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The synergistic effect of maleimide and phosphaphenanthrene groups on a reactive flame-retarded epoxy resin system

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ABSTRACT

A novel reactive flame-retarded epoxy resin system was prepared by copolymerizing diglycidyl ether of bisphenol-A (DGEBA) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), N,N'-bis-maleimide-4,4'-diphenylmethane (BDM) and 4,4'-diamino-diphenyl sulfone (DDS). Curing behavior, thermal and flame-retardant properties of the cured epoxy resins were investigated by differential scanning calorimeter (DSC), thermogravimeric analysis (TGA), limited oxygen index (LOI) measurement, UL94 test and cone calorimeter. The results indicated that phosphaphenanthrene group was introduced into the multicomponent system by addition reaction of DOPO with BDM. Compared with traditional DOPO-DGEBA systems, the EP/DDS/BDM/DOPO thermosets showed greatly improved glass transition temperatures (210–223 °C). The results of combustion tests indicated that the addition of BDM or DOPO into DGEBA could improve the flame resistance of the thermosets. Most importantly, the flame-retardant property was further improved when BDM and DOPO coexisted in the epoxy resin systems. For example, compared to the control samples, the EP/DDS/BDM/DOPO-15 thermoset displayed better flame retardancy with higher LOI value and UL94 rating, lower peak of heat release rate (pk-HRR) and average of effective heat of combustion (av-EHC) under the same content of BDM and phosphorus, strongly confirming the synergistic effect of BDM and DOPO. In addition, in a particular proportion, BDM and DOPO synergistically functioned in the condensed-phase and gaseous-phase at the same time. The flame retardant mechanism was studied by TGA and cone calorimeter coupled with the analysis of the char residues.

1. Introduction

Epoxy resins (EPs) are widely used in coating, adhesive, laminating, and electronic industry due to their attractive characteristics of high tensile strength and modulus, high adhesion to substrates, good chemical and corrosion resistance, excellent dimensional stability and superior electrical properties [1–5]. However, conventional epoxy resins are flammable and can not satisfy high flame-resistance requirement of advanced materials [6,7]. So far, research works on improving the flame retardancy of epoxy resins are very attractive for advanced application. The incorporation of halogen into the epoxy resins can increase flame resistance. Currently, halogen-containing compounds are not preferred for environmental reasons [8,9]. Therefore, there is a trend to develop and apply halogen-free flame retardants.

Epoxy resins modified by phosphorus-containing flame retardants are considered to be more environmentally friendly and have been widely used [10–14]. Among the phosphorus-containing flame retardants, DOPO and its derivatives have received considerable attention due to their high reactivity and flame retarded efficiency [15–17]. Without co-additive, epoxy resins modified with DOPO can not show high thermal stability and good mechanical properties due to the decreased crosslinking density, and single flame retardant composition limits the further enhancing of flame retardancy of the modified epoxy resins [18–20]. Therefore, flame retardants with multiple flame-retardant functional groups have been used. A few works have been reported about the synergistic effect of multiple flame-retardant functional groups on flame retardancy of epoxy resins [21–27].

Maleimide modified epoxy resins provide a convenient approach of enhancing the thermal stability, flame retardancy and

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mechanical properties due to their high crosslink density and thermal stable maleimide groups [28–30]. Therefore, when maleimide and phosphaphenanthrene groups coexist in epoxy resin systems, the cured products may exhibit outstanding integrated properties.

In this work, a novel flame-retarded epoxy resin system was prepared by copolymerizing DGEBA with DOPO, BDM and DDS. Research on the curing behavior of the multicomponent system revealed that phosphaphenanthrene and maleimide groups were integrated into one molecule which functioned as reactive flame retardant. Thermal and flame retardant properties of the cured epoxy resins were investigated by differential scanning calorimeter (DSC), thermogravimeric analysis (TGA), limited oxygen index (LOI) measurement, UL94 test and cone calorimeter. Compared to the traditional DGEBA-DOPO system, the EP/DDS/BDM/DOPO systems showed enhanced thermal stability and flame retardancy. The flame retardant mechanism of the EP composites based on BDM and DOPO was studied.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight (EEW) of about 188 g/equiv was provided by Yueyang Baling Huaxing Petrochemical Co., Ltd. N,N'-bismaleimide-4,4'-diphenylmethane (BDM) was obtained from Puyang Willing Chemicals Co., Ltd. 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Huizhou Sunstar Technology Co., Ltd. 4,4′-Diamino-diphenyl sulfone (DDS) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of EP/DDS/BDM/DOPO thermosets and the control samples

EP/DDS/BDM/DOPO thermosets were prepared via a thermal curing process. At first, BDM was dissolved in DGEBA at 120 °C under vigorous stirring. After complete dissolution of BDM, DOPO was added under N_2 atmosphere. After stirring at 120 °C for 20 min, stoichiometric DDS (with respect to epoxy) was thoroughly blended at 120 °C until a homogeneous solution was obtained. The mixture was then degassed under vacuum for 5 min to remove trapped air, and then poured directly into preheated mould and thermally cured in air convection oven for 2 h at 125 °C, 150 °C, 180 °C, 200 °C and 230 °C, respectively.

The control samples were prepared as follows. EP/DDS/BDM thermoset was obtained similar to the way of EP/DDS/BDM/DOPO thermosets without the addition of DOPO and thermally cured for 2 h at 160 °C, 180 °C, 200 °C and 230 °C, respectively. EP/DDS and EP/DDS/DOPO thermosets were prepared with the method reported in the literature [10]. All the details of formula are listed in Table 1.

2.3. Preparation of uncured samples for DSC analysis

The EP/DOPO mixture (the weight ratio is 2:1) was obtained by dissolving DOPO in DGEBA at 125 °C and then cooled to room temperature. The BDM/DOPO mixture (the molar ratio is 1:2) was prepared by grinding BDM and DOPO in an agate mortar. In addition, tiny amounts of the uncured EP/DDS/BDM and EP/DDS/BDM/DOPO mixtures prepared in 2.2 were taken out for DSC measurement.

2.4. Preparation of prepolymers for IR analysis

The EP/DOPO (the weight ratio is 2:1) mixture were placed in air convection oven at 125 °C for 2 h, and marked as EP/DOPO-125°C-2h.

Table 1
Formulas of the cured epoxy resins.

Sample code	DGEBA (g)	DDS (g)	BDM (g)	DOPO (g)	BDM content (wt.%)	P content (wt.%)
EP/DDS	100	33	0	0	0	0
EP/DDS/BDM	100	33	26.95	0	16.85	0
EP/DDS/DOPO	100	33	0	12.25	0	1.21
EP/DDS/BDM/DOPO-5	100	33	30	5	17.86	0.43
EP/DDS/BDM/DOPO-10	100	33	30	10	17.34	0.83
EP/DDS/BDM/DOPO-15	100	33	30	15	16.85	1.21
EP/DDS/BDM/DOPO-20	100	33	30	20	16.39	1.57

In addition, tiny amounts of EP/DDS/DOPO and EP/DDS/BDM/DOPO mixtures prepared in 2.2 were taken out after cured for 2 h at 125 °C, and labeled as EP/DDS/DOPO-125°C-2h and EP/DDS/BDM/DOPO-x-125°C-2h (x = 5,10, 15, 20).

2.5. Measurements

Fourier Transform Infrared (FTIR) spectra were obtained using a Nicolet 6700 infrared spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets.

Differential scanning calorimetry (DSC thermograms were recorded with Perkin–Elmer DSC 4000 at a heating rate of 10 °C/min under nitrogen atmosphere from 50 to 320 °C.

Thermogravimetric analysis (TGA) was performed using NETZSCH STA449F3 at a heating rate of 10 °C/min under nitrogen atmosphere from 50 to 800 °C.

The LOI values were measured at room temperature on a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO4589-1984 standard and dimensions of all samples were 130 × 6.5 × 3 mm^3. Vertical burning (UL-94) tests were carried out on the NK8017A instrument (Nklsky Instrument Co., Ltd, China) with the dimension of 130 × 13 × 3 mm^3 according to UL-94 test standard. Cone calorimeter measurements were performed on an FTT cone calorimeter according to ISO 5660 under an external heat flux of 50 kW/m^2. The dimension of samples was 100 × 100 × 3 mm^3.

Morphological studies on the residual chars were conducted using a JSM-5610LV scanning electron microscope (SEM) at an acceleration voltage of 25 kV.

3. Results and discussion

3.1. Research on the reactivity of the mixtures

The curing behavior of a multivariate copolymerization system determines its crosslinking network, and thereby the properties of the thermoset, so the curing behavior is the first issue needing to be studied. In our study, the reactivity of the EP/DDS/BDM/DOPO mixtures was investigated by DSC at a heating rate 10 °C/min under nitrogen atmosphere.

As shown in Fig. 1, the EP/DOPO mixture did not show obvious exothermic peak before 160 °C, indicating that the low reactivity between DGEBA and DOPO at this temperature region. The BDM/DOPO mixture showed a sharp endothermic peak at 110 °C, which was ascribed to the melting of DOPO. However, the curve of BDM/DOPO mixture went downwards immediately after the melting of DOPO, and then a very distinct exothermic peak appeared, indicating a much higher reactivity of BDM/DOPO mixture compared with that of DGEBA/DOPO mixture before 160 °C. In addition, the EP/DDS/BDM mixture exhibited only one exothermic peak, which involved with the ring-opening reaction, homopolymerization of maleimide groups and Michael-addition reaction between diamine