VALORIZATION OF POLYETHYLENE COMPOUNDS: INCORPORATION OF HALOGEN-FREE FLAME RETARDANTS AND HEAT STABILIZERS

A. Porfyris[1],*, A. Andronopoulou[1], K. Lountzis[1], D. Korres[1], S. Shahid[2], S. Gasmi[2], S. Vouyiouka[1], A.S. Luyt[2], R. Pfaendner[3], C. Papaspyrides[1]

[1]Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens 157 80, Greece,
[2]Center for Advanced Materials (CAM), Qatar University, PO Box 2713, Doha, Qatar,
[3]Fraunhofer Institute for Structural Durability and System Reliability LBF, Schlossgartenstr. 6, 64289 Darmstadt, Germany *(*than.porf@gmail.com)*

ABSTRACT

The effect of six halogen-free flame retardant (FR) formulations was investigated on the thermal stability of two low-density polyethylenes (LDPE) and one linear low-density polyethylene (LLDPE), by means of thermogravimetric analysis (TGA) under nitrogen and air atmosphere. The relative data were combined with UL94V flammability properties. In terms of flammability, the addition of a triazine derivative and ammonium polyphosphate at a loading of 35 % wt. was found to be the most efficient, leading to UL-94 V0 ranking in the case of the LDPE grade produced in an autoclave reactor. Turning to the heat stabilization of the polyethylene compounds, four different UV/heat additives were incorporated into the raw PE materials and the resulting formulations were subjected in accelerated thermal ageing experiments at 100°C. The results showed good stabilization against heat for almost four months of exposure.

INTRODUCTION

Polyethylenes (PEs) are the most widely used commodity polymers with a high potential of value-adding via proper compounding. An increasing fraction of PEs is nowadays used in inhouse and outdoor piping and the relevant applications need to be flame retarded in order to comply with stringent fire safety standards [1]. In addition, resistance to heat is very important especially when it comes to outdoor applications, such as pipes, gardening hoses etc. and in countries where average temperature is very high (e.g. Middle East).

In order to improve the flame resistance, halogen-containing flame retardants (HFRs), such as brominated FRs, e.g. decabromodiphenyl ether, are mainly used in combination with antimony oxide [2]. Nevertheless, HFRs present significant disadvantages, namely corrosion of the equipment during processing, and production of highly toxic gases (e.g. brominated and chlorinated furans and dioxins) during combustion. The need to substitute HFRs by halogen-free alternatives is therefore rising due to environmental legislations and EU directives, but also due to industrial initiatives and public consciousness [3],[4]. Therefore, inorganic flame retardants, e.g. $Al(OH)_3$ or $Mg(OH)_2$, need to be added in high loadings (>50 %wt.) in order to be effective. Consequently, the end products show poor mechanical, physical and rheological properties meanwhile showing difficulties in compounding [2]. Alternatively, phosphorus- and nitrogen-based compounds, including intumescent flame-retardant systems (IFRs), present a viable alternative. IFRs play an effective role mainly by the condensed-phase mechanism forming a carbonaceous foam residue (swollen char) on the surface of the polymer that acts as a heat insulator and a physical barrier to the transport of oxygen and pyrolysis products [5].

On the other hand, regarding heat stabilization, additives such as hindered amines and/or triazine derivatives which are known for UV stabilization, can offer also protection against heat. These additives can be effective in very low loadings (e.g. 0.1-0.5 %wt.) without affecting the end properties of the polymer, nevertheless their high cost should be taken into account.

In this work the effect of six halogen-free flame retardant (FR) formulations was investigated on the

thermal stability of two low-density polyethylenes (LDPE) and one linear low-density polyethylene (LLDPE), by means of thermogravimetric analysis (TGA) under nitrogen and air atmosphere and flammability properties (UL94V). Furthermore, four different UV/heat additives were incorporated to the raw PE materials and the resulting twelve formulations were subjected in accelerated thermal ageing experiments in an air circulating oven at 100°C. The samples were removed once a month and the mechanical properties were measured (tensile strength) and were compared to the respective values of the neat polymers. The results showed high FR efficiency when a combination of a triazine compound and ammonium polyphosphate was used and also good stabilization against heat for almost four months of exposure.

EXPERIMENTAL
Starting materials
Two commercial low-density polyethylene grades (LDPE-A, LDPE-T) and one linear low-density polyethylene (LLDPE, co-monomer 1-butene) were provided by Qatar Petrochemical Company (QAPCO). LDPE-A refers to the LDPE manufactured in the autoclave (batch process) and LDPE-T to the one manufactured in the tubular reactor (continuous process). The herein examined halogen-free flame retardants (FRs) were provided by BASF (FlamestabNOR116), MCA Technologies GmbH (PPM Triazine 765 and PPM Triazine HF), Clariant (Exolit AP422), Perstorp (Charmor DP40 and PP100) and ADEKA (ADK Stab FP2200) Similarly, the herein examined UV/heat stabilizers (HS) were provided by BASF (FlamestabNOR116, Chimassorb81, Chimassorb944 and Tinuvin1577) and Sabo Chemicals (Sabostab119) (Table 1).

Preparation of polyethylene compounds
The halogen-free FR systems were examined in a total content of 5-35 % wt (Table 1) with ratios of the char-forming agent to the acid source (CFA:APP) equal to 1:3 and 1:1.5. The incorporation was performed in a twin-screw extruder (extruder-Lab compounder, KETSE 20/40 EC, model 838106, 170-200°C, 70 rpm) following a dry mixing stage. The compounded material was then injection molded (Arburg All-rounder 570 C golden edition, 180-215°C) to prepare specimens for UL 94 with dimensions 127 mm x 12.7 mm x 1.6 mm. On the other hand, the heat stabilized (HS) polyethylene compounds were similarly compounded via twin screw extrusion according to the formulations shown in Table 1. Subsequently, the HS compounds were injection molded similarly and dumbbell shaped specimens with dimensions 160 mm x 13 mm x 3 mm were received.

Table 1. *Composition of FR and HS formulations in wt% for polyethylene grades. All formulations contained 0.05wt% calcium stearate, apart from FR4 which contains 0.1wt%.*

	Flamestab NOR116	PPM Triazine 765	PPM Triazine HF	Charmor DP40	Charmor PP100	Exolit AP422	ADK Stab FP2200	Total FR (%wt)	CFA: APP
Flame retarded (FR) compounds									
FR1	5							5	
FR2		30						30	
FR3			8.75			26.25		35	1:3
FR4*							30	30	
FR5				7		21	7	35	1:1.5
FR6					7	21	7	35	1:1.5

	Flamestab NOR116	Chimassorb 81	Chimassorb 944	Sabostab 119	Tinuvin 1577	Total HS (%wt)
Heat stabilized (HS) compounds						
HS1	5					5
HS2	5	0.1				5.1
HS3		0.1	0.1			0.2
HS4				0.1	0.1	0.2

Thermogravimetric analysis (TGA)

The thermal decomposition was studied via thermogravimetric analysis in a Mettler Toledo TGA/DSC 1 HT instrument. 15 mg of sample was heated from 30 to 800°C at 10°C·min^{-1} under air (thermo-oxidative decomposition) and nitrogen (thermal decomposition) atmospheres. The onset of decomposition temperature was defined as the temperature at 5% weight loss ($T_{d,5\%}$), the degradation temperature (T_d) was determined at the maximum rate of weight loss, and the char yield as the % residue at 600 and 800°C.

UL 94 V testing

The flammability was assessed according to UL 94 vertical burning tests (ASTM D3801) on injection molded bars, following a pre-treatment of the specimens for 45 h at 23°C and 50% RH. UL 94 tests are widely used to evaluate the flame resistance of polymers. The results fall into three categories with burning ratings V0, V1, and V2, with V0 corresponding to the highest level of flame resistance. All other results are anticipated as non-classified (NC).

Accelerated Thermal Ageing

Dumbbell specimens (in sets of 4) of each HS formulation and the respective neat grades were placed in an air circulating oven controlled at 100°C. Sampling was performed once a month and the tensile tests were performed. LDPE-A and LLDPE were compared.

Mechanical properties

The tensile testing was performed at an elongation rate of 10 mm·min^{-1} using an Instron4466 apparatus. Dumbbell shaped specimens with dimensions of 160 mm x 13 mm x 3 mm were used. The gauge length was 50 mm. Tensile strength (σ_{max}) was determined.

RESULTS AND DISCUSSION

Thermal decomposition of FR-containing compounds

Starting with the pure polymers, all three grades exhibited a one-step decomposition with the onset of the polyethylene backbone degradation in the range of 419-448°C ($T_{d,5\%}$) under nitrogen. The maximum rate of weight loss was observed at 460°C and 466°C for LDPE-A and LDPE-T respectively, while for LLDPE at a higher value of 476°C. All the grades had negligible residue values, verifying the little char formation which characterizes polyolefins. Turning to the FR-containing compounds, it was found that their thermal decomposition involved two or even more degradation steps, with lower onset temperature compared to the onset of the neat grades, obviously due to the earlier degradation of the additives (Fig. 1): the $T_{d,5\%}$ value was decreased in the range of 330-422°C under nitrogen, which was found in other polyethylene FR systems and was attributed to the lower stability of the bonds in the FR molecules (such as P-O and C-N) compared to the uniform C-C bonds in polyethylene[5,6]. The lowest $T_{d,5\%}$ values were observed in the cases of FR5 and FR6, i.e. when the pentaerythritol derivatives and APP were used, and can be attributed to the formation of thermally unstable ester mixtures between the -P-OH group in the APP molecules and the -OH group in the CFA[7]. When comparing the T_d values (Fig 1), the addition of FRs resulted in an increase in T_d, proving the formation of a protective char layer thus improving the thermal stability of the grades[6,8]: for the two LDPE grades, T_d reached 478°C *vs.* 460 and 465°C (ca. 15°C increase), while for the LLDPE compounds the increase was almost insignificant (up to 2°C). The trend was found similar under thermo-oxidative degradation (Fig. 1b), with the difference that the temperatures ($T_{d,5\%}$, T_d) were shifted to lower values under air, as was the case with the pure polymers.
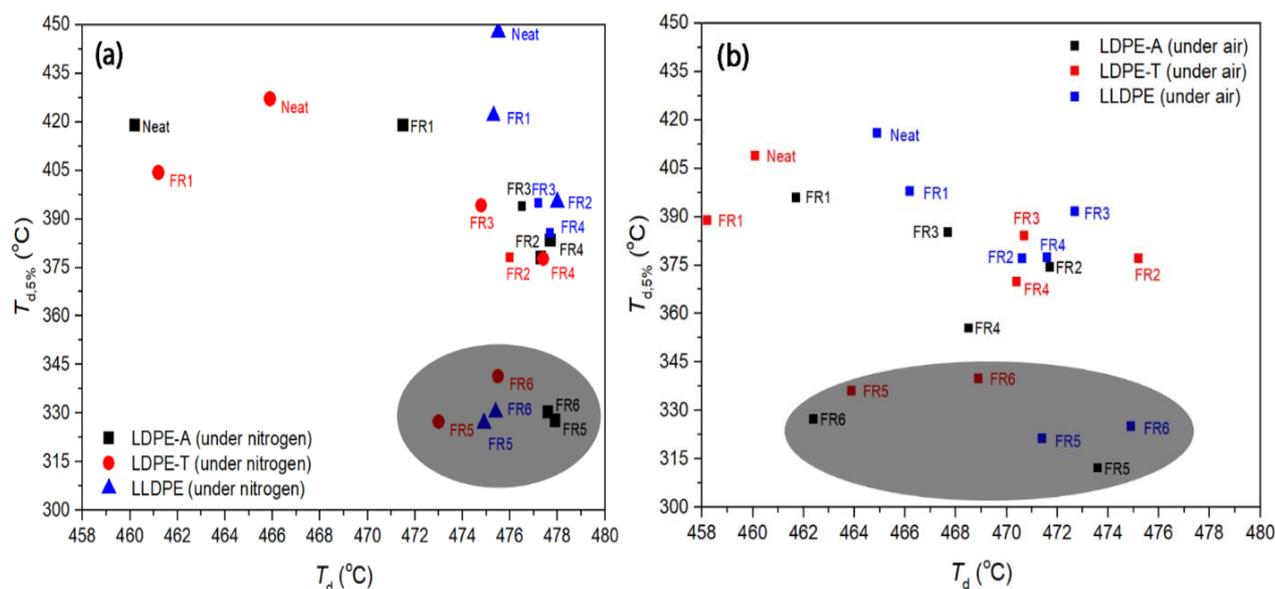
Figure 1. *Correlation between the onset of thermal degradation ($T_{d,5\%}$) vs. the temperature at the maximum rate of weight loss (T_d) for the FR-containing compounds under (a) nitrogen and (b) air atmosphere.*

The residue in the TGA can also be correlated with the formation of a protective char layer during the polymer combustion[6,7,9,10] (Fig. 2). FR1, which contained a nitrogen-based additive, failed to increase the char yield, so it is anticipated that the relevant formulation will not be efficient due to a lack of the acid source. On the other hand, the addition of the other FRs dramatically increased the residue under air and nitrogen atmospheres, reaching almost 19% under nitrogen at 800°C, with the highest value observed for FR4 (16.2%) in the case of LDPE-A, FR5 (19%) in the case of LDPE-T, and FR6 (18%) for LLDPE. These findings from the TGA study can predict a good flammability behavior in the UL94 test, nevertheless is not necessary that the highest amount of char or the lowest $T_{d,5\%}$ value will result in V0 in UL94 ranking. This also has to do with the proper ratio of charring agent to acid source, so as to produce the optimum char layer morphology and a compact and continuous intumescent char[9].
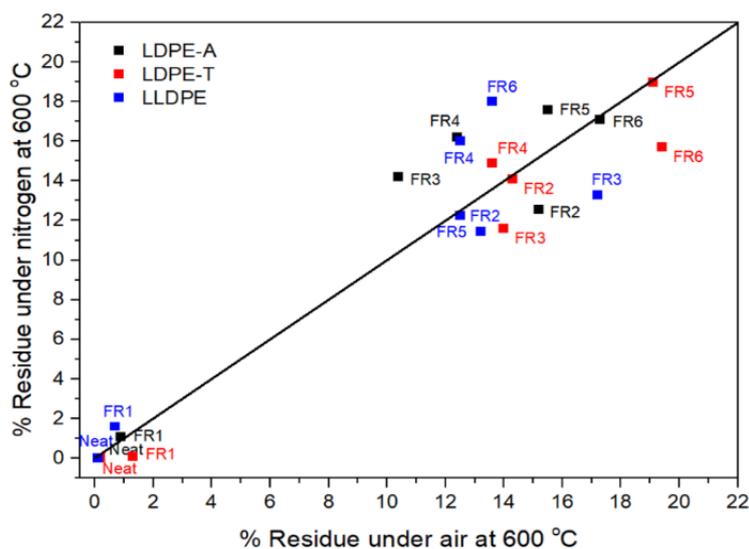

Figure 2. *TGA residue (%) under nitrogen and air atmosphere for the FR-containing compounds.*

Flammability

The results of the FR-containing polyethylene grades are given in Fig. 3. In all the grades, FR1 presented a low flame resistance since the total burning time was the longest and the samples failed in the UL 94 testing (NC). It is in agreement with the TGA results where the char yield was low (up to 2%), and this proves that nitrogen-based compounds alone cannot achieve a V0 rating for polyethylene[10].
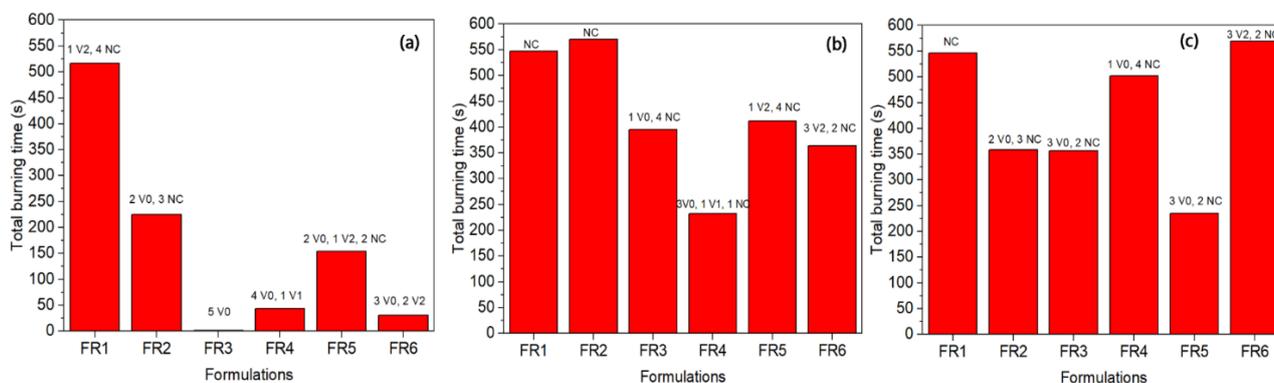

Figure 3. *UL94V results (total burning time, ranking) for FR-containing polyethylene grades. (a) LDPE-A, (b) LDPE-T, (c) LLDPE*

In the case of LDPE-A (Fig. 3a), FR3 was proved significantly efficient reaching a UL 94 V0 rating and a low total burning time (1.4 s). FR3 is the mixture of a triazine derivative and APP in 1:3 CFA:APP with a total loading of 35wt%; the mechanism of phosphorus-nitrogen synergism is considered to be provided by the ultimate formation of phosphorous oxynitride, which is a high-temperature resistant material[11]. FR3 performance is in line with the TGA results, where it presented the highest onset of thermal degradation for the LDPE-A FR-compounds, with an increase in T_d by 16°C and a char yield of almost 10% at 800°C under nitrogen. FR4 presented the next lower burning time (43.3s), a performance which can again be correlated with the high char yield in the TGA (14% at 800°C) and an increase in T_d by almost 18°C. The other formulations (FR2, FR5, FR6) presented poorer results in terms of UL 94 ranking. The performance of all the examined LDPE-T FRs was poorer than that of LDPE-A. Again, FR3 and FR4 can be considered to be the most promising, but they failed to obtain a safe UL 94 ranking. In the case of LLDPE, FR3 and FR5 presented lower burning times of 356 and 235 s respectively, but again they failed in presenting a safe UL 94 ranking.

Accelerated thermal ageing

Turning to the heat stabilization of the herein polyethylene compounds, the relevant formulations are presented in Table 1. The results (Fig. 4) show that the tensile strength shows an insignificant variation for 120-150 days of heat exposure, including the case of the reference materials. Sampling periods need to be increased to one year of exposure so as to produce safe results on the performance of the selected UV/heat stabilizers.
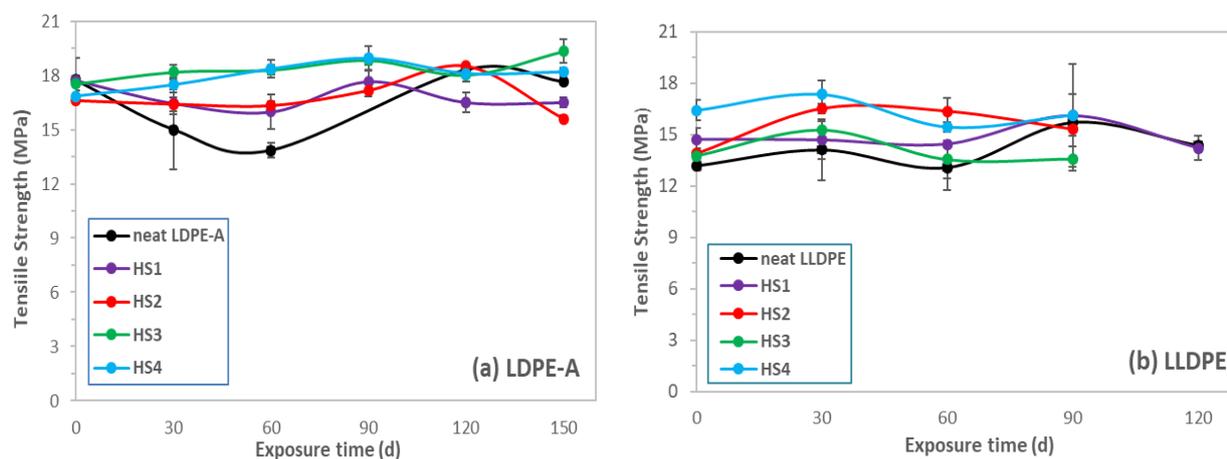
Figure 4. *Tensile strength vs. exposure time at 100°C of the HS compounds. a) LDPE-A, b) LLDPE.*

CONCLUSIONS

The performance of six FR formulations was investigated for LDPE-A, LDPE-T and LLDPE. The thermal decomposition of the FR grades was studied in TGA and was further correlated to the UL94 flammability results. FR3 formulation of LDPE-A, i.e. a triazine derivative and APP at a ratio of 1:3 and a total loading of 35 wt.%, was found to be the most efficient, achieving a UL 94 V0 ranking and upgrading the thermal stability of the polymer: the thermal degradation temperature was increased by more than 15 °C, along with a char residue which reached 10% at 800 °C. Turning to the heat ageing of the polyethylene grades all 4 HS formulations showed good stabilization against heat for up to 150 days of exposure, however ageing experiments are still ongoing and the mechanical behavior will be evaluated up to 1 year (365 days) of exposure.

ACKNOWLEDGMENT

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