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Synergistic flame-retardant behavior and mechanisms of aluminum poly-hexamethylenephosphinate and phosphaphenanthrene in epoxy resin

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ABSTRACT

The flame retardants aluminum poly-hexamethylenephosphinate (APHP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide(DOPO) were incorporated into diglycidyl ether of bisphenol A (EP) thermoset, and then the synergistic flame-retardant behavior and mechanism of APHP/DOPO were investigated. Comparing with the thermosets with 6%APHP and 6%DOPO alone, 2%APHP/4%DOPO/EP thermosets obtained the higher limited oxygen index, higher UL94 rating, decreased peak of heat release rate and less total heat release from cone calorimeter test. The results reveal a synergistic effect between APHP and DOPO. The synergistic effect of APHP/DOPO in gaseous phase obviously reduced effective heat of combustion, which implies the better flame inhibition effect through quenching free radical chain reaction of combustion. The synergistic charring effect in condensed phase led to the higher char yield, which locked more carbonaceous contents in residue and form more barrier to heat spreading. All the results were caused by the early decomposed DOPO that interacted with the later decomposed APHP to produce more char and decease release of the inflammable gas. Therefore, the burning intensity of APHP/DOPO thermosets obviously was weakened by the synergistic effect of APHP/DOPO.

1. Introduction

In the past several decades, flame-retardant epoxy resins have become important advanced materials in electronic and electrical equipment industries due to their excellent adhering, physical-mechanical, electric, and flame-retardant properties [1–6]. Therefore, they are widely applied as binders in printed circuit boards and as packaging materials in light-emitting diode illuminators [7–12]. To enhance flame-retardant efficiency and comprehensive properties of epoxy resins, a series of novel flame retardants especially for phosphorus-based flame retardants were prepared and incorporated into epoxy resins because of their halogen-free and high flame retardancy properties [13–19]. Among these flame retardants, some reactive and additive phosphorus flame retardants are the most important ones [20–29].

As an important reactive phosphorus flame retardant, 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide(DOPO) was widely used to react with epoxy resin to prepare flame-retardant thermosets and also introduced into curing agent to obtain flame-retardant curing system [20,30,31]. Recently, most of the studies about DOPO have focused on the novel additives constructed by phosphaphenanthrene and several functional groups such as cyclotriphosphazene [14,32], silsesquioxane [33], triazene [16,34,35], and other groups [36–38]. These additives can endow epoxy resin thermosets by high flame retardancy, and confirm flame-retardant group synergistic effect between DOPO and other functional groups by constructing novel molecules. Though the studies on constructing DOPO-based additives have made progress on developing novel and various high efficiency flame retardants, it is still essential to explore the flame-retardant behavior of composites because it has access to seek for flame-retardant epoxy resin thermosets with higher performance [23,39–43].

Recently, a novel alkyl-phosphinate flame retardant, aluminum poly-hexamethylenephosphinate (APHP, Scheme 1), was prepared in our laboratory [44]. In former study, APHP can endow diglycidyl ether of bisphenol A (EP) thermosets with better flame retardancy in both condensed and gas phase. But the APHP/EP thermosets still failed to V-0 rating. In this study, we applied APHP into a diglycidyl

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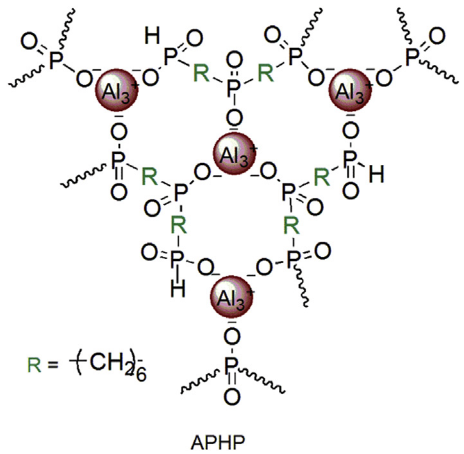


Scheme 1. Molecular structures of APHP.

ether of bisphenol A (DGEBA) pre-reacted with DODO and then cured with 4,4′-diamino-diphenyl methane (DDM). After the thermosets were investigated, a rising flame retardancy and significantly synergistic effect between APHP and DOPO were obtained in the flame-retardant epoxy resin thermosets. In this study, quantitative assessment on the synergistic effect of APHP and DOPO also was carried out [45].

2. Experimental

2.1. Material

Aluminum poly-hexamethylenephosphinate(APHP) was prepared in our laboratory. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was supplied by Shanghai Eutec Chemical Co., China. The molecular structures of APHP were shown in Scheme 1. The diglycidyl ether of bisphenol A (EP, commercial name: E-51), was purchased from Blue Star New Chemical Material Co. Ltd., China. 4,4′-Diamino-diphenyl methane (DDM) was purchased from Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Preparation of flame-retardant EP thermosets and the control samples

Typically, the 2%APHP/4%DOPO/EP thermoset sample with 2 wt% APHP and 4 wt% DOPO was prepared via the method: DOPO (5.28 g) was melted in DGEBA (100 g) at 150 °C, and then P—H bond in DOPO reacted with the epoxy group from DGEBA in ring opening reaction for 5 h. The reaction formula is as shown in Scheme 2. Then APHP (2.64 g) was incorporated into the mixture. After APHP was evenly dispersed in DGEBA, the equivalent mole DDM (24.07 g) of the reserved epoxy groups (decreased by the mole of addition DOPO) was added into the mixture at 110 °C and blended thoroughly. After the mixture was degassed at 120 °C for 3 min, it was poured into preheated mold and cured at 120 °C for 2 h and then at 170 °C for 4 h. Then, 2%APHP/4%DOPO/EP thermoset sample was obtained. Other samples were prepared using the same method after changing their compositions according to Table 1.

The samples were labeled based on the mass fraction of APHP and DOPO in the epoxy resin thermoset. The thermosets with 6% APHP and 6%DOPO alone was labeled as 6%APHP/EP and 6%DOPO. The control sample, DGEBA was cured to prepare thermoset in the same manner but without the addition of the flame retardant APHP and DOPO, and the sample was named as pure EP. The formulations of DGEBA, DDM, APHP and DOPO in each epoxy resin thermosets are listed in Table 1.

2.3. Characterizations

Thermogravimetric analysis (TGA) was performed using a TA instrument Q5000 IR thermal gravimetric analyzer. The sample was placed in an alumina crucible and heated from 50 °C to 700 °C at the rate of 20 °C/min in N_2 atmosphere.

The limited oxygen index (LOI) value was measured using an FTT (Fire Testing Technology, UK) Dynisco LOI instrument according to ASTM D2863-97 (sample dimension: 130 mm × 6.5 mm × 3.2 mm). The LOI measurement for each specimen was repeated three times, and their error values were ±0.5%. The vertical burning test for the UL 94 combustion level was performed according to ASTM D 3801 (sample dimension: 125 mm × 12.7 mm × 3.2 mm). Fire behavior was characterized using FTT cone calorimeter according to ISO5660 at an external heat flux of 50 kW/m^2 (sample dimension: 100 mm × 100 mm × 3 mm). The measurement for each specimen was repeated two times, and the error values of the typical cone calorimeter data were reproducible within ±10%. All the data were collected during combustion.

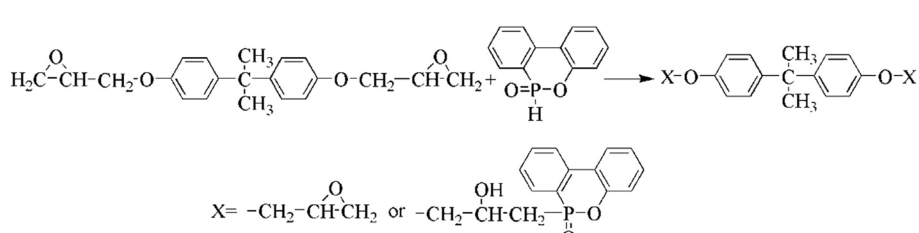
The micromorphology images of the residues after cone calorimeter test were obtained using a FEI Quanta 250 FEG field-emission scanning electron microscope at high vacuum conditions with a voltage of 30 kV. The element contents of residues from cone calorimeter test were investigated via an AMETEK Quanta 250 FEG/EDS Energy Dispersive Spectrometer. The tested specimens were obtained from the mixture of residues with sufficiently mixed and grinded, and the results were the average of the three times repeated tests which were all reproducible within ±5%.

To recognize the pyrolysis fragments of APHP/DOPO/EP thermosets, a Shimadzu GC-MS-QP5050A gas chromatography-mass spectrometer equipped with a PYR-4A pyrolyzer was employed. The helium (He) was utilized as carrier gas for the volatile products. The injector temperature was 250 °C, the temperature of GC/MS interface was 280 °C and the cracker temperature was 550 °C.

3. Results and discussion

3.1. Fire behavior: LOI and UL94 test

The flame-retardant properties of all the thermosets were determined using LOI and UL94 vertical burning tests. And the



Scheme 2. Ring opening reaction between DGEBA and DOPO.