Non-isothermal Cure Kinetics of Diglycidyl Ether of Bisphenol-A with Various Aromatic Diamines

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Cure kinetics of the reaction of diglycidyl ether of a bisphenol-A based epoxy resin (DGEBA) with aromatic diamines, such as 3,6-diaminocarbazole (DAC) and N-[7-(acetyl-4-aminoanilino)-9,9-dioctylfluoren-2-yl]-N'-4-aminophenyl acetamide (ADOAc) as curing agents have been studied by using non-isothermal differential scanning calorimetry (DSC). DAC was prepared according to literature and ADOAc was prepared via the reaction of 2,7-dibromo-9,9-dioctylfluorene with 4-aminoacetanilide in the presence of 10 mol% CuI and 20 mol% N,N’-dimethylethylene diamine(DMEDA) as catalysts and K2CO3 as a base. The parameters of non-isothermal curing kinetics, activation energy (Ea), pre-exponential factor (A) and rate constant (k) were obtained according to Kissinger, Ozawa, and iso-conversion equations. The activation energy (Ea) values for DGEBA/DAC and DGEBA/ADOAc systems obtained by Kissinger method are 88.11 and 59.50 kJ/mol, by Ozawa method are 90.75 and 64.15 kJ/mol and by iso-conversion equation are 91.45 and 65.49 kJ/mol, respectively. The values of pre-exponential factors (A) obtained for DGEBA/DAC and DGEBA/ADOAc systems are 1.29×1010 and 9.03×105 s-1 with rate constants (K) of 0.90 and 0.12 s-1, respectively. The results show that DGEBA/ADOAc system has lower Ea and K values than the DGEBA/DAC system. The exothermic curing thermograms of DGEBA with ADOAc are much broader than the curing exothermic peak of DGEBA with DAC. At 300ºC both cured systems start to lose weight and the final weight loss is higher for DGEBA/ADOAc system.

INTRODUCTION

Epoxy resins are widely used in coatings and structural applications [1,2] because these thermosets can be tailored to suit specific performance characteristics. As a result of their high cross-link density and aromatic backbone, most epoxy resins are rigid materials and fail by brittle fracture. The aromatic curing agents improve the thermal stability, chemical resistance, and mechanical properties of the cured resin [3-5].

The curing kinetics of epoxy resins have been studied with various techniques such as infrared spectroscopy [6,7] and differential scanning calorimetry [8-12]. Because of the complex chemistry involved in epoxy curing, a popular phenomenological approach is adopted to study these systems. The models arising from proposed kinetics mechanisms are based on...
autocatalytic cure kinetics [8,13]. In general, a good fit to experimental data is observed in the early stage of the cure, but deviations are observed in the latter stages particularly near vitrification, when the reaction is primarily diffusion controlled. Kinetic characterization of the thermoset resins is essential in understanding the structure/property/processing relationships for manufacture and utilization of high performance composites. These kinetic data provide information for the curing cycles of epoxies to ensure that the cured epoxy is adequately able to meet the requirements of its end use [14-18].

The main objective of the present work was to study the kinetics of cure reaction of DGEBA epoxy with two new aromatic diamines (DAC and ADOAc) by using dynamic DSC data of the curing process and different non-isothermal kinetic approaches such as the Kissinger, Ozawa, and iso-conversion methods. The thermal stability of cured systems was also studied by using thermogravimetry analysis. In addition, 3,6-diamino-9-octylcarbazole (DAOC) was prepared and its cure reaction with DGEBA was also compared with the curing of DGEBA/DAC system.

**EXPERIMENTAL**

**Materials**

Diglycidyl ether of a bisphenol A-based epoxy (DGEBA) was purchased from Sigma-Aldrich Co, with the following specification of $M_n \approx 377$, epoxide equivalent 188.5, clear liquid, viscosity (25°C) 100-150 poise, density 1.16 g/mL (25°C). All other chemicals were purchased either from Merck or Fluka and used directly without purification. Toluene was purified by distillation over sodium.

**Equipments**

FTIR spectra were recorded with potassium bromide plates on a Bruker FTIR spectrometer, Vector 22 over 400-4000 cm$^{-1}$ range. $^1$H NMR spectra were recorded using a Bruker DRX 500 MHz Advance instrument, using CDCl$_3$ and DMSO-$d_6$ as solvents. Elemental analysis was performed by a CHN-600 Leco elemental analyzer. Melting points were also measured with a Branstead Electrothermal Engineering LTD 9200 apparatus. Differential scanning calorimetry (DSC) curves were recorded on a Perkin Elmer Pyris 6 DSC under nitrogen atmosphere (20 cm$^3$/min). Thermogravimetric analysis (TGA) was performed with a Du Pont (TGA 951) analyzer well equipped with a PC at a heating rate of 10°C/min under nitrogen atmosphere (20 cm$^3$/min) in the temperature range of 30-700°C.

**Synthesis**

3,6-Diaminocarbazole

3,6-Diaminocarbazole (DAC) was prepared according to the procedure given in literature [19,20]. The reaction mechanism is presented in Scheme I. The yield obtained is 73% and the product has a melting point in the temperature range 276-279°C. The

![Scheme I. Preparation of 3,6-diaminocarbazole.](image-url)
characterization data of $^1$H NMR (500 MHz, acquisition time: 1.5860 s, delay time: 6.0 s, number of scan: 16, temperature: 300.0 K, and solvent: DMSO-d$_6$), $\delta$ (ppm): 10.07 (s, 1H), 7.05 (d, 4H), 6.64 (q, 2H), 4.51 (s, 4H).

FTIR (KBr plate), $\nu$ (cm$^{-1}$): 3393 (N 9-H), 3287, 3195 (-NH$_2$), 1636, 1575, 1508, 1466, 1332, 1219, 1163, 870, and 803.

Elemental analysis calculated: C, 73.10%; H, 5.58%; N, 21.32%; found: C, 72.92%; H, 6.10%; N, 21.25%.

3,6-Diamino-9-octylcarbazole

3,6-Dimino-9-octylcarbazole (DAOC) was prepared according to the procedure given in the literature [21,22]. The reaction mechanisms for the synthesis of the monomer are presented in Scheme II. The yield of the product was obtained to be 76% with a melting temperature range 140-142°C. The characterization data of $^1$H NMR (500 MHz, pulse program: zg 30, acquisition time: 3.1720 s, delay time: 5.00 s, number of scan: 16, temperature: 299.0 K and solvent: DMSO-d$_6$), $\delta$ (ppm): 7.14(d, 2H), 7.09(d, 2H), 6.73(dd, 2H), 4.62(br, 4H), 4.13(t, 2H), 1.66(br, 2H), 1.24-1.19(m, 10H), 0.83(t, 3H), FTIR (KBr plate), $\nu$ (cm$^{-1}$): 3393-3302-3191(-NH$_2$), 3021(Ar-H), 2923-2857(aliphatic C-H stretching), 1638, 1583, 1476, 1330, 1224, 1178, 1153, 875, 799, and 744.

Elemental analysis calculated: C: 77.63%, H: 8.79%, N: 13.58%; found: C: 77.35%, H: 8.93%, N: 13.68%.

$N'$-[7-(Acetyl-4-aminoanilino)-9,9-dioctylfluoren-2-yl]-$N'$-4-aminophenyl acetamide (ADOAc) DAOC derivative was prepared according to the following procedure: A 100 mL two-necked flask equipped with a magnetic stirrer, a condenser, and a argon inlet/outlet tube was charged with Cul (0.192 g, 1 mmol, 10 mol%), 9,9-dioctyl-2,7-dibromofluorene (2.74 g, 5 mmol), 4-aminoacetanilide (1.88 g, 12.5 mmol) and K$_2$CO$_3$ (2.8 g, 20.3 mmol), briefly evacuated, and backfilled with argon. $N,N'$-dimethylene diamine (DMEDA) (0.2152 mL, 2 mmol) and toluene (20 mL) were added under argon atmosphere. The reaction mixture was stirred at 110-115°C for 36 h. During this time, progress of the reaction was monitored by thin-layer chromatography (TLC) [23]. The resulting pale-brown suspension was allowed to reach room temperature and then filtered through a 0.5×1 cm pad of silica gel eluting with

![Scheme II. Preparation of 3,6-diamino-9-octylcarbazole.](image-url)
1:1 ethylacetate/dichloromethane (100 mL). The filtrate was evaporated, and then purified with column chromatography (SiO₂, ethylacetate/dichloromethane 1:4). Pale-brown crystalline product was obtained with the overall yield of 89.6% (3.8 g), and melting point of about 119-121°C [23]. The characterization data, ¹H NMR (500 MHz, pulse program: zg 30, acquisition time: 1.5860 s, delay time: 5.00 s, number of scan: 16, temperature: 296.2 K, and solvent: CDCl₃), δ (ppm): 7.63 (b, 2H), 7.26-7.20 (m, 4H), 7.09 (d, 4H), 6.70 (b, 4H), 3.78 (s, 4H), 2.11 (s, 6H), 1.91 (b, 4H), 1.26-1.04 (m, 20H), 0.88 (t, 6H), and 0.66 (b, 4H).

FTIR (KBr plate), ν (cm⁻¹): 3459-3357-3225 (-NH₂), 3033 (Ar-H), 2926-2860 (aliphatic C-H stretching), 1656 (C=O), 1583, 1466 (aromatic C=C), 1405 (C-N stretching), and 725 (-C=O, out of plane deformation).

Elemental analysis calculated: C, 78.71%; H, 8.45%; N, 8.16%; found: C, 78.58%; H, 8.56%; N, 8.31%.

The reaction mechanism for the synthesis of the monomer is presented in Scheme III.

Sample Mixing
Curing agents were carefully mixed with DGEBA by continuous stirring at room temperature to form a homogeneous viscous mixture. The stoichiometric amounts of DAC (21 phr), DAOC (41 phr), and ADOAc (58.5 phr) based on the number of active hydrogens in the curing agents and epoxy equivalent weight were used. The homogeneous viscous mixtures were stored in a refrigerator to be used for DSC tests.

DSC Analysis
Five milligrams of the uniform viscous mixture was put into a DSC sample pan, covered with an aluminium lid and closed tightly under pressure. The sample pan in the DSC sample cell together with an empty pan in the reference cell were heated under N₂ atmosphere (20 cm³/min) from room temperature to 350°C at different heating rates of 5, 10, 15, and 20°C/min.

TGA Analysis
Thermal stability of the cured samples was measured by using TGA in the temperature range of 50-700°C at the heating rate of 10°C/min under nitrogen atmosphere (20 cm³/min). Samples were prepared by pouring each uniform viscous mixture into an aluminium cell and cured in an oven at 100°C for 2 h, at 150°C for 1 h and at 180°C for 30 min. About 3 mg of each cured sample was cut into small discs for TGA tests.

RESULTS AND DISCUSSION
¹H NMR and FTIR spectra of DAC are shown in Figures 1 and 2. FTIR spectrum of DAC show characteristic bands at 3393 cm⁻¹ (N₉-H), 3287, 3195
(N–H stretching), and 1575 (C=C). The $^1$H NMR spectrum show the characteristic signals at 10.07 ppm for N$_\text{O}$-H, 7.05 and 6.64 ppm for aromatic protons and 4.51 ppm for NH$_2$ protons. The detailed conditions for the syntheses are reported by Chen [19] and Grotta [20] and the corresponding reactions are shown in Scheme I.

DAOC was characterized by FTIR and $^1$H NMR spectroscopy and elemental analysis. FTIR and $^1$H NMR spectrum of DAOC are shown in Figures 3 and 4, respectively. FTIR spectrum of DAOC, as identical to reported literature data, showed characteristic bands at 3393, 3302 and 3191 cm$^{-1}$ (N–H stretching), 3021 cm$^{-1}$ (Ar–CH), and 2923-2857 cm$^{-1}$ (aliphatic stretching C-H). $^1$H NMR spectrum showed the characteristic signals at 7.14, 7.09, and 6.73 ppm related to aromatic protons and 4.62 ppm related to NH$_2$ protons. The detailed conditions for the syntheses shown in Scheme II are reported in literature [21,22].

Figure 1. $^1$H NMR spectrum of DAC.

Figure 2. FTIR spectrum of DAC.

Figure 3. FTIR spectrum of DAOC.
ADOAc was synthesized in one step by the CuI/DMEDA catalytic C(aryl)–N coupling reaction (amidation) of 2,7-dibromo-9,9-dioctyfluorene with 4-aminoacetanilide in the presence of K2CO3 as base. The detailed conditions of the synthesis are presented in Scheme III. FTIR and 1H NMR spectra of ADOAc are shown in Figures 5 and 6, respectively. FTIR spectrum of ADOAc show the characteristic bands at 3459-3357 cm\(^{-1}\) (N–H stretching), 3033 cm\(^{-1}\) (Ar–CH), 2926-2860 cm\(^{-1}\) (aliphatic stretching C-H), 1656 cm\(^{-1}\) (C=O), and 1583 cm\(^{-1}\) (C=C). The 1H NMR spectrum show the characteristic signals at 3.78 ppm related to NH\(_2\) protons.

Kinetic Methods
The curing reaction of epoxy resins depends on the structure and reactivity of a specific curing agent. The onset of the curing exotherm depends on the nucleophilicity of the amino group. Although the aromatic amines containing an electron donor substituent initiate the curing process of epoxy resin at lower temperature, the chemical structure of the amine is not the only factor. In this respect the steric restrictions to the epoxy-amine addition reaction, physical interactions among different functional groups of the constituent components, and the curing extension can also influence the cure kinetics [4, 24-26].

The exothermic transition is characterized by noting the following parameters: T\(_{\text{onset}}\) (exothermic onset temperature obtained by extrapolation of the steepest portion of the initial side of the exotherm), T\(_{\text{p}}\)
(exothermic temperature of the peak position), and $\Delta H$ (the heat of curing calculated by the measurement of area under the exothermic transition).

Figure 7 shows the DSC diagram of DGEBA cured with DAC and DAOC as curing agents with similar heating rates (15°C/min). DAC (mp at ~279°C) is soluble in DGEBA at temperature above 80°C and its curing reaction with DGEBA occurs above 150°C with $T_p$ at 170°C. DAC has primary and secondary amine groups in its structure which both can react with the epoxy groups. This may be the reason that the exothermic peak of DGEBA/DAC system shows a very steep slope as the cure reaction takes place rapidly in a short period of time and in a narrow temperature range of 170-200°C. Alkylation of DAC at the –NH– position yielded DAOC with the melting point of 142°C which is soluble in DGEBA at above 80°C. DAOC contains primary and tertiary amine groups in its structure and both can react with epoxy groups. The tertiary amine cures epoxy resin catalytically at lower temperature and it may be accounted for the cure reaction of DGEBA/DAOC system starting at 100°C with $T_p$ at ~140°C.

Figure 8 shows the dynamic DSC curves for DGEBA resin cured with ADOAc at four different heating rates. All curves show only one exothermic peak regardless of the heating rate and shift towards higher temperatures as heating rate increases. ADOAc with the melting point of almost 120°C is not soluble in DGEBA before melting. DSC thermograms of DGEBA/ADOAc system show an
Figure 8. Dynamic DSC thermograms for DGEBA cured with ADOAc at different heating rates.

endothermic peak around 100°C due to the melting temperature of ADOAc and the curing reaction occurs immediately after, in a wide temperature range. ADOAc similar to DAOC has two types of amine groups in its structure. It can react with the epoxy groups catalytically through the tertiary amines and also by transferring hydrogen atom by the primary amines. DSC thermograms of DGEBA/ADOAc system show slower cure reaction at low temperature in comparison with those observed in DGEBA/DAOC system. This can be correlated to the steric hindrance of tertiary amines in ADOAc.

Table 1 shows all the data obtained from DSC thermograms. The exothermic peaks ($T_p$) with an almost $10^\circ$C difference in their maximum were attributed to the generation of heat during the cure reaction. The dynamic DSC data in Table 2 are the temperatures at which the instant conversion rate was maximum ($T_p$) and the heating rates ($\beta$) are used for calculation of kinetic parameters by using Kissinger, Ozawa, and iso-conversion methods.

Many models including the nth order reaction, the autocatalytic reaction, and the diffusion control models have been developed to investigate the cure kinetics of the epoxy system [27-30]. All kinetic studies rely on the fundamental equation that governs the rate of conversion at constant temperature as a function of the concentration of the reactants:

$$\frac{d\alpha}{dt} = kf(\alpha)$$

Or in the integrated form:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{\alpha_i}^\gamma kdt$$

where,

- $g(\alpha)$ : integrated form of the conversion-dependence function,
- $\frac{d\alpha}{dt}$ : the rate of cure, $\alpha$ is the fractional conversion at any time $t$,
- $k$ : the Arrhenius rate constant, and
- $f(\alpha)$ : a function form of $\alpha$ that depends on the

Table 1. DSC data for curing of DGEBA with DAC and ADOAc.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc (phr)</th>
<th>$\beta$ (°C/min)</th>
<th>$T_i$ (K)</th>
<th>$T_p$ (K)</th>
<th>$1/T_p \times 10^3$ (K$^{-1}$)</th>
<th>Ln$\beta$</th>
<th>Ln($\beta/T_p^2$)</th>
<th>Exo heat (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/DAC</td>
<td>21</td>
<td>5</td>
<td>422.72</td>
<td>431.68</td>
<td>2.32</td>
<td>1.61</td>
<td>10.53</td>
<td>-357.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>433.48</td>
<td>443.56</td>
<td>2.25</td>
<td>2.30</td>
<td>9.89</td>
<td>-364.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>439.93</td>
<td>450.31</td>
<td>2.22</td>
<td>2.71</td>
<td>9.51</td>
<td>-373.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>444.95</td>
<td>455.45</td>
<td>2.20</td>
<td>3.00</td>
<td>9.25</td>
<td>-381.12</td>
</tr>
<tr>
<td>DGEBA/DAOC</td>
<td>41</td>
<td>15</td>
<td>373.28</td>
<td>418.23</td>
<td>2.39</td>
<td>2.71</td>
<td>9.36</td>
<td>-450.870</td>
</tr>
<tr>
<td>DGEBA/ADOAc</td>
<td>58.5</td>
<td>5</td>
<td>424.85</td>
<td>461.67</td>
<td>2.17</td>
<td>1.61</td>
<td>10.66</td>
<td>-299.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>437.92</td>
<td>481.02</td>
<td>2.08</td>
<td>2.30</td>
<td>10.5</td>
<td>-284.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>445.60</td>
<td>492.67</td>
<td>2.03</td>
<td>2.71</td>
<td>9.69</td>
<td>-259.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>448.01</td>
<td>501.13</td>
<td>1.99</td>
<td>3.00</td>
<td>9.44</td>
<td>-260.10</td>
</tr>
</tbody>
</table>

$\beta$ = Heating rate; $T_i$ = onset temperature of the exotherm peak; $T_p$ = maximum temperature of the exotherm peak.
reaction mechanism.

Kissinger has extended the following equation [31,32] for when the temperature varies with time at a constant heating rate, $\beta = \frac{dT}{dt}$:

$$-\ln(\beta / T_p^2) = \frac{E_a}{RT_p} - \ln(A/R)$$

where,

$\beta$ : the heating rate,
$T_p$ : temperature at which $d\alpha/dt$ is maximum,
$E_a$ : the activation energy,
$A$ : a pre-exponential factor and,
$R$ : gas constant.

The data of the fifth and seventh columns in Table 1 were introduced into the Kissinger equation (eqn (3)), and $-\ln(\beta / T_p^2)$ versus $1/T_p$ was plotted. The linear plots in Figure 9 are expressed by the following equations for DGEBA/DAC and DGEBA/ADOAc systems, respectively:

$$-\ln(\beta / T_p^2) = 10.60 \times 10^3 (1/T_p) - 10.02$$

and

$$-\ln(\beta / T_p^2) = 7.16 \times 10^3 (1/T_p) - 4.84$$

The activation energies ($E_a$) and the pre-exponential factors ($A$) were calculated from the slopes of the linear plots and the $y$ intercept in Figure 9, respectively. The $E_a$ and $A$ values are listed in Table 3. The activation energy and the pre-exponential factor for DGEBA/DAC system are larger than those for DGEBA/ADOAc system. To compare the cure rates

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**Table 2.** Kinetic parameters of curing DGEBA resin with DAC and ADOAc at stoichiometric amount.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a^a$ (kJ/mol)</th>
<th>$E_a^b$ (kJ/mol)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$k^c$ (s$^{-1}$)</th>
<th>$E_a^d$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAC</td>
<td>88.11</td>
<td>90.75</td>
<td>1.29 $\times 10^{10}$</td>
<td>0.90</td>
<td>91.45</td>
</tr>
<tr>
<td>ADOAc</td>
<td>59.50</td>
<td>64.15</td>
<td>9.03 $\times 10^{5}$</td>
<td>0.12</td>
<td>65.49</td>
</tr>
</tbody>
</table>

(a) Kissinger’s method, (b) Ozawa’s method, (c) Arrhenius rate constant at 453 K, and (d) Iso-conversion.

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**Table 3.** Data of $\ln \beta$ vs. $T^{-1}$ for DGEBA/DAC system.

<table>
<thead>
<tr>
<th>Ln $\beta$</th>
<th>$1/T \times 10^3$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conversion</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>1.61</td>
<td>2.37</td>
</tr>
<tr>
<td>2.30</td>
<td>2.30</td>
</tr>
<tr>
<td>2.71</td>
<td>2.29</td>
</tr>
<tr>
<td>3.00</td>
<td>2.25</td>
</tr>
</tbody>
</table>

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**Figure 9.** Kissinger and Ozawa plots for DGEBA cured with DAC or ADOAc.
in both systems, pre-exponential factor and activation energy values were introduced into the Arrhenius equation (eqn (6)) to obtain the rate constants at a selected temperature shown in Table 2.

\[ k = A \exp\left(-\frac{E_a}{RT}\right) \]  

(6)

where \( k \) is the rate constant and \( T \) is a selected temperature (453 K). The rate constant for DGEBA/DAC system is higher than that of DGEBA/ADOAc system at the selected temperature.

Ozawa-Flynn-Wall method based on Doyle’s approximation [33,34] is expressed as an alternative method for the calculation of \( E_a \):

\[ \ln(\beta) = \text{Const} - 1.052 \frac{E_a}{RT_p} \]  

(7)

where \( \beta, E_a, T_p, \) and \( R \) are the same terms used in the Kissinger equation. The data of fifth and sixth columns in Table 1 have been also introduced into the Ozawa equation which linear plots of \( \ln(\beta) \) versus \( 1/(T_p) \) are shown in Figure 9. The slope of the linear plots is equal \(-1.052E_a/R\) where \( E_a \) values are calculated and listed in Table 2.

The Kissinger and Ozawa equations give only one set of \( E_a \) from \( T_p \) data. A more complete determination of \( E_a \) at any selected conversion can be calculated by the iso-conversion equation [35,36] as follows:

\[ E_a = -R \frac{d(\ln(\beta))}{d(T^{-1})} \]  

(8)

\[ \frac{1}{T} \times 10^3 \]  

Figure 1. Iso-conversional plots at various conversions for the DGEBA/ADOAc system.

where \( E, \beta, \) and \( R \) are the same terms used in the Kissinger equation and \( T \) is the temperature of a selected conversion at each heating rate. Figure 10 shows the conversion curves versus temperature at four different heating rates of DGEBA cured with DAC. These curves are obtained by integrating the DSC curves of Figures 8. The iso-conversion temperatures were obtained from the conversion curves at any selected conversion and \( 1/T \times 10^3 \) according to \( \ln(\beta) \) are listed in Table 3. To determine the activation energy at each conversion, the relationships of the variables at conversion range 0.1-0.9 were discerned (Figure 11) and for each straight line the linear expres-
A cure reaction was obtained. Changes in $E_a$ versus conversion are shown in Figure 12. The average values of the activation energies of DGEBA/DAC and DGEBA/ADOAc systems are 91.45 and 65.49 kJ/mol, respectively.

The activation energies of the cure reaction of DGEBA/PAP system using data from DSC scans (Table 1) and three kinetic models (Kissinger, Ozawa, and iso-conversion equations) are given in Table 4 for comparison.

The thermal stabilities of cured resin are determined by thermogravimetric analysis in N$_2$ atmosphere at the heating rate of 10°C/min. The obtained results are collected in Table 5 and the representative TGA curves are shown in Figure 13. The 2% decomposition temperatures ($T_2$) of DGEBA/DAC and DGEBA/ADOAc systems were about 278 and 303°C and their temperatures of 10% weight loss ($T_{10}$) were about 336 and 344°C, respectively which are important criteria for thermal stability evaluations. Furthermore, the char yields of the cured DGEBA/DAC and DGEBA/ADOAc systems at 700°C are found to be about 26.14% and 22.45%, respectively.

### Table 4. Activation energy for two curing systems with different kinetics models.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ (kJ/mol)</th>
<th>Kissinger’s method</th>
<th>Ozawa’s method</th>
<th>Iso-conversion equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/DAC</td>
<td>88.11</td>
<td>90.75</td>
<td>64.15</td>
<td>91.45</td>
</tr>
<tr>
<td>DGEBA/ADOAc</td>
<td>59.50</td>
<td></td>
<td></td>
<td>65.49</td>
</tr>
</tbody>
</table>

### Table 5. Thermal characteristic data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_2$ a (°C)</th>
<th>$T_5$ b (°C)</th>
<th>$T_{10}$ c (°C)</th>
<th>$T_{max}$ d (°C)</th>
<th>Char yield at 700°C e (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/DAC</td>
<td>278</td>
<td>316</td>
<td>336</td>
<td>377</td>
<td>26.14</td>
</tr>
<tr>
<td>DGEBA/ADOAc</td>
<td>303</td>
<td>329</td>
<td>344</td>
<td>374</td>
<td>22.45</td>
</tr>
</tbody>
</table>

(a) Temperature for 2% weight loss, (b) temperature for 5% weight loss, (c) temperature for 10% weight loss, (d) maximum decomposition temperature, and (e) weight of polymer remained at 700°C.

### CONCLUSION

The mechanisms and kinetics of the cure reaction of DGEBA with two aromatic diamines DAC and ADOAc have been studied by DSC scanning technique, three kinetic models: Kissinger, Ozawa, and iso-conversion equations. All dynamic DSC curves have shown only one sharp exothermic peak, regardless of the heating rate; which is an indication of the cure reactions taking place at the same stage between the epoxide groups and primary or secondary amine groups. However, the DSC thermograms have shifted to lower temperature with increasing amount of diamine, and shifted to higher temperatures with increased heating rate. The

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**Figure 13.** The TGA curves of two cured systems.
activation energy and the pre-exponential factor for DGEBA/DAC system are obtained to be higher than DGEBA/ADOAc system. The increase in the pre-exponential factor is due to the higher probability of collisions between the reactant groups. The rate constant of DGEBA/DAC system also has increased compared to DGEBA/ADOAc system. The activation energies obtained by three kinetic methods are almost in agreement all together. The thermal stability of two cured systems has been examined by TGA technique. The 2% decomposition of the cured DGEBA/DAC and DGEBA/ADOAc systems occur at 278°C and 303°C and the char yields at 700°C for these two systems are found to be about 26.14 and 22.45%, respectively.

REFERENCES

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