



Synthesis and characterization of aluminum poly-hexamethylenephosphinate and its flame-retardant application in epoxy resin



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ABSTRACT

A flame retardant additive, aluminum poly-hexamethylenephosphinate (APHP) with a polymeric structure was synthesized from 1,5-hexadiene, hypophosphorous acid and aluminum ions. The molecular structure of APHP and thermal stability were characterized by solid nuclear magnetic resonance, Fourier transform infrared and thermogravimetric analysis. Then, APHP was applied into diglycidyl ether of bisphenol-A cured by 4,4'-diamino-diphenylmethane. APHP showed flame-retardant effect on the epoxy thermosets in limited oxygen index (LOI), UL94 vertical test and cone calorimeter. The thermosets with only 4 wt.% APHP obtained an LOI value of 32.7% and reached the UL94 V-1 rating. The APHP/EP thermosets decreased the $pk-HRR$, THR and $av-EHC$ values, decreased CO_2Y and enhanced the COY ratios, and also reserved more residual char comparing with neat thermoset. The less incorporation of APHP in thermosets will impose the better flame retardancy to epoxy thermosets. The flame-retardant effect of APHP was resulted by its two main pyrolyzed contents phosphorus and alkyl-phosphinic fragments. In condensed phase, the phosphorus-containing contents facilitated to the higher char yields and the formation of intumescent char layer, which led to a reduction of the released fuel and a strong barrier effect to weaken the combustion intensity. In gas phase, the PO, PO₂ and alkyl-phosphinic fragments with quenching effect were released from the phosphorus-containing contents, and can decrease the heat release and weaken the combustion intensity.

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1. Introduction

In the recent years, high-performance halogen-free flame-retardant systems have become one of the most noteworthy topics in flame retardant fields to avoid the environment problems of several halogen-containing flame retardants [1]. Phosphorus-based flame retardants like phosphaphenanthrene, phosphazene, phosphate and phosphinate were all considered as effective contents to most of polymers [2,3]. Due to outstanding flame-retardant effect and water resistance, alkyl-substituted phosphinates were especially taken more attention in both commercial application and scientific research [4].

Alkyl-substituted phosphinates were first prepared and commercialized by Clariant Co. Series of metal alkyl-substituted

phosphinates, especially aluminum salt of diethylphosphinic acid (AlPi), have been designed, synthesized and applied [5–9]. It is reported that AlPi and its composites are commercially available as Exolit OP1230, 1240, 1312, 1200, 1311 [10–14]. AlPi was found to be well working in polyamides and glass fiber reinforced polyamides, poly(ethylene terephthalate) and poly(butylene terephthalate) [4,15–18], also in poly(methyl methacrylate), polyurethane, and polyolefin [19–22]. In addition, some other kinds of alkyl-substituted phosphinates, e.g. aluminum diisobutylphosphinate and aluminum phenylphosphinate, were also proven to be effectively flame retardant in some certain polymer composites [23–25]. Polyamides and polyesters system were most researched in the flame-retardant application of AlPi. Ramani et al. investigated the flame-retardant mechanism of AlPi in combination with melamine polyphosphate and organically modified montmorillonite nanoclay in PA6 [26]. Schartel et al. applied AlPi in synergize with melamine polyphosphate and zinc borate in glass-fiber-reinforced PA66 and found that the AlPi acted mainly by flame inhibition [10]. Horrocks et al. investigated the combined effects and

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burning behavior of AlPi and zinc stannate on HTPA [12]. Hao et al. found the synergistic effect between nano-Sb₂O₃ and AlPi on the flame retardancy of PET [27]. Gallo et al. investigated the flame retardancy of PBT containing AlPi and nanometric metal oxides and found that AlPi acted mainly in the gas phase through the release of diethylphosphonic acid [28].

In addition, studies on alkyl-substituted phosphinates with similar structure to AlPi have been further investigated. While the alkyl-substituted phosphinates change their metal type and structure of the alkyl groups, they will cause different flame-retardant effect on polymers. Wang et al. investigated that the mixture of diisobutylphosphonic and monoisobutylphosphonic aluminums were found to be effective on glass fiber reinforced PA6 [23,24]. Fang et al. prepared cerium phenylphosphonate and found low synergistic flame-retardant effect with decabromodiphenyl oxide in glass-fiber reinforced PET [29]. Liu et al. prepared zinc methylethylphosphinate and applied it into epoxy thermoset (EP) [30].

Normally, the phosphorus-based flame retardants can endow EP well flame retardancy [31], such as the aromatic phosphates [32], phosphaphenanthrene [33–35], cyclotriphosphazene [36], phosphorus-containing silsesquioxane [37], pentaerythritol diphosphate [38,39]. The flame retardant application of alkyl-substituted phosphinate were seldom reported in the previous literature.

To further explore the influencing rule on flame retardancy of different molecular structures of alkane in alkyl-substituted phosphinates, the alkyl-substituted phosphinates was attempted to be constructed to a polymeric macromolecule. According to this assumption, a flame retardant additive, aluminum polyhexamethylenephosphinate (APHP) with a polymeric structure, was synthesized and characterized. The flame retardancy, the pyrolysis route and flame-retardant mechanism of APHP in epoxy thermosets were also investigated.

2. Experimental

2.1. Materials

1,5-hexadiene was purchased from Tokyo Chemical Industry Co. Ltd., Japan. The diglycidyl ether of bisphenol-A (commercial name: E-51), was obtained from Blue Star New Chemical Material Co. Ltd., China. Hypophosphorous acid, aluminum chloride hexahydrate, 4,4'-diamino-diphenylmethane (DDM), 2,2'-azobis(2-methylpropionitrile), and propanol were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Synthesis of APHP

Hypophosphorous acid (50% wt.% H₂O) (137.3 g, 1.04 mol) was melted in propanol(350.0 g, 5.83 mol) with mechanical stirring in a three-neck flask. Then 1,5-hexadiene (65.6 g, 0.80 mol) was added into the mixed solution with reflux condensing, and 2,2'-azobis(2-methylpropionitrile) (1.3 g, 0.008 mol) was added into the reaction system as initiator. The reaction temperature was then elevated to 65 °C within 20 min, and the mixture was stirred for 24 h. While the mixture turn to white emulsion, aluminum chloride hexahydrate (83.6 g, 0.35 mol) dispersed in 100 mL propanol was dripped into the reaction system within 60 min. After another 16 h, more white granules appeared. The resulting solids were then filtered off. The solids were washed and filtrated with water at 80 °C till the PH value of the filtrate was 7. The reaction formula is shown in Scheme 1. Finally the products were dried at 120 °C and the yields was >92.0%. FT-IR (KBr, cm⁻¹): 2924 and 2857 (C–H); 2356 (P–H); 1459 and 1405 (P–CH₂); 1176 (P=O); 1093 (P–O); 716 (P–C). ¹H NMR (ppm): δ = 2.29 (C–H), δ = 4.51 (P–H); ¹³C NMR: δ = 31.54

(–CH₂–CH₂–CH₂–), 22.82 (CH₂–CH₂–PO₂–); ³¹P NMR (ppm): δ = 37.54 (–(CH₂)₆–PO₂[–]–(CH₂)₆–), 18.98 (–(CH₂)₆–PO₂–H); ²⁷Al NMR (ppm): δ = 13.61. Phosphorus content: 20.3 wt.%.

2.3. Preparation of flame-retardant EP and the control sample

DGEBA and APHP were heated to 120 °C and stirred till APHP was completely dispersed in DGEBA. DDM was then 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 the preheated molds and cured at 120 °C for 2 h and then at 170 °C for 4 h. The samples were labeled as 1%APHP/EP, 2%APHP/EP, 3%APHP/EP, 4% APHP/EP and 6%APHP/EP based on the mass fraction of APHP in EP thermosets. The control sample, EP, was also prepared in the same manner but without the addition of the flame retardant APHP. The formulas of DGEBA, DDM, and APHP in each epoxy thermosets are listed in Table 1.

2.4. Characterizations

FTIR spectra were obtained using a Nicolet iN10MX-type spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets. The ¹H NMR, ¹³C NMR, ²⁷Al NMR and ³¹P NMR data were obtained using a Bruker 400 MHz WB Solid-State NMR Spectrometer.

The phosphorus content was detected using Perkin Elmer Optima 8000 inductively coupled plasma optical emission spectrometry (ICP-OES).

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 N₂ atmosphere. All the tests were repeated three times, and the typical TGA data were reproducible within ±5%.

To detect volatile pyrolysis products, a Mettler-Toledo TGA/DSC-1 thermogravimetric analyzer was coupled to a Bruker Tensor 27 Fourier-transform infrared spectrometer (TGA-FTIR). Each sample was placed in an alumina crucible and heated from 50 to 700 °C at a heating rate of 20 °C/min under N₂ atmosphere. The thermogravimetric analyzer and FTIR spectrometer were connected by a quartz capillary at 230 °C.

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: 130.0 mm × 6.5 mm × 3.2 mm). The vertical burning test for the UL 94 combustion level was performed using an FTT0082 instrument according to ASTM D3801 (sample dimension: 125.0 mm × 12.7 mm × 3.2 mm). The cone calorimeter test was performed using an FTT0007 cone calorimeter according to ISO5660 at an external heat flux of 50 kW/m² (sample dimension: 100 mm × 100 mm × 3 mm). The measurement for each specimen was repeated three times, and the error values of the typical cone calorimeter data were reproducible within ±10%.

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 surface 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, a Shimadzu GC-MS-QP5050A gas chromatography-mass spectrometer equipped with a PYR-4A pyrolyzer was employed. The helium (He) was

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