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Polystyrene with reduced flammability containing halogen-free flame retardants

Summary — Additives that reduce the flammability of plastics were synthesized by a modification of expandable graphite (EG) using melamine salts (phosphate or cyanurate). Polystyrene (PS) was prepared by suspension polymerization of styrene in the presence of the obtained EG/melamine salt compounds. The resulting PS composites achieved horizontal FH-1 and vertical V-0 flammability ratings in the UL-94 burning test and the limiting oxygen index values increased by over 50 % compared with non-modified polystyrene. An advantageous effect of EG/melamine salt additives on the suppression of polystyrene combustion processes was also indicated by cone calorimetry and thermogravimetric analysis.

Keywords: halogen-free flame retardants, polystyrene of limited flammability, expandable graphite, melamine cyanurate, melamine phosphate.

POLISTYREN O OGRANICZONEJ PALNOŚCI ZAWIERAJĄCY BEZHALOGENOWE ANTYPIRENY

Streszczenie — W wyniku modyfikacji grafitu solami melaminy (cyjanuran lub fosforan) otrzymano bezhalogenowe dodatki ograniczające palność tworzyw polimerowych. Przeprowadzono syntezy polistyrenu metodą polimeryzacji suspensyjnej styrenu, w obecności uzyskanych dodatków grafitowych. Wytworzone produkty charakteryzowały się klasą palności poziomej FH-1, pionowej V-0 (UL-94) oraz wskaźnikiem tlenowym o wartości większej o ponad 50 % od wartości *OI* niemodyfikowanego polistyrenu. Korzystny wpływ dodatków grafitowych na ograniczenie procesu spalania polistyrenu wykazano w badaniach termograwimetrycznych oraz przy użyciu kalorymetru stożkowego.

Słowa kluczowe: bezhalogenowe dodatki ograniczające palność, polistyren o ograniczonej palności, grafit ekspandujący, cyjanuran melaminy, fosforan melaminy.

INTRODUCTION

In most practical applications of plastic materials restricted flammability is required. To achieve this goal, flame retardant (FR) agents have been introduced into the plastics to inhibit the polymer pyrolysis processes [1]. Most often aluminum or magnesium hydroxide, bromine, chlorine and phosphorus compounds, oxide of antimony and other metals as well as tin, zinc, boron, molybdenum and nitrogen compounds have been used for this purpose.

Halogen containing FR agents are often used as a additives for plastics. A significant disadvantage of halogen additives is the emission of very toxic and corrosive fumes from the fire area to the environment during combustion. Therefore, their use is gradually limited to ensure environmental protection. On the other hand, non-halogen FR additives are usually less efficient in decreasing the flammability. Consequently, they have to be used in greater amounts, which may adversely affect the mechanical properties of a polymeric material.

The action of graphite as a FR agent in polymers consists mainly in the formation of carbonaceous barrier which prevents access of the flame and oxygen to the polymeric material. This effect is achieved by the use of the so called expandable graphite (EG), which swells up on heating to several hundred percent of its volume with formation of a foamed insulation layer protecting the burning polymer. EG is employed to reduce flammability of various plastic materials, usually in combination with other FR additives [2—4], including halogen — containing compounds, *e.g.* decabromodiphenyl ethane [5] and it plays a supporting role in fire retardancy as an additional filler improving the insulation properties of the plastic [6—11]. However, such solutions are not environmen-

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[*)] Author for correspondence; e-mail: piotr.jankowski@ichp.pl tally friendly because of the presence of undesirable halogen compounds.

Mixtures of EG with melamine salts, like cyanurate (MC) and phosphate (MP) were used as additives supporting other FR agents [12]. Other examples are plastics with EG added to primary fire retardants such as phosphorus [13—25] nitrogen and boron compounds [26]. EG and MC were applied as FR additives in coating compositions for plastic fibers [27]. Expandable graphite compounds intercalated with metal salts can be used along with MC and MP to improve the fire properties of the coatings for various substrates [28]. Coatings containing, among others, graphite compound and MC can be applied to steel, wood and plastic substrates [29]. Graphite and melamine salts were also components for the production of decorative materials [30]. In the case of FR agents prepared by condensation of the derivatives of urea, cyanic acid, isocyanic acid and other organic compounds [31—35], graphite together with MC can be used as fillers. The composition obtained in this way can be applied to reduce the flammability of various plastic materials like polyurethanes, polyesters and epoxides.

Polystyrene (PS) is one of the most easily flammable polymers. Currently, the most commonly practised method to decrease PS flammability is the use of additives based on organic halogen derivatives [36—41]. They are mainly bromine-containing compounds, either aromatic like bromodiphenyl or bromodibenzyl ether [42] or aliphatic such as hexabromocyclododecane [40, 43].

Various graphite compounds were also applied as FR additives for polystyrene. They were introduced to the polymer during the reaction of cationic [44] or anionic [45] polymerization or compounded with the previously prepared polymer [46]. Graphite intercalated with potassium salts was used to prepare PS/graphite nanocomposites [47, 48].

Graphite additives can perform various functions. Zheng *et al.* carried out the polymerization of styrene and acrylonitrile in the presence of exfoliated graphite prepared by oxidation of natural graphite flakes with subsequent thermal expansion at 600 °C. The resulting composite showed relatively high electrical conductivity [49].

The results of investigations on PS/graphite composites emphasize the increased thermal insulation [50] and electricity conduction properties of these materials, however, they do not indicate a significant increase of thermal stability and other parameters related to fire resistance [51, 52]. In other cases the graphite introduced into polystyrene in aim to improve heat-insulating properties did not reduce sufficiently the flammability of polymer and the addition of halogen-containing FR agents was necessary [53, 54].

On the other hand, some authors reported the possibility of more remarkable improvement in fire properties of PS by using graphite compounds. Their conclusions were based on cone calorimetry and thermogravimetry analysis [45—47]. Research group from University of Science and Technology of China prepared polystyrene/graphite nanocomposite with increased thermal stability by emulsion polymerization of styrene carried out in the presence of graphite oxide (GO). TGA analysis showed that the presence of intercalated and exfoliated GO particles increased the char residue of the PS matrix [55]. Efficiency of graphite as FR additive for polystyrene can be enhanced by its combination with some phosphorus compounds [56].

The investigations on fire properties of PS/graphite composites were also conducted at Industrial Chemistry Research Institute in Warsaw [57, 58]. A method of reducing the flammability of PS synthesized in aqueous suspension polymerization process was developed, by using *in situ* addition of organic phosphorus compounds or their composition with organically modified aluminosilicates of montmorillonite type [59, 60]. Further studies are needed to increase an efficiency of expandable graphite additives and to achieve an appropriate fire retarding effect in polystyrene without the necessity to use high additive loadings.

The aim of present work was to investigate the efficiency of expandable graphite modified with selected melamine salts as FR additives, which could be introduced during the suspension polymerization of styrene. Besides fire retardancy action such EG/melamine salt compounds were expected to form more homogeneous compositions with the polymer than EG itself. Additionally in an industrial practice it is more favorable to use one efficient FR agent instead of the mixture of components.

EXPERIMENTAL

Materials

The reagents used for modification of expandable graphite (EG 290, supplied by Sinograf SA) were: melamine (Aldrich), cyanuric acid (Aldrich), ortophosphoric acid (POCh, 85 %). Polystyrene prepared using styrene (POCh, purified by destillation under reduced pressure) as a monomer, and benzoyl peroxide (Aldrich, white crystals) as a polymerization catalyst. For the stabilization of suspensions polyvinyl alcohol (PVA, molecular weight 35 000—40 000, produced by Shin-Etsu Chemical Co., Ltd.), bentonite (KBS Kremnica) and gelatin (BZŻ Sp. z o.o.) were used.

Syntheses

Modification of expandable graphite with melamine cyanurate

Into a 250 cm^3 reactor, equipped with mechanical stirrer, heating mantle, temperature controller, reflux condenser and inert gas inlet, 174.00 g of demineralized water was placed. Then, with vigorous stirring (400 rpm), 3.21 g (0,026 mol) melamine and 3.31 g (0,026 mol) cyanuric acid were added to give an aqueous dispersion, followed by the addition of 19.57 g expandable graphite (EG). The synthesis was carried out at ambient temperature for 1 hour and at 90 °C for 4 hours. The reaction mixture was then cooled to ambient temperature and the resulting product was separated by filtration and dried at 30 °C.

Syntheses were performed at various EG:MC ratio, while maintaining the constant weight ratio of all the reagents to water of 1 to 6.7. The obtained products (EG/MC compounds) were in the form of grey particles containing from 75 to 85 % graphite.

Modification of expandable graphite with melamine phosphate

Into a 250 cm^3 reactor, equipped with mechanical stirrer, heating mantle, temperature controller, reflux condenser and inert gas inlet, 187.30 g of demineralized water was placed. Then, with vigorous stirring (400 rpm), 8.65 g (0.069 mol) melamine was added to give an aqueous dispersion followed by the addition of 46.13 g expandable graphite (EG). After heating to 80 °C, 7.92 g (0.069 mol) 85 % ortophosphoric acid was added dropwise. The synthesis was carried out at 90 °C for 4 hours. The reaction mixture was then cooled to ambient temperature and the resulting product was separated by filtration and dried at 30 °C.

Syntheses were performed at various EG:MP ratio, while maintaining the constant weight ratio of all the reagents to water of 1 to 3. The obtained products (EG/MP compounds) were in the form of grey particles containing from 15 to 85 % graphite.

Suspension polymerization of styrene in the presence of the expandable graphite modified with melamine salts

The synthesis was carried out in an aqueous suspension stabilized with poly(vinyl alcohol) (PVA), using 700 cm^3 pressure reactor Arter-Variator VMSRD 30F, equipped with mechanical stirrer, cooling-heating jacket, inert gas inlet and manometer. Demineralized water (337.5 g) and 0.24 g PVA were placed in the reactor. Then, with vigorous stirring, 112.5 g styrene was added, followed by the addition of EG/MC compound in an amount between 16.9 g and 22.5 g. Benzoyl peroxide was used as a polymerization initiator. The reaction was carried out at 90 °C for 8 hours. The obtained polymer in the form of grey pellets was filtered-off and dried at 30 °C. The same procedure was applied for the synthesis of polystyrene in the presence of EG/MP compound in an amount between 12.4 g and 22.5 g or non-modified EG. As a suspension stabilizer, bentonite/gelatin system can be used instead of PVA. The as prepared polystyrene compositions contained 10 to 20 weight parts of graphite additives per 100 parts of polystyrene.

Preparation of polystyrene samples

Polystyrene pellets were pressed at temperatures between 170 and 190 °C for 4 min in a hydraulic press. The obtained plates of dimensions 100 × 160 × 4 mm were used to cut out the specimens for flammability testing according to the relevant standards.

Methods of testing

— The flammability properties of the prepared PS composites were examined by using vertical and horizontal burning tests (UL-94) and limiting oxygen index according to ASTM D 2863-97. The oxygen index (*OI*) is defined as a lowest oxygen concentration expressed as volume percent in a mixture of oxygen and nitrogen that will support combustion of the sample under equilibrium conditions of candle like burning. At lower oxygen concentrations the examined material extinguishes when the flame source is removed. During the horizontal and vertical flame test, a specimen marked with two lines is ignited with a gas burner. Then, the flame spreading rate between two marks is determined. The results are classified according to vertical burning test from FH-1 (the lowest flammability) to FH-3 and according to horizontal burning test from V-0 (the lowest flammability) to V-2. The most flammable specimens may not reach any horizontal burning classification.

— The measurements of the combustion behaviours of the samples were performed according to ISO 5660-2002 using the cone calorimeter (Fire Testing Technology) at an external heat flux of 50 kW/m^2. The combustion reaction was initiated by ignition with spark igniter. The specimens were placed in a horizontal orientation in relation to the radiator.

— Thermogravimetric analyses were performed using Mettler Toledo equipment TGA/SDTA851e. The samples (10 ± 2 mg) were placed in a platinum crucible of 0.15 cm^3 volume. The measurements were carried out in the air atmosphere.

All the analytical work was done at the Industrial Chemistry Research Institute in Warsaw except the flammability measurements on a cone calorimeter, that were performed at The Main School of Fire Service in Warsaw.

RESULTS AND DISCUSSION

Modification of graphite

Expandable graphite (EG) is commonly produced by intercalation of sulphuric acid into graphite in the presence of strong oxidizing agent. The product is mainly composed of graphite sulphate solvated by an excess of the acid, of general formula $C_{24n}^{+}\ HSO_4^{-} \cdot mH_2SO_4$ [61]. On heating above an onset temperature (between 100 and 200 °C), EG decomposes according to the reaction [62]:

$$C + 2\,H_2SO_4 \rightarrow CO_2 + 2\,H_2O + 2\,SO_2$$

In case of rapid heating (such as in a fire), the volatile products of EG decomposition cause the graphite layers to expand with formation of a foamed char layer, which acts as a physical barrier to heat and mass transfer between the flame and the burning material. This so called intumescent effect is responsible for the fire retardant action of EG filler in polymers.

In our study, expandable graphite was additionally modified using melamine salts: cyanurate (MC) and phosphate (MP). The modification was carried out by *in situ* synthesis of the salt in an aqueous suspension of EG particles. The most important problem that occur during the synthesis is an increase in the viscosity of reaction medium at the beginning of the process. This causes overheating of the reaction mixture. We solved this problem by optimizing the concentration of solid parts in the aqueous dispersion. Additionally, the heating of the reaction medium was delayed until the reaction mixture became homogeneous. The process was conducted at various weight ratio of EG to melamine salts (Table 1) and changing the water content in aim to maintain the viscosity of reaction system at the level which enables the reaction to proceed.

Table 1. Expandable graphites modified with melamine salts (cyanurate MC and phosphate MP)

No.	Symbol	Composition, wt. %
1	MG-2	graphite EG-290, 75 MC, 25
2	MG-5	graphite EG-290, 80 MC, 20
3	MG-6	graphite EG-290, 85 MC, 15
4	FMG-1	graphite EG-290, 70 MP, 30
5	FMG-2	graphite EG-290, 50 MP, 50
6	FMG-3	graphite EG-290, 85 MP, 15
7	FMG-4	graphite EG-290, 75 MP, 25
8	FMG-5	graphite EG-290, 15 MP, 85

Finally, the optimal total concentration of solid parts (EG, melamine salts) in aqueous dispersions used for EG modification was specified at the level of 13 % for modification by MC salt and 25 % for modification by MP salt.

Synthesis of polystyrene by suspension polymerization with the use of flame retardant additives

The procedure of suspension polymerization of styrene in the presence of FR additives was optimized by selecting the appropriate process parameters such as: the ratio of aqueous to organic phase, type and amount of suspension stabilizer, type and amount of FR agent and time of its addition to the reaction mixture.

The suspension stabilizer prevents coalescence of styrene droplets and the formed polystyrene beads. For this purpose, polyvinyl alcohol, which is an efficient stabilizing agent or bentonite/gelatin system, commonly used in the industrial practice, were employed. The optimal suspension compositions were determined as: styrene to water weight ratio of 1 to 3 with PVA in the amount of 0.07 % by weight of water or styrene to water weight ratio of 1.0 to 2.5—3.0 with 0.07—0.10 % bentonite and 0.2—0.3 % gelatin by weight of water.

The styrene and polymerization initiator (benzoyl peroxide, 0.5 % by weight of styrene monomer) were added with vigorous stirring to water containing the suspension stabilizing agent. Then, after heating to a predetermined temperature, stirring was continued and suitable amounts of EG/melamine salt compounds were introduced into the reaction system. The polymerization carried out at 90 °C for eight hours gave polystyrene pellets filled with graphite additives. The obtained granulate was then pressed and cut into the specimens for examination of horizontal and vertical flammability, limiting oxygen index and analysis of the combustion behaviour in cone calorimeter.

As it was observed during the polymerization process and by assessment of the quality of the produced PS specimens, the EG/melamine salt compounds are more homogeneously dispersed in the polymer than the non-modified EG.

The methods of preparation of halogen-free fire retardants (EG/melamine salt compounds) and a method of introduction them into polystyrene are a subjects of patent applications [63, 64].

Flammability study of the modified polystyrenes

Polystyrene synthesized in the presence of graphite additives was tested for flammability categories in the horizontal and vertical position (UL-94) and limiting oxygen index (ASTM D 2863-97) (Table 2).

The EG/melamine salt compounds introduced into polystyrene are suitable to achieve the required level of fire retardancy in most of practical applications. In some cases the maximum FH-1 and V-0 classifications were obtained in UL-94 flammability test, while usually they are difficult to be reached without the addition of halogen-containing FR agents to polystyrene. The maximum *OI* value of 27.1 % was obtained, which is an increase by 56 % compared with non-modified PS.

The effectiveness in reducing PS flammability was influenced not only by the content of EG/melamine salt compound in polymer, but also by the weight ratio of graphite to melamine salt. The most efficient were additives: MG-2 — graphite (75 %) modified with MC (25 %)

in the amount of 15—20 weight parts per 100 parts of polystyrene (Table 2, pos. 5, 6), MG-5 — graphite (80 %) modified with MC (20 %) in the amount of 15 weight parts per 100 parts of polystyrene (Table 2, pos. 7), MG-6 — graphite (85 %) modified with MC (15 %) in the amount of 15 weight parts per 100 parts of polystyrene (Table 2, pos. 8), FMG-1 — graphite (70 %) modified with MP (30 %) in the amount of 15 weight parts per 100 parts of polystyrene (Table 2, pos. 10), FMG-3 — graphite (85 %) modified with MP (15 %) in the amount of 15 weight parts per 100 parts of polystyrene (Table 2, pos. 14), FMG-4 — graphite (75 %) modified with MP (25 %) in the amount of 20 weight parts per 100 parts of polystyrene (Table 2, pos. 17).

Table 2. Examination of horizontal and vertical flammability

No.	Additive designation	Additive content (parts per 100 parts of PS by weight)	Oxygen index %	Horizontal flammability class	Vertical flammability class
1	—	—	17.4	FH-3/18	*)
2	EG-290	10	—	FH-1	*)
3	EG-290	15	—	FH-1	V-1
4	EG-290	20	—	FH-1	V-0
5	MG-2	15	24.8	FH-1	V-1/V-0
6	MG-2	20	26.1	FH-1	V-0
7	MG-5	15	25.1	—	V-0
8	MG-6	15	23.9	—	V-0
9	FM	15	19.7	*)	*)
10	FMG-1	15	26.1	FH-1	V-1/V-0
11	FMG-2	11	24.6	FH-1	*)
12	FMG-2	15	25.6	FH-1	*)
13	FMG-3	12	—	FH-1	*)
14	FMG-3	15	24.5	FH-1	V-0
15	FMG-4	11	24.2	—	*)
16	FMG-4	15	25.7	FH-1	V-1
17	FMG-4	20	27.1	FH-1	V-0
18	FMG-5	15	20.1	FH-3/11	*)

*) Non classified.

For a more detailed assessment of the examined PS composites, the notation V-1/V-0 was introduced, which denotes the specimens classified near the boundary between V-1 and V-0 categories. Due to a specific behaviour of polystyrene (burning is accompanied by melting of polymer, which complicates the oxygen index measurements) the determined *OI* values have only indicative character.

Cone calorimetry studies

A range of parameters corresponding to the combustion of the specimens were determined including among others: heat release rate per unit area (*HRR*), maximum heat release rate per unit area (HRR_{max}), mass loss rate (*MLR*), total heat released (*THR*), specific extinction area (*SEA*), total smoke released (*TSR*).

The obtained results allow to conclude that the EG/melamine salt compounds have a significant influence on the process of combustion of polystyrene composites. It was clearly demonstrated in the measurements of the heat released by a burning specimen expressed as the amount of energy per exposed surface area. The maximum value of this parameter (HRR_{max}) was decreased by 84 % in the PS containing 20 wt. % EG/MP compound (FMG-4/20) in comparison with the non-modified polystyrene (Fig. 1).

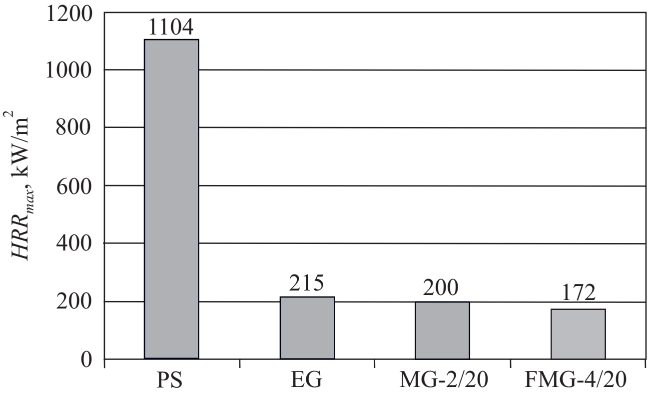

Fig. 1. Maximum heat release rate per unit area, PS — non-modified polystyrene, EG — polystyrene with expandable graphite, MG-2/20 — polystyrene with MG-2, FMG-4/20 — polystyrene with FMG-4

On the graphs showing *HRR* values plotted against time (Fig. 2) marked differences can be seen between the control sample of neat polystyrene (PS) and PS composites with expandable graphite (EG) or EG/melamine salt compounds (MG-2/20 and FMG-4/20). All FR additives were used in an amount 20 weight parts per 100 parts of polystyrene.

Substantial differences are noticed between 50 and 250 seconds of burning time. The combustion characteristics is dependent on the type of additive. PS modified with expandable graphite alone (sample EG) burns with a higher heat release rate than PS with EG/melamine salt compounds. This can be seen both in the graph of HRR_{max} (Fig. 1) and from the plot of HRR against time (Fig. 2). The modification of PS results in about 81 % decrease in average *HRR* value as can be observed in the Fig. 3.

The emission of smoke is another important problem, apart from the flammability, arising from the combustion of plastics. The smoke not only inhibits rescue action due to a limited visibility but, first of all, it contains toxic gaseous substances, which are harmful to the people in the fire area. Most of the victims killed by fire die in a result of smoke poisoning. Because of that, among many

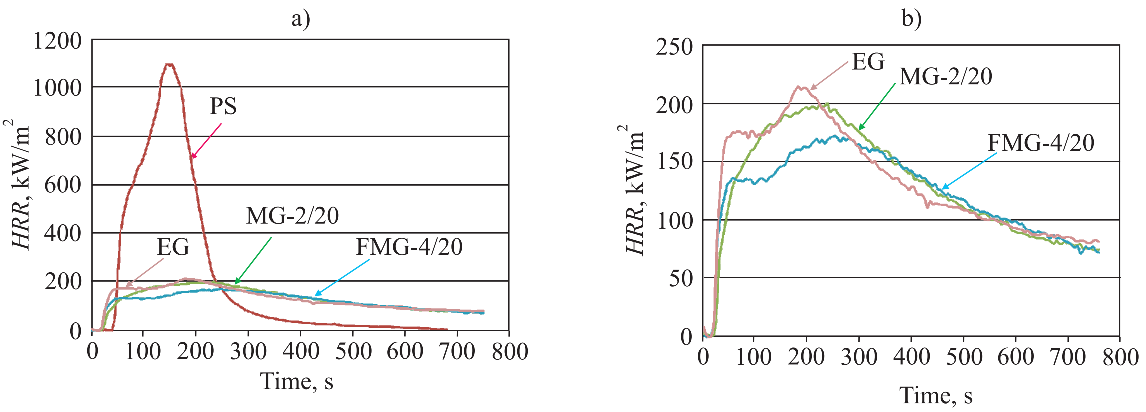

Fig. 2. Heat release rate per unit area as a function of time, with and without the control PS sample: PS — non-modified polystyrene, MG-2/20 — polystyrene with MG-2, FMG-4/20 — polystyrene with FMG-4, EG — polystyrene with expandable graphite

parameters of material combustion, which can be determined using the cone calorimeter method, the data describing the smoke produced by a burning sample are particularly important, such as the total smoke released (TSR), total smoke production (TSP), specific extinction area SEA_{av} — which can be indirectly taken as a measure of smoke emitted from the burning sample. All these parameters describe the same process — smoke emission — therefore one of them was discussed. Analyzed SEA_{av}, it can be clearly seen that PS containing expandable graphite releases much less smoke during the combustion. This effect is further enhanced when the compounds of EG with melamine phosphate salts are used as FR agents (FMG-4/20) (Fig. 4). For PS containing EG/MP compound the specific extinction area was decreased by 62 % in relation to the non-modified polystyrene. Summing up, all the parameters related to the smoke (SEA_{av}, TSR, TSP) were significantly improved as a result of the addition of expandable graphite and its compounds with melamine salts.

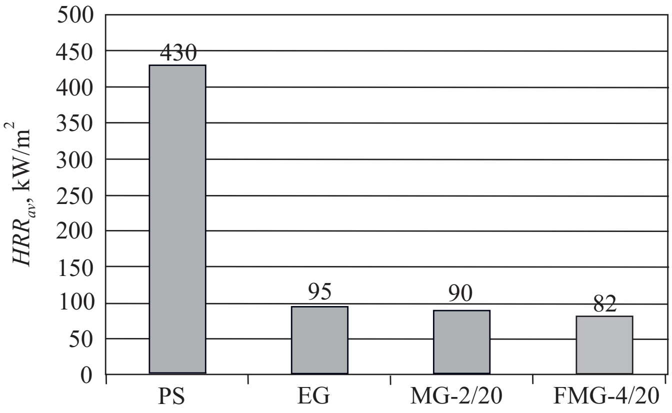

Fig. 3. Average heat release rate per unit area, PS — non-modified polystyrene, EG — polystyrene with expandable graphite, MG-2/20 — polystyrene with MG-2, FMG-4/20 — polystyrene with FMG-4

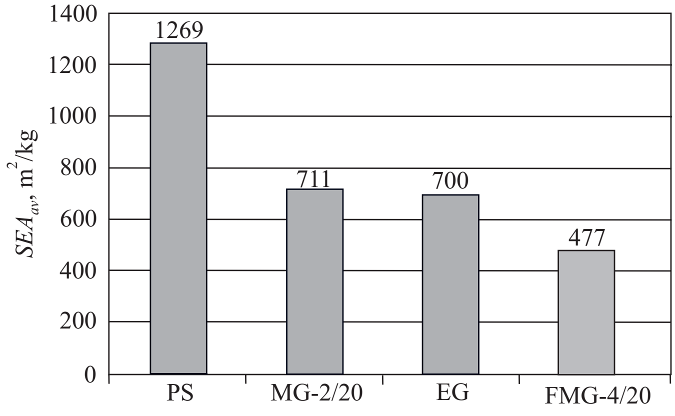

Fig. 4. Specific extinction area, PS — non-modified polystyrene, MG-2/20 — polystyrene with MG-2, EG — polystyrene with expandable graphite, FMG-4/20 — polystyrene with FMG-4

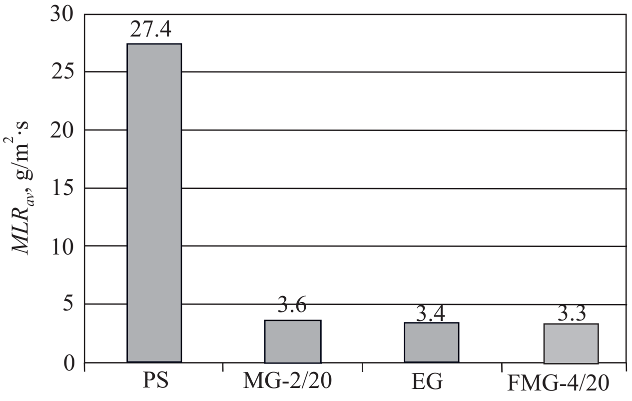

Fig. 5. Average mass loss rate, PS — non-modified polystyrene, FMG-4/20 — polystyrene with FMG-4, EG — polystyrene with expandable graphite, MG-2/20 — polystyrene with MG-2

Another example of the significant influence of the modified graphite additives on the burning properties of polystyrene can be drawn from the analysis of an average mass loss rate MLR_{av}. For the compositions of PS with EG and it compounds with melamine salts the MLR_{av} value is several times lower than that of the control sample of neat PS (Fig. 5).

Thermogravimetric study

The non-modified polystyrene and the selected composites of PS with the EG/melamine salt compounds were investigated by means of thermogravimetric analysis. For all samples the process of thermal decomposition begins slightly above 200 °C (Fig. 6). At the temperatures above 300 °C the differences in weight loss from various samples appear and they become more distinct with an increasing temperature. The non-modified polystyrene loses 98 % of its weight at 450 °C due to almost complete combustion in air atmosphere. According to expectations, polystyrene with the compound of EG (80 wt. %) and MC (20 wt. %) used in an amount of 15 weight parts per 100 parts of PS (MG-5/15), has a lower weight loss (84 %) at the same temperature. This is partly due to high thermal stability of EG component, which loses only about 25 % of its weight at 450 °C. For PS containing the compound of EG (85 wt. %) and MP (15 wt. %) used in the amount of 15 weight parts per 100 parts of PS and denoted as FMG-3/15, a slightly higher weight loss (87 %) was observed. The same weight loss at 450 °C was obtained for PS modified with the compound of EG (75 wt. %) and MP (25 wt. %) used in the amount of 20 weight parts per 100 parts of PS and denoted as FMG-4/20. All the PS composites modified with EG/melamine salt additives yield about 10 wt. % of char residue at 600 °C, which also may contribute to their fire retardant action shown on the basis of flammability studies.

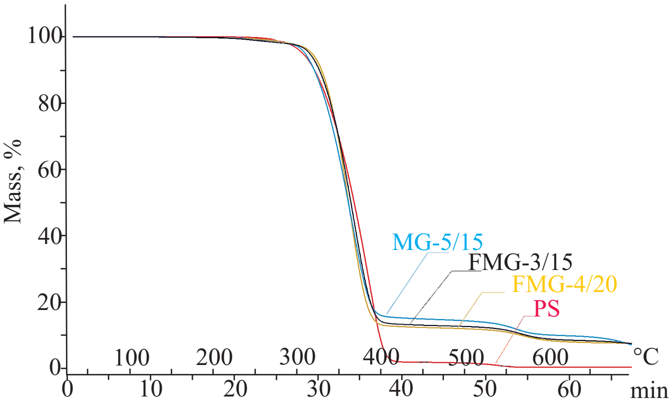

Fig. 6. Thermogravimetric analysis of PS with and without graphite additives

CONCLUSIONS

A method of preparation of halogen-free fire retardant additives for polystyrene was developed using *in situ* synthesis of melamine salts (cyanurate or phosphate) in the presence of expandable graphite. The obtained products with various compositions were introduced as FR additives during the suspension polymerization of styrene. The polymerization was optimized by changing the process parameters such as: the ratio of aqueous to organic phase, type and amount of suspension stabilizer [poly(vinyl alcohol) or bentonite/gelatin system], type and amount of FR additive and time of its addition to the reaction mixture. The flammability properties of the obtained PS composites were investigated.

The maximum FH-1 and V-0 classifications were obtained using 15 weight parts of the additives per 100 parts of polystyrene (*OI* values increased by about 44 % for EG/MC compound and 50 % for EG/MP compound compared to non-modified polystyrene). When 20 weight parts of the additive per 100 parts of polystyrene was used, the *OI* increased by about 50 % for EG/MC compound and 56 % for EG/MP compound.

Futhermore, the fire performance of modified polystyrenes were studied using cone calorimetry. The experiments demonstrated a beneficial effect of the EG/melamine salt additives on the suppression of polystyrene combustion processes and the fire characteristics (reduction in the heat release rate per unit area, decrease in the smoke emission and average weight loss). The selected flame retarded PS composites were investigated by means of thermogravimetric analysis and their thermal stability compared to that of non-modified PS.

In conclusion, the presented results show that expandable graphite modified with melamine salts act as efficient flame retardant additives in polystyrene composites. The additives can be introduced into polystyrene during the polymerization of styrene carried out in an aqueous suspension, which is particularly important for industrial practice.

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