



## Synthesis of maleimido-substituted aromatic s-triazine and its application in flame-retarded epoxy resins



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### ABSTRACT

In this study, a maleimido-substituted aromatic s-triazine (TMT) was synthesized successfully via the nucleophilic substitution reaction between cyanuric chloride and N-(4-hydroxyphenyl) maleimide (HPM) formed from paraaminophenol and maleic anhydride; and its structure was characterized by Fourier transform infrared spectroscopy (FT-IR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR), and elemental analysis (EA). The studied flame-retarded epoxy resins were obtained via thermal curing reactions among 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) modified epoxy prepolymer (DOPOER), 4,4'-diaminodiphenyl ethane (DDM) and TMT. Cure kinetics, flame-retardant, thermal and mechanical properties of the cured epoxy resins were characterized by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), limited oxygen index (LOI) measurement, UL 94 vertical burning test and mechanical test. The results indicate that TMT can promote the curing reaction of epoxy resins and decrease its apparent activation energy ( $E_a$ ). Introduction of TMT can greatly improve flame-retardant, thermal and mechanical properties of the cured epoxy resins. Compared with the DOPOER/DDM system without TMT, LOI value of the cured epoxy resin can increase from 36.4% to 51.8%, and all samples can pass UL 94 V-0 rate when TMT content ranges from 1.98 wt% to 7.44 wt%. Its initial degradation temperature and glass transition temperature ( $T_g$ ) can increase maximally by 37.6 °C and 12.6 °C, respectively when TMT content is 3.88 wt%.

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### 1. Introduction

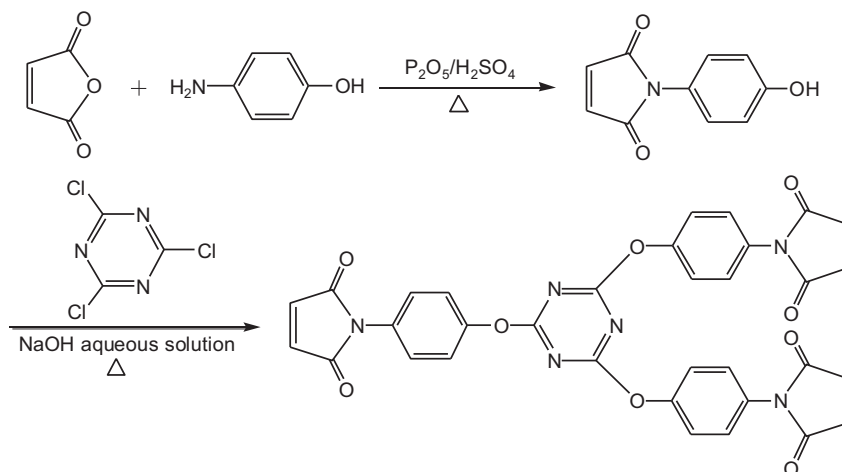
Due to its dimensional stability, outstanding adherence to many substrates, excellent solvent and chemical resistance, distinguished electrical and mechanical properties, and versatility in formula, epoxy resins are widely used in adhesive, laminating, coating, and casting areas [1,2]. However, conventional epoxy resins are flammable and cannot satisfy high flame-resistance requirement of advanced materials [3–5]. Halogenated monomers or additives have been widely used to obtain flame-retarded epoxy materials. But they produce poisonous and corrosive smoke and highly toxic halogenated dibenzodioxins and dibenzofurans during combustion [4]. Therefore, development and application of halogen-free flame-retarded epoxy resins has become an extremely important subject.

In the past few decades, reactive organo-phosphorous compounds have attracted much attention because their incorporation into epoxy network, via either curing agents or epoxy oligomers, which was proved to powerfully increase the resin's flame resistance [6–10]. However, their incorporation was also found may decrease the glass transition temperature ( $T_g$ ), initial degradation temperature and mechanical properties of the cured resins [11–15]. Some studies indicate a significant enhancement of flame-retarded efficiency when phosphorus and nitrogen with triazine structure coexist in epoxy resins [16,17]. And the incorporation of maleimide groups into epoxy resins can bring them higher glass transition temperatures and better thermal stability [18,19]. Therefore, the concomitance of phosphorus, nitrogen with triazine structure and maleimide groups in epoxy resin is supposed to enable it to display outstanding comprehensive properties.

In literature [20], 2,4,6-tris[4-(maleimido)phenoxy]-s-triazine (TMT) containing both triazine and maleimide structures was first synthesized with maleic anhydride and 2,4,6-Tris(4-Aminophenoxy)-s-Triazine (TAT). However, the synthesis process of precursor TAT comprised complex reactions and therefore

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**Scheme 1.** Synthesis process of TMT.

increased the synthesis difficulty of TMT. In our study, TMT was conveniently synthesized via the nucleophilic substitution reaction between cyanuric chloride and N-(4-hydroxyphenyl)maleimide (HPM), and its structure was characterized with Fourier transform infrared spectra (FT-IR),  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) and element analysis (EA). Then TMT was incorporated into phosphoric epoxy resins with 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide (DOPO) structure. Cure kinetics, flame-retardant, thermal and mechanical properties of the obtained epoxy resins were characterized by differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), limited oxygen index (LOI) measurement, UL 94 vertical burning test and mechanical test.

## 2. Experimental

### 2.1. Materials

DOPO-containing epoxy resin (DOPOER, epoxide value 0.475 mol/100 g, phosphorus 1.0 wt%) was self-prepared according to Literature [21]. Herein, diglycidyl ether of bisphenol A (EPON 828) and DOPO were purchased from Momentive Specialty Chemicals Inc. and Eutec Trading (Shanghai) Co., Ltd, respectively. Paraaminophenol, maleic anhydride, cyanuric chloride and 4,4'-diaminodiphenyl ethane (DDM) were obtained from Aladdin Reagents (Shanghai) Co., Ltd. Phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and sodium hydroxide (NaOH) were purchased from Guangzhou Chemical Reagent Factory.

### 2.2. Synthesis of TMT

Prior to synthesizing TMT, synthesis of HPM was carried out according to the modified reported procedure [22,23]. 50 ml DMF solution containing 10.9 g (0.1 mol) paraaminophenol was poured into a four-neck flask equipped with a mechanical stirrer, a thermometer and a nitrogen inlet, then 15 ml dimethylformamide (DMF) solution containing 10.7 g maleic anhydride (0.11 mol) was added in dropwise in 30 min. The mixture was stirred for 2 h at 30 °C and an amic acid solution was obtained. Subsequently, 4.14 g  $\text{P}_2\text{O}_5$  was added into the solution in batches in 5 min, followed by 3.25 g  $\text{H}_2\text{SO}_4$ , which was added in dropwise in 10 min. Then the solution was heated to 80 °C in 30 min and stirred for 3 h. After cooled down, the mixture was poured into 1000 ml ice water and filtered to obtain the precipitate. After washed three times with

deionized water, the precipitate was further recrystallized three times in isopropanol and vacuum-dried at 70 °C for 24 h. Yellow HPM crystal with a melting point of 183.5 °C was obtained. The yield was 73.2%. FT-IR parameters are 3481  $\text{cm}^{-1}$  (O–H), 3110  $\text{cm}^{-1}$  (HC=CH), 1705  $\text{cm}^{-1}$  (C=O), 1601  $\text{cm}^{-1}$  (aromatic ring), 1392  $\text{cm}^{-1}$  (C–N) and 828  $\text{cm}^{-1}$  (HC=CH of maleimide). NMR parameters are  $^1\text{H}$  NMR (DMSO- $\text{D}_6$ ) 9.71 (s, 1H, –OH), 6.82–6.84 (d, HC=CH of maleimide) and 7.07–7.13 (m, 4H, aromatic) ppm;  $^{13}\text{C}$  NMR (DMSO- $\text{D}_6$ ) 170.79 (C=O), 157.44, 134.37 (HC=CH of maleimide), 128.23 and 112.00 (C=C, aromatic) ppm.

TMT was synthesized via a two-step route shown in Scheme 1. Briefly, 11.4 g (0.06 mol) HPM and 2.48 g (0.062 mol) NaOH were dissolved in dioxane: deionized water (1:1, v:v) in a four-neck flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a refluxing condenser. Then 50 ml dioxane containing 4.1 g cyanuric chloride (0.022 mol) was added in dropwise. After 10 h reflux, the mixture was distilled to remove dioxane, and then was filtered to obtain the precipitate. The precipitate was washed successively for 3 times with ethyl acetate, 0.5 wt%  $\text{H}_2\text{SO}_4$  solution, 5 wt% NaOH solution and deionized water, and vacuum-dried at 60 °C for 24 h. Gray–yellow TMT powder was obtained. The yield was 74%. Element analysis details are C: 61.53 (cal 61.69), N: 12.86 (cal 13.08) and H: 3.09 (cal 2.82).

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

Flame-retarded epoxy resins were prepared via thermal curing reactions among DOPOER, DDM and TMT. According to the stoichiometric ratio of reactive groups, the amount of NH functionalities of DDM was equal to the sum of epoxy groups and alkenyl groups of DOPOER and TMT, respectively. Amounts of TMT, DOPOER

**Table 1**  
Detailed component amounts used to synthesize flame-retarded epoxy resins in this study.

DOPOER (g)	TMT (g)	DDM (g)	Content of TMT (wt%)	Content of P (wt%)
100	0	23.56	0	0.81
100	2.5	23.75	1.98	0.79
100	5	23.94	3.88	0.77
100	7.5	24.14	5.70	0.76
100	10	24.33	7.44	0.74
100	15	24.72	10.74	0.72

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