3.1 INTRODUCTION

The most valuable property of thermosetting resins is their ability to be transformed readily from the liquid state to tough, hard thermoset solids. Thermosets are the polymeric materials having permanent three dimensional network structures via the formation of intermolecular cross links and thus cannot be remelted. Among the large variety of polymeric thermosets, epoxides enjoy the most widespread uses and are certainly the most studied.

The transformation from low molecular weight resin to highly cross linked, tough network structure is brought about by the use chemically active compounds known as curing agents and the process is termed as ‘curing’. Curing agents, which later become an integral part of the cured resin, exert marked effect on its thermal stability although, they have very little effect on the mechanism of degradation.

A number of various curing agents have been suggested for the curing of thermosetting resins depending upon the location of reactive groups in the resin and their reactivity towards the curing agents. The curing agents (i.e. cross linking agents) used to crosslink the epoxy resins are aliphatic amines, cycloaliphatic amines, polyamides, aromatic diamines, polymercaptans, acid anhydrides, Lewis acids and bases etc. They are selectively employed according to the required properties of the cured resin, i.e. the end – use applications\textsuperscript{1-14}.

The choice of resin and curing agent depends on the handling characteristics (viscosity, gel time), curing temperature and time, toxicological aspects, environmental limitations and the cost factor. Hence, the systematic study of these factors are desirable, especially the evaluation of degree of cure as a function of cure conditions.
In the present investigation diethylenetriamine (DETA) and 4,4’-diaminodiphenyl sulfone (DDS), the commercially widely used crosslinking agents were chosen to study the curing behavior of the prepared epoxy resins.

3.2 PROCEDURE

3.2.1 ISOTHERMAL CURING

As it is evident from the title itself that the curing process is to be carried out at a constant temperature (isothermal), the mass should be carefully stirred and enough attention is required to recognize the gelling stage. One has to be very attentive and anxious even at the end of the curing process to observe the shoot-up in the temperature, which is to be considered as the peak exotherm temperature. Gel time is the period required by the resin/curing agent system to attain gel state during the curing process. The actual procedure is as follows.

In a wide mouth test tube (1” diameter), the resin sample was introduced carefully so that it fell at the bottom of the test tube directly. Cross linking agent and catalyst satisfying the stoichiometric amount were added and the mass was briskly stirred by a stout thermometer. The test tube was then immediately placed in a previously heated oil bath maintained at the required temperature and simultaneously the time was started to count. The temperature of the oil bath was carefully kept constant throughout the procedure. As the inside temperature of the test tube was raised, stirring became more and more difficult indicating the onset of the reaction. The time was noted at the stage when the resin set to a gel and stirring became literally impossible. This time period was considered as the gel time as defined above. At the same time, temperature of the gelled mass was also recorded and considered as peak exotherm temperature.
After gelation, post curing was carried out for two hours. After post curing, the selected cured resin samples were analyzed by either thermo gravimetrically or differential thermal analysis, which are discussed in section 3.2 and 3.3 respectively.

### 3.2.1.1 INTERPRETATIONS

The gel time and peak exotherm temperature of epoxy resins are presented in Tables 3.1 and 3.2. The conclusion drawn from the data are as follow.

The resin/curing agent system decides the gel time and peak exotherm temperature. The resin/DDS system is more reactive than resin/DETA system.

#### Table 3.1 Isothermal curing parameters for epoxy resins cured with diethylenetriamine (DETA) at 30 °C.

The quantity of DETA was 0.2 mole with respect to EEW.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Gel Time Minutes</th>
<th>Gel Temp. (°C)</th>
<th>Peak exotherm temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHDA1EP10</td>
<td>36</td>
<td>98</td>
<td>154</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>38</td>
<td>92</td>
<td>142</td>
</tr>
<tr>
<td>BHDA1EP50</td>
<td>34</td>
<td>94</td>
<td>130</td>
</tr>
<tr>
<td>BHDA1EP70</td>
<td>35</td>
<td>97</td>
<td>132</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>34</td>
<td>95</td>
<td>125</td>
</tr>
<tr>
<td>BHDA2EP10</td>
<td>37</td>
<td>96</td>
<td>158</td>
</tr>
<tr>
<td>BHDA2EP30</td>
<td>38</td>
<td>94</td>
<td>144</td>
</tr>
<tr>
<td>BHDA2EP50</td>
<td>32</td>
<td>95</td>
<td>136</td>
</tr>
<tr>
<td>BHDA2EP70</td>
<td>36</td>
<td>97</td>
<td>130</td>
</tr>
<tr>
<td>BHDA2EP100</td>
<td>34</td>
<td>94</td>
<td>126</td>
</tr>
<tr>
<td>BHDA3EP10</td>
<td>39</td>
<td>97</td>
<td>156</td>
</tr>
<tr>
<td>BHDA3EP30</td>
<td>30</td>
<td>92</td>
<td>140</td>
</tr>
<tr>
<td>BHDA3EP50</td>
<td>36</td>
<td>95</td>
<td>135</td>
</tr>
<tr>
<td>BHDA3EP70</td>
<td>32</td>
<td>96</td>
<td>130</td>
</tr>
<tr>
<td>BHDA3EP100</td>
<td>39</td>
<td>94</td>
<td>125</td>
</tr>
</tbody>
</table>
Table 3.2 Isothermal curing parameters for epoxy resins cured with dianinophenyl sulfone (DDS) at 160 °C.

The quantity of DDS was 0.2 mole with respect to EEW.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Gel Time (Minutes)</th>
<th>Gel Temp. (°C)</th>
<th>Peak exotherm temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHDA1EP10</td>
<td>24</td>
<td>168</td>
<td>204</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>22</td>
<td>172</td>
<td>198</td>
</tr>
<tr>
<td>BHDA1EP50</td>
<td>28</td>
<td>164</td>
<td>196</td>
</tr>
<tr>
<td>BHDA1EP70</td>
<td>30</td>
<td>168</td>
<td>210</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>32</td>
<td>170</td>
<td>192</td>
</tr>
<tr>
<td>BHDA2EP10</td>
<td>35</td>
<td>178</td>
<td>170</td>
</tr>
<tr>
<td>BHDA2EP30</td>
<td>24</td>
<td>164</td>
<td>185</td>
</tr>
<tr>
<td>BHDA2EP50</td>
<td>22</td>
<td>162</td>
<td>172</td>
</tr>
<tr>
<td>BHDA2EP70</td>
<td>28</td>
<td>166</td>
<td>170</td>
</tr>
<tr>
<td>BHDA2EP100</td>
<td>30</td>
<td>168</td>
<td>204</td>
</tr>
<tr>
<td>BHDA3EP10</td>
<td>26</td>
<td>172</td>
<td>190</td>
</tr>
<tr>
<td>BHDA3EP30</td>
<td>30</td>
<td>168</td>
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</tr>
<tr>
<td>BHDA3EP50</td>
<td>28</td>
<td>170</td>
<td>190</td>
</tr>
<tr>
<td>BHDA3EP70</td>
<td>35</td>
<td>166</td>
<td>185</td>
</tr>
<tr>
<td>BHDA3EP100</td>
<td>29</td>
<td>164</td>
<td>202</td>
</tr>
</tbody>
</table>

The curing data also reveal that the cure time of resin increases as the distance between epoxy rings in the polymer chain increases.

3.2.2 DYNAMIC CURING

In the recent years, Differential scanning calorimetry (DSC) is widely used to study the mechanism and kinetics of curing. It has proved to be a valuable tool for investigating parameters of the curing reaction of the thermoset polymers. This technique is applied to evaluate curing characteristics like the degree of cure, temperature and duration of the curing reaction, and the magnitude and variability of the heat of reaction as a function of time and temperature for thermosetting materials such as phenolics /15,16/, diallyl phthalate /17/, unsaturated polyesters /18/ and epoxy resins /19-30/.
Fava, R.A. /19/ has reported an application of DSC to amine catalyzed curing reaction of epoxy resin system. Three techniques were used to obtain information directly related to the curing reaction and rate processes. The change in electrical resistivity during the curing of epoxies was interpreted considering ionic conduction /20/.

Prime, R.B. /21, 22/ studied the isothermal and dynamic cure kinetics of DGEBA resin using DSC. A method was given for the determination of the cure parameters, Arhenious pre exponential, activation energy, and reaction order. Similar type of study was also carried out by Barton. J.M. /23/ and Penczek, P. /27/.

Now a days with the aid of advanced facilities of computer programmable methods, curing kinetics studies have been performed more easily. Patel, S.R. and Patel, R.G. /28/ have studied curing kinetics of the epoxy resins with various amines as curing agents by DSC using Borchardt Daniel method proposed by Du Pont. They reported the activation energy and order of reaction for each resin-curing agent systems. Patel, V.S. and his coworkers /29/ investigated curing parameters of Triglycidyl aminophenol with aromatic diamines by DSC. Compton, D.A.C. and his coworkers /30/ gave a combined DSC-FTIR approach to study the polymeric materials. DSC-FTIR technique is useful for spectroscopic and thermo degradation information about solid or liquid sample undergoing thermal modifications.

In the present work, the DSC technique was applied to study the cure kinetics of various epoxy resins using DETA and DDS as crosslinking agents. The overall kinetic parameters of the curing reactions were estimated using Barrett method /31/.
3.2.2.1 Experimental details

A Du Pont 900 differential scanning calorimeter was employed to study the exothermic curing reactions. The DSC cell was calibrated using standard materials and procedures /32/. The sample weights used for the investigation were in the range of 5.0 to 6.0 mg. The samples were scanned from 30 °C to 300 °C at a scanning rate of 10 °C min⁻¹.

3.2.2.2 Analysis of DSC scans

The employed instrument has the advantage that even by using small quantity of the sample, the energy changes involved in the reaction can be measured directly. Hence it is very easy to measure the values required for the evaluation of cure parameters. A DSC plot, actually a differential enthalpic analysis curve, is represented below.

![DSC plot](image)

The heat change involved in a reaction can be measured directly from the plot. The total area ‘A’ under the curve corresponds to the total heat evolved during the reaction (ΔH in m.cal.). the area ‘a’ corresponds to the heat evolved up to stage ‘S’, i.e. up to time ‘t’ after the commencement of the reaction.

Barrett has derived the following relation to determine the rate constant ‘K’.

\[
\frac{dH}{dt} = \text{Heat change}
\]

\[
S \quad \text{Temperature} \quad K
\]
Thus, the evaluation of ‘K’ requires measurement of \( \frac{dH}{dt} \) and \((A-a)\) at various time intervals as described below.

The heat changes in m.cal., i.e. area under the curve ‘A’ and ‘a’ are measured by Planimeter or by counting squares under the plot. The height of the ordinate at a given temperature (time) gives \( \frac{dH}{dt} \). It is expressed in units of m.cal.min\(^{-1}\). Using this information the rate constant ‘K’ was calculated at various temperatures. After getting ‘K’ at different temperatures, the regression analysis was made on the data using the Arrhenious relation to obtain the energy of activation for the curing reactions.

\[
K = A \times e^{-\frac{E}{RT}}
\]

Therefore,

\[
\ln K = \ln A - \frac{E}{RT}
\]

In the computation of the data it was assumed that the reactions follow a \( n \)^{th} order Arrhenious type kinetics.

The DSC scans obtained on curing of resin- curing agent systems were almost similar in shape giving an exotherm in some definite temperature range. In this range, no exotherms were observed in the case of DSC scans for the resin only and for the cured resin. This indicates that the exotherms obtained in all the above resin systems were due to curing reactions only. The curing of various systems containing different types of epoxy resins were found to differ with respect to total heat of reaction and the temperature at which the reactions were initiated, peaked and terminated. The DSC scans are reproduced in Fig. 3.1 and 3.2. The data obtained from DSC scan are shown in Table 3.3. The cure characteristics such as temperature at which the reactions were initiated (\( T_i \)), attained a maxima (\( T_p \)) and completed (\( T_f \)), along with the temperature range for curing as well as curing time and the activation energy were evaluated and are presented in Table 3.4.
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Hence, it is reasonable to assume that any change in the curing mechanism with curing temperature does not affect the overall reaction rate.

The use of the Barrett equation to obtain kinetic parameters associated with the epoxy curing reaction involves certain assumptions implicit in the theoretical analysis of curing. First, it is assumed that the chemistry of the process is independent of curing temperature; thus, in effect, single activation energy and a single $dH$ value would apply at all temperatures, and hence the area or fractional area under a DSC curve would always directly proportional to the number of crosslinks formed. Secondly, it is assumed that the area under the DSC curve has no contribution from thermal phenomena other than crosslinking. Therefore, the activation energy and reaction order thus obtained must be related to the average overall process of curing. In addition, the overall curing process follows first-order kinetics up to 80% conversion.
Figure 3.1 A Typical DSC Scan for curing of BHDA1E50-DETA system
Chapter 3

Figure 3.1 B Typical DSC Scan for curing of BHDA1EP100-DETA system
Figure 3.2 A Typical DSC Scan for curing of BHDA1EP30-DDS system
Figure 3.2 B Typical DSC Scan for curing of BHDA1EP50-DDS system
### Table 3.3 Kinetic parameters evaluated from single DSC scan for selected epoxy resins cured with DETA and DDS

<table>
<thead>
<tr>
<th>Resin</th>
<th>Activation Energy E. kJ. Mole⁻¹</th>
<th>Log Z min⁻¹</th>
<th>Order of reaction n</th>
<th>Heat of reaction ∆H J.gm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DETA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHDA1EP10</td>
<td>143.3</td>
<td>15.44</td>
<td>1.75</td>
<td>126.4</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>447.5</td>
<td>44.05</td>
<td>1.79</td>
<td>17.5</td>
</tr>
<tr>
<td>BHDA1EP50</td>
<td>64.9</td>
<td>5.31</td>
<td>0.20</td>
<td>191.9</td>
</tr>
<tr>
<td>BHDA1EP70</td>
<td>153.0</td>
<td>15.47</td>
<td>1.09</td>
<td>54.4</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>251.8</td>
<td>26.55</td>
<td>2.37</td>
<td>12.2</td>
</tr>
<tr>
<td>DDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHDA1EP10</td>
<td>266.2</td>
<td>28.01</td>
<td>1.37</td>
<td>44.8</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>255.7</td>
<td>21.38</td>
<td>2.12</td>
<td>287.3</td>
</tr>
<tr>
<td>BHDA1EP50</td>
<td>181.4</td>
<td>15.67</td>
<td>0.76</td>
<td>178.2</td>
</tr>
<tr>
<td>BHDA1EP70</td>
<td>665.6</td>
<td>62.51</td>
<td>3.82</td>
<td>250.3</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>553.0</td>
<td>53.18</td>
<td>3.65</td>
<td>308.2</td>
</tr>
</tbody>
</table>

### Table 3.4 Thermal parameters obtained from single DSC scan for selected epoxy resins cured with DETA and DDS

<table>
<thead>
<tr>
<th>Resin</th>
<th>Tᵢ °C</th>
<th>Tₚ °C</th>
<th>Tᵣ °C</th>
<th>Curing range (Tᵣ - Tᵢ) °C</th>
<th>Cure time min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DETA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHDA1EP10</td>
<td>174.58</td>
<td>208.45</td>
<td>243.18</td>
<td>68.60</td>
<td>24.32</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>249.88</td>
<td>266.74</td>
<td>270.45</td>
<td>20.57</td>
<td>27.05</td>
</tr>
<tr>
<td>BHDA1EP50</td>
<td>255.05</td>
<td>289.97</td>
<td>344.31</td>
<td>89.26</td>
<td>34.43</td>
</tr>
<tr>
<td>BHDA1EP70</td>
<td>204.21</td>
<td>236.0</td>
<td>262.96</td>
<td>58.75</td>
<td>26.30</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>108.43</td>
<td>141.77</td>
<td>166.67</td>
<td>58.22</td>
<td>16.67</td>
</tr>
<tr>
<td>DDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BHDA1EP10</td>
<td>204.10</td>
<td>225.21</td>
<td>250.0</td>
<td>43.09</td>
<td>23.00</td>
</tr>
<tr>
<td>BHDA1EP30</td>
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<td>345.14</td>
<td>365.91</td>
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<td>36.60</td>
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<tr>
<td>BHDA1EP50</td>
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<td>343.18</td>
<td>128.19</td>
<td>34.32</td>
</tr>
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<td>286.73</td>
<td>349.98</td>
<td>76.65</td>
<td>35.00</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>257.07</td>
<td>273.06</td>
<td>335.22</td>
<td>78.13</td>
<td>33.52</td>
</tr>
</tbody>
</table>
3.3 THERMOGRAVIMETRIC STUDY

3.3.1 INTRODUCTION

Thermal analysis has a unique role in the characterization of polymeric materials. Thermo gravimetric analysis (TGA) is one of the well-established thermal techniques like DSC, DTA and TMA. TGA measures and automatically records change in weight as a function of temperature or as a function of time at a constant temperature. The nature of TG curve for a given sample depends on nature of the sample, size of the sample, shape of the cell, the mode of heating and the atmosphere in the immediate vicinity of the sample during analysis. These are important factors and to be controlled during thermal analysis. From the information furnished by TGA and DTA, it is possible to note the temperature at which the material starts to decompose. It is also possible to know whether the decomposition occurs in one step or in multistep.

Besides this information, the order of reaction can be also determined by the analysis of the thermal data furnished by either DTA or TGA. Numbers of reports concerning thermal analysis of the epoxy resins are available in the literature./33-40/

The present work deals with the study of thermal behavior of isothermally cured epoxy resins.

3.3.2 THERMOGRAVIMETRIC ANALYSIS

The thermal behavior of the selected cured polymer samples described in section 3.1 has been studied by TGA. The loss in weight due to pyrolysis of the polymeric material with increase in temperature forms a TG curve. /41/ Normally a polymer sample starts to lose the weight at very slow rate up to a particular temperature. Therefore, the rate of loss in weight becomes larger over a narrow range of temperature. After this stage, the loss in
weight levels off. The shape of the TG curve depends on the nature of the degradation reaction. The analysis of these data by Broido method is often carried out with a view to estimate the activation energy of the degradation reaction.\footnote{42}

The advantages of TGA are enumerated below.\footnote{41-42}

- A relatively small set of data is to be treated.
- Continuous recording of weight loss as a function of temperature ensures equal weightage for examination over the whole range of study.
- As a single sample is analyzed over the whole range of temperature, the variation in the value of the kinetic parameters, if any, will be indicated.
- For the estimation of kinetic parameters, several methods may be employed. All of them involve two assumptions. It is assumed that the difference in the thermal and diffusion processes is negligible. Since small quantity of material is employed in TG analysis, the barrier between the thermal and diffusion processes is quite negligible. Hence, it is reasonable to ignore it. It is also assumed that the Arrhenious reaction is valid over the whole range of temperature.\footnote{42}
- Various methods are proposed to analyze the TG data depending upon the nature of experimentation.\footnote{42-48} Out of these, the method proposed by Broido, which is applied to a single set of TG data was selected for the analysis of the TG data.\footnote{42} in the present investigation.
3.3.2.1 Experimentation and Method of Calculation of Activation Energy

The thermo gravimetric analyses of samples have been carried out using a “Du Pont Thermo gravimetric Analyzer 9900” in a slow stream of air. The boat prepared from platinum foil was used to hold the polymer sample for analysis. First, it was properly washed and dried and then, suspended on a quartz rod in the TGA balance. The powdered sample (about 5 to 10 mg) was placed in the boat. The sample in the boat was covered by a quartz tube in which the flow of air was maintained. The weight of the sample was noted on the TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was performed by heating the system at a constant rate of 25°C.min⁻¹. Simultaneously, change in the weight was recorded automatically with time (temperature). This will reveal the percentage weight loss of the material as a function of time and also temperature. The experiment was stopped at 650 °C where no further decrease in weight was observed.

The thermo grams were analyzed to obtain information about the percentage weight loss at different temperatures. The results of these analyses are presented in Table 3.5 and Table 3.6. Selected thermograms are shown in Fig. 3.3 and 3.4.

Broido method was used to calculate activation energy (Ea) as follows.

When a polymeric substance is heated, it undergoes pyrolysis. It is assumed that the pyrolysis products are volatile. The progress of the reaction is followed by continuous weighing of the sample with time. It is reasonable to assume that the weight of the material (Wt) at time ‘t’ is related to the fraction of the number of initial molecules not yet decomposed ‘y’ and is expressed by the equation (3.1).
Where, ‘\(W_\infty\)’ is the weight when the reaction is completed and ‘\(W_0\)’ is the initial weight of the material.

If the pyrolysis is carried out isothermally, the reaction rate is given by
\[
\frac{dy}{dt} = -Ky^n \quad \text{.........(3.2)}
\]

Where, ‘\(n\)’ is the order of reaction. The rate constant ‘\(K\)’ changes with the absolute temperature according to the Arrhenioues equation.
\[
K = y^n \quad \text{.........(3.3)}
\]

From equation 3.2 and 3.3, it follows
\[
\frac{dy}{y^n} = -K \, dt \quad \text{.........(3.4)}
\]

If instead of operating the reaction isothermally, the reaction is operated by increasing temperature, and if temperature ‘\(T\)’ is a linear function of time ‘\(t\)’, then
\[
T = T_0 + ut \quad \text{.........(3.5)}
\]
\[
dT = u \, dt \quad \text{.........(3.6)}
\]

From the equation 3.4 and 3.6, it follows
\[
\frac{dy}{y^n} = -\left(\frac{A}{u}\right) e^{-E/RT} \, dT \quad \text{.........(3.7)}
\]

The TGA curve of such reaction represents this last equation integrated form a temperature ‘\(T_0\)’ at which \(y = 1\).

Thus,
\[
\int_{y}^{1} \frac{dy}{y^n} = \left(\frac{A}{u}\right) \int_{T_0}^{T} e^{-E/RT} \, dT \quad \text{.........(3.8)}
\]

A large number of pyrolysis processes are known to be first order reactions, and only these reactions are considered. As \(n = 1\),
the integration of left hand side (L.H.S.) becomes simple.

\[ \int_{\gamma}^{1} \frac{dy}{y^n} = \int_{y}^{1} \frac{dy}{y} = -\ln y = \ln \left( \frac{1}{y} \right) \]  \hspace{1cm} (3.9)

Conversely the integration of the right hand side (R.H.S.) part of the equation (3.9) is not that simple. However, Vallet, P. [49], in a monograph published in 1961, reported values of integration of terms like those involved in equation (3.8). From these data, the values of integration of the L.H.S. was obtained by Broido, A. [42].

Van. K. D. [50] and his co-workers revealed that almost the entire measurable reaction usually occurs in +10% of \( T_m \), the temperature of maximum reaction rate, and they applied certain approximations and obtained the following relation.

\[ \ln[\ln(1/y)] = \left( \frac{E}{R} \times T_m + 1 \right) \ln T + \text{const.} \]  \hspace{1cm} (3.10)

According to this relation (3.10) a plot of \( \ln[\ln(1/y)] \) vs. 1000/T would be linear and its slope is related to the activation energy.

Horowitz, H. H., et. al. [51] introduced two alternate approximations and developed relations (3.11) and (3.12).

\[ \ln[\ln(1/y)] = \left( \frac{E}{R} \times T_m^2 + 1 \right) T + \text{const.} \]  \hspace{1cm} (3.11)

\[ = \left( \frac{E}{R} \times T_m^2 + 1 \right) T + \text{const} \]  \hspace{1cm} (3.12)

The expression (3.12) has been found to be the most accurate of all three equations (3.10, 3.11, 3.12). The last equation is employed here to correlate the experimental data of all the polymer samples. The estimated values of activation energy (Ea) for polymer samples are included in Table 3.7 and Table 3.8. Integral procedural decomposition temperature (IPDT) values which were obtained by using Doyle’s method [52] are given in Table 3.7 and Table 3.8.

The other temperature characteristics such as Ti (initial decomposition temperature), T_{10} (temperature at 10% weight loss) and T_{max} (temperature of maximum rate of decomposition) are simultaneously presented in Table 3.7 and Table 3.8.
Table 3.5  Thermogravimetric data of epoxy resins cured with DETA

<table>
<thead>
<tr>
<th>Resin</th>
<th>Percentage weight loss at temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>BHDA1EP10</td>
<td>3.39</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>5.74</td>
</tr>
<tr>
<td>BHDA1EP50</td>
<td>6.64</td>
</tr>
<tr>
<td>BHDA1EP70</td>
<td>7.09</td>
</tr>
<tr>
<td>BHDA1EP100</td>
<td>2.94</td>
</tr>
<tr>
<td>BHDA2EP10</td>
<td>2.88</td>
</tr>
<tr>
<td>BHDA2EP30</td>
<td>9.2</td>
</tr>
<tr>
<td>BHDA2EP50</td>
<td>7.92</td>
</tr>
<tr>
<td>BHDA2EP70</td>
<td>10.29</td>
</tr>
<tr>
<td>BHDA2EP100</td>
<td>10.45</td>
</tr>
<tr>
<td>BHDA3EP10</td>
<td>3.33</td>
</tr>
<tr>
<td>BHDA3EP30</td>
<td>7.42</td>
</tr>
<tr>
<td>BHDA3EP50</td>
<td>12.47</td>
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<tr>
<td>BHDA3EP70</td>
<td>14.37</td>
</tr>
<tr>
<td>BHDA3EP100</td>
<td>14.31</td>
</tr>
</tbody>
</table>

Table 3.6  Thermogravimetric data of epoxy resins cured with DDS

<table>
<thead>
<tr>
<th>Resin</th>
<th>Percentage weight loss at temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>BHDA1EP10</td>
<td>5.11</td>
</tr>
<tr>
<td>BHDA1EP30</td>
<td>5.41</td>
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<tr>
<td>BHDA1EP50</td>
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<td>5.86</td>
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<tr>
<td>BHDA1EP100</td>
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<tr>
<td>BHDA2EP10</td>
<td>2.08</td>
</tr>
<tr>
<td>BHDA2EP30</td>
<td>7.7</td>
</tr>
<tr>
<td>BHDA2EP50</td>
<td>6.42</td>
</tr>
<tr>
<td>BHDA2EP70</td>
<td>6.54</td>
</tr>
<tr>
<td>BHDA2EP100</td>
<td>2.89</td>
</tr>
<tr>
<td>BHDA3EP10</td>
<td>10.17</td>
</tr>
<tr>
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<td>BHDA3EP50</td>
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<td>11.02</td>
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<tr>
<td>BHDA3EP100</td>
<td>8.58</td>
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</tbody>
</table>
Figure 3.3 Thermogravimetric data of epoxy resins cured with DETA
Figure 3.3 Thermogravimetric data of epoxy resins cured with DDS
3.3.3 INTERPRETATIONS

Examination of the thermo grams and TG data presented in Table 3.7 and Table 3.8 reveals the following.

The thermal stability of epoxy resins described in the present work is higher than that of DGEBA, the conventional epoxy resins. The introduction of azomethine (-C=N-) groups in the main chain of the epoxy resins remarkably increases thermal stability. The epoxy resins cured with DETA are less thermally stable compared to those cured with DDS.

The results indicate that the epoxy equivalent weight as well as the thermal stability increases upon addition of Schiff bases. At the same time, both the parameters increases as the steric hindrance decreases due to the structural features of the monomers. It is found that at the initial decomposition stage BHDA1EP30 degrades first compared to other prepared epoxy resins and BHDA3EP10 last. The highest $T_{\text{max}}$ (maximum decomposition temperature) were observed in case of BHDA1EP10 and BHDA1EP50 which is 340 °C. In the case of final decomposition temperature almost reverse trend is observed, which reveals that the order of $T_{\text{max}}$ is $p < m < o$. It can also be noted that it decreases upon increase in the concentration of monomers (Schiff bases). In short BHDA3EP100 shows the least $T_f$ value i.e. 510 °C. The activation energy of synthesized resins is observed in the range of 50 kJ/mol to 95 kJ/mol. The IPDT value of synthesized resins is ranging from 625 to 700. $T_{50}$ values of all the resins are ranging from 510 °C to 630 °C.
The above results indicate that the epoxy equivalent weight and the thermal stability increase upon addition of Schiff bases. At the same time, both the parameters increase as the steric hindrance decreases, which may be due to the structural features of the monomers. It is also observed that at the initial decomposition stage BHDA1EP30 degrades first compared to other prepared epoxy resins and BHDA3EP10 last. The highest $T_{\text{max}}$ (maximum decomposition temperature) were observed in case of BHDA1EP70 and BHDA2EP30 which is 340 °C. In the case of final decomposition temperature almost different trend is observed, which reveals that the order of $T_{\text{max}}$ is $p<o<m$. It can also be noted that it decreases upon increase in the concentration of monomers. In short BHDA3EP100 and BHDA3EP100 show the least $T_f$ values i.e. 510 °C. The activation energy of synthesized resins is observed in the range of 50 kJ/mol to 95 kJ/mol. The IPDT value of synthesized resins is ranging from 625 to 700. $T_{50}$ values of all the resins are ranging from 510 °C to 630 °C.
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