Study of Polymerization Mechanism and Kinetics of DGEBA with BF₃-amine Complexes Using FT-IR and Dynamic DSC

Mousa Ghaemy and Mohammad Hossein Khandani
Department of Chemistry, University of Mazandaran, Babolsar, I.R.Iran.

Received: 30 October 1996; accepted 28 January 1997

ABSTRACT

The diglycidyl ether of bisphenol A and boron trifluoride-diethylamine, monoallylamine and piperidine complexes are used in a model system to investigate the cure reaction which occur during polymerization. Experiments using FT-IR at different temperatures show that boron trifluoride-amine complexes break down rapidly to tetrafluoroborlic acid at 100 °C and above. Tetrafluoroboric acid forms complexes with epoxy groups, producing an activated monomer that reacts with epoxy in an etherification reaction. Dynamic DSC thermograms also show a small exotherm peak due to complex formation before the large exotherm peak of etherification reaction. A phenomenological approach is used to characterize the cure kinetics. Kinetic analysis, using integral procedure on dynamic data, indicates that the cure reaction data of diglycidyl ether of bisphenol A with boron trifluoride-amine complexes can be described well with the homogeneous first-order reaction model. The activation energies are found to be in the range of 90.85 kJ/mol for boron trifluoride-diethylamine; 96.88 kJ/mol for boron trifluoride-monoallylamine; and 94.45 kJ/mol for boron trifluoride-piperidine complexes.

Key Words: resins, thermoset, cure, kinetics, DSC

INTRODUCTION

Epoxy resins are widely used in diverse applications including surface coatings, printed circuit boards, the potting of electronic composites, rigid foams, adhesives, and fibre-reinforced composites. In all these applications a curing process is involved in which the monomeric or oligomeric polyfunctional epoxide is transformed into a cross-linked macromolecular structure. An understanding of these curing reactions, together with the availability of reliable methods of monitoring them, are important in order to obtain consistent products with the desired physical and mechanical properties. One of the important classes of catalytic curing agents of epoxy resins are boron trifluoride(BF₃)-amine complexes. These types of complexes are added to epoxy resins to accelerate the curing reactions at temperatures 120—160 °C [1]. Primary aliphatic or aromatic amines are able to form 1:1 complex with
BF₃ [2]. Although varieties of BF₃ complexes are introduced, only BF₃-monoethylamine (BF₃-MEA) complex has been used widely for polymerization of epoxy resin [3, 4], as a curing agent for coating [5], varnishes [6], electrical insulation [7], epoxy foam [8], finishing of PVC as leather substitutes [9] and glass fibre reinforcing material [10]. The BF₃-MEA cured epoxy resins have good strength, heat resistance, and electrical properties. The complex BF₃-MEA can be used as a co-curing agent for epoxy resins. It can also work as an accelerator for diaminodiphenyl-sulphone (DDS)-cure epoxy resins [3]. The activation energies of gelling epoxy with 0.030—0.093 mol of BF₃-MEA is 23 kcal/mol [11]. The temperature at which the rate of exothermic polymerization reaction is the fastest has been reported at 130 °C [11], 166 °C [12] or 178 °C [13]. These differences are probably due to different ratios of curing agent to various epoxy resins. The complex BF₃-MEA is used extensively since it is not easily affected by moisture.

A variety of experimental techniques has been developed to follow the cure reaction of thermosetting systems, one of them being differential scanning calorimeter (DSC). The DSC technique finds several applications in different industries and in determination of reaction kinetics, degree of crystallinity, melting point and glass transition temperature of polymers and materials purity [14—18]. The cure reaction of BF₃-MEA/epoxy resin using DSC technique under dynamic condition was studied by Tackle [19]. They showed that BF₃-MEA breaks down rapidly into HBF₄ and an amine salt at 85 °C and above. This finding agrees with the conclusion of Smith and Smith [1, 20], and it was also reported that HBF₄ does not catalyze epoxy resin polymerization at room temperature [21]. Our findings on epoxy/BF₃-amine systems using isothermal DSC [23] are in agreement with the results on epoxy/BF₃-DEA [18—21] showing that a rapid thermal conversion of the complex to HBF₄ occurs in resins. Therefore, it is HBF₄, and not BF₃-amine, which is the actual catalyst.

In the present work we have used FT-IR and dynamic DSC techniques to investigate the mechanism and kinetics of cure reaction of DGEBA/BF₃-amine complexes systems. The purpose of the work is to delineate the reaction mechanism and kinetics of DGEBA with BF₃-DEA, BF₃-MAA and BF₃-PP complexes.

**EXPERIMENTAL**

**Materials**

The epoxy compound used in this study was a diglycidyl ether of bisphenol-A (DGEBA) from Shell Chemical Co., Epon 828. Boron trifluoride diethyl ether was obtained from Aldrich. Diethylamine (DEA), allylamine (MAA) and piperidine (PP) were obtained from Fluka.

**Synthesis of Complexes of BF₃-amines**

The complexes of BF₃ and the amines (BF₃-DEA, BF₃-MAA and BF₃-PP) have been prepared according to the method proposed in the literature [22]. The reaction was carried out at 0 °C by direct addition of amine to pure solution of BF₃(Et₂O). The precipitated complex was filtered, washed repeatedly with ether, and dried under vacuum at a specific temperature for a given complex for 24 h. The characteristics of the prepared complexes were given elsewhere [23].

\[
\text{BF}_3\text{-NH} \left(\text{CH}_2\text{—CH}_3\right)_2
\]

BF₃-DEA: Boron trifluoride diethylamine

\[
\text{BF}_3\text{-NH}_2\text{—CH}_2\text{—CH} \equiv \text{CH}_2
\]

BF₃-MAA: Boron trifluoride monoallylamine

\[
\text{BF}_3\text{-NH}\bigg(\bigg)
\]

BF₃-PP: Boron trifluoride piperidine

**Hydrolysis of BF₃-amine Complexes**

Hydrolysis of BF₃-amine complexes was studied with a Bruker IFS88 FT-IR equipped with a
thermostatted sample holder to allow analysis at different temperatures. The thermal conversion of each complex was recorded over the temperature range 30 to 200 °C. The BF₃-DEA and BF₃-MAA products were dissolved in acetone first and then placed on a KBr pellet as a thin layer. These
samples were kept at room temperature for 1 h to allow the solvent to vaporize before recording the spectrum. The BF$_3$-PP complex was a viscous liquid and placed on a KBr pellet directly. In these experiments, a spectrum was recorded at room temperature for each BF$_3$-amine complex and then the sample holder was heated to the required temperature. Infra-red spectra of mixtures of DGEBA/BF$_3$-amine complexes were also recorded at different temperatures. Samples of the mixtures of DGEBA and 10 phr BF$_3$-amine complexes were prepared by the same above procedure.

Dynamic DSC Experiments

Samples of DGEBA containing the required amounts of BF$_3$-amine complexes (6, 8, 10 and 15 parts per 100 by weight of DGEBA, phr) were cured dynamically with a Perkin-Elmer DSC-4. The samples were prepared with dissolving the required amounts of resin and solid hardeners (BF$_3$-DEA and BF$_3$-PP) in the least amount of acetone to allow to mix together at room temperature. After vaporization of solvent, the sample had been weighed out into aluminium DSC sample pan and it was covered with an aluminium lid; then it was placed in the DSC cell at ambient temperature and the temperature was increased at a controlled heating rate. The heating rates were 10, 15 and 20 °C/min over a temperature range from 25 to 300 °C that guarantee reaction completion. Sample sizes were about 10 mg and an empty covered aluminium DSC sample pan was used as the reference which was placed in the right hand cell of the DSC. The complete heat of cure was estimated as the area under the cure exotherm, measured with a planimeter. The DSC was calibrated with a high purity indium.

RESULTS AND DISCUSSION

The amines alone, DEA, MAA and PP did not cure epoxy resin to a thermoset material at concentration of 10 phr and at temperature of 60 °C in more than 5 h, while their complexes with BF$_3$ did cure epoxy resin, at the same concentration and temperature, to a hard glassy material in less than 5 h.

The thermal breakdown of BF$_3$-amine complex was monitored with FT-IR at different temperatures. For these experiments, a spectrum was recorded for each BF$_3$-amine complex at room temperature; then the cell was heated to higher temperatures. Typical FT-IR spectrum of the complex is shown in Figure 1. The peaks of FT-IR spectrum at room temperature are many and quite sharp which appear at: 3557 cm$^{-1}$ due to NH stretching, around 3000 cm$^{-1}$ due to CH stretching, at 1609 cm$^{-1}$ due to NH bending, at 945 and 1145 cm$^{-1}$ due to BF symmetric and asymmetric stretching in BF$_3$. The peak at 1070 cm$^{-1}$ is caused by BF$_4$ anion [19]. It is seen in Figure 1 that the FT-IR spectrum of the BF$_3$-amine complex changes greatly and gradually as the temperature increases. We are interested in increase of peak at 1070 cm$^{-1}$ which is consistent with the conversion of BF$_3$-DEA complex to HBF$_4$. The conversion of BF$_3$-amine complex to HBF$_4$ occurs above 100 °C. The BF$_3$ peaks decrease rapidly with heating, while the BF$_4$ anion peak grows larger. The peak of BF$_4$ is very strong even at temperature of 200 °C, indicating that the reaction which produced it may be irreversible. The peaks at 3000 cm$^{-1}$ are changed but the CH stretch is clearly visible, whereas the NH absorbances at 1609 and 3557 cm$^{-1}$ are not. The peaks that were present between 1200 and 1750 cm$^{-1}$ have either disappeared or are greatly diminished in size. This is unexpected and may be indicative of a low boiling component, such as alkylamine, being vaporized from the KBr pellet [19]. The results from FT-IR spectrum show that BF$_3$-amine complexes convert to HBF$_4$ at higher temperatures and, therefore, the true catalyst is proved to be HBF$_4$, and not the BF$_3$-amine complex.

In addition to the rapid thermal breakdown of BF$_3$-amine complex, the IR studies show the persistence of the fluoroborate anion. This observation is in agreement with the findings of other workers [1, 19, 20, 21] for BF$_3$-MEA complex. These results support the mechanism whereby 2 moles of BF$_3$-amine complex react to form 1 mole
Figure 2. FT-IR spectrum of DGEBA/BF$_3$-MAA (10 phr) system at different temperatures.

Iranian Polymer Journal / Volume 6 Number 1 (1997)
of the catalytically active species in a rapid, thermally activated reaction. The proposed reactions are:

\begin{align}
2F_3B-NHR_2 & \longrightarrow F_2B^-N^+H_2R_2 + F_2B^-N^-R_2 \quad (1) \\
F_2B^-N^+H_2R_2 & \longrightarrow HBF_4 + NHR_2 \quad (2)
\end{align}

The following mechanism is also suggested in the presence of water in solvents or humidity:

\begin{align}
F_3B-NH_2R \text{ or } F_3B-NHR_2 + H_2O & \longrightarrow HBF_3OH + (RNH_2 \text{ or } R_2NH) \quad (3) \\
HBF_3OH + H_2O & \longrightarrow HBF_2(OH)_2 + HF \quad (4) \\
2 HBF_3OH & \longrightarrow HBF_4 + HBF_2(OH)_2 \quad (5) \\
2HBF_2(OH)_2 & \longrightarrow HBF_4 + B(OH)_3 + H_2O \quad (6)
\end{align}

The results presented here on the FT-IR spectrum of BF₃-DEA, BF₃-MAA and BF₃-PP complexes are also in agreement with the findings of BF₃-MEA complex by several authors [1, 19, 20]. Samples of DGEBA containing 10 phr of BF₃-DEA, BF₃-MAA or BF₃-PP complex were tested in FT-IR spectrum over a temperature range of 50 to 200 °C. Figure 2 shows a typical spectrum obtained for BF₃-MAA/DGEBA system. The concentration-temperature curves for DGEBA containing BF₃-amine complexes as curing agent were generated by monitoring the area of the epoxy peak at 914 cm⁻¹ to the reference peak at 1184 cm⁻¹ (epoxy index) with temperature and time; these curves are shown in Figure 3. The concentration of epoxy groups decrease at temperatures above about 140 °C, but it decreases sharply at 200 °C after a period of 20 minutes. The cationic polymerization of epoxy molecules occurs through the terminal carbon atom [3]. In this case, HBF₄ opens an epoxide ring to form a protonated oxonium ion, which yields an activated monomer. The activated monomer polymerizes other epoxy groups, with the BF₄ anion, a non-nucleophilic anion, associated with the oxygen. Typical dynamic thermograms of DSC for DGEBA containing 15 phr of BF₃-DEA, BF₃-MAA and BF₃-PP complexes are shown in Figures 4–6, respectively. Two exotherm peaks were observed for each DGEBA/BF₃-amine system: the first small peak is assigned to the formation of the complex of HBF₄ and DGEBA, and the second large peak is caused by etherification reaction [19]. These assignments are consistent with the mechanism of complex formation and epoxy curing. Figure 4, for example, shows complex formation peak at 85 °C.
Endo e rel A 75 155 235
Temperature (°C)

Figure 5. Dynamic scan of resin+BF3-MAA; concentration of complex: 15 phr; heating rate: 20 °C/min; sample size: 2.18 mg.

and etherification reaction at 185 °C. The reaction mechanism upon which the subsequent kinetics experiments were predicted is shown in Figure 7. According to this mechanism, therefore, dynamic DSC thermogram indicates two exotherm peaks; a small peak is caused by the complex formation of HBF4 and DGEBA, and a large peak is caused by etherification reactions which is responsible for network formation and it was used for calculation of kinetic parameters in the present work.

The total area under the DSC thermogram, based on the extrapolated baseline at the end of reaction, was used to calculate the total heat of reaction. The size of the peak increased over the concentration range of 6–15 phr for BF3-amine complexes. Table 1 shows typical results obtained from dynamic DSC thermograms of DGEBA/BF3-amine systems. The maximum of exotherm peak, for a specific concentration, shifts to higher temperature as the heating rate increases. That is, as the heating rate increases the time for cure at a particular temperature decreases. The maximum of exotherm peak, for a specific heating rate, shifts to lower temperature as the concentration of the curing complex increases. As it is seen in Table 1, the exotherm peaks of DGEBA/BF3-MAA system reaches to the maximum at lower temperatures in comparison with those of BF3-DEA and BF3-PP at the same concentration and heating rate, which indicates that BF3-MAA is more active than the other two complexes. Therefore, the average cure temperature (maximum peak) for BF3-DEA and BF3-PP complexes is about 180 °C and for BF3-MAA is 160 °C very close to BF3-MEA complex found by Tackie et al. [19]. The BF3-MAA and BF3-MEA are complexes of primary amines but BF3-DEA and BF3-PP are complexes of secondary amines. The primary amines having only one electron donating group, their complexes with BF3 are less stable in comparison with the secondary amines having two electron donating groups. The
Study of Polymerization Mechanism and Kinetics of DGEBA

\[ BF_3 \text{-amine complex} \xrightarrow{} HBF_4 \]

\[ HBF_4 \xleftrightarrow{} H + BF_4 \]

\[ H + BF_4 + H_2C\text{-CH-CH}_2\text{-O} - C(CH_3)_2 \xrightarrow{\text{complex formation}} \]

\[ \text{etherification reaction} \]

Figure 7. Mechanism of complex formation and etherification reactions.

Less stable complex would hydrolyze and convert to the activated species at lower temperatures. The kinetic parameters of the curing reaction was obtained from the dynamic DSC experiments using the classic Barrett's method (24). The extent of reaction, \( a \), is given by:

\[ a = \Delta H_i / H \]

(11)

Where \( H_i \) is the partial area under a DSC trace up to a certain temperature (heat evolved up to a certain temperature) divided by the total area (total heat of reaction, \( \Delta H \)). Since the cure reaction is the only thermal event, then the reaction rate \( da/dt \) is directly proportional to the rate of heat generation \( dH/dt \) (which is the ordinate of a DSC trace):

\[ da/dt = 1/\Delta H \times dH/dt \]

(12)

The phenomenological reaction rate can also be expressed in differential form [25]:

\[ da/dt = k f(a) \]

(13)

where \( k \) is the Arrhenius rate constant, and \( f(a) \) a functional form of \( a \), that depends on the reaction mechanism. By incorporating the Arrhenius form of the rate constant \( k \), i.e. \( k = A \exp(-E_a/RT) \), equation 13 can be rearranged in the following form:

\[ da/dt = A \exp(-E_a / RT) \times f(a) \]

(14)

where \( A \) is the frequency factor, \( E_a \) the activation energy, \( R \) the gas constant and \( T \) the temperature in K. Integration of equation 14 yields:

\[ \ln[(da/dt)/f(a)] = \ln k = \ln A - E_a / RT \]

(15)

which form the starting equation for the derivative analysis of the dynamic data. The computer program reads in the dynamic data from the data file and calculates \( \ln[(da/dt)/f(a)] \) for each conversion point using the functional form for the chosen...
Table 1. Kinetic parameters of DGEBA curing with BF₃-amine complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conc. (phr)</th>
<th>Heating rate (°C/min)</th>
<th>Eₐ (kJ/mol)</th>
<th>A (s⁻¹)</th>
<th>Average Eₐ (kJ/mol)</th>
<th>Average A (s⁻¹)</th>
<th>Temp. of peak (max °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃-DEA</td>
<td>6</td>
<td>15</td>
<td>84.87</td>
<td>3.48 × 10⁷</td>
<td>84.87</td>
<td>3.48 × 10⁷</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>15</td>
<td>87.78</td>
<td>6.07 × 10⁷</td>
<td>87.78</td>
<td>6.07 × 10⁷</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>90.06</td>
<td>1.41 × 10⁸</td>
<td>90.06</td>
<td>1.41 × 10⁸</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>15</td>
<td>90.34</td>
<td>1.75 × 10⁸</td>
<td>90.34</td>
<td>1.75 × 10⁸</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>92.17</td>
<td>2.01 × 10⁸</td>
<td>92.17</td>
<td>2.01 × 10⁸</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>10</td>
<td>92.17</td>
<td>3.01 × 10⁸</td>
<td>92.17</td>
<td>3.01 × 10⁸</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>15</td>
<td>92.27</td>
<td>3.24 × 10⁸</td>
<td>92.27</td>
<td>3.24 × 10⁸</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>20</td>
<td>93.99</td>
<td>3.95 × 10⁸</td>
<td>93.99</td>
<td>3.95 × 10⁸</td>
<td>184</td>
</tr>
<tr>
<td>BF₃-MAA</td>
<td>6</td>
<td>15</td>
<td>86.44</td>
<td>9.16 × 10⁷</td>
<td>86.44</td>
<td>9.16 × 10⁷</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>15</td>
<td>92.57</td>
<td>7.24 × 10⁸</td>
<td>92.57</td>
<td>7.24 × 10⁸</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>96.07</td>
<td>1.24 × 10⁹</td>
<td>96.07</td>
<td>1.24 × 10⁹</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>15</td>
<td>96.46</td>
<td>1.46 × 10⁹</td>
<td>96.46</td>
<td>1.46 × 10⁹</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>96.10</td>
<td>2.23 × 10⁹</td>
<td>96.10</td>
<td>2.23 × 10⁹</td>
<td>167.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>10</td>
<td>99.11</td>
<td>4.84 × 10⁹</td>
<td>99.11</td>
<td>4.84 × 10⁹</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>15</td>
<td>99.79</td>
<td>6.70 × 10⁹</td>
<td>99.79</td>
<td>6.70 × 10⁹</td>
<td>155.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>20</td>
<td>101.85</td>
<td>1.38 × 10¹⁰</td>
<td>101.85</td>
<td>1.38 × 10¹⁰</td>
<td>161</td>
</tr>
<tr>
<td>BF₃-PP</td>
<td>6</td>
<td>15</td>
<td>85.79</td>
<td>5.67 × 10⁷</td>
<td>85.79</td>
<td>5.67 × 10⁷</td>
<td>188.5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>15</td>
<td>91.93</td>
<td>3.46 × 10⁸</td>
<td>91.93</td>
<td>3.46 × 10⁸</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>93.47</td>
<td>3.26 × 10⁸</td>
<td>93.47</td>
<td>3.26 × 10⁸</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>15</td>
<td>94.67</td>
<td>3.89 × 10⁸</td>
<td>94.67</td>
<td>3.89 × 10⁸</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>95.22</td>
<td>3.91 × 10⁸</td>
<td>95.22</td>
<td>3.91 × 10⁸</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>10</td>
<td>97.79</td>
<td>8.93 × 10⁸</td>
<td>97.79</td>
<td>8.93 × 10⁸</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>15</td>
<td>97.92</td>
<td>1.49 × 10⁹</td>
<td>97.92</td>
<td>1.49 × 10⁹</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>20</td>
<td>101.76</td>
<td>1.56 × 10⁹</td>
<td>101.76</td>
<td>1.56 × 10⁹</td>
<td>187</td>
</tr>
</tbody>
</table>

model. A plot of the left-hand side of the above equation, ln k, against 1 / T should give a straight line with a slope of -Eₐ / R for the correct functional form f(x). The intercept is lnA from which the frequency factor can be evaluated. The homogenous models are often used to describe cure reactions in literature [26, 27]. We have, therefore, chosen the nth order homogeneous reaction model for dynamic experiments of DGEBA/BF₃-amine system; and for homogeneous model the functional form f(x) in equation 15 can be replaced by (1-x)ⁿ. Equation 15 can be written as:

\[
\ln[(da/dt)/(1-x)^n] = \ln A - E/RT
\]  

According to equation 16 a plot of the left-hand side, ln[(da/dt)/(1-x)^n], against 1/T should
give a straight line with a slope of $-E_a/R$ and intercept of $\ln A$ for a suitable and correct value of $n$. Figure 8 shows typical plots of $\ln[(da/dt)/(1-a)]$ vs. $1/T$, in which the fractional conversions, $a$, were determined from dynamic DSC thermograms of DGEBA/BF$_3$-amine systems of Figures 4–6. The straight lines obtained with the best correlation coefficients when the chosen values of $n$ were in the range of 0.97 to 0.99 for the three BF$_3$-amine complexes used as curing agents of DGEBA in the present work. The results, therefore, indicate that the best suitable value of $n$ is one ($n=1$). Table 1 shows activation energies ($E_a$) and frequency factors ($A$) of each of the DGEBA/BF$_3$-amine systems at different concentrations of 6, 8, 10 and 15 phr. It also shows the average values of $E_a$ of etherification reaction of 89 kJ/mol for DGEBA/BF$_3$-DEA, 94 kJ/mol for DGEBA/BF$_3$-MAA and 92.83 kJ/mol for DGEBA/BF$_3$-PP systems. The activation energy changes with the concentration of curing agent slightly, but as it is seen in Figure 9 the frequency factor increases as the initial BF$_3$-amine complex concentration increases. The increase in the frequency factor is indicative of the formation of a greater number of active sites as the concentration of BF$_3$-amine complex increases. The same results were obtained by Tackie et al. [19] for BF$_3$-MEA complex. Figure 10 shows plots of the average reaction rate $(da/dt)$ vs. concentration of BF$_3$-amine complexes. The reaction rate increases sharply with the concentration up to 10 phr, and it is higher in magnitudes for BF$_3$-MAA complex/DGEBA system in comparison with the two other systems. This could also indicate that BF$_3$-MAA complex is more reactive than BF$_3$-DEA and BF$_3$-PP complexes.

If the dynamic cure of epoxy resin is considered to be a homogeneous reaction, the equation 13 can be rewritten as follows:

$$\frac{da}{dt} = k(1-a)^n$$  \hspace{1cm} (17)

or

$$\frac{da}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1-a)^n$$  \hspace{1cm} (18)

For calculation of activation energy and frequency factor the value of $n = 1$ was used. To verify the
validity of this, activation energy and frequency factor of dynamic experiment of DGEBA/BF₃-PP system at 6 phr concentration monitored at a heating rate of 15 °C/min was used:

\[
\frac{d\alpha}{dt} = 5.67 \times 10^7 \exp(-85.79/RT)(1-a) \quad (19)
\]
or

\[
\frac{d\alpha}{dt} = 5.67 \times 10^7 \exp(-10319.58/T) (1-a) \quad (20)
\]

Thus, if \( q=\alpha T/dt \) is the constant heating rate,

\[
\int_0^\alpha \frac{d\alpha}{(1-a)} = 5.67 \times 10^7 /q \int_{T_a}^T \exp(-10319.58/T)dT \quad (21)
\]

By calling \( Z=10319.58/T, \) \( dZ=-Z^2 dT/10319.58 \) and \( da/(1-a)=\ln(1-a), \) equation 21 may be written as:

\[
-\ln(1-a) = -[3.51 \times 10^{13}/q \exp(-Z/Z^2)]dZ \quad (22)
\]

According to the mathematical calculations given in the literature [28], for \( Z>15 \) which cover the actual using range of our experiments, the integral

\[
F(z) = [\exp(-Z)/Z^2]dZ \quad (23)
\]

may be calculated as:

\[
\ln F(z) = -5.330 - 1.0516 Z \exp[\ln F(z)]
\]

\[
= \exp(-5.33) \times \exp(-1.0516Z) \quad (24)
\]

By applying the above value and the value of \( Z \) in equation 22:

\[
-\ln(1-a) = -[1.7 \times 10^{11}/q (°C/min)] \exp(-10852.07/T) - \exp(-10852.07/T_a) \quad (25)
\]

In our experiments \( T_a \) is room temperature and due to higher value of \( T \) we can neglect the term of \( T_a. \)

\[
-\ln(1-a) = -[1.7 \times 10^{11}/q (°C/min)] \exp(-10852.07/T) \]

Then:

\[
\ln[-\ln(1-a)] = \ln[1.7 \times 10^{11}/q] - 10852.07/T \quad (26)
\]

and

\[
\ln\{[-\ln(1-a)]q/ax7\times10^{11}\} = -10852.07/T \quad (27)
\]

In equation 27, \( q=15 °C/min; \) by applying the value of conversion at the related temperatures , the left hand side of the equation:

\[
Y=[-\ln(1-a)] q/1.7 \times 10^{11}
\]

can be plotted against the right hand side:

\[
X=10852.07/T
\]

which has to be a straight line if the reaction is to
be first order. Figures 11 and 12 show typical plots of such attempts for DGEBA/BF$_3$-PP and DGEBA/BF$_3$-DEA systems at 6 and 15 phr concentrations, respectively. The same results were obtained for all concentrations (6, 8, 10 and 15 phr) of DGEBA/BF$_3$-amine systems studied in the present work. These results confirm the reasonable accuracy of the proposed first order kinetic equation.

CONCLUSION

The FT-IR and dynamic DSC experiments were used to delineate the mechanisms for the BF$_3$-amine complexes/DGEBA homopolymerization reaction. BF$_3$-amine complexes undergo a rapid thermal conversion to HBF$_4$, which is the catalytic species. This finding agrees with the conclusions of Smith and Smith [1] and Tackle [19]. A phenomenological kinetic model has been proposed with which it is possible to calculate accurately the degree of conversion of epoxy/ BF$_3$-amine systems over the whole range of cure processes.

From the analysis presented above using the integral procedures on data obtained from dynamic experiments, it can be concluded that cure reactions can be represented by the first-order homogeneous reaction mechanism. Analysis of the reaction between DGEBA and BF$_3$-amine complexes showed that the curing proceeds by a two step mechanisms: The first step is the complex formation reaction of DGEBA and the active species (HBF$_4$) formed from thermal breakdown of BF$_3$-amine complexes, and the second step is the etherification reactions through which cross-links form. It may then be concluded that given the typical cure conditions for an epoxy (temperatures of 140–200 °C), the BF$_3$-amine complexes would be completely converted to HBF$_4$ before the cross-linking reactions began in the resin system.

The maximum temperature of exothermal peaks (cure temperatures) shifts to a higher value as the heating rate increases, and shifts to the lower values when at a particular heating rate the concentration of the curing agent increases. The cure temperatures of BF$_3$-MAA , BF$_3$-DEA and BF$_3$-PP complexes are, respectively, 157, 174 and 176 °C at the heating rate of 10 °C/min and concentration of 10 phr in DGEBA. The activation energies of the above systems are in the range of 90–96 kJ/mol at the same above heating rates and concentrations, while the frequency factor changes with concentration of BF$_3$-amine complex.

REFERENCES

15. Fava R. S.; Polymer, 137, 1968.
<table>
<thead>
<tr>
<th>Number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>Ghaemy M., Khandani M. H.; in press</td>
</tr>
</tbody>
</table>