

Synthesis, curing behavior and properties of siloxane and imide-containing tetrafunctional epoxy

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Abstract A novel tetrafunctional epoxy resin containing siloxane and imide groups, i.e., *N,N,N',N'*-tetraglycidyl-bis(4-aminophenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxane-bisnorbornane-2,3-dicaroximide), was synthesized and characterized. The curing behavior of this resin and the properties of its cocured material with commercial tetraglycidyl meta-xylene (GA-240) was studied. Functional group changes during cocuring reactions were investigated with FTIR. Kinetic parameters were analyzed with dynamic DSC. Thermal properties were measured with TGA, TMA and DMA. Curing kinetics revealed that this novel tetrafunctional epoxy indicated a lower activation energy and lower curing temperature than GA-240. The cocured materials, due to the presence of siloxane and imide groups in the polymer matrix, show higher glass transition temperature, better dimensional stability and toughness, and also enhanced properties than pure GA-240.

Keywords Siloxane and imide-containing tetrafunctional epoxy · Co-cured materials · Toughness · Enhanced properties

Introduction

Epoxy resin, because of its easy processing and excellent adhesion, is one of the most widely used thermosets, especially in the field of package and PC board in electronics industry. Demand for the epoxy resin in the

new era of electronic application lies in improved thermal properties, better toughness, lower dielectric constant, lower curing temperature and easy processing, etc. Furthermore, the verification of the bulk state curing would result in internal residual stress in the polymer matrix, and subsequently leads to device failure. Siloxane, due to its flexibility, when incorporated in the epoxy chain, would therefore improve the toughness and lower the internal residual stress. In addition, since siloxane is an excellent water repelling material, an epoxy resin containing such a siloxane group would somehow show a lower dielectric constant. Similar ideal of molecular design was also applied to imide group for its good mechanical property and long term reliability. Tetrafunctional epoxide was deliberately designed in this new resin to enhance the cross-linking and further improve its glass transition temperature and mechanical properties. Synthesis and characterization of other tetrafunctional epoxies can also be referred from literature [1, 2]. Since the commercially available tetraglycidyl meta-xylydiamine (electronic grade, GA-240) is relatively hard and brittle, When GA-240 is blended with this siloxane and imide-containing tetrafunctional epoxy, the cocured material apparently show enhanced thermal properties and toughness, but lower residual stress. In this work, we would like to report such a study.

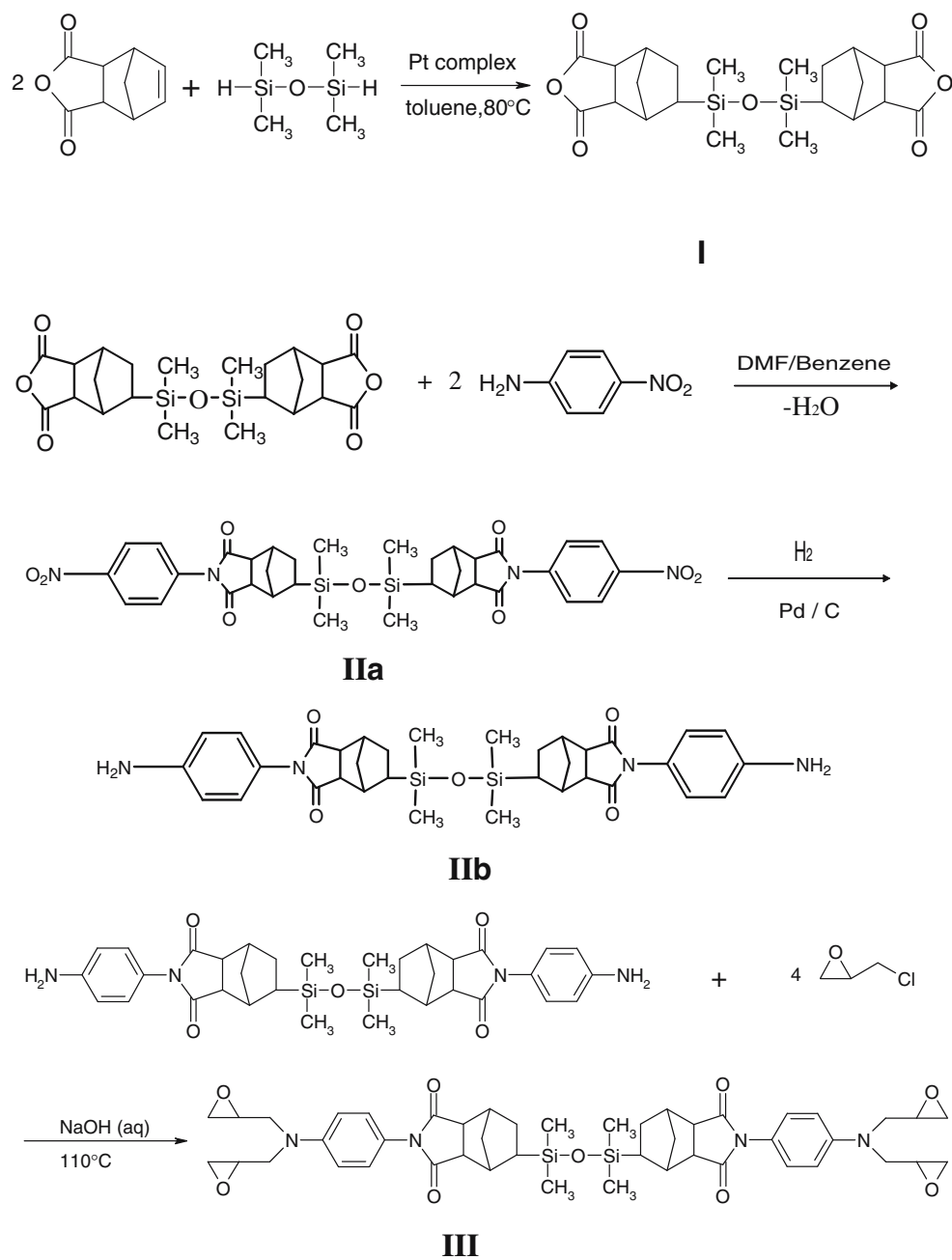
Experimental

Chemicals

5-norbornane-2,3-dicarboxylic anhydride (i.e., nadic anhydride) was purchased from Merck Co. Tetramethyldisiloxane was bought from Lancaster Co., catalyst. Platinum-cyclovinyl-methylsiloxane complex (as catalyst for

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Scheme 1 Synthesis of tetrafunctional epoxy (III)



hydrosilation) was provided from UCT, and 4,4'-methylene diamine, from CVC, epichlorohydrin from Tedia Co., and 4-nitroaniline from Janssen Co. Solvents toluene and *N,N*-dimethyl formamide were purified by adding calcium chloride and were distilled. All other chemicals were used directly without further purification.

Instruments

All ^1H NMR spectra were obtained with Varian Unity 300 MHz NMR, using CDCl_3 as solvent. IR spectra were obtained from Avatar 360 FT-IR (Nicolet Co.) with a

resolution of 4 cm^{-1} . Dynamic differential scanning calorimeter (DSC) thermograms were performed with Seiko Instrument DSC 200 under 100 ml/min of nitrogen flow with heating rates of 3, 5, 10 and 15 $^\circ\text{C}/\text{min}$. Thermogravimetric analyzer (TGA) and thermomechanical analyzer (TMA) thermograms were performed with Du Pont TA 2950 and 2940 with a heating rate of 10 $^\circ\text{C}/\text{min}$. Samples with dimension of $4 \times 1 \times 0.2\text{ cm}$ were tested with dynamic mechanical analyzer (DMA) at 1 Hz with a heating rate of 3 $^\circ\text{C}/\text{min}$., temperature ranging from 30 to 300 $^\circ\text{C}$. Dielectric constants of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1 MHz.

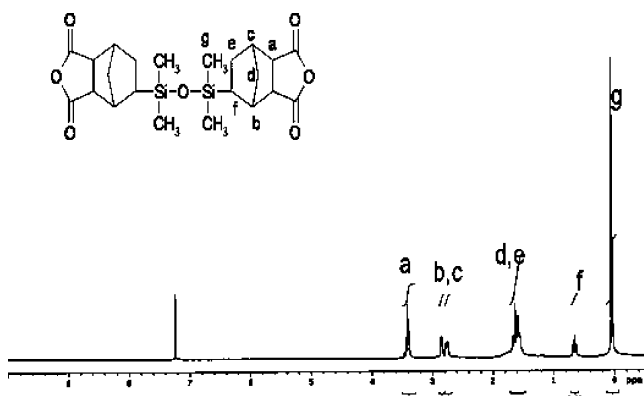


Fig. 1 ^1H NMR spectrum of compound I

Preparation of materials (Scheme 1)

Synthesis of 5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxane-diallyl) bisnorbornane-2,3-dicarboxylic anhydride (I) Nadic anhydride (131.33 g, 0.8 mole) in 500 ml of toluene, to which tetramethyldisiloxane (53.6 g, 0.4 mole) and catalyst platinum-cyclovinyl methyl-siloxane complex were added and stirred at 80 °C for 46 h. The reaction mixture was concentrated to precipitate the product. The product was recrystallized from ether, giving a white crystal with mp. of 135–7 °C (70% yield), which shows $^1\text{H-NMR}$ (CDCl_3 , ppm): δ : 0.03–0.05 (m, 12H), 0.63–0.68 (m, 2H), 1.56–1.68 (m, 8H), 2.75–2.78 (m, 2H), 2.85 (m, 2H), 3.39–3.43 (m, 4H).

IR: anhydride $\nu_{\text{C=O}}$ 1,856, 1,780 cm^{-1} ; siloxane, $\nu_{\text{Si-O-Si}}$ 1,082 cm^{-1} , $\nu_{\text{C-Si}}$ 1,225 cm^{-1} .

Synthesis of N,N'-bis(4-aminophenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxane-diallyl)-bisnorbornane-2,3-dicarboximide (IIb) Into a three necked flask, I (11.58 g, 0.025 mole) in 20 ml DMF and 4-nitroaniline (7.60 g, 0.055 mole) in 20 ml DMF were charged. Reaction proceeded at ambient temperature for 6 h, then benzene was

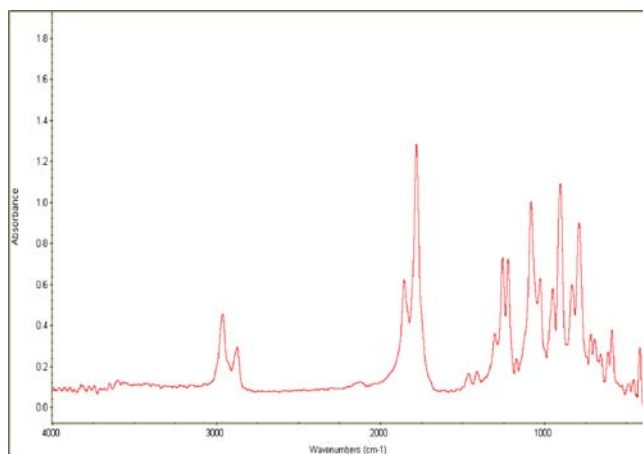


Fig. 2 FT-IR spectrum of compound I

Table 1 Curing conditions of samples

Sample	Equivalent ratio	Curing conditions [temp (°C)/time (h)]
GA-240/III/MDA	A(1/0/1)	150/2+180/4+200/2
	B(0.95/0.05/1)	140/2+170/4+200/2
	C(0.9/0.1/1)	140/2+170/4+200/2
	D(0.85/0.15/1)	130/2+160/4+200/2
	E(0.8/0.2/1)	130/2+160/4+200/2

added, imidization proceeded in a Dean-Stark apparatus. After removal of water, a yellow solid (IIa) was obtained. IIa (7.07 g, 0.01 mole) was dissolved in 300 ml ethanol and Pd/C (0.4 g) was added under Hydrogen atmosphere to reduce the nitro group into NH_2 at room temperature for 24 h. A red product of IIb was obtained (5.67 g, 88% yield). $^1\text{H-NMR}$ (CDCl_3 , ppm) shows: δ : 0.00–0.01 (m, 12H), 0.61 (m, 2H), 1.54–1.61 (m, 8H), 2.72 (m, 2H), 2.78 (m, 2H), 3.15 (m, 4H), 3.66 (s, 4H), 6.59–6.63 (d, 4H), 6.87–6.90 (d, 4H).

IR: imide, $\nu_{\text{C=O}}$ 1,768, 1,705 cm^{-1} ; siloxane, $\nu_{\text{Si-O-Si}}$ 1,082 cm^{-1} , $\nu_{\text{C-Si}}$ 1,225 cm^{-1} .

Synthesis of N,N',N',N'-tetraglycidyl-bis(4-aminophenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxane-diallyl)-bisnorboenane-2,3-dicarboximide (III) IIb (20.00 g, 0.031 mole), epichlorohydrin (96.79 ml, 1.24 mole), NaOH (7.44 g, 0.186 mole) in 15 ml H_2O were charged into a flask and was refluxed at 110 °C for 8 h. Product III was extracted with dichloromethane, washed with water and dried with MgSO_4 . A greenish solid (20.6 g, 76.7% of yield) with mp of 127–31 °C was isolated. $^1\text{H-NMR}$ and IR spectra of compound III are given in Figs. 1 and 2, where $^1\text{H-NMR}$ (CDCl_3 , ppm) shows: δ : 0.04–0.06 (m, 12H), 0.67 (m, 2H), 1.60 (m, 8H), 1.82–1.87 (m, 4H), 2.57 (m, 4H), 2.78–2.85 (m, 8H), 3.16–3.23 (m, 8H), 6.83–6.85 (d, 4H), 7.04 (d, 4H).

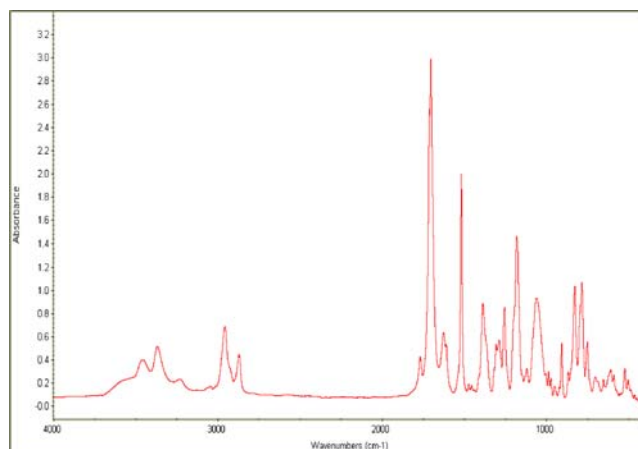


Fig. 3 FT-IR spectrum of compound II b

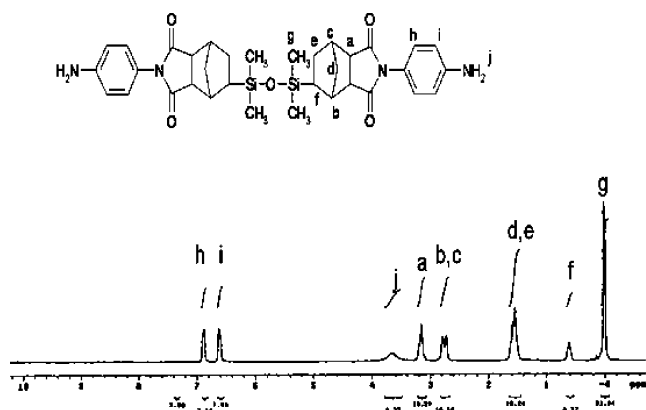


Fig. 4 ^1H NMR spectrum of compound II b

IR shows: epoxide, ν 910 cm^{-1} .

This tetrafunctional epoxy (III) was titrated by the pyridinium chloride method [3] to find an epoxide equivalent weight (EEW) of 432.

Preparation of cocured materials

Blends of GA-240/III/MDA in equivalent ratios of (A) 1/0/1, (B) 0.95/0.05/1, (C) 0.9/0.1/1, (D) 0.85/0.15/1, (E) 0.8/0.2/1, and (F) 0/1/1 were mixed thoroughly and was each filled into DSC aluminum pan and scanned from 30 to 300 $^{\circ}\text{C}$ under 100 ml/min of nitrogen flow at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Maximum curing exothermic peak for each sample was found at (A) 129.9 $^{\circ}\text{C}$, (B) 173.1 $^{\circ}\text{C}$, (C) 170.3 $^{\circ}\text{C}$, (D) 166.6 $^{\circ}\text{C}$, (E) 165.2 $^{\circ}\text{C}$ and (F) 152.2 $^{\circ}\text{C}$. Test samples were then cured at the three stages shown in Table 1.

Results and discussions

The synthesis of siloxane and imide containing tetrafunctional epoxy (III) is given in Scheme 1.

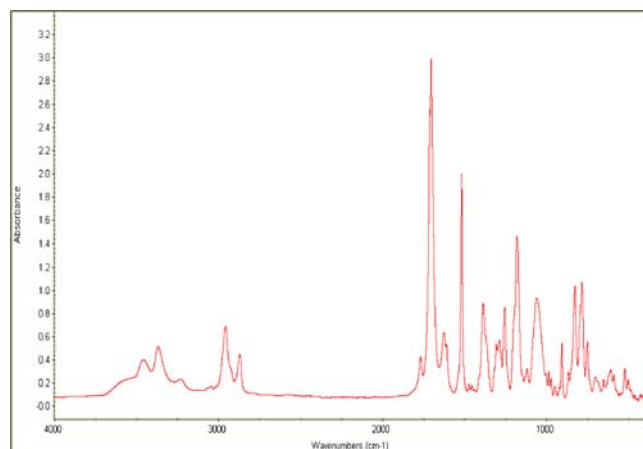


Fig. 5 FT-IR spectrum of compound III

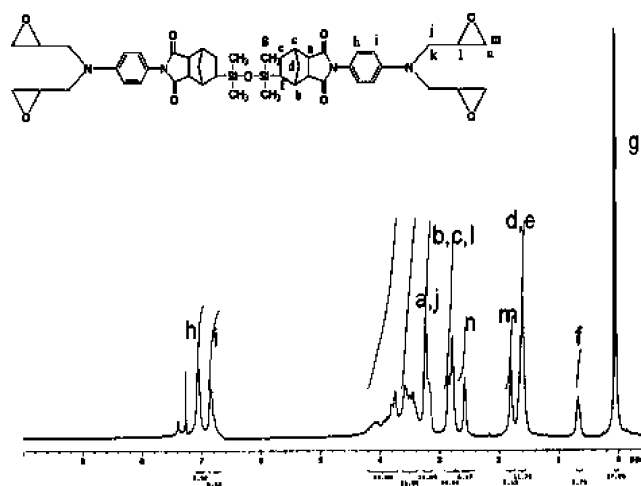


Fig. 6 ^1H NMR spectrum of compound III

Structures determination

Compound I was prepared from the hydrosilylation of nadic anhydride and tetramethyldisiloxane in the molar ratio of 2:1 under the catalysis of active Pd complex. Trace of the reaction was monitored with ^1H -NMR (Fig. 1). In the beginning, the two vinylic H's in norbornene occurs at δ 0.63 ppm, and the two Si-H's in tetramethyldisiloxane occurs at δ 4.7 ppm. After 24 h of reaction, both absorption disappeared and a new absorption at δ 0.6 ppm was observed, indicating 2 H's at the C-Si, while δ 0.03 to 0.05 ppm indicating 12 H's of the four methyl groups on Si, and those at δ 0.63 to 3.43 ppm indicating the 4 H's on anhydride, an evidence of producing I. FT-IR spectrum of I (Fig. 2) shows an absorption of anhydride at 1,782, 1,852 cm^{-1} (anhydride, C=O stretching) and 1,220 cm^{-1} (anhydride, C-O-C stretching). The disappearance of absorption at 1,680 cm^{-1} (C=C stretching) of norbornene, the new absorptions at 1,083 cm^{-1} (Si-O-Si stretching),

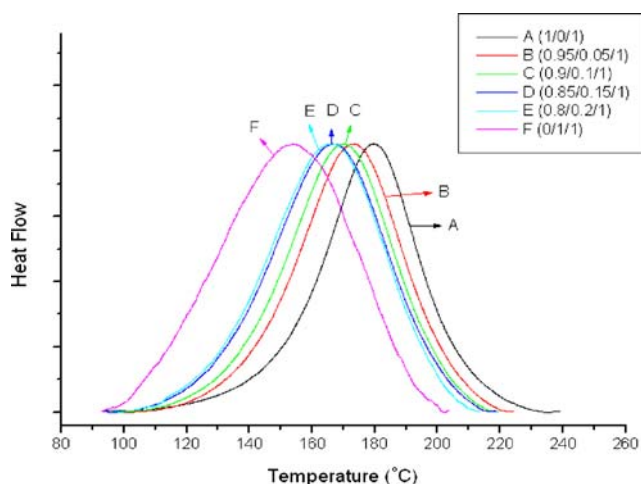
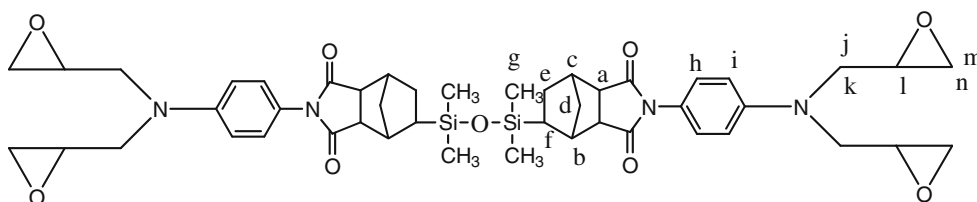


Fig. 7 Dynamic DSC of samples (GA-240/III/MDA), A=1/0/1; B=0.95/0.05/1; C=0.9/0.1/1; D=0.85/0.15/1; E=0.8/0.2/1; F=0/1/1

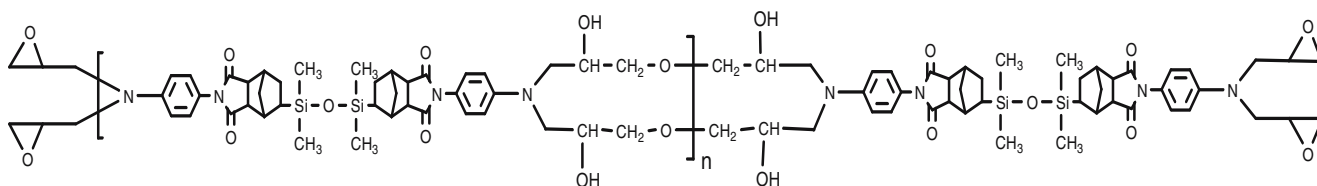
and $1,258\text{ cm}^{-1}$ (Si-CH₃ stretching) of the product confirms the structure of I.

For the structure determination of IIb, the IR absorption at $1,768, 1,705\text{ cm}^{-1}$ (imide, C=O stretching) strongly supports the existence of imide group (Fig. 3). The coupled doublet of asymmetric N-H stretching occurring at $3,460$ and $3,369\text{ cm}^{-1}$ proves the reduction of nitro group into primary amine. ¹H-NMR spectrum (Fig. 4) shows 12 H's of tetramethyl groups in the siloxane at $\delta 0.00\sim 0.01$ ppm, 4 H's at $\delta 3.66$ ppm for the two primary amine, and $\delta 6.59\sim 6.90$ ppm for the 8 H's on benzene rings. All these evidence conforms the structure of IIb.

IR absorption (Fig. 5) at 910 cm^{-1} (epoxy ring stretching) and broad absorption at $3,200\sim 3,500\text{ cm}^{-1}$, ($\nu_{\text{O-H}}$) indicates that III is an oligomer. The ¹H-NMR spectrum (Fig. 6) shows H_g at $\delta 0.04\sim 0.06$ ppm (12H), H_f at $\delta 0.67$ ppm (2H), $H_{d,e}$ at $\delta 1.60$ ppm (8H), H_m : at $\delta 1.82\sim 1.87$ ppm (4H), H_n at $\delta 2.57$ ppm (4H), $H_{b,c,l}$ at $\delta 2.78\sim 2.85$ ppm (8H), $H_{a,j}$ at $\delta 3.16\sim 3.23$ ppm (8H), H_i at $\delta 6.83\sim 6.85$ ppm (4H), H_h at $\delta 7.04$ ppm (4H). Where H_h represents one H on the benzene ring, H_m represents one H on the epoxide, and from the structure of III, one molecule of III contains 4 H_h 's, and 4 H_m 's. If the product III contains tetraglycidyl group, the ratio of integrated areas of H_h to H_m :1: 1. It is observed that ¹H-NMR spectrum (Fig. 6) shows this is the case, thus conforms the structure of III. A reasonable structure of III is giving in the following:



III was titrated by the HCl-pyridine method [3], and an epoxide equivalent weight (EEW) of 432 was found, which means III has a molecular weight of 1728. The calculated repeating unit, n , is 0.97, very close to 1, which reveals that the tetrafunctional epoxy thus prepared is a dimer.



$$n = 0.095$$

Table 2 The maximum exothermic temp. of samples (MDA)

Sample	Equivalent ratio	Max. exothermic temp (°C)
GA-240/III/MDA	A(1/0/1)	179.9
	B(0.95/0.05/1)	173.1
	C(0.9/0.1/1)	170.3
	D(0.85/0.15/1)	166.6
	E(0.8/0.2/1)	165.2
	F(0/1/1)	152.2

Dynamic DSC

Maximum exothermic peaks for various blends of GA-240/III/MDA are listed in Fig. 7 and are summarized in Table 2.

It is obvious that Sample A, GA-240 cured with equivalent MDA, shows the highest curing temperature at $179.9\text{ }^{\circ}\text{C}$. As more III incorporated into GA 240, The curing reaction shifts to lower temperature. Sample F, only III cured with equivalent MDA, shows a maximum exothermic temperature at $152.2\text{ }^{\circ}\text{C}$. As III contains a tertiary amine, (imide group), which played a catalytic effect on the epoxy cure [4]. This explain the reason why blends containing more quantity of III would show lower exothermic temperature.

Curing kinetics

The activation energy of curing reaction can be studied with dynamic DSC [5–9]. Figure 8 gives the typical dynamic DSC thermograms for sample E at heating rates of 3; 5; 10° , and $15\text{ }^{\circ}\text{C}/\text{min}$. According to the method developed by

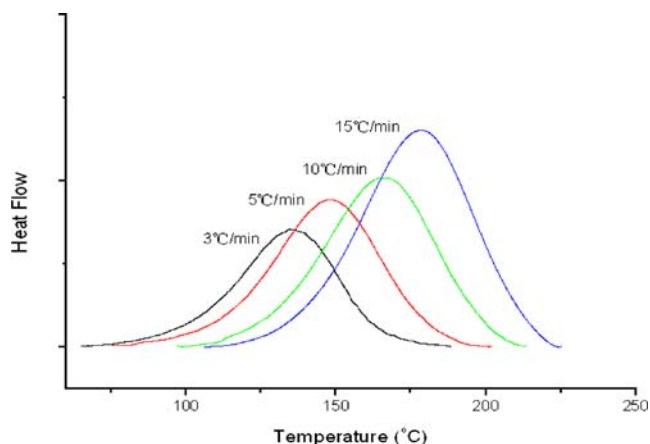


Fig. 8 Typical dynamic DSC of sample (GA-240/III/MDA=0.8/0.2/1) with different heating rate

Kissinger [5, 6, 10], the activation energy, E_a , can be calculated by:

$$2.303 d \log (\Phi / T_m^2) / d(1 / T_m) = -E_a / R \quad (1)$$

where T_m is the Maximum peak temperature in K, Φ is the heating rate in °C/min, R is Gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), and E_a is the activation energy (kJ/mol). A plot of $\ln(\Phi / T_m^2)$ versus $1/T_m$ is given in Fig. 9. The calculated E_a values are listed in Table 3.

Result shows that Sample A has the highest activation energy of 55.51 kJ/mol. As more III blended into GA-240, lower activation energies were found. This result is in consistent with the finding in Maximum exothermic peak shift (Fig. 7 and Table 2), because imide group played a catalytic role during curing reaction. Furthermore, the tetrafunctional epoxy III contains a flexible siloxane in the main chain which may, in part, show higher chain mobility and thus account for its easy processing.

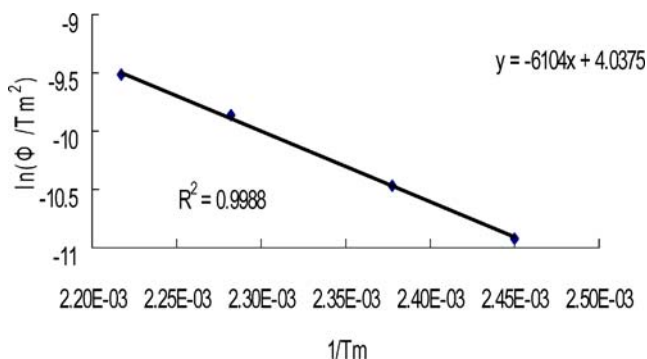


Fig. 9 Plot of $\ln(\Phi / T_m^2)$ vs $1/T_m$ of sample (GA-240/III/MDA=0.8/0.2/1)

Table 3 Kinetic data of samples

Sample	Equivalent ratio	Heating rate (°C/min)				Ea, kJ/mol
		3	5	10	15	
GA-240/	A(1/0/1)	151	163.1	179.9	193.6	55.51
III/MDA	B(0.95/0.05/1)	142.8	156	173.1	184.9	53.80
	C(0.9/0.1/1)	139.6	151.7	170.3	181	52.97
	D(0.85/0.15/1)	137.1	148.3	166.6	179.1	51.81
	E(0.8/0.2/1)	135.2	147.6	165.2	178.1	50.75

Functional group changes during curing reaction

Typical functional group changes during curing reactions for Sample E is given in Fig. 10, and the difference spectra using the absorbance of Si–O–Si at $1,050$ to $1,060 \text{ cm}^{-1}$ as internal reference, is giving in Fig. 11. The absorption of epoxide at 910 cm^{-1} decreases with time. The absorptions of NH_2 (from the curing agent, MDA) at $3,460$ and $3,369 \text{ cm}^{-1}$ are clearly decreased, and eventually broadened because of overlapping with the absorption of newly produced OH group.

Gel fractions

The fully cured samples were continuously extracted with acetone in Soxhlet extractor for 24 h to extract the uncured portions. Gel fractions of samples are listed in Table 4. It is found that all the gel fractions of the five samples are high enough over 97%, meaning that these samples are potentially easy to process and contains high cross-linking.

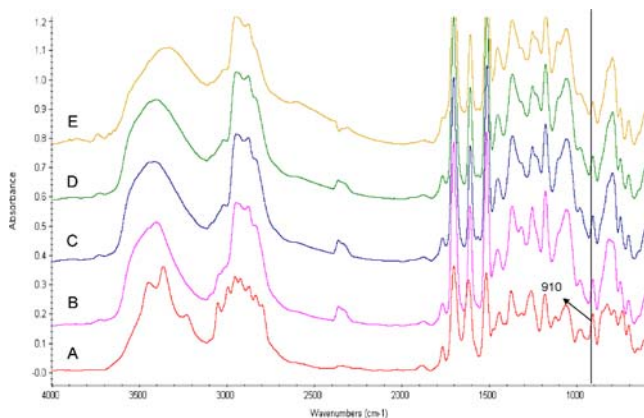


Fig. 10 FT-IR spectrum of sample (GA-240/III/MDA=0.8/0.2/1), A=initial; B=130 °C/10 min; C=160 °C/10 min; D=160 °C/20 min; E=200 °C/10 min

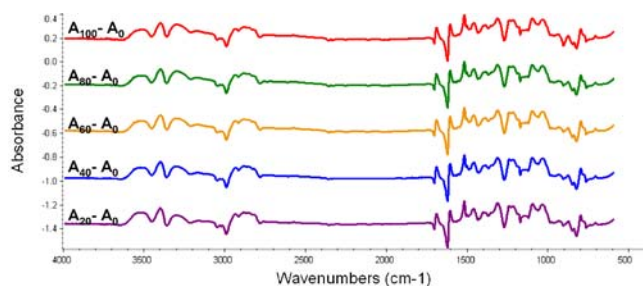


Fig. 11 Different spectra ($A_t - A_0$, t in min), showing the increase and decrease of absorbances during curing reaction at 160°C

Coefficients of thermal expansion (CTE)

Thermal expansion coefficient of each sample was measured from the smooth slope of TMA thermogram before Tg (Fig. 12) and the values are listed in Table 5. Although each TMA was tested in a temperature range of 30 to 280 °C, the TMA thermogram after Tg appears not very regular, and the CTE after Tg is difficult to be found. Since all these samples are highly cross-linked with high gel fractions as indicated in Table 4, they are, therefore, thermally stable and show relatively low coefficient of thermal expansion. Compared the pure GA-240 (sample A in which GA-240/III/MDA=1/0/1) with other co-cured samples, It is found that as III is added into GA-240, thermal expansion coefficient can be effectively reduced. That means these co-cured materials have improved dimensional stability and are good for device fabrication. The low thermal expansion coefficient and good dimensional stability of these samples are due to high cross-linking and, also are, probably in part, due to the presence of hard and strong molecular interaction of imide group in III.

Thermal stability

The on-set temperature of 5% weight loss and %residual weight at 450 °C are found from TGA thermograms (Fig. 13) and are listed in Table 6.

TGA thermogram of Sample A indicates one stage of pyrolysis. While other samples pyrolyze in two stages but

Table 4 Gel fraction results of samples

Sample	Equivalent ratio	Gel fraction (%)
GA-240/III/MDA	A (1/0/1)	98.3
	B (0.95/0.05/1)	97.6
	C (0.9/0.1/1)	97.4
	D (0.85/0.15/1)	98.0
	E (0.8/0.2/1)	97.1

Table 5 Thermal expansion coefficients of samples

Sample	Equivalent ratio	CTE α ($\mu\text{m}/\text{m}^\circ\text{C}$) ^a
GA-240/III/MDA	A (1/0/1)	79.6
	B (0.95/0.05/1)	56.55
	C (0.9/0.1/1)	55.95
	D (0.85/0.15/1)	53.68
	E (0.8/0.2/1)	55.33

^a The value of CTE was measured from the smooth slope of TMA thermogram before Tg.

show higher residual weight, which is probably due to the presence of thermally stable imide group [11].

Dynamic mechanical analyzer

Damping peaks ($\tan \delta$) and Storage Modulus (G') of samples are giving in Figs. 14 and 15 and data are listed in Table 7.

GA-240 has a Tg of 217.1 °C, as III incorporated into GA-240, these co-cured samples still have relatively high Tg's. Sample E shows two Tg's at 228.5 °C and a shoulder at 185.5 °C (probably a transition of siloxane), indicating possible phase separation. Therefore, 20% of III is the maximum amount that can be incorporated into GA-240, or otherwise, more III might cause drawback in the mechanical property because of phase separation [12]. Sample A has a storage modulus of 1,775 MPa, other samples indicate storage modulus decreases as III incorporated. This is because the existence of soft siloxane in the samples. However, the rubber siloxane play a toughness role in the samples [12]. In general, high cross-linking materials are hard and brittle. The siloxane portions in III, when incorporated into a high cross-linking material, clearly improve the toughness of these samples, as can be seen from the increased damping peak height and the area of $\tan \delta$ in Table 8. This phenomenon has been discussed in literature [13, 14]. Furthermore, it appears that the G'

Table 6 Thermogravimetric analysis of samples

Sample	Equivalent ratio	5% Weight loss temp(°C)	Residue weight (%) at 450°C
GA-240/III/MDA	A(1/0/1)	302.2	43.3
	B(0.95/0.05/1)	278.3	47.8
	C(0.9/0.1/1)	283.6	53.4
	D(0.85/0.15/1)	257.4	54.8
	E(0.8/0.2/1)	251.4	60.7

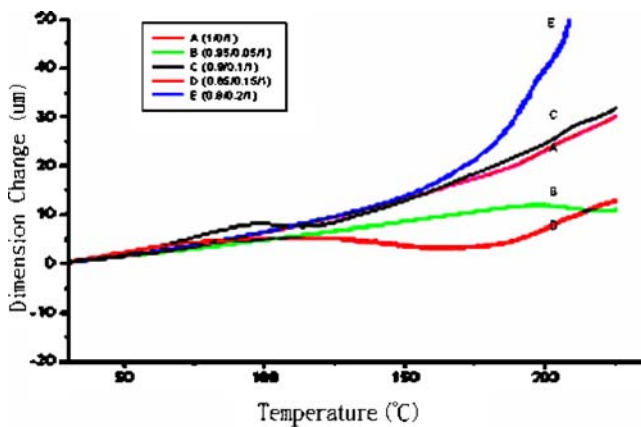


Fig. 12 TMA thermograms of samples (GA-240/III/MDA), $A=1/0/1$; $B=0.95/0.05/1$; $C=0.9/0.1/1$; $D=0.85/0.15/1$; $E=0.8/0.2/1$

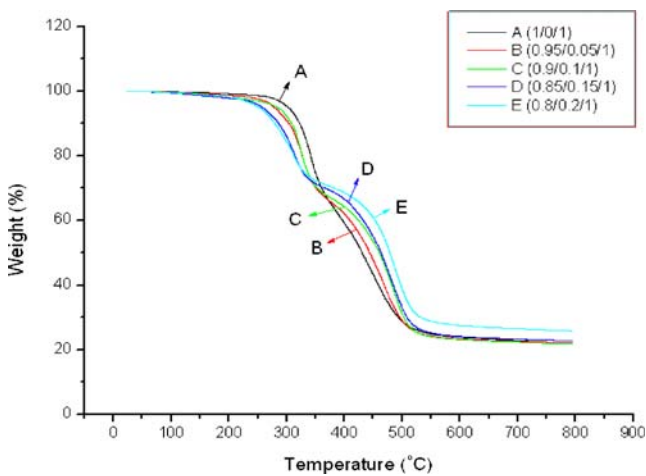


Fig. 13 TGA thermograms of samples (GA-240/III/MDA), $A=1/0/1$; $B=0.95/0.05/1$; $C=0.9/0.1/1$; $D=0.85/0.15/1$; $E=0.8/0.2/1$

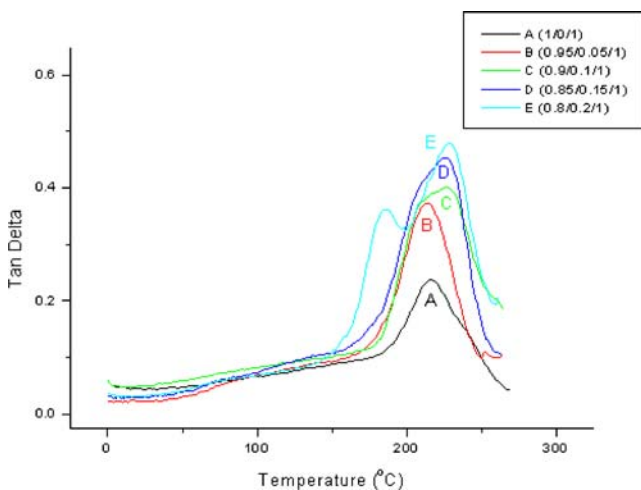


Fig. 14 Tan δ of samples (GA-240/III/MDA), $A=1/0/1$; $B=0.95/0.05/1$; $C=0.9/0.1/1$; $D=0.85/0.15/1$; $E=0.8/0.2/1$

Table 7 Storage modulus and glass transition temperatures of samples

Sample	Equivalent ratio	Storage modulus (MPa)	T _g (°C)
GA-240/III/MDA	A(1/0/1)	1,775	217.1
	B(0.95/0.05/1)	1,210	213.8
	C(0.9/0.1/1)	1,099	226.3
	D(0.85/0.15/1)	636	227.1
	E(0.8/0.2/1)	443	185.5, 228.5

Table 8 DMA results (peak height and area of Tan δ) of samples

Sample	Equivalent ratio	Peak height	Area of Tan δ
GA-240/III/MDA	A(1/0/1)	0.24	13.8
	B(0.95/0.05/1)	0.37	20.6
	C(0.9/0.1/1)	0.40	25.4
	D(0.85/0.15/1)	0.45	29.0
	E(0.8/0.2/1)	0.48	34.4

profiles of samples A, C and D near T_g's are not regular (Figs. 14, 15). This phenomenon happens presumably because of incomplete cure. As incompletely cured samples are reheated during DMA test, probably post-cure would occur to some extent, leading to some fluctuations as observed from the G' profiles.

Dielectric constants

Dielectric constants and dissipation factor of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1 MHz of frequency and data are listed in Table 9. In general, dielectric constant and dissipation factor would be reduced as water repellent material is incorporated in a polymer blend [8]. Unfortunately, this is

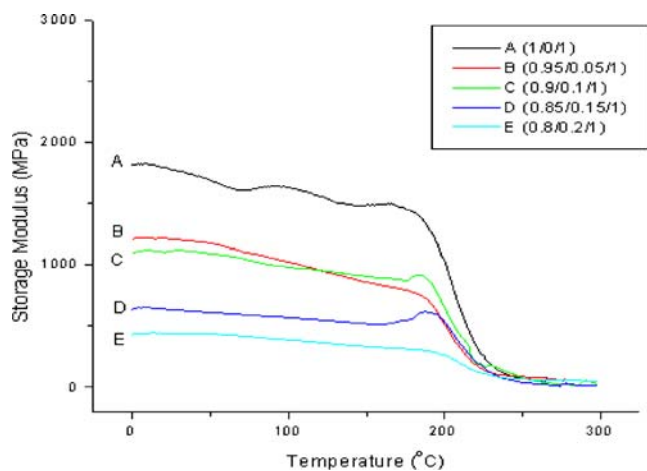


Fig. 15 Storage modulus of samples (GA-240/III/MDA), $A=1/0/1$; $B=0.95/0.05/1$; $C=0.9/0.1/1$; $D=0.85/0.15/1$; $E=0.8/0.2/1$

Table 9 Dielectric constant and dissipation factor of samples

Sample	Equivalent ratio	Dielectric constant	Dissipation factor
GA-240/III/	A(1/0/1)	5.71	0.036
MDA	B(0.95/0.05/1)	5.16	0.036
	C(0.9/0.1/1)	5.43	0.038
	D(0.85/0.15/1)	7.21	0.081
	E(0.8/0.2/1)	6.02	0.069

not the case expected as observed from data. As it is well known that OH group produces when epoxy cures [4]. The high polarity of OH group in III would no doubt play a drawback in dielectric constant and dissipation factor. Furthermore, since GA-240 and III each contains four epoxides which must produce lots of OH groups after they are cured. This probably explain why relative high dielectric constants and dissipation factors are observed for these samples. Use of less MDA as curing agent could be one way to lower the dielectric constant and dissipation factor. Because less diamine used would produce less OH's but in the meantime cause less cross-linking. It seems apparently, dielectric constant and mechanical properties must compromise in some way.

Conclusion

Since commercial tetrafunctional GA-240 is a relatively hard and brittle material. Blending siloxane and imide-containing tetrafunctional epoxy III into GA-240 to improve the physical properties appears permissible. The imide group in III contains tertiary amine and played a catalytic role to the curing reaction of epoxy and lower the

activation energy and curing temperature. The soft rubber section of siloxane played a toughness role. The co-cured materials apparently showed improved dimensional stability, lower thermal expansion coefficient, and enhanced toughness. However, increased dielectric constant of samples is the drawback because more OH's were produced in the cured material. This drawback could be possibly improved by using less MDA as curing agent.

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