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Highly effective flame retarded epoxy resin cured by DOPO-based co-curing agent

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ABSTRACT

A highly effective 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-based flame retardant (D-bp) was successfully synthesized via the addition reaction between DOPO and Schiff-base obtained in advance by the condensation of 4,4'-diaminodiphenyl methane (DDM) and 4-hydroxybenzaldehyde. D-bp was used as co-curing agent to improve the flame retardancy of DDM/diglycidyl ether of bisphenol A (DGEBA) system. Non-isothermal curing kinetics, thermal and flame-retardant properties of cured epoxy resins were studied by differential scanning calorimeter (DSC), thermogravimeric analysis (TGA), UL94 vertical burning test, limited oxygen index (LOI) and cone calorimeter test. The morphology of residues after cone calorimeter test was observed by scanning electron microscope (SEM). The results revealed that the epoxy thermosets exhibited excellent flame-retardancy and passed V-0 rating of UL 94 test with LOI of 39.7% when the phosphorus content was only 0.5 wt%.

1. Introduction

Epoxy resin, one of the most important industrial materials, displays the characteristics of good chemical and corrosion resistance, high tensile strength and modulus, excellent dimensional stability and superior electrical properties, and has been widely used as the polymeric matrix of advanced composites, especially in semiconductor encapsulation applications [1–3]. Unfortunately, due to the flammability of epoxy resin, the utilization in some fields that require high flame resistance is limited [4].

Traditionally, halogen compounds are useful for improving the flame retardancy of epoxy resin [5–7]. However, the employment of bromine or chlorine-containing compounds would produce poisonous and corrosive smoke during combustion. Therefore, the development of halogen-free flame-retarded epoxy resin has become an extremely important subject [8–10]. In recent years, organophosphorous compounds have exhibited remarkable results in environment-friendly flame retarded epoxy resin [11–16]. However, in order to achieve an excellent flame retardancy, the high addition amount of phosphorus element needs to be introduced, which consequently brings negative effects on the other properties of cured epoxy resins [17,18]. In addition, from the commercial point of view, the decrement in addition amount of flame retardants is beneficial to the reduction of cost. It is still worth challenging that the load of flame retardant reduces as low as possible in the cured epoxy resins via the improvement in flame-retardation efficiency.

Some studies indicated that the utilization of other flame-retardant elements, such as nitrogen, silicon, etc., would give a significant enhancement in the flame-retardation efficiency of phosphorus-based compound through the synergistic flame retardation effect [19–21]. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) exhibited great potential to construct such synergism by utilizing the high reactivity of P—H bond [22–24]. Triazine [25], Schiff-base [26] or hexachlorocyclotriphosphazene [27,28] structures have attached into DOPO molecule to produce phosphorus-nitrogen synergism in the flame retardation of epoxy resin. It was found that the addition product between DOPO and Schiff-base presented a considerable enhancement in flame-retardation efficiency for epoxy resin [26,29–31]. Gu et al. [29] synthesized two novel DOPO-containing Schiff-base, which performed excellent flame retardancy with

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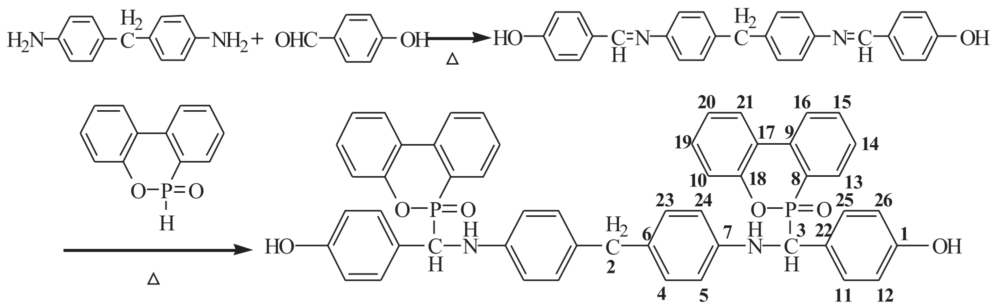

Scheme 1. Synthesis of D-bp.

Table 1
Formulations of the flame-retarded epoxy resins.

Sample	DGEBA (g)	DDM (g)	D-bp (g)	P (wt%)	N (wt%)
EP-0	100	25.3	0	0	2.85
EP-0.25	100	24.3	4.4	0.25	2.78
EP-0.5	100	23.2	8.9	0.5	2.70
EP-1	100	20.8	18.9	1	2.55

Table 2
Exothermic peak temperatures of D-bp/DDM/DGEBA cured at varying heating rates.

Heating rate (°C/min)	EP-0 (°C)	EP-0.25 (°C)	EP-0.5 (°C)	EP-1 (°C)
5	147.1	136.4	127.4	120.3
10	164.5	153.5	143.6	137.5
15	175.6	164.0	153.9	148.5
20	183.6	172.7	163.6	155.3

0.73 wt% phosphorus content. However, T_g of the cured epoxy resin decreased significantly from 160.3 °C to 141 °C. What's more, the structure of flame retardant contained methoxy group, which brought the negative effect to the flame-retardation efficiency. In order to achieve a breakthrough in flame retardancy, it is necessary to design the structure of DOPO-containing Schiff-base compounds.

In this paper, a highly effective DOPO-containing Schiff-base flame retardant (D-bp) was successfully synthesized by a simple one-pot method and used as co-curing agent to improve the flame retardancy of DDM/DGEBA system. The cured epoxy resins exhibited superior flame retardancy, which may attributed to the phosphorus-nitrogen synergistic flame retardation effect and well-maintained crosslink density of the thermoset by introducing D-bp.

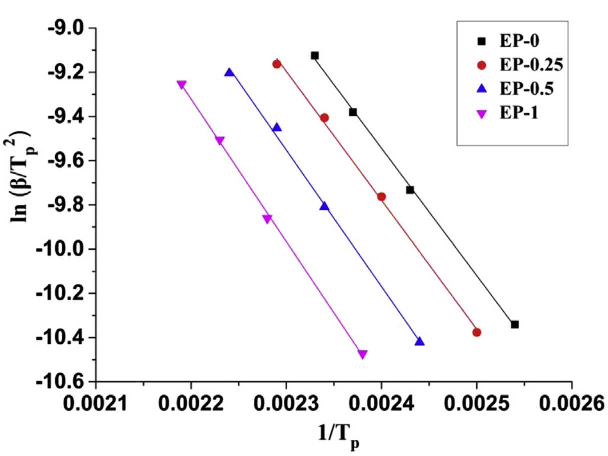

Fig. 1. The linear plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ of D-bp/DDM/DGEBA according to Kissinger's method.

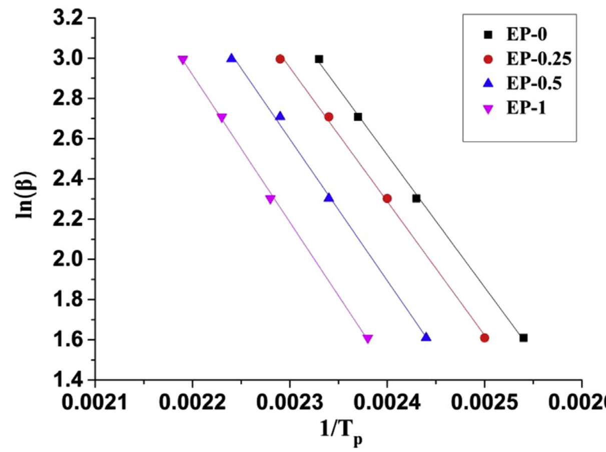

Fig. 2. The linear plot of $\ln(\beta)$ versus $1/T_p$ of D-bp/DDM/DGEBA according to Ozawa's method.

Table 3
Apparent activation energy of D-bp/DDM/DGEBA.

Sample	E_a^a (kJ/mol)	R^2	E_a^b (kJ/mol)	R^2
EP-0	53.6	0.999	60.9	0.999
EP-0.25	51.3	0.996	58.4	0.999
EP-0.5	48.5	0.997	55.3	0.999
EP-1	47.9	0.998	54.6	0.999

E_a^a: Calculated by Kissinger's method.
E_a^b: Calculated by Ozawa's method.

2. Experimental

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and diglycidyl ether of bisphenol A (DGEBA, epoxide value of 0.51 mol/100 g) were purchased from Eutec Trading (Shanghai) Co., Ltd and Momentive Specialty Chemicals Inc., respectively. 4,4′-Diaminodiphenyl methane (DDM) and 4-hydroxybenzaldehyde

Table 4
Thermal properties data of cured epoxy resins at different contents of D-bp.

Sample	T_g (°C)	$T_{d\ 5\%}$ (°C)	$T_{d\ max}$ (°C)	Residues (%)
EP-0	161.1	368.0	386.7	15.7
EP-0.25	158.4	353.6	382.9	21.6
EP-0.5	157.9	336.5	381.1	26.9
EP-1	155.9	332.2	370.9	27.9