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Chemical modification of dicyclopentadiene-based epoxy resins to improve compatibility and thermal properties

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Abstract

A series of siloxane-containing epoxy resins was obtained by curing dicyclopentadiene-containing epoxy DG with the silicon-containing curing agents TS, DS, and AS. Curing behavior was studied using DSC, and the activation energies of the DG curing reaction with curing agents TA, DS, and AS were found to be 59, 80, and 157 KJ/mol. Meanwhile, the curing reaction of DG with diamines was found to be a first-order reaction using Arrhenius plots. In addition, thermal stability and the weight loss behavior of the cured polymers were studied via TGA. The silicon-containing resins displayed higher weight loss temperatures and higher char yields than the silicon-free resin. The activation energies of degradation ranged from 108 to 206 KJ/mol. The morphology of the cured pieces were investigated using SEM. The DG/TS and DG/DS are more compatible between the epoxy and the curing agents than DG/AS. The limited oxygen index (LOI) values of 31 to 34 for the DG-based resin confirmed the effectiveness of silicon-containing epoxy resins as flame retardants. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Flame-retardant; Dicyclopentadiene; Epoxy resin; Siloxane

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1. Introduction

Epoxies are used in diverse areas such as molding compounds, surface coating and painting materials, composites, microelectronic encapsulated materials, printed circuit boards, and adhesives owing to their satisfactory mechanical properties, including suitable weather, chemical and thermal resistance [1–3]. Epoxy resins have previously been prepared by condensing hydroxyl-containing aromatic compounds and aldehydes and ketones. Commercially available high performance resins such as phenol-formaldehyde resins possess excellent properties. However, certain properties, such as a lack of moisture or chemical resistance properties, electrical properties, or fire retardation properties, have limited their applications [4]. Moreover, highly closslinked epoxy resins are relatively brittle, accounting for why a second component such as a rubber or a thermoplastic modifier is added to enhance the fracture toughness of the epoxy resin. The introduction of incompatible materials, such as siloxanes, to epoxy resins [5–9] is attracting more and more attention because siloxanes possess numerous unique properties, including low glass transition temperature, low surface tension, good flexibility, non-flammability and high resistance to thermal oxidation.

Generally, flame-retardants are added during processing and, although relatively inexpensive, they have several disadvantages. Flame-retardant additives may be leached from the polymer, particularly if used for external applications, or may even volatilize during use. They also have to be used in significantly high concentrations in order to be effective, which may in turn affect the physical and mechanical properties of the polymer. Novel approaches for developing new flame-retardant polymers focus on various alternatives: high-temperature stable materials that decompose generating flame suppressants [10] or nonflammable polymers [11], mixtures of plastics with surface-active flame retardants [12], or materials that slow radiative or conductive heating of the polymer by forming porous insulating char or by endothermic phase transitions or decomposition processes. Besides halogens, metal oxides, phosphorus, and nitrogen, related investigations have demonstrated that silicon is a feasible alternative for use

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as a flame-retardant element [13–19] owing to its stability at extremely high temperatures. Additional investigation suggested that the enhancement of LOI caused by incorporating silicon into the polymers resulted from the production of continuous layers of silica that retarded in char oxidation [15]. Such layers are especially effective in materials with high oxygen content, like polyesters, polyurethanes, epoxies or cellulose.

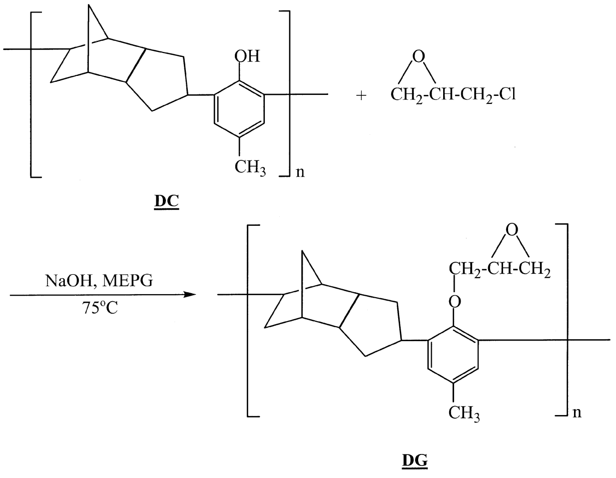
Moreover, compounding the two incompatible silicone- and carbon-based ingredients in the epoxy formulations always caused problems. Therefore, synthesizing a polymer with both siloxane and epoxide moieties is a relevant task. The epoxy resin used in the present invention, which has in some instances improved mould shrink property by introducing DCPD into epoxy resin [4], was cured with three types of silicone-containing curing agent. In the epoxy curing reaction, the quantity of curing agent is relative less and the phase separation of the siloxane component from the epoxy matrix can be improved. Based on the above concept, the present work attempts to discuss the reactivity, curing behavior, thermal properties, degradation behavior, morphology, and flame-retardant properties of the above-mentioned cured siloxane-containing epoxy resins.

2. Experimental

2.1. Materials

Poly(dicyclopentadiene-co-p-cresol) (DC) from Aldrich Co. was used as received. The DCPD-containing epoxy resin (DG) was synthesized according to literature [4] and shown in Scheme 1.

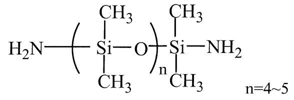
Curing agents of amino-terminated ploy(dimethylsiloxane) (AS) ($M_w = 450$, from ShinEtsu Chemical Co.) was used as received. Bis(p-aminophenoxy) dimethylsilane (DS) and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisilane (TS) came from Lancaster Co. and were also used as received. 4,4-Diaminodiphenylmethane (DDM) was acquired from Aldrich and used as received. Fig. 1 illustrates the chemical structure of the AS, DS, TS, and DDM.



Scheme 1. Synthesis of dicyclopentadiene-containing epoxy.

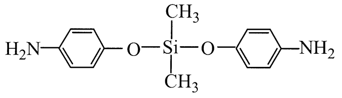
2.2. Characterization

The FT-IR spectra were measured using a Bio-Rad FTS-155 spectrometer. Samples were cast onto a KBr tablet for measurement. Differential scanning calorimeter (DSC) thermograms were recorded with a Seiko SSC 5200 at heating rates of 5, 10 and 20°C/min under nitrogen atmosphere. Meanwhile, thermal gravimetric analysis (TGA) was performed by a Seiko Exstar 6000 Thermogravimetric Analyzer at heating rates of 10, 20, 30 and 40°/min under nitrogen atmosphere. The limiting oxygen index (LOI) values were measured on a Stanton Redcroft flame meter via a modified method. Power samples were placed in a glass cup situated in the middle of the chimney. A flame was then applied from the top of the chimney for 10 s, while the flow rate ($N_2 + O_2$) was maintained at 17 l/min. The percentage of the O_2–N_2 mixture that was just sufficient to sustain the flame was taken as the LOI [20]. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were carried out using the normal and back-scattered electron modes to determine silicon dispersion and analyze impact fracture surfaces.

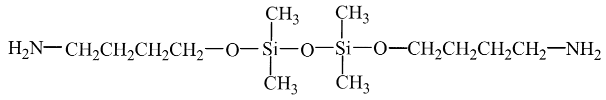


$$H_2N\!-\!\left(\underset{CH_3}{\overset{CH_3}{Si}}\!-\!O\right)_n\!\underset{CH_3}{\overset{CH_3}{Si}}\!-\!NH_2 \quad n=4\sim5$$

Amino-terminated poly (dimethylsiloxane) (AS)

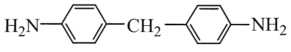


Bis (p-aminophenoxy) dimethylsilane (DS)



$$H_2N\!-\!CH_2CH_2CH_2CH_2\!-\!O\!-\!\underset{CH_3}{\overset{CH_3}{Si}}\!-\!O\!-\!\underset{CH_3}{\overset{CH_3}{Si}}\!-\!O\!-\!CH_2CH_2CH_2CH_2\!-\!NH_2$$

1,3-bis (3-aminopropyl)-1,1,3,3-tetramethyldisilane (TS)



4,4-diaminodiphenylmethane (DDM)

Fig. 1. The chemical structure of the epoxy DG, and diamine curing agent AS, DS, TS, DDM.

2.3. Curing procedure for advanced epoxy resins

The epoxy polymers were obtained by thermally curing DG with various curing agents, namely AS, DS, and TS. The reactant compositions were mixed homogeneously in a 1:1 equivalent ratio. Meanwhile, the curing cycles were determined through DSC tracing of the respective epoxy/curing agent compositions: DG/TS was cured at 85°C for 4 h and post-cure at 150°C for 4 h; DG/DS was cured at 100°C for 2 h and post-cure at 135°C for 2 h.; DG/AS was cured at 125°C for 2 h and post-cure at 140°C for 2 h. After that, samples were allowed to cool slowly to room temperature in order to prevent cracking.

2.4. Kinetic studies of curing reaction

Kinetic studies of the DG curing reaction were performed by a differential scanning calorimetry (DSC) technique combined with two analytical methods, termed dynamic method A and dynamic method B.

2.4.1. Dynamic method A [21,22]

This method only analyzes one reaction curve. When the temperature of the system is increased continuously, a series of rare constants at various temperatures can be obtained by

$$k = (\mathrm{d}H/\mathrm{d}T)/\Delta H \tag{1}$$

Where $\Delta H = \Delta H_{\mathrm{O}} - \Delta H_{\mathrm{T}}$. ΔH_{T} denotes the enthalpy at temperature T while ΔH_{O} represents the enthalpy of the whole curing reaction. The activation energy can be determined by employing these rate constants at various temperatures. This formula is based on the assumption that the curing reaction is first order.

2.4.2. Dynamic method B

This method is based on a simple correlation relationship between activation energy (E_{a}), heating rate (ψ), and temperature of the exothermic peak (T_{p}) as

$$E_{\mathrm{a}} = \frac{-R}{1.052} \frac{\Delta \ln \varphi}{\Delta (1/T_{\mathrm{p}})} \tag{2}$$

This method provides an easy method of calculating the activation energy.

2.4.3. Kinetic studies of degradation process

The activation energy of degradation for a given weight fraction (wt.%) is determined by Ozawa's method [23,24]. He reported the following equation:

$$\begin{aligned} \log\beta &= \frac{1}{2.303} \ln\beta \\ &= -0.4567 \frac{E}{RT} + \left(\log \frac{AE}{R} - \log F(x) - 2.315 \right) \end{aligned} \tag{3}$$

where β denotes the heating rate, E represents the activation energy, R is the ideal gas constant and $F(x)$ denotes the conversion dependent term.

3. Results and discussion

3.1. Characterization of polymers

Epoxy resins containing silicon were obtained using silicon-containing diamine compound as a curing agent. Fig. 2 shows the FT-IR spectrum of the curing epoxy resins. The characteristic peaks appear at 1091 cm^{-1} (Si–O–Si), 1261 and 801 cm^{-1} (Si–CH$_3$) for DG/AS, 915 cm^{-1} (Si–O–Ph) and 825 cm^{-1} (Si–CH$_3$) for DG/DS, 1057 cm^{-1} (Si–O–CH$_2$) and 838 cm^{-1} (Si–CH$_3$) for DG/TS. Furthermore, the EDS analysis is also used to identify the level of silicon content in the cure epoxy resins and the results are shown in Table 1. These characteristic absorption peaks and data are consistent with the proposed curing of the chemical structure of epoxy resins.

3.2. Curing reactivity and kinetics

The curing behavior of epoxy resin depends on the curing conditions. Curing conditions can greatly influence not only the curing kinetics but also the physical properties of the resulting material. The curing reactions of the diamine compounds toward DG were studied using DSC. Fig. 3 displays typical DSC thermograms of various curing agents toward DG. These thermograms, as well as isothermal DSC curing studies, provide information for determining the conditions of curing reactions. Table 1 lists the results and uses them as curing cycles for preparing cured epoxy resins. The reactivities of the curing agents were read directly from the starting temperatures of the exothermic peaks. Therefore, as the DSC thermograms demonstrate, the relative reactivity of the three curing agents towards the epoxy DG was TS > DS > AS. The observed variation in reactivity is probably due to the electronic effect. An electron-donating group in the amine compound would enrich the electron density of the amine group and thus increase the reactivity of the amine toward oxirane rings. For TS and DS, owing to the butyl group having

Table 1
Silicon content in the cured epoxy resins from EDS analysis

	Si content (%)	
Epoxy resin compositions	Calculated value	Experiment value
DG/TS	1.96	2.34
DG/DS	1.93	2.90
DG/AS	6.22	7.16

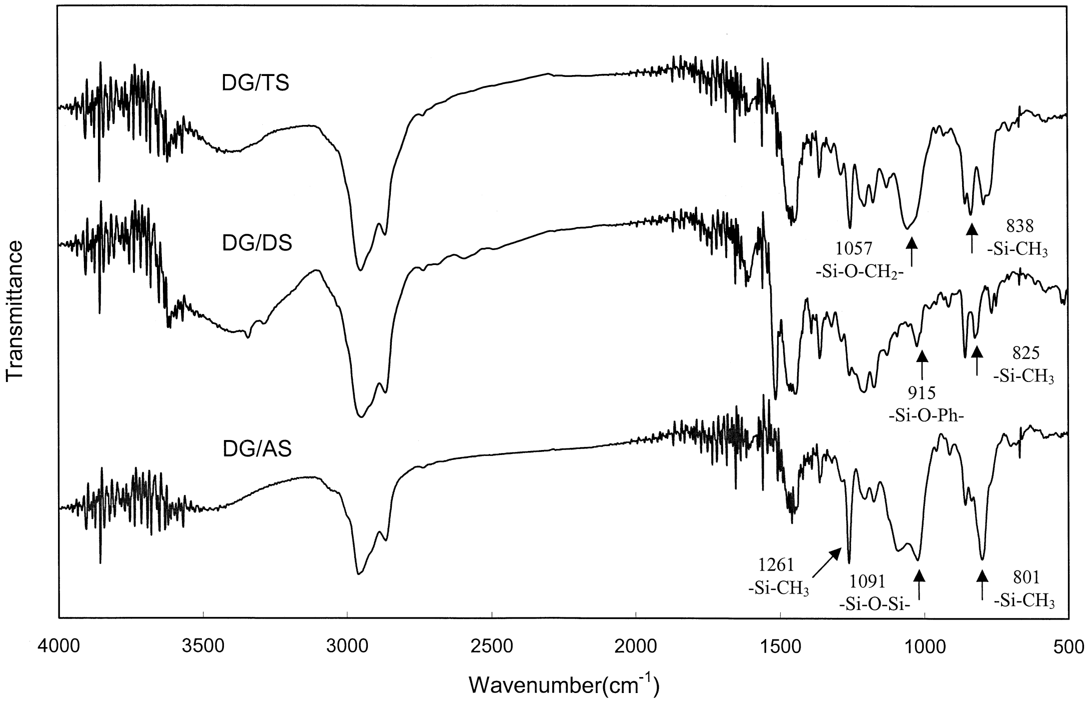


Fig. 2. FT-IR spectrums of the curing epoxy resins.

more capacity to donate electrons than the phenyl group, thus the butyl group increasing the electron density of the amine group, and increase the reactivity toward epoxy resins. For DS and AS, because the carbon atom has more electron-donating ability than silicon, consequently the activity in cure with epoxies increases. Furthermore, the kinetics of DG curing reactions were studied. Two mathematical methods were employed: Dynamic method A and Dynamic method B. The enthalpy of complete curing reaction was first obtained from the DSC dynamic scan. Enthalpy values were observed at several heating rates and are listed in Table 2. Variation in heating rate did not significantly affect the value of the complete curing enthalpy. Meanwhile, the reaction enthalpies were found to be 78.41, 48.41, and 4.94 J/g for DG/TS, DG/DS, and DG/AS, respectively.

To calculate the activation energy via Eq. (1), the reaction is assumed to be first-order reaction. The dH/dT and ΔH were then obtained at various temperatures from the DSC thermograms. Table 3 lists the rate constants k of the curing epoxy resins DG/TS, DG/DS, and DG/AS at a heating rate of 10°C/min. This table reveals that the maximum value of dH/dT increased with an increasing heating rate. On the other hand, the value of rate constant k at a constant temperature decreased with an increasing heating rate. This phenomenon arises because the temperature error between the sample and the instrument increases with heating rate, while the reaction rate constants decrease. The reactivity of the diamine curing agents could also be obtained from these

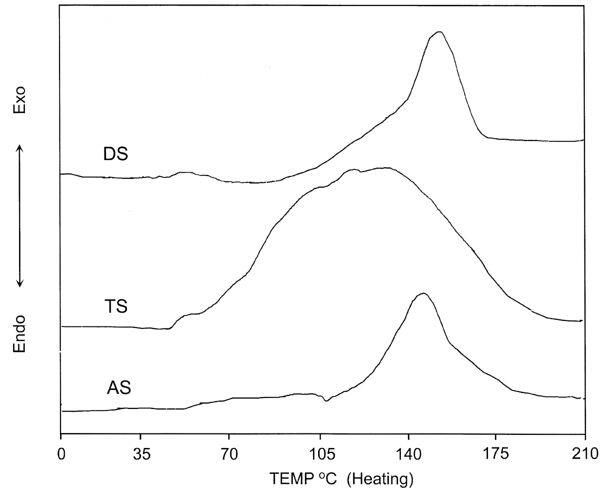


Fig. 3. Typical DSC thermograms of various curing agents toward DG.

Table 2
Enthalpies of the curing reaction of DG with various curing agents

Curing agent	Heating rate (°C/min)	Enthalpy (J/g)
TS	5	78.41
TS	10	68.10
TS	20	42.52
DS	5	48.41
DS	10	24.93
DS	20	15.72
AS	5	4.94
AS	10	4.09
AS	20	3.37

three tables. If the reaction rate constant of a given curing agent can be obtained at a relative lower temperature, the reactivity of this curing agent toward DG is relative higher. The beginning temperature of the curing reaction from the table reveals that TS is the most reactive toward DG among the curing agents employed. This phenomenon is also confirmed by the rate constants obtained for these curing reactions at a certain temperature.

The activation energy was obtained from the Arrhenius plots (Figs. 4 and 5). Notably, the Arrhenius plots for all curing reactions are linear. This pattern confirms that the assumption of first-order reaction is correct. The observed activation energy varies with heating rate. However, the variation is not very significant. More values of activation energy are summarized in Table 4.

Dynamic method B provides another convenient way to obtain the activation energy of a curing reaction without resorting to evaluating the reaction order and reaction rate constant. Table 4 also lists the activation energies determined based on Eq. (2). The activation energies of the curing reactions for DG with various curing agents were found to be ordered as TS < DS < AS. Table 4 clearly displays that dynamic method B gave smaller activation energies than dynamic method A. The literature has described this difference. Activation energy based on the variation of peak position with different heating rates (dynamic method B) generally yields smaller values than dynamic method A.

Table 3
Rate constant of DG curing reaction from dynamic method A

Ciring agent	Temperature (°C)	Rate constant $K \times 10^3$ (s^{-1})
TS	57.88	1.615
TS	62.94	2.320
TS	67.87	3.759
TS	72.89	5.404
TS	77.91	6.784
DS	95.33	6.338
DS	100.24	6.526
DS	105.29	26.233
DS	110.25	31.609
DS	115.27	42.118
AS	111.15	45.994
AS	113.12	54.896
AS	115.09	66.766
AS	117.08	71.217
AS	119.05	86.053

3.3. Morphology of the cured epoxy resins

Fig. 6(a)–(d) displays the SEM micrographs of fracture surfaces of silicon-containing and silicon-free epoxies. In Fig. 6(a), the cured silicon-free network exhibits an extremely smooth surface. When silicon-containing diamines were employed as the curing agents, the fracture surfaces become rougher and even exhibited a distinct phase separation in the matrix. DG/TS exhibit a uniformly fractured surface owing to TS having a long methylene chain, which can move easily to form a homogeneous network. For the DG/DS blend, the fracture surface is obviously rougher. This phenomenon is due to DS having a hard phenyl segment and making the network more closed. Fig. 6(d)

Table 4
Activation energies (kJ/mol) of DG curing reaction with various curing agents at different heating rate

Curing agent	Dynamic method A			Dynamic method B
	5°C/min	10°C/min	20°C/min	
TS	64.0	58.8	34.2	27.7
DS	86.0	79.6	75.1	65.4
AS	184.6	157.2	153.6	133.5

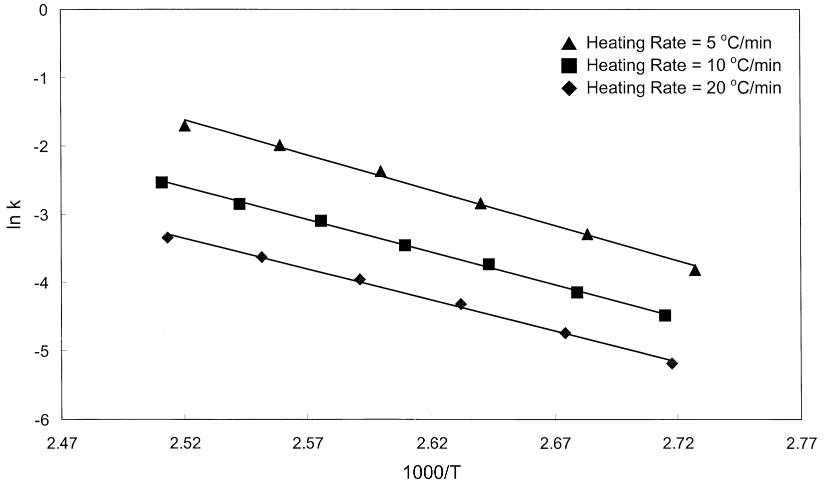


Fig. 4. Arrehenius plot from dynamic method A of DG/TS curing reaction.

displays that DG/AS has an apparent phase separation. Increasing the polysiloxane chain length may results in incomplete mixing owing to gross incompatibility between the polydimethylsiloxane and epoxy resin prior to curing.

3.4. Thermal properties

The glass transition temperature, T_g, can be obtained from the DSC thermogram. Being a second order thermal transition,T_g provides information regarding soft-

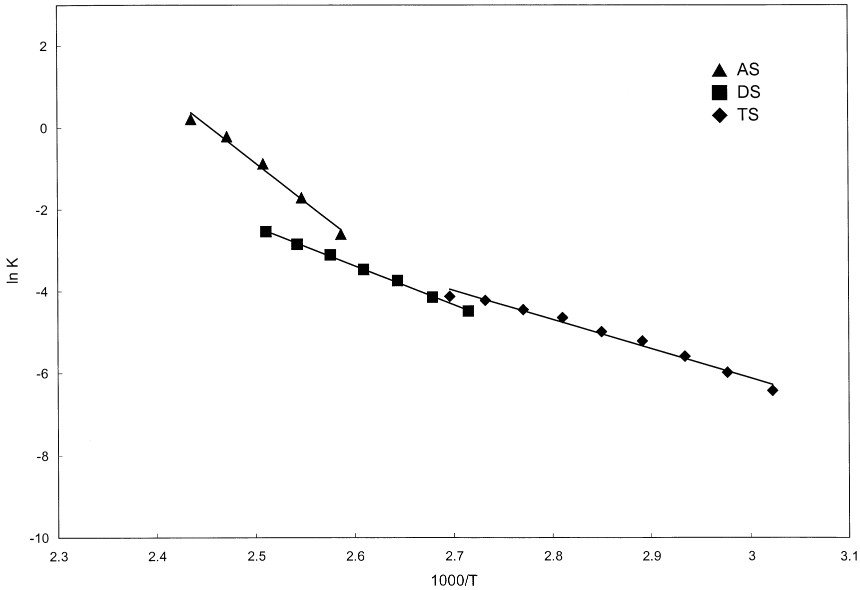
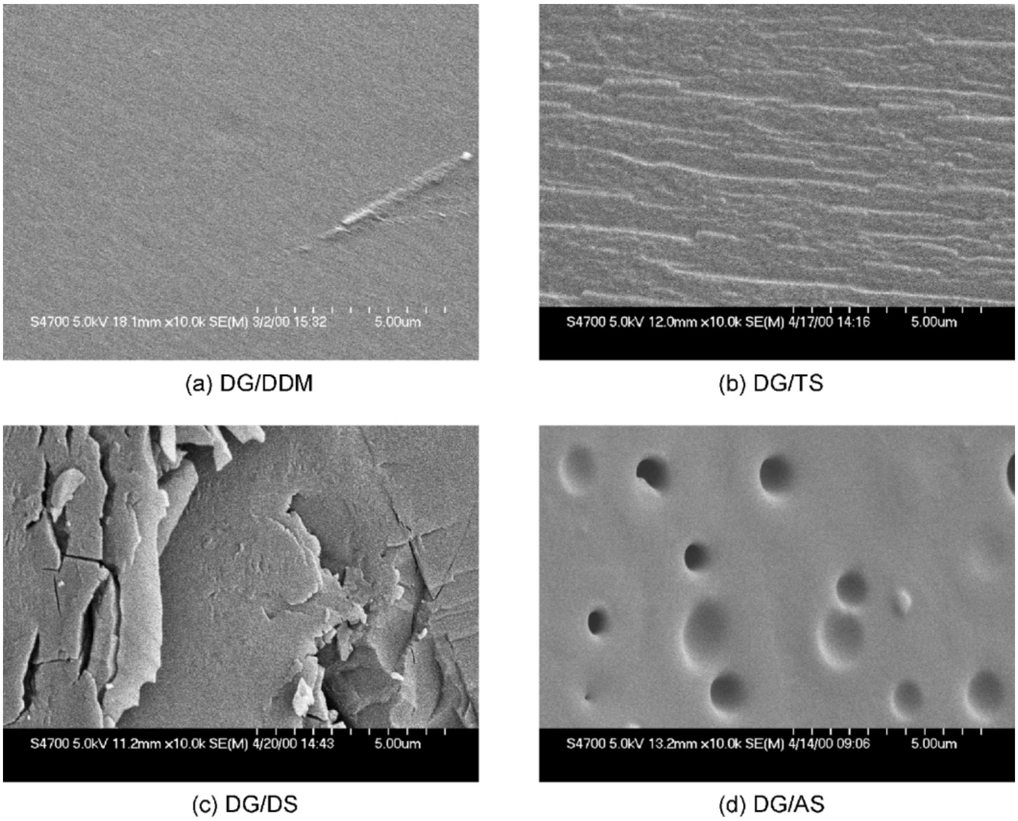


Fig. 5. Arrehenius plot from dynamic method A at 10°C/min.



(a) DG/DDM

(b) DG/TS

(c) DG/DS

(d) DG/AS

Fig. 6. SEM micrographs of fracture surfaces of silicon-containing and silicon-free epoxies.

ening of the amorphous portion of a polymer as the temperature is raised. Fig. 7 shows DSC thermograms of the curing epoxy resins. DG/TS, DG/DS, and DG/AS display a second order transition at 85.8, 99.7, and 44.5°C, respectively. DG/AS containing long flexible siloxane linkage derived from amino-terminated poly(-dimethylsiloxane) exhibits the lowest T_g, while DG/DS containing aromatic moiety derived from Bis(p-aminophenoxy) dimethylsilane exhibits the highest T_g.

TGA traces of these epoxies provide additional information regarding their thermal stability and thermal degradation behavior. Fig. 8 shows the TGA curves of various samples at heating of 10°C/min under N_2. Two-stage weight loss behavior was observed for all epoxy resins. Table 5 illustrates the calculated results: the on-set degradation temperature (T_d), maximum-rate degradation temperature (T_{max}) and maximum rate (R_{max}) of the various samples. DG/DDM resin exhibited a 5% weight loss around 220°C, followed by two rapid weight losses at 397 and 442°C. The silicon-containing epoxy resins show degradation temperatures (T_d 5%) in nitrogen ranging from 277 to 295°C, while the char yields at 700°C ranged from 4.9 to 6.2%. The pyrolysis temperatures and char yield of the resins increased when the silicon-containing curing agents were incorporated. The decomposition of silane groups in all curing agents formed a silicon-rich residue after the initial stage of weight loss slowed further decomposition of the resins. This phenomenon plays an important role in improving the flame-retardant properties of the resins. Meanwhile in fire, the silane groups first decompose and then SiO_2 is formed. This silicon-rich residue can prevent further decomposition of the polymer, raise the decomposition temperature of the polymer, and increase char yield.

Table 5
The calculated data from TGA curves of various samples under N_2[a]

Epoxy resin composition	T_d (°C)	T_{1max} (°C)	T_{2max} (°C)	Char (%)
DG/DDM	220.1	397.3	442.1	2.1
DG/TS	277.8	373.6	454.2	5.0
DG/DS	276.6	366.9	440.7	6.2
DG/AS	295.0	387.0	447.4	4.9

[a] The heating rate was 10 °C/min; T_d was the on-set degradation temperature; T_{1max} and T_{2max} were the maximum rate degradation temperature in the first stage and second stage, respectively.

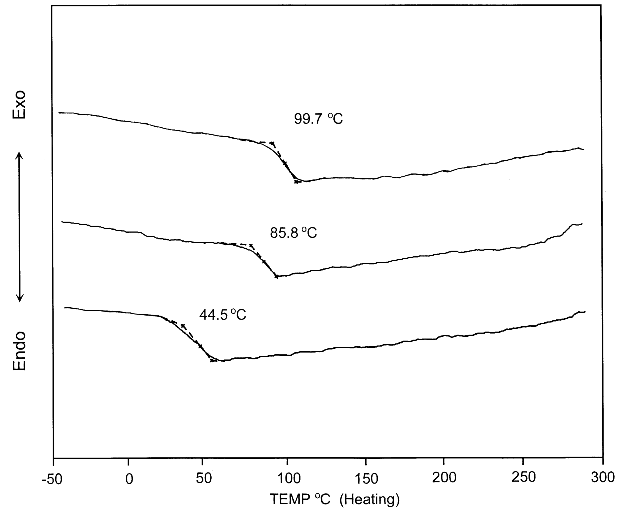


Fig. 7. DSC thermograms of the curing epoxy resins.

3.5. Degradation kinetics

Dynamic thermogravimetric analysis has frequently been used to study the overall thermal degradation kinetics of polymers because it provides reliable information on activation energy. The relationship between weight loss fraction (α) and apparent activation energy (*E*) can be determined via Ozawa's method. First, every sample was heated at different heating rates (β) to obtain the thermal degradation curves; then at the same conversion of weight loss, a plot of ln(β) versus T^{-1} should be a straight line with a slope of $(2.303\times0.4567)E/R$. Therefore, the activation energy can be obtained as a function of conversion. Fig. 9 displays the typical TG

Table 6
The apparent activation energies at different conversions for various samples under thermal degradation in N_2

Epoxy resin composition	Activation energy, *E*, by Ozawa's method (J/mol)							
	Conversion, α[a]							
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
DG/DDM	90.1	126.4	142.9	153.5	159.6	166.7	170.8	178.6
DG/TS	121.7	142.1	154.9	163.5	175.3	184.7	190.8	206.2
DG/DS	120.5	122.2	127.7	131.1	133.1	137.7	147.5	152.4
DG/AS	108.7	136.7	145.7	145.4	146.2	154.6	172.9	187.4

[a] α=[100-residual weight (%) in TGA]/100

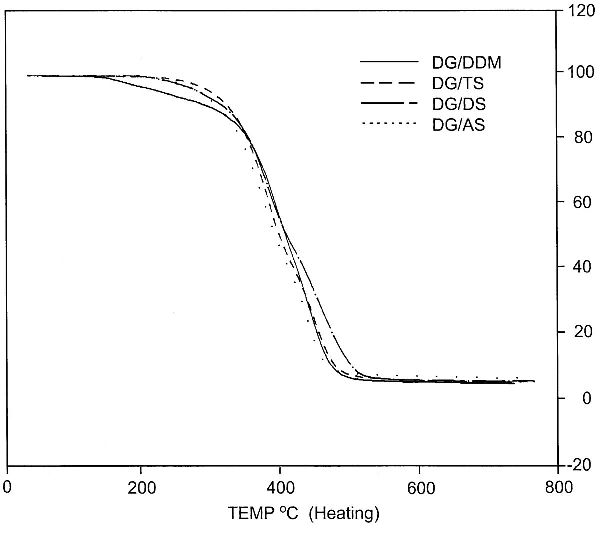


Fig. 8. TGA curves of various samples at heating of 10°C/min under N_2.

curves for epoxy resins heated in nitrogen atmosphere at various heating rates. The figure reveals that the curves were displaced to higher temperatures due to the heat transfer lag with increased heating rate. Straight lines are drawn according to the least squares method (Fig. 10). Table 6 lists all the apparent activation energies at different conversions for various samples. The dynamic method proposed herein gave apparent activation energies of 90.1–178.6, 121.7–206.2, 120.5–152.4 and 108.7–187.4 kJ/mol for DG/DDM, DG/TS, DG/DS, and DG/AS, respectively. As TS and AS were used as curing agents, the activation energies were increased in the two degradation stages compared with DG/DDM system. This increase is probably because the formation of thermally stable compounds covered the materials and prevented further decomposition of the polymer.

3.6. Flame retardant properties

The flame-retardant properties of these epoxy resins were further examined by measuring the limiting oxygen index (LOI). Fig. 11 displays the resulting values. Silicon-based resins exhibited LOI values of around 31–34 while the silicon-free DG/DDM epoxy resin exhibited an LOI value of below 19. Meanwhile, the flame-retarding effect of the silicon-containing curing agents was demonstrated. Furthermore, the increase in LOI values with silicon content was not previously observed.

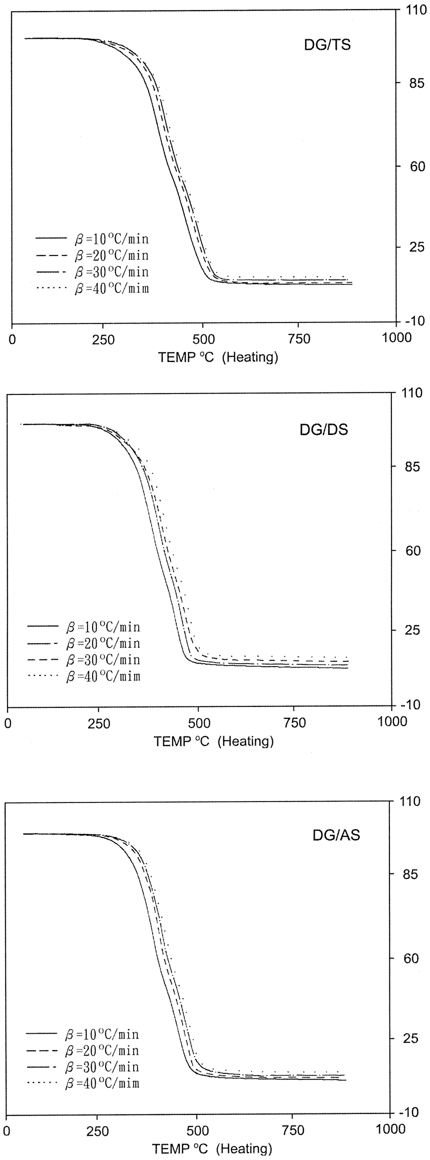


Fig. 9. Typical TG curves for epoxy resins heated in nitrogen atmosphere at various heating rates.

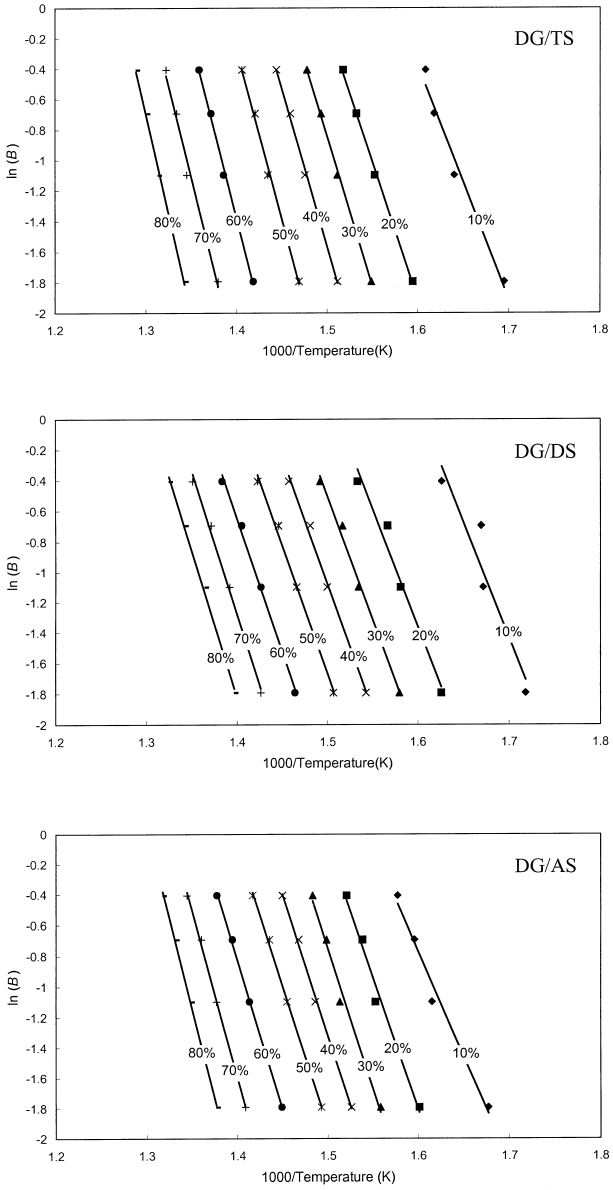


Fig. 10. Straight lines of cured epoxy resins according to the least square method.

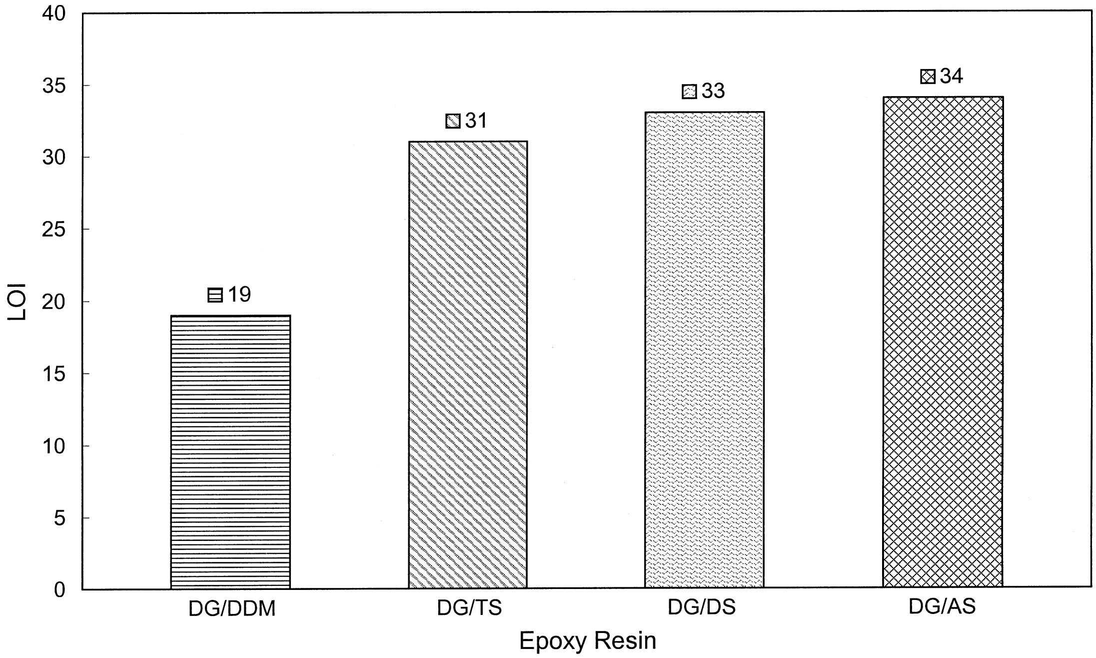


Fig. 11. The LOI values of silicon-based and silicon-free epoxy resins.

The LOI values of these cured epoxy resins are high enough to be considered flame-retardant systems.

4. Conclusions

In this study, a series of silicon containing epoxy resins were obtained by curing dicyclopentadiene-containing epoxy DG with silicon-containing curing agents TS, DS, and AS. The structures of the cured epoxies were characterized by FT-IR and EDS. The reactivity of curing agents to DG is ordered as TS > DS > AS. For TS and DS, the butyl group has greater electron-donating ability than the phenyl group, and can increase the electron density of the amine group while also increasing reactivity to epoxy resins. Meanwhile, for DS and AS, carbon atoms have more electron-donating ability than silicon, and thus increase activity in curing with epoxies. The activation energies of the DG curing reaction with various curing agents TA, DS, and AS are found to be 59, 80, and 157 KJ/mol. The morphology of the cured epoxies investigated by SEM demonstrates that DG/TS and DG/DS are more compatible between the epoxy and the curing agents than DG/AS, which has a distinct phase separation. Furthermore, TGA analysis revealed that the silicon-containing resins showed higher weight loss temperatures (277–295°C) and higher char yields (4.9–6.2%) than the silicon-free resin ($T_d = 220°C$, char yield = 2.1%). The degradation activation energies for silicon-base epoxies ranged from 108 KJ/mol to 206 KJ/mol, and thus are higher than those for DG/DDM. Finally, the limited oxygen index (LOI) values of 31–34 for the DG-based resin confirmed the effectiveness of silicon-containing epoxy resins as flame retardants.

Acknowledgements

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