

Flame Retardancy Effects of Phosphorus-Containing Compounds and Cationic Photoinitiators on Photopolymerized Cycloaliphatic Epoxy Resins

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ABSTRACT: This study presents a promising ultraviolet (UV)-curable epoxy resin formulation with improved flame-retardant properties. The formulation is based on the cycloaliphatic epoxide 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL4221) and a novel silicon, phosphorous containing flame-retardant additive. The additive, 1,3,5,7-tetramethyl-1,3,5,7-tetra 2-(6-oxido-6-H-dibenzo(c,e) (1,2)oxaphosphorin-6-yl) ethylcyclotetrasiloxane (DOPO-SiD), was synthesized by the addition reaction of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D₄Vi) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Formulations containing the cycloaliphatic epoxy resin ERL4221 and the flame-retardant DOPO-SiD additive were prepared in various concentrations and crosslinked by UV irradiation. The effects of DOPO-SiD and photoinitiators, such as the cyclopentadienyl iron complex of carbazole (In-Fe) and diphenyl-(4-(phenylthiol) phenyl) sulfonium hexafluorophosphate (In-S), on the flame-retardant properties and thermal stabilities of UV-cured ERL4221/DOPO-SiD composites were investigated with limiting oxygen index, UL-94 vertical test, and thermogravimetric analysis, respectively. The results showed that DOPO-SiD can increase the thermal stabilities of the ERL4221/DOPO-SiD. The char yield was improved when DOPO-SiD and In-Fe were simultaneously used. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40011.

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INTRODUCTION

Ultraviolet (UV) curing provides numerous advantages over traditional thermal curing, such as their rapid curing, high efficiency, and low amount of volatile organic compounds. UV curing systems are widely used for coatings, printing inks, vanishes, adhesives, and electronics.^{1,2} Cationic UV-curable materials, and epoxide resins in particular, have the advantages of efficient adhesion, low shrinkage, and the absence of oxygen inhibition. Cationic UV-initiated photopolymerization allows dark curing after photoinitiation and thermal post-cure thanks to its long active center lifetimes.^{3–5} However, most conventional UV-curable epoxides are flammable, which creates a demand for flame-retardant UV-curable epoxide systems. This is particularly relevant in applications where fire hazards are more of a concern, such as in electronic and wood coatings.

Cycloaliphatic epoxy resins are widely used as encapsulants in the microelectronic industry due to the high photopolymerization activity of the UV-curable epoxides.^{6,7} As electronic encapsulation materials, the flammability of cycloaliphatic epoxides is of great concern. Typical cycloaliphatic epoxy resins such as ERL4221 have a low limiting-oxygen index (LOI) of ~18 and a low melt viscosity, which can cause dripping during flame tests.^{8,9} Several approaches have been used to enhance the flame retardancy of cycloaliphatic epoxides. Fire resistance can be achieved with additive- and reactive-type flame retardants. For example, halogen- and phosphorus-containing monomers have been used to confer fire resistance. However, the halogen-containing epoxy resins can produce toxic gases and corrode metal components when overheated.^{10–12} Furthermore, phosphorus-containing monomers decrease the thermostability of resins as they begin to degrade because of the formation of less stable P–O–C bonds at lower temperatures. Phosphate

groups have a major contribution on compaction of char formation, but phosphorus-containing cycloaliphatic epoxy resins are reported to have very low char yield, usually less than 5%.^{8,13}

Several phosphorus-containing organic compounds have been reported as effective flame retardants.^{14–17} 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have received considerable attention as novel phosphorus-containing flame retardants in epoxy resins.^{18–22} Organosilicon compounds have likewise been known for their effective flame-retardant properties that are combined with excellent thermal and chemical properties, such as their high thermal-oxidative resistance and low toxicity.^{23,24} Both phosphorus-containing organic compounds and organosilicon compounds have been demonstrated as effective flame retardants for epoxy resins. Moreover, silicon and phosphorus were demonstrated to exhibit synergistic effects in their flame-retardant behaviors.^{25–28}

To obtain flame retardants with higher phosphorus and silicon content, DOPO-SiD was synthesized as a novel silicon- and phosphorus-containing flame retardant via the addition reaction of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4Vi) with DOPO. The flame-retardant cycloaliphatic epoxy resin from the ERL4221/DOPO-SiD system was obtained by UV irradiation and subsequently investigated. The effects of DOPO-SiD and photoinitiators on the flame-retardant properties, and thermal stabilities of UV-cured ERL4221/DOPO-SiD composites were investigated by LOI measurement, UL-94 vertical test, and thermogravimetric analysis (TGA), respectively.

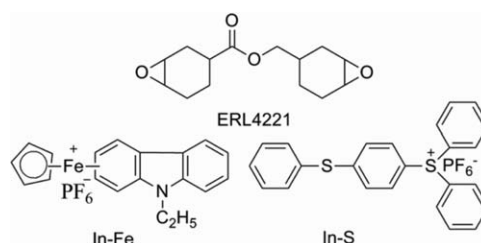
EXPERIMENTAL

Materials

D_4Vi , which was purchased from Jiangxi Duolin Co. (China), was reagent quality and used without further purification. DOPO was purchased from Huizhou Sunstar Technology Co. (China). The commercial epoxy compound used in this study is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL4221, epoxy value: 0.78 mol/100 g) which was purchased from Jiangsu Tetrachem Co. (China). The cationic photoinitiator diphenyl-(4-(phenylthio)phenyl) sulfonium hexafluorophosphate (In-S) was synthesized via the condensation of diphenyl sulfide and diphenylsulfoxide in the $MSA-P_2O_5$.²⁹ The cationic photoinitiator cyclopentadienyl iron complex of carbazole (In-Fe) was synthesized via the reported method.³⁰ Other reagents and solvents were commercially available and reagent quality. The abbreviations and structures of the epoxy compounds and photoinitiators employed in this study were summarized in Scheme 1.

Synthesis of DOPO-SiD

DOPO (43.2 g, 0.200 mol) and 120 mL toluene were placed into a 500 mL three-necked flask with a mechanical stirrer, reflux condenser, and dropping funnel under a nitrogen atmosphere. The temperature was maintained at 80°C. D_4Vi (16.5 g, 0.048 mol) and AIBN (1.2 g) were pre-dissolved in benzene. After DOPO was completely dissolved, the D_4Vi -AIBN mixture was added dropwise to the system for approximately 10 h and allowed to further react for 24 h in the dark. The products were purified by filtration, whereas the solvent was removed using a



Scheme 1. Structures of ERL4221, In-S, and In-Fe.

rotary evaporator. The crude product was purified by column chromatography. Finally, a faint yellow solid, which was named DOPO-SiD, was obtained (46.1 g, 79.3% yield). IR(KBr) ν_{max} (cm^{-1}): 911, 1067 (P–O–Ph), 1106 (Si–O–Si), 1231 (P=O), 1478, 1599 (P–Ph), 2870–2958 (aliphatic C–H), 3059 (Ph–H); 1H NMR ($CDCl_3$, 400 MHz): $\delta_{ppm} = -0.30$ to 0.24 (Si–CH₃), 0.42 – 0.84 (Si–CH₂), 1.74 – 2.17 (P–CH₂), 7.03 – 8.11 (aromatic H); ^{31}P NMR ($CDCl_3$, 400 MHz): $\delta_{ppm} = 35$ – 38 .

Sample Preparation

DOPO-SiD was mixed with ERL-4221 at 120°C in different ratios to obtain a series of homogenous blends. After the mixtures cooled to 80°C, 4 wt % photoinitiator (In-Fe or In-S) was added and mixed thoroughly. The blends were exposed to a high pressure Hg lamp (1 kW, BELSRI/UV-220V, China) at room temperature for 10 min and then thermally cured at 120°C for 30 min. Details of both thermal and UV curing methods have been reported in our previous article.^{31,32} The light intensity on the surface of sample was 1 mW/cm^2 , detected by a radiometer (UV-A, Beijing Normal University, China).

Measurements

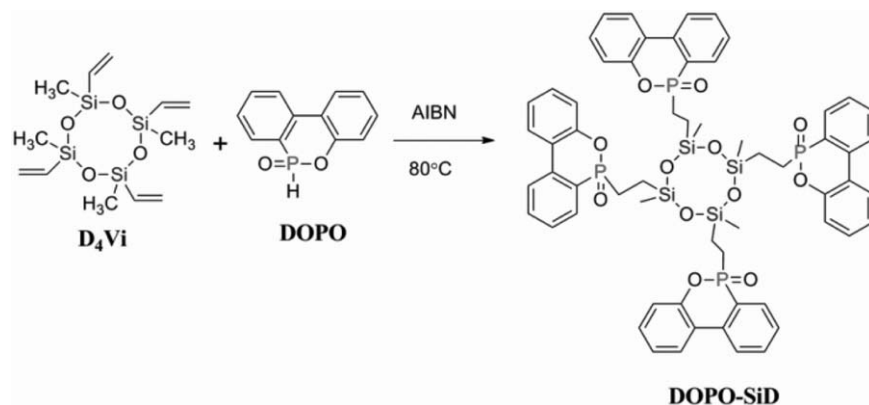
1H and ^{31}P NMR spectra were recorded on a Bruker AV400 unity spectrometer operated at 400MHz using $CDCl_3$ as deuterated solvent. FT-IR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA). Light intensity was recorded by a UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, China). The thermogravimetric analysis (TGA) was performed on STA-449C simultaneous thermal analyzer (Netzsch, Germany) with a heating rate of 10°C/min in a temperature range of 50–800°C under high purity nitrogen conditions. The mass of each sample was approximately 3–10 mg.

The limiting oxygen index (LOI) tests were carried out on a JF-3 type instrument (Jiangning, China), according to GB/T 2406-1993. The specimens used for the test were of dimensions 100 mm \times 6.5 mm \times 3 mm. The percentage of O_2 in the O_2/N_2 mixture was taken as the LOI which was just sufficient to sustain the combustion of plastics. The UL-94 vertical test was carried out on CZF-3 instrument (Jiangning Analysis Instrument Co., China) according to the UL-94 standard. The specimens used for the test were of dimensions 130 mm \times 13 mm \times 3 mm.

RESULTS AND DISCUSSION

Syntheses and Characterizations

DOPO-SiD was synthesized via the addition reaction of D_4Vi with DOPO. The P–H bond in the DOPO structure can react



Scheme 2. Synthesis of DOPO-SiD by the addition reaction of D₄Vi with DOPO.

with the vinyl group of D₄Vi in the presence of azobisisobutyronitrile (AIBN). The schematic outline for the synthesis of DOPO-SiD is given in Scheme 2.

The chemical structure of DOPO-SiD was characterized by FTIR (Figure 1), ¹H NMR (Figure 2), and ³¹P NMR (Figure 3). In Figure 1, the characteristic peaks at 911, 1067 (P–O–Ph), 1106 (Si–O–Si), 1231 (P=O), 1478, 1599 (P–Ph), 2870–2958 (aliphatic C–H), 3059 (Ph–H) can be observed in the FTIR spectra of DOPO-SiD. There is no absorption peaks at about 1633 cm⁻¹ (–CH=CH) and 2432 cm⁻¹ (P–H). In addition to the presence of a signal at 8.87 ppm (P–H), proton signals at 5.75–6.14 ppm (–CH=CH) had disappeared in the ¹H NMR. In the ³¹P NMR spectra, at about 35–38 ppm appeared new chemical shifts, and there were no peaks of DOPO to be observed.

All the results supported that DOPO-SiD was successfully synthesized via the addition reaction between DOPO and D₄Vi.

Flame-Retardant Properties

The flame retardancy of the UV-cured cycloaliphatic epoxy resins from ERL4221 and the ERL4221/DOPO-SiD system were evaluated by the LOI and UL-94 vertical tests. The effect of the

photoinitiators and the DOPO-SiD contents on the LOI values and UL-94 rates of UV-cured cycloaliphatic epoxy resins are presented in Table I.

Cationic cyclopentadienyl iron complexes of arene and triphenyl sulfonium salts are commonly used as photoinitiators in photo-cured epoxy resins.^{3–5} However, the flame-retardant effects of

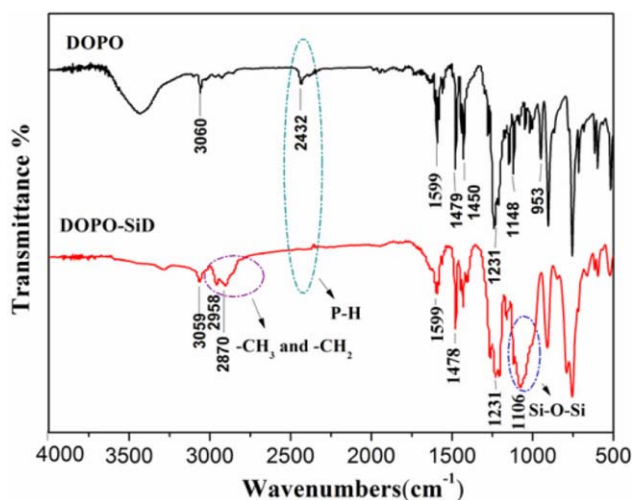


Figure 1. FTIR spectra of DOPO and DOPO-SiD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

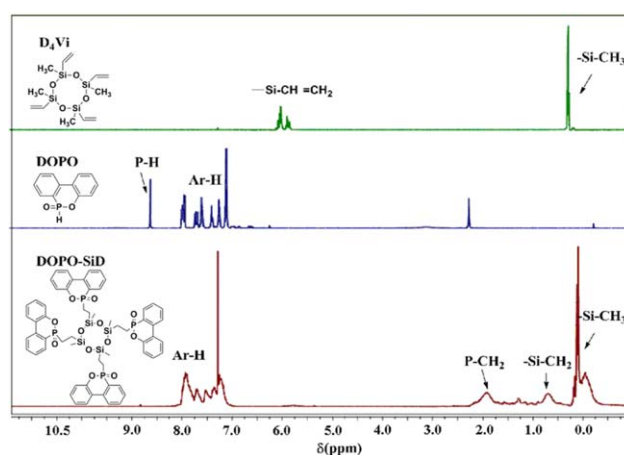


Figure 2. ¹H NMR spectra of DOPO and DOPO-SiD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

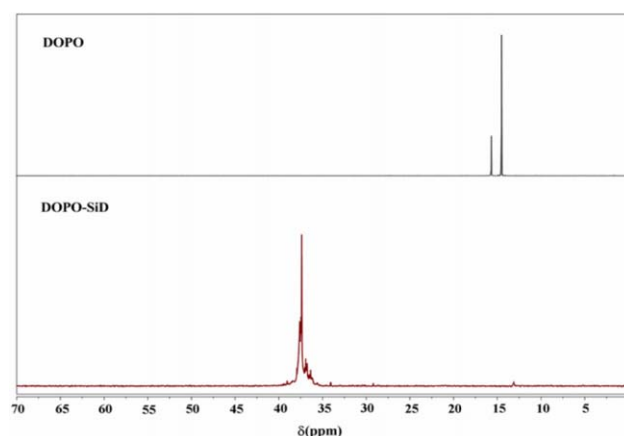


Figure 3. ³¹P NMR spectra of DOPO and DOPO-SiD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Compositions and Flame Retardancy of the UV-Cured Cycloaliphatic Epoxy Resins

Samples	In-Fe (wt %)	In-S (wt %)	DOPO-SiD		LOI	UL-94
			P (wt %)	Si (wt %)		
ERL-4221 ^a	0	0	0	0	18.2	NR
In-S2/ERL4221	0	2.0	0	0	20.9	NR
In-S3/ERL4221	0	3.0	0	0	21.5	NR
In-S4/ERL4221	0	4.0	0	0	22.2	NR
In-Fe2/ERL4221	2.0	0	0	0	20.8	NR
In-Fe3/ERL4221	3.0	0	0	0	21.7	NR
In-Fe4/ERL4221	4.0	0	0	0	22.5	NR
In-S4/ERL4221/DOPO-SiD1	0	4.0	1.0	1.2	22.8	NR
In-S4/ERL4221/DOPO-SiD1.5	0	4.0	1.5	1.8	23.9	NR
In-S4/ERL4221/DOPO-SiD2	0	4.0	2.0	2.4	24.8	V-2
In-Fe4/ERL4221/DOPO-SiD1	4.0	0	1.0	1.2	23.3	V-2
In-Fe4/ERL4221/DOPO-SiD1.5	4.0	0	1.5	1.8	24.2	V-2
In-Fe4/ERL4221/DOPO-SiD2	4.0	0	2.0	2.4	25.0	V-1
In-Fe2/ERL4221/DOPO-SiD2	2.0	0	2.0	2.4	24.3	V-1
In-Fe3/ERL4221/DOPO-SiD2	3.0	0	2.0	2.4	24.9	V-1

^aData were taken from Ref. 9.

NR, No rating; V-1, Burning stops within 60 s after two applications of ten seconds each of a flame to a test bar. No flaming drips are allowed; V-2, Burning stops within 60 s after two applications of ten seconds each of a flame to a test bar. Flaming drips are allowed.

these photoinitiators on the epoxy resin have not been previously reported. The varying LOI values of the UV-cured epoxy resin photoinitiated by In-Fe and In-S are shown in Figure 4. The LOI of epoxy resins in Figure 4 were obtained from ERL4221 photoinitiated by In-Fe and In-S without flame-retardant DOPO-SiD, and the data were summarized in Table I.

The LOI values from Figure 4 showed that the photoinitiators In-Fe and In-S confer flame-retardant properties to the epoxy resin. The LOI values increased with increasing photoinitiator content. The In-S/ERL4221 system with 2 wt % In-S produced a cured epoxy resin with a LOI value of 20.9. When the In-S content was increased to 4 wt %, the LOI value of the cured epoxy resin reached 22.2. Similar results were obtained in the

In-Fe/ERL4221 system. The flame-retardant properties of In-S and In-Fe are caused by the S atom and Fe²⁺ ion (respectively) that are present in these molecules. The In-Fe structure is similar to that of ferrocene. Several studies have reported that ferrocene can promote flame extinction and suppress smoke production by accelerating char formation.^{33–35}

The varying trends in the LOI values of ERL4221/DOPO-SiD with different DOPO-SiD contents are shown in Figure 5. When the P(DOPO-SiD) content was increased from 0 wt % to 2.0 wt % in the presence of 4 wt % photoinitiator, the LOI value increased from 22.2 to 25.0, and the UL-94 V-1 rate was achieved. Silicone derivatives have been reported to increase flame resistance by means of their gelation during combustion.^{23,24} When the DOPO group was introduced into the

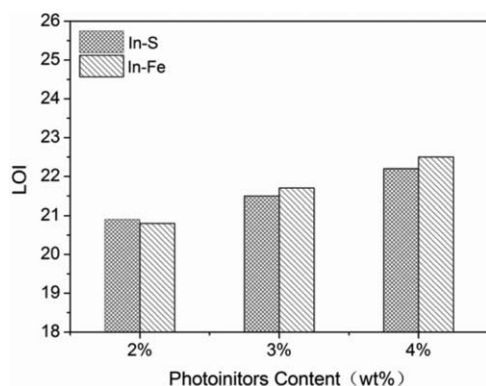


Figure 4. LOI value of UV-cured ERL4221/DOPO-SiD systems with 2 wt % of P (DOPO-SiD) photoinitiated by different contents of In-S and In-Fe.

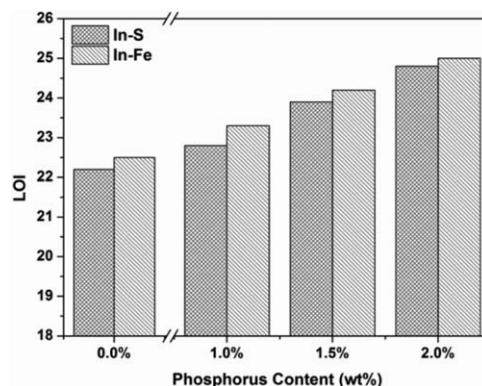


Figure 5. LOI value of UV-cured ERL4221/DOPO-SiD systems photoinitiated by 4 wt % content of In-S and In-Fe with different content of P (DOPO-SiD).

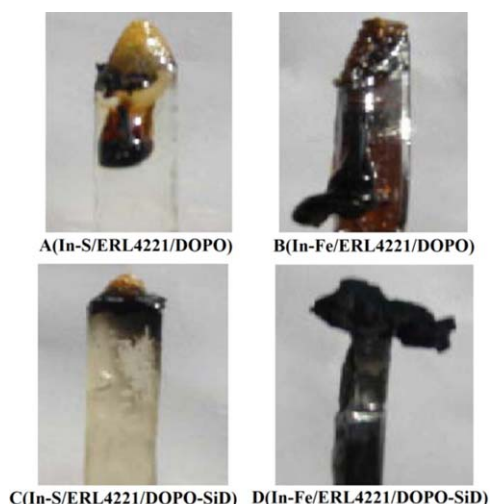


Figure 6. Dripping phenomenon and char residue of ERL4221/DOPO systems (A and B) and ERL4221/DOPO-SiD systems (C and D) (A and C: photoinitiated by In-S; B and D: photoinitiated by In-Fe; P%: 2.0 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

silicon derivatives, flame resistance was further enhanced, thereby demonstrating the silicon-phosphorus synergistic effect.^{25–28}

To fully characterize the synergistic effects of In-Fe4 and DOPO-SiD, the samples with different amount of In-Fe-4 and DOPO-SiD should have been measured. However, because the flame retardants had a negative effect on photopolymerization of the cycloaliphatic epoxy resins, complete curing of the epoxy system is difficult to obtain when the content of photoinitiator in ERL4221/DOPO-SiD system is less than 3 wt %. By comparison, when the content of photoinitiator is above 5 wt %, the upper layer cured quickly. This however makes the bottom of the epoxy system difficult to cure. Thus, higher concentrations of photoinitiator were not tested. The selection of the content of phosphorus was also limited because of the solubility of DOPO-SiD in ERL4221.

In this study, DOPO-SiD was found to effectively prevent the cycloaliphatic epoxy resin from softening and melting (dripping) during combustion. The pictures C and D in Figure 6 are the samples of In-S/ERL4221/DOPO-SiD and In-Fe/ERL4221/DOPO-SiD after the LOI test. For comparison, the flame-retardant effect of DOPO on the UV-cured ERL4221/DOPO system was also investigated by measuring LOI values [Figure 6(A,B)]. From Figure 6(A,B), it can be seen that during the combustion of the cured samples blended with DOPO, significant levels of melted polymer (drip) were always present. Thus, the precise LOI values could not be obtained. When DOPO-SiD was used [Figure 6(C,D)], dripping was not observed while the ERL4221/DOPO-SiD systems were burning. This result is due to the addition of DOPO-SiD, which increases the melt viscosity of the cured epoxy resin.

Compared with the cured epoxy resins from the In-S/ERL4221/DOPO-SiD systems, with In-S as the photoinitiator, an abun-

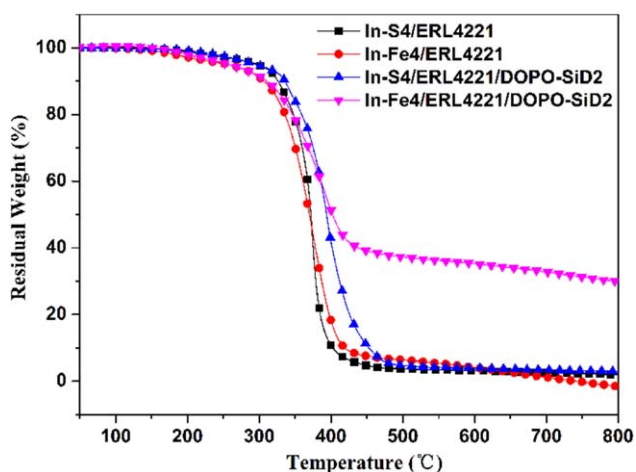


Figure 7. TGA curves of the UV-cured In-Fe/ERL4221 (In-Fe: 4 wt %), In-S/ERL4221 (In-S:4 wt %), In-Fe/ERL4221/DOPO-SiD [(In-Fe: 4 wt %; P%: 2 wt %) and In-S/ERL4221/DOPO-SiD (In-S: 4 wt %; P%: 2 wt %)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dant char layer was observed after the LOI testing of the cured epoxy resin from In-Fe/ERL4221/DOPO-SiD, with In-Fe as the photoinitiator [Figure 6(C,D)]. However, this phenomenon is not evident in the In-Fe/ERL4221 systems. These results indicated that, in comparison to In-S, the combined use of photoinitiator In-Fe and DOPO-SiD can increase the char yield of the cured epoxy system.

Thermal Stability

The thermal decomposition behaviors of the UV-cured systems with the flame retardant additive were investigated by TGA. The TGA thermograms and the differential weight loss (DTG) curves of the UV-cured In-S4/ERL4221/DOPO-SiD2 and In-Fe4/ERL4221/DOPO-SiD2 systems in a nitrogen atmosphere are shown in Figures 7 and 8, respectively. For comparison, the TGA and the DTG curves of the UV-cured In-S4/ERL4221 and

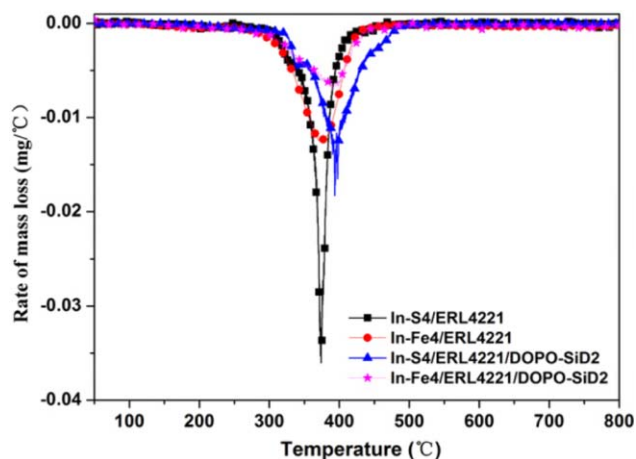


Figure 8. DTG curves of the UV-cured In-Fe/ERL4221 (In-Fe: 4 wt %), In-S/ERL4221 (In-S:4 wt %), In-Fe/ERL4221/DOPO-SiD [(In-Fe: 4 wt %; P%:2 wt %) and In-S/ERL4221/DOPO-SiD (In-S: 4 wt %; P%:2 wt %)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. TGA and DTG Dates of the UV-Cured Cycloaliphatic Epoxy Resins

Sample	T_{onset} (°C) ^a	$T_{0.5}$ (°C) ^b	T_{max} (°C) ^c	Residue (%) (800°C)
In-S4/ERL4221	358	372	374	2.0
In-Fe4/ERL4221	335	369	375	1.5
In-S4/ERL4221/DOPO-SiD2	363	393	394	3.0
In-Fe4/ERL4221/ DOPO-SiD2	334	402	391	29.9
ERL4221 ^d	316	/	368	1.3

^a T_{onset} is the initial decomposition temperature of the cured sample.

^b $T_{0.5}$ is the temperature when the weight loss is 50%.

^c T_{max} is temperature of the maximum weight loss rate.

^dData were taken from Ref. 9.

In-Fe4/ERL4221 were likewise obtained. The specific degradation temperatures and the final char yield at 800°C are summarized in Table II.

The UV-cured epoxy resin photoinitiated by both In-S and In-Fe (Table II) was degraded at a higher onset temperature than that reported in the literature for ERL4221 (316°C). The onset temperature of the cured epoxy resin from In-S4/ERL4221 is 358°C. When the same system was added with 2.0 wt % P(DOPO-SiD2), the onset temperature of the cured epoxy resin from In-S4/ERL4221/DOPO-SiD2 was 363°C. These results indicate that as an additive-type flame retardant, DOPO-SiD has little change on the thermal degradation temperature of the UV-cured epoxy resin. A similar conclusion was reached for the In-Fe/ERL4221 system.

One of the key criteria for flame-retardant systems is char formation. The amount of char residue can be determined by TGA. TGA results (Table II) showed that the UV-cured epoxy resin from In-S4/ERL4221, In-Fe4/ERL4221, and In-S4/ERL4221/DOPO-SiD2 have a maximum of 3.0% char residue at 800°C. However, the residual char increased sharply in the In-Fe4/ERL4221/DOPO-SiD2 system at 800°C (29.9 wt %), thereby implying that In-Fe and DOPO-SiD had a joint effect on the degradation of the UV-cured epoxy resin.

The difference in the degradation behavior of epoxy resins containing flame-retardant components could be observed by comparing their DTG curves (Figure 8). Once the decomposition temperature was reached, the UV-cured epoxy resin from ERL4221 without DOPO-SiD was quickly decomposed. However, the decomposition rate of the UV-cured epoxy resin was reduced when DOPO-SiD was used. The samples photoinitiated by In-Fe have a lower degradation rate and higher T_{max} temperature than those photoinitiated by In-S. The aforementioned results indicated that the In-Fe/DOPO-SiD system was better at protecting the UV-cured epoxy resin from further degradation.

CONCLUSION

The flame-retardant properties of the UV-curable cycloaliphatic epoxy systems were investigated. The photoinitiators In-Fe and In-S were found to confer flame-retardant properties to ERL4221. An additive-type silicon- and phosphorus-containing flame retardant, DOPO-SiD, was synthesized and found to effectively induce flame retardancy in UV-cured ERL4221.

DOPO-SiD was found to effectively prevent the cycloaliphatic epoxy resin from dripping during combustion. In-Fe and DOPO-SiD used together can increase the char residue of the UV-cured epoxy resin. By adding In-Fe and DOPO-SiD, a promising formulation for a halogen-free flame-retardant and UV-curable cycloaliphatic epoxy resin can be obtained.

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