Polym. Bull. (2009) 62:829–841
DOI 10.1007/s00289-009-0052-0

ORIGINAL PAPER

# Preparation and properties of halogen-free flame retardant epoxy resins with phosphorus-containing siloxanes

**Jiapei Ding · Zhiqiang Tao · Xiaobiao Zuo · Lin Fan ·**
**Shiyong Yang**

Received: 25 October 2008 / Revised: 27 December 2008 / Accepted: 15 February 2009 /

**Abstract** Novel epoxy resin modifiers, DOPO–TMDS and DOPO–DMDP were synthesized by addition reaction of divinylsiloxane with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Halogen-free flame retardant epoxy resins were obtained through modification of *o*-cresol novolac epoxy resin cured by phenol novolac resin using DOPO–TMDS and DOPO–DMDP which were characterized by $^{1}$H NMR, $^{13}$C NMR, $^{31}$P NMR and FT-IR measurements. Effects of the phosphorus-containing siloxanes on thermal stabilities, mechanical properties and flame retardant properties of the epoxy resins were investigated. The cured epoxy resins exhibited better mechanical properties and greatly improved flame retardant properties due to the presence of phosphorus-containing siloxanes. The cured epoxy resins with phosphorus loading of 2.0 wt% showed LOI values of 32–33 and achieved UL94V-0 ratings.

**Keywords** Epoxy · Flame retardancy · Mechanical properties · Phosphorus · Silicon

## Introduction

Epoxy resins have been widely used as microelectronics packaging materials due to their many attractive features such as excellent mechanical properties, good

---

J. Ding · Z. Tao (✉) · X. Zuo · L. Fan · S. Yang (✉)
Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences,
Zhongguancun, 100190 Beijing, China
e-mail: zqtao@iccas.ac.cn

S. Yang
e-mail: shiyang@iccas.ac.cn

J. Ding
e-mail: jpding@iccas.ac.cn

chemical and moisture resistance, long-term service time, low-cost and easy processing [1, 2]. However, epoxy resins always need flame retardant to ensure fire safety. Bromine-containing compounds or resins incorporated are usually employed as flame retardants. With the concerns of environmental problems caused by the toxic substances generated in combustion of bromine-containing flame retardants, developing of halogen-free flame retardants has been one of the hot research fields recently [3].

Phosphorus-containing organic compounds or resins have been demonstrated as effective flame retardants for epoxy resins and other polymer materials, attributed to their several advantages including high flame retardant efficiency, low production of corrosive and toxic gases in flames etc. [4]. Many kinds of phosphorus-containing organic compounds or resins as effective flame retardants have been reported [5–9]. A phosphorus-containing organic compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), has attracted intensive attention due to high flame retardant efficiency and thermal properties. Hence, various DOPO-based epoxy resins, curing agents and additives have been reported [10–17].

Organosilicon compounds have also been known for their good flame retardant properties combined with excellent thermal and chemical properties such as high thermal-oxidative resistance, low toxicity etc. Organosilicon compounds have been demonstrated as effective flame retardants for epoxy resins [18–21].

Moreover, silicon and phosphorus were demonstrated to exhibit a synergistic effect in their flame retarding behaviors. These combined compositions exhibit extremely high efficiency in flame retardancy and provide an approach for reducing the amounts of flame retardant used. Consequently, the cost was reduced and the epoxy resins' thermal properties were enhanced [22, 23]. However, the reports on P and Si synergy flame retardants only focus on flame retardant properties.

In this work, novel DOPO-based siloxanes have been prepared and evaluated as halogen-free flame retardants for epoxy resins. Effects of the siloxanes on the mechanical properties, thermal stabilities and flame retardant properties of epoxy resins were investigated.

## Experimental

### Materials

1,2-Divinyl-1,1,2,2-tetramethylsiloxane (TMDS), dichloromethylvinylsilane and bromobenzene (Acros) were purified by distillation prior to use. Magnesium turning (Acros) was used as received. Diethylether was purchased from Beijing Beihua Fine Chemicals Co., China, and freshly distilled in nitrogen over sodium prior to use. Petroleum ether, ethyl acetate, triethylamine, tetrahydrofuran (THF), and AIBN were obtained from Beijing Beihua Fine Chemicals Co., China and used without further purification. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

(DOPO) was prepared according to the literature [13]. Triphenylphosphine was used as received from Sinopharm Chemical Reagent Co. Phenol novolac resin (PN, trade name TD-2131, hydroxyl equivalent 105 g/mol, softening point 80 °C) was purchased from Dainippon Ink & Chemicals Inc., Japan. Cresol novolac epoxy (CNE, trade name 195LL, epoxy equivalent 195 g/mol, softening point 70 °C) was purchased from Yuka Shell Epoxy KK, Japan.

### Instruments

$^{1}$H, $^{13}$C and $^{31}$P NMR spectra were performed on a Bruker AVANCE 400 Spectrometer at 400 MHz using DMSO-$d_6$ as solvents. FT-IR spectra were recorded on a Perkin–Elmer 782 Fourier transform infrared spectrophotometer. Dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA) were measured on Perkin–Elmer 7 thermal analysis system. The mechanical properties were tested on an Instron 3365 tensile and flexural apparatus with specimen in agreement with GB/T 2570-1995 at a rate of 1.0 mm/min. The morphologies of the fracture surface after tensile tests for each sample were observed by a Hitachi S-4300 scanning electron microscope (SEM) at 15 kV acceleration voltages. Flame retardancy of the thermal-cured resins was determined by the limited oxygen index (LOI) method specified in ASTM D289. UL94 test was also used to evaluate the flame retardancy, which was performed using sheets (100 × 13.0 × 3.0 mm) according to ASTM D635-77. Combustion properties were evaluated by a cone calorimeter (Fire Testing Technology Co.) at heat flux of 50 kW/m$^2$.

### Synthesis of DOPO-1,2-diethylidene-1,1,2,2-tetramethyldisiloxane (DOPO–TMDS)

DOPO (108.0 g, 0.50 mol) and benzene (100 mL) were added into a 1,000 mL, three-necked round-bottom flask equipped with a stirrer and nitrogen inlet. The temperature was kept at the reflux temperature of benzene (80 °C). 1,2-Divinyl-1,1,2,2-tetramethylsiloxane (46.5 g, 0.25 mol) and AIBN (4.1 g, 0.025 mol) were dissolved in benzene, which was added dropwise into the system in about 6 h. After further reacted for 24 h, the reaction solution was cooled to ambient temperature. The solution was distilled to give the crude product (124.3 g) as a yellow solid. Purification was performed by column chromatography (using ethyl acetate/petroleum ether = 1/1 as eluent) to give fine product (71% yield). IR (KBr, cm$^{-1}$): 908 (P–O–Ph), 1,008–1,100 (Si–O–Si), 1,206 (P=O), 1,582 (P–Ph), 2,800–3,000 (aliphatic C–H), 3,064 (Ph–H). $^{1}$H NMR (DMSO-$d_6$, $\delta$, ppm): −0.06–0 (Si–CH$_3$, 12H), 0.51–0.60 (Si–CH$_2$, 4H), 1.93–2.00 (P–CH$_2$, 4H), 7.24–8.23 (Ph–H, 16H). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): −0.4 (s), 8.6 (s), 20.8 (d), 120.0 (d), 122.0 (d), 124.3(d), 124.5 (d), 124.6 (s), 125.6 (s), 128.6 (d), 129.7 (d), 130.7 (s), 133.2 (s), 134.8 (d), 148.8 (d). $^{31}$P NMR (DMSO-$d_6$, $\delta$, ppm): 39.1. Elem. Anal. Calcd. for $C_{32}H_{36}O_5P_2Si_2$: C, 62.12%; H, 5.86%; Found: C, 62.27%; H, 5.74%.

## Synthesis of DOPO-1, 2-diethylidene-1, 2-dimethyl-1, 2-diphenyldisiloxane (DOPO–DMDP)

### *Chlorophenylmethylvinylsilane*

A mixture of bromobenzene (46.8 g, 0.30 mol), magnesium (25.0 g, 1.04 mol) and freshly distilled diethyl ether (1,000 mL) were placed into a 2,000 mL three-necked round-bottom flask fitted with a dropping funnel, a drying tube, a nitrogen inlet and a reflux condenser. The flask was heated at 30°C to initialize the reaction. A mixture of bromobenzene (109.2 g, 0.70 mol) in freshly distilled diethyl ether (100 mL) was added dropwise into the flask in a period of 1 h. The reaction mixture was stirred at refluxing for 3 h to yield a black solution. After cooled to ambient temperature, dichloromethylvinylsilane (140.0 g, 1.00 mol) was added into the flask. The reaction mixture was heated at reflux temperature and kept for 2 h. Then distillation was performed to give a colorless liquid chlorophenylmethylvinylsilane (118.0 g, 65% in yield).

### *1,2-Divinyl-1,2-dimethyl-1,2-diphenyldisiloxane (DMDP)*

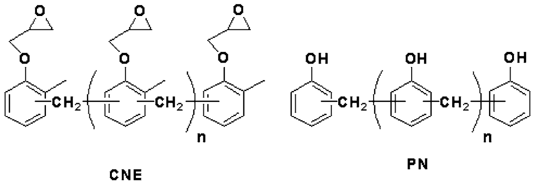
The obtained chlorophenylmethylvinylsilane (91.0 g, 0.50 mol) and triethylamine (202.0 g, 2.00 mol) were placed in a 500 mL, three-necked, round-bottom flask equipped with a dropping funnel, a nitrogen inlet and a reflux condenser. The flask was heated at 80°C and deionized water (5.0 g, 0.28 mol) was added dropwise in 1 h. The reaction mixture was refluxed for 4 h to give a viscous liquid. After cooled to ambient temperature, the reaction mixture was filtered to remove the solid and then washed by deionized water for 3 times. The product 1,2-divinyl-1,2-dimethyl-1,2- diphenylsiloxane (DMDP) was vacuum distilled to give 71.3 g colorless liquid (yield 92%). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 7.50–7.53 (q, 4H); 7.35–7.43 (m, 6H); 6.21–6.30 (q, 2H); 6.05–6.09 (q, 2H); 5.77–5.82 (q, 2H); 0.39 (s, 6H). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 0.2(s), 123.4(s), 125.2(s), 134.1(s), 133.6(s), 137.7(s). Elem. Anal. Calcd. for $C_{18}H_{22}OSi_2$: C, 69.62%; H, 7.14%; Found: C, 69.53%; H, 7.11%.

### *DOPO-1,2-diethylidene-1,2-dimethyl-1,2-diphenyldisiloxane (DOPO–DMDP)*

DOPO (108.0 g, 0.50 mol) and benzene (100 mL) were placed in a 1,000 mL, three-necked round-bottom flask equipped with a stirrer and nitrogen inlet. The solution was heated at the reflux temperature of benzene (80 °C). 1,2-Divinyl-1,2-dimethyl-1,2-diphenylsiloxane (77.5 g, 0.25 mol) and AIBN (4.1 g, 0.025 mol) were dissolved in benzene which was then added dropwise into the flask in 6 h. After further reacted for 24 h, the reaction solution was cooled to ambient temperature. The solution was distilled to remove the solvents and the crude product (151.7 g) as a yellow solid was obtained. The crude product was purified by column chromatography (using ethyl acetate/petroleum ether = 1/1 as eluent) to give fine product in 75% yield. IR (KBr, cm$^{-1}$): 909 (P–O–Ph), 1008–1100 (Si–O–Si), 1,230 (P=O), 1,583 (P–Ph), 2,800–3,000 (aliphatic C–H), 3,067 (Ph–H). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 0.21–0.25 (Si–$CH_3$, 6H), 0.79–0.90 (Si–$CH_2$, 4H), 1.84–1.93

**Table 1** Chemical compositions of the epoxy resins with phosphorus-containing siloxanes

| Samples | CNE (g) | DOPO–TMDS (g) | DOPO–DMDP (g) | PN (g) | P (wt%) | Si (wt%) |
|---|---|---|---|---|---|---|
| CNE-PN | 65 | 0 | 0 | 35 | 0 | 0 |
| EP-1a | 58.5 | 10 | 0 | 31.5 | 1 | 0.9 |
| EP-1b | 55.3 | 15 | 0 | 29.7 | 1.5 | 1.4 |
| EP-1c | 52 | 20 | 0 | 28 | 2 | 1.8 |
| EP-2a | 57.1 | 0 | 12 | 30.9 | 1 | 0.9 |
| EP-2b | 53.3 | 0 | 18 | 28.7 | 1.5 | 1.3 |
| EP-2c | 49.4 | 0 | 24 | 26.6 | 2 | 1.8 |



**Scheme 1** Chemical structure of CNE and PN

(P–CH$_2$, 4H), 7.23–8.18 (Ph–H, 26H). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): −1.9 (d), 7.5 (d), 20.9 (d), 120.0 (d), 122.0 (d), 124.3 (d), 124.3 (d), 124.6 (s), 125.7 (d), 127.8 (s), 128.6 (d), 129.6 (d), 129.8 (s), 130.7 (s), 132.8 (s), 133.3 (s), 134.8 (d), 136.3(s). $^{31}$P NMR (DMSO-$d_6$, $\delta$, ppm): 38.6. Elem. Anal. Calcd. for $C_{42}H_{40}O_5P_2Si_2$: C, 67.90%; H, 5.43%; Found: C, 68.03%; H, 5.39%.

### Preparation of the flame retardant epoxy resins with the phosphorus-containing siloxanes

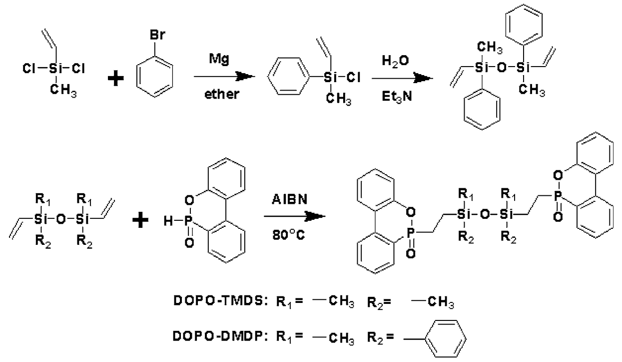
The flame retardant epoxy resins were prepared according to the resin chemical compositions (Table 1).

The CNE epoxy (Scheme 1) was blended with phenol novolac (PN) and synthesized siloxane at 150 °C to give homogeneous solution. Triphenylphosphine as the curing catalyst was added with mechanically stirring to ensure the catalyst well dispersed in the resin system. The epoxy resin samples were thermally cured at 150 °C for 2 h, followed by 180 °C for 2 h. After postcured at 200 °C for 1 h, the cured epoxy resins with different phosphorus loadings were obtained.

## Results and discussion

### Synthesis of the phosphorus-containing siloxanes

As DOPO has high reactive P–H group in molecule thereof, DOPO has been used to synthesize a series of novel DOPO derivatives by the addition reaction of DOPO and double bond containing compounds [17]. Recently simple and high yield



**Scheme 2** Synthesis of DOPO–TMDS and DOPO–DMDP

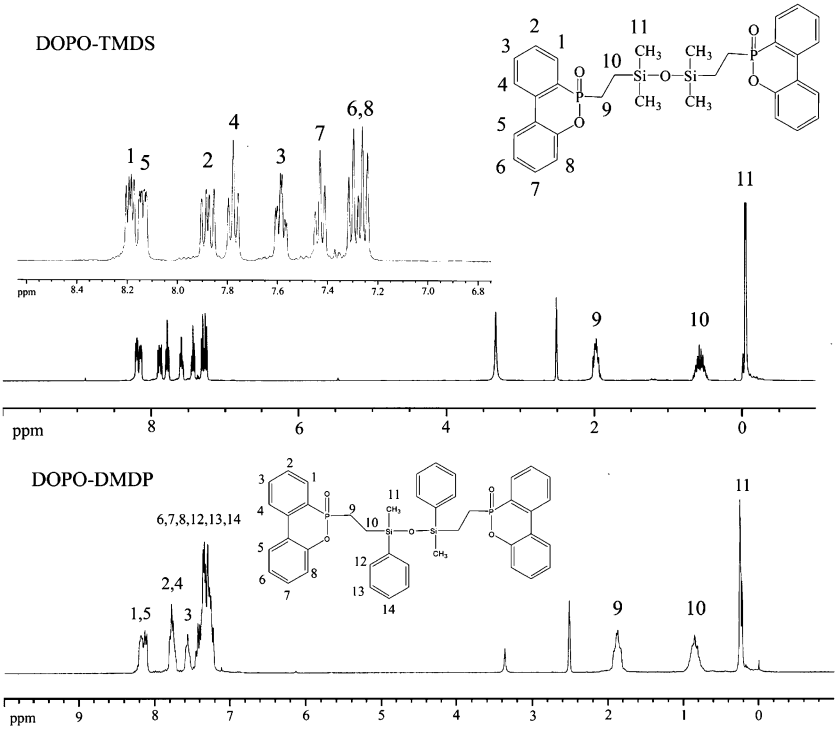


**Fig. 1** $^1$H NMR spectra of DOPO–TMDS and DOPO–DMDP

reaction between P–H group containing compounds and vinyl group containing compounds was reported [24]. Therefore, DOPO was provided herein for addition reaction with vinyl-siloxane resulting in DOPO-end-capped siloxanes (DOPO–TMDS and DOPO–DMDP, Scheme 2).

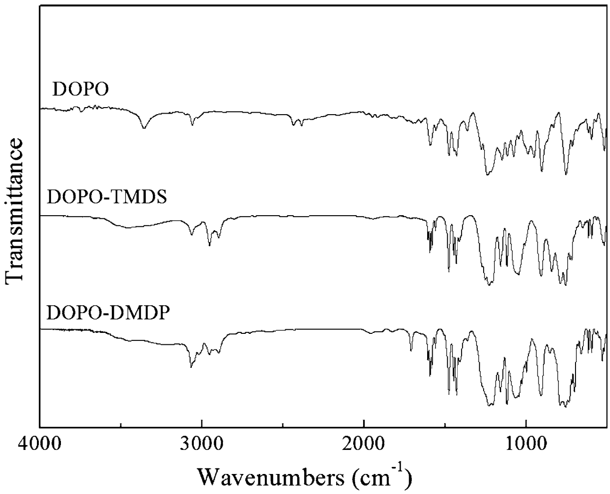


**Fig. 2** FT-IR spectra of DOPO–TMDS and DOPO–DMDP

The synthesized compounds were characterized with $^1$H (Fig. 1), $^{13}$C, $^{31}$P NMR, FT-IR (Fig. 2) and elemental analysis. The reaction process of P–H and vinyl group was monitored by FTIR instrument and NMR spectrometer, which was confirmed by disappearance of the absorption peaks at 2,385 cm$^{-1}$ (P–H), 1,633 cm$^{-1}$ (–CH=CH$_2$) by FTIR and the chemical shift at 8.8 ppm (P–H) and 6.0–6.4 ppm (–CH=CH$_2$) by $^1$H NMR. The appearance of the chemical shift at 39 ppm instead of 19 ppm (DOPO) in $^{31}$P NMR spectrum also indicated that P–H group had already reacted with the –CH=CH$_2$ group of vinyl-siloxanes.

## Mechanical properties of the cured epoxy resins

The mechanical properties of the cured epoxy resins are summarized in Table 2. The mechanical properties were apparently enhanced by the introduction of the phosphorus-containing siloxanes. Figure 3 shows the fracture morphology of EP-1c and EP-2c compared with CNE-PN. All the samples showed good homogeneity. It can be seen that three typical regions are observed, namely initiation, propagation and termination. The fracture surface of the tensile specimens exhibited remarkable difference in the rapid crack growing area. The termination region bring the main region reflects the differences in deformation. It was known that higher surface roughness was connected with higher energy which was required to fracture the specimens [25]. The toughening effect of the phosphorus-containing siloxanes is obvious based on the fact that the fracture surface of EP-1c and EP-2c are much rougher than that of CNE-PN.

## Thermal properties of cured epoxy resins

Thermal properties of the cured epoxy resins were investigated by DMA and TGA. Results are shown in Figs. 4, 5, 6 and data are summarized in Table 3.

**Table 2** Mechanical properties of cured epoxy resins

| Samples | Tensile strength (MPa) | Tensile modulus (GPa) | Flexural strength (MPa) | Flexural modulus (GPa) |
|---|---|---|---|---|
| CNE-PN | 68.4 | 2.59 | 127 | 2.88 |
| EP-1a | 76.7 | 2.60 | 136 | 3.11 |
| EP-1b | 94.2 | 2.72 | 152 | 3.30 |
| EP-1c | 97.4 | 2.73 | 152 | 3.31 |
| EP-2a | 86.6 | 2.80 | 144 | 3.13 |
| EP-2b | 92.5 | 2.81 | 158 | 3.32 |
| EP-2c | 94.7 | 2.81 | 164 | 3.41 |

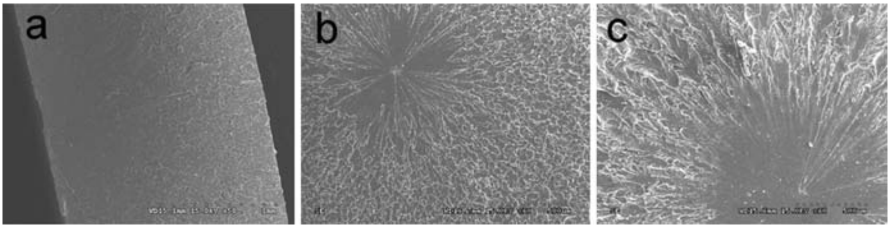


**Fig. 3** Tensile fracture SEM photos of CNE-PN (**a**), EP-1c (**b**) and EP-2c (**c**)

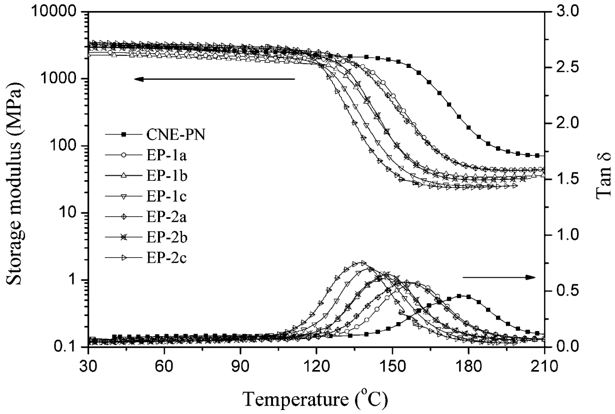


**Fig. 4** DMA curves of cured epoxy resins

It was obvious that the glass transition temperatures determined by DMA slightly decreased with the siloxane loading increasing. For instance, the glass transition temperature of CNE-PN was 177 °C determined by the peak temperature of the loss tangent (tan *δ*) curve, 30–40 °C higher than that of EP-1c (141 °C) and EP-2c (138 °C), respectively. This might be interpreted by the softening effect of the siloxane additives.

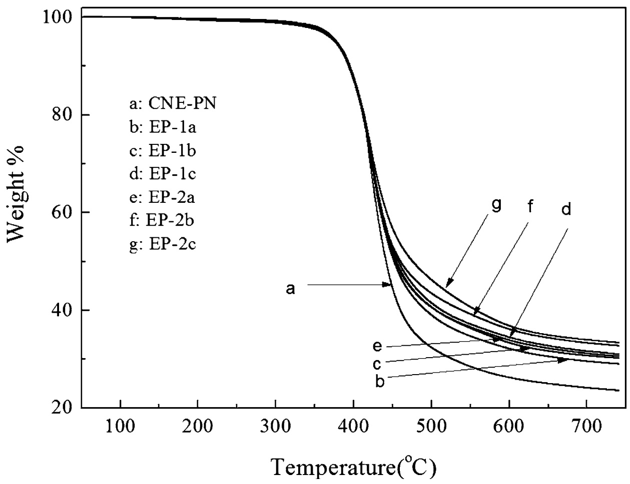


**Fig. 5** TGA curves of cured epoxy resins in nitrogen

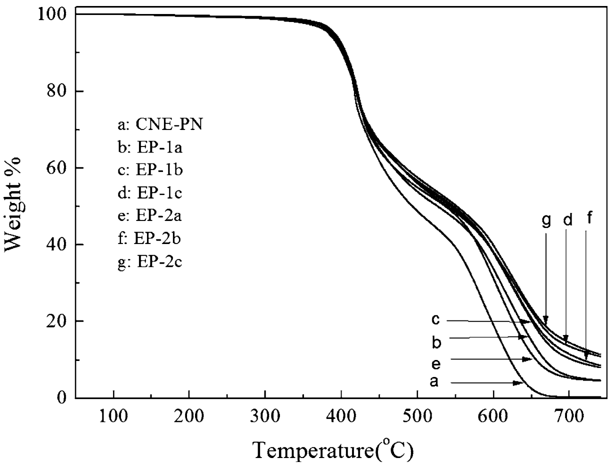


**Fig. 6** TGA curves of cured epoxy resins in air

The thermal stability and decomposition behavior of cured epoxy resins comprising the phosphorus-containing siloxanes were investigated by TGA. Figure 5 shows plots of weight versus temperature from 50 to 750 °C for the cured epoxy resins with different siloxane loadings in nitrogen atmosphere. It was found that almost no weight loss was detected below 350 °C. The initial decomposition temperatures at 5% weight loss were observed in the range of 376–378 °C in nitrogen and 384–391 °C in air. It was implied that initial thermal decomposition behavior of the cured resins was not affected strongly by DOPO–TMDS and DOPO–DMDP. However, the maximum weight loss rates were obviously decreased in nitrogen. The residual chars at 700 °C were measured in the range of 29.5–33.9%, much higher than that of CNE-PN. The char forming effect of

**Table 3** Thermal properties of the cured epoxy resins with phosphorus-containing siloxanes

| Samples | $T_g$ (°C) | $T_{d1}$ (°C) | $R_1$ (%/°C) | Char$_1$ (%) | $T_{d2}$ (°C) | $R_{2a}$ (%/°C) | $R_{2b}$ (%/°C) | Char$_2$ (%) |
|---|---|---|---|---|---|---|---|---|
| CNE-PN | 177 | 377 | 1.20 | 24.1 | 386 | 1.06 | 0.46 | 0.30 |
| EP-1a | 159 | 377 | 0.98 | 29.5 | 391 | 0.86 | 0.39 | 5.81 |
| EP-1b | 148 | 376 | 0.96 | 30.7 | 390 | 0.84 | 0.36 | 10.3 |
| EP-1c | 141 | 377 | 0.92 | 31.6 | 389 | 0.82 | 0.32 | 13.5 |
| EP-2a | 156 | 377 | 0.97 | 31.2 | 389 | 0.83 | 0.45 | 5.32 |
| EP-2b | 148 | 376 | 0.93 | 33.3 | 386 | 0.78 | 0.35 | 11.5 |
| EP-2c | 138 | 378 | 0.81 | 33.9 | 384 | 0.77 | 0.34 | 14.5 |

$T_{d1}$ 5% weight loss temperature in nitrogen; $R_1$ maximum weight loss rate in nitrogen; *Char*$_1$ weight at 700 °C in nitrogen; $T_{d2}$ 5% weight loss temperature in air; $R_{2a}$ 1st maximum weight loss rate in air; $R_{2b}$ 2nd maximum weight loss rate in air; *Char*$_2$: weight at 700 °C in air

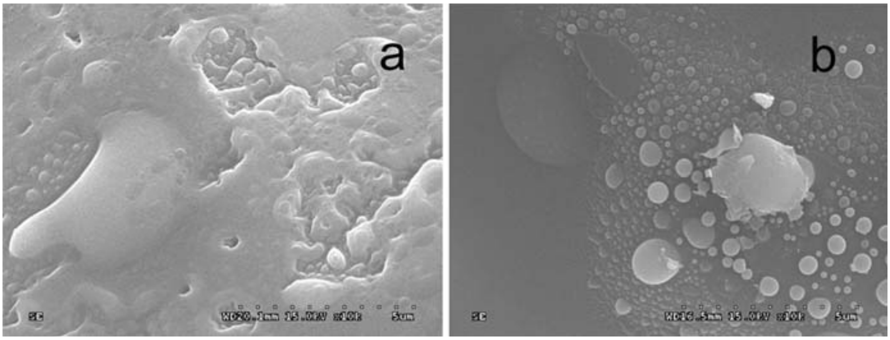


Fig. 7 Char surface SEM photos of EP-1c (**a**) and EP-2c (**b**)

the phosphorus and silicon content of siloxane are significant. Because char yield correlates with flame retardant property of polymers, the epoxy resins prepared were expected to have good flame retardant properties.

In air atmosphere, TGA curves show two decomposition stages (Figure 6), in which the first stage was assumed as the thermal degradation of polymer network and the second one as the oxidation process of the char moiety [26]. In the first stage, the maximum weight loss rates of the cured epoxy resins were decreased by 18.9–22.6% compared with that of the CNE-PN, while in the second char oxidation stage, the maximum weight loss rates were decreased by 15.2–30.4% compared with that of CNE-PN. These results indicated the cured epoxy resins combined with siloxanes possess improved thermal stability and thermo-oxide resistance compared with CNE-PN. The TGA residues of EP-1c and EP-2c in air were investigated by SEM (Fig. 7), while no residue was found in CNE-PN. The residues showed uneven surface which mainly consisted of silicon and phosphorus oxide determined by elemental analysis. This silicon-phosphorus oxide composite surface played important role in protecting inside resin as well as blocking heat and mass transfer [17].

**Table 4** Flame retardant properties of the epoxy resins with phosphorus-containing siloxanes

| Samples | LOI | UL94 | TTI (s) | pHRR (kW/m$^2$) | THR (MJ/m$^2$) |
|---|---|---|---|---|---|
| CNE-PN | 21 | NOT V-2 | 51 | 754 | 59.0 |
| EP-1a | 28 | V-1 | 57 | 630 | 58.2 |
| EP-1b | 31 | V-1 | – | – | – |
| EP-1c | 33 | V-0 | 61 | 360 | 49.8 |
| EP-2a | 27.5 | V-1 | 53 | 549 | 57.1 |
| EP-2b | 30 | V-1 | – | – | – |
| EP-2c | 32 | V-0 | 54 | 474 | 47.0 |

*TTI* time to ignition; *pHRR* peak of heat release rate; *THR* total heat release

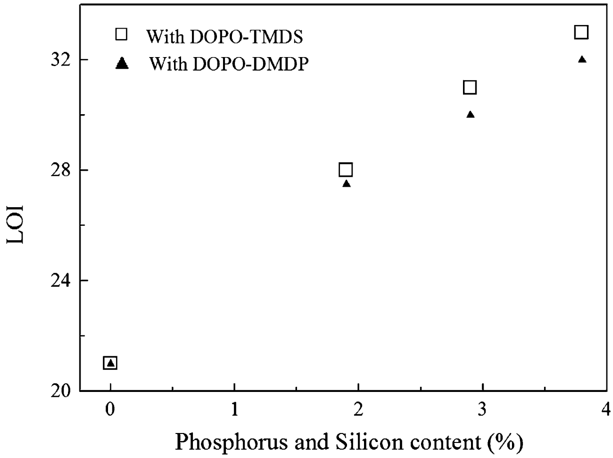


**Fig. 8** LOI versus P and Si content of epoxy resins

## Flame retardant properties of the cured epoxy resins

The flame retardant properties of the cured epoxy resins were investigated by LOI test and UL94 test. Data are summarized in Table 4. LOI values of the cured resins increased with increasing of the phosphorus and silicon loadings (Fig. 8).

The LOI value of pure CNE-PN was 21 and the UL94 rating was NOT V-2. LOI value was higher than 30 when the phosphorus loading was above 1.5 wt%. UL94 V-0 ratings could be achieved when the phosphorus loading was 2.0 wt%.

The combustion properties, including TTI, pHRR and THR of the cured epoxy resins were evaluated by cone calorimeter (Table 4).

It was clear that the introduction of the phosphorus-containing siloxanes in the epoxy resins extended the TTI values (53-61 s) compared with CNE-PN (51 s). However, pHRR value of the epoxy resins modified by siloxanes were greatly reduced (Fig. 9). For instance, pHRR values of EP-1c and EP-2c were 360 and 474 kW/m$^2$, 37.7–52.3% lower than that of CNE-PN (754 kW/m$^2$), which might be attributed to the self-extinguishing ability of the phosphorus-containing resins [27]. THR values were measured in the range of 47.0 MJ/m$^2$ for EP-1c and 49.8 MJ/m$^2$

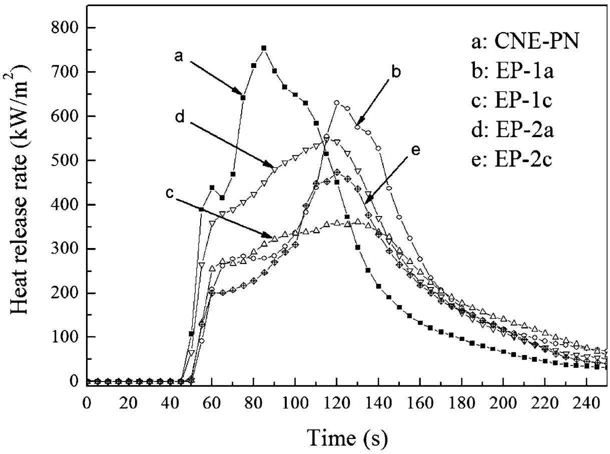


**Fig. 9** Heat release rate curves of cured epoxy resins

for EP-2c, respectively, 15.5–20% lower than that of CNE-PN (59 MJ/m$^2$), implying that P and Si have effect to reduce the heat release in the case of fire.

The burning behavior of polymeric materials is understood in terms of their ability to generate flammable volatile products and their subsequent ignition. The phosphorus-containing siloxanes tend to catalyze the polymer chain to form silicaceous char in condensed phase and inhibit the release of combustible gases [21]. This char yield acts like a stable barrier which may insulate the heat and mass transfer between the gaseous and condensed phases. Thus the flame retardant property was greatly improved.

## Conclusions

Halogen-free flame retardant epoxy resins with phosphorus-containing siloxanes have been prepared using DOPO-end-capped siloxane (DOPO–TMDS and DOPO–DMDP). The phosphorus-containing siloxanes showed obvious effect on the thermal stabilities, mechanical properties as well as flame retardancy of the epoxy resins. The cured epoxy resins exhibited improved mechanical properties and better thermal stabilities. Importantly, excellent flame retardant properties were founded for the cured epoxy resins. UL94 V-0 ratings and LOI values of 32–33 could be achieved for the cured epoxy resins with phosphorus loading of 2.0 wt%.

**Acknowledgment** The authors wish to thank for financial support of National Natural Science Foundation of China (Project Grant No. 50803069).

## References

1. Lee H, Neville K (eds) (1972) Handbook of epoxy resins. McGraw-Hill, New York
2. McAdams LV, Gannon JA (1988) Encyclopedia of Polymer Science and Engineering, vol 6. Wiley, New York, p 322

3. Bergman A (1999) In: Proceedings of international conference on halogen-free materials for electronic and electric products, Gotherburg, Sweden
4. Hsiue GH, Liu YL, Tsiao J (2000) Phosphorus-containing epoxy resins for flame retardancy V: synergistic effect of phosphorus–silicon on flame retardancy. J Appl Polym Sci 78:1
5. Li J, Chen S, Xu X (1990) Mechanism of flame-retardant action of tris (2,3-dichloropropyl) phosphate on epoxy resin. J Appl Polym Sci 40:417
6. Liu YI, Pearce EM, Weil ED (1999) Flame retardancy of dicyandiamide-crosslinked epoxy resins containing phenolphthalein structures and/or a phosphorus-containing additive. J Fire Sci 17:240
7. Zerda AS, Lesser AJ (2002) Organophosphorous additive for fortification, processibility, and flame retardance of epoxy resins. J Appl Polym Sci 84:302
8. Kodolov VI, Shuklin SG, Kuznetsov AP, Makarova LG, Bystrov SG, Demicheva OV, Rudakova TA (2002) Formation and investigation of epoxy intumescent compositions modified by active additives. J Appl Polym Sci 85:1477
9. Denq BL, Hu YS, Chen LW, Chiu WY, Wu TR (1999) The curing reaction and physical properties of DGEBA/DETA epoxy resin blended with propyl ester phosphazene. J Appl Polym Sci 74:229
10. Lin CH, Feng CC, Hwang TY (2007) Preparation, thermal properties, morphology, and microstructure of phosphorus containing epoxy/$SiO_2$ and polyimide/$SiO_2$ nanocomposites. Eur Polym J 43:725
11. Wang XD, Zhang Q (2004) Synthesis, characterization, and cure properties of phosphorus-containing epoxy resins for flame retardance. Eur Polym J 40:385
12. Lin CH, Wu CY, Wang CS (2000) Synthesis and properties of phosphorus-containing advanced epoxy resins. II. J Appl Polym Sci 78:228
13. Wang CS, Shieh JY (1998) Synthesis and properties of epoxy resins containing 2-(6-oxid-6H-dibenz<c,e> <1,2>oxaphosphorin-6-yl)1,4-benzenediol. Polymer 39:5819
14. Cho CS, Fu SC, Chen LW, Wu TR (1998) Aryl phosphinate anhydride curing for flame retardant epoxy networks. Polym Int 47:203
15. Liu YL, Wu CS, Hsu KY, Chang TC (2002) Flame-retardant epoxy resins from *o*-cresol novolac epoxy cured with a phosphorus containing aralkyl novolac. J Polym Sci Polym Chem 40:2329
16. Wang CS, Lin CH (1998) Properties and curing kinetic of diglycidyl ether of bisphenol A cured with a phosphorus-containing diamine. J Appl Polym Sci 74:1635
17. Levchik SV, Weil ED (2004) Thermal decomposition, combustion and flame-retardancy of epoxy resins—a review of the recent literature. Polym Int 53:1901
18. Hsiue GH, Wang WJ, Chang FC (1999) Synthesis, characterization, thermal and flame-retardant properties of silicon-based epoxy resins. J Appl Polym Sci 73:1231
19. Kashiwagi T, Gilman JW (2000) In: Grand AF, Wilkie GA (eds) Fire retardancy of polymeric materials. Marcel Dekker, New York
20. Hsiue GH, Wei HF, Shiao SJ, Kuo WJ, Sha YA (2001) Chemical modification of dicyclopentadiene-based epoxy resins to improve compatibility and thermal properties. Polym Degrad Stab 73:309
21. Mercado LA, Reina JA, Galia M (2006) Flame retardant epoxy resins based on diglycidyloxymethylphenylsilane. J Polym Sci Polym Chem 44:5580
22. Li Q, Jiang PK, Su ZP, Wei P, Wang GL, Tang XZ (2005) Synergistic effect of phosphorus, nitrogen, and silicon on flame-retardant properties and char yield in polypropylene. J Appl Polym Sci 96:854
23. Anna P, Marosi G, Bourbigot S, Le Bras M, Delobel R (2002) Intumescent flame retardant systems of modified rheology. Polym Degrad Stab 77:243
24. Han LB, Zhao CQ (2005) Stereospecific addition of H–P bond to alkenes: a simple method for the preparation of (Rp)-phenylphosphinates. J Org Chem 70:10121
25. Tang LX, Qu BJ, Shen XF (2004) Mechanical properties, morphological structure, and thermal behavior of dynamically photocrosslinked PP/EPDM blends. J Appl Polym Sci 92:3371
26. Wu CS, Liu YL, Chiu YC, Chiu YS (2002) Thermal stability of epoxy resins containing flame retardant components: an evaluation with thermogravimetric analysis. Polym Degrad Stab 78:41
27. Troitsch J (1990) International plastic flammability handbook, 2nd edn. Hanser, Munich