JEREMIE LOUISY[1)], SERGE BOURBIGOT[1),*)], SOPHIE DUQUESNE[1)], PHILIPPE DESBOIS[2)],
ALEXANDER KÖNIG[2)], MARTIN KLATT[2)]

Novel synergists for flame retarded glass-fiber reinforced poly(1,4-butylene terephthalate)

Summary — Poly(1,4-butylene terephthalate) (PBT) is an important engineering thermoplastic polymer which is very often reinforced by glass fibers (GF) to improve its mechanical properties. Applications of GF-PBT could be limited due to its high flammability and flame retardants (FRs) must be incorporated into the polymer. In this work, the selected FRs are aluminum diethylphosphinate (OP 1240) and a combination of melamine cyanurate and of aluminum diethylphosphinate (OP 1200). Synergists are investigated in formulations of GF-PBT containing OP 1200 or OP 1240 according to different fire scenarios [limiting oxygen index (*LOI*), UL-94 and mass loss calorimetry]. It is found that polyhedral silsesquioxanes (POSS)-based molecules are synergists of interest combined with OP 1200 and OP 1240. The combination of the layered potassium acetate modified kaolin with OP 1200 also appears to be beneficial.

Keywords: flame retardants, synergists, poly(1,4-butylene terephthalate), glass-fiber, (nano)filler, fire test, oxygen index, heat release rate.

NOWE SYNERGETYKI UNIEPALNIONEGO POLI(1,4-TEREFTALANU BUTYLENU) WZMACNIANEGO WŁÓKNEM SZKLANYM

Streszczenie — Badano potencjalne synergetyki, działające w układzie z handlowo dostępnymi opóźniaczami palenia (FR), stosowane do uniepalniania kompozytu poli(1,4-tereftalanu butylenu) napełnionego włóknem szklanym (GF-PBT). Palność wytworzonych materiałów (FR GF-PBT) oceniano na podstawie testu palności UL-94, wyznaczonego indeksu tlenowego (*LOI*) oraz określonej kalorymetrycznie szybkości wydzielania ciepła (*HRR*). Wykorzystano w pracy handlowe uniepalniacze: dietylofosfinian glinu (OP 1240) oraz układ cyjanuranu melaminy z dietylofosfinianem glinu (OP 1200), jako nanonapełniacze stosowano natomiast: Cloisite 30B, warstwowy kaolin modyfikowany octanem potasu, talk, krzemionkę, ekspandowany grafit i trzy rodzaje silseskwioksanów (POSS). Stwierdzono, że interesujący synergiczny układ z tradycyjnymi uniepalniaczami, poprawiający odporność na palenie otrzymywanych kompozytów, tworzy poliedryczny silseskwioksan a także warstwowa glinka kaolinowa modyfikowana octanem potasu.

Słowa kluczowe: uniepalniacze, synergizm, poli(1,4-tereftalan butylenu), włókno szklane, nanonapełniacze, test palności, indeks tlenowy, szybkość wydzielania ciepła.

INTRODUCTION

Engineering thermoplastic polymers such as polyamides, polycarbonates, semicrystalline aromatic polyesters and their blends are widely used in electrical and electronic appliances [1]. Poly(1,4-butylene terephthalate) (PBT) is one of them and it is a very important engineering thermoplastic polymer since it combines several desirable properties such as high strength and rigidity, low moisture absorption, excellent electrical properties and chemical resistance, rapid molding cycles and reproducible mold shrinkage [2]. It is very often reinforced by glass fibers to make various composites with high performance. Glass fibers are incorporated into PBT in order to improve properties such as stiffness, strength, creep and to increase the dimensional stability of the polymer [3]. The amount (20—50 wt. % typically) and length of fibers as well as their orientation in PBT are governing factors that enhance dramatically the mechanical properties of the composite material. Glass fiber reinforced PBT (GF-PBT) has largely penetrated the market and it represents nowadays about 70 % to 80 % of the global consumption of PBT [2].

The development and application of GF-PBT are limited due to its high flammability when subjected to elevated temperature or flame [4, 5]. An efficient method to

---

[1)] ISP/UMET — UMR/CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Avenue Dimitri Mendeleiev — Bât. C7a, BP 90108, 59652 Villeneuve d'Ascq Cedex, France.

[2)] BASF EG, B001, 67056 Ludwigshafen, Germany.

[*)] Corresponding Author; e-mail: serge.bourbigot@ensc-lille.fr

reduce the flammability of PBT and GF-PBT is to incorporate flame retardant (FR) into the polymer [6—9]. Several types of FRs are used in PBT and GF-PBT and they have been reviewed elsewhere [4, 5]. Gas phase active agents such as halogenated compounds or alkylphosphinate salts are effective substances with regard to the low propensity of PBT for charring. Good fire properties are also obtained when substituting part of these aforementioned substances by agents acting through fuel dilution such as melamine cyanurate. Char promoting flame retardants such as hypophosphite salts and red phosphorus provides high fire properties and they have been found to be synergistic with char former polymers such as polycarbonate or phenol formaldehyde resins. Halogenated compounds and red phosphorus are among all known families of flame retardants the most efficient. They nonetheless raised concerns regarding their potential toxicity or instability and therefore would get less and less consideration in academic and industrial researches. Phosphinates salts are very effective flame retardants and they may advantageously enhance the electrical properties of PBT. It was examined in details by Braun *et al.* [7, 10]. They investigated the mode of action of the aluminum and zinc salts of diethylphosphinic acid in glass fiber reinforced PBT and they found that the aluminum phosphinate salts released during the main decomposition step diethyl phosphinic acid in the gas phase. The diethylphosphinic acid acts in the gas phase by inhibition of the combustion reactions. This is accompanied by formation of aluminum phosphinate-terephthalate complexes in the condensed phase.

The pioneering work of Gilman *et al.* at NIST in the middle 90's showed that the use of organomodified montmorillonite (MMT) nanodispersed in polymers provided low flammability to them [11]. Numerous groups subscribed this approach and developed hybrid polymeric materials including organomodified clays [12], nanoparticles of Al_2O_3 or TiO_2 [13], nanoparticles of silica [14], layered double hydroxides (LDH) [15], carbon nanotubes (CNT) [16] or polyhedral silsesquioxanes (POSS) [17]. All those materials exhibit low flammability associated to other properties such as enhanced mechanical properties. This approach has been also applied to PBT but as far as we know, only the use of MMT [18, 19] and CNT [20] was reported in the literature so far. However, it shows some limitations because even if heat release rate (*HRR*) measured by cone calorimetry is decreased by 50 %, PBT nanocomposites fail to other tests, in particular those with samples in vertical position (*e.g. LOI*, UL-94). It is a general trend for all polymer nanocomposites and it is therefore useful to combine the nanofillers with conventional FRs [21]. Only few papers report the use of nanoparticles with conventional FRs while this approach seems to be very promising because it could create large synergistic effects. Yang *et al.* [22] showed that the substitution of aluminum hypophosphite by organomodified MMT could enhance the fire properties of the material. On the other hand, Gallo *et al.* [23, 24] reported that the combination of aluminum diethylphosphinate (Exolit OP 1240 of Clariant) with nanometric particles of metal oxides such as Fe_2O_3 and TiO_2 could remarkably improve the fire properties of unreinforced PBT. 10 wt. % OP 1240 in PBT achieve V-1 rating (3.2 mm) while substituting the phosphinate salt by 2 wt. % of the metal oxides allows reaching the V-0 ranking. V-0 classification was obtained with 5 wt. % OP 1240 and 2 wt. % Fe_2O_3. Both TiO_2 and Fe_2O_3 were evidenced to increase the char residue in the burning polymer. TiO_2 seems to favor polyarylate structures and polyaromatisation of PBT through coordinating with terephthalate residues, while Fe_2O_3 was assumed to induce the homolytic cleavage of PBT chains, hence favoring crosslinking of the later. According to the authors, high synergistic performances of metal oxides would be ascribed to their nanometric size and good dispersion in the PBT matrix.

Our survey of the literature has shown the benefit of combining (nano)fillers with conventional FRs in PBT. Based on those results, the goal of this paper is to examine potential synergists in flame retarded GF-PBT. The selected FRs are aluminum diethylphosphinate (OP 1240) and a combination of melamine cyanurate and of aluminum diethylphosphinate (OP 1200) because they are halogen-free FR and they have been found to be efficient in GF-PBT. The first part of the paper will examine the thermal stability of the (nano)fillers which will be evaluated in GF-PBT/OP-based materials as well as their processing in the flame retarded GF-PBT. The second part will be devoted to the evaluation of the fire performance of GF-PBT/OP-based materials containing the (nano)fillers. The benefit of the (nano)fillers will be finally discussed.

EXPERIMENTAL

Materials

Raw materials: PBT was a commercial grade supplied by BASF (Ludwigshafen, Germany) under the tradename PBT Ultradur B4520. Glass fibers were 3786 Evonik supplied by PPG (Pittsburg, USA).

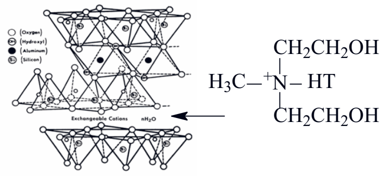
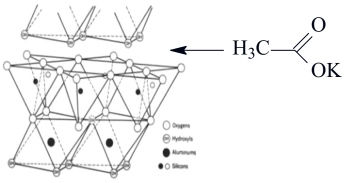
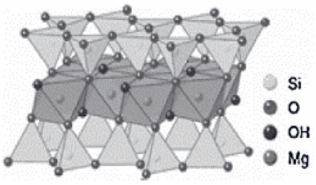
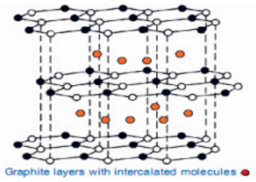
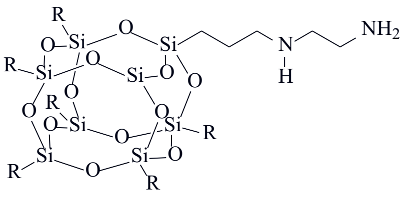
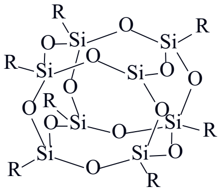
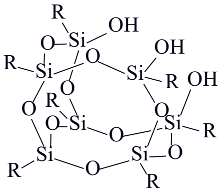
Flame retardants: Exolit OP 1240 and Exolit OP 1200 were supplied in powder by Clariant (Knappsak, Germany) and are aluminum diethylphosphinate salt and the combination of aluminum diethylphosphinate salt with melamine cyanurate, respectively.

(Nano)fillers: The (nano)fillers used in this study are detailed in Table 1.

Samples preparation

Masterbatch: PBT was melt-mixed with glass-fibers and FRs (OP 1200 or OP 1240) using a ZSK MC 26 mono-screw mega-compounder to get masterbatches. The rotational speed was 300 rpm and the temperature profile lies between 235 °C to 280 °C. The extrudates were

T a b l e 1. Characteristic of the (nano)fillers used in the formulations

Structure		Specifications
Cloisite® 30B (Southern Clay Product)		amino concentration: 125 meq/100g
Kaolin VP Cocoon 2125 (Benefit)		stability: ≈300 °C
Talc Jetfine® (Rio tinto Minerals)		median particle size: 1 μm
Fumed SiO_2 HDK® H30RM (Wacker)	—	BET-surface area silica: 270—330 m^2/g
Expandable Graphite ES 350 F5 (Graphit Kropfmül AG)		onset of thermal expansion: 175 °C, minimum expansion rate: 350 cm^3/g
Amino-ethyl-amino propyl-isobutyl POSS® (AEAPI POSS) (Hybrid plastic)	 R = *t*-butyl	resin solubility: aliphatic resins
Octamethyl POSS® (OM POSS) (Hybrid plastic)	 R = methyl	resin solubility: most thermoplastic resins (PA, PE, PP, PU)
Trisilanol phenyl POSS® (TSP POSS) (Hybrid plastic)	 R = *i*-butyl	resin solubility: aliphatic monomers, oligomers, PP, PE, PA

T a b l e 2. Composition of the masterbatches (GF-PBT/OP 1200 and GF-PBT/OP 1240

Components	Pellets and masterbatches, wt. %			
	PBT	GF-PBT	GF-PBT/OP 1200	GF-PBT/OP 1240
PBT Ultradur B4520 (BASF)	100	60	55	55
Glass Fibre PPG 3786 (Evonik)	—	40	25	25
Aluminum diethylphosphinate, Exolit® OP 1200 (Clariant)	—	—	20	—
Aluminum diethylphosphinate, Exolit® OP 1240 (Clariant)	—	—	—	20

then pelletized. The composition of the masterbatches is summarized in Table 2.

Mixing: Formulations [masterbatch and (nano)filler] were prepared in a Brabender internal mixer (type 350/EH roller blade, mixing conditions checked using the data processing torque recording by the rheometer system PL2000, constant shear rate at 50 rpm) in nitrogen flow (our Brabender mixer is equipped with home-made chamber limiting the oxidation of the polymer). Pellets of the flame retarded GF-PBT with the (nano)fillers were mixed at 250 °C for 10 minutes. The formulations were prepared in the way where the loading of GF is kept constant at 25 wt. % and that of FR + (nano)fillers is constant equaling 20 wt. %. In all cases, FR was substituted by the (nano)filler between 1 and 5 wt. %. All materials were dried overnight at 60 °C before use. The resulting materials were then cut off in small pieces and from those pieces polymer plates (100 × 10 × 3 mm, 100 × 12.7 × 0.8 mm, and 100 × 100 × 3 mm) were prepared using a Darragon molding press.

Methods of testing

Thermal analysis

Thermogravimetric analyses (TGA) was performed using a Setaram TG 92 microbalance. Samples of 10 mg were heated in open silica pans in nitrogen flow (cm^3/min) at heating rate of 10 °C/min from room temperature to 800 °C. Parameters obtained from the thermogravimetric analyses were the remaining mass as a function of temperature, the mass loss rate as a function of temperature, the mass loss starting temperature (T_{onset}), the maximal mass loss rate temperature (T_{max}), the mass loss at the processing temperature of PBT (250 °C) and the residue yield at 800 °C.

Fire testing

— Limiting Oxygen Index (*LOI*, minimum oxygen concentration to support candle-like combustion of plastics) was measured using a Fire Testing Technology (FTT) instrument on sheets (100 × 10 × 3 mm) according to the standard oxygen index test (ISO 4589). It measures the minimum concentration of oxygen in a nitrogen/oxygen mixture required to just support combustion of a test sample under specified test conditions in a vertical position (the top of the test sample is ignited with a burner).

— UL-94 test: UL-94 classification was obtained on sheets (100 × 12.7 × 1.6 mm) according to the conditions of the standard test (ASTM D 3801) *i.e.* in a vertical position (the bottom of the sample is ignited with a burner). This test provides only a qualitative classification of the samples (V-0, V-1 and V-2 labeled samples).

— Mass loss calorimetry: FTT Mass Loss Calorimeter was used to carry out measurements on FR GF-PBT 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 × 100 mm × 3 mm in horizontal orientation. External heat flux of 50 kW/m^2 was used for running the experiments. This flux corresponds to common heat flux in developed fire scenario. The mass loss calorimeter was used to determine heat release rate (*HRR*). When measured at 50 kW/m^2, *HRR* is reproducible to within ±10 %. The data reported in this paper are the average of three replicated experiments.

RESULTS AND DISCUSSION

Thermogravimetry

Thermogravimetric analyses (TGA) of the FR GF-PBTs and of the (nano)fillers (except talc and fumed silica) are shown in Figure 1 and the associated data is summarized in Table 3.

T a b l e 3. TGA data of the (nano)fillers compared to the FR GF-PBTs

Materials	T_{onset} °C	T_{max} °C	Mass loss at 250 °C wt. %	Residue yield at 800 °C wt. %
GF-PBT/OP 1200 (55/25/20)	302	396	0	35
GF-PBT/OP 1240 (55/25/20)	330	391	0	38
Cloisite 30B	186	269	3	76
Kaolin	290	355	0	83
Graphite	188	236	14	71
AEIP POSS	211	322	2	9
TSP POSS	215	570	1	74
OM POSS	171	278	15	6

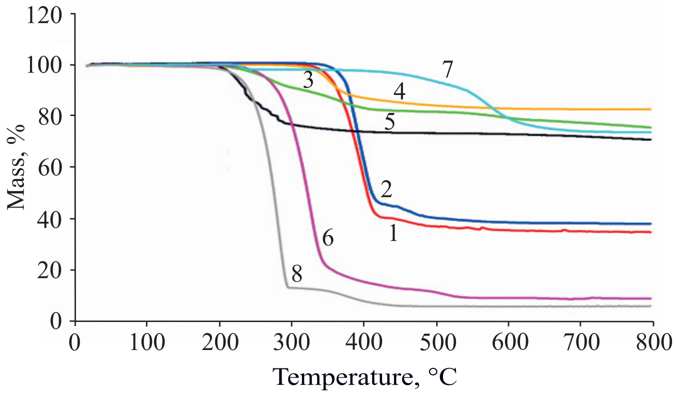


Fig. 1. TG curves of the (nano)fillers compared to the FR GF-PBTs: 1 — PBT/GF/OP 1200 (55/25/20), 2 — PBT/GF/OP 1240 (55/25/20), 3 — Cloisite 30B, 4 — Kaolin VP Cocoon 2125, 5 — Graphite ES350F5, 6 — AEAPI POSS, 7 — TSP POSS, 8 — OM POSS

TG curve of GF-PBT/OP 1240 is characterized by a main decomposition process with a maximal mass loss rate at 391 °C. An additional minor decomposition process corresponding to a weight loss of about 8 wt. % occurs around 460 °C. A residue of 38 wt. % remains with a large part which can be attributed to the glass fiber content (25 wt. %). For the GF-PBT/OP 1200 material, the onset temperature is shifted to lower values while the main decomposition step is observed at similar temperature (396 °C vs. 391 °C). The additional minor decomposition process was also found (5 wt. %) and a residue of 35 wt. % remains. Based on the work of Braun *et al.* [7, 10], the main decomposition step of OP 1240 and OP 1200 containing GF-PBT materials are characterized by release of tetrahydrofurane (THF) and H_2O that are produced by the hydrolytic and thermal scission of polyester bonds. Ester and butadiene are the main products evolved during the maximum of mass loss rate. Simultaneously diethylphosphinic acid is released. During the second minor decomposition process ethene, CO_2 and benzene are given off. According to this study the melamine cyanurate decomposes mainly independently of the polymer and the phosphinate salt yields to fuel dilution gases (isocyanide acid and carbon dioxide). These later are released at the beginning of the main decomposition process of the polymer which would explain that the GF-PBT/OP 1200 material exhibited a lower starting mass loss temperature than the GF-PBT/OP 1240 material.

TG curves of the (nano)fillers are consistent with data reported in literature and it will be commented in the following. Degradation of the graphite ES 350 F5 starts at 188 °C and it exhibits a maximal mass loss rate at about 236 °C. Here we can assume that graphite expansion caused by evolution of the inserted chemicals and release of gaseous species should occur during PBT processing.

According to previous work [25], thermal decomposition of the organoclay Cloisite 30B takes place into four stages, starting with loss of free water residing between montmorillonite crystallites and gaseous species at about 180 °C. This is followed by the decomposition and evolution of ammonium-based surfactants between 200 and 470 °C then, dehydroxylation of aluminosilicate lattice occurs from 470 to 700 °C and finally, evolution of products associated with residual organic carbonaceous matter occurs from 700 °C. It is consistent with our TG curves even if the first stage is not observed. On the other hand, it is noteworthy that decomposition of the ammonium-based surfactant should occur during the processing of PBT.

The first mass loss of the potassium acetate modified kaolin starts around 300 °C and it is followed by a slower mass loss step over a wide temperature range between 400 and 550 °C. Gabor *et al.* [26] found that both evolution steps of the organomodified kaolin correspond to dehydroxylation processes of the kaolin crystallites accompanied with the decomposition of the intercalated potassium acetate. The remarkable feature of the organomodified kaolin is it exhibits onset temperature degradation similar as that of the GF-PBT/OP 1200 sample. Through releasing water during PBT decomposition, we can assume that organomodified kaolin could lead to a further improvement of the fire performances of the polymer in addition to the expected barrier effect.

Thermal behavior of the polyhedral oligomeric silsesquioxane (POSS) compounds appears somewhat different depending on the nature of the side groups and also on whether the nano-cage is opened or closed. A major degradation process step occurs for both closed nano-cages (OM POSS and AEAIP POSS) well before decomposition of the PBT materials, followed by a minor decomposition step (over a range of 200 to 450 °C and 220 to 550 °C, respectively). Almost no residue remains at 800 °C for these POSS (6 wt. % for OM POSS and 9 wt. % for AEAIP POSS). On the contrary, the opened nano-cage TSP POSS exhibits better thermal stability up to 400 °C, with a char yield of about 74 wt. % at 800 °C. According to the literature [25], the decomposition process of the TSP POSS includes the evolution of the cyclic organosilanes starting at 400 °C, followed by the loss of hydrocarbon fragments between 450 and 550 °C, and finally POSS cage degradation between 550 and 680 °C.

In this section, the thermal degradation of the materials has been fully commented. It shows that some of the selected (nano)fillers could be degraded during the PBT processing and it is expected it could be play a role on the fire performance of the formulations. Nevertheless, all of them will be evaluated in FR GF-PBT since they could bring additional performance to the materials.

Processing

Processing of the formulations has been done using mixer and additional information can be obtained measuring the torque changes as a function of time. Part of the 20 wt. % of the OP 1200 or OP 1240 contained in the

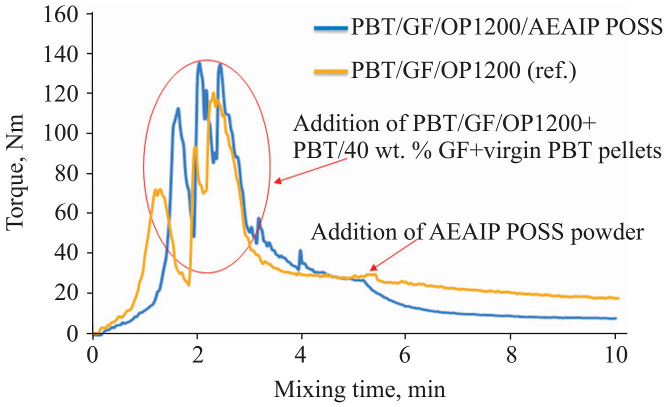


Fig. 2. Torque as a function of time measured during the mixing of GF-PBT/OP 1200 with and without AEAIP POSS

flame retarded GF-PBT masterbatches has been substituted by the potential synergists presented above. During compounding, it was observed that some additives, namely AEAIP POSS, TSP POSS, Cloisite 30B, kaolin, talc and graphite, lead to a decrease of the polymer viscosity. This decrease was particularly significant for AEAIP POSS, Cloisite 30B and kaolin as illustrated in Fig. 2 by the sharp decrease of the torque during mixing when incorporating AEAIP POSS to the mixture of PBT/GF/OP 1200. Two phenomena may explain this: (i) a lubricating effect and (ii) a chemical effect through rupture of the ester bonds of PBT because of the functional groups such as hydroxyls or amines, present in the additive structure. It is out of the scope of this paper to investigate the modifications of the material during processing but this information should be useful for upscaling and we have to recognize it could play a role on the fire properties.

Reaction to fire

LOI and UL-94 test results of the different formulations are shown in Table 4. GF-PBT flame retarded by either OP 1240 or by OP 1200 exhibits good fire performance as previously reported [7]. Both reference materials achieve a V-0 rating associated to *LOI* higher than 40 vol. %. Substitution of OP 1240 by synergists decreases UL-94 classification from V-0 to V-1 (except for AEAIP POSS and OM POSS). In particular, significant increase of the total burning time is observed for the substitution of OP 1240 by 2 wt. % Cloisite 30B and 2 wt. % TSP POSS (98 s and 82 s, respectively). OM POSS and AEAIP POSS are the fillers keeping V-0 classification and decreasing maximum total burning time. Concerning *LOI* values, a maximum increase of 4 vol. % is measured with 3 wt. %

Table 4. LOI and UL-94 results of materials prepared via mixing

	FR, wt. %	Synergist, wt. %	*LOI* vol. %	UL-94 (0.8 mm, conditioning temp. 23 °C)				
				UL-94 rating	total burning time, s	cotton inflamed	drops	break
PBT + 25 % GF	20 % OP 1200	—	42 ± 1	V-0	36	0	0	0
	18 % OP 1200	2 % AEAIP POSS	36 ± 1	V-0	25	0	0	0
	18 % OP 1200	2 % OM POSS	43 ± 1	V-0	37	0	0	0
	18 % OP 1200	2 % TSP POSS	38 ± 1	V-1	63	0	0	0
	19 % OP 1200	1 % kaolin	(<45)	V-0	40	0	0	0
	18 % OP 1200	2 % kaolin	53 ± 1	V-0	32	0	0	0
	17 % OP 1200	3 % kaolin	49 ± 1	V-0	36	0	0	0
	17.1 % OP 1200	1.9 % kaolin	48 ± 1	V-0	35	0	0	0
	16.2 % OP 1200	1.8 % kaolin	48 ± 1	V-0	34	0	0	0
	15.3 % OP 1200	1.7 % kaolin	46 ± 1	V-2	47	1	0	0
	17 % OP 1200	3 % graphite	39 ± 1	V-1	67	0	0	0
	18 % OP 1200	2 % SiO_2	43 ± 1	V-1	68	0	0	0
	18 % OP 1200	2 % talc	44 ± 1	V-0	41	0	0	0
	18 % OP 1200	2 % Cloisite 30B	39 ± 1	V-1	51	0	0	0
	20 % OP 1240	—	40 ± 1	V-0	40	0	0	0
	18 % OP 1240	2 % AEAIP POSS	38 ± 1	V-0	29	0	0	0
	18 % OP 1240	2 % OM POSS	42 ± 1	V-0	35	0	0	0
	18 % OP 1240	2 % TSP POSS	38 ± 1	V-1	82	0	0	0
	17 % OP 1240	3 % kaolin	44 ± 1	V-1	59	0	0	0
	17 % OP 1240	3 % graphite	44 ± 1	V-1	73	0	0	0
	18 % OP 1240	2 % SiO_2	40 ± 1	V-1	65	0	0	0
	18 % OP 1240	2 % talc	41 ± 1	V-1	71	0	0	0
	18 % OP 1240	2 % Cloisite 30B	39 ± 1	V-1	98	0	0	0

kaolin and 3 wt. % graphite containing materials. It is to be reminded that *LOI* and UL-94 results are not correlated as shown with our materials. For instance, the OP 1240/graphite material exhibits a superior *LOI* value of 44 vol. % while having a reduced UL-94 rating (V-1) with a noticeable increase of the total burning time (+33 s) as compared to the reference material. On the contrary the OP 1240/AEAIP POSS material achieves V-0 rating and exhibits a slightly better total burning time along with a 2 vol. % decrease of the *LOI* value compared to the reference material.

OP 1200 containing materials show to some extent comparable flammability results. However, it should be noticed that V-0 rating is achieved with the OP 1200/talc composite (which is not the case with the corresponding OP 1240 containing material). A much lower total burning time value is obtained for the OP 1200/Cloisite 30B composite compared to the OP 1240/Cloisite 30B composite (51 s versus 98 s). On the other hand, a 2 or 3 wt. % substitution of the OP 1200 by kaolin improves dramatically *LOI* value of the material without modifying UL-94 classification. In particular, the 2 wt. % substituted material achieves a *LOI* value of 53 vol. % which is the best result among all the evaluated materials. Such increase in *LOI* value is not observed for the 1 wt. % neither the 3 wt. % kaolin containing material even if the value is higher than that of GF-PBT/OP 1200 which evidences that the optimum efficiency of kaolin is around 2 wt. % for a total loading of 20 wt. % FRs. The higher performance achieved by the OP 1200/kaolin material compared to the corresponding OP 1240 material could be linked to the similar temperature degradation range observed for GF-PBT/OP 1200 and kaolin (see the previous section and Fig. 1).

T a b l e 5. Mass loss calorimeter data of FR GF-PBT with and without synergist

FR formulations	p*HRR*, kW/m^2	*t ing*, s
OP 1200 (20)	250	66
OP 1200-talc (18/2)	222 (-11 %)	70
OP 1200-SiO_2 (18/2)	213 (-15 %)	69
OP 1200-graphite (17/3)	172 (-31.2 %)	67
OP 1200-kaolin (17/3)	206 (-17.6 %)	56
OP 1200-TSP POSS (18/2)	214 (-14.4 %)	70
OP 1200-OM POSS (18/2)	172 (-31.2 %)	62
OP 1240 (20)	191	67
OP 1240-talc (18/2)	203 (+6 %)	67
OP 1240-SiO_2 (18/2)	213 (+12 %)	79
OP 1240-graphite (17/3)	217 (14 %)	70
OP 1240-kaolin (17/3)	191 (0 %)	62
OP 1240-TSP POSS (18/2)	134 (-30 %)	64
OP 1240-OM POSS (18/2)	135 (-29 %)	70

The materials have been also evaluated by mass loss calorimetry. Peak of heat release rate (p*HRR*) and time to ignition (*t ign*) of the evaluated formulations as well as p*HRR* reductions compared to the references are summarized in Table 5.

HRR curves show that p*HRR* values of OP 1200 based materials (except for the formulation containing OM POSS and graphite) are only slightly decreased compared to the reference (Table 5 and Fig. 3). p*HRR* reduction of GF-PBT/OP 1200/(nano)fillers compared to GF-PBT/OP 1200 lies between 11 % and 18 % which is not really significant. It is noteworthy that the OP 1200/kaolin composite exhibits the shortest time to ignition (56 s) which is 10 seconds shorter than that of the reference material. On the other hand, substitution of OP 1200 by graphite or OM POSS leads to a 31 % decrease of the p*HRR* value.

HRR curves (Fig. 4) show that some OP 1240 based materials (namely those containing 2 wt. % talc, 2 wt. % silica, 3 wt. % kaolin and 3 wt. % graphite) exhibit higher (or similar) p*HRR* than that of the reference (GF-PBT/OP

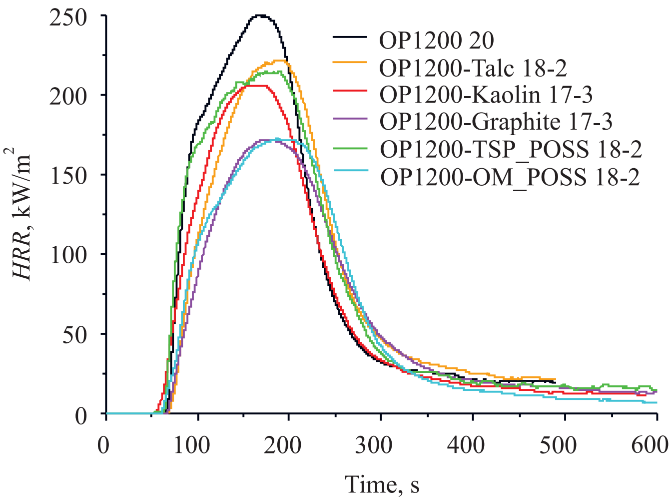


Fig. 3. HRR as a function of time of GF-PBT/OP 1200 formulations and of GF-PBT/OP 1200 for comparison purposes

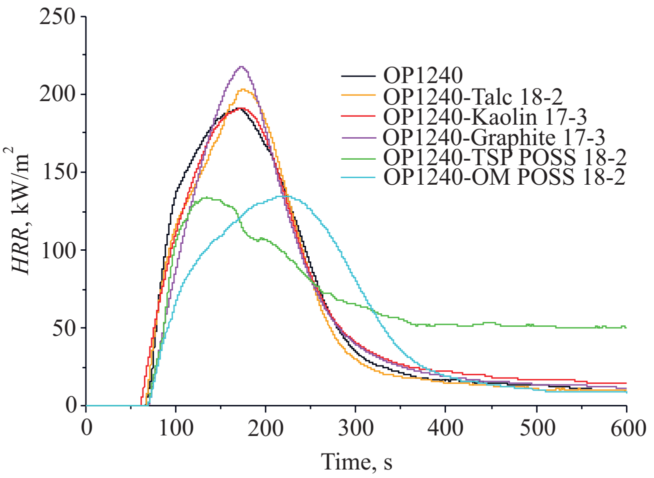
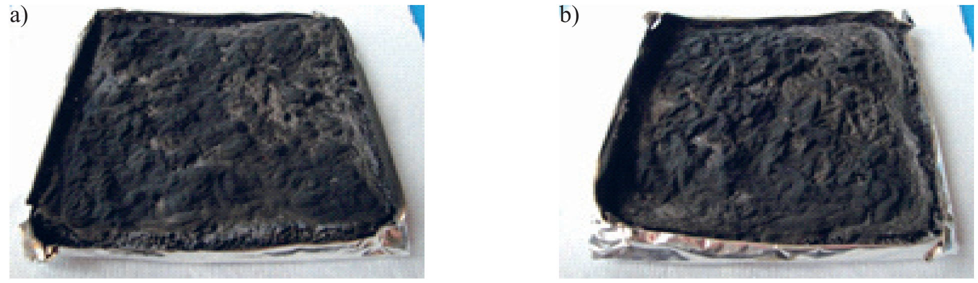
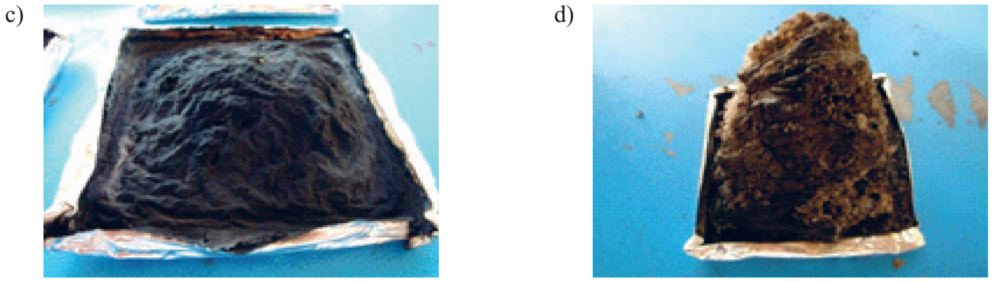


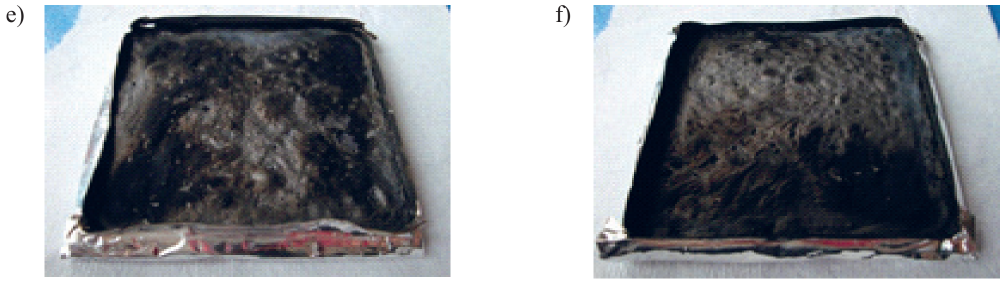
Fig. 4. HRR as a function of time of GF-PBT/OP 1240 formulations and of GF-PBT/OP 1240 for comparison purposes



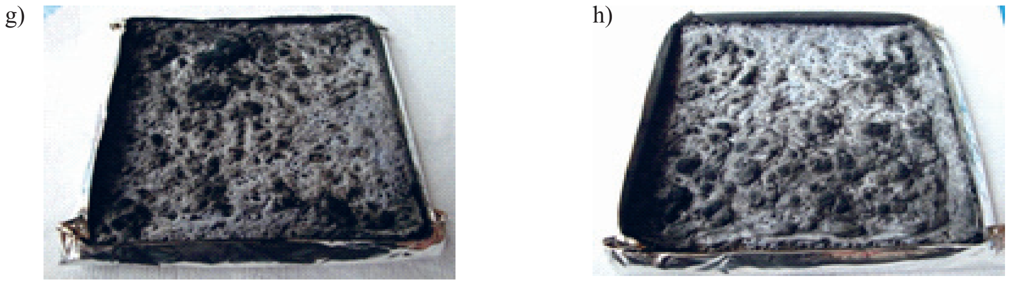
GF-PBT/OP1200 GF-PBT/OP1240



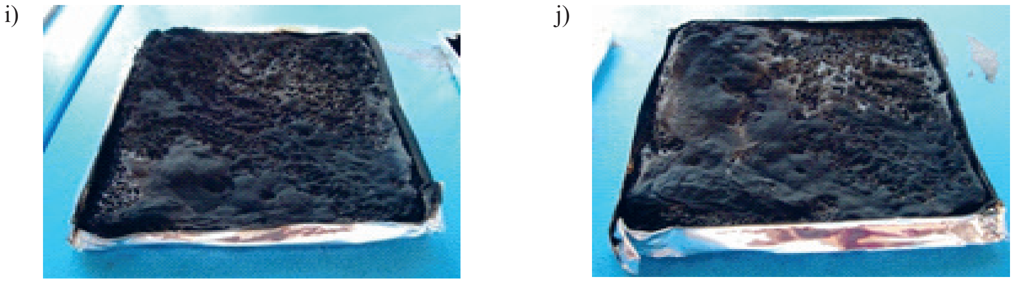
GF-PBT/OP1200/OM POSS GF-PBT/OP1240/TSP POSS



GF-PBT1200/Graphite GF-PBT1240/Graphite



GF-PBT/OP1200/Kaolin GF-PBT1240/Kaolin



GF-PBT/OP1200/SiO_2 GF-PBT/OP1240/SiO_2

Fig. 5. The residues after mass loss calorimeter experiments of the FR GF-PBT composites

1240). The OP 1240/graphite composite exhibits the highest p*HRR* increase (14 %) while substituting OP 1200 by graphite leaded to a significant decrease of p*HRR* (31 %) (Table 5). A synergistic effect between melamine cyanurate and graphite can thus be suggested. On the contrary TSP POSS which exhibited a low p*HRR* reduction when substituting OP 1200 (-14 %), leads to 30 % p*HRR* reduction when substituting OP 1240. The OP 1240/OM POSS composite also exhibits a significant p*HRR* reduction compared to the reference material (-29 %). It is noteworthy that both OP 1240/TSP and OP 1200/OM POSS composites exhibit the lowest p*HRR* value (respectively 134 and 135 kW/m^2) among all the investigated samples which is a p*HRR* reduction of about 45 % compared to GF-PBT/OP 1200 (p*HRR* = 250 kW/m^2).

The visual observations of the residues after mass loss calorimeter experiments reveal interesting behavior for OP 1240/TSP POSS and OP 1240/OM POSS composites. The OP 1240/TSP POSS composite exhibits an intumescent behavior forming a swollen char layer (expansion of about 2900 %) at the end of experiments (Fig. 5d). The OP 1240/OM POSS composite intumesces as well but with a lower expansion (about 900 %) (Fig. 5c). Similar behavior was previously reported in the literature when combining OM POSS with zinc phosphinate (Exolit OP 950 from Clariant) in PET [27, 28]. This intumescent behavior suggests that the mechanism of action involves the formation of a heat barrier protecting the underlying material and hence permitting a significant p*HRR* reduction. The graphite containing materials do not expand as we could expect but on the contrary the sample surface is flat after combustion (visual observations during the experiments do not show any expansion of the material as well) and its aspect looks similar as a continuous graphite layer scattered by holes (Fig. 5e and Fig. 5f). It is assumed that the molecules intercalated between the initial graphite layers give off during processing (degradation temperature of graphite occurs at 188 °C) avoiding additional expansion of the char upon heating. Surface aspects of the other composites after combustion look similar as the references (Figure 5a, b, g, h, i, j) except for the color (formulations containing kaolin) or for the roughness (formulations containing kaolin and silica).

CONCLUSIONS

Table 6 summarizes fire performance of the evaluated formulations compared to the references. The symbols with their obvious meaning –, + or = are attributed depending on how the substituting (nano)fillers modify the fire properties of the materials (see the caption of Table 6).

Each fire scenarios associated to fire testing are specific and the fire behavior of the material depends on them. It means that there is no direct correlation between a fire test and another. A typical example is that involving GF-PBT/OP 1240 with TSP POSS which shows large p*HRR* reduction *via* an intumescent behavior while worsening UL-94 classification because of long burning time and while decreasing *LOI* as well.

Table 6. Fire performances of the various formulations compared to the references[*)]

	FR wt. %	Synergist wt. %	*LOI* vol. %	UL-94 rating	p*HRR* kW/m^2
PBT + 25 % GF	20 % OP 1200	—	42 ± 1	V-0	250
	18 % OP 1200	2 % AEAIP POSS	—	=	
	18 % OP 1200	2 % OM POSS	=	=	+
	18 % OP 1200	2 % TSP POSS	=	—	=
	19 % OP 1200	1 % kaolin	(<45)	=	
	18 % OP 1200	2 % kaolin	+/+	=	
	17 % OP 1200	3 % kaolin	+	=	=
	17.1 % OP 1200	1.9 % kaolin	+	=	
	16.2 % OP 1200	1.8 % kaolin	+	=	
	15.3 % OP 1200	1.7 % kaolin	=	-/-	
	17 % OP 1200	3 % graphite	=	—	+
	18 % OP 1200	2 % SiO_2	=	—	=
	18 % OP 1200	2 % talc	=	=	=
	18 % OP 1200	2 % cloisite 30B	=	—	
	20 % OP 1240	—	40 ± 1	V-0	191
	18 % OP 1240	2 % AEAIP POSS	=	=	
	18 % OP 1240	2 % OM POSS	=	=	+
	18 % OP 1240	2 % TSP POSS	=	—	+
	17 % OP 1240	3 % kaolin	=	—	=
	17 % OP 1240	3 % graphite	=	—	=
	18 % OP 1240	2 % SiO_2	=	—	=
	18 % OP 1240	2 % talc	=	—	=
	18 % OP 1240	2 % cloisite 30B	=	—	

[*)] *LOI*: -/+ → -/+ 5 vol. %; UL-94: -/+ → </> rating; p*HRR*: -/+ → +/- 25 %.

AEAIP and OM POSS exhibits lower thermal stability than TSP POSS (Fig. 1) but they provide higher performance than TSP POSS in terms of UL-94 when combined with OP 1200 and OP 1240. OM POSS does not modify UL-94 classification and *LOI* (same behavior with AEIP POSS) while it favors p*HRR* reduction especially when combined to OP 1240 (AEIP POSS has not been evaluated in FR GF-PBT by mass loss calorimetry). Those results suggest therefore that POSS compounds are synergists to be considered to be combined with phosphinate salts in GF-PBT. It extends works done by Vannier *et al.* [28, 29] pointing out the large increase of fire performance in poly(ethylene terephthalate) containing phosphinate salts with OM POSS.

Use of kaolin as synergist also shows interesting effects increasing dramatically *LOI* values of GF-PBT/OP 1200. UL-94 classification is not modified and the material still achieves V-0 rating (without further modification of the total burning time) when the total loading in OP 1200/kaolin drops down from 20 wt. % to 18 wt. %. It is assumed that the enhancement of the performance is due to a release of water (evolving from kaolin) when the polymer starts to decompose (as suggested by TGA). By mass loss calorimetry, the use of kaolin leads to weak p*HRR* reduction when combined with OP 1200 while no reduction is observed in OP 1240 based material. The better performance achieved for OP 1200/kaolin composite compared with OP 1240/kaolin composite could be partially explained by a closer range of degradation temperature for the kaolin and PBT/GF/OP 1200 material. We may also assume such difference of performance by potential interactions between kaolin and melamine cyanurate. Those aspects will be further examined and it will be published in a separate paper. Taking into consideration UL-94 results, none of the other (nano)fillers permits enhancing the fire performance compared to the references. *LOI* and p*HRR* are moderately modified (with the exception of the OP 1200/graphite containing material in mass loss calorimeter).

REFERENCES

1. Acquasanta F., Berti C., Colonna M., Fiorini M., Karanam S.: *Polym. Degrad. Stab.* 2011, **96**, 2098.
2. Bienmüller M., Wanders M:. *Kunstst. Int.* 2011, **101**, 48.
3. Hine P. J., Duckett R. A.: *Polym. Compos.* 2004, **25**, 237.
4. Weil E. D., Levchik S. V.: *J. Fire Sci.* 2004, **22**, 339.
5. Levchik S. V., Weil E. D.: *Polym. Int.* 2005, **54**, 11.
6. Braun U., Schartel B., Fichera M. A., Jäger C.: *Polym. Degrad. Stab.* 2007, **92**, 1528.
7. Braun U., Bahr H., Sturm H., Schartel B.: *Polym. Adv. Technol.* 2008, **19**, 680.
8. Brehme S., Schartel B., Goebbels J., Fischer O., Pospiech D., Bykov Y., *et al.*: *Polym. Degrad. Stab.* 2011, **96**, 875.
9. Chen L., Luo Y., Hu Z., Lin G. P., Zhao B., Wang Y. Z.: *Polym. Degrad. Stab.* 2012, **97**, 158.
10. Braun U., Schartel B.: *Macromol. Mater. Eng.* 2008, **293**, 206.
11. Gilman J. W., Kashiwagi T., Lichtenhan J. D.: *SAMPE J.* 1997, **33**, 40.
12. Zhu J., Morgan A. B., Lamelas F. J., Wilkie C. A.: *Chem. Mater.* 2001, **13**, 3774.
13. Laachachi A., Cochez M., Leroy E., Gaudon P., Ferriol M., Lopez Cuesta J. M.: *Polym. Adv. Technol.* 2006, **17**, 327.
14. Kashiwagi T., Morgan A. B., Antonucci J. M., VanLandingham M. R., Harris Jr R. H., Awad W. H., *et al.*: *J. Appl. Polym. Sci.* 2003, **89**, 2072.
15. Zammarano M., Franceschi M., Bellayer S., Gilman J. W., Meriani S.: *Polymer* 2005, **46**, 9314.
16. Kashiwagi T., Grulke E., Hilding J., Harris R., Awad W., Douglas J.: *Macromol. Rapid Commun.* 2002, **23**, 761.
17. Bourbigot S., Turf T., Bellayer S., Duquesne S.: *Polym. Degrad. Stab.* 2009, **94**, 1230.
18. Samyn F., Bourbigot S., Jama C., Bellayer S., Nazare S., Hull R., *et al.*: *Eur. Polym. J.* 2008, **44**, 1642.
19. Yang W., Kan Y., Song L., Hu Y., Lu H., Yuen R. K. K.: *Polym. Adv. Technol.* 2011, **22**, 2564.
20. Aranberri I., Germán L., Matellanes L., Suárez M. J., Abascal E., Iturrondobeitia M., *et al.*: *Plast. Rubber Compos.* 2011, **40**, 133.
21. Bourbigot S., Duquesne S.: *J. Mater. Chem.* 2007, **17**, 2283.
22. Yang W., Hu Y., Tai Q., Lu H., Song L., Yuen R. K. K.: *Composites Part A: Appl. Sci. Manuf.* 2011, **42**, 794.
23. Gallo E., Braun U., Schartel B., Russo P., Acierno D.: *Polym. Degrad. Stab.* 2009, **94**, 1245.
24. Gallo E., Schartel B., Braun U., Russo P., Acierno D.: *Polym. Adv. Technol.* 2011, **22**, 2382.
25. Dasari A., Yu Z. Z., Mai Y. W., Cai G., Song H.: *Polymer* 2009, **50**, 1577.
26. Gabor M., Toth M., Kristof J., Komaromi-Hiller G.: *Clay Clay Miner.* 1995, **43**, 223.
27. Vannier A., Duquesne S., Bourbigot S., Alongi J., Camino G., Delobel R.: *Thermochim. Acta* 2009, **495**, 155.
28. Vannier A., Duquesne S., Bourbigot S., Castrovinci A., Camino G., Delobel R.: *Polym. Degrad. Stab.* 2008, **93**, 818.

Received 23 VII 2012.