



Synergistic flame-retardant effect of expandable graphite and phosphorus-containing compounds for epoxy resin: Strong bonding of different carbon residues



Shuang Yang^{*}, Jun Wang, Siqi Huo, Mei Wang, Junpeng Wang, Bin Zhang

School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, People's Republic of China

ARTICLE INFO

Article history:

Received 11 December 2015

Received in revised form

25 February 2016

Accepted 12 March 2016

Available online 14 March 2016

Keywords:

Epoxy resin

Flame retardant

Expandable graphite

Phosphazene

Phosphaphenanthrene

ABSTRACT

In this paper, phosphorus-based compounds, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and hexa-phenoxy-cyclotriphosphazene (HPCP), and expandable graphite (EG) were adopted as flame retardants for epoxy resin (EP). The resulting EP composites were investigated using thermogravimetric analysis (TGA), limited oxygen index (LOI), vertical burning (UL94), cone calorimeter, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), Fourier Transform Infrared (FTIR) and scanning electron microscope/energy dispersive X-ray (SEM-EDX). The results disclosed that EG affected the thermal decomposition process of EP composites and led to the earlier arisen *pk*-HRR and later lower HRR due to its high thermal conductivity and strong barrier effect. The further enhanced flame retardancy of EP composites containing both EG and phosphorus-containing compounds indicated the synergy between different flame retardant components. The morphology study showed that the residual char of EP/EG exhibited an intumescent but fluffy and wormlike structure with low adhesion. However, those of EP/EG/DOPO and EP/EG/HPCP revealed compact and tough structures composed of wormlike graphite and carbonized EP matrix. The strong interfacial bonding between these two different carbon residues strengthened the integrality and continuity of the intumescent char layers, leading to a stronger barrier effect in condensed phase. In addition, DOPO and HPCP provided flame retardant effect in gaseous phase for EG-containing epoxy resin.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, non-halogen flame retardants have attracted more and more attention since the applications of traditional halogenated compounds are restrained for environmental reasons [1–5]. Among them, phosphorus-based compounds are considered to be the most promising ones due to their strong carbonization effect in condensed phase and free radical quenching effect in gaseous phase [6–11]. Based on previous studies, low smoke generation, low toxicity, low add-on and high efficiency were obtained when phosphorus-containing compounds were applied to polymer matrixes in combination with other flame retardants to form intumescent flame retardant systems [12–17]. Therefore, there is a

trend to develop and apply halogen-free intumescent flame retardant (IFR).

Expandable graphite (EG), a commercially available inorganic IFR can expand in the perpendicular direction and generate a vermicular structured layer when exposed to heat source [18–20]. Many studies have confirmed that EG has a high flame retarding effect, low toxicity and no-smoke production [21–23]. However, the wormlike char layers formed during combustion are normally lack of sufficient adhesion, and thus are easily destroyed by heat convection and flame pressure during combustion process [24–27]. If the char layers become more compact, the flame retardancy of EG filled polymer composites may be further enhanced. In addition, EG cannot exert flame retardant effect in gaseous phase.

As kinds of phosphorus-containing flame retardants, phosphaphenanthrene, cyclotriphosphazene and their corresponding derivatives have been widely used in flame-retarded polymers due to their high reactivity, high thermal stability and excellent flame-retardant efficiency [28–33]. However, when they are used alone, the smoke production amounts of modified systems are not

^{*} Corresponding author. School of Materials Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Hongshan District, Wuhan 430070, People's Republic of China.

E-mail address: ys583377051@163.com (S. Yang).

obviously decreased and even dramatically increased sometimes. The formed residual chars after combustion are compact and tough with a certain degree of swelling. However, the expansion ratio is lower than that of a typical compounded IFR system which may restrain the further improvement of flame retardant performance.

According to the above discussion, if EG is used together with phosphaphenanthrene or cyclotriphosphazene, the advantages of these two components may be combined. The char layer of modified polymer matrix may exhibit a highly expansive, compact and integrated structure, which is beneficial to retard combustion.

In this paper, bisphenol A epoxy resin (DGEBA) was selected as resin matrix due to its excellent comprehensive performance and broaden application in advanced fields but flammable characteristic [34–38]. So far, no one reported the application of EG together with phosphaphenanthrene or cyclotriphosphazene in epoxy resins. We selected typical phosphaphenanthrene-based and cyclotriphosphazene-based flame retardants, DOPO and HPCP, and then mixed them with EG and DGEBA to prepare flame retardant EP composites. A series of characterization methods were employed to evaluate the thermal properties, flame retardant properties as well as mechanism.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight (EEW) of about 188 g/equiv was provided by Yueyang Baling Huaxing Petrochemical Co., Ltd. 4,4'-Diaminodiphenyl sulfone (DDS) was purchased from Sinopharm Chemical Reagent Co., Ltd. DOPO was purchased from Huizhou Sunstar Technology Co., Ltd. HPCP was purchased from Zibo Lanyin Chemical Co., Ltd. EG was bought from Qingdao Baixing Graphite Company, China. All the reagents were used as received.

2.2. Preparation of EP composites

EG and DOPO or HPCP were directly mixed with DGEBA at 125 °C under continuous stirring for 30 min. Then, stoichiometric DDS (with respect to epoxy) was added into the mixture. After stirring for 20 min, the mixture was degassed under vacuum and poured directly into a preheated mold and thermally cured in an air convection oven at 160 °C for 2 h and then at 180 °C for 5 h. The total content of flame retardants in each sample was consistent.

The preparation process of control samples, neat EP/DDS, EP/DOPO, EP/HPCP and EP/EG was similar to the above method with the same curing cycle. All the compositions of EP composites are listed in Table 1.

Table 1
Formulas of the cured epoxy resins.

Sample code	DGEBA/DDS (g)	EG (g)	DOPO (g)	HPCP (g)	EG content (wt%)	P content (wt%)
EP/DDS	100	0	0	0	0	0
EP/EG	80	20	0	0	20	0
EP/DOPO	92.3	0	7.7	0	0	1.1
EP/HPCP	91.8	0	0	8.2	0	1.1
EP/EG/DOPO-1	80	16	4	0	16	0.57
EP/EG/DOPO-2	80	14	6	0	14	0.86
EP/EG/DOPO-3	80	12	8	0	12	1.15
EP/EG/DOPO-4	80	10	10	0	10	1.44
EP/EG/HPCP-1	80	16	0	4	16	0.54
EP/EG/HPCP-2	80	14	0	6	14	0.81
EP/EG/HPCP-3	80	12	0	8	12	1.07
EP/EG/HPCP-4	80	10	0	10	10	1.34

2.3. Measurements

Thermogravimetric analysis (TGA) was performed using NETZSCH STA449F3 at a heating rate of 10 °C/min under nitrogen atmosphere from 50 to 800 °C.

The LOI values were measured at room temperature on a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO 4589-1984 standard and dimensions of all samples were 130 × 6.5 × 3 mm³. Vertical burning (UL94) tests were carried out on the NK8017A instrument (Nklsky Instrument Co., Ltd, China) with the dimension of 130 × 13 × 3 mm³ according to UL94 test standard. Cone calorimeter measurements were performed on an FIT cone calorimeter according to ISO 5660 under an external heat flux of 50 kW/m². The dimension of samples was 100 × 100 × 3 mm³. The measurement for each specimen was repeated three times, and the error values of the typical cone calorimeter data were reproducible within ±5%.

Py-GC/MS analysis was carried out with Agilent 7890/5975 GC/MS. The injector temperature was 250 °C, 1 min at 50 °C, temperature increase to 280 °C at a rate of 8 °C/min. The temperature of GC/MS interface was 280 °C, and the cracker temperature was 500 °C.

Morphological studies on the residual chars were conducted using a JSM-5610LV scanning electron microscope (SEM) at an acceleration voltage of 20 kV. The SEM instrument was integrated with an energy dispersive X-ray (EDX) microanalyser for elemental analysis.

Fourier Transform Infrared (FTIR) spectra were obtained using a Nicolet 6700 infrared spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets.

3. Results and discussion

3.1. Thermal analysis

The weight loss behavior was detected by TGA for exploring the basic degradation information. The TGA curves of all the samples under N₂ atmosphere are shown in Fig. 1. The characteristic thermal decomposition data, such as temperature at 5% weight loss (T_{5%}), temperature at maximum weight loss rate (T_{max}) and char yields at 800 °C are listed in Table 2.

As shown in Fig. 1(a) and Table 2, EG had a T_{5%} of 333 °C and a high char yield of 89% at 800 °C. With the incorporation of EG, DOPO and HPCP, the T_{5%} of the corresponding EP composites were dramatically decreased compared with that of the neat EP/DDS. The decrease in T_{5%} of phosphorus-containing samples was partially due to the formation of phosphorus-based compounds which catalyzed the decomposition of EP matrix in advance. However, it should be noted that T_{5%} of the phosphorus-containing samples

Download English Version:

<https://daneshyari.com/en/article/5201184>

Download Persian Version:

<https://daneshyari.com/article/5201184>

[Daneshyari.com](https://daneshyari.com)