

# The influence of parameters of manufacturing hybrid flame retardant additives containing graphite on their effectiveness

Piotr Jankowski<sup>1), \*</sup>, Dorota Kijowska<sup>1)</sup>

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**Abstract:** Syntheses of hybrid flame retardant (HFR) additives were done on a semi-industrial scale. HFRs were obtained by *in situ* synthesis of melamine cyanurate in the presence of expandable graphite. HFRs have been used to reduce the flammability of selected polymers: polyester, epoxide, polystyrene. Compositions characterized by high oxygen indexes (in the case of the polyester compositions – 39.8 %) and improved horizontal FH-1 and vertical V-0 flammability parameters were obtained. The influence of the production parameters (including methods and parameters of drying), the grain size and expansion of the received HFRs on their effectiveness in the reduced flammability of selected plastics were investigated.

**Keywords:** hybrid flame retardant additives, expandable graphite, melamine cyanurate, flammability, polystyrene, polyester resin, epoxy resin.

## Wpływ parametrów wytwarzania hybrydowych, zawierających grafit uniepalniaczy na efektywność ich działania

**Streszczenie:** Hybrydowe uniepalniacze (HFR) otrzymano na drodze syntezy cyjanuranu melaminy w obecności grafitu ekspandującego (proces w skali ½-technicznej). HFR użyto do zmniejszenia palności poliestru, epoksydu i polistyrenu. Otrzymane kompozycje charakteryzowały się wysokimi wskaźnikami tlenowymi (w przypadku kompozycji poliestrowych – 39.8 %) oraz parametrami palności poziomej FH-1 i pionowej V-0. Zbadano zależność pomiędzy parametrami wytwarzania (w tym metodami i parametrami suszenia), wymiarami ziaren oraz parametrami ekspansji otrzymanych HFR a ich efektywnością w ograniczaniu palności tworzyw polimerowych.

**Słowa kluczowe:** hybrydowe uniepalniacze, grafit ekspandujący, cyjanuran melaminy, palność, polistyren, żywica poliestrowa, żywica epoksydowa.

The use of plastics in practice usually requires reducing their flammability. This is usually achieved through flame retardant additives. The legislation of the European Union has gradually limited the use of halogen containing flame retardants. A significant disadvantage of halogen additives is the emission of very toxic and corrosive fumes from the fire area to the environment during combustion. For the above mentioned reasons, halogen containing flame retardants are consistently substituted by halogen free additives. Unfortunately, the halogen free additives are often characterized by a lower efficiency in decreasing the flammability. Intumescent flame retardant systems are mostly used as halogen-free, flame retardant additives. They usually consist of: an acid catalyst (e.g. phosphate or phosphate esters, charring agents), small molecule compounds such as pentaerythritol and

a blowing agent (a compound responsible for the expansion of the char layer) [1]. The most reported intumescent systems contain phosphorus-nitrogen compounds.

An interesting solution in flame retardant compositions is the use of expandable graphite (EG). It swells during combustion to form a char layer, which prevents the access of oxygen to the combustion zone. Expandable graphite is one of the intumescent flame retardant additives that is produced by intercalation of sulphuric acid into graphite in the presence of a strong oxidizing agent. At elevated temperatures, expandable graphite decomposes with an emission of volatile products. This causes the formation of a foamed char layer, which is a physical barrier that reduces heat and mass transfer between burning materials and the environment [2]. The effect of the char layer on the flaming plastic was emphasized by Mochane and Luyt [3] in their publication. The influence of the introduction of flame retardant additives into poly(ethylene-co-vinyl acetate) copolymer (EVA) and an EVA/wax blend on the thermal stability and flammability of the compositions was described. As

<sup>1)</sup> Industrial Chemistry Research Institute, Department of Polyesters, Epoxides and Polyurethanes, Rydygiera 8 Str., 01-793 Warszawa, Poland.

<sup>\*</sup>) Author for correspondence; e-mail: [piotr.jankowski@ichp.pl](mailto:piotr.jankowski@ichp.pl)

flame retardant additives, EG, as well as combinations of EG with Cloisite 15A clay, and diammonium phosphate were used. The improvement in the thermal stability of the composition of the polymer with the flame retardant additive was proved [3]. It seems interesting to compare EG with natural graphite and the graphite oxide used as flame retardant additives for EVA.

The flammability, combustion process, quantity of residual char, morphology of the residual chars and thermal stability of the chars were investigated by cone calorimetry, scanning electron microscopy and thermal gravimetric analysis. It was found that the flame retardance of EVA is improved due to the addition of graphite, especially for EG [4]. The authors of other publications used EG modified with phosphorus oxychloride and pentaerythritol as a flame retardant for the epoxy resin. Although the obtained results were better than in the case of unmodified EG, the proposed solution is not environmentally friendly due to the presence of a halogen derivative [5].

Graphite oxides and graphene may be also used as flame retardant additives for polystyrene (PS). The flammability of nanocomposites was evaluated by thermal gravimetric analysis and cone calorimetry. The optimal reduction of flammability was obtained with the addition of 5 wt % of graphene. In this case, the reduction in the peak heat release rate (HRR) was almost 50 % compared to pure PS [6]. Bai *et al.* [7] described EG and an intumescent flame retardant that consists of a novel triazine char forming agent and ammonium polyphosphate (APP). These additives were used in wood flour-polypropylene composites. The synergistic effect between EG and the intumescent flame retardant on the mechanical properties, flame retardancy and thermal degradation of wood flour-polypropylene composites was investigated. The combination of EG and the intumescent flame retardant was proven to be a promising flame retardant system for wood flour-polypropylene [7]. EG shows a synergistic effect also with melamine polyphosphate and layered double hydroxide [8] or with diethyl ethylphosphonate and organically modified nanoclay (such as organically-modified montmorillonite or organically-modified layered double hydroxide) in polyisocyanurate-polyurethane foam nanocomposites [9]. In both cases, improving the flame retardancy and the fire behavior was achieved. Moreover, a synergistic effect was observed between EG and APP on flame retardant polylactide. Polylactide compositions with 15 wt % of combined additives showed a limiting oxygen index value of 36.5 and V-0 rating in UL-94 tests. A significant improvement in flame retardant properties of the above mentioned compositions in comparison with the compositions with APP or EG alone was observed [10]. Zhang *et al.* [11] used EG, APP and diethyl ethylphosphate as flame retardants for rigid polyurethane foams made from a polyol derived from melamine and cardanol. The flame retardant-filled polyurethane displayed a better compressive strength, thermal stabil-

ity, char residue, heat release and smoke emission than non-filled foams. The most effective additive proved to be EG. Han *et al.* [12] used EG with APP, or with intumescent flame retardant, for reduced flammability of polyethylene. The efficiency of EG alone and in compositions with other flame retardant additives was studied. The results of limiting oxygen index revealed stronger synergistic effects of EG with intumescent flame retardant than that with APP. Bahramian [13] used a graphite nano-crystal and nano-clay as an alternative to traditional fire retardants to improve the thermal stability and flammability resistance of polymeric materials in particular novolac type phenolic resins. Nano-graphite has a great potential in applications as a flame retardant [13]. EG was used together with silicon compounds, hydrotalcite and ammonium polyphosphate as a flame retardant composition for different plastics, *e.g.* EVA and polyurethane [14, 15]. In turn, the authors of another publication investigated the thermal degradation of polypropylene compositions containing EG with magnesium hydroxide [16]. The limiting oxygen index, vertical and horizontal flammability according to UL-94, as well as thermogravimetric parameters, were examined. The effect of an additional reduction of flame retardant properties in the presence of EG was observed. An increase in the decomposition temperature and thermal stability of the polypropylene composition was proven.

It is apparent from the literature that, in most cases, graphite is not used alone. From a variety of solutions, to increase its efficiency, the modification of EG by the melamine salt can be carried out. The method of obtaining this type of hybrid flame retardant (HFR) additives has been developed in our Institute on the laboratory scale [17, 18]. Modified graphite was used as a flame retardant additive for polystyrene, epoxy resin and polyester resin [19]. The highest flame retardancy classes FH-1 and V-0, as well as high limiting oxygen indexes, were observed. The mechanical properties of the selected compositions were measured. There were no adverse effects of the additive on the mechanical properties of the final compositions. After the completion of laboratory tests, our investigations were directed towards the implementation of the developed solutions on the industrial scale.

The aim of the present work was to investigate the influence of the method of the commercial production of HFRs on their flame retardant properties in compositions with selected plastics.

## EXPERIMENTAL PART

### Materials

For the syntheses of HFRs, the following materials were used:

- expandable graphite (EG) with trade name EG 290 characterized by particle size >200  $\mu\text{m}$  (Sinograf SA, Poland),

- melamine (Zakłady Azotowe Puławy S.A., Poland),
- cyanuric acid (Hebei HaiDa Chemical Industry Co., Ltd., China).

The prepared HFRs were tested as flame retardants with the following polymers:

- epoxy resin with trade name Epidian 5 (EP5, „Organika Sarzyna”, Poland),
- polyester resin named Polimal 109 (P109, „Organika Sarzyna”),
- polystyrene (PS), which was synthesized from styrene (POCh, purified by distillation under reduced pressure) with benzoyl peroxide (Aldrich) used as a polymerization catalyst.

Polyvinyl alcohol (PVA, molecular weight 35 000–40 000 produced by Shin-Etsu Chemical Co., Ltd.) was used for the stabilization of suspensions.

### Syntheses of HFRs

The syntheses were performed using various contents of EG according to the formulations listed in Table 1. The HFR names include the percentage content of EG and sum of melamine and cyanuric acid. Furthermore, the HFR samples were obtained using different speeds of the stirrer in the dissolver, different speeds of the rotor in the LGM, different temperatures at the inlet and outlet of the LGM, as well as different quantities and the types of beaters (blades) in the rotor inside the LGM (Table 2).

The synthesis of an exemplary sample of a HFR containing 75 wt % of EG was as follows. Into a 120 dm<sup>3</sup> dissolver (Niemann production), equipped with a mechanical disc stirrer with a diameter of 200 mm and maximum speed of 4000 rpm, four beaters (kind of blades inside the dissolver) to increase turbulence, heating jacket, temperature controller and bottom blowdown, 60 l of demineralized water was placed. Then, with stirring – 400 rpm, 2.47 kg (19.6 mol) of melamine and 2.53 kg (19.6 mol) of cyanuric acid were added to give an aqueous dispersion. Subsequently, 15 kg of expandable graphite (EG) was added. The synthesis was carried out at ambient tempera-

**Table 1. Hybrid flame retardant additives recipe**

Symbol of additive	Graphite kg	Melamine kg	Cyanuric acid, kg	Water kg
CMG40/60	9.0	2.97	3.03	60
CMG25/75-1	15.0	2.47	2.53	60
CMG25/75-2	15.0	2.47	2.53	60
CMG25/75-3	15.0	2.47	2.53	60
CMG15/85	8.5	0.74	0.76	30
CMG20/80	8.0	0.99	1.01	30
CMG50/50	10.0	4.94	5.03	60

ture for 1 h and at 90 °C for 1.5 h. Then, the reaction mixture was cooled to ambient temperature and the resultant product was pumped to the mill dryer – long gap mill (LGM, Hosokawa Alpine production). Part of the product was retrieved directly from the dissolver and, after filtration, dried in a conventional dryer and then crushed. After drying, the product was packaged into plastic bags.

The obtained HFR products were in the form of grey particles containing from 50 to 85 wt % of EG.

### Preparation of polymer compositions with reduced flammability

The compositions of polyester and epoxy resins were obtained by blending 20 parts of HFR per 100 parts of a particular polymer by weight. For this purpose, a slow-speed stirrer (IKA-Werke) was used. Specimens for flammability testing with dimensions according to the relevant standards were cast in molds.

PS compositions were prepared by suspension polymerization of styrene in the presence of the previously obtained HFR (15 or 20 parts per 100 parts of PS by weight) according to the method described in previous publications [17, 20]. The syntheses were carried out in an aqueous suspension stabilized by PVA and in the presence of benzoyl peroxide as a polymerization catalyst. PS pellets were pressed for 4 min in a hydraulic press at temperatures between 170 and 190 °C. The specimens for flamma-

**Table 2. The effect of drying method on grain dimension of additives**

Symbol of additive	Method of drying						
	conventional		LGM with air flow of 1800 m <sup>3</sup> /h				
	$d_{90}$ μm	speed rpm	$d_{90}$ μm	speed rpm	input temperature °C	output temperature °C	technical information
CMG40/60	486	700	64	3000	350	124	A
CMG25/75-1	386	400	179	3000	350	110	A
CMG25/75-2	459	400	267	3000	170	95	A
CMG25/75-3	404	500	295	3000	170	90	B
CMG15/85	379	400	378	3000	170	90	B
CMG20/80	482	400	229	3000	350	110	B
CMG50/50	507	400	148	3000	350	110	C

A – 4 long and 12 short beaters in LGM, B – 4 long beaters in LGM, C – 4 long and 4 short beaters in LGM,  $d_{90}$  – the particle diameter, below which are 90 % of the analyzed material.

bility testing were cut from the obtained plates according to the relevant standards.

### Methods of testing

The flammability properties of the prepared polymer compositions were examined with a horizontal-vertical flame chamber tester (Fire Testing Technology) according to the PN-EN 60695-11-10:2014-2 standard. The limiting oxygen index was determined using a special testing apparatus (Fire Testing Technology) according to ISO 4589-2:2006. Cone calorimetry studies were performed according to ISO 5660-2:2002 using a cone calorimeter (Fire Testing Technology) with an external heat flux of 50 kW/m<sup>2</sup>. The combustion reaction was initiated by ignition with a spark igniter. The specimens were placed in a horizontal orientation in relation to the radiator.

The grain size was characterized with a Malvern Mastersizer 3000.

The expansion of additives was measured according to our own Industrial Research Institute's method by measuring the percentage increase in volume of samples after heating to 600 °C [21].

## RESULTS AND DISCUSSION

### Production of HFR additives

Syntheses of HFRs were done in an analogous manner to that described previously [17, 18] but this time on a semi-industrial scale. All processes of the production of HFRs consist of *in situ* synthesis of melamine cyanurate in the presence of expandable graphite in dissolver, drying the product in a long gap mill (LGM) and packing into plastic bags. Syntheses were carried out according to the formulations shown in Table 1. Additives containing from 50 to 85 wt % of expandable graphite were obtained. The HFR production process was optimized by changing the speed of the stirrer in the dissolver, changing the speed of the rotor in the LGM, changing the temperature at the inlet and outlet of the LGM, as well as changing the quantity and the type of beaters (kind of blades) in the rotor inside the LGM. Two types of products were analyzed. The first of them was HFRs after synthesis in the dissolver and LGM drying, the second group was the additives after synthesis in the dissolver and conventional drying. In this latter group, the samples were separated by filtration and dried in a standard vacuum dryer.

The values of grain size for the prepared HFRs are listed in Table 2. Significant differences in grain size between individual samples (depending on the method of drying) were observed. In general, it can be stated that drying in the LGM significantly reduced the grain size of the final HFR products. However, depending on the drying parameters, described above, it is possible to reduce this phenomenon. It was possible to obtain HFR characteristics with very similar grain size regardless of the drying

method – 379 μm ( $d_{90}$ ) after drying in a standard vacuum dryer and 378 μm ( $d_{90}$ ) after LGM drying (Table 2, sample CMG15/85). The grain size of the products is dependent not only on the stirrer speed in the dissolver and the rotor speed in the LGM but also on the inlet and outlet temperature and the quantity and type of beaters in the rotor.

The expansions of the obtained additives are collected in Table 3. The value of the expansion depends on the method of obtaining additives (including the method of drying) and indirectly on their grain sizes. The additives with a smaller grain size are mostly characterized by lower expansion parameters. However, there are situations in which an additive after LGM, regardless of the grain size, is characterized by the smallest expansion (sample CMG15/85). The expansion of the final HFR depends not only on the particle dimension but also on other factors. As mentioned in the introduction, expandable graphite owes its properties due to the intercalation of sulfuric acid. The manner of the synthesis of HFRs in an aqueous environment (stirrer speed in dissolver, rotor speed in LGM, temperature of drying and other previously mentioned parameters) has presumably a direct impact on the reduction of the amount of sulfuric acid in the graphite thus reducing the expansion parameters of the final product.

### Flammability study of polymer compositions

The obtained additives have been used in the preparation of flame retardant polymeric compositions. Different types of HFR were introduced into polyester (P109), epoxide (EP5) and PS in an amount of 15 or 20 weight parts per 100 parts of polymer. Oxygen index values for the composition of EP5 or P109 with 20 weight parts of HFR per 100 parts of polymer (HFR dried using one of two methods) are listed in Table 4 together with values for neat polymers. The oxygen index decreased by 10 to 42 % for the samples with HFRs dried using the LGM in comparison with those containing HFRs dried directly after the dissolver. EP5 + CMG50/50 with HFR dried conventionally was characterized by the highest parameter of the oxygen index (33.4 %).

The highest oxygen index (39.8 %) for P109 compositions was observed for sample P109 + CMG25/75-2. The HFR used in this composition was separated by filtra-

**Table 3. The effect of drying method on expansion of additives (in %)**

Symbol of additives	Expansion, %	
	conventional drying	LGM drying
CMG25/75-1	112	40
CMG25/75-2	100	52
CMG25/75-3	80	64
CMG15/85	108	56
CMG20/80	136	68
CMG50/50	76	20



**Table 4.** The effect of drying method of HFR additives on oxygen index of composition EP5 or P109 with HFR

Symbol of composition	Oxygen index, %	
EP5	22.1	
P109	18.5	
	conventional drying	LGM drying
EP5+CMG25/75-1	27.6	24.8
EP5+CMG25/75-2	29.6	26.5
EP5+CMG25/75-3	31.9	27.9
EP5+CMG15/85	29.2	25.0
EP5+CMG20/80	28.5	25.7
EP5+CMG50/50	33.4	26.0
P109+CMG25/75-1	39.5	22.8
P109+CMG25/75-2	39.8	23.6
P109+CMG25/75-3	39.2	26.6
P109+CMG15/85	33.5	25.3
P109+CMG20/80	33.4	24.6
P109+CMG50/50	33.4	23.9

tion directly after the reaction and dried conventionally in a vacuum dryer. The polymers with significantly reduced flammability easily achieved the best parameters of vertical and horizontal flammability.

Polystyrene is one of the most flammable polymers. Taking into account the influence of drying on the effectiveness in reducing the flammability of the obtained HFRs, mainly the additives extracted by filtration directly after the reaction and dried in a vacuum dryer were used. The results of the flammability tests are listed in Table 5. The best parameters of vertical and horizontal flammability (V-0 and FH-1) were achieved for PS containing 15 weight parts per 100 parts of PS sample PS+CMG15/85. The use of other additives (CMG40/60, CMG25/75-1, CMG20/80, CMG50/50) requires the addition of larger quantities (20 weight parts per 100 parts of PS) to achieve the above mentioned parameters of flammability. The oxygen index of these compositions ranges

from 23.8 to 25.0 %. It should be taken into account that the growth of the limiting oxygen index in comparison with unmodified polystyrene is approximately 44 %. This growth is satisfactory in comparison with halogen-free flame retardants, which often must be used in much higher quantities to obtain similar results.

### Cone calorimetry studies

HFRs in compositions with polyester or epoxide were tested using the cone calorimeter method. Polymers including 20 weight parts of additives per 100 parts of polyester or epoxide were analyzed. Because of the influence of the drying method on the effectiveness of reducing the flammability of HFRs and on the value of the oxygen index, additives extracted by filtration directly after the reaction and dried in a vacuum dryer were used. Many parameters relating to the flammability of the samples were determined including: maximum and average heat release rate per unit area  $HRR_{max}$  and  $HRR_{avr}$  respectively, average specific extinction area ( $SEA_{avr}$ ), average mass loss rate ( $MLR_{avr}$ ), average emission of CO and CO<sub>2</sub> ( $CO_{avr}$  and  $CO_{2avr}$  respectively – both given as mass of combustion products resulting from 1 kg of combusted material). The measurements of the combustion behavior of the samples were performed with an external heat flux of 30 kW/m<sup>2</sup> or 50 kW/m<sup>2</sup>. The composites of P109 or EP5 with CMG25/75-3 and EP5 with CMG50/50 were tested. The results are listed in Table 6. The type of the HFR in the polymer compositions has a significant influence on the process of their combustion. In the case of the use of the additive CMG25/75-3, the  $HRR_{max}$  value decreased 83.7–88.6 % for P109 compositions and 76.1–76.7 % for EP5 compositions in comparison with the unmodified polymer. A beneficial action of additive CMG50/50 was also shown. The  $HRR_{max}$  decreased by 75.3–84.2 % for EP5 samples. In Figs. 1 and 2, showing heat release rate ( $HRR$ ) values plotted against time, large differences can be seen between the control sample of neat P109 or EP5 and compositions with HFRs. The main differences are noted between 50 and

**Table 5.** Examination of oxygen index and horizontal and vertical flammability of PS composition

Symbol of composition	Method of drying	HFR content, weight parts per 100 parts of PS	Flammability		
			oxygen index, %	horizontal flammability class	vertical flammability class
PS+CMG40/60	LGM	15	19,2	–	–
PS+CMG40/60		15	23,9	FH-1	V-1
		20	24,6	FH-1	V-0
PS+CMG15/85		15	23,8	FH-1	V-0
		20	25,0	FH-1	V-0
PS+CMG25/75-1	conventional	15	23,6	–	BK
		20	24,2	FH-1	V-0
PS+CMG20/80		15	24,0	–	BK
		20	24,0	FH-1	V-0
PS+CMG50/50		15	23,7	–	BK
		20	24,5	FH-1	V-0

Table 6. The results of cone calorimetry studies

External heat flux	Symbol of sample	$HRR_{max}$ kW/m	$HRR_{av}$ kW/m	$SEA_{av}$ m/kg	$MLR_{av}$ g/s	$CO_{av}$	$CO_{2av}$
30	P109	676	208	473	0.094	0.051	1.85
	P109+CMG25/75-3	77	46	105	0.021	0.095	1.69
	EP5	1035	247	487	0.099	0.062	1.77
	EP5+CMG25/75-3	248	96	–	–	–	–
	EP5+CMG50/50	256	95	2046	0.041	0.060	1.57
50	P109	696	236	464	0.117	0.056	1.65
	P109+CMG25/75-3	113	60	106	0.032	0.091	1.53
	EP5	1542	284	508	0.111	–	1.87
	EP5+CMG25/75-3	359	82	236	0.032	–	1.7613
	EP5+CMG50/50	243	101	227	0.040	–	1.76

300 s of burning time. In this time range, the effect of the used additives is most noticeable. Burning out, they form a charred layer that isolates the flammable polymer from the environment. In the case of EP5 addition of CMG50/50 proved to be slightly better – we can observe 7.5 % better reduction of  $HRR_{max}$  in comparison with CMG25/75-3 (Fig. 2, 50 kW/m<sup>2</sup>).

$SEA_{av}$  is the parameter, which can be indirectly taken as a measure of the smoke emitted from the burning polymer. This describes the smoke emission process. The fumes, in case of fire, are even more dangerous than the high temperatures. They limit visibility at the fire location and mostly contain toxic gaseous substances harmful to people. As is clear from the research, HFR additives, used for the prep-

aration of the polymer compositions, reduce the average specific extinction area in comparison with the unmodified polyester or epoxide. In the case of the P109 composition, the reduction of  $SEA_{av}$  reached 77.3–77.7 % (CMG25/75-3 additive) and in the case of EP5 53.4 % (CMG25/75-3 additive) or 58.1–55.3 % (CMG50/50 additive, Table 6).

A second parameter, which describes the process of combustion, is  $MLR_{av}$  and it is affected by the addition of HFRs to the polymer. The use of CMG25/75-3 for modification of P109 decreased the  $MLR_{av}$  of compositions by 72.6–77.2 % in comparison with the unmodified polymer and in the case of EP5 with the same additive by 71.5 %. Modification of EP5 by the CMG50/50 additive resulted in the reduction of  $MLR_{av}$  by 58.2–63.8 % (Table 6).

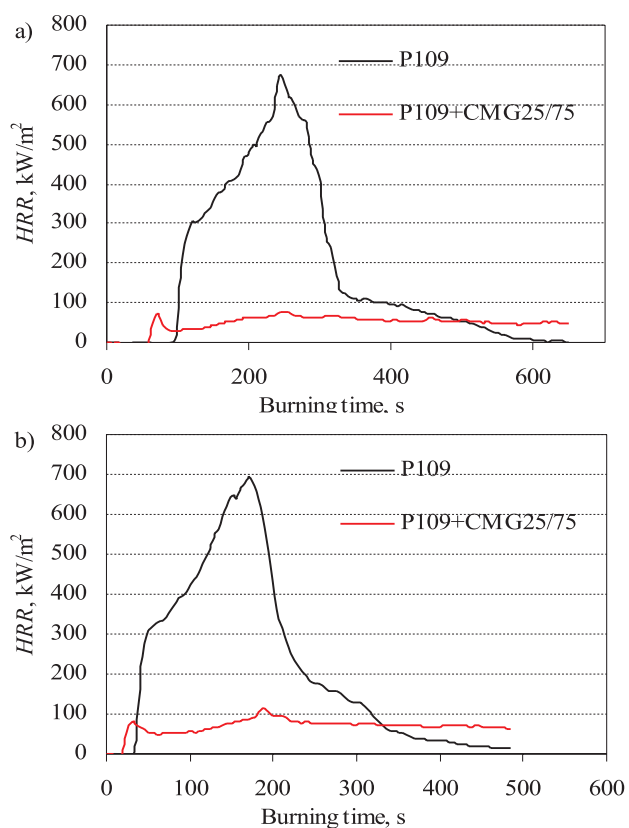


Fig. 1. Heat release rate per unit area ( $HRR$ ) as a function of time for polyester samples, at an external heat flux of: a) 30 kW/m<sup>2</sup>, b) 50 kW/m<sup>2</sup>

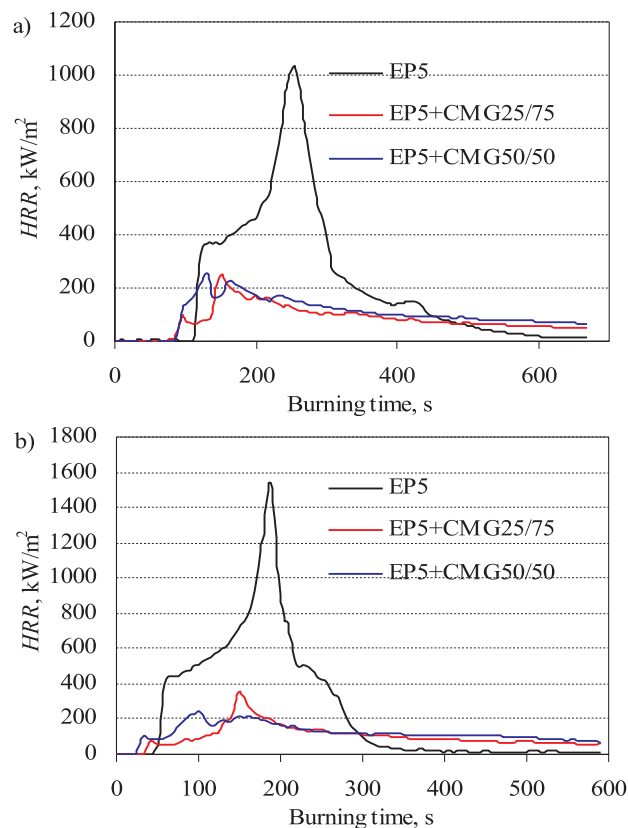


Fig. 2. Heat release rate per unit area ( $HRR$ ) as a function of time for epoxide samples, at an external heat flux of: a) 30 kW/m<sup>2</sup>, b) 50 kW/m<sup>2</sup>

The impact of HFRs on  $CO_{av}$  and  $CO_{2av}$  is also very interesting. The presence of most of the flame retardants in the polymers cause a general increase in the CO content in the fumes. On the other hand, HFRs have virtually no effect on  $CO_2$  emissions (Table 6).

It is clear from the above analysis that HFRs have a significant influence on the process of combustion of the polyester, the epoxide or polystyrene compositions.

### CONCLUSION

HFRs (expandable graphite modified by melamine cyanurate) with different grain size, were obtained by syntheses on a semi-industrial scale. These additives were introduced as flame retardants into the polyester, the epoxide or polystyrene. The flammability of polymer compositions – oxygen index, vertical and horizontal flammability, cone calorimetry studies – were investigated. The relationships between the production parameters, the grain size, expansion and the effectiveness of additives as flame retardants for different plastics have been found.

Depending on the HFR production conditions, products with different effectiveness were obtained. A key step was the drying method and parameters. It was possible to obtain additives with a grain size from 148 to 507  $\mu\text{m}$  ( $d_{90}$ ) and expansion from 20 to 136 %. The grain size and expansion have a direct impact on the flammability of the compositions of HFRs with different polymers. The oxygen index of P109 with the same HFR, but dried in a different way, ranged from 22.8 to 39.8 %. An analogous situation took place with EP5 – the oxygen index ranged from 24.8 to 31.9 %. PS with additives characterized by expansion parameters higher than 100 % reached flammability V-0 (vertical flammability class), FH-1 (horizontal flammability class) and oxygen index 25 %. On the other hand, PS compositions with additives characterized by too small expansion parameters could not be classified according to the vertical and horizontal flammability standard.

The flame retardant effect is greater when the grain size is larger and the tendency of the additives to expand is greater. Excessive fragmentation of the HFRs in the course of their production causes a reduction in the expansion properties of expandable graphite contained therein. This phenomenon is particularly evident during the second stage of production when the product is dried in the LGM. It can be concluded that the manner of production of HFRs has a significant influence on the properties of expandable graphite contained therein and thus on the flame retardant effectiveness of HFRs in their final compositions with polyester, epoxide or polystyrene.

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