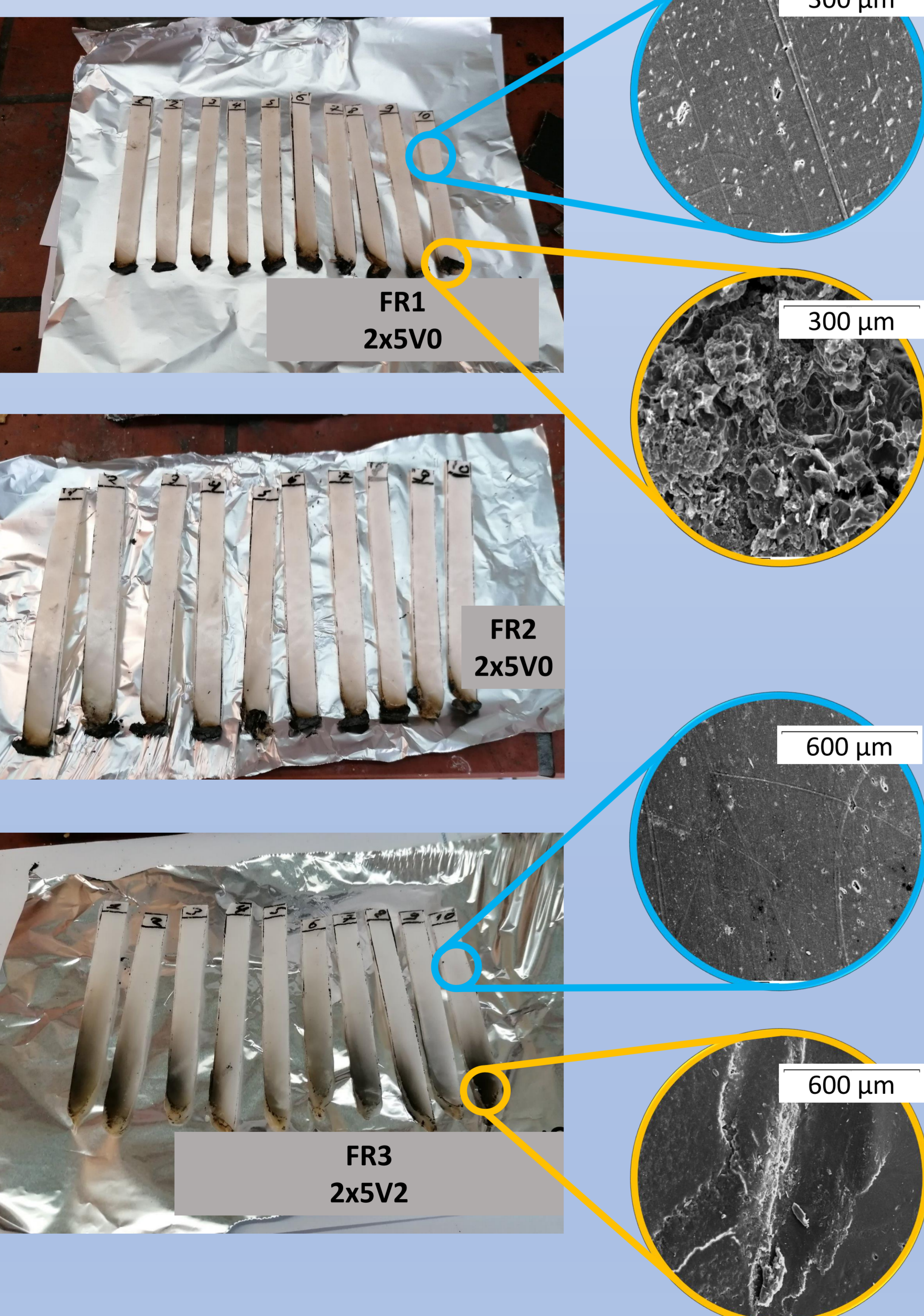


Figure 1. UL94 specimens after the test. SEM on the surface prior to and after the UL94 test.

Formulations	Triazine [wt%]	APP [wt%]	Low halogen additive [wt%]	FR load [wt%]	UL94V Class	T _m [°C]	X _c [%]	T _{d5%} [°C]	T _d [°C]	MFR [g/10 min]
PP	-	-	-	-	NC	167.0 ± 0.2	27.8 ± 2.5	391.7 ± 0.0	433.5 ± 1.2	1.31 ± 0.01
FR1	6.25	18.75	-	25	V0	170.5 ± 0.5	21.5 ± 3.9	371.8 ± 3.9	447.3 ± 1.3	0.95 ± 0.01
FR2	5	20	-	25	V0	170.0 ± 0.6	28.3 ± 3.2	360.4 ± 3.2	444.6 ± 2.0	0.93 ± 0.01
FR3	-	-	2	2	V2	172.0 ± 0.8	25.7 ± 0.3	348.2 ± 7.0	413.7 ± 6.1	3.63 ± 0.40

PP: Polypropylene (REPSOL ISPLEN PB131N5E). Heterophasic co-polymer (iPP), superior impact strength
 Triazine: Triazine-morpholine-piperazine derivative (MCA Technologies GmbH)
 APP: Ammonium polyphosphate (Clariant)
 Low halogen additive: Aluminum hypophosphite (AHP), along with a phosphorous-bromine salt and a dripping meltable synergic (Italmatch Chemicals)

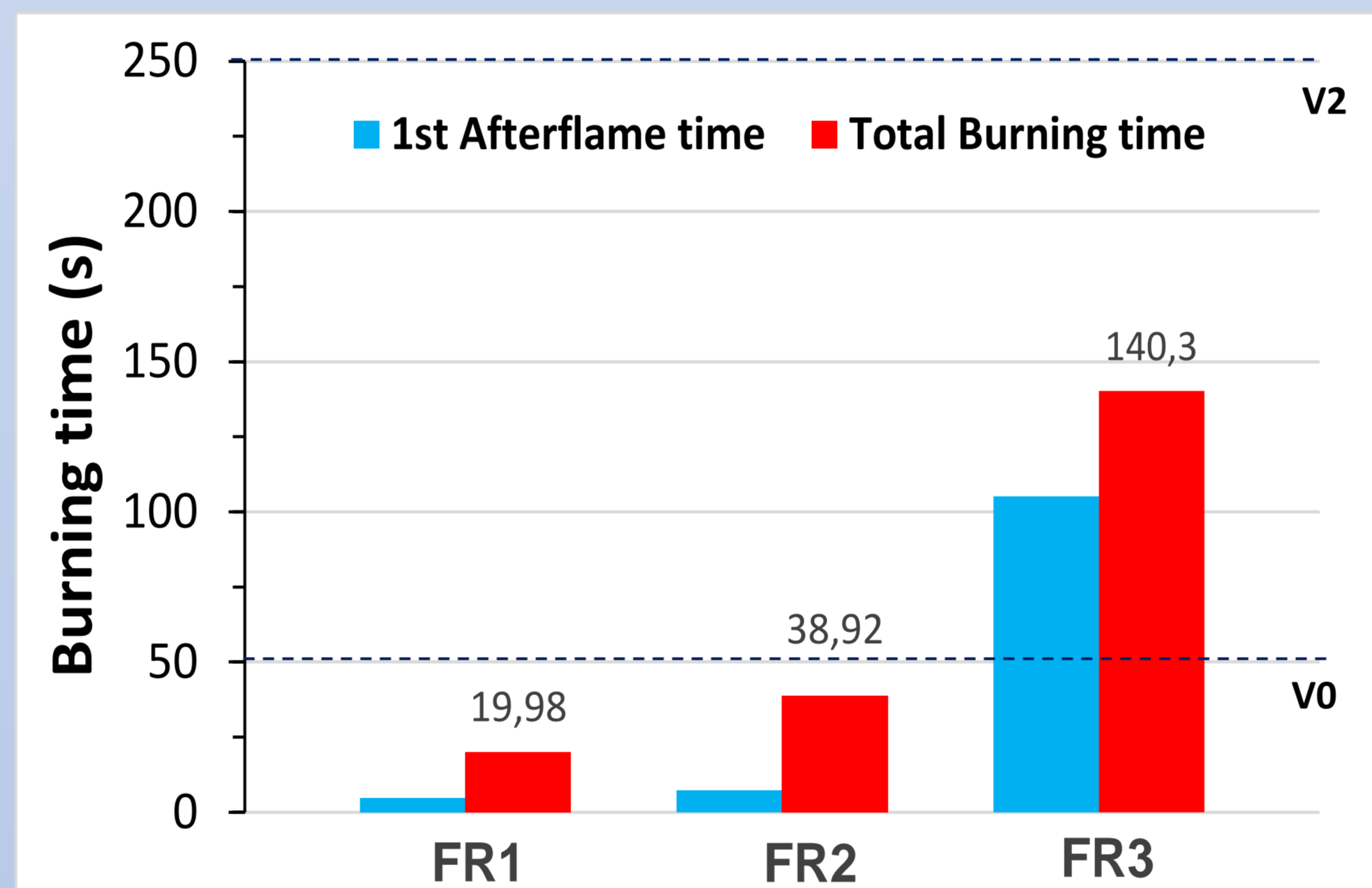


Figure 2. Determined burning times per formulation from the UL94V tests.

Regarding the **low-halogen FR formulation**, FR3 reached successfully **V2 class** (Fig.2) and can be considered as a promising low-cost alternative, offering flame retardance at very low concentrations, while complying with EN50642 standard. The UL94 specimens after the burn test exhibited smooth surface, while melt flow was evidenced by SEM (Fig. 1).

Formation of swollen char was not observed, thus proving the different FR mechanism of this system. Accordingly, the dripping meltable synergist promoted intensive dripping, thus removing portions of heat and fuel from the flame zone. The phosphorous-bromine salt generated Br[•], while AHP decomposed upon heating, releasing PH₃ and H₂O, thus further diluting and cooling the gas phase and assisting flame termination [5]. The latter led to a **decrease in both T_{d5%}** (by 44 °C) and T_d (by 20 °C) in the FR3 compound compared to neat PP, while the final residue was similar, verifying that no significant char was formed (Fig. 4).

Turning to the DSC analysis, T_m was increased (by ca. 5 °C), but the crystallinity was slightly decreased compared to PP. (Table 1). The FR3 compound also **presented intense MFR increase** to 3.63 g/10min, probably due to the melt dripping synergist.

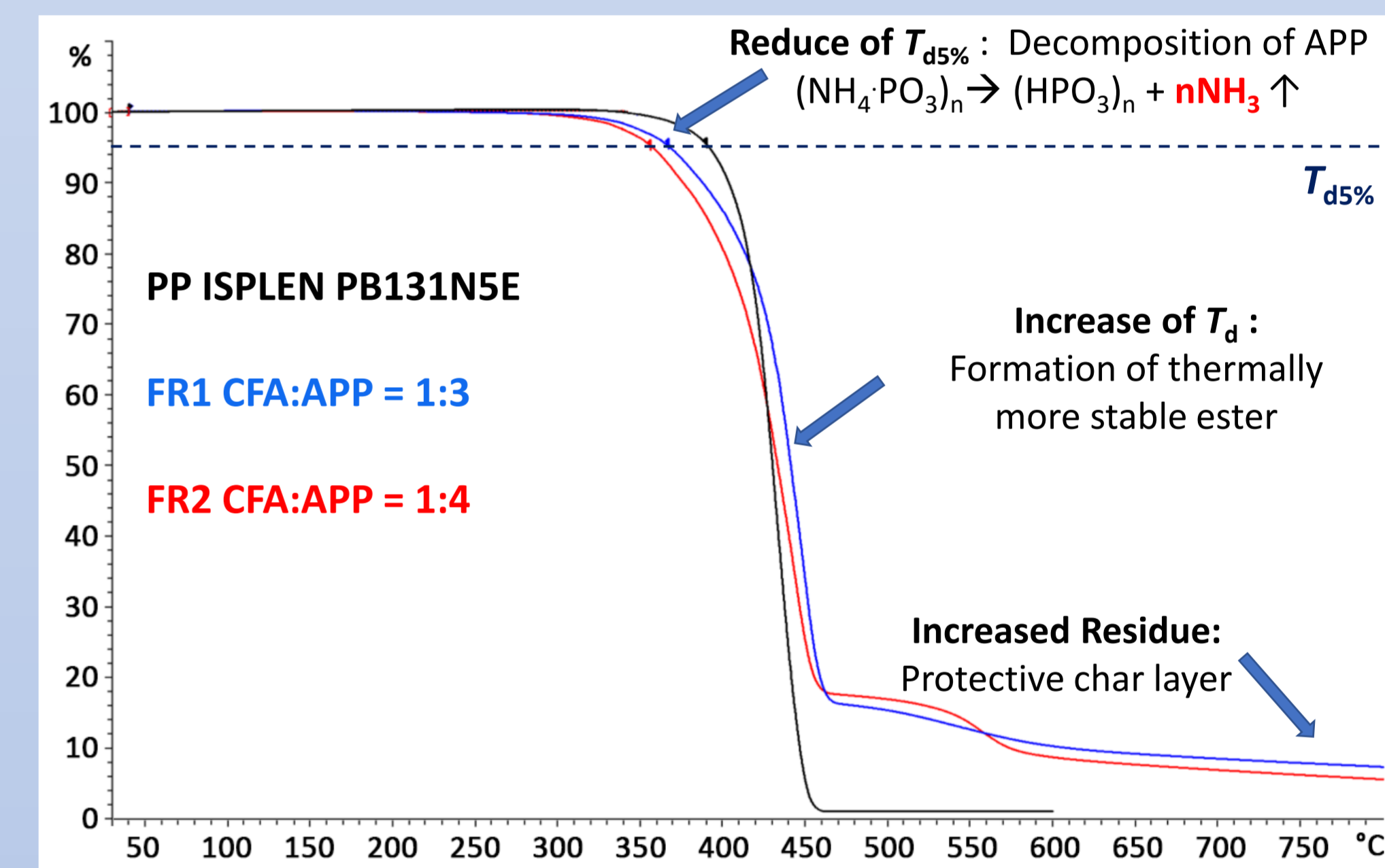


Figure 3. TGA curves of HFLS compounds of the intumescent system (PP vs. FR1 vs. FR2)

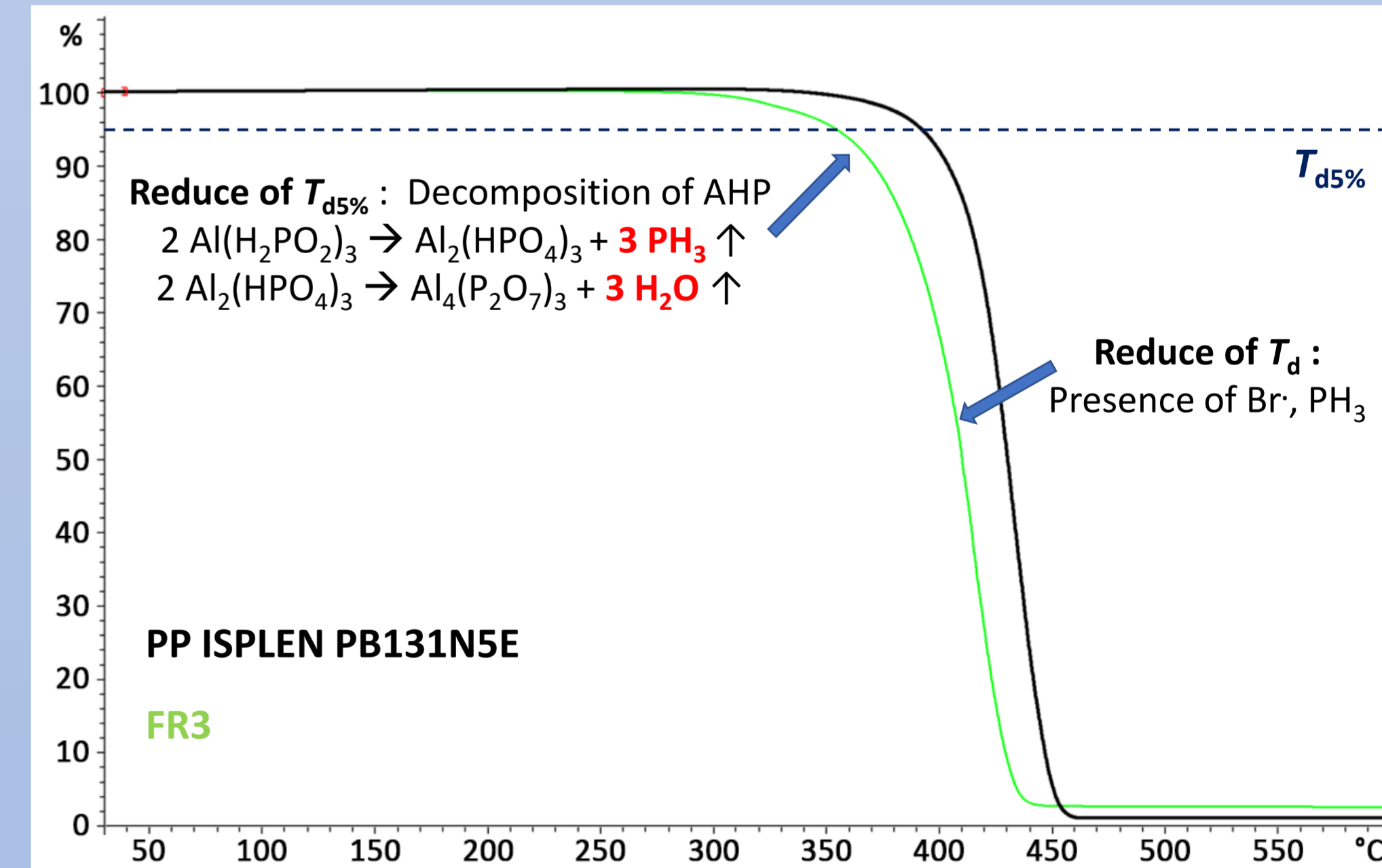


Figure 4. TGA curves of HFLS compounds of the gas-phase system (PP vs. FR3)

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CONCLUSIONS

The performance of two FR systems was tested on PP. The first system (halogen-free) consisted of ammonium polyphosphate and a polymeric triazine derivative (CFA) acting as an intumescent system in the condensed phase. Two formulations were developed (FR1 and FR2) at total loading of 25 wt%, but two different ratios of the FR components were used, i.e. CFA:APP 1:3 (FR1) and 1:4 (FR2). Both reached V0 classification with FR1 showing overall better performance. On the other hand, the second system (low-halogen) comprised aluminum hypophosphite, a bromine-phosphorous salt and a dripping meltable synergic compound. This particular system operated in the gas phase, by releasing Br radicals and gases (PH₃, H₂O), while intense dripping removed polymer from the flame zone, thus suspending the fire. It resulted in V2 classification with significant increase in the melt flow rate (MFR) value, while halogen content was complying with the EN50642 standard.