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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, pyrolysis-combustion 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.

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 g/cm^3, mean diameter d_{50} = 5–7 μm, BET specific surface area = 23.1 m^2/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^3 min^{-1} with alumina crucibles (150 μl) containing 20–25 mg of sample. The run was carried out in dynamic conditions at the constant heating rate of 10 °C min^{-1}. 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 × 50 × 4 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^{-2}) 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_2 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 °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 in-depth are involved. In this way only the thermal conduction properties (density, heat capacity and thermal diffusivity) affect the temperature rise of the rear side.

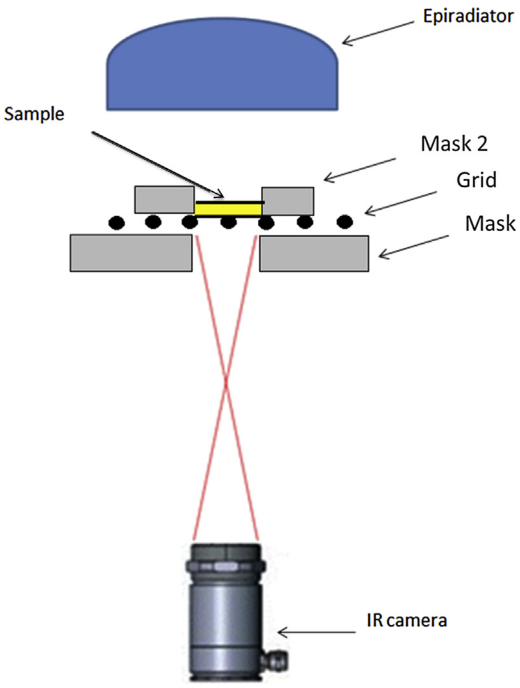

Fig. 1. Scheme of the experimental set up with an epiradiator and an infrared camera.