Study of the Cure Reaction of DGEBA/ABS Blend in the Presence of Aromatic Diamine

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A B S T R A C T

The kinetics and mechanism of cure reaction of DGEBA with 4,4'-oxydianiline(ODA) as curing agent in the presence of thermoplastic ABS was studied using isothermal FTIR and dynamic DSC techniques. The activation energy (Ea) by FTIR analysis was evaluated as 36 kJ/mol and decreased to 31 kJ/mol when the amount of ABS was increased from 10% to 30% by weight. Thermodynamic parameters (ΔH#, ΔS# and ΔG#) for isothermal curing were calculated and the value of ΔG# did not change significantly by increasing the amount of ABS, while it increased with increasing isothermal curing temperature. The maximum temperature (T_p) of the exothermal peak in DSC thermogram increased with increasing heating rate. The values of E_a by using DSC data and Kissinger, Ozawa-Flynn-Wall, and isoconversional equations were in the range of 55-65 kJ/mol. There was a small decrease in the E_a value by increasing the amount of ABS which can be related to the ease of diffusion of functional groups through the network and/or the catalytic influence of the nitrile group (-CN) on the mechanism of cure reaction.

INTRODUCTION

Epoxy resins as one of the most important high performance thermosetting polymeric materials are used widely as polymer matrices for fibre composites and structural adhesives. Many applications of the epoxy resins usually require a high level of cross-linking which is influenced by the stoichiometric ratio and also the cure schedule. The result is a material with a brittle behaviour and poor resistance to crack propagation.

In order to modify this behaviour, the impact resistance of epoxy networks has been increased by blending with high-performance ductile thermoplastics as an alter-
native to the reactive rubbers which leads to a reduction in some mechanical and thermal properties [1]. It has been reported that engineering thermoplastics are interesting materials as modifiers for epoxy resins from the viewpoint of retaining the mechanical and thermal properties of the matrix resins [2-5]. Kinetics of the curing of epoxy resin have been widely studied by using DSC [6-8] and FTIR [9-11], most of the studies on thermoplastic/thermoset blends are mainly focused on the mechanical properties and final morphology [12], and recently the effect of modifiers on the kinetics of curing has been investigated by some researchers [13-15].

Recently, Barral et al. [15] have reported the effect of ABS on the curing kinetics of an epoxy/cycloaliphatic system by using DSC. Their report indicates that Ea of the cure reaction increases in the presence of ABS without changing the mechanism of cure reaction. Curing kinetics of epoxy resins is normally very complex because many reactive processes such as gelation, vitrification, and changes from chemical kinetic control to diffusion control occur simultaneously in the progression of curing [16]. However, kinetic study of thermoset resins is useful for a variety of applications, including shelf-life prediction and the optimization of processing conditions.

The objectives of our study are to check the mechanism of cure reaction of DGEBA/aromatic diamine system in the presence of higher amounts of ABS by using: (1) FTIR technique, (2) DSC technique to determine parameters such as activation energy by applying isoconversional equation in addition to Kissinger and Ozawa equations, and (3) to perform a thermodynamic study to determine the amounts of enthalpy (ΔH#), entropy (ΔS#), and Gibbs free energy (ΔG#) changes for this new epoxy/ABS blend system.

**EXPERIMENTAL**

**Materials**

The epoxy resin studied was based on a commercial DGEBA, Epidian 5, purchased from Iran Petrochemical Co. (Khuzestan, Iran); with epoxide equivalent 196-208 and it was a clear yellow liquid of viscosity (at 25°C) 25000 mpa.s. Acrylonitrile-butadiene-styrene (ABS) was a commercial product and purchased from Iran Petrochemical Co. (Tabriz, Iran). 4,4’-oxydianiline(ODA) mp 190ºC was purchased from Fluka.

**Preparation of ABS/Epoxy and Curing Agent Blend**

ABS was held in vacuum oven at 70°C for 5 h in order to dry, and then was dissolved in dichloromethane. The resulting polymer solution was mixed with the required amount of epoxy resin at room temperature. The solvent in the mixture was removed in a thermic bath at 80°C. Subsequently, 25.0 g of ODA per 100 g of DGEBA was slowly added to the DGEBA/ABS mixture with continuous stirring at room temperature.

**DSC Analysis**

DSC thermograms were recorded using a DSC V4.0B Dupont 2000 instrument, USA. Six mg of the blends of DGEBA/ODA and DGEBA/ODA/ABS were scanned in DSC from room temperature to 300°C at four heating rates of 5, 10, 15, and 20°C/min.

![Diagram](https://via.placeholder.com/150)

**Scheme I**

DGEBA (composed principally of two homologs n = 0 and n = 1 ).
FTIR Analysis

FTIR Spectra were obtained using Bruker, Vector 22, Germany. Samples were prepared by casting a thin film of the blends on KBr discs covered with another KBr plate. The samples were cured at constant temperatures (100, 120, 140 and 160ºC) for various times and the partially cured samples were analyzed by FTIR spectroscopy.

RESULTS AND DISCUSSION

FTIR Studies

The chemistry of curing is initiated through the formation and linear growth of the chains, which soon begin to branch and eventually cross-link. As the cure reactions go forward, the concentration of epoxide groups decreases with a simultaneous increase in the concentration of hydroxyl groups.

The study of curing mechanism of DGBA/ODA system in the presence of ABS was carried out by FTIR analysis on the most important absorption band of the epoxide group at 916 cm⁻¹ which is quite distinctive from other peaks and selected for quantitative analysis because its intensity decreases during cure reactions. The absorption around 1589-1631 cm⁻¹ related to C=C stretching vibration of the phenylene group was taken as the reference peak in order to calculate the conversion of epoxide groups. Three samples were used for monitoring FTIR spectra for each isothermal temperature and the average values of the three readings were used for calculation of kinetic parameters. From the spectra, the reaction rate in relation to the concentration of epoxide group (C) and time can be expressed by [17]:

\[
\frac{dc}{dt} = -kC
\]  

(1)

rearrangement and integration of eqn (1) yield:

\[
\ln\left(\frac{C_t}{C_0}\right) = -kt
\]  

(2)

where, \(C_t\) and \(C_0\) are the concentration of epoxide groups at time \(t\) and \(t_0\), respectively. It is obvious that concentration of epoxide group is directly proportional to the area under the epoxide absorption band and it is therefore expressed as follows:

\[
(t) = \frac{(C_0 - C_t)}{C_0} = \frac{(A_{t_0} - A_t)}{A_{t_0}}
\]  

(3)

The dependence of the epoxy group conversion on the curing time at different isothermal temperatures for the blend containing 30% ABS is shown in Figure 1.

By incorporating the \(C_t/C_0\) ratio from eqn (3) into eqn (2) we have:

\[
\ln(1- \alpha_t) = -kt
\]  

(4)

according to this equation, a plot of the left-hand side of the eqn (4), \(-\ln(1-\alpha_t)\), versus \(t\) should give a straight line with a slope of \((k)\). These plots are shown in Figure 2. The activation energy can be calculated by Arrhenius form of a plot of \(\ln(k)\) versus \(1000/T\).
The activated complex (AC) theory which has been given in the earlier publications [7,18]. According to this theory, the specific rate constant \( k \) is given as:

\[
  k = k^\# K_B T/h
\]

where \( K_B \) and \( h \) are Boltzmann and Planck constants respectively and \( k^\# \) is the equilibrium constant for formation of activated complex. This equation is fundamental in the calculation of the thermodynamic parameters in the curing reaction of epoxy systems based on AC theory. \( k^\# \) is related to the \( \Delta G^\# \) as follows:

\[
  \Delta G^\# = -RT \ln k^\# = \Delta H^\# - T(\Delta S^\#)
\]

Eqn (5) can be rewritten as:

\[
  k = K_B T/h \exp(-\Delta G^\#/RT)
\]

or

\[
  k = K_B T/h \exp(-\Delta S^#/RT) \exp(-\Delta H^#/RT)
\]

taking natural logarithms of the last equation, one can obtain:

\[
  \ln(k/T) = \ln [K_B/h \exp(\Delta S^#/R)] - \Delta H^#/RT
\]
Figure 4. Arrhenius plots of ln(k/T) vs. 1000/T.

The plot of ln(k/T) versus 1/T gives a linear line with a slope of $-\Delta H^\# / R$ and an intercept on the y axis equal to ln[KB/h exp(ΔS^#/R)].

These thermodynamic quantities are calculated with rate constants obtained from isothermal FTIR experiments given in Table 1. The corresponding plots of ln(k/T) versus 1/T are shown in Figure 4, and the values of ΔH^# and ΔS^# are given in Table 1. The magnitudes of ΔH^# and ΔS^# reflect the transition-state structure. The reaction bonds will be partially formed and partially broken in the transition state and the energy required for bond reorganization is reflected in the higher potential energy of the activated complex and corresponds to the enthalpy of activation ΔH^#.

The ΔS^# is a measure of the degree of order produced in the formation of the activated complex and it decreases or increases with the relative degree of freedom, respectively.

By using equation $\Delta G^\# = \Delta H^\# - T \Delta S^\#$, the values of ΔG^# were calculated and listed in Table 1. The values of ΔG^# did not change much with increasing the amount of ABS but increased with increasing isothermal curing temperature.

**DSC Studies**

Figure 5 shows typical dynamic DSC thermograms for DGEBA/ABS mixture cured with 4,4’-oxydianiline at four different heating rates. All samples showed only one sharp exothermic peak regardless of the heating rate and the endothermic peak of melting of ODA was not observed. It can be seen that the exothermic peak shifted towards higher temperature with increasing heating rate.

The DSC data of dynamic curing of DGEBA/ODA/ABS system are shown in Table 2. The exothermic peak is caused by polymerization and etherification reactions which are responsible for network formation, and it was used for calculation of kinetic parameters. The total area under the DSC thermograms based on the extrapolated baseline at the end of reaction was used to calculate the total heat of reaction generated to reach full conversion. The average value of the heats of reactions calculated in each thermogram and for each blend is the overall heat evolved in the reaction. It was observed that the average value of heat of reaction decreased for the blend containing 30% of ABS.

Kinetic analysis of the DSC data for the DGEBA/
ABS/ODA blend was performed using three kinetic equations: Kissinger [19], Flynn-Wall-Ozawa [20], and isoconversional equations [21]. These methods were used because they exempt us of having a prior knowledge of the reaction mechanism to quantify kinetic parameters.

According to the method of Kissinger, $E_a$ is obtained with specific assumption on the conversion dependent function. The resulting relation, for the analysis of DSC data, can be expressed as:

$$-\ln \left( \frac{\beta}{T_p^2} \right) = \frac{E_a}{RT_p} - \ln(AR/E_a) \quad (10)$$

where, $T_p$ is the temperature at which the instant conversion rate is maximum and $\beta$ is the constant heating rate and these are given in Table 2. The $E_a$ was calculated from the slope of the linear plot of $-\ln(\beta/T_p^2)$ against $(1/T_p)$ as shown in Figure 6 and given in Table 3.

The Ozawa-Flynn-Wall method based on Doyle’s approximation [22] is an alternative method for the calculation of $E_a$ and is expressed as follow:

$$\ln \beta = \text{Const.} - 1.052 \frac{E_a}{RT_p} \quad (11)$$

plot of $\ln(\beta)$ versus $1/T_p$ should give a straight line, as shown in Figure 7, with a slope of $1.052 E_a/R$. This can provide $E_a$ for different levels of conversion, but at the present study, however, it is only applied to the maximum rate where the peak appears and it was assumed that when the exothermic peak is reached, the degree of conversion is independent of the heating rate.

The calculated $E_a$ based on Ozawa’s method is given in Table 3. It can be seen from this table that $E_a$ values obtained by Kissinger and Ozawa equations are 61 kJ/mol and 64.8 kJ/mol, respectively. The $E_a$ value of this system is 20 kJ/mol higher than the value

<table>
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<th>Conc. of ABS (phr)</th>
<th>$\beta$ (°C/min)</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>Exothermic heat (J/g)</th>
<th>Ave. exo. heat (J/g)</th>
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Table 2. DSC Data of the curing reaction of DGEBA blends.
reported by Barral et al. [15] for curing the DGEBA/cycloaliphatic amine system. This comparison shows that DGEBA/ODA system is less reactive and gives a longer pot life. Also, $T_p$ of 154°C for DGEBA/ODA system is compared with $T_p$ of 100°C for the system reported by Barral et al. [15] at the same heating rate.

Frequency factor ($A$) decreased from $1.17 \times 10^7$ min$^{-1}$ in the absence of ABS to $8.84 \times 10^5$ min$^{-1}$ in the presence of 30% ABS due to lower probability of collision between epoxide and amine functional groups. Our results show a small initial decrease in the $E_a$ values in the presence of ABS thermoplastic, in Table 3, which is in contrast to the results reported by other researchers [15]. The decrease in $E_a$ value can probably be attributed to the ease of diffusion of the functional groups through the network in the presence of thermoplastic ABS and/or the catalytic influence of the nitrile group (-CN) on the cure reaction.

Table 3 also shows that the rate constant obtained from the Arrhenius equation at 423 K decreased in the presence of ABS which can be due to the decrease in the amount of curing system and frequency factor ($A$).

The Kissinger and Ozawa equations give only one $E_a$ from the data of $T_p$. A more complete determination of $E_a$ at any selected conversion can be calculated by the isoconversional equation [23] which is expressed as:

$$d(\ln \beta_i) = -\frac{E_a}{R} \frac{d(T)}{T} \quad (12)$$

where $\beta_i$ is different heating rates and $T$ is the temperature for a selected conversion at each heating rate.

Figure 8 shows the conversion curves which were obtained by integrating the DSC curves in Figure 5. The isoconversional temperatures were obtained from the conversion curves at any selected conversion. The values of $1/T \times 10^3$ according to $\ln(\beta_i)$ were listed in Table 4. To obtain the $E_a$ value at each conversion, the relationships of the variables in the conversion range of 0.1-0.9 were discerned and the linear expression for each straight line was obtained.

Typical and selected linear curves of $\ln(\beta_i)$ versus $1/T \times 10^3$ were shown in Figure 9. The slopes of these curves correspond to $-E_a/R$ at each particular

<table>
<thead>
<tr>
<th>Conc. of ABS (phr)</th>
<th>$E_a^a$ (kJ/mol)</th>
<th>$E_a^b$ (kJ/mol)</th>
<th>$A$ (min$^{-1}$)</th>
<th>$K^c$ (min$^{-1}$)</th>
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<td>$1.17 \times 10^7$</td>
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(a) Kissinger’s method; (b) Ozawa’s method; (c) Arrhenius rate constant at 423K.
conversion. The calculated $E_a$ values are listed in Table 5. It may be observed that there is a small decrease in $E_a$ values as the amount of ABS increases in the blend from 10% to 30%. The decrease in the $E_a$ value can be related to decrease in the viscosity of the curing mixture as a result of the presence of thermoplastic ABS which induces easier diffusion of the functional groups through the network. There is also the possibility of catalytic influence of the nitrile groups (-CN) of ABS on the mechanism of cure reaction of DGEBA/ODA system. Another noticeable result in Table 5 is that the $E_a$ values are decreased gradually with the increase in conversion. The decrease in the $E_a$ values with the increase in conversion can probably be due to catalytic effect of the increasing amount of hydroxyl groups formed during curing reaction process. The decrease in $E_a$ value with increasing conversion can be related to decrease in viscosity of the curing mixture in the presence of

<table>
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<tr>
<th>Concentration (phr)</th>
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Table 4. Data of ln($β$) and $T^{-1}$ for DGEBA/ABS blends at different conversions.

Figure 9. Isoconversional plots at various conversions for the 30 phr ABS/epoxy blend.
thermoplastic ABS because of rising temperature which causes the easier mobility of the functional groups through the network.

The exothermic peak in DSC thermogram is mainly caused by the sum of non-catalytic (reactions 1 and 4), catalytic (reactions 2 and 3), and etherification reactions which are shown in Scheme II.

The reaction between amine and epoxide groups can be influenced by the catalytic action of hydroxyl groups (Reaction 3) and also in this case, can be suggested by the catalytic action of the nitrile groups (Reaction 2). There is also etherification reaction (Reaction 5) which may be neglected for stoichiometric mixtures of epoxy with diamines since the reactivity of the diamines towards the epoxide rings is much higher than the hydroxyl groups. This reaction can be significant when diamine concentration is lower than the stoichiometric value.

Scheme II. Non-catalytic (reactions 1 and 4), catalytic (reactions 2 and 3), and etherification (reaction 5) reactions of epoxide groups.

**CONCLUSION**

Measurement of isothermal curing of DGEBA/ABS/ODA system by FTIR has shown that the maximum conversion is achieved at 160 and 100°C after 40 and 80 min, respectively. The \( E_a \) value of 36 kJ/mol is dropped to 31 kJ/mol in the presence of 30% ABS. Thermodynamic parameters (\( \Delta H^\# \), \( \Delta S^\# \), and \( \Delta G^\# \)) for isothermal curing were calculated and the value of \( \Delta G^\# \) did not change much with the increasing in the amount of ABS while it increased by increasing isothermal curing temperature. Dynamic curing of the blends in DSC shows one large exothermic peak, which its position has not changed very much as the amount of ABS is increased to 30%. The \( E_a \) values obtained by analyzing DSC data and using different kinetic methods lie in the range of 55-65 kJ/mol. The difference in the \( E_a \) values
obtained by FTIR and DSC data can be due to the fact that these two techniques measure different parameters during curing reactions. The values of $E_a$ obtained by analyzing DSC data have shown a small decrease with increasing the amount of ABS which can be due to decrease in viscosity and easier diffusion of functional groups through the network and/or due to possible catalytic effect of the nitrile groups on the mechanism of curing.

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