

# Study of Curing Kinetics of Siloxane-Modified DGEBA Epoxy Resins

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## SYNOPSIS

The curing kinetics of some epoxy resins of siloxane-modified diglycidyl ether of bisphenol A (ESDG) were studied by the dynamic differential scanning calorimetry method. The curing kinetic parameters are calculated by using the Ozawa method and are further verified by the Kissinger method. The results indicate a first-order curing kinetics for ESDG. The curing characteristics of ESDG have been observed to be influenced by the phenyl content of the siloxanes. The curing activation energies in the range of 80.3 to 88.1 KJ mol<sup>-1</sup> are obtained for these ESDG. The thermograms indicate that the ESDG exhibits a slightly higher initial temperature, as well as peak temperature, but a significantly narrower curing temperature range. The reason for the narrow curing temperature range may due to the low concentration of —OH group in the ESDG, and thus little process of ether linkage is taken place in the curing process. This suggests that ESDG can be cured more efficiently than the normal DGEBA epoxy resins. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Functional siloxane oligomers are often being used as the epoxy modifiers.<sup>1-10</sup> Siloxane has been known to possess many unique properties, such as low glass transition temperature, low surface energy, high resistance to thermal oxidation, and imparting non-flammability to the resins.<sup>11-12</sup> The epoxy resins become brittle due to the self-polymerization that occurs during the curing process, which is inherited from its formation of a highly crosslinked networks.<sup>13</sup> In order to obtain epoxy resins suitable for high-tech applications, such as print circuit boards, electronic components, and aerospace composites and coatings,<sup>13-15</sup> a toughening agent is often required to be added during their formulation. Among a large variety of possible toughening agents, various flexible siloxane oligomers offer promising prospects.<sup>6-10</sup> However, the epoxy resins of a diglycidyl ether of the bis-phenol A (DGEBA) are carbon-based, whereas the siloxane oligomers are silicone-based and are hence immiscible with each other. Even the siloxane oligomers containing organic

moieties such as methylphenyl groups in the poly-methylphenyl siloxane (PMPS) or dimethyl groups in the polydimethyl siloxane (PDMS) are also immiscible with the carbon-based epoxy resins.<sup>16</sup> The end results of blending of such components often depend on the state of the art. Furthermore, the curing optimum conditions are often required to be compromised due to the different requirements of curing temperature and curing agent for such different components.

In the course of previous investigations aimed at achieving improvements in the thermal stability and impact strength of the epoxy resins, incorporation of siloxane oligomer into the DGEBA epoxy resin as a nonreactive segment in the epoxy structure has been achieved.<sup>9,10</sup> This epoxy resin of siloxane-modified DGEBA (abbreviated as ESDG) exhibited remarkable molecular properties, such as lowering of the glass transition temperature ( $T_g$ ), improved the thermal stability and nonflammability and a four-fold increase in the impact strength.<sup>9,10</sup>

Since these ESDG are expected to be used along with the conventional epoxy resins with the established curing process, the curing behaviors of the ESDG are hence investigated and compared with the unmodified DGEBA epoxy resins, namely, Epi-

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kotes 1001 and 1004. These ESDGs provide better observations of the siloxane effects on the curing behavior of the specimen because siloxane is a part of the epoxy structure and not merely one of the ingredients in the siloxane/epoxy coblended state. Notably, this approach of using a single component for specimen preparation eliminates the elaborate mixing of incompatible siloxane with epoxy resin and hence provides better understanding of the siloxane effects on the curing kinetics.

The objectives of the present study are to analyze the curing behavior of various epoxy resins of siloxane-modified DGEBA ESDG and to study the effects of structurally different siloxane segments in the epoxy resin on the curing kinetics. The comparison of ESDG with the conventional Epikote series epoxy resins (DGEBA) is made for the purpose of obtaining a better understanding of the curing behavior as a function of curing process for both the resin systems. A variety of ESDG, obtained by modifying the Epikote 1001 epoxy resin with linear PMPS and PDMS, have been used in this study. The kinetic investigations are carried out by using differential scanning calorimetry (DSC) in a dynamic mode, and the kinetic data are evaluated by following the Ozawa<sup>17,18</sup> and Kissinger<sup>19</sup> methods.

## EXPERIMENTAL

### Materials

Methoxy-terminated PMPS of DC-3074 and DC-3037 and hydroxyl-terminated PDMS of Q2-1484 were gifts from Dow Corning Co., Taiwan, with product descriptions as shown in Table I. Epoxy resins of DGEBA (Epikotes 1001 and 1004) were procured from Shell Oil Co. and were used directly without further purification. Tetraisopropyl titanate (TPT) was supplied by Du Pont Co. and used directly as catalyst. Solvents were analytical grade and were used directly.

### Synthesis of Epoxy Resins of Siloxane-modified DGEBA (ESDG)

The epoxy resins of siloxane-modified DGEBA (ESDG) were synthesized by a hot melt polycondensation method.

A typical procedure is described in the following. A 2 L three-neck round-bottom flask, equipped with mechanical stirring and thermometer, was charged with 700 g of Epikote 1001 epoxy resin and heated until the epoxy resin melted. The mixture of siloxane (300 g of DC-3074) and TPT catalyst (1.5 g) was added at this stage while maintaining the reaction temperature at 130°C for 2 h. Completion of the reaction was confirmed by noting the disappearance of the infrared (IR) active vibrational mode of the Si-OCH<sub>3</sub> functional group of siloxane in the reaction mixture and was further confirmed by titrimetric determination of the epoxy equivalent weight (EEW). The IR spectrum of ESDG-7430 (cast on NaCl plate) exhibits major absorptions (cm<sup>-1</sup>) at 3418 (OH), 2956, 1259, 805 (Si-CH<sub>3</sub>), 1590, 1427, 696, 487 (Si-phenyl), 1381 [(CH<sub>3</sub>)<sub>2</sub>C], 1108 (Si-O-C), 1085-1038 (Si-O-Si), and 912 (oxirane). The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) shows major chemical shifts (δ, in ppm from TMS = 0) at 7.59, 7.24 (Si-phenyl), 7.13, 6.82 (C-phenyl-), 3.35 [oxirane (CH)], 2.89, 2.74 [oxirane (CH<sub>2</sub>)], 1.65 [(CH<sub>3</sub>)<sub>2</sub>C], and 0.21 (Si-CH<sub>3</sub>). The <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) shows major peaks (δ, in ppm from TMS = 0) at 156.17, 143.53, 127.68, 113.91 (C-phenyl), 134.00, 130.00, 127.20, 127.20 (Si-phenyl), 50.13, 44.67 (oxirane), and 41.61, 30.96 [(CH<sub>3</sub>)<sub>2</sub>C].

The structures of these ESDG were determined by using IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopies, the details of which have been described in the previous reports.<sup>9-10</sup>

### Instrument Measurements

Infrared spectra of the ESDG were recorded on Jasco IR-700 spectrophotometer. A small amount of sam-

**Table I** The Properties of some PMPS and PDMS Oligomers

Code	Type	Phenyl <sup>a</sup> (%) <sup>c</sup>	T <sub>g</sub> (°C) <sup>b</sup>	M <sub>w</sub>	Crosslinking Density <sup>c</sup>
DC-3074	methyl phenyl	50	-63	1800	1.8
DC-3037	methyl phenyl	23	-100	1850	1.8
Q2-1484	dimethyl	0	-112	—	2.0

Code, type, M<sub>w</sub>, and cross-linking density were provided by Dow Corning on data sheets.

<sup>a</sup> Phenyl content was measured by <sup>1</sup>H NMR.

<sup>b</sup> T<sub>g</sub> was measured by DSC at a scanning rate of 10°C/min.

<sup>c</sup> Density of 1.0 is defined as complete cross-linking, and density of 2.0 is a linear oligomer (from Dow Corning information).

ple was dissolved in appropriate solvent and cast on NaCl plate to enable the IR measurements.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-300 WB FT-NMR with deuterated  $\text{CDCl}_3$  solvent.

A Physical Spectra P1000 HPLC system, equipped with a column series containing four Waters (Ultrastayragel) columns  $300 \times 7.7$  mm (100, 500,  $10^3$ ,  $10^4$  Å in a series), was used for the GPC analysis. Tetrahydrofuran (THF) was employed as the mobile phase with a flow rate of 1 mL/min. The eluents were monitored with a Spectra 100 UV detector operating at the 254 nm. A series of 10 polystyrene standards was used to establish a calibration curve of logarithm (molecular weight) versus retention time, in order to obtain the relative molecular weight of ESDG copolymers to the standards.

The HCl/pyridine method<sup>20</sup> was used to determine the epoxy equivalent weights. Samples weighing 1–1.5 g, sufficient to determine the EEW value, were used for this purpose.

### Measurement of the Curing Kinetics

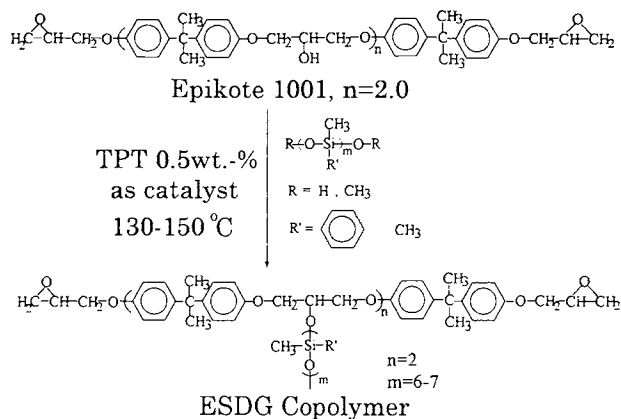
Samples for the measuring the thermal data were prepared by mixing epoxy resin with 2 wt % curing agent, followed by milling, to obtain a fine powder. 5–10 mg of this powder was then placed in the DSC cell, and the normal scanning procedures were carried out with a Du Pont 9000 Thermal Analyzer, coupled with a TA 2000 data analysis system. A dynamic DSC scanning was carried out up to  $300^\circ\text{C}$  at a few discrete selected heating rates, 2.5, 5.0, 10, and  $20^\circ\text{C}/\text{min}$ , under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Preparation of Epoxy Resins of Siloxane-modified DGEBA (ESDG)

The general preparation procedures and curing conditions are shown in Figure 1. Preparation of the ESDG has been carried out by polycondensation of the hydroxyl groups in Epikote 1001 epoxy resin and either with the methoxy-terminated groups of the PMPS or hydroxyl groups in PDMS. The stripping of methanol or water in these preparations require high temperatures. The details of these procedures have been described previously.<sup>9,10</sup>

The molecular properties of these ESDG are listed in Table II. It can be seen that the ESDG show a moderate increase in the epoxy equivalent weight (EEW) and exhibit a higher molecular weight



**Figure 1** Preparation of siloxane-modified DGEBA epoxy resins.

( $M_w$ ) with a wider molecular distribution (MWD) as compared to the unmodified resin, indicating that ESDG is a larger epoxy resin with siloxane oligomers incorporated in the structure. These molecular properties and their effects on the curing kinetics will be discussed in this paper.

### Theoretical Background

DSC has been used extensively for the curing kinetic characterizations of thermosetting materials, such as epoxides,<sup>21,22</sup> unsaturated polyesters,<sup>23</sup> and polyurethanes.<sup>24</sup> The data from dynamic DSC measurements are analyzed by following the kinetic equation [eq. (1)]:

$$r = dx/dt = \beta dx/dT = k(T)f(x) = k(T)(1-x)^n \quad (1)$$

Temperature dependence of the constant  $k(T)$  may be described by Arrhenius expression, as shown in eq. (2)

$$k(T) = A \exp(-E_a/RT) \quad (2)$$

where  $f(x)$  is the kinetic function;  $x$ , fraction conversion;  $k(T)$ , rate constant;  $\beta$ , heating rate ( $^\circ\text{C}/\text{min}$ );  $E_a$ , activation energy (J/mol);  $A$ , preexponential factor;  $R$ , gas constant; and  $T$ , the temperature (K).

Combining eqs. (1) and (2), we obtain, as shown in eq. (3),

$$dx/dt = \beta(dx/dT) = A \exp(-E_a/RT)(1-x)^n \quad (3)$$

Since the maximum rate occurs when  $d(dx/dt)/dt$  is zero, differentiation of eq. (3) with respect to time and equating the resulting expression with zero gives:

**Table II Fundamental Properties of Epoxy Resins of Siloxane-modified DGEBA**

Epoxy Resins	Siloxane Content (wt %)	$M_n^a$	$M_w^a$	MWD <sup>a</sup>	$T_g$ (°C) <sup>b</sup>		EEW <sup>c</sup>
					Uncured	Cured	
Epikote 1001	0	1650	2640	1.6	33–40	99	522
Epikote 1004	0	2600	4680	1.8	50–60	98	840
ESDG-3710 <sup>d</sup>	10	1780	3160	1.8	30–37	99	670
ESDG-3720 <sup>d</sup>	20	2130	13550	6.4	29–35	96	710
ESDG-3730 <sup>d</sup>	30	3064	40300	13.1	28–34	88	834
ESDG-3740 <sup>d</sup>	40	3024	42940	13.5	27–33	86	960
ESDG-7430 <sup>e</sup>	30	2770	18790	6.8	28–44	99	866
ESDG-8430 <sup>f</sup>	30	3767	67040	17.8	36–44	97	822

<sup>a</sup> Based on polystyrene.

<sup>b</sup>  $T_g$  was measured by DSC at a scanning rate of 10°C/min. The first and last values represent the initial and final temperature in the baseline changed for the measurement of  $T_g$ .

<sup>c</sup> EEW was determined by the of HCl/pyridine method.

<sup>d</sup> The notation is as follows: ESDG is the abbreviation of the epoxy resins of siloxane-modified DGEBA; the first two digits indicate the siloxane origin, and the last two digits represent the wt % of siloxane. For example, ESDG-37Y (Y = 10, 20, 30, and 40) is the epoxy resin of PMPS-modified DGEBA containing 10, 20, 30, and 40 wt % DC-3037.

<sup>e</sup> ESDG-7430 is the epoxy resin of PMPS-modified DGEBA containing 30 wt % DC-3074.

<sup>f</sup> ESDG-8430 is the epoxy resin of PDMS-modified DGEBA containing 30 wt % Q2-1484.

$$\beta E_a/RT_p^2 = An(1-x)p^{n-1}\exp(-E_a/RT_p) \quad (4)$$

where  $T_p$  is the maximum-rate temperature (peak temperature in the DSC thermogram). The Kissinger method<sup>19</sup> assumes that the product  $n(1-x)p^{n-1}$  is independent of  $\beta$ , so that eqs. (4) and (5) can be written in the natural logarithm form as shown in

$$-\ln(\beta/T_p^2) = \ln(E_a/R) - \ln(An) - (n-1)\ln(1-x)_p + E_a/RT_p \quad (5)$$

$$-\ln(\beta/T_p^2) = -\ln(AR/E_a) + E_a/RT_p \quad (6)$$

The above expressions yield linear plots of  $-\ln(\beta/T_p^2)$  against  $1/T_p$ , and the activation energy can be obtained from the slope of the corresponding straight line. Another theoretical treatment, namely, the Ozawa method<sup>17-18</sup> can also be applied to the thermal data. The method has been modified by Doyle<sup>25</sup> and is shown in the following:

$$-\ln \beta_1 - 1.052E_a/RT_1 = -\ln \beta_2 - 1.052E_a/RT_2 = \dots \quad (7)$$

where  $E_a$  is an activation energy (J/mol);  $R$ , the gas constant (8.31441 J/mol K); and  $\beta$  (or  $dT/dt$ ), the heating rate (°C/min).

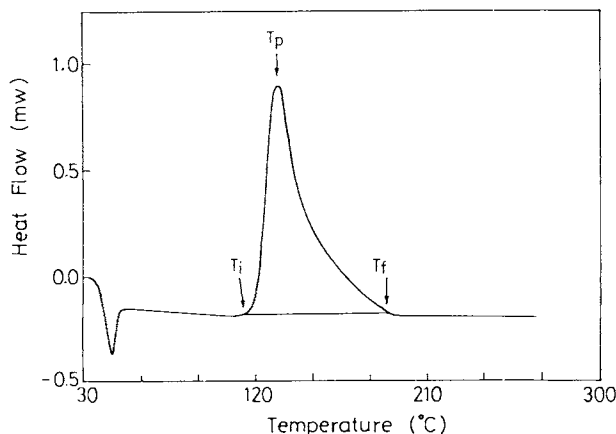
The activation energy for the curing of epoxy resin can be obtained by plotting natural logarithm  $\beta$  against the reciprocal of the temperature at the

reacted maximum temperature and using the eq. (8), as shown in

$$E_a = -R/1.052 \times \Delta \ln(\beta)/\Delta(1/T_p) \quad (8)$$

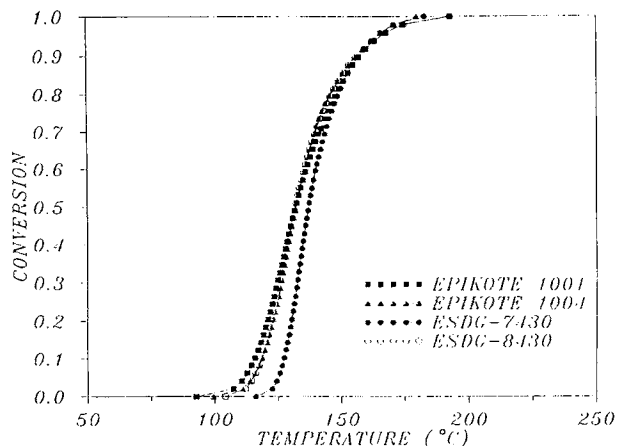
### Curing Kinetics of ESDG

The curing behavior of epoxy resin depends upon the curing conditions. The curing condition can greatly affect not only the curing kinetics but also the physical properties of the resulting material. There is a large variety of factors, such as epoxy structure and its EEW, molecular weight and its distribution, properties of curing agent, and many others<sup>26-27</sup> that influence the curing kinetics. In the present study, only one epoxy resin with a constant amount of a curing agent was used in order to simplify the system for the kinetic study. A typical DSC thermogram for ESDG-7430 with a dynamic mode of the heating rate of 2.5°C/min is shown in Figure 2, where  $T_i$  is the initial curing temperature,  $T_p$  is the peak curing temperature, and  $T_f$  is the completing curing temperature. A single exothermic peak was observed for the epoxy self-polymerization process. The area under the DSC curve represents the magnitude of exothermic heat. The curing characteristics of the ESDG and epoxy resins sans siloxane modifications of Epikotes 1001 and 1004 are summarized in Table III. A higher initial reaction temperature but a narrower temperature range than Epikote 1001 was observed for ESDG, which may be attributed to the necessity of higher temperature



**Figure 2** Dynamic DSC thermograms of ESDG-7430 at a heating rate of 2.5°C/min.

that is required for the larger molecules with attached siloxane segments to align the oxirane groups for self-polymerization and to lower probability of etherification.<sup>28</sup> The curing reaction rate of epoxy with curing agent is directly related to the probability of mutual diffusion of the reaction molecules. This probability generally decreases as the viscosity of the reaction mixture and the epoxy equivalent weight value of the epoxy increases.<sup>28</sup> In other words, the probability would decrease when foreign relative inactive substance are present in the reacting mixture. Since there are fewer epoxy groups in ESDG (with higher EEW values) than Epikote 1001, less energy is evolved during the curing process. The peak temperatures for Epikote 1001, ESDG-7430, ESDG-3730, and ESDG-8430 were observed to be 122, 133, 129, and 127°C, respectively, and their corresponding exothermic energies in (J/g) were 102, 75, 80, and 82 for the scanning rate of 2.5°C/min. The fractional conversion at various temperatures was calculated by the following equation:



**Figure 3** Fractional conversion as a function of temperature for the heating rate of 2.5°C/min of ESDG and DGEBA epoxy resins.

$$x = H_T/H_{\text{total}} \quad (9)$$

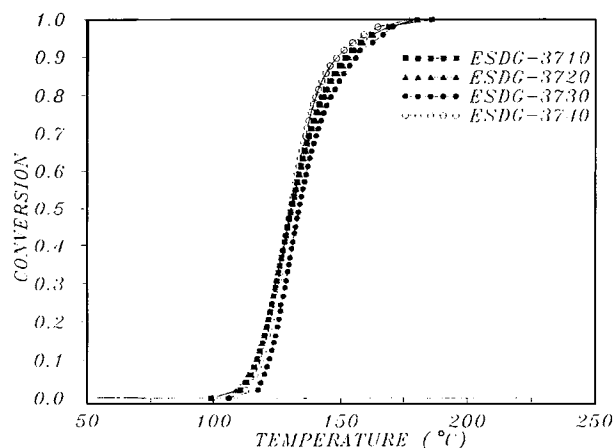
where  $H_{\text{total}}$  is the total amount of exothermic heat evolved, and  $H_T$  is the heat evolved at temperature  $T$ . Figure 3 shows the fractional conversion as a function of curing temperature for ESDG and reference epoxy resins. ESDG-7430 exhibited the lowest fractional conversion among the ESDG-8430, Epikote 1004, and Epikote 1001 at constant temperature. This result thus suggests that ESDG-7430, which contains more number of phenyl group (50 mol %) of DC-3074, may offer a steric hindrance in the curing process.

The curing characteristics in terms of fractional conversion as a function of curing temperature for a series of ESDG series containing of increasing amounts of siloxane oligomer (DC-3037) in epoxy resins are shown in Figure 4 (ESDG-37Y series, where Y is 10 to 40). A trend of slight increase in

**Table III** Typical Curing Characteristics of the ESDG from the DSC Measurements at a Heating Rate of 2.5°C/min

Epoxy Resins	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)	Curing Range (°C)	Curing Time (min)	$x_p^a$	$\Delta H$ (J/g)
Epikote 1001	92	122	193	101	40.4	0.25	102
Epikote 1004	97	126	180	83	33.2	0.31	69
ESDG-3710	99	123	185	86	34.4	0.27	94
ESDG-3720	100	124	185	85	34.0	0.31	89
ESDG-3730	106	129	180	74	29.6	0.35	80
ESDG-3740	106	127	178	72	28.8	0.39	68
ESDG-7430	116	133	185	69	27.6	0.33	75
ESDG-8430	104	127	195	91	36.4	0.37	82

<sup>a</sup> Conversion of peak temperature.



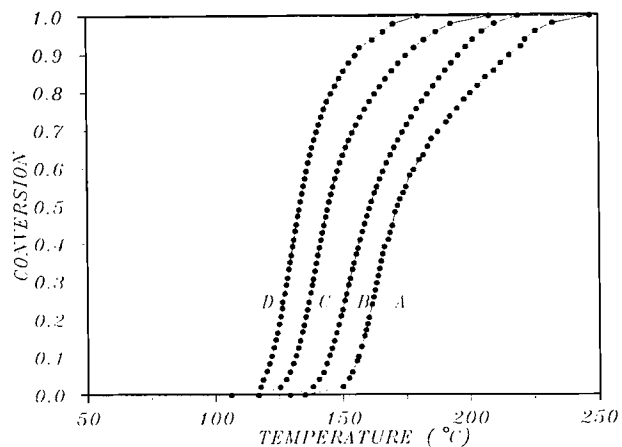
**Figure 4** Fractional conversion as a function of temperature for the heating rate of 2.5°C/min of DC-3037-modified Epikote 1001 with various siloxane contents.

the initial temperatures but lowering of the completing temperatures was observed for increasing contents of siloxane oligomers in the epoxy resins. In other words, at an initial lower conversion stage, the curing rate for ESDG-37Y, which contains a low DC-3037 content, was faster than that of high DC-3037 content; while in the high conversion stage, the curing reaction rate was slower for the lower DC-3037 content in the ESDG-37Y system. This phenomenon will be discussed as follows.

As mentioned before, in the present study, only a small amount of a curing agent (2.0 wt %) was used in the curing system for the kinetic study. Therefore, most reaction was the self-polymerization in the epoxy curing process. At the high temperature, the possible etherification reaction will occur between the epoxy ring and the —OH group in the epoxy itself. Mijovic and coworkers<sup>29</sup> have evidenced the epoxy-hydroxyl reaction for the curing reaction of *N,N,N',N'*-tetraglycidyl-4-4'-diaminodiphenyl methane (TGDDM) with diaminodiphenyl sulfone (DDS). Riccardi and Williams<sup>30</sup> have shown the etherification for curing reaction of DGEBA and DDS and indicated that the reaction was significant at temperature higher than 150°C. The possibility of etherification is enhanced with a stoichiometric excess of the epoxy compound. Bokare and Gandhi<sup>31</sup> and Macosko and Miller<sup>32</sup> have studied the kinetic effect of simultaneous etherification on the curing reaction of epoxides with amine.<sup>32</sup> The etherification reaction is to be significant only when an initial excess of epoxy over amine groups is assumed. Bokare and Gandhi<sup>31</sup> also reported that the epoxy conversion at gelation decreases when the etherification rate increases, i.e., the etherification accelerates the

gelation of the system. Since the ESDG were prepared from Epikote 1001 and with siloxane by polycondensation, the hydroxyl group content of ESDG is decreased with the increase of the incorporation of siloxane content. This is due mainly to the reacting sites for epoxy and siloxane were C—OH for epoxy resin and Si—OCH<sub>3</sub> or Si—OH for siloxane, respectively. For ESDG-3740, the concentration of —OH group presented in the curing system was rather low due to the 40 wt % of the siloxane in respect to 60 wt % of the epoxy resin. Hence, very little etherification between —OH group with epoxy group could occur. Table III shows the conversion for ESDG and reference epoxy resins at peak temperature. It can be clearly observed that the conversion was increased with the DC-3037 content increasing in the ESDG-37Y series. An other possible explanation for the faster curing rate at higher conversion for ESDG is due to the flexible ESDG, especially for high content of siloxane in ESDG. The flexible siloxane in ESDG lowers the *T<sub>g</sub>* of ESDG to around 27–44°C for all ESDG than 33–40°C for Epikote 1001 or 50–60°C for Epikote 1004, as shown in Table II. In a sense, the cross-linked epoxy network of ESDG is plasticized by the siloxane oligomeric molecules. Once the cure reaction reaches the gel point, the reacting species in the neat epoxy would have less molecular mobility than those modified by siloxane, as in the ESDG system. For this reason, the retardation effect on the epoxy cure of the ESDG was relatively small. The phenomenon has occurred in thermoplastic-epoxy blend system, such as polyether imide-TGDDM/DDS,<sup>33</sup> polycarbonate-TGDDM/DDS,<sup>34</sup> and polyether sulfone-DGEBA/DDS.<sup>28</sup>

Epoxy curing with narrower curing temperature range is desirable and is a curing property that is often sought for the epoxy resins. A narrower curing temperature range often means better curing and more stability during the process for making of specimens. Furthermore, epoxy resin with a narrow curing temperature range, along with a higher initial curing temperature, often imparts longer shelf life for the storage and transportation. Sometimes, the diffusion control<sup>35</sup> also indicates the system of the larger molecules; however, in this case, the effect may be due to the flexibility of the siloxane segment in the incorporated epoxy structure, which mobilizes the ESDG more easily during the curing process and the low possibility of etherification between —OH and epoxy groups. The *T<sub>p</sub>* data and curing times, presented in the Table III, also suggest better curing efficiency of the ESDG. Higher *T<sub>p</sub>*s and lower *T<sub>g</sub>*s represent better curing. Curing times have also been



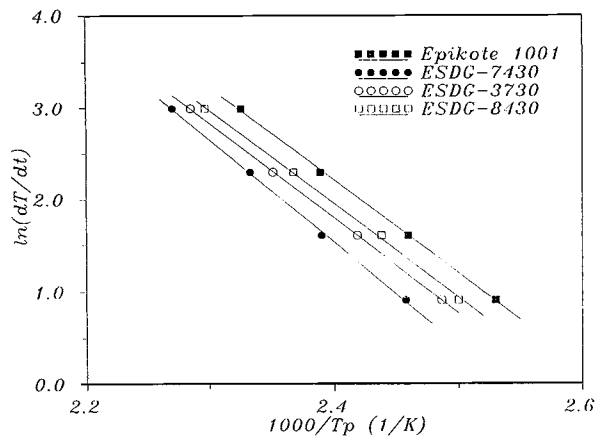
**Figure 5** Fractional conversion as a function of temperature for different heating rates of ESDG-3730. Curve A: 20°C/min. Curve B: 10°C/min. Curve C: 5°C/min. Curve D: 2.5°C/min.

observed to exhibit a decreasing trend with increasing siloxane contents (40.4 min for Epikote 1001 to 28.8 min for ESDG-3740). For the PDMS-incorporated ESDG-8430, a slight reduction in the curing range and curing time is indicated, which can be attributed to the phase separation in the ESDG-8430 and correlates well with the subsequent observation of its less effectiveness in impact strength improvement<sup>9,10</sup> as compared to that of the PMPS-modified ESDG. This DSC study on the  $T_i$ ,  $T_p$ , and  $T_s$  thus indicates that PMPS-modified epoxy resins are better than the PDMS-oligomer-modified epoxy resin. Apparently, the dimethylsilyl structure is less compatible with the BPA-based DGEBA epoxy resin than the methylphenylsilyl structure.

The overall curing behaviors of ESDG are quite similar to that of the DGEBA system but with better properties so that the ESDG can be comfortably cured, along with the DGEBA epoxy resins. This is significant since these modified series can be used in the industry without alternating the existing curing process, and yet offer the advantages of the siloxane oligomer and present a segment in the ESDG, such as better thermal stability and quadruple improvement in the impact strength.<sup>9,10</sup>

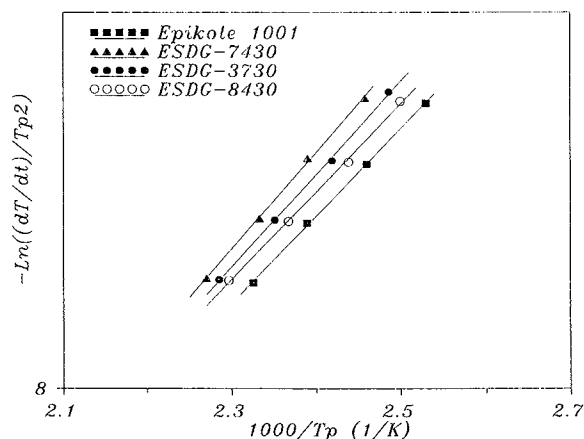
The fractional conversions of ESDG-3730 as a function of curing temperature, with heating rates of 2.5, 5, 10, and 20°C/min, respectively, are shown in Figure 5. From this figure, one noteworthy phenomenon has been observed: at a constant curing agent, the initial cure temperature and the temperature at a constant conversion increase with the increase of the heating rate. This result is similar to the other systems reports.<sup>36-38</sup>

A plot of  $\ln(\beta)$  versus  $1/T_p$  and  $-\ln(\beta/T_p^2)$  versus



**Figure 6** Determination of the  $E_a$  and  $\ln A$  values for ESDG resins by using the Ozawa's equation.

$1/T_p$ , according to eqs. (6) and (8), allows the determination of activation energies, which are shown in Figs. 6 and 7, respectively. A linear correlation was observed for each sample (shown in Fig. 6), and the constant magnitude of slopes for these samples indicates similar activation energies for the opening of the epoxy ring is concerned. This result means the ESDG and DGEBA have the same curing mechanism. The existence of activation energy for opening of the epoxy resin can be explained as follows. The samples used in the present study belong to a system that has been specifically designed and simplified for studying the kinetics of self-polymerization, with a minimum amount of curing agent. This system is set for conditions associated with either for zero or for the first kinetic order of reaction. To verify the result, the Kissinger treatment of the first order kinetics was applied. The linear correlation of the ESDG system with the Kissinger treatment, as



**Figure 7** Determination of the  $E_a$  and  $\ln A$  values for ESDG resins by using the Kissinger's equation.

**Table IV Kinetic Parameters of the ESDG Obtained by Using the Ozawa and Kissinger's Equations**

Epoxy	Ozawa			Kissinger		
	$E_a$ (KJ/mol)	ln A (min <sup>-1</sup> )	Regression	$E_a$ (KJ/mol)	ln A (min <sup>-1</sup> )	Regression
Epikote 1001	80.0	22.7	0.99969	77.5	21.7	0.99966
Epikote 1004	81.3	22.8	0.99922	78.0	22.0	0.98665
ESDG-3710	81.9	23.2	0.99906	79.2	22.2	0.99895
ESDG-3720	82.9	23.4	0.99916	80.3	22.4	0.99844
ESDG-3730	83.5	23.7	0.99998	82.0	22.6	0.99956
ESDG-3740	84.8	23.8	0.99385	82.3	22.9	0.99952
ESDG-7430	88.1	24.3	0.99947	85.6	23.4	0.99941
ESDG-8430	80.3	22.5	0.99944	77.6	21.4	0.99931

shown in Figure 7, confirms the first-order kinetics. The magnitudes of  $E_a$  and ln A for ESDG and DGEBA epoxy systems are calculated from Ozawa and Kissinger equations and are in good agreement, as shown in Table IV. The curing process of ESDG series can hence be assumed to follow a first-order mechanism, indicating that the siloxane segment in the epoxy structure is not participating during the cure, just like other epoxy systems.<sup>27</sup>

Although variations of a few KJ/mol in the activation energies for increasing siloxane contents in the ESDG-37Y series are small, the trend of increase in activation energy with increase in the siloxane content is clearly visible. The highest activation energy observed for ESDG-3740 is in accordance with the largest  $M_w$  values of the corresponding resin, as shown in Table II. The bulky ESDG-3740, as the molecular weight indicates, requires more energy to overcome as the steric hindrance of siloxane segments and induces a molecular motion during curing. The small increase in the curing activation energy with the increasing molecular weight have been observed<sup>39</sup> for the cyanated poly(ether sulfone)s of different molecular weights but the maintaining the same curing mechanism. Other reports such as Ohtsuga and coworkers<sup>40,41</sup> also have studied the curing kinetics of epoxy resin of *o*-cresol novlac (EOCN)<sup>40</sup> and urethane elastomers-modified epoxy resin<sup>41</sup> with various molecular distribution. Again, the activation energy increases as the molecular weight increases. Part of reason is due to the increasing rate of entangled molecular chain increased with melt viscosity; therefore, the molecular motion is decreased.

The higher activation energy for the epoxy resin containing siloxane (DC-3074) with a higher phenyl content is also reflected in the copolymeric structure of the corresponding resins, as a higher magnitude

of collision factor in A values as compared to the other modified epoxy resins (ESDG-3730 and ESDG-8430). However, the epoxy resin modified either with a linear siloxane of PMPS of DC-3074, DC-3037, or with PDMS of Q2-1484 in the weight ratio up to 30 wt % can be cured more efficiently due to the narrower temperature range in the curing conditions than the conventional DGEBA epoxy resins.

## CONCLUSIONS

ESDG and the conventional DGEBA epoxy resins have been observed to follow a similar curing pattern under the same curing process and curing agent. The slightly higher peak temperature ( $T_p$ ) exhibited by ESDG containing PMPS with a high phenyl content is offset by a significant narrowing of the curing range and hence can be cured more efficiently at the settings for conventional DGEBA system. The higher activation energy of the ESDG-7430 may be attributed to the steric hindrance of the bulky phenyl group of the siloxane oligomer in the epoxy resin.

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