



Synthesis of a novel reactive flame retardant containing phosphaphenanthrene and piperidine groups and its application in epoxy resin



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ABSTRACT

A novel reactive flame retardant (DPT) for epoxy resin (EP) was successfully synthesized through the reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), 1,4-phthalaldehyde and triacetone-diamine. DPT was used as co-curing agent of 4,4'-diaminodiphenyl methane (DDM) to prepare intrinsic flame-retardant EP (EP/DDM/DPT) thermosets. DSC results indicated that DPT was capable of curing EP and only a slight decline in glass transition temperatures of EP/DDM/DPT thermosets (162–173 °C) was observed. The incorporation of DPT led to the improvement of the char yields for EP/DDM/DPT thermosets at 800 °C. The EP/DDM/DPT-4 sample displayed a LOI value of 38.3% and a UL94 V-0 rating when the phosphorus content was only 1.0 wt %. Compared with comparable values for a EP/DDM sample, the peak of heat release rate (pk-HRR), average of heat release rate (av-HRR) and total heat release (THR) for EP/DDM/DPT-4 sample were decreased by 38.7%, 31.6% and 36.4%, respectively. During combustion, DOPO groups decomposed to generate phosphorus-containing compounds which promoted the formation of protective char layers in the condensed phase, and produced phosphorus-containing radicals which quenched the active radicals in the gaseous phase. Large quantities of hindered amine radicals with quenching effect and incombustible gases with diluting effect were released into the gaseous phase from the pyrolysis of piperidine groups. The presence of piperidine groups served to reinforce the action of phosphaphenanthrene groups. The piperidine and DOPO groups exerted flame retardant effect in both gaseous and condensed phases to endow EP thermosets with excellent flame retardancy.

1. Introduction

As a high performance resin, epoxy resin (EP) has motivated a worldwide interest due to its outstanding properties such as excellent chemical and heat resistance, adhesion, mechanical properties, and superior electrical insulating properties [1–3]. Therefore, it is widely applied as an adhesive, coating and resin matrix for advanced fiber-reinforced composites [4–6]. However, the flammability of epoxy resins restricts their application in many fields, so finding high-efficiency flame retardants to improve the flame retardancy of EP has received extensive attention [7,8].

In recent years, phosphorus-containing flame retardants, as one kind of halogen-free compounds, have been widely used in flame-retardant epoxy resins since the use of traditional halogenated

compounds is restrained for environmental reasons [9–11]. Among these flame retardants, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is regarded as the most promising due to its high reactivity, good thermal stability and applicability in epoxy resin [12,13]. However, an ideal flame-retardant property can only be achieved under high phosphorus content when DOPO is used alone. It is generally known that the flame-retardant influence of DOPO-based compounds can be enhanced by introducing other flame-retardant groups such as maleimide [14,15], s-triazine [16,17], triazine-trione [18,19], phosphazene [20,21], or silsesquioxane [22,23]. These DOPO-based compounds, either as reactive or additive flame retardants endow excellent flame retardancy for EP at low phosphorus content. However, compared with additive flame retardants, the incorporation of reactive flame retardants can avoid migration and result in more stable flame-

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retardant effect. Therefore, identification of new functional groups which display certain flame-retardant effects and combination of these with a phosphaphenanthrene group to prepare novel reactive flame retardants have become a research focus in recent years.

Recently, it has been reported that piperidine-containing compounds may contribute to improving the flame retardancy of polyolefins through an excellent radical quenching effect in the gaseous phase [24–28]. A novel macromolecular charring agent containing piperidine groups has been synthesized and combined with ammonium polyphosphate (APP) to improve the flame retardancy of polypropylene (PP) [24]. In addition, the synthesis and use of a multifunctional radical generator containing piperidine groups which can effectively provide flame retardancy to both PP films and plaques has been reported [25]. Previous studies have demonstrated that piperidine group exerts a flame-retardant effect in the gaseous phase through radical quenching effect [24,25]. However, the combination of piperidine group with phosphorus-containing functional groups in flame retardants had not been extensively reported. Moreover, as a hindered amine, covalently combining piperidine with phosphaphenanthrene groups into one molecule might produce a novel reactive flame retardant for epoxy resin.

Thus, in this work, a novel phosphaphenanthrene/piperidine-containing reactive flame retardant (DPT) was successfully synthesized by one-pot reaction between triacetonediamine, 1,4-phthalaldehyde and DOPO. DPT was incorporated into EP/DDM system as co-curing agent to prepare an intrinsic flame-retardant EP thermoset. The thermal properties, flammability and combustion behaviors of the modified EP thermosets was investigated by a series of tests.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight (EEW) of about 188 g/eq was provided by Yueyang Baling Huaxing Petrochemical Co., Ltd. Triacetonediamine was purchased from Zhengzhou Alfa Chemical Co., Ltd. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from Huizhou Sunstar Technology Co., Ltd. 1,4-Phthalaldehyde, ethanol and 4,4'-diamino-diphenyl methane (DDM) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of DPT

The synthesis route of DPT is presented in Scheme 1.

1,4-Phthalaldehyde (1.34 g, 0.01 mol) was dissolved in 20 mL of ethanol in a 100 mL, three-necked round-bottomed glass flask equipped with a mechanical stirrer, reflux condenser, and thermometer. Then, triacetonediamine (3.13 g, 0.02 mol) dissolved in 10 mL of ethanol was added dropwise over 0.5 h at room temperature. The mixture was heated to 50 °C and stirred for 2 h. After that, DOPO (4.32 g, 0.02 mol) was added, and the mixture was further heated to 80 °C and stirred for 8 h. After the reaction was finished, the mixture was allowed to cool to room temperature, and the crude product was collected by filtration, washed with ethanol and dried at reduced pressure and 60 °C for 24 h. The yield was 89%.

2.3. Preparation of the cured EP samples

DPT served as co-curing agent of DDM. The amount of active protons of amino groups in DPT and DDM was equal to the amount of epoxy groups in DGEBA. As presented in Table 1, appropriate quantities of DPT and DGEBA were mixed at 160 °C for 30 min to form a clear liquid. And then, the mixture was cooled to 80 °C and blended with DDM until DDM was completely dissolved. Finally, the mixture was degassed at reduced pressure for 5 min and poured into a preheated mold in an oven. The flame-retardant epoxy system was respectively

cured at 120 °C, 140 °C, 160 °C, and 180 °C for 2 h. The epoxy thermoset was cooled slowly to room temperature to prevent cracking. The EP/DDM thermoset was prepared in a similar way without the addition of DPT. Additionally, EP/DDM/DOPO thermoset was prepared similarly with the addition of DOPO at 80 °C.

2.4. Preparation of uncured EP mixtures for DSC test

The EP/DPT mixture (the mass ratio was 1:1.1) was prepared by dispersing EP and DPT in acetone under ultrasonic dispersion. The solution was evaporated at room temperature at reduced pressure. The EP/DDM and EP/DDM/DPT mixtures (the mass ratios were reported in Table 1) were obtained in a manner similar to that for the preparation of the EP/DPT mixture.

2.5. Measurements

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.

¹H and ³¹P NMR spectra were obtained using a Bruker AV400 NMR spectrometer and DMSO-*d*₆ as the solvent.

Elemental analysis (EA) was performed using a Vario EL cube Elemental Analyzer.

Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin-Elmer DSC 4000 at a heating rate of 10 °C/min from 80 to 240 °C in a nitrogen atmosphere.

The LOI values were measured at room temperature using a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM D2863. Dimensions of all samples were 100 × 6.5 × 3 mm³. Vertical burning (UL-94) tests were carried out using a NK8017A instrument (Nklsky Instrument Co., Ltd., China) and dimensions of specimens were 130 × 13 × 3 mm³ according to the UL-94 test standard. Cone calorimeter measurements were performed using a FTT cone calorimeter according to the ISO 5660 standard under an external heat flux of 50 kW/m². The dimensions of samples were 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%.

Thermogravimetric analysis (TGA) was performed using a NETZSCH STA449F3 at a heating rate of 10 °C/min from 40 to 800 °C in a nitrogen atmosphere.

Thermogravimetric analysis/infrared spectrometry (TGA-FTIR) was performed using a NETZSCH TGA 209F3 that was interfaced with a Nicolet 6700 FTIR spectrophotometer. About 6.0 mg of sample was put in an alumina crucible and heated from 40 to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

Py-GC/MS analysis was carried out with an Agilent 7890/5975 GC/MS. The injector temperature was 250 °C; 1 min at 50 °C then the temperature was increased to 280 °C at a rate of 8 °C/min. The temperature of the 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 10 kV. The SEM instrument was integrated with an energy dispersive X-ray (EDX) microanalyser for elemental analysis.

3. Results and discussion

3.1. Synthesis and characterization of DPT

DPT was prepared using a one-pot synthesis composed of two procedures: the Schiff base (DP) was obtained via the dehydration reaction between 1,4-phthalaldehyde and triacetonediamine; DPT was synthesized through the addition reaction between DP and DOPO.

The FTIR spectra of DP, DOPO and DPT are presented in Fig. 1. As

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