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Dynamics and thermal properties of epoxy resin cured by new diamino disiloxanes

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ABSTRACT: Two disiloxane compounds, 3,3′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**C1**) and 4,4′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**C2**) were synthesized and used as new curing agents of **DGEBA** epoxy resin with an epoxy value of 0.51 (**E-51**). The curing kinetics of **E-51/C1** and **E-51/C2** systems was investigated by non-isothermal differential scanning calorimetry (DSC) analyses. The activation energy (ΔE) and the characteristic cure temperatures of the two systems were determined. The two systems have the similar activation energy. The reactivity of **E-51/C1** is higher than that of **E-51/C2**. The reaction orders of **E-51/C1** and **E-51/C2** are 0.88 and 0.87, respectively, illustrating that curing reaction between the epoxy resin and curing agent (**C1** or **C2**) is complicated. The DSC result shows that **E51** cured by **C2** has higher Tg; whereas thermogravimetric analysis results indicate that **E51** cured by **C1** has higher thermal stability. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42385.

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INTRODUCTION

Epoxy resins have found broad application in various fields as LED-packing materials, semiconductor encapsulations, advanced composite materials, coatings, and adhesives, due to their excellent mechanical properties, resistance to corrosion, good dielectric behavior, and thermal properties.[1–8] However, the disadvantages of cured epoxy resins, such as intrinsically brittle with poor fatigue properties and damage tolerance caused by high cross-link density, low toughness, poor anti-stripping, and impact resistance property, restrict their further application in high-tech areas. The research on improving the properties of epoxy resins has been an active subject.

Among the developed methods to enhance the toughness of epoxy resins, the chemical modification of epoxy resins by introducing flexible segment to improve the molecular chains activity between crosslinking sites of the cured epoxy resin has been an important route. Generally, the introduction of flexible segment into epoxy resins can be achieved by either synthesis of epoxy resins containing flexible segments,[8–11] or use of curing agents containing flexible structure units.[12,13] The unit of Si—O—Si with good flexibility and high resistance to thermal oxidation[14] has drawn intensive attention in the modification of epoxy resin. However, most of work is focused on the use of siloxane polymers[9,10] or oligomers[15–17] as modifiers, limited attention has been paid on the use of siloxaneyl monomers.[3,18] In addition, though siloxanes containing amine groups were used as curing agents of epoxy resins in the past few decades,[19,20] there has no report on the use of siloxaneyl unit containing aromatic diamine compound as curing agent so far.

4,4′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**C2**) was first synthesized in 1986 and used as the intermediate to generate disiloxanediyl diisocyanate.[21] The molecule can be seen as an analogue of 4,4′-diaminodiphenyl sulfone (DDS) or 4,4′-diaminodiphenylmethane (DDM), the common curing agent of epoxy resins, with disiloxanediyl replace sulfonyl or methylene, respectively. We envisioned that the Si—O—Si unit containing liquid aromatic diamine may be a good curing agent for toughening epoxy resin, due to its reactive aromatic amine group, the flexible organosilicon unit, and possible good miscibility from its liquid characteristics. To our surprise, there is no reported work on using the compound as curing agent of epoxy resins. For searching new route to high performance epoxy resin, in this article, we synthesized **C1** (3,3′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine)) and **C2** by slightly modifying the literature method, and further used them as curing reagents of epoxy **E-51** to investigate the curing reaction kinetics of **E-51/C1** and **E-51/C2**, respectively.

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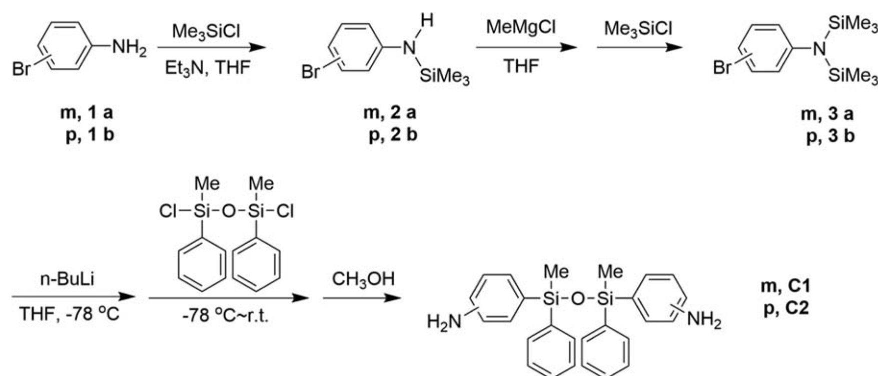

Figure 1. Synthesis route of **C1** and **C2.**

The influence of the structure of the curing agents on the curing reaction kinetics was also revealed.

EXPERIMENTAL

Materials

4-Bromaniline, 3-Bromaniline, chlorotrimethylsilane, methylmagnesium chloride (3.0*M* in THF) and DDM was obtained from J&K Chemical. *n*-BuLi (1.6*M* in hexane) was purchased from Acros Chemical. 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisiloxane was purchased from Gelest. THF, triethylamine, trichloromethane, petroleum ether (PE), ethyl acetate (EA), and magnesium sulfate were purchased from Beijing Chemical Reagents Company. DGEBA epoxy resin with an epoxy value of 0.51 (**E-51**, number-average molecular weight: 307) was supplied by Wuxi Diaish Epoxy Company.

All solvents were purified by standard methods. All reactions were carried out under an argon or a nitrogen atmosphere.

Synthesis of Curing Agent C1 and C2

Synthesis of 2a and 2b. 1a (Figure 1) (12.90 g, 75 mmol) and THF (75 mL) were added into a 250 mL three-necked flask equipped with magnetic stirring, reflux condenser, and nitrogen inlet. The flask was heated to 45°C, then chlorotrimethylsilane (19.2 mL, 150 mmol) was added dropwise. The reaction mixture was stirred for 6 h, and then filtered. The solvent was removed under reduced pressure to obtain the product **2a** (Figure 1), as an orange viscous liquid in 97% yield.

Compound **2b** was prepared in the same manner as described for **2a** from **1b**, as a red viscous liquid in 97% yield.

2a (*N*-(trimethylsilyl)−3-bromoaniline): ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.01 (t, J = 16 Hz, 1H, Ar H), 6.84 (d, J = 8 Hz, 1H, Ar H), 6.79 (s, 1H, Ar H), 6.58 (d, J = 8 Hz, 1H, Ar H),3.47(s, 1H; NH), 0.28(s, 9H; CH_3);

2b (*N*-(trimethylsilyl)−4-bromoaniline): ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.21 (d, J = 8.7 Hz, 2H, Ar H), 6.52 (d, J = 8.8 Hz, 2H, Ar H), 3.43 (s, 1H; NH), 0.26 (s, 9H; CH_3).

Synthesis of 3a and 3b. 2a (17.69 g, 72.4 mmol) and THF (75 mL) were added into a 250 mL three-necked flask equipped with magnetic stirring. The flask was cooled to 0°C, and then methylmagnesium chloride (3.0*M* in THF, 36.3 mL, 108.8 mmol) was added dropwise. After stirred for 45 min at the temperature, to the mixture, chlorotrimethylsilane (18.5 mL, 145 mmol) was then added dropwise, and stirred at room temperature for another 4.5 h. The mixture was filtered with 300 mL *n*-hexane; the solvent was removed under reduced pressure to give **3a** as a light yellow viscous liquid, in 80% yield. **3b** was synthesized in the same method as described for **3a** (Figure 1) from **2b**, as a yellow viscous liquid in 88% yield.

3a (*N,N*-bis(trimethy1silyl)−3-bromoaniline): ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.20 (d, J = 8 Hz, 1H, Ar H), 7.08 (s, 1H, Ar H), 7.06 (t, J = 8 Hz, 1H, Ar H), 6.83 (d, J = 8 Hz, 1H, Ar H), 0.07 (s, 18H; CH_3);

3b (*N,N*-bis(trimethy1silyl)−4-bromoaniline): ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.30 (d, J = 8.6 Hz, 2H Ar H), 6.75 (d, J = 8.6 Hz, 2H Ar H), 0.05 (s, 18H; CH_3).

Synthesis of C1 and C2. To a solution of **3a** (11.03 g, 34.9 mmol) in THF (120 mL) was added a hexane solution of *n*-BuLi (1.6*M*, 22.9 mL, 36.65 mmol) dropwise at −78°C. After stirring for 45 min, 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane was added into the system within 10 min at −78°C and then stirred at room temperature for 3 h. Then 2 mL triethylamine and 40 mL saturated ammonium chloride solution was added to the reaction mixture, and the resulting solution was washed with deionized water. The separated organic phase was dried with anhydrous magnesium sulfate, filtrated, and concentrated to produce an orange viscosity liquid, which was then dispersed into the mixture of 20 mL trichloromethane and 20 mL methanol. After stirred for 15 h at room temperature, the mixture was rotary evaporated to remove the solvent to give crude product, which was then purified by silica gel column chromatography (Eluted with a mixed solvent, PE : EA = 2 : 1, R_f = 0.22) to give **C1** (Figure 1) as a yellow viscous liquid in 62% yield.

Compound **C2** was synthesized in the same manner as described for **C1** as a brownish yellow viscous liquid in 64% yield from **3b**.

C1 (3,3′-(1,3-Dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine)): ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.55 (d, J = 8Hz,4H, Ar H), 7.40–7.30 (m, 6H, Ar H), 7.15 (t, J = 16Hz, 2H, Ar H), 6.93 (d, J = 8Hz,2H, Ar H), 6.76 (s, 2H, Ar H), 6.71 (d, J = 8Hz,2H, Ar H), 3.53 (s, 4H; NH), 0.55 (s, 6H; CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 145.78, 138.82, 138.02, 134.25,

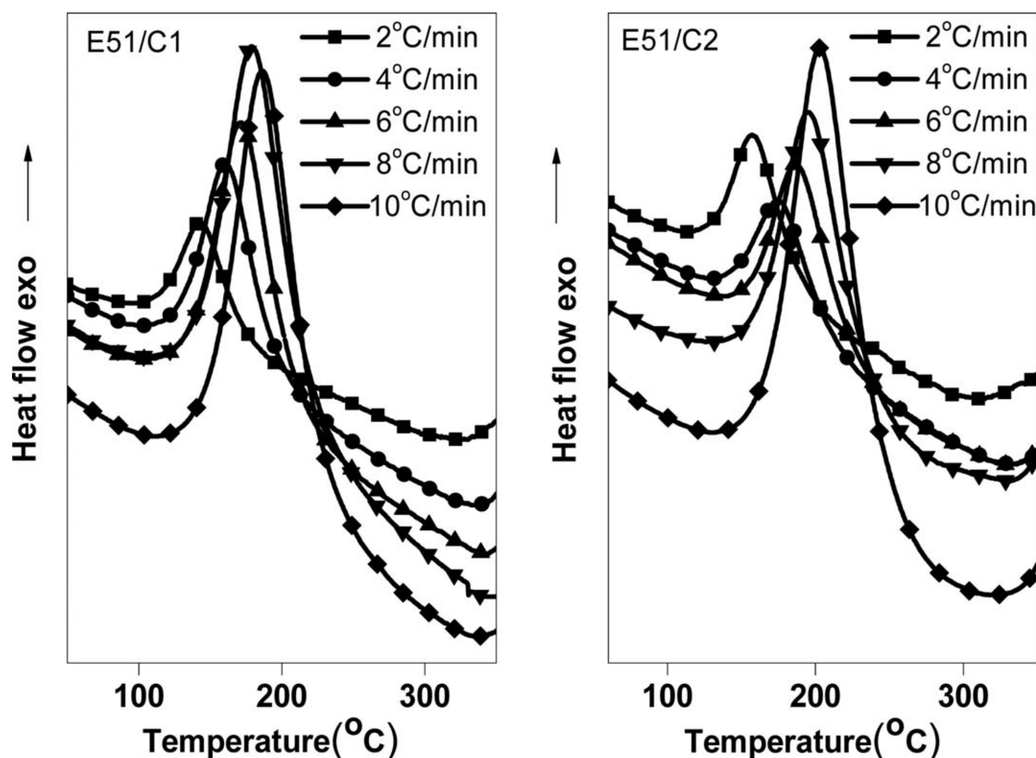

Figure 2. Dynamic DSC thermograms for the **E-51/C1** and **E-51/C2** systems at heating rates of 2, 4, 6, 8, 10°C/min.

129.66, 128.84, 127.85, 124.44, 120.91, 116.54, 0.41 ppm. ^{29}Si-NMR (60 MHz, $CDCl_3$, δ): −10.33. High-resolution mass spectrometry (HRMS; EI, *m/z*): $[M + H]^+$ calcd. for $C_{26}H_{28}N_2OSi_2$, 440.1740; found, 440.1745; Fourier transform infrared spectra (FTIR; KBr, cm^{-1}): 3453.71, 3370.84, 3219.12, 3067.29, 3046.72, 3021.36, 2958.08, 1292.07, 1254.89, 1171.45, 1056.88, 892.79, 698.33.

C2 (4,4′-(1,3-Dimet hyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine)): ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.52 (d, J = 6.4 Hz, 4H, Ar H), 7.39–7.27 (m, 10H, Ar H), 6.64 (d, J = 8.3 Hz, 4H, Ar H), 3.69 (s, 4H; NH), 0.51 (s, 6H; CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 147.79, 138.65, 135.53, 134.09, 129.31, 127.63, 125.85, 114.45, −0.26 ppm. ^{29}Si-NMR (60 MHz, $CDCl_3$, δ): −10.77 ppm. HRMS (EI, *m/z*): $[M + H]^+$ calcd. for $C_{26}H_{28}N_2OSi_2$, 440.1740; found, 440.1746. FTIR (KBr, cm^{-1}): 3380, 3018, 2957, 1619, 1597, 1505, 1427, 1271, 1256, 1115, 1050, 821, 787, 731.

Measurement

The ^{1}H-NMR and ^{13}C-NMR were measured with a BRUKER AVANCE 400 MHz NMR spectrometer in deuterated chloroform. ^{29}Si-NMR was evaluated on a Bruker DMX 300MHz

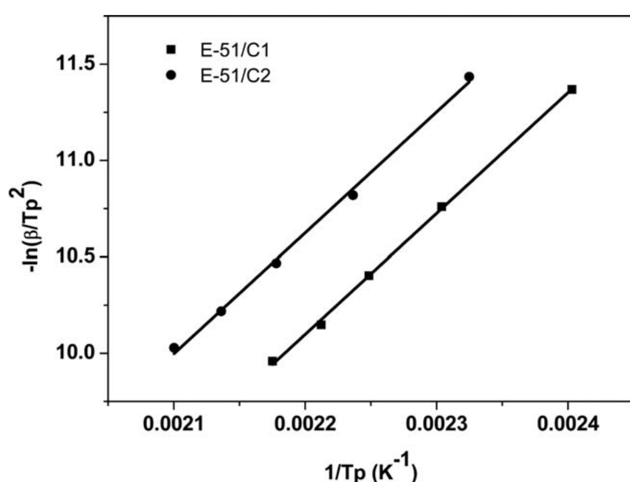

Figure 3. Plot for determination of ΔE and A.

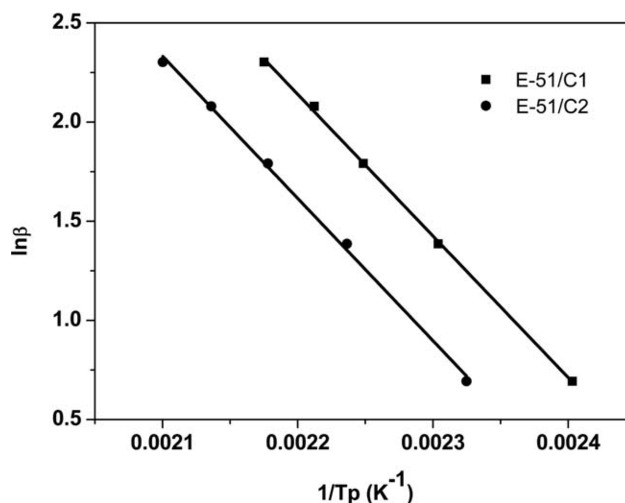

Figure 4. Plot for determination of n.

Table I. Characteristic Temperatures (°C) and Enthalpy Changes (ΔH, J/g) of Cure Exotherms for **E-51/C1** and **E-51/C2** at Different Heating Rates (β, °C/min)

	E51/C1				E51/C2			
β	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
2	96.5	143.0	189.1	233	87.8	157.2	232.1	296
4	97.7	160.9	216.7	248	97.4	173.8	232.1	307
6	115.2	171.6	228.7	229	106.7	186.3	272.8	267
8	118.2	178.9	235.8	244	112.8	195.1	288.4	287
10	122.9	186.6	251.8	233	122.2	202.5	307.6	271

spectrometer with deuterated chloroform as solvent. FTIR were conducted on a BRUKER TENSOR-27 FTIR spectrometer at room temperature in the range of 4000–400 cm^{-1}. HRMS were determined by using Waters Micromass GCT, EI as ionization source.

Differential scanning calorimetry (DSC) was performed on a SII EXSTAR DSC6200 under nitrogen atmosphere (100 mL/min) at heating rates of 2, 4, 6, 8, 10°C/min, respectively, using 5 mg samples. The sample of epoxy resin **E-51** and curing agent **C1** or **C2** was mixed homogeneously according to the molar ratio of epoxy group and **N-H** in 1 : 1. For measuring the glass transition temperatures (Tg) of the cured epoxy resins, the samples were first cured in the oven, then heated from 30 to 350°C at a heating rate of 10°C/min, cooled down to room temperature at the same rate to eliminate the thermal history. Then, the samples were heated to 350°C again.

Thermogravimetric analysis (TGA) was run on a STA7300 thermal analyzer at a heating rate of 10°C/min in nitrogen.

RESULTS AND DISCUSSION

Synthesis and Characterization of C1 and C2

C2 (4,4′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine)) was first synthesized in 1986 and used as an intermediate to generate disiloxanediyl diisocyanate.[21] In this work, we slightly modified the literature method to improve the synthetic yield. By decreasing the ratio of Me_3SiCl in reactants, replacing the homocondensation reaction of amino silanols with the lithium halogen exchange reaction and coupling reaction, the **C2** was synthesized in 64% isolated yield, which is increased by 10% from that of the literature method.[21] The synthetic schemes of diamino disiloxanes **C1** and **C2** are shown in Figure 1. Thus, bromoaniline reacted directly with chlorotrimethylsilane to give compounds **2a** or **2b** by elimination HCl in the first step. According to the method of Weisenfeld[21] and Milano *et al.*,[22] the treatment of **2a** and **2b** with MeMgCl and then Me_3SiCl gave **3a** and **3b**, respectively. Then the sequenced halogen lithium exchange reactions of **3a** or **3b** with *n*-BuLi, coupling reaction of the lithiated intermediates with 1,3-dichloro-1,3-dimethyl-1,3-diphenyl-disiloxane, and deprotection reaction of trimethylsilyl group produced the final products **C1** and **C2** in yield of 62% and 64%, respectively. The chemical structures of these products were characterized with ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, and HRMS. The disiloxanes have good solubility in common organic solvents such as THF, acetone, dichloromethane, acetic ether, and *n*-hexane.

Curing Reaction Kinetics

In previous studies about epoxy resins cured by silicon-containing amine compounds, the mainly used molecules are siloxane polymers or oligomers with relatively high molecular weights, which generally suffered from incompatibility. The monomer disiloxanes **C1** and **C2** have low molecular weights, and their structures of terminal aromatic amine groups are similar as those of DDM and DDS, which may benefit for their compatibility and reactivity with epoxy resins. The preliminary test on using them as epoxy resin curing agents confirmed our speculation. Then we further investigated the curing reaction kinetics using **C1** and **C2** as curing agents of **E-51** epoxy resin, respectively (Figure 2).

There are several methods on kinetics study such as FTIR, TMA, and DSC.[23] DSC is the frequently used method due to lower dosage and higher accuracy. In the DSC reaction kinetic practices, the heat release from DSC experiments is proportional to the reaction degree (fractional conversion/reaction rate). Therefore, the heat flow collected from DSC is assumed to obey the following expression:

$$\alpha=\frac{\int_{o}^{t}\frac{dH}{dt}dt}{\Delta H} \tag{1}$$

where dH/dt represents the DSC heat flow, t is the reaction time, ΔH is the overall reaction heat, α is the reaction degree (conversion rate).[24–27] From eq. (1), various kinds of curing kinetics models can be obtained to imitate the conversion rate

Table II. Curing Kinetic Parameters of **E-51/C1** and **E-51/C2** Using Kissinger Method

Samples	ΔE (KJ mol^{-1})	A (s^{-1})	n	Curing model
E-51/C1	52.13	2.51×10^5	0.88	$\gamma = 2.51 \times 10^5 \exp(-52.13/RT)(1-\alpha)^{0.88}$
E-51/C2	52.15	1.49×10^5	0.87	$\gamma = 1.49 \times 10^5 \exp(-52.15/RT)(1-\alpha)^{0.87}$

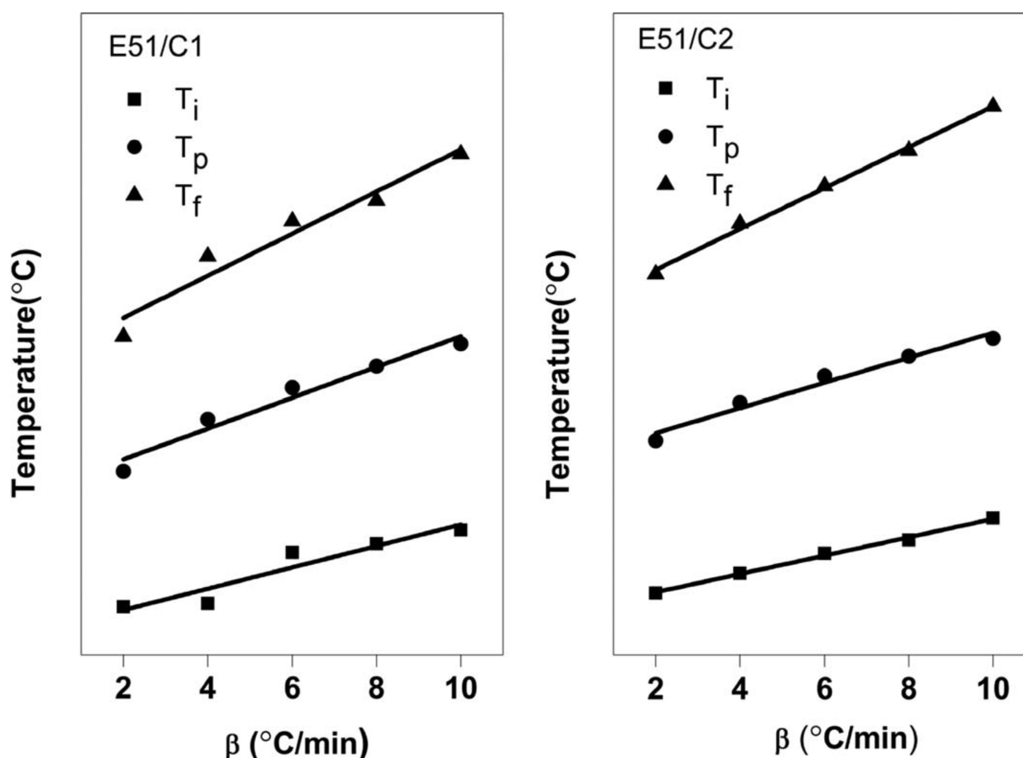

Figure 5. Plots for determination of curing process.

of epoxy resins, among which the *n*th–order curing model[28] and autocatalytic Kamal model[29,30] are the most commonly adopted. In this work, the *n*th-order curing model was used:

$$\gamma = \frac{d\alpha}{dt} = K(T)\,(1-\alpha)^n \tag{2}$$

where, α is the conversion ratio, n is the reaction order, $K(T)$ represents the rate constant related to temperature, calculated by Arrhenius equation:

$$K(T) = A\exp\left(-\frac{\Delta E}{RT}\right)$$

Thus, the *n*th-order curing model (2) can be described as eq. (3):

$$\gamma = \frac{d\alpha}{dt}\,A\exp\left(-\frac{\Delta E}{RT}\right)\,(1-\alpha)^n \tag{3}$$

where A is the pre-exponential, T is the thermodynamic temperature. ΔE is the activation energy. R is the ideal gas constant, 8.3144 J mol^{-1} K^{-1}.

Activation energy (ΔE) can be calculated in Kissinger's method assuming that the maximum rate of curing reaction occurred in the peak temperature of exothermic reaction and the reaction order n remained unchanged during the curing process.

Table III. Characteristic Temperature of **E-51/C1** and **E-51/C2** by Liner Relationship of T and β

Samples	T_i^i (°C)	T_p^i (°C)	T_f^i (°C)
E-51/C1	88	136	181
E-51/C2	80	149	215

Kissinger's method is expressed as eq. (4):

$$\ln\left(\frac{\beta}{T_p^2}\right)=\ln\left(\frac{AR}{\Delta E}\right)-\frac{\Delta E}{RT_p} \tag{4}$$

where, β is the heating rate, T_p is the thermodynamic peak temperature, ΔE is the activation energy, which can be obtained from the slope of $-\ln(\beta/T_p{}^2)$ versus $1/T_p$ (Figure 3).

Also, pre-exponential (A) can be calculated as eq. (4) from the intercept of $-\ln(\beta/T_p{}^2)$ versus $1/T_p$ (Figure 3).

The curing reaction order (n) can be gained in Crane method depicted as eq. (5):

$$\frac{d(\ln\beta)}{d\left(\frac{1}{T_p}\right)}=-\left(\frac{\Delta E}{nR}+2T_P\right) \tag{5}$$

where ΔE is activation energy calculated by Kissinger's method, n can be obtained from the slope of $\ln\beta$ versus $1/T_p$ (Figure 4) when $\Delta E/n$R is far greater than $2T_p$.

The non-isothermal DSC thermograms of **E-51/C1** and **E-51/C2** obtained at different heating rates are shown in Figure 2, the corresponding characteristic temperatures and the enthalpy changes of the curing reaction are summarized in Table I. It can be found that the exothermic characteristic temperatures (T_i, T_p, T_f) shift to higher with the heating rates increasing for both **E-51/C1** and **E-51/C2** systems. Furthermore, the shapes of peaks gradually become sharper. From Table I, the enthalpy changes have maximum values at the heating rate of 10°C/min for **E-51/C1** and **E-51/C2** systems, in other words, the systems have the highest curing degree when heated at 10°C/min.

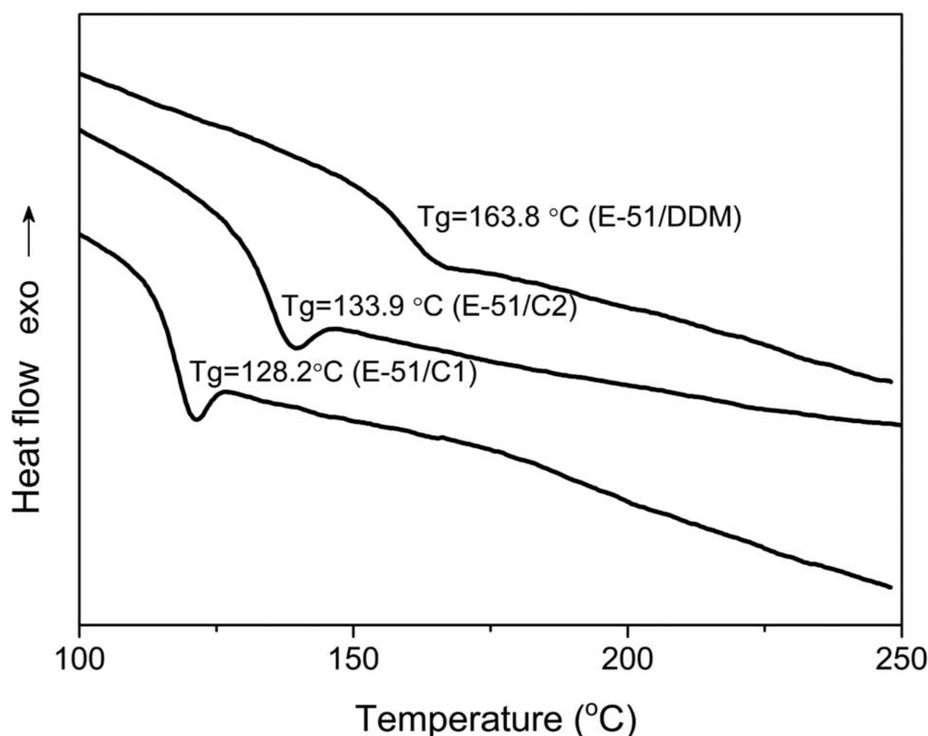

Figure 6. The glass transition temperatures of epoxy resin cured by DDM, **C1,** and **C2.**

Figures 3 and 4 are the relationship curves of $1/T_p$ versus $-\ln(\beta/T_p^2)$ and $\ln\beta$, respectively. The curing reaction kinetic parameters ΔE, A, and n obtained from the plots are summarized in Table II. The values of ΔE for **E-51/C1** and **E-51/C2** are 52.13 KJ mol^{-1} and 52.15 KJ mol^{-1}, respectively. This fact suggests that the position of —NH_2 group in **C1** and **C2** has negligible influence on their curing reactivity. The curing reaction orders n are 0.88 and 0.87 for **E-51/C1** and **E-51/C2**, respectively, illustrating that the curing reactions may proceed complicatedly. The pre-exponentials A of **E-51/C1** is 2.51×10^5 s^{-1} and 1.49×10^5 s^{-1} for **E-51/C2**, indicating that **E-51/C1** system is more active than **E-51/C2** system when curing reaction occurs.

In view of the curing kinetic parameters above, the curing models are summarized in Table II. The systems of **E-51/C1** and **E-51/C2** have almost the same curing model.

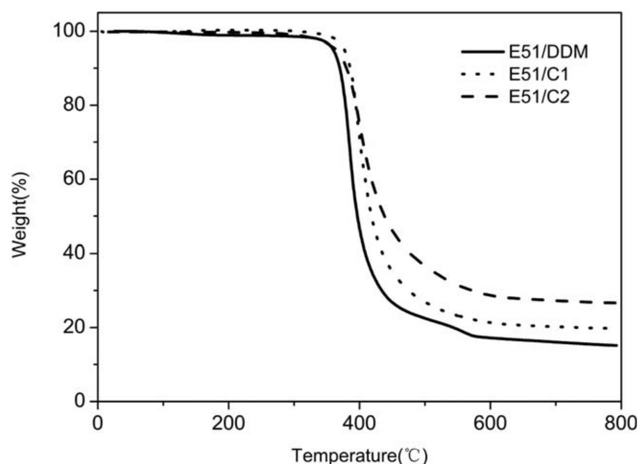

Figure 7. TGA thermograms of epoxy resin cured by DDM, **C1,** and **C2.**

Initial curing temperature T_i^i, peak temperature T_p^i, and final temperature T_f^i versus diverse heating rates β are plotted as shown in Figure 5. When extrapolating $\beta = 0$, T_i^i, T_p^i, T_f^i can be obtained and shown in Table III. From Table III, T_i^i of **E-51/C1** is close to that of **E-51/C2**, T_p^i and T_f^i are lower than those of **E-51/C2**, this is consistent with the result above that **E-51/C1** has more active spots, the maximum curing rate could appear at relative low temperature.

Thermal Properties of Cured Epoxy Resin

As we know, Tg is affected both by backbone rigidity of the thermosetting resins and by crosslink density, reflected the temperature of mobility of chain segments. Introduction of rigid groups into the backbone of the cured polymers or increase of crosslink density can result in the increase of Tg. Figure 6 shows the DSC charts of epoxy resins cured by DDM (sample for reference), **C1** and **C2**, respectively, and from which Tg of each sample can be obtained. Both Tg of **E-51/C1** and **E-51/C2** curing system are lower than that of **E-51/DDM** system, indicating the introduction of —Si—O—Si— flexible segment decreases chain rigidity. Tg of **E-51/C1** is lower than that of **E51/C2**, this fact may be explained as followings, para-NH_2 groups in **C2** make the molecule have better structure regularity than **C1.**

Table IV. Thermal Stability Data of Different Cured System

Samples	T_d (°C)	$T_{5\%}$ (°C)	Char (%)
E-51/DDM	360.1	359.9	15.1
E-51/C1	370.3	371.8	19.4
E-51/C2	363.7	363.9	26.6

Figure 7 exhibits the TGA scans of **E-51**/DDM, **E-51/C1,** and **E-51/C2**, and the results are summarized in Table IV. It is interesting to find that both T_d and $T_{5\%}$ are in the order of **E-51/C1** > **E-51/C2** > **E-51**/DDM. **E-51/C1** and **E-51**/DDM have the closed $T_{5\%}$, and **E-51/C2** has the highest $T_{5\%}$, which is higher than that of **E-51/C1** by 20°C. The result indicates an improvement on the thermal stability of the network cured by new curing agents. Considering the only difference between **C1** and **C2** is the position of substituent —NH_2 groups, the result that the **E51/C2** has higher $T_{5\%}$ may be explained from their different compact arrangement caused by different structure regularity.

CONCLUSIONS

Two diamino disiloxanes (**C1** and **C2**) were synthesized and used as the new curing agents of diglycidyl ether of bisphenol-A epoxy resin (**E-51**). The curing kinetics were studied by DSC using Kissiger's method and Crane's method. The systems of **E-51/C1** and **E-51/C2** exhibit the same curing mechanism and show similar activation energy. The pre-exponential (A) of **E-51/C1** system is higher than that of **E-51/C2** system. The reaction orders of **E-51/C1** and **E-51/C2** are both less than 1, implying that curing reaction with the new curing agents is complicated. The epoxy resins cured by **C1** and **C2** show improved thermal stability and higher char residue than **E51**/DDM.

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