

Effect of a novel P/N/S-containing reactive flame retardant on curing behavior, thermal and flame-retardant properties of epoxy resin



Rongkun Jian^{a,b,*}, Pan Wang^a, Long Xia^a, Xuelin Zheng^{a,b,*}

^a College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China

^b Fujian Key Laboratory of Polymer Materials, Fujian Normal University, Fuzhou 350007, China

ARTICLE INFO

Keywords:

Epoxy resin
Curing behavior
Flammability
Thermo-mechanical property
Pyrolysis behavior

ABSTRACT

A novel P/N/S-containing flame retardant DHBZ was synthesized with 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, *p*-hydroxybenzaldehyde and 2-aminothiazole, and used as a co-curing agent for epoxy resin (EP). With the aid of DHBZ, EP/7.5% DHBZ passed UL-94 V-0 rating, and owned a LOI value of 31.4%. Besides, DHBZ also played a positive role in inhibiting the release of heat and the production of smoke. Through non-isothermal DSC tests it revealed that in the presence of DHBZ, epoxy resin was cured at a lower temperature and showed lower curing-reaction activity energy. DMA analyses indicated that EP/7.5% DHBZ showed an increased storage modulus, and it had a close glass transition temperature with EP. While, DHBZ presented a decreased effect on the thermal stability of epoxy resin acquired from TG analyses. Finally, the flame-retardant mechanism studied by TG-FTIR and py-GC/MS deduced that DHBZ worked in the gaseous phase by producing P·, PO· and incombustible gases.

1. Introduction

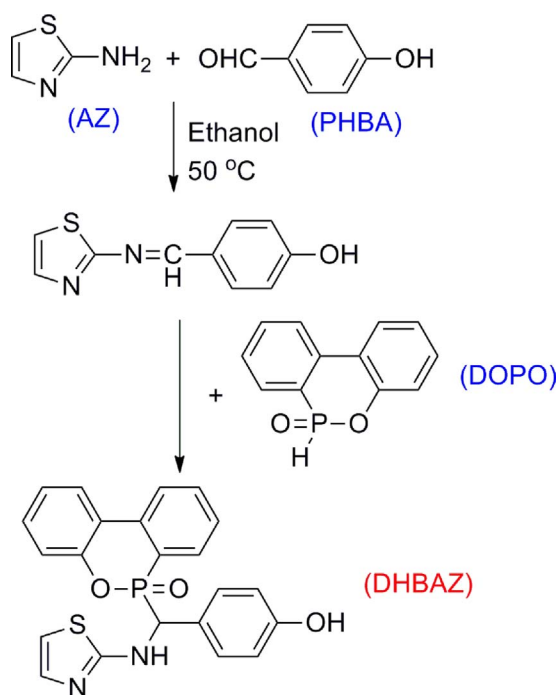
Epoxy resin (EP) regarded as one of the most important thermosets, has been widely used in the industrial applications, thanks to its high performances, such as excellent mechanical properties, good resistance to chemicals, solvent and moisture, and low dielectric constant [1–4]. However, the inherent flammability of epoxy resin is one of the drawbacks which has severely restricted the applications of epoxy resins in the fields where require high fire resistance [2,5,6]. Therefore, the research on improving the flame retardance of epoxy resin is very important. To meet the considerable requirement and focus on the environment-friendly, halogen-free flame retardants have been rapidly developed [7–12].

To date, phosphorus-containing flame retardants [13–16] have been largely reported due to variable flame retardant mechanism combined with other functional groups, such as intumescent flame retardant system composed of ammonium polyphosphate (APP) [17–19], and other P/N containing flame retardants [20–24]. As expected, the flammability of epoxy resin can be easily improved by incorporating the referred flame retardants through physical-mixing and covalently combination. Generally, although the former is an easy and important way, the addition of large amount of flame retardants plays a negative effect on the mechanical properties of epoxy resin [25,26]. By contrast, the latter chemically connected to the polymer chain is more stable and

effective, and it can endow epoxy resin with flame retardance, good compatibility, and the retentive physical and mechanical properties [10,27–34]. DOPO and its derivatives [35–38] are widely used to flame-retard epoxy resins, because of its strong gaseous flame-retardant mechanism and binary flame-retardant mechanism with other elements such as nitrogen [39–41], silicon [42–44], and sulfur [45,46]. Hence, it is meaningful to design and synthesize such P/N/S-containing DOPO-based reactive flame retardant. To achieve this, we use DOPO, *p*-hydroxybenzaldehyde (PHAB) and 2-aminothiazole (AZ) as reactants to prepare a novel P/N/S-containing reactive flame retardant.

In this work, DHBZ was successfully synthesized by the combination of DOPO, PHAB and AZ through a two-step reaction, and used as a flame-retardant co-curing agent of epoxy resin. The chemical structure of DHBZ was characterized by Fourier transform infrared spectroscopy (FTIR), ¹H, and ³¹P-nuclear magnetic resonance (NMR), and high resolution electrospray ionization mass spectrum (HRESI-MS), respectively. The curing behavior of epoxy resin in the presence of DHBZ was investigated by non-isothermal differential scanning calorimetry (DSC). Dynamic mechanical analysis (DMA) tests were used to evaluate the effect of DHBZ on the viscoelastic properties of EP. The effect of DHBZ on the thermal properties of epoxy thermosets were studied by thermo-gravimetric analysis (TG). The limited oxygen index (LOI), underwriter laboratory 94 vertical burning test (UL 94) and cone calorimeter tests were experimented to assess the flammability of

* Corresponding authors at: College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China
E-mail addresses: scujianrongkun@126.com (R. Jian), parrowxg@163.com (X. Zheng).



Scheme 1. Synthetic route of DHBAZ.

Table 1
The fabrications of epoxy thermostets and relevant results after UL-94 and LOI tests.

Samples	DGEBA (g)	DDM (g)	DHBAZ (g)	P (wt%)	UL-94 (3.2 mm)		LOI (%)
					$t_1^a + t_2^b$ (s)	Rating	
EP	100	25	0	0	> 50	No rating	25.5
EP/5.0% DHBAZ	100	20.29	6.32	0.37	5.0 + 5.0	V-1	30.5
EP/7.5% DHBAZ	100	19.48	9.73	0.56	3.3 + 4.2	V-0	31.4
EP/10.0% DHBAZ	100	18.64	13.33	0.74	2.4 + 2.5	V-0	32.3
EP/12.5% DHBAZ	100	17.74	17.14	0.95	3.0 + 2.8	V-0	33.3

^a Average burning time after the first ignition.

^b Average burning time after the second ignition.

flame-retardant epoxy thermostets. The pyrolysis products or volatiles of DHBAZ were also characterized by means of TG-FTIR and pyrolysis-gas chromatograph/mass spectrometer (py-GC/MS).

2. Experimental

2.1. Materials

9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was commercially obtained from Huizhou Sunstar Technology Co., Ltd. (Huizhou, China). 2-aminothiazole (AZ) was provided by J&K Chemical Ltd. (Shanghai, China). P-hydroxybenzaldehyde (PHBA) and 4, 4'-Diamino-diphenylmethane (DDM) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Diglycidyl ether of bisphenol-A (DGEBA, E-44) was available from Nantong Xingchen Synthetic material Co., Ltd. (Nantong, China).

2.2. Synthesis of DHBAZ

The chemical DHBAZ was synthesized by two-step reaction as shown in Scheme 1. First, 2-aminothiazole (10.0 g, 0.1 mol), p-hydroxybenzaldehyde (12.2 g, 0.1 mol) and absolute ethanol (100 mL) were introduced into a 500 mL three-necked round-bottomed glass flask equipped with a condenser, a mechanical stirrer, and a nitrogen inlet. The mixture was stirred at 50 °C for 2 h to obtain the intermediate

Schiff base. Subsequently, DOPO (21.6 g, 0.1 mol) dissolved in absolute ethanol (100 mL) was added dropwise into the obtained Schiff base solution, and the reaction was kept for another 12 h. Finally, the solution was cooled naturally to the room temperature. The resulting precipitate was filtered and washed twice with ethanol, and then dried at 80 °C for 8 h to get light brown powder (DHBAZ, yield: 88 wt%). FTIR (KBr, cm^{-1}), 3393 (O–H), 3235 (N–H), 3066 (C=C–H), 3012 (Ar–H), 2812 (C–H), 1613, 1518, 1473, and 1444 (C=C), 1238 (P=O). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): 9.50, 9.46 (s, OH); 8.63 (dd, $J = 1.6$ Hz, 10 Hz, NH), 8.48 (dd, $J = 2.8$ Hz, 10 Hz, NH); 8.22–8.15 (m, 2H); 7.79–7.71 (m, 2H); 7.59–7.50 (m, 1H); 7.46–7.41 (m, 1H); 7.34–3.31 (m, 1H); 7.16–7.02 (m, 3H); 6.88, 6.77 (d, $J = 3.6$ Hz, 1H); 6.72–6.67 (m, 2H); 6.58, 6.51 (d, $J = 3.6$ Hz, 1H); 5.70, 5.41 (dd, $J = 10$ Hz, 14 Hz, 1H); ^{31}P NMR (162 MHz, $\text{DMSO}-d_6$, ppm): 30.24, 28.84. HRMS(ESI⁺): calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3\text{PS}[\text{M}+\text{H}]^+$ 421.0776, found 421.0764.

2.3. Preparation of EP/DHBAZ samples

EP/DHBAZ thermostets were prepared through an appointed thermal curing process. In order to make sure that each pre-curing epoxy mixture contained equal active hydrogen supplied by DDM and DHBAZ, the proportions of DDM and DHBAZ were adjusted, and the formulation was listed in Table 1. First, DGEBA and DHBAZ were mixed together and stirred at 130 °C for 30 min to obtain homogeneous solution. Then the mixture was cooled down to 90 °C, and DDM was added with stirring for 5 min. Afterwards, the mixture was poured rapidly into a preheated stainless steel mold and thermally cured at 100 °C for 3 h, 150 °C for 2 h, and 180 °C for 2 h. Finally, the epoxy thermostets were obtained after cooled naturally to the room temperature. The obtained thermostets were directly used for the relevant tests.

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded in the range of 500–4000 cm^{-1} (KBr pellets) on a Thermo Nicolet 5700 FT-IR instruments.

2.4.2. Nuclear magnetic resonance (NMR)

^1H and ^{13}P NMR spectra were obtained with a Bruker AVANCE AV II-400 NMR instrument using $\text{DMSO}-d_6$ as the solvent and tetramethylsilane (TMS) as the internal standard. High resolution electrospray ionization mass spectrum (HRESI-MS) was conducted on a Bruker compact Q-TOF apparatus.

2.4.3. Fire tests

LOI values were evaluated on a HC-2C oxygen index meter (Jiangning, China) according to ASTM D2863-97, and the samples for LOI tests were with the three-dimensional size of $130 \times 6.5 \times 3.2 \text{ mm}^3$; UL-94 vertical burning ratings were assessed CZF-2 instrument (Jiangning, China) according to ASTM D3801, and the samples for UL-94 tests were with the three-dimensional size of $130 \times 13 \times 3.2 \text{ mm}^3$. Besides, combustion behaviors of the samples were measured on a cone calorimeter device (Fire Testing Technology, East Grinstead, UK) according to ISO 5660-1, and the samples for cone tests with three-dimensional size of $100 \times 100 \times 3 \text{ mm}^3$ were exposed to a radiant cone at a heat flux of 35 kW/m^2 .

2.4.4. Dynamic mechanical analysis (DMA)

DMA was performed on a DMA Q800 apparatus (TA instruments). The specimen with dimensions of $40 \times 10 \times 4 \text{ mm}^3$ was mounted on a single cantilever clip, the frequency was set as 1.0 Hz, the oscillation amplitude was fixed at 20.0 μm , and the samples were tested from 40 to 240 °C with a heating rate of 10 °C/min under air.

Download English Version:

<https://daneshyari.com/en/article/5134453>

Download Persian Version:

<https://daneshyari.com/article/5134453>

[Daneshyari.com](https://daneshyari.com)