Polymer Degradation and Stability 149 (2018) 69–77

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Flame-retarding epoxy resin with an efficient P/N/S-containing flame retardant: Preparation, thermal stability, and flame retardance

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ARTICLE INFO

Keywords:
Epoxy resin
Flame retardance
Thermal stability
Mechanism

ABSTRACT

To further study the effect of the phosphorus, sulfur, and nitrogen-containing flame retardant on epoxy resin, a DOPO-based phenol derivative 4-[(benzothiazolyl 2-amino)(6-oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl) methyl] phenol namely D-P-A, was successfully synthesized from 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), *p*-hydroxybenzaldehyde (PHBA), and 2-aminobenzothiazole (ABZ), and used to flame retard epoxy resin (EP). As expected, D-P-A imparted flame retardance to epoxy resin. For example, with 7.5 wt% loading of D-P-A, epoxy thermoset passed a UL-94 V-0 rating, and got a LOI value of 29.6%. Besides, D-P-A played an effective role in inhibiting heat release of EP, that EP/7.5% D-P-A showed a peak of heat release rate (PHRR) of 713 kW/m^2 much lower than 1137 kW/m^2 of EP. However, it decomposed in advance owing to the lower thermal stability of D-P-A. Finally, through Scanning electron microscopy (SEM), Raman spectra and X-ray photoelectron spectroscopy (XPS) and pyrolysis-gas chromatograph/mass spectrometer (Py-GC/MS), it disclosed that D-P-A exerted its flame-retardant activity both in the vapor and condensed phase.

1. Introduction

Epoxy resin (EP) is one of most popular thermosetting polymers, and widely used in coatings, adhesives, composites etc. Due to its good resistance to chemical and corrosion, low dielectric property and excellent mechanical strength [1–3]. While, it needs to satisfy the requirement of flame-retardant standard in some fields, since EP is flammable and cannot be self-extinguished, resulting in a high risk for people's lives and properties. Therefore, it is urgent to adopt proper ways to reduce the flammability of epoxy resins.

To achieve this aim, in the past decades, halogen-containing additives have been largely developed, and showed high effectiveness in flame-retarding polymers, while some of them are now restricted to use in consideration of their harm to the environment [4–7]. To date, lots of researchers have reported their own development in flame retarding epoxy resins, and series of work are presented. For example, epoxy nanocomposites with metal hydroxides [8,9] and carbon-family materials [10] are gradually becoming a focus. Although they have apparent improvement in terms of the cone calorimeter (CC) results, mechanical and thermal properties, they cannot give the direct answer to the flammability of epoxy resin. As for organic flame retardants, phosphorus [11,12] or phosphorus uniting other elements such as nitrogen [13–17], silicon [18–20], and sulfur [21–24] based flame retardants are now most prevalent due to their high efficiencies on enhancing the extinguished ability of epoxy resins. To date, DOPO based derivatives are largely reported to modify epoxy resins [25–30]. For instance, Wang reported a novel reactive DOPO-based triazol compound, and it imparted flame retardance to epoxy resin with 4 wt% loading [31]. Recently, it is reported by our group that P/N/S-containing flame retardants including DOPO-ABZ, D-AZ and DHBAZ (see Scheme 1) were effective on flame-retarding epoxy resins [23,32,33]. Inspired by the chemical structures of them, D-P-A with the similar structure is designed and used in epoxy resin. It is found that D-P-A also works well in flame-retarding epoxy resins; moreover, it shows less negative effect on the thermal stability of epoxy resin compared to DOPO-ABZ, D-AZ and DHBAZ, that EP/D-P-A has higher initial decomposition temperature than EP/DOPO-ABZ, EP/D-AZ and EP/DHBAZ with the same loading of flame retardants. In order to further understand the effect of this

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https://doi.org/10.1016/j.polymdegradstab.2018.01.026
Received 26 October 2017; Received in revised form 21 January 2018; Accepted 28 January 2018
Available online 31 January 2018
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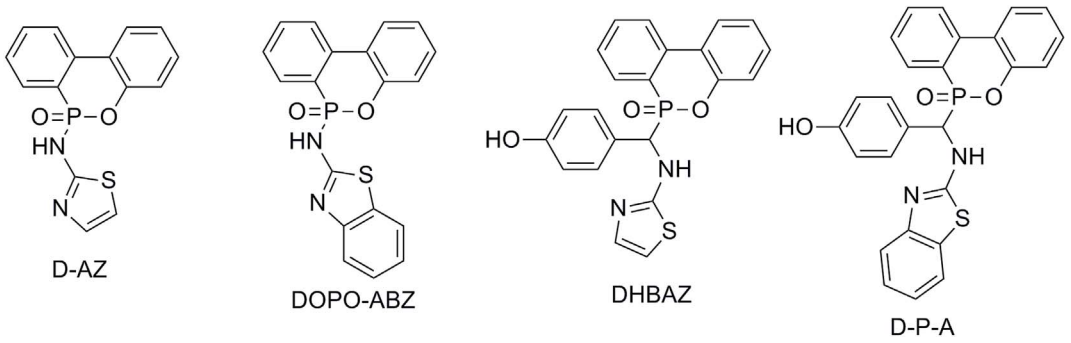


Scheme 1. The chemical structures of D-AZ, DOPO-ABZ, DHBAZ and D-P-A.

compound on epoxy resin, the detailed work has been carried out.

In this paper, a DOPO-based flame retardant namely D-P-A derived from DOPO, PHBA, and ABZ was synthesized through a two-step reaction. Then D-P-A was used to modify epoxy resin. The chemical structure of D-P-A was characterized and confirmed. Thermal properties of epoxy thermosets were studied. The flammability and combustion tests were experimented to assess the flame retardance and fire performance of flame-retardant epoxy thermosets. Finally, the flame retardant mechanism of D-P-A was also investigated.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA, E-44) was available from Xingchen Synthetic Material Co., Ltd. (Nantong, China). 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was commercially obtained from Sunstar Technology Co., Ltd. (Huizhou, China). Absolute ethanol, 4, 4′-diamino-diphenylmethane (DDM) and *p*-hydroxybenzaldehyde (PHBA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2-aminobenzothiazole (ABZ) was provided by Macklin Biochemical Co., Ltd. (Shanghai, China).

2.2. Synthesis of D-P-A

The synthetic route of D-P-A was shown in Scheme 2. To a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet, 2-aminobenzothiazole (0.1 mol, 15.0 g) and *p*-hydroxybenzaldehyde (0.1 mol, 12.2 g) dissolved in 100 ml absolute ethanol were added and the solution were stirred at 50 °C for 2 h. Afterwards, the ethanol solution of DOPO (0.1 mol, 21.6 g) was gradually added into the reaction system accompanied with vigorous stirring. And then the reaction was kept at 50 °C for another 12 h. Finally, the solution was cooled down to the room temperature. The resulting precipitate was filtered, and then washed with ethanol under ultrasonic, and the process was repeated by twice. The product was dried at 80 °C for 8 h to obtain white powder (D-P-A, yield: 65%). FTIR (KBr, cm^{-1}), 3407 (-OH), 3227 (-NH-), 3034 (aromatic-H), 2918, 2811 (aliphatic C-H), 1601, 1529, and 1446 (benzene ring), 1220 (P = O). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 9.54, 9.51 (s, OH), 9.09, 8.99 (d, J = 9.6 Hz, N-H), 8.21–8.15 (m, 2H), 7.78–6.96 (m, 12H), 6.74–6.69 (m, 2H), 5.70, 5.41 (m, 1H); ^{31}P NMR (162 MHz, DMSO-d_6, ppm): 30.01, 28.58. HRMS (ESI^+): calcd. for $C_{22}H_{18}N_2O_3PS$ $[M+H]^+$ 471.0932, found 471.0896.

2.3. Preparation of EP/D-P-A samples

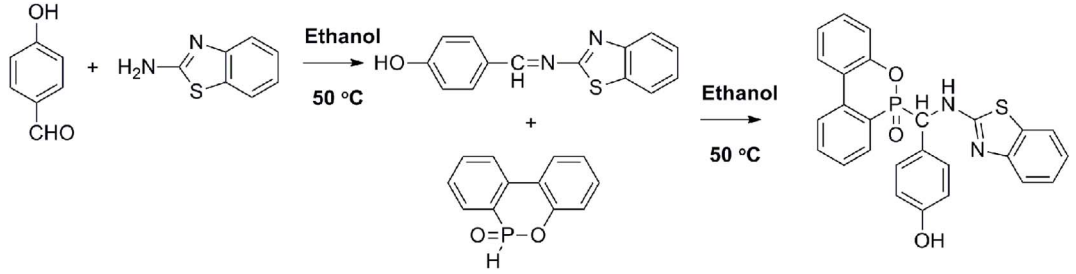
EP and D-P-A were firstly added to a stand-up flask, and mixed homogeneously at 130 °C for 30 min under rapid agitation using a mechanical stirrer. Secondly, after the solution was cooled down to 90 °C, DDM was added, and the mixture was vigorously stirred for 5 min. Then the resulting mixture was rapidly poured into preheated stainless steel molds and cured at 100 °C for 3 h, 150 °C for 2 h, and 180 °C for 2 h, respectively. Besides, EP obtained as a control was cured at 100 °C for 3 h and 150 °C for 2 h. It should be noted that the total amount of active protons of D-P-A and DDM used simultaneously as curing agents was equal to that of DDM used individually. The corresponding formulations of epoxy thermosets are listed in Table 1.

2.4. Characterization

The FTIR spectra of DOPO, PHB, ABZ and D-P-A were recorded in the range of 400–4000 cm^{-1} (KBr pellets) on a Thermo Nicolet 5700 FT-IR instrument. ^{1}H and ^{13}P NMR spectra of D-P-A were recorded on a Bruker AVANCE AV II-400 NMR instrument, and DMSO-d_6 was used as the solvent.

LOI tests were carried out through a HC-2C oxygen index meter (Jiangning, China) according to ASTM D2863, and the samples made into the dimensions of 130 mm × 6.5 mm × 3.2 mm were adopted; UL-94 vertical burning experiments were conducted through a CZF-2 instrument (Jiangning, China) according to ASTM D3801, and the samples with the dimensions of 130 mm × 13 mm × 3.2 mm were used. Burning behaviors were evaluated on a cone calorimeter device (Fire Testing Technology, East Grinstead, UK) according to ISO 5660-1, and the samples with dimensions of 100 mm × 100 mm × 3 mm were exposed to a radiant cone at a heat flux of 35 kW/m^2.

The glass transition temperature (T_g) was determined under nitrogen atmosphere by using a TA Q10 DSC instrument. The thermal



Scheme 2. Synthetic route of D-P-A.