

MICHAŁ KĘDZIERSKI^{*)}, PIOTR JANKOWSKI, GRAŻYNA JAWORSKA, ANNA NISKA

Industrial Chemistry Research Institute
Department of Polyesters, Epoxide Resins and Polyurethanes
ul. Rydygiera 8, 01-793 Warsaw, Poland

Graphite oxide as an intumescent flame retardant for polystyrene

Summary — In this work the possibility to apply graphite oxide (GO) as an intumescent flame retardant added *in situ* during suspension polymerization of styrene was studied. Synthesis of GO was carried out starting from natural flake graphites with different carbon content and particle size (between 45 and 500 μm). The obtained products were examined using elemental and scanning electron microscopy (SEM) analysis, Fourier transform infrared spectroscopy (FT-IR) as well as X-ray powder diffractometry (XRD). Thermal stability and expansion properties of GO were also investigated. It was stated that with an increase in particle size GO exhibited a lower degree of oxidation while the temperature of maximum decomposition rate increased. The highest expansion volume at 600 °C was observed for GO prepared from graphite with large-sized plates (300 and 500 μm). In order to prevent the dispersion of hydrophilic GO in an aqueous phase during the polymerization of styrene, GO was modified with organofunctional silane. Polystyrene with added GO (15 wt. %) reached HF-1 rating in the UL 94 horizontal burning test, however it failed to pass the required vertical flame test. The modification with melamine-formaldehyde resin (MF) resulted in an increase of GO thermal stability. Polystyrene with 15 wt. % of GO-MF additive obtained maximum ratings HF-1 and V-O in the UL 94 flame test. An attention should be paid to safe handling of GO which, although stable at ambient conditions, may undergo highly exothermic decomposition, *e.g.* when subjected to mechanical impact at moderately elevated temperature.

Keywords: graphite oxide, thermal expansion, intumescent flame retardants, polystyrene.

TLENEK GRAFITU JAKO PĘCZNIEJĄCY ANTYPIREN STOSOWANY DO POLISTYRENU

Streszczenie — W ramach pracy badano możliwości wykorzystania tlenku grafitu (GO) jako antypirenu pęczniejącego dodawanego *in situ* w procesie syntezy polistyrenu suspensyjnego. Przeprowadzono syntezę GO wychodząc z naturalnych grafitów płatkowych różniących się zawartością węgla oraz wielkością cząstek (od 45 do 500 μm). Uzyskane produkty analizowano metodami analizy elementarnej, skaningowej mikroskopii elektronowej (SEM), spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) oraz rentgenowskiej dyfraktometrii proszkowej (XRD). Wykonano również badania stabilności termicznej metodą termogravimetrii oraz badanie zdolności ekspandujących otrzymanych tlenków grafitu. Stwierdzono, że ze wzrostem wielkości cząstek grafitu zmniejsza się stopień utlenienia GO, natomiast wzrasta temperatura maksymalnej szybkości rozkładu. Największe objętości ekspansji w temp. 600 °C wykazywały tlenki otrzymane z grafitów o dużych rozmiarach płatków (300 i 500 μm). Aby w trakcie polimeryzacji styrenu zapobiec dyspersji hydrofilowego GO w fazie wodnej, poddano go modyfikacji organofunkcyjnym silanem. Polistyren z dodatkiem 15 % mas. GO osiągnął klasę HF-1 w teście poziomego palenia się UL 94, jednak nie spełnił wymaganych kryteriów palności pionowej. Modyfikacja GO żywicą melaminoformaldehydową (MF) prowadziła do zwiększenia stabilności termicznej GO, a polistyren z dodatkiem 15 % mas. kompozycji GO-MF osiągał maksymalne kategorie HF-1 i V-0 w teście palności UL 94. Należy zwrócić uwagę na kwestię bezpieczeństwa stosowania GO, który jest stabilny w temperaturze pokojowej, jednak w wyniku np. oddziaływania mechanicznego może nastąpić jego silnie egzotermiczny rozkład już w umiarkowanie podwyższonej temperaturze.

Słowa kluczowe: tlenek grafitu, ekspansja termiczna, antypireny pęczniejące, polistyren.

Graphite oxide (GO) is a common name of a non-stoichiometric compound formed by oxidation of gra-

phite flakes. This reaction was first reported by Brodie about 150 years ago [1], however the interest in GO has recently been renewed, as oxidized graphite turned out to be a convenient precursor of graphene-like materials

^{*)} Author for correspondence; e-mail: michal.kedzierski@ichp.pl

[2, 3]. Thermal exfoliation of GO leads to formation of very thin platelets consisting of tens to hundreds stacked graphene layers, while sonication of aqueous GO suspensions can result even in single-layer graphene oxide [4]. The exfoliation process is accompanied by a large volume expansion along the crystallographic c-axis of graphite, accordingly GO can be classified as a so-called expandable graphite compound. This class of carbon materials has found many industrial applications, among them are intumescent fire retardants for polymers. The term „intumescence“ refers to the ability of some substances (or mixtures) to expand on heating into a foamed char layer that acts as an insulating barrier to heat and mass transfer between the flame and the burning material. Unlike in classical intumescent systems comprising a combination of several ingredients, including char former, carbonization catalyst and blowing agent [5], expandable graphite combines all functions needed for intumescence in a single compound. Graphite is a carbon source, while the gases evolved during the decomposition of intercalated species perform the blowing action. The intumescent effect of expandable graphite incorporated into polystyrene (PS) is demonstrated in Figure 1.



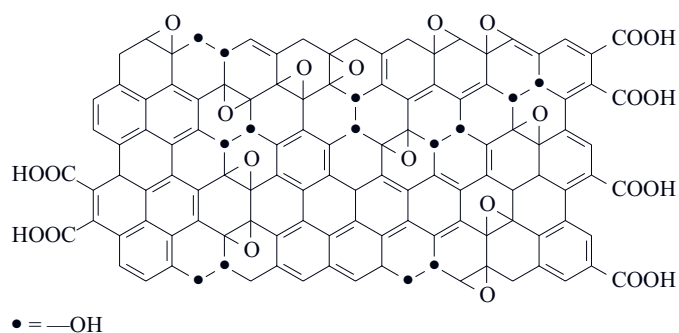
Fig. 1. A specimen of polystyrene-expandable graphite composite burned in limiting oxygen index test

Commercial expandable graphite compounds are usually prepared by intercalation of sulfuric acid into graphite in the presence of a strong oxidizing agent, which extracts electrons from the carbon layers. The product is graphite salt solvated by acid molecules of general formula $C_{24n}^+ HSO_4^- \cdot m H_2SO_4$ [6] and the process of exfoliation at elevated temperature involves reaction [7]:



High volume of volatile reaction products contributes to good intumescent properties, however some amount of toxic sulfur dioxide is evolved. Another drawback of sulfuric acid intercalated graphite (GSA) compounds is a poor miscibility with organic polymers. High loadings of GSA compounds needed to achieve the required level of fire retardancy may adversely affect mechanical properties of the final composite [8].

Graphite oxide is also synthesized using strong acids and oxidants, however it contains much less residual acid than GSA compounds. This is because intercalation/oxidation process is followed with hydrolysis of intermediate graphite salt and washing out the excess acid. Carbon layers in GO are functionalized with hydroxyl, carboxyl and epoxide groups (see Scheme A) which can be modified in order to improve the compatibility of graphite compound with organic matrices. Due to hydrophilic nature of GO these reactions can be carried out in an aqueous medium.



Scheme A. Structure of functionalized graphite oxide (according to Lerf-Klinowski model [9])

Several publications have been devoted to the use of GO as a flame retardant (FR) for polymers. Uhl and Wilkie [10] used GO modified with several ammonium salts as additives for polystyrene. Two approaches were tried: melt blending and *in situ* bulk polymerization of styrene monomer in the presence of modified GO. X-ray diffraction (XRD) analysis of the modified PS indicated the formation of nanocomposites, while cone calorimetry studies showed a significant reduction in peak heat release rate (comparable to that of clay – polystyrene nanocomposites) for the *in situ* polymerized product. The melt blended nanocomposites showed a smaller improvement in fire properties [10]. Zhang and coworkers [11] prepared nanocomposites of styrene-butyl acrylate copolymer with GO and observed a decrease of the peak heat release rate by 45 % in a cone calorimeter test at 1 wt. % of GO content. GO was also used as an efficient flame retardant additive for polycarbonate, acrylonitrile-butadiene-styrene copolymer and high impact polystyrene [12]. The group of Yu [13] used graphene oxide prepared by sonication of alkaline GO suspension for the modification of epoxy resin. They obtained exfoliated nanocomposites with slightly improved fire properties at GO content of 1 wt. %. Wang and Han [14] studied how the degree of GO dispersion influences the fire properties of several polymer matrices. An increase in limiting oxygen index (from 18.8 to 24.5) and a decrease by over 50 % of the heat release rate measured by cone calorimetry, were observed for polyacrylate-GO nano-

composites, while the microcomposites showed only a slight enhancement in fire resistance.

In this work we aimed at using GO as a non-halogen flame retardant added *in situ* during the suspension polymerization of styrene.

EXPERIMENTAL

Materials

All chemicals used were of reagent grade. Various grades of flake graphite were kindly supplied by Sinograf S.A. (Toruń, Poland). Silane U-511 (3-metacryloxypropyltrimethoxysilane) was purchased from Unisil Sp. z o.o. (Tarnów, Poland). Graphite-sulfuric acid compound, with trade name Grafguard 160-80N, was provided by GrafTech International. Its elemental analysis showed 70.41 % of C, 1.28 % of H, and 7.70 % of S, while the expansion volume determined at 600 °C was 80 cm³/g.

Preparation of graphite oxide

Concentrated sulfuric acid (450 g) was placed in reactor (3 dm³ capacity) and cooled to 0 °C, then graphite (22.5 g) was added. The resulting slurry was stirred for 30 min, then potassium manganate(VII) (67.5 g) was added in small portions during 70 min, while maintaining the temperature below 20 °C. The stirring and cooling was continued for 90 min, then ice-cold water (50 cm³) was added dropwise during 60 min (highly exothermic process!) followed by further addition of 850 cm³ of water over 60 min. The reaction mixture was stirred until it reached the room temperature and left overnight. Then 30 % solution of hydrogen peroxide (75 cm³) diluted with 500 cm³ of water was added dropwise during 120 min. The resulting precipitate was washed twice with 3 % solution of hydrochloric acid (500 cm³) and subsequently with aqueous sodium hydrogen carbonate (to pH value about 6) and separated by centrifugation. The final product was dried at 65 °C under vacuum to yield 28.4 g of dark grey solid.

Modification of GO with melamine-formaldehyde resin (GO-MF)

Melamine (3.75 g), 37 wt. % solution of formalin (7.5 g) and water (75 cm³) were placed in a 250 cm³ reactor and the pH of the mixture was adjusted to 8.4. Then the temperature was raised to 75 °C and maintained until melamine dissolved. The mixture was cooled to 40 °C, graphite oxide (12.5 g) was added and stirring was continued for 30 min. Then 36 % solution of hydrochloric acid was added (16.8 g), the mixture was heated up to 70 °C for 120 min and left for 64 h at the room temperature. The solid product was filtered and washed with water until pH was constant (about 4), then dried at 65 °C under

vacuum to yield 13.4 g of product. Elemental analysis showed the composition of the product GO-MF to be 60.50 % of C, 2.14 % of H and 8.60 % of N.

Modification with silane

The solution of 3-metacryloxypropyltrimethoxysilane in 400 cm³ of ethanol-water mixture (9:1 by volume) was acidified with acetic acid to pH = 5 and stirred for 1 h. Then graphite compound (30 g) was added, the slurry was stirred for 60 min, the product was filtered and washed twice with 100 cm³ of ethanol and finally dried at 60 °C under vacuum.

Methods of testing

Infrared spectra (KBr pellets) were obtained with Perkin Elmer System 2000 FT-IR spectrometer.

Elemental analysis was carried out using a Series II CHNS/O Perkin-Elmer analyser.

Scanning electron microscopy (SEM) analysis was performed using JEOL JSM-6100 microscope.

Powder X-ray diffraction (XRD) patterns were recorded using Bruker-AXS D8 Advance Series 2 powder diffractometer working with Co-K α radiation ($k = 0.179$ nm).

Thermogravimetric analysis (TGA) was performed on TGA/SDTA 851e Mettler Toledo thermoanalyzer under nitrogen atmosphere using the heating program: the heating rate from the ambient temperature up to 100 °C and from 400 to 700 °C was 10 °C/min, but only 5 °C/min between 100 and 400 °C.

Expansion volume was determined by heating up 0.5 g of GO samples to 600 °C and maintaining at this temperature for 5 min, then exfoliated graphite was transferred into a graduated cylinder and its volume was measured. The content of volatile substances was also examined by measuring weight loss during exfoliation.

RESULTS AND DISCUSSION

Four types of flake graphite with different carbon content (in the range of 87–99.9 wt. %) and particle size (from 45 to 500 μ m) were oxidized using modified Hummers-Offemmann method [15]. The oxidizing agent was potassium manganate(VII) in concentrated sulfuric acid medium and the process was terminated with the addition of hydrogen peroxide in order to reduce excess KMnO₄ and by-product MnO₂ to a water soluble Mn(II) salt. Finally, sulfuric acid and the formed salts were removed from the reaction mixture by washing with water.

The obtained graphite oxides were denoted according to the average particle size of the starting graphite as it is listed in Table 1. As a result of the oxidation process, carbon content in GO products was decreased by 25–43 percentage points compared to the initial graphite (Table 1). The extent of oxidation increases with lowering

Table 1. Characteristics of investigated graphite oxides

Product designation	Properties of the starting flake graphite		Properties of graphite oxide				
	particle size μm	carbon content wt. %	elemental composition			Δm at 600 °C ^{a)} wt. %	expansion volume at 600 °C, cm^3/g
			% of C	% of H	% of S		
GO 45	45	94	50.72	2.54	0.47	83	2
GO 180	180	99	56.11	2.87	0.67	69	32
GO 300	300	99.9	61.03	3.52	2.25	55	76
GO 300/2	300	94	53.14	1.95	2.85	77	20
GO 500	500	87	61.83	1.66	2.93	56	60

^{a)} Δm at 600 °C — percentage weight loss after 5 min at 600 °C.

of graphite particle size, consequently the finest grade GO 45 has the lowest carbon content (50.7 %) while GO 500 particles lost only about one quarter of the initial carbon content. GO synthesized from coarse grained graphite types (300 and 500 μm) contains 2 to 3 wt. % of sulfur, *i.e.* significantly more than GO from the finer grades (45 and 180 μm). This indicates that the increased crystallite size is more favorable to the permanent intercalation of sulfate anions in the interlayer space of oxidized graphite.

SEM images of two types of graphite and its oxidation products are presented in Figure 2. They show plate-like particle morphology typical for crystalline graphite, however, after the oxidation flat and sharply edged graphite platelets become more irregular with rounded edges and altered surface appearance. FT-IR spectra of

the obtained graphite oxides presented in Figure 3 show absorption bands corresponding to stretching vibrations of O-H group (at 3400 cm^{-1}), C-H and C-O bonds (near 2900 cm^{-1} and 1100 cm^{-1} , respectively) as well as the overlapping bands in the range 1550–1650 cm^{-1} , which may be assigned to bending O-H and C=C ring stretching vibrations. Additionally, C=O absorption band appears near 1700 cm^{-1} indicating the presence of COOH groups in oxidized graphites. The intensity of the carbonyl band is rather weak for GO synthesized from the coarse graphite types, however it becomes more significant in the case of the fine-sized GO 45. These differences can be explained by higher content of the edge carbon atoms (that are more susceptible to oxidation [9]) in finer graphite particles. In effect, GO 45 consisting of small-sized plates is more oxidized and exhibits more acidic character than

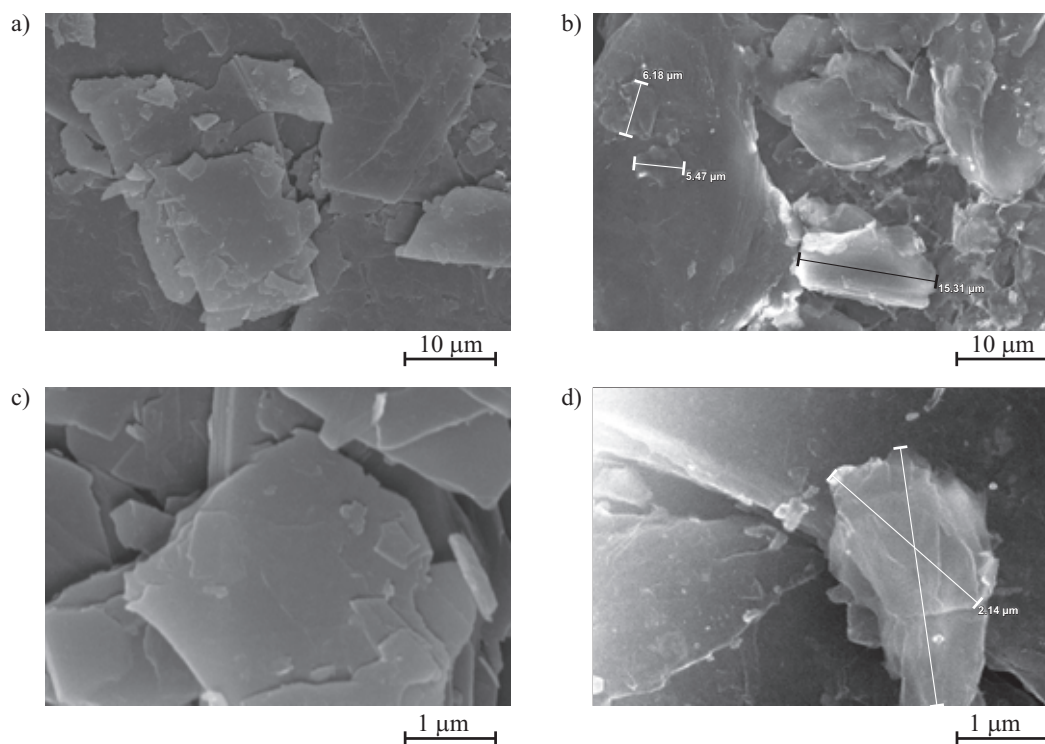


Fig. 2. SEM images of selected graphites and their oxidation products: a) graphite 180 μm , b) GO 180, c) graphite 45 μm , d) GO 45

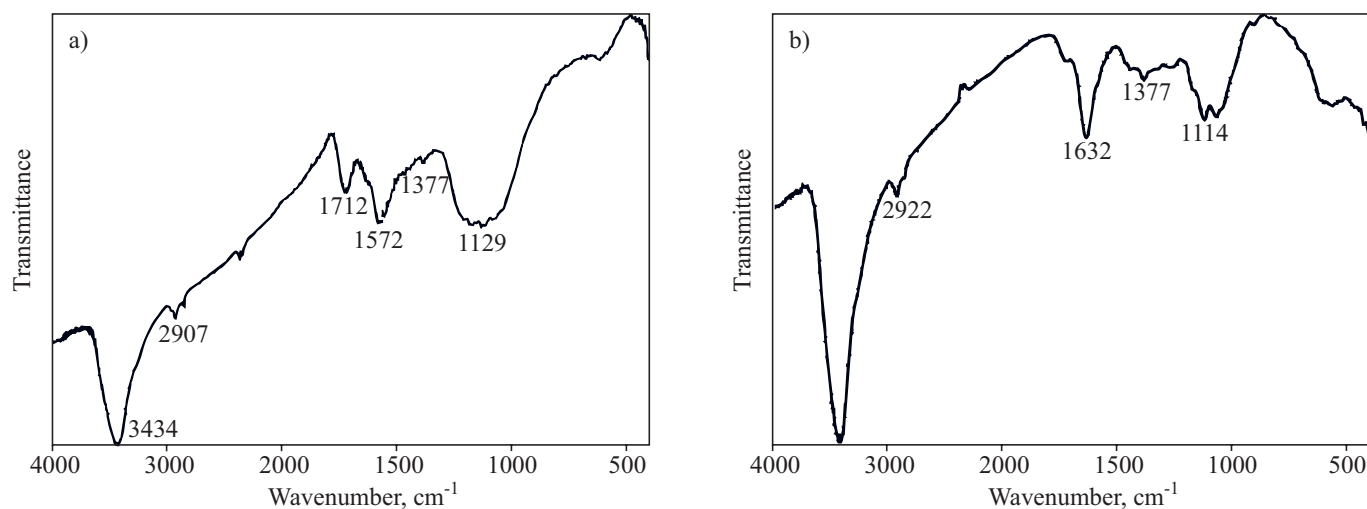


Fig. 3. FT-IR spectra of graphite oxides: a) GO 45, b) GO 180

other examined graphite oxides. The presence of carboxyl groups was also indicated by pH values of GO aqueous suspensions — 4.7 and 4.1 for GO 180 and GO 45 products, respectively.

X-ray diffraction patterns of graphite oxides presented in Figure 4 contain (002) basal plane reflections at $2\theta = 30^\circ$ and 13° , corresponding to the interlayer distances of 0.336 and about 0.8 nm. They can be assigned to the pristine and oxidized form of graphite, respectively. The presence of polar oxygen-containing groups facilitates a penetration of water molecules into the graphite interlayer space and consequently causes an increase in the distance between graphite layers [16]. The relative intensity of the lower angle reflection increases in the sequence of $\text{GO 300} < \text{GO 180} < \text{GO 45}$, *i.e.*, in accordance with the increasing extent of oxidation.

In order to make a preliminary evaluation of GO products as intumescent additives, the volume expansion after the rapid heat treatment at 600°C was determined and results are presented in Table 1. The finest grade GO 45 shows minimum expansion volume ($2\text{ cm}^3/\text{g}$) despite

of high weight loss (above 80 %). This indicates that gaseous decomposition products in fine-sized graphites do not interact with graphite layers. It is known from the literature that exfoliation does not occur when the particle size of graphite is lower than $75\ \mu\text{m}$ [17]. A significant increase in exfoliation volume (up to $70\text{ cm}^3/\text{g}$) is observed with an increase of the particle size to $300\ \mu\text{m}$.

Besides the expansion ability, many other factors influence the effectiveness of intumescent fire retardant additives. A coordination of the reactions leading to the formation of a foamed char as well as the processes of melting, pyrolysis and combustion of the polymer is necessary. The expanding agent should be stable at temperatures high enough to prevent its premature foaming action (before the polymer melts and reaches an appropriate viscosity). PS, used as a polymer matrix in this study, melts at 160°C and starts to depolymerize at 275°C [18]. Commercial expandable graphite (GSA) starts to decompose with expansion at 160°C and reaches a maximum decomposition rate at $230\text{--}250^\circ\text{C}$. GSA added to polystyrene in the amount of 15 wt. % is sufficient to warrant

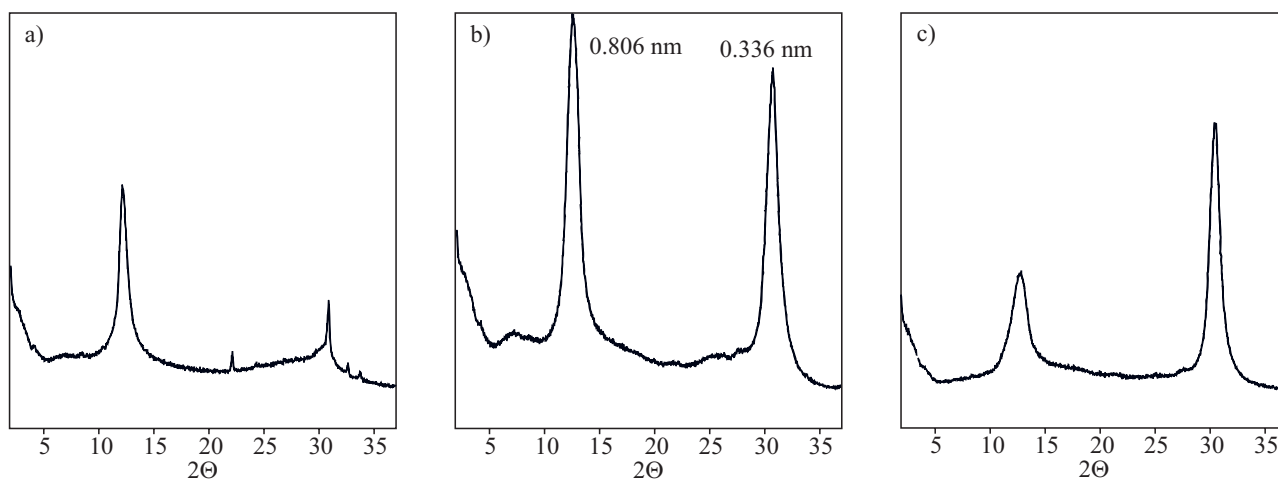


Fig. 4. X-ray diffraction patterns of graphite oxides (low angle region): a) GO 45, b) GO 180, c) GO 300

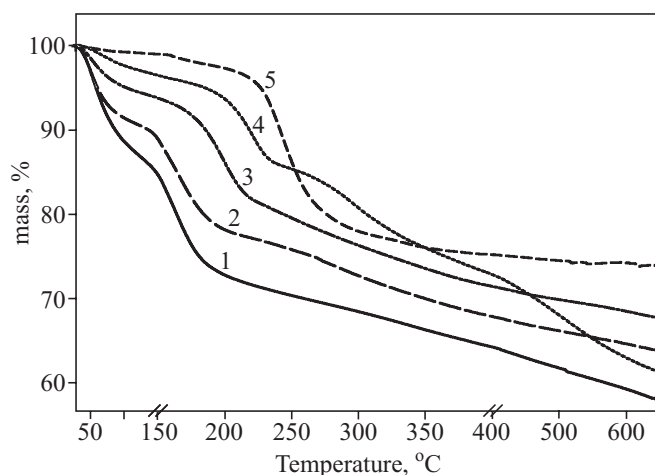


Fig. 5. TGA profiles of: 1 – GO 45, 2 – GO 180, 3 – GO 300, 4 – GO-MF, 5 – GSA

maximum FH-1 classification in the UL 94 horizontal burning test, however in the vertical flame test such modified PS does not reach V-0 rating required in some applications.

Thermogravimetric analysis profiles of three GO products with different particle size are shown in Figure 5. The first weight loss, below 130 °C can be attributed to the evaporation of absorbed water. Then between 130 and 250 °C, oxygen functional groups decompose, releasing mainly carbon dioxide [19]. The temperature of maximum decomposition rate increases with the GO particle size, from 160 °C for GO 45 to 200 °C for GO 300. For commercial GSA compound heated in the same conditions, rapid decomposition begins at 200 °C and maximum decomposition rate is observed near 240 °C. As it can be seen, graphite oxides are less thermally stable than graphite intercalate with sulfuric acid.

In recent work of de Farias *et al.* [20] it was reported that the compound of graphite oxide with hexamethylenetetramine is more thermally stable than pure GO showing a reduced by half mass loss and relatively high char residue. In this study we used another nitrogen compound, *i.e.* melamine, for the purpose to modify the thermal degradation profile of GO, as well as to achieve possible synergy, since melamine is known as an effective blowing agent in intumescent systems. In order to bind melamine inside the GO matrix, we prepared *in situ* melamine-formaldehyde resin in the alkaline aqueous GO suspension, with subsequent acidification and curing of the synthesized resin. The obtained product, denoted as GO-MF, contains 8.6 wt. % of nitrogen and as it is shown in Figure 6, its XRD spectrum shows an increase in the interlayer distance of GO from 0.8 to 0.9 nm, probably due to intercalation of the melamine resin. The temperature of maximum decomposition rate observed in the TGA profile of GO-MF is higher by 20 °C than that of unmodified GO.

Unmodified and modified graphite oxides were mixed with polystyrene by *in situ* addition during the

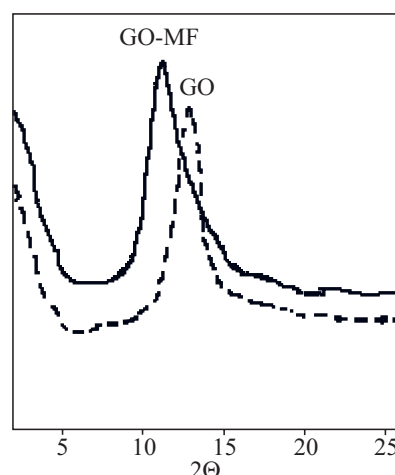


Fig. 6. XRD (002) reflection of GO and its compound with melamine resin (GO-MF)

suspension polymerization of styrene. In order to suppress the solubility of GO in the aqueous phase and to improve the miscibility with polystyrene particles, both GO products were previously subjected to silane treatment. The polymerization procedure and the flame test methods are described in our previous work [21].

Table 2. UL 94 burning ratings of polystyrene and its compositions with graphite additives

type	Additive		Horizontal burning	Vertical burning
	amount, wt. %			
Pure PS	—		FH-3/18	non classified
GSA	15		FH-1	V-1/V-2
GO	15		FH-1	non classified
GO-MF	15		FH-1	V-0

Table 2 presents the flammability ratings of polystyrene containing equal amounts of GSA and GO compounds evaluated in UL 94 tests. PS modified with graphite oxide obtained maximum FH-1 rating in the horizontal burning test, however it failed to pass the vertical flame test. The lower efficiency of GO compared to GSA can be attributed to the higher thermal stability of the latter. The best resistance to ignition, *i.e.* burning rate categories of V-0 and FH-1, was achieved for PS modified with GO-melamine resin compound. This can be explained, on one hand, by the action of an additional flame resistant (FR) agent (melamine sublimes above 250 °C and decomposes above 350 °C with evolution of ammonia and self-condensation to multi-ring structures which improve the thermal stability of char [22]) and on the other hand, by the delayed decomposition of GO intercalated with MF resin. From these preliminary results, we may suppose that graphite oxide can be a valuable non-halogenated fire retardant if used in combination with other FR additives. Further work is needed to study

the interactions between GO and various FR agents, especially intumescent systems.

Although known for one and half century, graphite oxide has been rediscovered in recent years and has been a subject of numerous studies focused on its exfoliated „graphene oxide“ form. As it was pointed out recently [23], an attention should be paid to the safe handling of GO. Even though it is stable at the ambient temperature {Lerf and coworkers [24] examined 30-years old sample of GO and observed only minor changes in its ^{13}C magic-angle-spinning nuclear magnetic resonance (^{13}C MAS NMR) spectrum} GO easily undergoes highly exothermic self-propagating deoxygenating reaction under the influence of temperature or even a close exposure to a photo camera flash [25]. We have also experienced this highly energetic nature of GO, which accidentally subjected to a mechanical impact at moderate temperature (below 60 °C) underwent self-ignition and explosive decomposition. Another problem to be solved in prospect of GO commercialization is still an inconvenient method of its preparation, involving the use of high volumes of concentrated sulfuric acid, strongly exothermic hydrolysis stage, voluminous acidic effluents, etc. Studies in this field are continuously carried out [26].

CONCLUSIONS

The expanding properties of graphite oxide depend primarily on its particle size. GO obtained from 300 and 500 μm graphite flakes exhibits a high expansion volume at 600 °C, comparable to the commercial expandable graphite-sulfuric acid salts. In part, it may result from some amount of sulfuric acid incorporated into the GO structure, however the sulfur content in the most expanding GO 300 was over three times lower than in GSA. On the other hand, GO decomposition occurs at a lower temperature range than in the case of GSA, consequently GO is less efficient as an intumescent fire retardant for polystyrene. The thermal stability of GO and its performance as FR agent can be improved by modification with melamine resin, which probably intercalates within graphite interlayer. The resulting GO-MF compound, containing approximately 10 wt. % of melamine can be made hydrophobic by organosilane treatment. When added in the amount of 15 wt. % during the suspension polymerization of styrene, it enables the resulting polymer to achieve maximum FH-1 and V-0 ratings in the UL 94 burning test.

As indicated by other authors [14], graphite oxide introduced into a polymer matrix as a nanofiller can give better FR agent properties than popular layered aluminosilicate clays. However, such effects are possible when GO particles disperse into nanometric platelets. With reference to our study this aspect needs further investigations. At the moment, it seems that GO can act as an intumescent FR agent, especially when combined with other FR additives.

REFERENCES

1. Brodie B. C.: *Ann. Chim. Phys.* 1860, **59**, 466.
2. Potts J. R., Dreyer D. R., Bielawski C. W., Ruoff R. S.: *Polymer* 2011, **52**, 5.
3. Kuilla T., Bhadra S., Dahu Y., Kim N. H., Bose S., Lee J. H.: *Prog. Polym. Sci.* 2010, **35**, 1350.
4. Boehm H. P., Clauss A., Fischer G. O., Hofmann U. Z.: *Naturforsch.* 1962, **17b**, 150.
5. Bourbigot S., Duquesne S.: „Intumescence-based fire retardants“ in: „Fire retardancy of polymeric materials“ (Eds. Wilkie C. A., Morgan A. B.), Taylor and Francis Group 2010, p. 129.
6. Rudorff W., Hofmann U.: *Z. Anorg. Allg. Chem.* 1938, **238**, 1.
7. Duquesne S., Le Bras M., Bourbigot S., Delobel R., Camino G., Eling B., Lindsay Ch., Roels T.: *Polym. Degrad. Stab.* 2001, **74**, 493.
8. Ye L., Meng X. Y., Ji X., Li Z. M., Tang J. H.: *Polym. Degrad. Stab.* 2009, **94**, 971.
9. Lerf A., He H., Forster M., Klinowski J.: *J. Phys. Chem. B* 1998, **102**, 4477.
10. Uhl F. W., Wilkie C. A.: *Polym. Degrad. Stab.* 2004, **84**, 215.
11. Zhang R., Hu Y., Xu J., Fan W., Chen Z.: *Polym. Degrad. Stab.* 2004, **85**, 583.
12. Higginbotham A., Lomeda J., Morgan A. B., Tour J. T.: *ACS Appl. Mater. Interfaces* 2009, **1**, 2256.
13. Wang Z., Tang X. Z., Yu Z. Z., Guo P., Song H. H., Du X. S.: *Chin. J. Polym. Sci.* 2011, **3**, 368.
14. Wang J., Han Z.: „Comparative Study of Nanoeffect on Fire Retardancy of Polymer — Graphite Oxide Nanocomposites“ in „Fire Retardancy of Polymers: New application of Mineral Fillers“ (Ed. Le Bras M.), Springer Verlag 2005, chapter 12, p. 161.
15. Titelman G. I., Gelman V., Bron S., Khalfin R. L., Cohen Y., Bianco-Peled H.: *Carbon* 2005, **43**, 641.
16. Hontoria-Lucas C., Lopez-Peinado A. J., Lopez-Gonzalez J. D. D., Rojas-Cervantes M. L., Martin-Aranda R. M.: *Carbon* 1995, **33**, 1585.
17. *Pat. Ger. (East)* DD 150 739 (1981).
18. Mehta S., Biederman S., Shivkumar S.: *J. Mater. Sci.* 1995, **30**, 2944.
19. Shulga Y. M., Martynenko V. M., Muradyan V. E., Baskakov S. A., Smirnov V. A., Gutsev G. L.: *Chem. Phys. Lett.* 2010, **498**, 287.
20. de Farias R. F., Airoidi C.: *J. Serb. Chem. Soc.* 2010, **75**, 497.
21. Jankowski P., Kędzierski M.: *Polimery* 2011, **56**, 20.
22. Chattopadhyay D. K., Webster D. C.: *Prog. Polym. Sci.* 2009, **34**, 1068.
23. Kim F., Luo J., Cruz-Silva R., Cote L. J., Sohn K., Huang J.: *Adv. Fun. Mater.* 2010, **20**, 2867.
24. Lerf A., He H. Y., Riedl T., Forster M., Klinowski J.: *Solid State Ionics* 1997, **101**, 857.
25. Cote L. J., Cruz-Silva R., Huang J.: *J. Am. Chem. Soc.* 2009, **131**, 11 027.
26. Marcano D. C., Kosynkin D. V., Berlin J. M., Sinitskii A., Sun Z., Slesarev A., Alemany L. B., Lu W., Tour J. M.: *ACS Nano* 2010, **4**, 4806.