

# Synthesis, properties and pyrolysis of siloxane- and imide-modified epoxy resin cured with siloxane-containing dianhydride

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**Abstract:** Hydrosilylation of nadic anhydride with tetramethyl disiloxane yielded 5,5'-(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboxylic anhydride (I), which further reacted with 4-aminophenol to give *N,N'*-bis(4-hydroxyphenyl)-5,5'-bis-(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboximide (II). Epoxidation of II with excess epichlorohydrin formed a siloxane- and imide-modified epoxy oligomer (*ie* diglycidyl ether of *N,N'*-bis(4-hydroxyphenyl)-5,5'-bis(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboximide) (III). Equivalent ratios of III/I of 1/1 and 1/0.8 were prepared and cured to produce crosslinked materials. Thermal mechanical and dynamic mechanical properties were investigated by TMA and DMA, respectively. It was noted that each of these two materials showed a glass transition temperature ( $T_g$ ) higher than 160 °C with moderate moduli. The thermal degradation kinetics was studied with dynamic thermogravimetric analysis (TGA) and the estimated apparent activation energies were 111.4 kJ mol<sup>-1</sup> (in N<sub>2</sub>), 117.1 kJ mol<sup>-1</sup> (in air) for III/I = 1/0.8, and 149.2 kJ mol<sup>-1</sup> (in N<sub>2</sub>), 147.6 kJ mol<sup>-1</sup> (in air) for III/I = 1/1. The white flaky residue of the TGA char was confirmed to be silicon dioxide, which formed a barrier at the surface of the polymer matrix and, in part, accounted for the unique heat resistance of this material.

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**Keywords:** siloxane- and imide-modified epoxy oligomer; crosslinking; dynamic mechanical properties; thermal degradation kinetics; apparent activation energy; SiO<sub>2</sub> char residual

## INTRODUCTION

In the development of electronic devices, electronic packaging has a tendency towards lower cost, finer pitch, higher electrical performance and better reliability. Flip chip technology prevails among chip packaging candidates to meet these trends.<sup>1–9</sup> The widespread use of epoxy resins in the flip chip package interests people in the development of higher performance for encapsulants. Epoxy resin exhibits many desirable properties, such as high strength and modulus, excellent chemical and solvent resistance, good thermal and electrical properties, outstanding adhesion, and easy processing. However, cured epoxy resins are generally hard and relatively brittle because of their rigid crosslinked networks.

Modification with elastomers such as carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN) and silicone rubber has been considered as a successful method to improve the toughness of epoxy resin after many efforts, while there are inevitable drawbacks in mechanical properties and thermal stability. Moreover, if epoxy is directly blended with silicone elastomer, phase separation occurs because of the incompatibility of the two components, and this worsens the mechanical properties.<sup>10–17</sup> Consequently,

we are interested in developing modified epoxy to enhance the flexibility and toughness while sustaining the thermo-mechanical properties with improving dielectric constants. In order to improve the mechanical properties, modification of silicone-epoxy with a rigid segment, such as an imide group, is essential owing to the superior thermo-mechanical properties obtained: high crosslinking ability, high glass transition temperature ( $T_g$ ), high thermal stability, high char yield, and excellent heat resistance and mechanical modulus. In this study, we synthesized and characterized a novel siloxane- and imide-modified epoxy resin and cured it with siloxane-containing dianhydride for possible electronic applications. The thermal mechanical properties and thermal degradation kinetics of the cured epoxy were also investigated. The main pyrolysis product of the materials was characterized as SiO<sub>2</sub> in this study.

## EXPERIMENTAL

### Materials

5-Norbornene-2,3-dicarboxylic anhydride (nadix anhydride), and tetramethyl disiloxane were purchased from Merck Co. Platinum divinyl tetramethyl

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disiloxane complex was purchased from UCT Co. Epichlorohydrin was purchased from TCI. All chemicals were purified before use. Electronic grade of diglycidyl ether of bisphenol-F (830LVP) was obtained from DIC Co, and 2-ethyl-4-methyl-1-ethylcyanoimidazole (2E4MZCN) was purchased from Shikoku Chemicals Co and used as the catalyst for curing the epoxy and anhydride.

### Synthesis of 5,5'-(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboxylic anhydride (I)

The synthesis of siloxane-containing dianhydride (**I**) was performed according to the method reported in the literature (Scheme 1).<sup>18</sup> The chemical structure of the white product was confirmed with proton and <sup>13</sup>C nuclear magnetic resonance spectroscopy (Unity 300 MHz NMR, Varian Inc., Walnut Creek, CA, USA). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm) δ: 0.03–0.05 (m, 12H), 0.65 (t, 2H), 1.55–1.66 (m, 8H), 2.73–2.78 (m, 2H), 2.84 (m, 2H), 3.39–3.43 (m, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm) δ: –1.20–0.94, 25.75, 26.74, 40.32, 41.00–41.03, 41.64, 49.46, 52.62, 171.98–172.25.

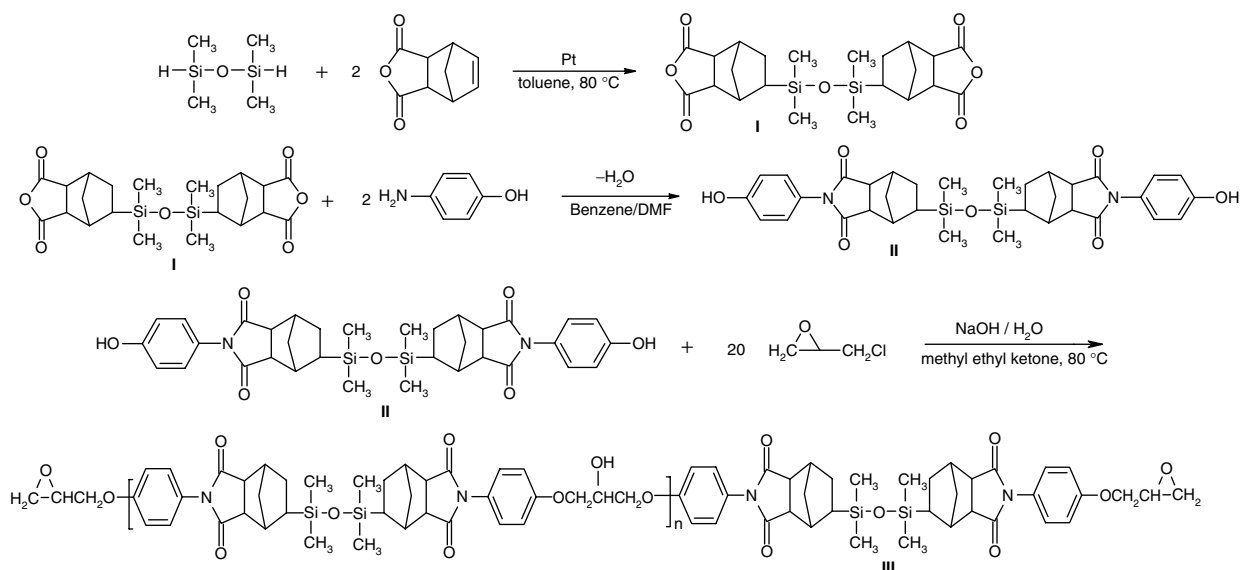
### Synthesis of *N,N'*-bis(4-hydroxyphenyl)-5,5'-bis(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboximide (II)

The siloxane-containing dianhydride (**I**) (30 g, 0.065 mol) was dissolved in 90 ml of dimethylformamide (DMF), and 4-aminophenol (14.9 g, 0.136 mol) in 40 ml of DMF was gradually added (Scheme 1). The solution was stirred for 8 h at ice-bath conditions, followed by imidization using a Dean-Stark instrument. Compound **II** in solid powder was obtained after vacuum drying, and it was recrystallized from isopropanol (38 g, yield = 91 %, mp = 123 °C). An Avatar 360 FT-IR (Nicolet Instrument Corporation, Madison, WI, USA) was used for IR analysis.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm) δ: 0.01–0.02 (m, 12H), 0.61 (m, 2H), 1.54–1.62 (m, 8H), 2.74 (m, 2H), 2.78 (m, 2H), 3.12–3.17 (m, 4H), 6.70–6.73 (d, 4H), 6.90–6.94 (d, 4H), 7.42 (s, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm) δ: –0.88, –0.84, 25.64, 26.54, 39.70, 40.57, 41.33, 48.54, 51.09, 116.16, 123.45, 127.81, 156.62, 178.57, 178.60, 178.82. IR: imide 1789 and 1720 cm<sup>-1</sup>, OH 3100–3500 cm<sup>-1</sup> (broad band).

### Synthesis of diglycidyl ether of *N,N'*-bis(4-hydroxyphenyl)-5,5'-bis(1,1,3,3-tetramethyl disiloxane-1,3-diyl)-bis-norborane-2,3-dicarboximide oligomer (III)

The synthesis of siloxane- and imide-containing epoxy (**III**) was carried out according to a method described previously.<sup>19</sup> A three-necked flask equipped with an addition funnel was filled with a solution of **II** (12.88 g, 0.02 mol) and epichlorohydrin (37 g, 0.4 mol) (Scheme 1). A solution of NaOH (1.6 g NaOH, 0.04 mol in 3.2 ml of H<sub>2</sub>O) was added dropwise to the mixture, which was stirred for 6 h at 65 °C. The product was extracted three times with toluene. The solvent and residual reactants were removed by vacuum drying. The product was then purified by column chromatography using n-hexane/ethyl acetate (v/v = 1/1) as eluent to obtain an oligomer of siloxane- and imide-containing epoxy (**III**) with an epoxy equivalent weight (EEW) of 477 g eq<sup>-1</sup> by titration with HBr, and a calculated average repeating unit of 0.34 (**III** in Scheme 1, where n = 0.34; yield = 92.6 %; mp = 100–103 °C). Elemental analysis for **III**: (calculated) C = 64.84 %, N = 3.78 %, H = 6.53 %, O = 17.27 %; (found) C = 64.00 %, N = 3.78 %, H = 6.73 %, O = 17.16 %. IR: absorption of epoxide at 910 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm) δ: 0.01–0.16, 0.63, 1.54–1.64, 2.69–2.89, 3.20–3.21, 3.29–3.30, 3.92–3.94, 4.18–4.22, 6.93–6.97, 7.09–7.12. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm) δ: –0.85, 25.62, 26.54, 39.76,



**Scheme 1.** Synthesis of compounds **I** and **II** and oligomer **III**.

40.62, 41.33, 44.50, 48.50, 49.90, 51.07, 68.95, 115.17, 125.00, 127.72, 158.30, 177.35–177.57.

### Preparation of epoxy curing systems

The siloxane- and imide-modified epoxy oligomer (**III**) and the siloxane-containing dianhydride (**I**) in molar ratios of 1/1 and 1/0.8, together with 1 phr of 2-ethyl-4-methyl-1-ethylcyanoimidazole, were dissolved in acetone and then vacuum dried at 50 °C to obtain well-mixed blends. For comparison, control systems of similar blend with bisphenol-F epoxy in place of **III** were prepared exactly by the same formulation and procedure.

### Characterization

#### Thermal mechanical properties

The epoxy curing systems were poured onto aluminium plates and cured according to the profile 130 °C for 30 min, 150 °C for 180 min and 200 °C for 30 min. The thermal mechanical behaviour was investigated by TMA (TA 2940, DuPont) and the dynamic mechanical properties were analysed using a DuPont DMA2980 with a dual cantilever head on cured film with dimensions of 60 mm × 8 mm × 0.1 mm at a frequency of 1 Hz and heating rate of 3 °C min<sup>-1</sup> from 30 °C to 250 °C.

#### Thermal degradation kinetics

The thermal degradation kinetics of the cured epoxy were investigated using thermogravimetric analysis (TGA) (DuPont TA 2950). The system was operated in the dynamic mode over the temperature range 50–800 °C, at various heating rates: 5, 10, 15 and 20 °C min<sup>-1</sup>. All the experiments were carried out under dry nitrogen and under air atmospheres

## RESULTS AND DISCUSSION

### Thermal mechanical properties

The thermal mechanical properties of these four curing materials are shown in Fig 1 and summarized in Table 1. It should be noted that the  $T_g$  values of all these systems were higher than 160 °C.

### Dynamic mechanical properties

Figures 2 and 3 compare DMA data for the four crosslinked materials. It is noted that the  $T_g$  values of the **III/I** systems showed a consistent tendency with the data obtained from TMA (Fig 1). In addition, the **III/I**

systems showed higher damping peaks ( $\tan \delta$ ), higher area of  $\tan \delta$  peaks and lower loss modulus than those of bisphenol-F epoxy/**I** systems. Among these systems, the one with **III/I** = 1/0.8 had the lowest storage modulus  $E'$  but showed the highest damping peak ( $\tan \delta_{\max}$ ), and also the highest area of  $\tan \delta$ . All of the DMA data confirmed the stress–release, enhancement of flexibility and toughness of the **III/I** systems. Although **III/I** systems had lower  $T_g$  values than the corresponding bisphenol-F/**I** systems (Figs 1, 2 and 3), all these systems exhibited excellent flexibility and toughness, because of the proper balance of soft siloxane and rigid imide segments in the polymer matrices. In addition, it was found that both the  $\tan \delta$  and  $E'$  curves of the **III/I** systems had a large main transition peak with a small second transition, implying

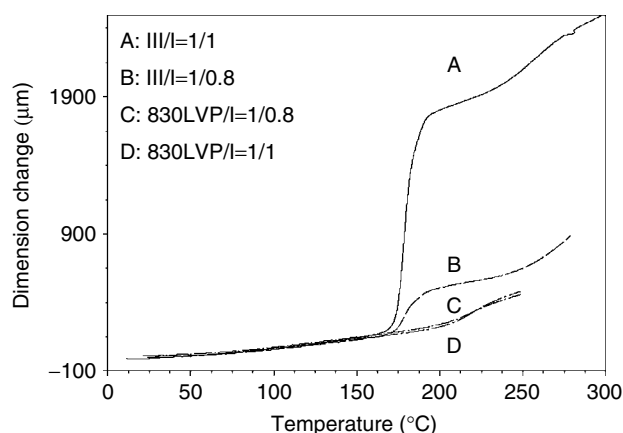


Figure 1. TMA thermograms of 830LVP/**I** and **III/I** systems.

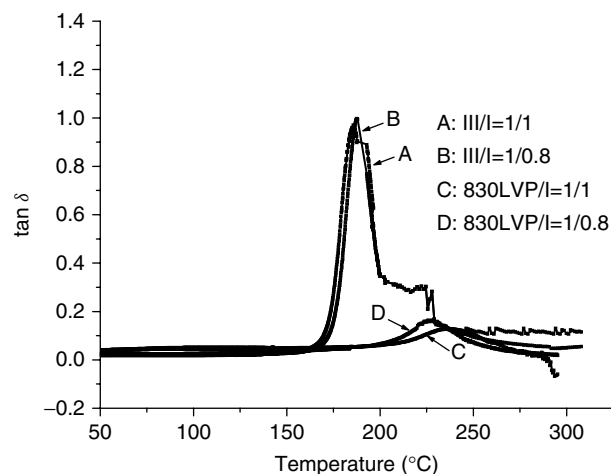


Figure 2. Damping curves of 830LVP/**I** and **III/I** systems.

Table 1. Comparisons of thermal mechanical properties of **III/I** and 830LVP/**I** systems

System	$T_g^a$	$\tan \delta$ (°C)	Peak height <sup>b</sup>	Area of $\tan \delta$	$E'_{\text{glass}}$ (MPa)	$E'_{\text{rubber}}$ (Mpa)
<b>III/I</b> = 1/1	173.2	185.6	0.970	36.90	1903.7	6.604
<b>III/I</b> = 1/0.8	171.1	187.6	0.996	37.76	1122.0	6.604
830LVP/ <b>I</b> = 1/1	204.1	227.7	0.163	14.37	2012.5	92.17
830LVP/ <b>I</b> = 1/0.8	201.9	237.2	0.128	14.91	1436.9	95.92

<sup>a</sup>  $T_g$  values obtained from the TMA thermograms.

<sup>b</sup> Peak height was measured from the damping curve of the DMA thermograms.

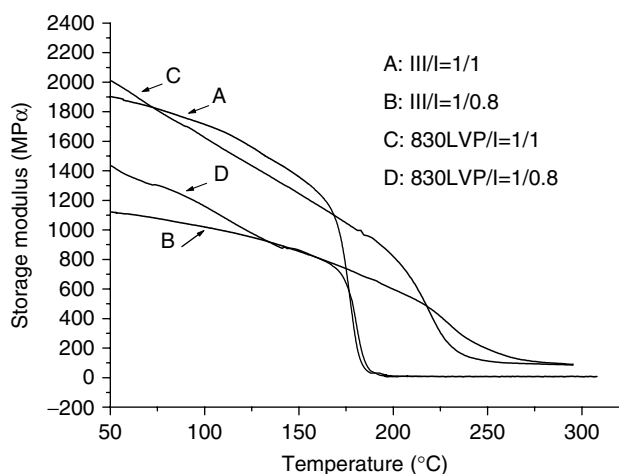


Figure 3. Storage moduli of 830LVP/I and III/I systems.

compatibility of the system with possibly some phase separation. This small second transition may also possibly have been due to the segmental motion of the flexible siloxane. Nevertheless, it was noted that the siloxane moiety was well dispersed in the crosslinked network and it was hard to see phase separation in the cured systems. This inference was confirmed by the homogeneity of carbon-mapping scanning electron microscopy (SEM), oxygen-mapping SEM and silicon-mapping SEM of the cured systems (Fig 4). All the mapping SEM results indicated homogeneity and compatibility of the cured matrices.

**Thermal degradation behaviour**

The TGA thermograms of cured epoxy provided valuable information regarding their thermal stability and thermal degradation behaviour. TGA data of these systems (Table 2 and Fig 5) indicated that 5 % weight loss in nitrogen atmosphere for III/I =

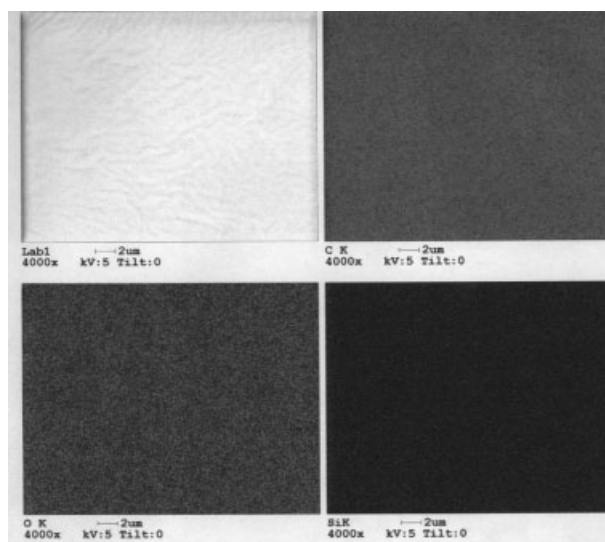


Figure 4. Typical mapping SEM images of III/I = 1/1: (upper left) SEM photo; (upper right) carbon-mapping; (lower left) oxygen-mapping; (lower right) silicon-mapping.

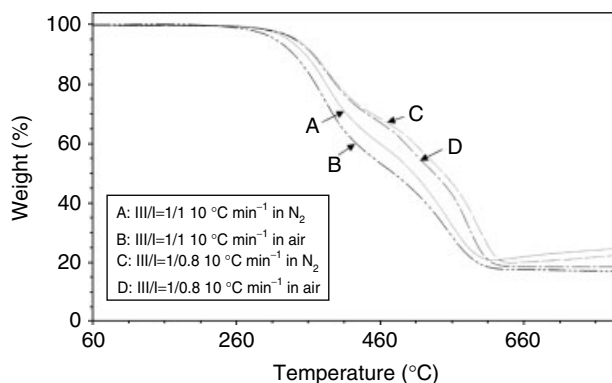
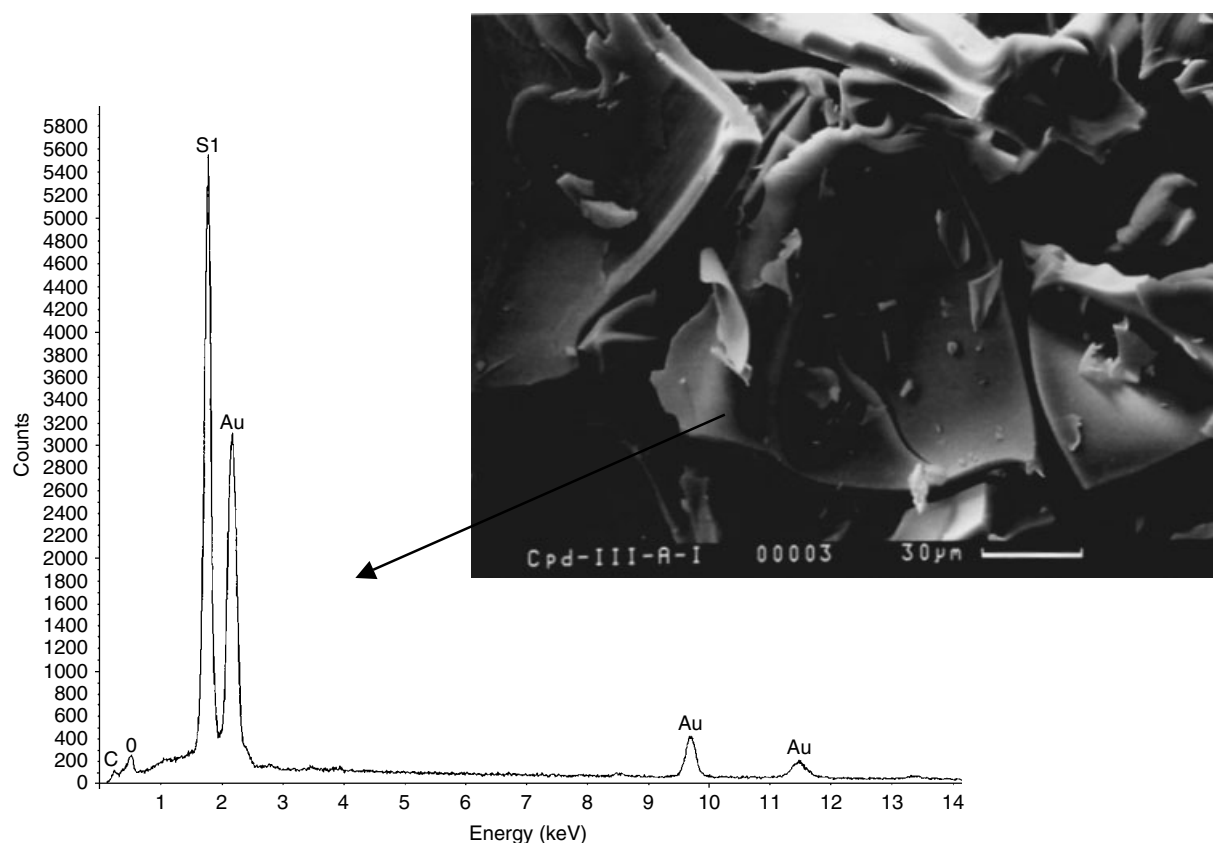


Figure 5. TGA thermograms of III/I system.

Table 2. Dynamic TGA and activation energy  $E_a^a$  by the Kissinger method

Atmosphere	Heating rate (°C min <sup>-1</sup> )	5 % weight loss T (°C)	Peak 1 T (°C)	Yield (%)	$E_{a1}$ (kJ mol <sup>-1</sup> )	Peak 2 T (°C)	Yield (%)	Char yield (%)	$E_{a2}$ (kJ mol <sup>-1</sup> )
<b>III/I = 1/0.8</b>									
N <sub>2</sub>	20	365.9	408.4	84.17	111.4	642.0	36.09	14.35	75.1
	15	350.3	396.3	82.99		610.3	29.29	12.44	
	10	344.6	384.3	83.12		593.3	34.29	18.81	
	5	320.7	366.9	81.65		543.3	33.68	23.22	
Air	20	347.0	394.9	79.35	117.1	593.8	31.02	16.49	72.9
	15	357.5	400.6	81.06		634.2	33.00	18.30	
	10	346.3	382.1	85.33		579.1	34.35	18.46	
	5	321.8	365.1	81.94		557.2	28.85	18.26	
<b>III/I = 1/1</b>									
N <sub>2</sub>	20	356.6	401.3	78.45	149.2	576.1	35.46	19.13	78.0
	15	350.3	399.7	78.85		602.1	28.71	24.94	
	10	342.1	386.1	80.12		553.4	35.10	24.71	
	5	319.7	373.2	74.67		532.7	27.80	24.62	
Air	20	356.9	397.5	81.14	147.6	596.1	31.11	18.01	82.7
	15	350.2	386.0	83.53		586.2	28.47	18.04	
	10	317.1	382.8	74.60		558.3	29.11	16.59	
	5	310.2	365.6	76.64		517.1	32.81	16.76	

<sup>a</sup>  $E_a$  = activation energy



**Figure 6.** ESCA spectrum showing the TGA residual of the **III/I** system, identified as silicon dioxide; the residue itself is shown in the SEM photo.

1/0.8 occurred in the range 320.7–365.7 °C, and in the range 319.7–356.4 °C for **III/I** = 1/1. The 5 % weight loss in air atmosphere for **III/I** = 1/0.8 occurred 321.7–357.5 °C, and at 310.2–356.9 °C for **III/I** = 1/1. Furthermore, flaky residuals with char yields in the range 12–24.9 % were found as the pyrolysis products. The main composition of the residual was characterized to be silicon dioxide, as shown in the SEM and electron spectroscopy for chemical analysis (ESCA) spectrum in Fig 6. All of the experimental results indicated that the transformation of these silicon-containing polymers into stable silicon dioxide could form a flaky layer on the polymer surface, which is believed to inhibit the propagation of decomposition, and thus to improve the heat resistance of the cured materials.

### Thermal degradation kinetics

Dynamic TGA has frequently been used to study the thermal degradation kinetics of polymers. We applied Kissinger's method<sup>20–22</sup> to determine the activation energy ( $E_a$ ) of solid–gas reactions using the following equation:

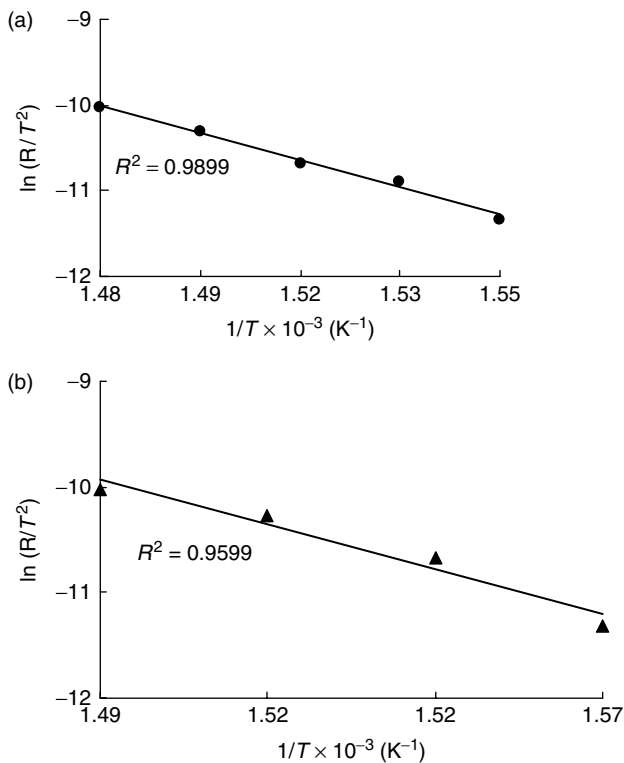
$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln(n(1 - \alpha_{\max})^{n-1}) - \frac{E_a}{RT_{\max}}$$

where  $\beta$  is the heating rate,  $T_{\max}$  is the temperature of the inflection point of the thermograms that

corresponds to the maximum reaction rate,  $A$  is the pre-exponential factor,  $\alpha_{\max}$  is the maximum conversion,  $n$  is the reaction order, and  $R$  is the molar gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>). The straight lines were obtained according to the least-squares method for both systems (Fig 7). The dynamic method proposed herein gave apparent activation energies of degradation of 111.4 kJ mol<sup>-1</sup> (in N<sub>2</sub>), 117.1 kJ mol<sup>-1</sup> (in air) for **III/I** = 1/0.8 system, and 149.2 kJ mol<sup>-1</sup> (in N<sub>2</sub>), 147.6 kJ mol<sup>-1</sup> (in air) for **III/I** = 1/1 system. The higher the siloxane and imide content in the crosslinked material, the higher the activation energy. Moreover, there was a unique phenomenon that the apparent activation energies obtained in air were very close to those obtained in nitrogen atmosphere. It can be inferred that the formation of thermally stable silicon dioxide creates a barrier on the material surface and prevents further decomposition in the inner polymer matrix, thus explaining this experimental finding.

### CONCLUSION

A novel siloxane- and imide-modified epoxy oligomer (**III**) was successfully synthesized, and characterized by elemental analysis, IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR. This novel epoxy oligomer was then cured with a siloxane-containing dianhydride (**I**). Unlike with most silicone-containing compounds, there was no apparent phase separation in the cured epoxy. The TMA and DMA data revealed that the flexible siloxane group



**Figure 7.** Typical dynamic TGA of III/I systems: (a) III/I = 1/1 in  $N_2$ ; (b) III/I = 1/1 in air;  $R^2$  corresponds to the correlation of the points.

and the rigid imide group improved the toughness as well as the mechanical properties. The thermal degradation kinetic data, the SEM micrographs and the ESCA results showed that during pyrolysis the siloxane groups had been transformed into flaky silicon dioxide as char residual, which further improved its heat resistance by inhibiting the propagation of thermal decomposition in the polymer matrix. This evidence accounts for the fact that this siloxane- and imide-containing epoxy material exhibited good thermal stability with similar thermal degradation behaviour in both  $N_2$  and air atmospheres.

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