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Pyrolysis route of a novel flame retardant constructed by phosphaphenanthrene and triazine-trione groups and its flame-retardant effect on epoxy resin

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ABSTRACT

A novel flame retardant TGIC-DOPO, which was constructed by phosphaphenanthrene and triazine-trione groups, was synthesized via a controllable ring-opening addition reaction between 1,3,5-triglycidyl isocyanurate (TGIC) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The flame-retardant effect of TGIC-DOPO on an epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), cured with 4,4′-diamino-diphenyl sulfone was investigated. The results of the limited oxygen index (LOI), UL94 vertical burning test, and cone calorimeter test indicated that the TGIC-DOPO imparted flame-retardant properties to DGEBA thermosets. When the mass fraction of TGIC-DOPO reached 12wt.%, the DGEBA thermoset acquired a LOI value of 33.3%, UL94 V-0 rating, and the lower peak of heat release rate (pk-HRR) at 481 kW/m^2. Specifically, the DGEBA thermoset with 6wt.% TGIC-DOPO had an LOI value of 33.3%, whereas the DGEBA thermoset with 10wt.% TGIC-DOPO had the highest LOI value of 35.2% among the specimens. Meanwhile, the time to ignition, pk-HRR, average of effective heat of combustion (av-EHC), and total heat release of the DGEBA thermoset were all negatively correlated with the mass fraction of TGIC-DOPO. Moreover, the average CO_2 and CO yields exhibited a downtrend with increasing mass fraction of TGIC-DOPO from 6wt.%. The reduction of av-EHC with increase of TGIC-DOPO content in thermosets confirmed the free radical quenching effect of TGIC-DOPO in gaseous phase during combustion. The macromorphology, micromorphology and element content of the residues from the cone calorimeter test revealed the bi-phase flame-retardant effect of TGIC-DOPO. Furthermore, the pyrolysis route of TGIC-DOPO were investigated via Py-GC/MS, which disclosed that the decomposed TGIC-DOPO with double flame-retardant groups released various fragments with quenching effect on free radical chain reaction of combustion. The fragments enhanced the flame-retardant performance of DGEBA thermosets both in gaseous and condensed phases. The flame-retardant performance of TGIC-DOPO was resulted by the quenching effect of TGIC-DOPO and the synergistic effect of phosphaphenanthrene and triazine-trione groups.

1. Introduction

In the past several decades, epoxy resin has been rapidly and significantly developed in theory and in practical application [1–5]. In the electronic and electrical industry, various epoxy resins are used as adhesives [6,7] and electrical encapsulation materials [8,9] because of their excellent electrical insulation and adhesive properties as well as corrosion resistance. However, most epoxy resins are flammable, which pose potential risks. Thus, to impart flame-retardant properties to epoxy resin is necessary for its practical demands [10,11].

The synthesis of novel phosphorus-containing flame-retardant additives and the preparation of phosphorus-containing flame-retardant epoxy resins have already been conducted [12–15]. To obtain a highly efficient flame-retardant epoxy resin, several flame-retardant chemical structures composed of single or multiple flame-retardant functional groups have been utilized, such as phosphaphenanthrene [16–18], cyclotriphosphazene [19,20], phosphorus-containing silsesquioxane [21], pentaerythritol diphosphonate [22,23], triazine [24,25], and triazine-trione [26–28] structures. Moreover, several novel flame retardant

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additive structures with a high flame-retardant efficiency have been discovered for the synergistic effect of flame retardant groups [20,29].

In the present work, a novel addition-type flame retardant TGIC-DOPO, which was based on phosphaphenanthrene and triazine-trione groups, was prepared via a one-step controllable ring-opening addition reaction. Then, the epoxy resin thermosets incorporated TGIC-DOPO were investigated to evaluate the flame-retardant behavior. The pyrolysis route of TGIC-DOPO was also explored to find out its flame-retardant mechanism on epoxy resin thermosets.

2. Experimental

2.1. Materials

1,3,5-Triglycidyl isocyanurate (TGIC) was provided by Shanghai Fangruida Chemical Co. Ltd., China. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was supplied by Shanghai Eutec Chemical Co., China. The epoxy resin, diglycidyl ether of bisphenol-A (DGEBA, commercial name: E-51), was purchased from Blue Star New Chemical Material Co. Ltd., China. 4,4′-Diamino-diphenyl sulfone (DDS) was purchased from Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Synthesis of TGIC-DOPO

DOPO (63.7 g, 0.295 mol) was melted at 135 °C with mechanical stirring in a three-neck flask. After the DOPO was completely melted, TGIC (29.7 g, 0.100 mol) was added into the reaction system at the rate of 2.97 g per 20 min. The reaction temperature was then elevated to 170 °C within 30 min, and the mixture was stirred for 3 h. The white powders of TGIC-DOPO were obtained after the cooled products were grinded at room temperature. The products were refined by washing with toluene and then drying. The reaction formula is shown in Scheme 1. The yield was >98.2%. The purity of TGIC-DOPO was 93.6% investigated by high performance liquid chromatography (HPLC). The impurities were mainly from incomplete addition reaction between TGIC and DOPO. The obtained peaks in the Fourier transform infrared (FT-IR) spectra (KBr, cm^{-1}) were 3369 (OH), 3065 (Ar—H), 2905 (C—H), 1690 (C═O), 1595 (C_6H_6), 1464 (C—N), 1203 (P═O), 915 (P-O-Ph), and 756 (o-R_1-Ph-R_2). The ^{1}H nuclear magnetic resonance (^{1}H NMR) data obtained (DMSO-d_6, ppm) were δ = 7.1 to 8.3 (Ar—H, 24H), δ = 5.1 and 5.4 (CH, 3H), δ = 3.8 and 4.2 (DOPO-CH_2, 6H), δ = 3.7 ($C_3N_3O_3$—CH_2, 6H), and δ = 2.1 to 2.3 (OH, 3H). The ^{31}P nuclear magnetic resonance (^{31}P NMR) datum obtained (DMSO-d_6, ppm) was δ = 35.9.

2.3. Preparation of flame retardant DGEBA and the control sample

DGEBA and TGIC-DOPO were heated to 185 °C and stirred until TGIC-DOPO was completely dissolved in DGEBA. DDS was then added into the mixture at 185 °C and blended thoroughly. After the mixture was degassed at 185 °C for 3 min, it was poured into preheated molds and cured at 150 °C for 3 h and then at 180 °C for 5 h. The samples were labeled as 6%TGIC-DOPO/DGEBA/DDS, 8% TGIC-DOPO/DGEBA/DDS, 10%TGIC-DOPO/DGEBA/DDS, and 12% TGIC-DOPO/DGEBA/DDS based on the mass fraction of TGIC-DOPO in the DGEBA thermoset. The control sample, DGEBA/DDS, was also prepared in the same manner but without the addition of the flame retardant TGIC-DOPO. The formulations of DGEBA, DDS, and TGIC-DOPO in each epoxy resin thermosets are listed in Table 1.

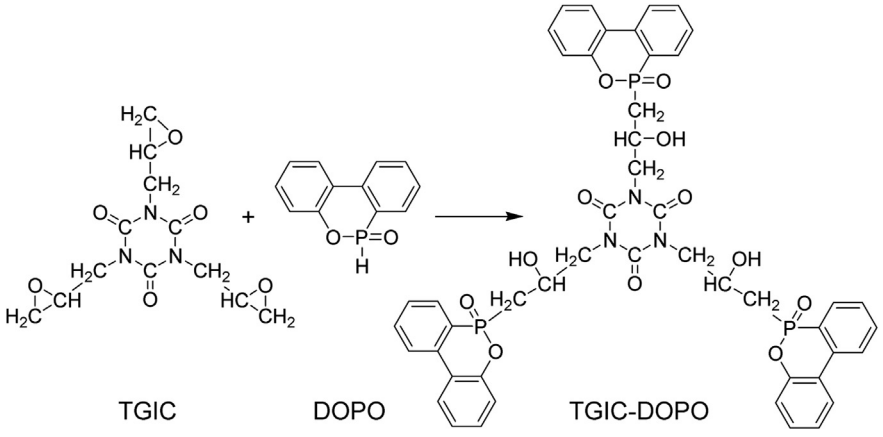
2.4. Characterizations

FT-IR spectra were obtained using a Nicolet iN10MX-type spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets. The ^{1}H NMR and ^{31}P NMR data were obtained using a Bruker AV300MB NMR spectrometer and a DMSO-d_6 solvent.

The purity of TGIC-DOPO was investigated by Shimadzu HPLC LC10AT with C-18 column. The detection wavelength was 254 nm. The mobile phase was the mixture of methanol and water, whose volume ratio was 90:10. The flowing rate of mobile phase was 1 mL/min.

The glass transition temperature (T_g) was determined under N_2 atmosphere by using a TA instrument Q100 differential scanning calorimeter. The thermal history of the TGIC-DOPO sample was eliminated by heating at 140 °C for 1 min and then cooling down to 40 °C at the rate of 10 °C/min. The T_g of sample was then determined by heating to 200 °C at 10 °C/min. The thermal history of the DGEBA thermoset samples were eliminated by heating at 210 °C for 1 min and then cooling down to 40 °C at 10 °C/min. The T_g of samples were then determined by heating to 250 °C at 10 °C/min. All the tests were repeated three times, and all of the T_g values were reproducible within ±3%.

Thermogravimetric analysis (TGA) was performed using a TA instrument Q5000 IR thermal gravimetric analyzer. The sample was placed in a platinum crucible and heated from 50 °C to 700 °C at the rate of 20 °C/min in N_2 atmosphere. All the tests were repeated three times, and the typical TGA data were reproducible within ±5%.



Scheme 1. Synthesis of TGIC-DOPO.