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Epoxy resins possessing flame retardant elements from silicon incorporated epoxy compounds cured with phosphorus or nitrogen containing curing agents

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Abstract

New silicon-containing epoxy compounds were obtained by reacting a bisphenol-A type epoxy and an *o*-cresol–formaldehyde novolac type epoxy with diphenylsilandiol and triphenylsilanol, respectively. The reactions were performed with tin(II) chloride as a catalyst at 140–170 °C. With various feeding ratios of reactants, the epoxy compounds contained various silicon contents. The thermal stability and the flame retardant property of the cured epoxy resins were improved with this incorporation of silicon. Synergistic effects of phosphorus/silicon and nitrogen/silicon on enhancing limited oxygen index values were also observed for the epoxy resins from the silicon-containing epoxy compounds cured with phosphorus- and melamine-containing agents. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Silicon; Flame retardant

1. Introduction

Epoxy resins have been commercially available for about 50 years and are widely used in modern industries. Up to now, research efforts on improving the properties of the epoxy resins are under progress for meeting the requirements from the versatile and advanced application. For epoxy resins utilized in electronics, superior thermal stability, electrical properties, and halogen-free in flame retardation were especially focused [1,2]. Some achievements have been reached with incorporating imido [3,4] and maleimido [5,6] groups into epoxy structures, introducing silicon-containing group into epoxy resins [7,8], using phosphorus flame retardant to replace the traditional halogenated compounds [2,9–13], and utilizing rigid and aromatic compounds as curing agents [14,15]. Among these work, introducing silicon and its groups into epoxy was attractive for its significant improvement on the electrical properties of the epoxy resins, thermal stability, and flame retardancy [7,8,16–18]. Some other properties, such as high resistance to thermal oxidation, low surface energy, and low toxicity, were also observed for organosilicon compounds and polymers [19–21].

The excellent thermal stability of silicon-containing epoxy compounds satisfy the requirements for application in advanced electronics. Another attractive character of silicon was its improvement on flammability of the polymers [7,8]. While heating, low surface energy of silicon renders it to migrate to the surface of epoxy resin and to form a protective layer with high heat-resistance to avoid polymer residue from thermal degradation. Silicon was therefore considered as one of the 'environment friendly' flame-retarding elements, including phosphorus and nitrogen. Phosphorus compounds have been demonstrated to exhibit notable efficiency on improving flame retardancy of the polymers through a condensed mechanism [22–25]. On the other hand, the nitrogen-rich melamine group was also widely utilized which is expected to impart flame retardancy to polymers [26,27], since melamine groups could form polymeric products of melam and melem via deammoniation reaction [28–30]. The high heat-insulating and heat-resistant products and incombustible ammonia gas from melamine thermal degradation played a significant effect on reducing flammability of the materials. Moreover, effective synergistic effect of silicon and phosphorus on enhancing char formation and improving flame retardancy

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of the polymers was also observed [31,32]. A novel approach to obtain epoxy resins with excellent thermal properties as well as high flame retardancy was reached with simultaneously incorporating silicon and phosphorus into the epoxy resins.

In this work, incorporation of silicon onto epoxy compounds was performed by reacting phenylsilanol compounds with epoxy compounds. Both of the commercially available bisphenol-A type epoxy (BE188) and *o*-cresol–formaldehyde novolac epoxy (CNE200) were reacted with diphenylsilandiol (DPSD) and triphenylsilanol (TPSO), respectively, through the addition reaction between the oxirane ring and silanol group. The silicon-containing epoxy compounds were cured with various curing agents, including phosphorus- and melamine-containing compounds. The preparation of silicon-containing epoxy compounds, curing reactions, thermal properties, and flammability of the cured resins were discussed.

2. Experimental section

2.1. Materials

DPSD and TPSO were purchased from Aldrich Co. Diglycidylether of bisphenol-A (epoxy equivalent weight, EEW = 188) and *o*-cresol–formaldehyde novolac epoxy (EEW = 200) were supplied from Chang Chun Plastic Co. in Taiwan with their commercial codes of BE188 and CNE200, respectively. Dicyandiamide (DICY), 4,4′-diaminodiphenylmethane (DDM), and triphenylphosphine (TPP) were from Tokyo Kasei Kogyo Co. Ltd. Tin(II) chloride was from Aldrich Co. Bis(aminophenyl)phenylphosphine oxide (BAPPPO) was prepared in the laboratory according to the literature [28–30]. Diamine compound 2DOPO-A [33] and novolac resin DOPO-PN [34], both bearing 9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl (DOPO) substituent, were obtained according to the reported methods. Melamine-modified phenol–formaldehyde novolac (MPFN) was received from Hitachi Chemical Co., Japan, with the commercial code of Melan 9000 (nitrogen content: 7 wt%, –OH equivalent weight: 118). All of the amine and novolac compounds were used as curing agents with epoxy compounds. The chemical structures of the earlier-mentioned compounds were shown in Fig. 1.

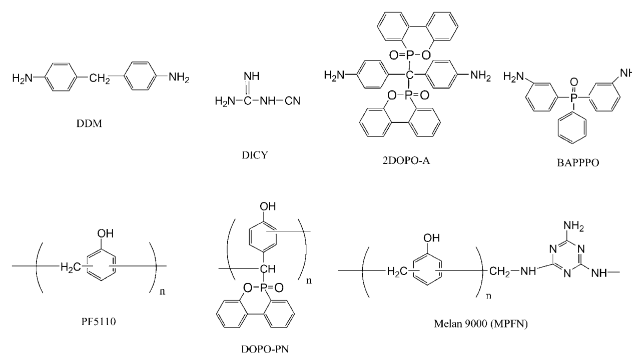


Fig. 1. The chemical structures of the curing agents.

2.2. Synthesis of BE–Si epoxy compounds

BE–Si series epoxy compounds were prepared by reacting BE188 with DPSD with 500 ppm tin(II) chloride as a catalyst. Various compositions of reactants were fed to result in epoxy compounds with different silicon contents (Table 1). A typical procedure for preparing BE–Si20 was represented as an example. 18.8 g of BE188, 7.9 g of DPSD, and 0.013 g of tin(II) chloride were taken in a 50 ml round-bottomed flask. The reaction mixture was stirred at 140 °C for 2 h. A transparent product was obtained with 100% yield. Instrumental analysis on BE–Si20: EEW = 505 (calculated: 485); softening point: 55 °C; FT-IR (KBr, cm^{-1}): 1323 (Si–O–CH_2–), 1582 (Si–Ph), 915 (oxirane ring). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.77$ ppm (–C(CH_3)$_2$–), $\delta = 2.84$ and 2.97 ppm (oxirane ring, –CH_2–CH(O)CH_2), $\delta = 3.43$ ppm (oxirane ring, –CH_2–CH(O)CH_2), $\delta =$ 3.81–4.31 ppm (other protons in cyclic and opened oxirane ring), and $\delta = 6.94$–7.77 ppm (aromatic protons).

Table 1
Synthesis of silicon-incorporated epoxy resins

Epoxy resin	Epoxy	Silanol compound	Feeding ratio[a]		EEW (g/mol)		Softening point (°C)
			Epoxy	Silano compound	Calculated	Measured	
BE–Si20	BE188	DPSD	2	1	484	505	55
BE–Si25	BE188	DPSD	2.5	1	385	400	43
BE–Si30	BE188	DPSD	3.0	1	336	339	–[b]
BE–Si35	BE188	DPSD	3.5	1	306	310	–[b]
CNE–Si20	CNE200	TPSO	1	0.2	250	288	87
CNE–Si30	CNE200	TPSO	1	0.3	286	334	98
CNE–Si40	CNE200	TPSO	1	0.4	334	355	102
CNE–Si50	CNE200	TPSO	1	0.5	413	415	110

[a] In equivalent molar ratios.
[b] Not measurable.

Table 2
Curing compositions and reaction data for preparing cured epoxy resins

Cured epoxy resin	Epoxy monomer	Curing agent	Curing condition (°C, min)	Post cure condition (°C, min)
BE–Si20-I	BE–Si20	DDM	140, 60	185, 80
BE–Si25-I	BE–Si25	DDM	140, 60	185, 80
BE–Si30-I	BE–Si30	DDM	155, 60	190, 80
BE–Si35-I	BE–Si35	DDM	155, 60	190, 80
BE–Si20-II	BE–Si20	DICY	205, 80	230, 100
BE–Si20-III	BE–Si20	BAPPPO	200, 80	220, 100
BE–Si20-IV	BE–Si20	2DOPO-A	190, 80	210, 100
CNE–Si20-I	CNE–Si20	PF5110	140, 60	185, 80
CNE–Si30-I	CNE–Si30	PF5110	140, 60	185, 80
CNE–Si40-I	CNE–Si40	PF5100	155, 60	190, 80
CNE–Si50-I	CNE–Si50	PF5100	155, 60	190, 80
CNE–Si40-II	CNE–Si40	DOPO-PN	205, 80	230, 100
CNE–Si40-III	CNE–Si40	MPFN	200, 80	220, 100

2.3. Synthesis of CNE–Si epoxy compounds

CNE–Si epoxy compounds were obtained by reacting CNE200 and TPSO with various feeding ratios of reactants (Table 1). 500 ppm of tin(II) chloride was added as a catalyst. The reactions were performed with similar manners for preparing BE–Si epoxy compounds, with a different reaction temperature of 170 °C. Instrumental analysis on CNE–Si40: EEW = 355 (calculated: 334); softening point: 102 °C; FT-IR (KBr, cm^{-1}): 1330 (Si–O–CH_2–), 1588 (Si–Ph), 910 (oxirane ring). ^1H NMR ($CDCl_3$, ppm): $\delta = 2.27$ ppm (–Ph–CH_3), $\delta = 2.66$ ppm (–Ph–CH_2–Ph), $\delta = 2.83$ and 2.97 ppm (oxirane ring, –CH_2–CH(O)CH_2), $\delta = 3.30$ ppm (oxirane ring, –CH_2–C*H*(O)CH_2), $\delta = 3.73$–4.24 ppm (other protons in cyclic and opened oxirane ring), and $\delta = 6.85$–7.73 ppm (aromatic protons).

2.4. Preparation of epoxy resins

The cured epoxy resins were obtained from thermally curing silicon-containing epoxy compounds (BE–Si and CNE–Si series) with various curing agents. To obtain a highly crosslinking polymer with good thermal stability, one EEW of the epoxy was cured with one functional equivalent weight of the curing agent. Good miscibility between the silicon-containing epoxy compounds and the curing agents were observed from their mixtures. TPP (500 ppm) was added to each of the curing composition of the CNE–Si epoxy compounds as a promoter to curing reactions. The curing compositions and curing reaction conditions (determined from DSC scanning traces of the reactions) were shown in Table 2.

2.5. Determination of the epoxy equivalent weights of the epoxy compounds

The EEWs of the epoxy compounds were determined by titration. 3.00 g of epoxy compound was taken in a 250 ml round-bottomed flask and 25 ml of 0.2N HCl/pyridine solution was added. The mixture was then heated to 40 °C. While the epoxy compound was dissolving in the HCl/pyridine solution, the solution was heated to reflux for 20 min, cooled to room temperature, and then 6 ml of water and 0.2 ml of phenolphthalein solution (0.1 wt% in methanol) were added as an indicator. The solution was then titrated with NaOH solution (0.1N in methanol). The EEW value of the epoxy compound was determined with EEW = $10\,000W/f(B - S)$, where W is the weight of the epoxy compound (g), B the used amount of 0.1N NaOH solution for blank test (ml), S the used amount of 0.1N NaOH solution for sample titration (ml), and f is the calibration factor for NaOH solution.

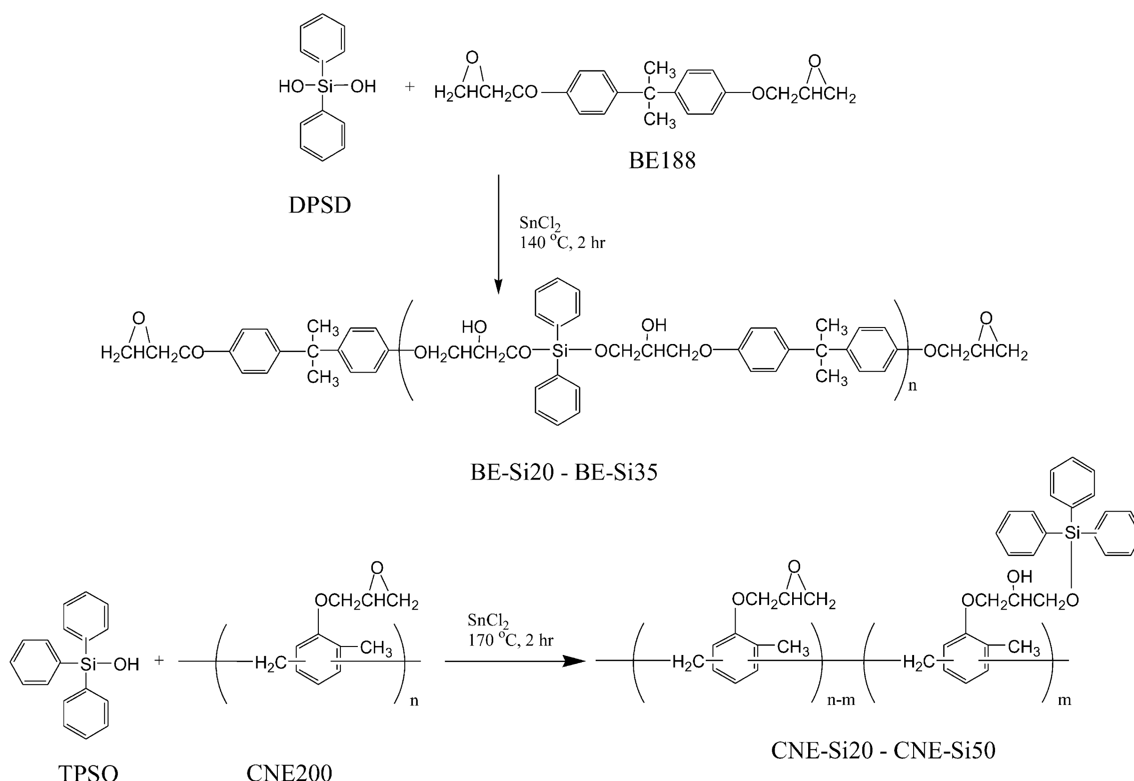
2.6. Instrumental measurements

Infrared spectra (FT-IR) were obtained from a Perkin–Elmer 2000 FT-IR. ^1H NMR spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer with $CDCl_3$ as a solvent. Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin–Elmer DSC 7 at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a Perkin–Elmer TGA 7 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air atmosphere. Limited oxygen index (LOI) values were measured on a Stanton Redcraft flame meter. The percentage in the O_2–N_2 mixture, deemed sufficient to sustain the flame and was taken as the LOI.

3. Results and discussion

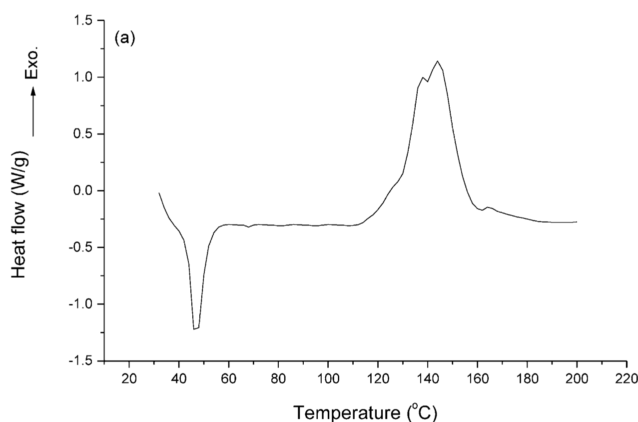
3.1. Preparation of silicon-containing epoxy compounds

The chain extension process was often utilized for preparing high molecular weight epoxy, by reacting the difunctional and low molecular weight epoxy with di-phenol compounds at temperatures between 180 and 200 °C [35,36] (Scheme 1). A catalyst, for example, TPP and A1



Scheme 1. Preparation of the silicon-containing epoxy compounds.

catalyst (ethyltriphenylphosphonium acetate/acetic acid complex) [37], was usually employed for promoting this reaction and limiting the side reactions. However, these two ordinary catalysts were not very powerful for the extension reaction of BE188 and DPSD. The reaction conversion was not high enough even at reaction temperature over 190 °C and a long period of reaction time over 3 h. Therefore, another compound of tin(II) chloride was used as the catalyst for BE188/DPSD reaction. Fig. 2 showed the DSC thermograms monitoring the above reaction catalyzed with tin(II) chloride. Heating scan on the reaction mixture gave an exothermic peak to imply an optimum reaction temperature of 140 °C. Isothermal scan at 140 °C indicated the reaction got completed in 80 min. Therefore, a reaction condition of 140 °C for 2 h was taken for the addition reaction between BE188 and DPSD promoted with tin(II) chloride. Moreover, for incorporating silyl groups onto CNE200, a monofunctional silanol TPSO was reacted with CNE200. From DSC measurements the reaction condition for TPSO/CNE200 addition reaction promoted with tin(II) chloride was determined to be at 170 °C for 2 h. The reactivity of TPSO onto oxirane ring was found to be lower than that of DPSD. With the earlier-mentioned reaction conditions, various feeding compositions of epoxy compounds and silanol compounds were charged to result in silicon-incorporated epoxy compounds with different silicon contents (Table 1). The performance of the addition reaction between silanol and the oxirane groups was observed with FT-IR spectra. The disappearance of the Si–OH absorption peak at 2900 cm^{-1} and the appearance of the Si–O–C (aliphatic carbon) at 1323 cm^{-1} demonstrated the occurrence of the reaction between Si–OH and oxirane ring. The band at 1582 cm^{-1} (Si–Ph) was observed for all the resultant products, further to indicate the incorporation of silyl groups onto epoxy compounds. ^{1}H NMR analysis gave another evidence to the preparation of silicon-containing epoxy compounds. All the absorption peaks gave good coincidence with the chemical structures of the epoxy compounds (see the analysis data collected in Section 2). The ratios of the peak area integration from the ^{1}H NMR spectra were also comparable to the ratios of the proton numbers of the desired chemical structures. The EEWs of the resulted epoxy compounds measured by titration were comparable but a little higher with the values calculated from the reaction feeding compositions (Table 1). The relatively high measured EEW values of the obtained epoxy compounds might be from the occurrence of the reaction between C–OH group and oxirane ring. The high reaction temperature of CNE200/TPSO reaction promoted the C–OH/oxirane ring reaction, to result in epoxy compounds with high EEW values. However, the reactivity of C–OH/oxirane ring was still very low at the reaction temperatures. Therefore, transparent epoxy compounds were obtained from the reaction. Otherwise, high degree of C–OH/oxirane ring reaction might lead to gel products during the reactions. Moreover, the softening points of the epoxy compounds were measurable and increased with increasing feeding ratios of the silicon



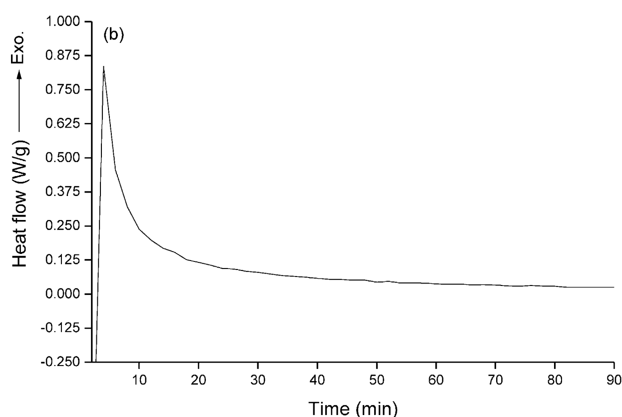


Fig. 2. DSC monitoring on the BE188/DPSD reaction catalyzed with $SnCl_2$: (a) heating scan at 10 °C/min; (b) isothermal scan at 140 °C.

compounds, since high feeding ratios of the silicon compounds resulted in epoxy compounds with high molecular weights, i.e. high EEW values.

3.2. Reactivity of the Si-containing epoxy compounds

The curing reactions of the silicon-containing epoxy compounds with various curing agents were monitored with DSC to determine the curing conditions. Introducing silicon group into BE188 increased the resulted reactivity of the epoxy compounds toward DDM (Fig. 3). The high electronegativity of silicon reduced the electron density of the oxirane ring, therefore to increase its ring opening reactivity. However, increase of reactivity was not observed for CNE–Si epoxy compounds. This result was reasonable since less electron-withdrawing effect of the silicon could be done on the oxirane rings of the epoxy compounds. For CNE–Si epoxy compounds, the bulk triphenylsilane group even brought a steric hindrance to the oxirane group to bring a counteraction on increasing the ring opening reactivity of CNE–Si epoxy compounds. Moreover, the enthalpies of the epoxy curing reactions were also obtained from peak integration of the DSC thermograms. The oxirane molar

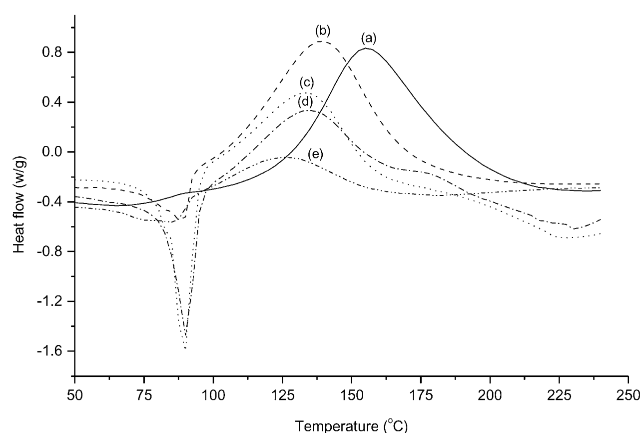


Fig. 3. DSC thermograms on the curing reactions of epoxy compounds with DDM: (a) BE188/DDM; (b) BE–Si35/DDM; (c) BE–Si30/DDM; (d) BE–Si25/DDM; (e) BE–Si20/DDM.

ratios of the silicon-containing epoxy compounds (over BE188) were plotted against the reaction enthalpies of these epoxy compounds cured with DDM (Fig. 4). The linear plot indicated the high conversion of the reaction between silicon compound (DPSD) and BE188. Moreover, the curing reactions of BE–Si epoxy compounds with DDM were also demonstrated to achieve high conversions, since the enthalpies of the curing reactions were dependent on the number of oxirane groups participating in the curing reaction.

From DSC heating and isothermal scans on the curing reactions, the reaction conditions for various curing compositions were determined (Table 2). Commercial compounds, DDM and PF5110, were cured with the silicon-containing BE–Si epoxy compounds and CNE–Si epoxy compounds, respectively. Other curing agents, including phosphorus- and melamine-containing compounds, were also applied to cure with the prepared epoxy compounds to check their

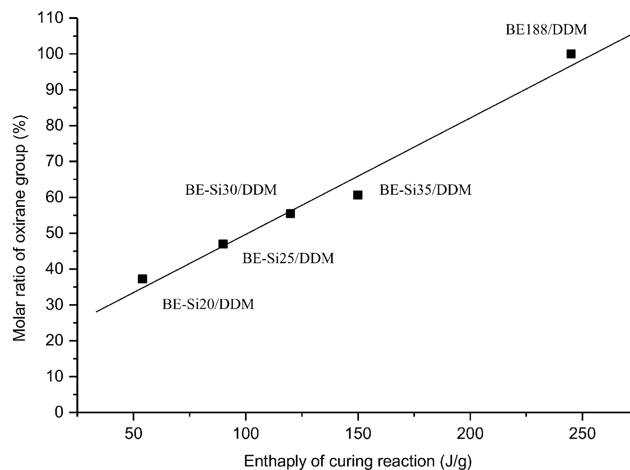


Fig. 4. The plot of oxirane molar ratio of Si–BE epoxy compounds over BE188 vs. their enthalpies of curing reactions with DDM. The enthalpies of the curing reactions were obtained from peak integration of the DSC thermograms of the reactions (heating rate: 5 °C/min).

Table 3
Thermal analysis data and LOI values of the cured epoxy resins

Cured epoxy resin	Si content (wt%)	P content (%)	T_g (°C)	Thermal stability (°C)[a]		Char yield at 700 °C (wt%)		LOI
				In N_2	In air	In N_2	In air	
BE188/DDM	0.00	0.00	143	379	376	22.1	0.0	21
BE–Si20-I	5.46	0.00	97	376	387	31.5	13.8	22.5
BE–Si25-I	4.46	0.00	103	362	392	26.9	6.5	22.5
BE–Si30-I	3.77	0.00	104	358	385	25.0	6.7	22
BE–Si35-I	3.26	0.00	107	360	390	24.8	4.8	21.5
BE–Si20-II	5.83	0.00	114	357	351	21.8	7.5	23
BE–Si20-III	5.20	1.33	120	315	317	29.3	23.6	29.5
BE–Si20-IV	4.57	2.35	164	313	315	24.9	14.6	35
CNE200/PF5110	0.00	0.00	181	363	371	36.2	11.2	21
CNE–Si20-I	1.66	0.00	118	354	354	53.9	23.2	23
CNE–Si30-I	2.34	0.00	115	356	358	50.6	26.0	24
CNE–Si40-I	2.88	0.00	109	344	342	46.0	27.7	26
CNE–Si50-I	3.42	0.00	106	352	358	44.8	25.7	27
CNE–Si40-II	2.22	4.71	151	319	335	40.4	43.8	49
CNE–Si40-III	3.29	0.00	131	345	355	43.8	18.2	31

[a] [a]Temperature at the onset point of weight loss.

influence on the thermal and flame retardant properties of the cured resins.

3.3. Thermal properties of the cured epoxy resins

Glass transition temperatures (T_g) of the cured epoxy resins were determined from DSC measurements. Introducing silyl groups into the epoxy compounds lowered the T_g of the cured resins, for both BE–Si and CNE–Si series epoxy compounds. The silicon-containing epoxy compounds possessed relatively high EEW values, to result in cured resins with low crosslinking density, consequently to lower the T_g of the resins. The low T_g of the BE–Si series resins might also result from the flexible linkage of Si–O–Ph in the backbones of the resins. Moreover, for CNE–Si series resins, incorporating silicon group onto the multifunctional epoxy would result in epoxy compounds with bulk pendants. The bulk pendants might simultaneously increase the free volume and reduce the crosslinking density of the cured resins, to lower the T_g of the resins. The T_g of the epoxy resins might be enhanced by utilizing curing agents with rigid groups in the backbones or at the pendants. Curing agents with TPP oxide group (BAPPPO), DOPO group (2DOPO-A and DOPO-PN), and melamine group (MPFN) were therefore used. High T_gs were observed for epoxy resins of BE–Si20-III (cured with BAPPPO, $T_g = 120$ °C), BE–Si20-IV (cured with 2DOPO-A, $T_g = 164$ °C), CNE–Si40-II (cured with DOPO-PN, $T_g = 151$ °C), and CNE–Si40-III (cured with MPFN, $T_g = 131$ °C).

The thermal properties of the cured epoxy resins were characterized with TGA. The initial decomposition temperature (assigned as onset point of weight loss) was 376 and 387 °C for BE–Si20-I heated in nitrogen and air, respectively. The decomposition temperatures of BE–Si20-I were very close to those of BE188/DDM resin to suggest that incorporating silyl groups into the epoxy compounds did not apparently alter the thermal stability of the epoxy resins. The earlier-mentioned results were reasonable since the oxydiphenylsilane group (O–$SiPh_2$–) was reported to exhibit a high thermal stability over 400 °C [38–40]. Same result was also observed for the silicon-containing *o*-cresol–formaldehyde novolac epoxy compounds (CNE–Si epoxy compounds) cured with PF5110 (Table 3).

On the other hand, the thermal stability of the cured resins was significantly lowered to about 315 °C while curing with phosphorus-containing curing agents (BE–Si20-III, BE–Si20-IV, and SNE–Si40-II). Owing to the less strength of phosphorous bonds, phosphorus-containing groups in polymers decompose at relatively low temperature region than the ordinary polymer chains [41–43]. However, the thermal stability of the cured resins were higher than the thermal stability of other phosphorylated epoxy resins (220–281 °C) [9–13,28–30], and were comparable with the thermal stability of the other DOPO-epoxy resins designed for application at high temperatures [34]. High thermal stability over 300 °C is especially important for epoxy resins being utilized in the advanced electronics, while associating with the surface mounting technology and lead-free soldering processes [44].

The weight loss behavior (the decomposition pattern) of the epoxy resins at temperature over 600 °C being altered with the incorporation of silicon was noteworthy (Figs. 5 and 6). Both heated in air and nitrogen, incorporation of silicon into epoxy resins enhanced the char formation at high temperature region (Table 3). The char formation increased with the increasing silicon contents of the epoxy resins, both for BE–Si and CNE–Si series resins. The high thermal stability of the formed char at high temperatures region was noteworthy, especially for samples heated in air. For BE–Si epoxy resins heated in air, weight loss was

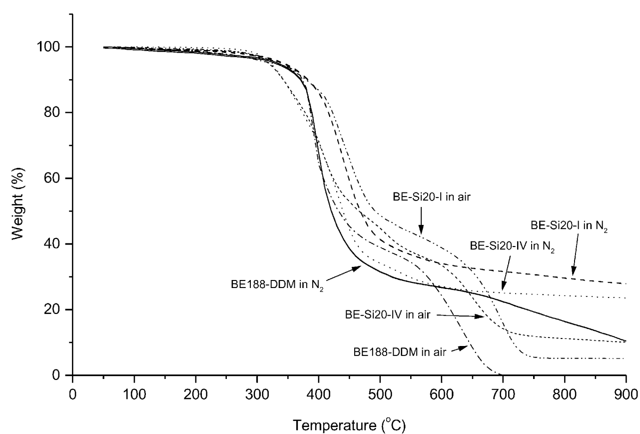


Fig. 5. Typical TGA thermograms of cured epoxy resins based on BE–Si epoxy compounds.

almost not observed at temperatures over 700 °C (Fig. 5). However, weight loss derived from char oxidation at this temperature region was usually observed for silicon-free epoxy resins [9–13,34]. The weight loss was preventing from silicon migration to char surface (due to the low surface energy of silicon) and formation of a silicon-protecting layer to char (accompanied with the anti-oxidant property and high thermal stability of silicon) [31,32]. However, weight loss was still observed for CNE–Si epoxy resins at temperature over 700 °C. The less efficiency of silicon on reserving char from oxidation for CNE–Si resins might be owing to the low silicon contents of the resins. Being compared with the silicon-free resin of CNE200/PF5110, the weight loss of epoxy resins at such high temperature region was still retarded with incorporated silicon.

The char formation of the silicon-containing epoxy resins could be further enhanced by using phosphorus-containing curing agents. High char yields at 700 °C of 23.6 and 43.8% were observed for BE–Si20-III (cured with BAPPPO) and CNE–Si40-II (cured with 2DOPO-A) heated in air, respectively. Phosphorylation is generally known to affect the decomposition pattern of the polymeric materials associated

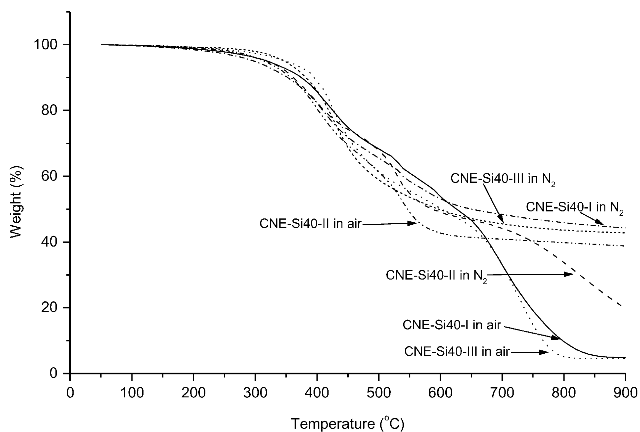


Fig. 6. Typical TGA thermograms of cured epoxy resins based on CNE–Si epoxy compounds.

with the formation of phosphorus-rich char with good heat-insulation and heat-resistance [41–43]. However, while heated in air, weight loss from oxidation was still observed for the phosphorus-rich char at high temperatures [45]. The oxidation of char might be prevented with the protecting effect of silicon, while phosphorus and silicon were both associated in the epoxy resins [31,32]. On the other hand, from Fig. 6 it was observed that introduction of melamine (nitrogen group) into epoxy resins did not show obvious enhancement on char formation (CNE–Si40-III). The less char formation of CNE–Si40-III might come from the low melamine content of MPFN [46]. Since the char yield has been correlated to denote the flame retardancy of the polymer [34,47], the epoxy resins prepared in this work were expected to possess good flame retardant property.

3.4. Flame retardancy of the cured epoxy resins

The flame retardant property of the cured epoxy resins was evaluated by measuring their LOI values (Table 3). With silicon incorporation, the LOI values of the epoxy resins were leveled up from 21 to 22.5 and from 21 to 27 for BE–Si20-I and CNE–Si50-I, respectively. The LOI enhancement for BE–Si epoxy resins was not as significant as observed for CNE–Si epoxy resins. This result is reasonable since CNE/PF5110 based epoxy resins gave high char yield (11.2 wt% in air) than did BE188/DDM (0.0 wt% in air) (Table 3), and silicon showed its significant LOI-enhancement for polymers with high char yields [48]. While cured with phosphorus-containing curing agents, the resulted epoxy resins showed extremely high LOI values of 35 and 49 for BE–Si20-IV and CNE–Si40-II, respectively. Phosphorus acting char enrichment on polymeric materials has been demonstrated [41–43]. Therefore, the high LOI values for BE–Si20-IV and CNE–Si40-II have come from the char enrichment of phosphorus and the char protecting effect of silicon, both acted to exhibit the synergistic effect on LOI enhancement [22–25]. On the other hand, the LOI value of the cured epoxy resin was also leveled up by employing the melamine-containing curing agent MPFN (CNE–Si40-III, LOI = 30). However, char enhancement was not observed for the MPFN cured epoxy, since the char yield of CNE–Si40-III (18.2%) heated at 700 °C in air was not as high as CNE–Si40-I (27.7%). The LOI enhancement of melamine should not derive from char formation. Under heat, melamine group transformed to melam and melem via deammoniation reaction [28–30]. The formed ammonia gas and heat-resistant melam and melem could enhance LOI through gas-phase and condensed phase mechanism. The same result was also observed for other epoxy resins cured with melamine-containing curing agent [46].

4. Conclusion

Silyl groups were successfully introduced into epoxy

compounds with various silicon contents. The thermal stability and flame retardancy of the epoxy resins were improved with silicon incorporation. Curing with phosphorus and melamine-containing curing agents, the resulted LOI values of the epoxy resins were further enhanced. From the earlier result, the synergistic effect of phosphorus/silicon and nitrogen/silicon on LOI improvement were observed and demonstrated for the prepared epoxy resins. The epoxy resins, possessing good thermal stability, high glass transition temperature, and excellent flame retardancy were expected to be applied in the advanced electronics.

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