Effects of Nitriles on Curing of Epoxy Resin

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Abstract: Cure kinetics of diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA) systems with three nitriles were investigated by DSC analysis. Nitriles as reactive additives were malononitrile(MN), succinonitrile (SN) and glutaronitrile (GN). To estimate the kinetic parameters, Kissinger equation (dynamic run) and Fractional-life equation (isothermal run) were employed. The activation energy of DGEBA/MDA system is 11.11 kcal/mol and those of the DGEBA/MDA systems with MN, SN and GN are 11.38 kcal/mol, 11.48 kcal/mol and 11.32 kcal/mol, respectively. Due to the disturbance of nitrile compound to the reaction of amine and epoxide group, the activation energy is considered to increase while the cure rate is decreased.

1. Introduction

The development of modified epoxy resin has needed in the area of commercial and military equipments. Many scientists have modified epoxy resin systems to obtain appropriate properties by several methods [1-8]. We introduced three nitrile compounds as reactive additives to improve the toughness of DGEBA/MDA system and determined the cure kinetics of those systems. The physical, mechanical and electrical properties of cured epoxy resins strongly depend on the degree of cure. To investigate the cure kinetics, scientists have developed various creative methods [9-13], such as chemical analysis, FT-IR analysis, torsional braid analysis, or differential scanning calorimetry (DSC) techniques. DSC has been a useful technique for studying cure kinetics of crosslinking reactions in thermosetting epoxy resins. The basic assumption was that the heat evolution recorded by DSC was proportional to the extent of consumption of the functional groups [14-17].

In this study, cure kinetics were studied and analyzed by Kissinger equation and Fractional-life equation. To obtain the activation energy and the pre-exponential factor from the relationship between the heating rates and the exothermic peaks, Kissinger equation [12] was employed. It is

\[-\ln \left( \frac{q}{T_p^2} \right) = \frac{E_a}{RT_p} - \ln \left( \frac{AR}{E_a} \right) \]

where, q is the heating rate, T_p the temperature at which the maximum cure rate takes place, E_a activation energy, R gas constant and A pre-exponential factor.

The reaction order, n is calculated from the following Fractional-life equation [13].

\[\log t_n = \log \frac{a^{1-n} - 1}{k(A)^{n-1}} - (n-1) \log \frac{(A)_0}{(A)_f} \]

where, t_n is the fractional life which means the time required for initial concentration, (A)_0 to fall into a (A)_f. n reaction order, k rate constant and (A)_0/(A)_f unreacted fraction.

2. Experimental

2.1. Materials
The epoxy resin was diglycidyl ether of bisphenol
A (DGEBA), Epon 828 supplied by Shell Co. The epoxy equivalent weight was 184 g/eq. Curing agent was 4,4'-methylene dianiline (MDA) and the reactive additives are nitrile compounds such as malononitrile (MN), succinonitrile (SN) and glutaronitrile (GN). These agents were supplied by Fluka Chemie AG [18, 19].

2.2. Dynamic DSC Analysis
The calorimetric measurements were carried out with the Cahn-DSC. DGEBA/MDA (30 phr) systems with nitriles (5 phr) were well-mixed and 3 mg of the sample was accurately weighed at an aluminum DSC pan. Dynamic DSC analysis was performed in the various heating rates of 2, 5, 10, 20 °C/min under the nitrogen atmosphere of 40 mL/min.

2.3. Isothermal DSC Analysis
2-3 mg of the same sample used in dynamic analysis was placed in a DSC pan, cured at 85, 105, 120 and 150 °C in oven for a required time and quenched at -3 °C to stop the reaction of epoxy resin. Residual exothermic heat was determined by dynamic DSC scan at a heating rate of 20 °C/min and the isothermal curing curve was constructed by the proportional relationship between the residual exothermic heat and the unreacted fraction.

3. Results and Discussion

3.1. Kinetic Results of Dynamic DSC Analysis
DSC scans from room temperature to 350 °C at different heating rates of 2, 5, 10, 20 °C/min for DGEBA/MDA system with (dashed curve) and without (solid curve) SN are shown in Fig. 1. To obtain the activation energy and the pre-exponential factor from the relationship between the heating rates, q and the temperature, \( T_p \), at which the maximum cure rate takes place in Kissinger equation, Table 1 is constructed and the relationship between \( 1/T_p \times 10^5 \) and \(-\ln(q/T_p^2)\) is illustrated in Fig. 2. The activation energy could be calculated from the slope and the pre-exponential factor from the \( y \)-intersection. These values are listed in Table 2.

With the addition of SN, the temperatures at which cure reaction starts and those at which the maximum cure rate takes place were shown at about 4 °C higher than those in the system without SN as shown in Fig. 1. Moreover, the activation energy of DGEBA/MDA system is 11.11 kcal/mol and that of DGEBA/MDA/SN system was somewhat higher value, 11.38 kcal/mol. The results of the increasing temperatures and activation energy imply that the cure reaction of DGEBA/MDA/SN system is more difficult and needs more energy than that of DGEBA/MDA system. In DGEBA/MDA system, the reaction between the primary amine and epoxide group is significant in the beginning of the cure reaction. As the reaction proceeded, the reaction with the secondary amine and epoxide group and that of the epoxide and hydroxyl group were taken place. On the other hand, with an incorporation of nitrile compound to the DGEBA/MDA system the reaction of the amine and epoxide group is inhibited [8] by the nitrile compound which may disturb the contact of the functional groups. To confirm the possibility of the disturbance of nitrile compounds, DSC analysis for DGEBA/MDA system with various contents of SN

![Fig. 1. DSC scans for DGEBA/MDA system with (dashed curve) and without (solid curve) SN (5 phr) at various heating rates. (A) 20 °C/min, (B) 10 °C/min, (C) 5 °C/min, and (D) 2 °C/min.](image)

**Table 1.** The Relationship between the Heating Rates, q, and the Temperature at which the Maximum Cure Rate take Place, \( T_p \)

<table>
<thead>
<tr>
<th>System</th>
<th>Heating rate, ( q/\text{°C/min} )</th>
<th>Temp. at peak, ( T_p/\text{°C} )</th>
<th>( 1/T_p \times 10^6 )</th>
<th>(-\ln(q/T_p^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/MDA</td>
<td>2</td>
<td>393.3</td>
<td>2.54</td>
<td>11.25</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>414.8</td>
<td>2.41</td>
<td>10.45</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>434.2</td>
<td>2.30</td>
<td>9.84</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>457.9</td>
<td>2.18</td>
<td>9.26</td>
</tr>
<tr>
<td>DGEBA/MDA/GN</td>
<td>2</td>
<td>396.2</td>
<td>2.52</td>
<td>11.27</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>419.1</td>
<td>2.39</td>
<td>10.47</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>438.5</td>
<td>2.28</td>
<td>9.86</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>459.3</td>
<td>2.18</td>
<td>9.26</td>
</tr>
</tbody>
</table>
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Fig. 2. Plots of $-\ln(q/T_p^2)$ vs. $(1/T_p) \times 10^3$ by Kissinger equation for DGEBA/MDA system with (□) and without (○) SN (5 phr).

Table 2. Kinetic Parameters for DGEBA/MDA/Nitrile (5 phr) Systems

<table>
<thead>
<tr>
<th>System</th>
<th>$E_a$ (kcal/mol)</th>
<th>$A \times 10^7$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/MDA</td>
<td>11.11</td>
<td>1.86</td>
</tr>
<tr>
<td>DGEBA/MDA/MN</td>
<td>11.38</td>
<td>2.95</td>
</tr>
<tr>
<td>DGEBA/MDA/SN</td>
<td>11.48</td>
<td>5.24</td>
</tr>
<tr>
<td>DGEBA/MDA/GN</td>
<td>11.32</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Fig. 3. DSC scans for DGEBA/MDA system with various SN contents at the heating rate of 10 °C/min (A) 15 phr, (B) 10 phr, (C) 5 phr and (D) 0 phr.

Fig. 4. DSC scans for DGEBA/MDA system with three nitrile (5 phr) compounds at the heating rate of 10 °C/min (A) DGEBA/MDA/GN, (B) DGEBA/MDA/SN, (C) DGEBA/MDA/MN and (D) DGEBA/MDA.

Fig. 5. Isothermal curing curves for DGEBA/MDA/SN (5 phr) system at various temperatures (○) 85 °C, (□) 105 °C, (△) 120 °C and (◇) 150 °C.

is performed and is shown in Fig. 3. The temperature at which the maximum cure rate takes place is increased with the increment of SN content, thereby this explains the effect of nitrile compound on the disturbance.

Using the same method in Figs. 1 and 2 for the other nitrile compounds, the activation energies and the pre-exponential factors are obtained and are listed in Table 2. The activation energies of the
Table 3. Calculation of \(-\log[(A)_0/(A)_T]\) and \(\log(t_{oa})\) based on the Isothermal curing Curve at 85 °C in Fig. 5

<table>
<thead>
<tr>
<th>((A)_0/(A)_T)</th>
<th>(t)</th>
<th>0.6 ((A)_0/(A)_T)</th>
<th>(t_{oa})</th>
<th>(-\log ((A)_0/(A)_T))</th>
<th>(\log(t_{oa}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>1.0</td>
<td>0.54</td>
<td>22.0-1.0=21.0</td>
<td>0.046</td>
<td>1.322</td>
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<tr>
<td>0.85</td>
<td>2.6</td>
<td>0.51</td>
<td>24.0-2.6=21.4</td>
<td>0.070</td>
<td>1.330</td>
</tr>
<tr>
<td>0.80</td>
<td>4.2</td>
<td>0.48</td>
<td>26.3-4.2=22.1</td>
<td>0.097</td>
<td>1.344</td>
</tr>
<tr>
<td>0.75</td>
<td>6.8</td>
<td>0.45</td>
<td>29.4-6.8=22.6</td>
<td>0.125</td>
<td>1.354</td>
</tr>
<tr>
<td>0.70</td>
<td>9.6</td>
<td>0.42</td>
<td>32.9-9.6=23.3</td>
<td>0.155</td>
<td>1.367</td>
</tr>
</tbody>
</table>

Table 4. Reaction Orders for DGEBA/MDA/Nitrile(5 phr) Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature</th>
<th>85 °C</th>
<th>105 °C</th>
<th>120 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/MDA</td>
<td>1.72</td>
<td>1.62</td>
<td>2.02</td>
<td>1.91</td>
<td></td>
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<tr>
<td>DGEBA/MDA/MN</td>
<td>1.43</td>
<td>1.36</td>
<td>1.47</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>DGEBA/MDA/SN</td>
<td>1.41</td>
<td>1.41</td>
<td>1.48</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>DGEBA/MDA/GN</td>
<td>0.70</td>
<td>0.83</td>
<td>0.79</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. Computation of reaction orders for DGEBA/MDA/SN (5 phr) system by Fractional-life equation (○) 85 °C, (□) 105 °C, (△) 120 °C and (◇) 150 °C.

systems with nitriles are somewhat larger than that of the system without nitrile. The temperature at which the maximum cure rate takes place for the other nitrile compounds is shown in Fig. 4. As mentioned before, nitrile compounds affected the temperature of the highest peak.

3.2. Kinetic Results of Isothermal DSC Analysis

Isothermal curing curves for DGEBA/MDA/SN

Fig. 7. Isothermal curing curves for DGEBA/MDA/ Nitrile (5 phr) systems at various temperatures (○) 85 °C, (□) 105 °C, (△) 120 °C and (◇) 150 °C.
system are shown in Fig. 5. In order to obtain the reaction order from the isothermal curing curve at 85 °C, $-\log([A]_0/(A)_1)$ and $\log[k]_0$ were calculated using the experimental data in Table 3, then the Fractional-life equation were employed and these values of the other temperatures were calculated by the same method. The relationship of $-\log([A]_0/(A)_1)$ and $\log[k]_0$ in Eq. 2 were plotted (Fig. 6) and reaction orders were gained from the slope, -(n-1), and are listed in Table 4. The reaction orders for DGEBA/MDA/SN system are varied between 1.41 and 1.50 in the employed temperature. In general, the reaction order for an elementary reaction is constant regardless of the reaction temperature. However, the reaction orders for the DGEBA/MDA/Nitrile system are varied with the temperature. The observed variation of the reaction order may be due to the complex reactions pathways. The pathways are composed of many simple reactions such as the primary amine and the epoxide reaction, the secondary amine and the epoxide reaction, the amine and the hydroxyl reaction, the primary amine and the nitrile reaction, the nitrile and the hydroxyl reaction, etc., and these reactions occurs at the same time. Therefore, it may be possible that each of the above pathway makes certain different contribution to the total reaction mechanism at different temperatures, so reaction orders may be varied [13].

The effect of temperature on the cure rates could be investigated in Fig. 5. As can be seen, cure rates are increased with the cure temperature. Cure time to be a selected conversion is inversely proportional to the cure rate. Thus, the average cure rates to be 60% conversion at other temperatures compared to that at 85 °C would be 2.4 times at 105 °C, 6.0 times at 120 °C and 7.6 times at 150 °C.

Fig. 7 shows isothermal curing curves for the other nitrile systems. As shown in Fig. 5, the cure rates was increased with the curing temperature. From these isothermal curing curves, the reaction orders could be calculated using Fractional-life equation and are listed in Table 4.

Fig. 8 shows isothermal curing curves for DGEBA/MDA system with various nitriles at 85 °C. As have seen above, the activation energies increase and the reaction orders decrease with the nitrile compounds. Therefore the cure rates decrease with the addition of nitrile compounds.

4. Conclusion

With an incorporation of nitrile compounds to DGEBA/MDA system, the activation energy increased and cure rate decreased. This may be comprised from the disturbance of the curing reaction between the amine and the epoxide groups by the nitrile compound. The activation energy of DGEBA/MDA system is 11.11 kcal/mol and those of the DGEBA/MDA systems with MN, SN and GN are 11.38 kcal/mol, 11.48 kcal/mol and 11.32 kcal/mol, respectively. The reaction orders varied with the curing temperature and those are 1.62 to 2.02 for DGEBA/MDA, 1.36 to 1.56 for DGEBA/MDA/MN, 1.41 to 1.50 for DGEBA/MDA/SN and 0.70 to 0.83 for DGEBA/MDA/GN.

References

8. S. W. Cho, M. J. Shim, and S. W. Kim,


