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### Is expanded graphite acting as flame retardant in epoxy resin?

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#### ABSTRACT

In this study, expanded graphite (EG) was investigated as flame retardant for epoxy resin based on DGEBA. Various amounts of EG (up to 50 wt%) were incorporated into the epoxy and the composites were studied using X-ray diffractometer, scanning electronic microscopy, cone calorimeter, pyrolysiscombustion flow calorimeter, thermogravimetric analysis, instrumented epiradiator and laser-flash method. Quite unexpectedly, EG leads to a significant increase in pHRR in cone calorimeter tests. Nevertheless, EG also allows delaying strongly the time-to-ignition. Such behavior was assigned mainly to the increase in thermal diffusivity which allows transferring heat faster from the surface to the bulk.

Keywords: Expanded graphite Flame retardant Mechanisms Polymer Epoxy resin

#### 1. Introduction

Expandable graphite is a well-known intumescent flame retardant additive. Its performance depends mainly on its ability to expand during heating [1-3]. Li et al. have also shown that the expandable graphite particle size has a significant effect on flame retardancy properties [4]. Even if it is not able to expand as expandable graphite, expanded graphite (EG) has also been assessed as flame retardant in various polymers, most generally as synergist in multicomponent systems.

Several flame retardant mechanisms, mainly in condensed phase, have been proposed to explain the reduced flammability of polymers in the presence of EG. EG particles can reinforce the char and increases its thermal stability [5–7]. Nevertheless, Wu et al. observed some differences between the chars obtained from EVA containing an intumescent flame retardant system and expandable graphite or natural graphite as synergists. These authors assesses that the char obtained with expandable graphite ensures a better thermal protection [2].

According to Murariu et al., the char can also swell in some extent improving its barrier properties. Hence, these authors observed that PLA with 3–6 wt% of EG forms a porous foamed char swollen during cone calorimeter test [8].

Another phenomenon was observed by Zang et al. consisting to the possibility of EG to migrate at the beginning of heating on the material surface. Such migration may improve its efficiency to act as a physical barrier [5].

The efficiency of various carbon-based fillers (multiwall carbon nanotubes, functionalized graphene, carbon black and expanded graphite) has been studied and compared in a flame retarded polypropylene [9]. The authors have shown that the onset temperature of degradation is related to the specific surface area of the fillers. EG does not exfoliate in PP and is poorly dispersed in comparison to other fillers. Therefore, the viscosity is not strongly enhanced and the composite containing EG can maintain a V-2 rating in UL-94 test due to its dripping behavior. Nevertheless, EG was not efficient as flame retardant according to cone calorimeter test.

The aim of the present paper was to highlight what happens exactly when EG is used as flame retardant and which is the most important parameter impacting the reaction to fire of EG filled polymer composite. For this purpose, EG was incorporated into

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epoxy resin at different weight fraction and thermal degradation and flame retardant mechanisms were investigated.

#### 2. Experimental

#### 2.1. Materials

The epoxy resin is a diglycidyl ether of bisphenol A (DGEBA) from Aldrich. The curing agent used was diphenyl diaminosulfone (DDS) from Aldrich. Expanded graphite (EG) was supplied by ECOPHIT G. According to the manufacturer data, the principal characteristics of the specific used GFG 5 grade of EG are: real density =  $2.25 \text{ g/cm}^3$ , mean diameter  $d_{50} = 5-7 \mu$ m, BET specific surface area =  $23.1 \text{ m}^2/\text{g}$  (slightly lower than the specific surface area of EG used in Dittrich's study [9]). It was used without any further purification.

#### 2.2. Preparation of composites

EG filled DGEBA composites were prepared by mixing EG into DGEBA resin at 130 °C, at respectively 5, 10, 15, 23 and 50 wt%. Both magnetic stirring and Hielscher Ultrasonic Processor UP400 methods were tested to disperse the EG into the DGEBA matrix. Both methods led to the same results. Nevertheless, results presented in this paper are only based on magnetic stirring samples. DDS hardener was then added in appropriate ratio to the mixture, regarding the same mixing procedure. Composites were then cured at 180 °C for 2H under press, followed by a 2H post-cure at 220 °C.

#### 2.3. SEM (scanning electron microscopy)

SEM micrographs of DGEBA-EG composites and the residues after flammability test were made using an environmental microscope (FEI-QUANTA 200 type).

#### 2.4. Thermogravimetric analysis

The thermal degradation was studied by thermogravimetric analysis (TGA). The TGA apparatus was a NETZSCH-STA 409 PC apparatus, operating in air environment under a gas flow of 100 cm<sup>3</sup> min<sup>-1</sup> with alumina crucibles (150  $\mu$ l) containing 20–25 mg of sample. The run was carried out in dynamic conditions at the constant heating rate of 10 °C min<sup>-1</sup>. The uncertainties on temperature and mass measurements were respectively estimated to 0.5 °C and 0.1 mg.

#### 2.5. Cone calorimeter

The flame retardancy of composites was measured with a cone calorimeter (Fire Testing Technology) according to ISO 5660-1 standard. Specimens with dimensions of  $50 \times 50 \times 4 \text{ mm}^3$  were positioned on a load cell to test the evolution of mass loss during the combustion test. Despite the non-standard sample sizes there are many studies that use small sample size [10–12]. A conical radiant electrical heater (at 50 kW m<sup>-2</sup>) uniformly irradiated the specimen, while the combustion was triggered by an electric spark. The measurements of the gas flow and oxygen concentration allowed computing the heat release rate (HRR) per surface area.

The cone calorimeter is one of the most effective bench scale methods for investigating the reaction to fire of polymer materials. Various parameters can be measured including time to ignition (TTI), time of flameout (TOF), heat release rate (HRR) as a function of time, peak of heat release rate (pHRR), total heat released (THR), mass loss rate (MLR), total smoke released (TSR), total CO and CO<sub>2</sub> produced. In the present paper, we shall focus on the three most

important parameters, i) TTI, ii) pHRR and iii) THR. Their reproducibility is within 5%.

#### 2.6. Pyrolysis-combustion flow calorimetry (PCFC)

The principle of PCFC relies on the separate reproduction of the solid state and gas phase processes of flaming combustion by a controlled pyrolysis of the sample in an inert gas stream, followed by a high temperature oxidation of the volatile products [13]. PCFC was performed in duplicate on about 3 mg samples using a Fire Testing Technology (FTT) calorimeter at a heating rate of  $1 \,^{\circ}\text{C s}^{-1}$  up to 750 °C under nitrogen in the pyrolysis zone. The combustion zone was set at 900 °C under nitrogen/oxygen atmosphere (80/20 by volume) for a complete combustion of gases.

#### 2.7. Instrumented epiradiator

Additional experiments were carried out using an epiradiator equipped with IR camera (Optris). The infrared camera was used in order to measure temperature of the lower surface giving an insight on the heat transfer. The infrared camera provides high level spatial resolution for surface temperature compared to thermocouples. A scheme of the experimental set up is shown in Fig. 1. It must be noted that the heating power and the distance grid/epiradiator are chosen to ensure a slow heating. The sample was placed on the metallic grid below epiradiator. The thickness of the samples used in this test is 6.5 mm. A hole on the center of the grid allows measuring the temperature of the lower surface. Prior to measurements, thin graphite layer was deposited on both sample surfaces to improve the signal-to-noise ratio of the infrared camera. Due to the graphite coating, the emissivity is believed to be equal to 1 and similar for all samples. On the lower surface, the infrared camera measures a true temperature. While the heat flux is absorbed at the upper surface, no reflection and no absorption indepth are involved. In this way only the thermal conduction properties (density, heat capacity and thermal diffusivity) affect the temperature rise of the rear side.



Fig. 1. Scheme of the experimental set up with an epiradiator and an infrared camera.



Fig. 2. XRD patterns of pure EG and DGEBA-EG composites at 5, 10 and 15 wt% of EG.

#### 2.8. Thermal diffusivity analysis

Thermal diffusivity ( $\alpha$ ) of the studied composites was measured by laser flash method at room temperature. This technique entails heating the front side of a small, usually disk-shaped plane-parallel, sample by a short ( $\leq 1$  ms) laser pulse. The temperature increase on the sample rear surface is measured versus time using an infrared detector. Disc shaped samples, with a diameter of 12 mm and a thickness of 1 mm, were used to measure the thermal diffusivity under an Argon flow. All samples were molded under compression and coated, on both faces, with a very thin layer of colloidal graphite. The error for the thermal diffusivity measurement is evaluated at  $\pm 3\%$ .

#### 2.9. X-ray diffraction

X-ray diffraction (XRD) experiments were performed with an INELFRANCE diffractometer. Samples were scanned in the reflection mode using the Cu-K $\alpha$ 1 radiation (wavelength: 1.5405 Å).

#### 3. Results

#### 3.1. Dispersion and morphology

To investigate the dispersion and the intercalation or exfoliation of the EG when incorporated into DGEBA at different EG content, X- ray diffraction (WAXS mode) and SEM were used. X-ray diffraction patterns of the EG and DGEBA-EG composites obtained after processing are presented in Fig. 2. It was observed that DGEBA-EG composites exhibited a broad amorphous hallow scattering and a sharp peak at  $2\theta \sim 26.5^\circ$  which corresponds to the stacking of single graphene lavers at a distance of 0.335 nm, regardless the EG content. The sharp peak at 26.5° confirms the presence of pure graphite based on stacks of parallel graphene sheets [14]. This result also points out the fact that even in advanced mixing conditions applied using the ultrasonic processor, exfoliation or complete separation of the graphene layers was not reached and some sheets still existed in the aggregate form. Even melt mixing does not allow achieving exfoliation of EG into thermoplastics as PP [9] and PLA [8]. However, SEM images show that EG platelets are well and homogeneously dispersed in DGEBA matrix without the presence of any large aggregates (Fig. 3).

#### 3.2. Flammability performances

The effect of varying EG amounts in DGEBA-EG composites on HRR curves measured using cone calorimeter is shown in Fig. 4. For a better illustration of the effect of EG on the reaction to fire, we have presented separately the following parameters: TTI, pHRR and THR as a function of EG content (Fig. 5).

The obtained results show that pHRR increases in presence of EG until about 25 wt%. For example at 10 and 23 wt%, pHRR is respectively higher by 150 and 200% in comparison to pure DGEBA. We have to point out that the effectiveness of any flame retardant system is measured by its ability to reduce the pHRR and not to increase it during the cone calorimeter test as in the present case. To the best of our knowledge, such increase with EG incorporation was not already reported in the literature. It is therefore of great importance to find an explication for this unexpected behavior.

As shown in Fig. 5, the THR decreased in the presence of EG. Nevertheless this decrease is proportional to the EG amount incorporated into the composite. The residual weight exactly corresponds to the mass fraction of EG plus the char from DGEBA which remains constant for all composites (i.e. around 10% of DGEBA - Fig. 6). It means that EG does not promote charring. Moreover combustion efficiency is constant. EHC value remains constant for all composites in the range 17–20 kJ/g confirming that EG does not act as flame inhibitor in gas phase.

However the time to ignition largely increases as the mass fraction of EG increases. Ignition occurs at 65 s, 102 s and 133 s respectively for pure DGEBA, DGEBA filled with 15 and 50 wt% of EG. Therefore the ratio between pHRR and TTI which is an empirical index measuring the flame spread properties [15] remains quite constant around 13–18 kW/m<sup>2</sup> s. While EG has a detrimental effect



Fig. 3. SEM images of DGEBA-EG composites at 5, 10 and 15 wt% of EG.



Fig. 4. Heat release rate (HRR) curves for DGEBA and its composites containing 5, 10, 15, 23 and 50wt% of EG measured by cone calorimeter at 50 kW/m<sup>2</sup>.

on pHRR and no influence on THR and EHC, such significant increase of TTI can be considered as the only positive effect of EG in DGEBA resin.

In the following, additional experiments are carried out to explain the results obtained in cone calorimeter test.

#### 3.3. Evidence of barrier effect?

Barrier effect has been reported as the mode-of-action of EG in various polymers [8,5]. While we observe an increase in pHRR, it is obvious that barrier effect is ineffective or counterbalanced by another phenomenon in our case. First, the shape of HRR curves does not correspond to thick charring materials [16]. We have also examined the morphology and the structure of residues after cone tests. The pictures of these residues (Fig. 7) show the presence of char for all samples including pure DGEBA sample. However we have already pointed out that EG does not promote the formation of the char. Fig. 7 also shows that the char layers obtained have many open holes and cracks except the sample with 50 wt% of EG which exhibits a better cohesion without visible holes at the surface. This can be related to the pHRR value obtained for samples containing less than 23 wt% of EG. It is noted from these pictures the absence of



Fig. 5. Time to ignition (TTI), peak of heat release rate (pHRR) and total of heat release (THR) values for DGEBA and its composites containing 5, 10, 15, 23 and 50 wt% of EG measured by cone calorimeter at 50 kW/m<sup>2</sup>.



Fig. 6. Residual weight collected after cone calorimeter tests for DGEBA and its composites with EG at different mass fraction.

any eventual expansion of these char layers because the thickness of the samples remains practically constant contrarily to the finding of Murariu et al. who observed the swelling of PLA filled with low amounts of EG [8]. The microstructure of the obtained residues has been analyzed by SEM at different scales with several magnifications to have complementary information (Fig. 8). The residues appeared as porous material but pores distribution is very large: some pores exceed one hundred microns. At higher magnification, individual EG platelets can be seen without any modification.

These observations (holes on the surface, large pores and absence of expansion) strongly exclude any gas and heat barrier effect of EG in the condensed phase. This explains the non-effectiveness of EG to reduce the pHRR (Fig. 5) because the



**Fig. 7.** Photos of the residues collected after cone calorimeter tests for DGEBA and its composites with EG at different weight fractions (given in yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

presence of a barrier layer could protect the material against heat flux and reduce the degradation kinetics of the composite during its pyrolysis and therefore the volatilization rate of degradation gases.

#### 3.4. Catalytic effect of EG in anaerobic atmosphere?

The increase in pHRR in presence of EG may be due to a catalytic effect. Then PCFC analyses were carried out to assist in the understanding of the fire behavior and to confirm our previous interpretations. In these experiments, pyrolysis was carried out in nitrogen atmosphere: Indeed, after ignition, the pyrolysis in cone calorimeter test is considered as mainly anaerobic. Table 1 presents the results of PCFC for DGEBA and its composites with EG at different weight fractions. The THR decreases proportionally to the EG content due to a simple physical dilution (less fuel when the weight fraction of EG increases in composite) as observed in cone calorimeter tests, confirming that EG does not promote the charring of DGEBA. The temperature at pHRR remains constant in the range 409–416 °C. Therefore we can assume that EG does not catalyze the degradation of DGEBA: the thermal stability of all composites is similar.

The pHRR remains constant up to 15 wt% of EG and decreases above. At 50 wt% of EG, the pHRR is approximately half the value of the pure DGEBA. These results are not in agreement with cone calorimeter results for which pHRR increases strongly in presence of EG.

It is well-known that PCFC and cone calorimeter are not wellcorrelated due to some additional effects occurring in cone tests [17]. Among these effects, barrier effect and flame inhibition cannot explain the discrepancy in the present study: barrier effect has been proved inefficient and EG does not act as flame inhibitor. Identically thermal stability is not modified by EG. Another explanation concerns the heat transfer: in PCFC, no strong heat gradient can be expected since the sample is as small as 2–5 mg (this explains why barrier effect is ineffective). On the contrary, in cone tests, the heat gradient along the sample thickness drives the front of pyrolysis. Heat gradient depends especially on some thermophysical and optical properties of the material. Before assessing the influence of EG on these properties and on the heat gradient, we must check that EG does not modify the thermo-oxidative stability of DGEBA.

#### 3.5. Influence of EG on thermo-oxidative stability of DGEBA

Indeed, before ignition, pyrolysis in cone calorimeter test is aerobic. Therefore the increase in TTI with EG may be due to an improvement of thermo-oxidative stability. In order to verify this hypothesis, thermogravimetric analyses were performed on pure DGEBA sample and its composites containing EG at different loading ratios in air atmosphere (Fig. 9). It appears from these data that EG has no particular effect on the thermal degradation of the matrix and this is valid for all weight fractions studied. In fact, compared to DGEBA, the other samples with EG have similar decomposition temperatures. Moreover, the char yield at 750 °C gradually raises with the increase of EG amount as shown in Fig. 3 by different arrows. The char formed at this temperature is composed only from EG, EG does not promote the charring of DGEBA in air.

#### 3.6. Influence of EG on thermal diffusivity and heat transfer

EG does not modify the degradation pathway of DGEBA whichever the atmosphere, and does not promote an effective barrier effect. To explain the increase in TTI and pHRR, other explanations must be proposed. An increase of the thermal diffusivity



Fig. 8. SEM images of residues obtained after combustion of the composite DGEBA-23EG.

of samples in the presence of EG due to its higher intrinsic thermal diffusivity can be invoked to explain this increase of TTI [18]. The thermal diffusivity is the ability of a material to transmit heat rather than to absorb it. It was questioned if the thermal diffusivity of the DGEBA can increase when adding EG and what is the impact of this intrinsic property on the reaction to fire of composites. Using the laser flash method, thermal diffusivity of the DGEBA samples and its composites with EG was measured (Fig. 10). The thermal diffusivity of DGEBA-EG composites is higher than that of pure DGEBA and this increase is more important when the weight fraction of EG is higher. For example, adding 10 and 50 wt% of EG led respectively to a thermal diffusivity three times and fifteen times higher than that of pure DGEBA. In order to highlight if a possible relation exists between the time to ignition and the thermal diffusivity, TTI and thermal diffusivity were plotted versus EG content. It clearly shows that TTI steadily increases with thermal diffusivity. This good correlation suggests that TTI seems to be somewhat related to thermal diffusivity [18]. Then, the question arises to know if the increase of thermal diffusivity significantly modifies the temperature profile of the sample during the cone calorimeter test. Indeed, it is wellknown that ignition occurs when the temperature of the surface reaches a given temperature (depending on the polymer) [19]. A lower increase of this temperature due to higher thermal diffusivity may allow delaying the ignition.

To verify this hypothesis, epiradiator test was carried out as described in the experimental section. The epiradiator was maintained above the sample during the whole test. The temperature of the lower surface was recorded from the infrared camera in the

 Table 1

 PCFC results for DGEBA composites filled with various amounts of EG.

EG (wt%)	Temperature at pHRR (°C)	pHRR (W/g)	THR (kJ/g)
0	416	555	28.1
5	414	558	27.1
10	415	525	24.8
15	409	553	23.2
50	414	275	14

presence of EG and was compared with pure DGEBA under the same conditions (Fig. 11). The results show a clear increase of the lower surface temperature of samples (more than 40 °C) when adding EG. The heating rate of the lower surface was faster which means that heat is faster dissipated from the upper surface. The strong heat dissipation at the upper surface caused by the EG delays the increase of the surface temperature and therefore the polymer degradation leading to a higher TTI.

#### 4. Discussion

To the best of our knowledge, it is the first article reporting that thermal diffusivity is the predominant parameter controlling the flame retardancy of a polymer filled with EG. Kuan et al. have studied polyethylene composites filled with 30 wt% of various expandable graphites [1]. These graphites were prepared from natural flake graphite. The composite with natural flake graphite was the only one exhibiting a strong increase of TTI (170 s versus 78 s for pure polyethylene). Moreover, the pHRR was increased from 411 to 461 kW/m<sup>2</sup>. These results are in agreement with ours but the authors did not discuss the influence of thermal diffusivity.

Zhang et al. have shown that a low content of EG (5 wt%) allows increasing the thermal diffusivity of a flame retarded paraffin/ polyethylene blend but they did not connect this increase to the flame retardancy properties [5].

Mhike et al. have studied polyethylene composites filled with flake graphite [20]. A strong increase in TTI was observed and assigned to an increased reflectivity only based on simulations using Thermakin software and not on a direct measurement of reflectivity.

Dittrich et al. have discussed the respective influence of indepth heat absorption and thermal conductivity on the TTI of flame retarded polypropylene filled with various carbon nanomaterials including expanded graphite [9]. In their study, the fillers are incorporated at a low content (5 wt%). Therefore they alter the in-depth absorption more than the thermal conductivity leading to a decrease – and not an increase – in TTI.



Fig. 9. TG curves for DGEBA and its composites containing 5, 10, 15, 23 and 50 wt% of EG.



**Fig. 10.** Thermal diffusivity and time to ignition as a function of EG content for DGEBA and its composites with EG.

Indeed in-depth heat absorption is another materials property influencing the ignition. If the radiative flux is absorbed in a thicker layer, the temperature of the surface rises more slowly and ignition is delayed [21]. The decrease of heat transmittance due to the



Fig. 11. Comparison of the lower surface temperature profiles under the same conditions for DGEBA and its composites with 10 and 50 wt% of EG.

presence of nanoparticles has already been invoked to explain the change in TTI.

Kashiwagi et al. have showed that both properties influence the ignition of PP filled with multiwalled carbon nanotubes (MWCNT) but their relative predominance depends on the filler content [22]. At low MWCNT content, in-depth heat absorption is predominant leading to a decrease in TTI but thermal conductivity allows increasing TTI after a critical MWCNT content (between 0.5 and 1 wt%).

In our study, EG content is significantly higher (5 wt% and more). Therefore, it is obvious that the decrease in heat transmittance cannot counterbalance the increase in thermal diffusivity.

Finally the increase in thermal diffusivity also allows explaining the increase in pHRR. Patel et al. has simulated the HRR curves in cone calorimeter using Thermakin software by varying single thermophysical and optical properties of materials [23]. As explained above, the increase in thermal inertia (which depends on thermal diffusivity) delays ignition by transferring faster the heat from the surface to the bulk. Material's bulk is then heated more quickly leading to a faster increase of HRR after ignition up to a higher pHRR.

#### 5. Conclusion

For thermoset matrix as epoxy resin, we have shown through this study that:

- EG has no particular effect on the thermal degradation of the matrix whatever the weight fraction used. EG does not promote or inhibit the charring. EG does not act as flame inhibitor. EG mainly acts in the condensed phase as chemically inert filler by diluting the combustible phase.
- Nevertheless EG changes the burning kinetics of thick samples due to its high intrinsic thermal diffusivity. We have assumed that the high heat dissipation at the surface caused by the EG delays the increase of surface temperature and therefore increases TTI. This is well pointed out by the relationship between the time to ignition (TTI) and thermal diffusivity.
- No barrier effect of EG is observed in the condensed phase due to the weak cohesion of the residue. This poor cohesive residue, combined with a fast heating of the condensed phase (due to the high thermal diffusivity of composites containing EG) leads to a strong increase in pHRR.

We hope this contribution to highlight the role of expanded graphite will lead to a better use of EG as part of multicomponent flame retardant systems in the future.

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