



Two novel phosphorus–nitrogen-containing halogen-free flame retardants of high performance for epoxy resin



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ABSTRACT

Two novel halogen-free flame retardants, DP-DDE and DP-DDS, were synthesized via a one-pot procedure based on the Pudovik reactions between 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and imines directly resulting from the condensation reactions of 3-methoxy-4-hydroxybenzaldehyde with two typical curing agents, 4,4'-oxydianiline (DDE) and 4,4'-diaminodiphenylsulfone (DDS), respectively. The fire-resistant properties of DP-DDE or DP-DDS modified epoxy resins (2,2-bis(4-glycidylphenoxy)propane) with 4,4'-methylenedianiline as hardener were been investigated by UL-94 vertical test. Their high flame-retarding performance has been found: the epoxy thermosets with a relatively low addition amount of DP-DDE or DP-DDS (on the account of phosphorus content of 0.75 wt.% or 0.73 wt.%) can reach UL-94 V-0 flammability rating. These thermosets demonstrated excellent thermal stability, high glass transition temperature ($T_g > 135$ °C) and high char yields (>22% at 800 °C). Moreover, the thermal degradation kinetics of the flame retardants and their corresponding epoxy thermosets were studied based on Kissinger, Ozawa and FWO methods by thermogravimetric analysis.

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1. Introduction

Flame-retarding epoxy resin has become one of the basic materials in the electronic industry. For example, brominated epoxy resins are used as main materials for the copper clad laminate, because of their good flame retardancy, low cost, excellent physical and mechanical properties [1–4]. However, halogenated epoxy resins or halogen-containing flame retardants cause serious environmental problems, i.e., emitting toxic and corrosive fumes during combustion [5–7]. Driven by the urgent need of environmental protection, halogen-free flame retardant (HFFR) has been being developed rapidly since 1970s [8–11]. Up to now, halogen-free flame-retarding copper clad laminate with high glass transition temperature (T_g) [12,13] and good mechanical properties [14–16] has been acquired. Nevertheless, there is still a key challenge for HFFRs, i.e., the optimization in two aspects: flame-retarding performance in terms of UL-94 V-0 grade, the addition amount of key flame-retarding element(s) [17–19]. For instance, as an important branch of HFFR family, the phosphorus-containing HFFR for epoxy

resin has to encounter limitation (or risk): phosphorus resource efficiency, potential eutrophication from phosphorous [20–22], as well as the performance of epoxy thermoset [23,24].

It has been reported that some epoxy resins modified with 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) group usually embody high T_g , excellent mechanical properties, and high adhesion [25–28]. Based on the Pudovik reaction, chemically introducing DOPO into various monomers has become a strategy for preparing HFFRs of epoxy resin [29–31]. Since the late 1990s, a series of flame retardants and hardeners covalently bonded with DOPO group have been prepared and tested in epoxy resins by Wang et al. [3,27,32,33], among which one reactive monomer containing DOPO group displayed the highest phosphorus resource efficiency to our knowledge: an epoxy thermoset using this HFFR reached UL 94 V-0 flammability rating, when the phosphorus content is as low as 0.81 wt.% [33]. Besides, laconic reaction condition has been invented, for example, Lin et al. reported a one-pot reaction of DOPO, amine and aldehyde in high yields [34]. Following these inventions as well as earlier work by Lin [34–36], we synthesized three HFFRs by covalently bonding DOPO and Schiff bases via a two-step procedure, and obtained epoxy thermosets meeting UL-94 V-0 flammability rating with LOI value as high as 35.6, when the phosphorus content was 1.0 wt.% [37], and found that the sites of hydroxyl in these HFFRs significantly affected LOI

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values of the as-prepared thermosets with identical phosphorus contents. To sum up, optimizing the flame-retarding performance and resource efficiency by selecting functional groups and adjusting their sites of DOPO-based reactive monomer is feasible.

In this work, two novel DOPO-based HFFRs via a one-pot procedure are synthesized. The as-synthesized HFFRs are characteristic of building blocks resembling the curing agents, 4,4'-oxydianiline (DDE) and 4,4'-diaminodiphenylsulfone (DDS). Thus, we considered them as co-curing agents which may covalently introduce rigid DOPO into the epoxy thermosets. Importantly, the two HFFRs-modified epoxy thermosets meet UL 94 V-0 flammability rating with phosphorus content only 0.75 wt.% and 0.73 wt.%, respectively.

2. Experimental section

2.1. Material

4,4'-Methylenedianiline (DDM), 4,4'-oxydianiline (DDE), 4,4'-diaminodiphenylsulfone (DDS) and 3-methoxy-4-hydroxybenzaldehyde (vanillin) from Aladdin Chemistry Co., Ltd., 2,2-bis(4-glycidyloxyphenyl)propane (also named as diglycidyl ether of bisphenol A, short for DGEBA, epoxy equivalent = 0.51 mol/100 g) from Wuxi Diaisheng Epoxy Co., Ltd., were used as received. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) was purchased from Eutec Trading (Shanghai) Co., Ltd., and was purified by recrystallization from absolute ethanol (EtOH). EtOH and ethyl acetate (EA), both from Guangdong Guanghua Sci-Tech Co., Ltd., were dried using anhydrous sodium sulfate (Na_2SO_4) prior to use.

2.2. Syntheses and reactions

2.2.1. Synthesis of DP-DDE

To a 500 mL three-neck round-bottom glass flask equipped with a reflux condenser and a mechanical stirrer, a solution of DDE (15.02 g, 0.075 mol) in EA (150 mL) was charged. A solution of vanillin (22.82 g, 0.15 mol) in EA (100 mL) was added dropwise into the flask within 30 min. After this solution had been added completely, the mixture was stirred at 40 °C for about 4 h, when only one dot was examined using thin layer chromatography (TLC). Then DOPO (32.43 g, 0.15 mol) was added into the mixture directly, and 80 mL of EtOH was added subsequently. The reaction mixture was stirred at 80 °C for another 18 h. Finally, the reaction mixture was filtered, washed repeatedly with hot EtOH and dried for more than 8 h in a vacuum oven, a white solid product (DP-DDE) was recovered (61.36 g, yield: 90.8%). ^1H NMR (400 MHz, DMSO-d_6) δ 9.02–8.92 (m, 2H), 8.12 (t, $J = 7.3$ Hz, 4H), 7.87 (dd, $J = 9.8$, 6.0 Hz, 1H), 7.66 (dd, $J = 14.4$, 4.6 Hz, 3H), 7.48–7.18 (m, 12H), 7.11 (d, $J = 8.1$ Hz, 1H), 6.99 (dd, $J = 7.8$, 3.1 Hz, 1H), 6.91 (d, $J = 18.2$ Hz, 2H), 6.76 (dt, $J = 13.7$, 7.8 Hz, 6H), 6.66–6.60 (m, 2H), 5.44 (dd, $J = 16.5$, 9.5 Hz, 1H), 5.17–5.07 (m, 1H), 3.67–3.59 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.34 (C1, C1', t, $J = 9.1$ Hz), 149.53 (C15, C15', dd, $J = 35.1$, 8.9 Hz), 147.73 (C12, C12', s), 146.83 (C13, C13', s), 136.34–135.76 (C6, C6', m), 134.14 (C21, C21', d, $J = 33.4$ Hz), 132.21 (C8, C8', d, $J = 8.9$ Hz), 131.09 (C23, C23', s), 129.98 (C17, C17', s), 128.79 (C25, C25', d, $J = 12.8$ Hz), 128.53 (C2, C2', C3, C3', s), 127.02 (C26, C26', d, $J = 18.5$ Hz), 126.06 (C24, C24', d, $J = 11.4$ Hz), 125.39–124.87 (C19, C19', m), 124.33 (C18, C18', t, $J = 8.8$ Hz), 123.81 (C22, C22', d, $J = 9.6$ Hz), 122.67 (C20, C20', d, $J = 12.3$ Hz), 122.12–121.66 (C9, C9', m), 121.53 (C11, C11', d, $J = 5.1$ Hz), 120.74–119.99 (C16, C16', m), 115.58 (C10, C10', s), 113.28 (C4, C4', C5, C5', dd, $J = 14.3$, 6.2 Hz), 54.62–56.80 (C7, C7', q), 56.06 (C14, C14', s).

^{31}P NMR (162 MHz, DMSO-d_6) δ 33.16 (s), 31.46 (s).

FTIR (KBr): 925 cm^{-1} , 1234 cm^{-1} (P–O–Ph); 1033 cm^{-1} (Ph–O–C); 1206 cm^{-1} (PO); 1514 cm^{-1} , 3367 cm^{-1} (N–H); 1594 cm^{-1} (P–Ph); 3510 cm^{-1} (O–H).

Elemental analysis values: C, 69.22; H, 4.614; N, 2.72. Calculated values on $\text{C}_{52}\text{H}_{42}\text{N}_2\text{O}_9\text{P}_2$: C, 69.33; H, 4.70; N, 3.11; O, 15.98; P, 6.88.

2.2.2. Synthesis of DP-DDS

Compound DP-DDE was prepared in a similar procedure of DP-DDE, using vanillin, DDS and DOPO as starting materials. A white solid (90.7% yield) was obtained. ^1H NMR (400 MHz, DMSO-d_6) δ 9.02–8.92 (m, 2H), 8.11 (dd, $J = 11.5$, 4.7 Hz, 4H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.75–7.59 (m, 3H), 7.47–7.18 (m, 12H), 7.11 (d, $J = 8.1$ Hz, 1H), 7.01–6.96 (m, 1H), 6.91 (d, $J = 17.9$ Hz, 2H), 6.74 (dd, $J = 15.1$, 10.4 Hz, 6H), 6.62 (dd, $J = 8.0$, 2.2 Hz, 2H), 5.43 (dd, $J = 16.2$, 9.6 Hz, 1H), 5.11 (dd, $J = 13.7$, 10.3 Hz, 1H), 3.62 (d, $J = 3.7$ Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.31 (C1, C1', t, $J = 9.4$ Hz), 149.52 (C15, C15', dd, $J = 35.1$, 9.1 Hz), 147.70 (C12, C12', s), 146.81 (C13, C13', s), 136.02 (C6, C6', dd, $J = 27.4$, 5.9 Hz), 134.12 (C21, C21', d, $J = 33.6$ Hz), 132.20 (C8, C8', d, $J = 7.4$ Hz), 131.08 (C23, C23', s), 129.95 (C17, C17', s), 128.77 (C25, C25', d, $J = 14.1$ Hz), 128.51 (C2, C2', C3, C3', s), 127.01 (C26, C26', d, $J = 18.7$ Hz), 126.06 (C24, C24', d, $J = 11.7$ Hz), 125.14 (C19, C19', dd, $J = 7.9$, 6.2 Hz), 124.33 (C18, C18', t, $J = 8.8$ Hz), 123.82 (C22, C22', d, $J = 10.0$ Hz), 122.68 (C20, C20', d, $J = 12.5$ Hz), 121.92 (C9, C9', dd, $J = 10.1$, 5.0 Hz), 121.63 (C11, C11', dd, $J = 25.3$, 5.4 Hz), 120.35 (C16, C16', dd, $J = 35.2$, 5.6 Hz), 115.55 (C10, C10', s), 113.55–113.05 (C4, C4', C5, C5', m), 56.75–55.70 (C7, C7', q), 56.04 (C14, C14', s).

^{31}P NMR (162 MHz, DMSO-d_6) δ 33.10 (s), 31.38 (t, $J = 8.1$ Hz).

FTIR (KBr): 926 cm^{-1} , 1236 cm^{-1} (P–O–Ph); 1034 cm^{-1} (Ph–O–C); 1207 cm^{-1} (PO); 1514 cm^{-1} , 3369 cm^{-1} (N–H); 1595 cm^{-1} (P–Ph); 3514 cm^{-1} (O–H).

Elemental analysis values: C, 64.25; H, 4.634; N, 2.69. Calculated values on $\text{C}_{52}\text{H}_{42}\text{N}_2\text{O}_{10}\text{P}_2\text{S}$: C, 65.82; H, 4.46; N, 2.95; O, 16.86; P, 6.53; S, 3.38.

2.3. Curing procedure of DP-DDE or DP-DDS epoxy resin

The DP-DDE (or DP-DDS)-modified epoxy resins with phosphorus content 0.75 wt.%, 1.0 wt.%, 1.5 wt.% (or 0.73 wt.%, 0.98 wt.%, 1.46 wt.%) were cured using DDM as a hardener. Due to the same active proton numbers between DP-DDE (or DP-DDS) and DDM, DP-DDE (or DP-DDS) were used as co-curing agents of DDM. The formulas of the pre-curing mixtures of DGEBA, DDM and DP-DDE (or DP-DDS) are listed in Table 1. The flame retardant DP-DDE (or DP-DDS) and epoxy resin were mixed and stirred at 160 °C for 2 h, then DDM was added when the mixtures were cooled to 100 °C. The products were cured at 140 °C for 2 h and then 180 °C for 2 h. Thereafter, the epoxy thermosets were cooled slowly to room temperature, in order to prevent cracking. They are labeled as DP-X/(P%-Y), where X denotes DDE or DDS, and P%-Y stands for the percentage content of phosphorus in the thermoset.

2.4. Instrumental analyses and measurements

FTIR spectra were recorded on a Bruker Vertex 70 infrared spectrophotometer by KBr disc method with the optical range of 400–4000 cm^{-1} . ^1H (400 MHz), ^{13}C (101 MHz) and ^{31}P (162 MHz) NMR spectra were registered with a Bruker AV-400 spectrometer using DMSO-d_6 as a solvent and TMS as an internal standard. The elemental analyses were performed with a CHNOS Elemental Analyzer-vario EL cube. DSC scans were obtained in the way that samples of approximately 8–15 mg, and scanned in the range of 25 °C–300 °C under argon atmosphere at a heating rate of 10 °C·min $^{-1}$ using a Mettler-Toledo DSC 823e. Moreover the glass transition temperature (T_g) was taken as midpoint of enthalpy

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