

# Preparation and flame retardancy of an intumescent flame-retardant epoxy resin system constructed by multiple flame-retardant compositions containing phosphorus and nitrogen heterocycle



Shuang Yang\*, Jun Wang, Siqi Huo, Liufeng Cheng, Mei Wang

School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

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## ABSTRACT

A phosphorus/nitrogen-containing reactive phenolic derivative (DOPO–HPM) was synthesized via the addition reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and N-(4-hydroxyphenyl) maleimide (HPM). The structure of DOPO–HPM was characterized by Fourier transform infrared spectroscopy (FTIR),  $^1\text{H}$  and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) and elemental analysis (EA). The studied flame-retardant epoxy resin systems were prepared by copolymerizing diglycidyl ether of bisphenol-A (DGEBA) with DOPO–HPM, triglycidyl isocyanurate (TGIC) and 4,4'-diamino-diphenyl sulfone (DDS). Thermal and flame retardant properties of the cured epoxy resins were investigated by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), limited oxygen index (LOI) measurement, UL94 test and cone calorimeter. The DSC results indicated that the modified epoxy resins showed little fluctuation in glass transition temperatures (197–205 °C). The results of combustion tests indicated that the modified epoxy resin systems exhibited excellent flame retardant properties. The P-1 and P-1.25 systems acquired LOI values of 37% and 38.5%, respectively, and achieved a UL94 V-0 rating. Compared with the P-0 system, the peak of heat release rate (pk-HRR), average of effective heat of combustion (av-EHC) and total heat release (THR) of P-1.25 system decreased by 61.4%, 23.4% and 34.9%, respectively. In addition, the total smoke production (TSP) of the modified epoxy resin systems decreased with the increasing content of flame retardants, indicating the smoke suppression effect of the flame-retardant systems. Through visual observation, the char residues after cone calorimetry test exhibited intumescent structures with continuous and compact surfaces. The flame retardant mechanism was studied by FTIR, scanning electron microscope (SEM), cone calorimeter and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

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## 1. Introduction

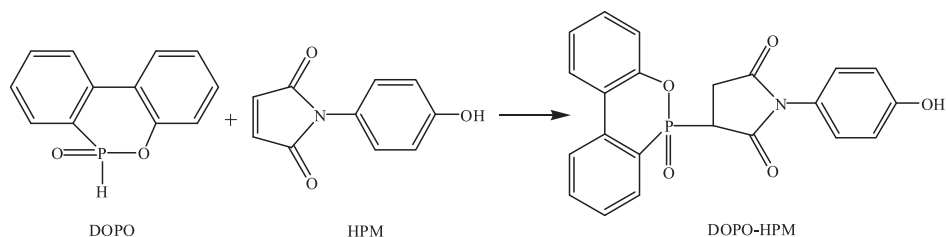
Epoxy resins (EPs) are widely used as advanced matrix resin in the electronic and electrical industries due to their attractive characteristics of high tensile strength and modulus, high adhesion to substrates, good chemical and corrosion resistance, excellent dimensional stability and superior electrical 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 retardation of

epoxy resins are very attractive for advanced application. Traditionally, halogenated compounds have been widely used to endow epoxy resins with flame resistance. Currently, halogen-containing compounds are not preferred for environmental reasons [8–10]. Therefore, there is a trend to develop and apply halogen-free flame retardants.

Phosphorus-containing flame retardants modified epoxy resins are considered to be more environmentally friendly and have received outstanding attention [11–16]. Among the phosphorus-containing flame retardants, DOPO and its derivatives have received considerable attention due to their high reactivity with epoxy monomers, high thermal stability and flame retardant efficiency [17–21]. However, single flame retardant composition limits the further enhancing of flame retardancy of the modified epoxy resins [22–24]. Therefore, DOPO-based epoxy resin systems with

\* Corresponding author. School of Materials Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Hongshan District, Wuhan 430070, China.

E-mail address: [ys583377051@163.com](mailto:ys583377051@163.com) (S. Yang).



Scheme 1. Synthesis route of DOPO–HPM.

multiple flame-retardant compositions have been prepared and the synergistic effect of multiple flame-retardant functional groups on flame retardancy of epoxy resins has been observed as reported in a few works [25–32].

In this work, a phosphorous/nitrogen-containing reactive phenolic derivative (DOPO–HPM) was synthesized via the addition reaction between DOPO and HPM. The structure of DOPO–HPM was characterized by Fourier transform infrared spectroscopy (FTIR),  $^1\text{H}$  and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) and elemental analysis (EA). The investigated flame-retarded epoxy resin systems were prepared by copolymerizing DGEBA with DOPO–HPM, TGIC and DDS. Thermal and flame-retardant properties of the cured epoxy resins were investigated by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), limited oxygen index (LOI) measurement, UL94 test and cone calorimeter. The flame retardant mechanism was studied by FTIR, SEM, cone calorimeter and Py-GC/MS.

## 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-(4-hydroxyphenyl) maleimide (HPM) was obtained from Puyang Willing Chemicals Co., Ltd. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Huizhou Sunstar

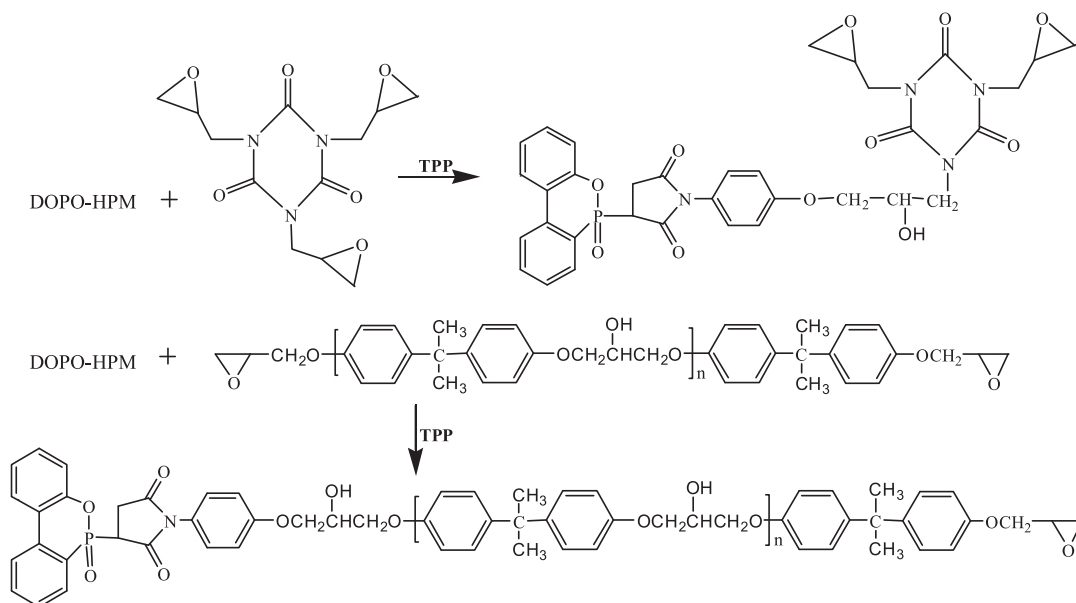
Technology Co., Ltd. Triglycidyl isocyanurate (TGIC) was purchased from Jinan Zian Chemicals Co., Ltd. Triphenyl phosphine (TPP), 4,4'-Diamino-diphenyl sulfone (DDS) and 1,4-dioxane were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used as received.

### 2.2. Synthesis of DOPO–HPM

DOPO (21.6 g, 0.1 mol), HPM (18.9 g, 0.1 mol) and 1,4-dioxane (150 ml) were introduced into a 250 mL, three-neck, round-bottom glass flask equipped with a mechanical stirrer, reflux condenser, thermometer and dry nitrogen inlet. The mixture was heated to 80 °C under nitrogen atmosphere and stirred until DOPO and HPM dissolved completely. The mixture was further heated to reflux for 5 h and then distilled to remove 1,4-dioxane. The products were washed with ethyl acetate and vacuum-dried at 70 °C for 24 h. The reaction formula is shown in Scheme 1. The yield was 90%. Elemental analysis: C: 64.99 (cal 65.2), N: 3.48 (cal 3.46), H: 3.97 (cal 3.95). IR (KBr,  $\text{cm}^{-1}$ ): 3224 (–OH), 1777 and 1706 (C=O), 1393 (C–N), 1189 (P=O), 937 and 758 (P–O–Ph).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm): 9.7 and 9.8 (–OH, 1H), 6.7–8.3 (Ar–H, 12H), 3.9–4.2 (CH, 1H), 3.0–3.3 (CH<sub>2</sub>, 2H).  $^{31}\text{P}$  NMR (DMSO- $d_6$ , ppm): a single peak at 29.7.

### 2.3. Preparation of flame-retarded epoxy resins

At first, DGEBA, TGIC, DOPO–HPM and TPP (0.4wt.%) were blended and prepolymerized at 135 °C until a homogeneous



Scheme 2. Reactions between DOPO–HPM, TGIC and DGEBA.

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