



Preparation and flame retardancy of a compounded epoxy resin system composed of phosphorus/nitrogen-containing active compounds



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ABSTRACT

Triazine derivative with active maleimide group (TMT) was synthesized via nucleophilic substitution reaction between N-(4-hydroxyphenyl) maleimide (HPM) and cyanuric chloride using a new method, and higher yield of TMT was obtained. The investigated flame-retardant epoxy resins were then prepared by copolymerizing diglycidyl ether of bisphenol-A (DGEBA) with TMT, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 4,4'-diamino-diphenyl methane (DDM). The study on the reactivity disclosed that DOPO was exclusively grafted on TMT. The glass transition temperatures (T_g s) of EP/TMT/DOPO thermosets (154–160 °C) were much higher than that of the traditional EP/DOPO thermoset (122 °C). Flame-retardant properties of the cured products were evaluated using limited oxygen index (LOI), vertical burning (UL94) and cone calorimeter tests. The results indicated that the flame retardancy of EP/TMT/DOPO thermosets was dramatically enhanced with low loading of phosphorus content. EP/TMT/DOPO-1.0 sample with phosphorus content of only 1.0 wt.% achieved a LOI value of 40.3% with UL94 V-0 rating, and the average of heat release rate (av-HRR), average of effective heat of combustion (av-EHC) and total heat release (THR) were decreased by 37%, 31.9% and 35.4%, respectively, compared with those of the neat EP. The excellent flame-retardant properties of EP/TMT/DOPO thermosets were ascribed to bi-phase flame-retardant effect. The morphologies of the char residues showed honeycombed and intumescent structures with a small number of holes on the surfaces. The char barrier served as protective layer. The small number of holes on the surface facilitated the concentrated release of free radicals to implement an intensive quenching effect. The enhanced flame retardancy was achieved by means of carbonization, swelling and high concentration of free radicals.

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1. Introduction

In the past couple of decades, flame-retarded epoxy resins (EPs) have been exploited for a variety of applications in many fields with the requirement of fire safety due to their attractive characteristics of high adhesion to substrates, outstanding physical–mechanical, electrical and flame-retardant properties [1–5]. Traditionally, halogenated compounds have been used to improve the flame retardancy of epoxy resins. Currently, the applications of halogen-containing compounds are restrained for environmental reasons [6–8]. Therefore, the development and application of halogen-free

flame retardants have attracted increasing attention in recent years.

To prepare halogen-free flame retardant epoxy resin systems, a plenty of flame retardants containing phosphorus [9–14], silicon [15–18] and boron [19–22] were utilized. Among them, phosphorus-based flame retardants are considered to be more efficient, especially 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives which have high reactivity, thermal stability and flame-retardant efficiency [23–28]. However, an ideal flame-retardant property could only be acquired under high phosphorus loading when DOPO-based compounds were used alone, and there was a sharp decrease in T_g values [29–31]. Therefore, many researches aimed at the development of novel epoxy resin systems with further enhanced flame-retardant properties under low loading of additives. In order to achieve this goal, DOPO-based flame retardants were used in conjunction with the

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other ones containing phosphazene [32], silsesquioxane [33–35], s-triazine [36,37], triazine–trione [38,39] and maleimide [40,41], and thus EP systems with excellent flame retardancy were obtained by means of the synergistic effect between different components. In addition, the different collaborative flame-retardant mechanisms were discussed in these studies as well. Although the former researches have made a contribution to the development of high efficiency flame-retardant epoxy resin systems, the research efforts on the exploitation of compounded epoxy resin systems with further enhanced flame retardancy and the disclosure of their flame-retardant mechanisms are still essential for providing new ideas.

In this paper, triazine derivative with active maleimide group (TMT) was synthesized by a more convenient method compared with the former reports [36]. The reactive flame-retarded epoxy resin blends were then prepared by copolymerizing DGEBA with TMT, DOPO and DDM. The results of curing behavior research disclosed that DOPO exclusively reacted with TMT. The LOI, vertical burning (UL94) and cone calorimeter tests were used to evaluate the flame-retardant properties of the EP thermosets. The flame-retardant mechanism was discussed in detail.

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. Cyanuric chloride, diglyme and triethylamine were obtained from Aladdin Reagents (Shanghai) Co., Ltd. 4,4'-diamino-diphenyl methane (DDM) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of TMT

HPM (31.2 g, 0.165 mol), triethylamine (16.7 g, 0.165 mol) and diglyme (200 mL) were introduced into a 500 mL, three-neck and round-bottom glass flask equipped with a mechanical stirrer, reflux condenser, thermometer and dry nitrogen inlet. The mixture was heated to 85 °C under nitrogen atmosphere and stirred until HPM dissolved completely. Cyanuric chloride (9.225 g, 0.05 mol) dissolved in 80 mL diglyme was added over 2 h. After that, the mixture was further heated to 110 °C and stirred for 6 h. Then the mixture was distilled to remove diglyme, the crude product was washed successively for 3 times with deionized water and ethyl acetate, and then vacuum-dried at 60 °C for 24 h. The reaction formula is shown in Scheme 1. Yield: 29.3 g (91.3%). Element analysis: C: 60.94 (cal

61.68), N: 12.87 (cal 13.08), H: 2.83 (cal 2.8). FTIR (KBr, cm^{-1}): 3101 and 691 (C=C), 1713 (C=O), 1508 (triazine ring skeleton). ^1H NMR (DMSO- d_6 , ppm): 7.2 (CH=CH, 6H), 7.38 and 7.39 (Ar-H, 12H). ^{13}C NMR (DMSO- d_6 , ppm): 170 (C=O), 135.5 (HC=CH of maleimide), 151 (C-O), 129.5 (C-N), 128.5 and 122 (C=C of aromatic ring).

2.3. Preparation of EP/TMT/DOPO thermosets and the control samples

At first, DDM, TMT and DOPO were blended at 125 °C and stirred for 30 min. After that, the temperature was decreased to 90 °C, and then DGEBA was added and blended thoroughly. The mixture was then degassed under vacuum and poured directly into preheated mould and thermally cured in air convection oven for 2 h at 120 °C, 140 °C, 160 °C and 180 °C, respectively.

The preparation process of control sample EP/TMT was similar to that of EP/TMT/DOPO samples. The content of TMT in EP/TMT sample is the same as that in EP/TMT/DOPO-1.0 sample.

The control samples neat EP and EP/DOPO were prepared as follows. DDM with or without DOPO was mixed with DGEBA at 100 °C. After well mixed, the mixture was degassed and then poured directly into preheated mould and thermally cured in air convection oven for 2 h at 120 °C, 140 °C, 160 °C and 180 °C, respectively. The phosphorus content of EP/DOPO sample is the same as that of EP/TMT/DOPO-1.0 sample. All the details of formula are listed in Table 1.

2.4. Preparation of mixed powders for DSC analysis

The TMT/DOPO (the molar ratio is 1:3) and DDM/DOPO (the weight ratio is 1:1) mixtures were prepared by grinding DOPO and TMT or DDM in an agate mortar.

2.5. Preparation of prepolymers for ^{31}P NMR test

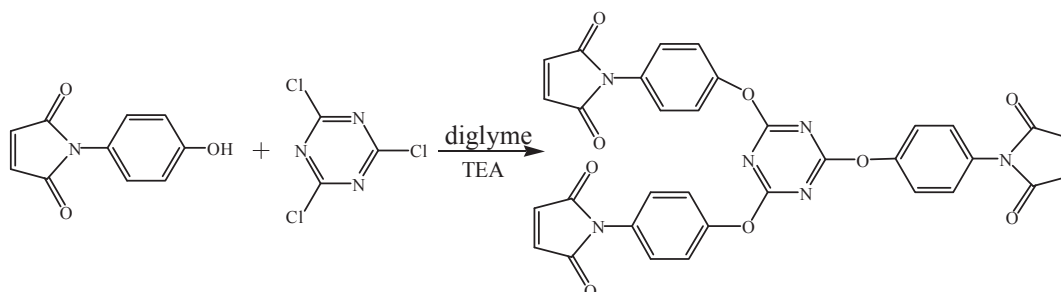
DDM/DOPO mixture prepared in 2.4 were maintained at 125 °C for 30 min, and coded as DDM/DOPO-30 min. In addition, tiny amounts of DDM/TMT/DOPO mixture prepared in 2.3 were taken out after prepolymerized at 125 °C for different times, and coded as DDM/TMT/DOPO-x (x = 15 and 30 min), where x was the mixing times.

2.6. Characterization

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.

^1H , ^{13}C and ^{31}P NMR spectra were obtained on a Bruker AV400 NMR spectrometer using DMSO- d_6 as solvent.

Elemental analysis (EA) was performed on a Vario EL cube Elemental Analyzer.



Scheme 1. Synthesis route of TMT.

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