Chapter 3

Cure Kinetics of Novolac epoxy-Diallyl Bisphenol A System

Part of the results discussed in this chapter has been published

1. "Kinetics of Triphenyl phosphine catalysed thermal cure of diallyl bisphenol A-Novolac epoxy blend"
   International conference Thermans, BARC, Mumbai, May 2002

3. "Triphenyl Phosphine catalysed curing of Diallyl bisphenol A-Novolac epoxy resin system – A kinetic study"
   communicated to J. of Appl. Polym. Science
Scope of the study

The kinetics of triphenyl phosphine (TRP) catalysed epoxy – phenol reaction in the reactive blend of 2,2'-diallyl bisphenol A (DABA) and an epoxy novolac (EPN) was investigated using differential scanning calorimetry. The evaluation of this resin system at the composite level involves the optimization of its processing conditions. In order to eliminate to excessive resin bleeding during the composite fabrication, the phenol -epoxy reaction is to be initiated at a comparatively lower temperature for which a suitable catalyst is to be used. This paper examines principally the effect of catalyst - triphenyl phosphine (TRP) – and its concentration on the kinetic parameters of epoxy -phenol reaction. The iso conversional kinetic analysis was done at different conversion levels and catalyst concentrations to study the change in overall activation energy with conversion. The evaluation of kinetic parameters enabled the prediction of its cure profile under given conditions of temperature and catalyst concentration. This kinetic study was useful for the first level optimisation of the processing window of the resin system for its composite fabrication.
3.1 Introduction

Epoxy resins are the most versatile class of thermosetting matrix resins. However, their limitations in respect of low glass transition temperature and brittle nature often demand matrix modification to widen their area of utility. Epoxy matrix properties can be tuned by proper selection of curatives like amines, acids, anhydrides and phenols. Although less preferred, polyphenols are used as curative, since the addition-cured, void-free product is comparatively tougher due to the formation of flexible ether network. Epoxy-phenol thermosets have been evaluated for many applications including void-free composite structures. Networks containing high compositions of epoxies cross linked with phenolic novolacs are used in microelectronics packaging applications. However, the low glass transition temperature \((T_g)\) of the epoxy-phenol system would be a limiting factor for its wide spread applications. One way to obviate this is to use modified phenolic curatives with multiple curing reaction. In this perspective, we have examined 2,2'-diallyl bisphenol-A as a dual curative for a novolac epoxy resin. The system can cure by the addition reaction of phenol-epoxy as well as by the addition polymerization of allyl groups. The mechanical properties of the cured composites are determined by the extent of cure, which depend on the processing conditions. Therefore, a clear understanding of the curing mechanism and the ability to develop suitable kinetic models to simulate the curing reaction are essential to predict and to control the end properties of the cross linked material. Variety of techniques such as DSC, thermal scanning rheometry, dielectric spectroscopy, Raman spectroscopy, FTIR, etc. have been used to monitor cure reaction of epoxies.

Femandez et al. studied the cure kinetics of an epoxy matrix based on tetraglycidyl diamino diphenyl methane polymerized with diamino diphenyl methane and its blends with poly(methyl methacrylate) and poly(ether sulphone)(PES). The activation energies reported for these cases (73 and 70 kJ/mole) are close to each other, suggesting that the unique activation energy could represent the over all curing reaction, as reported. This activation energy is also in close agreement with the value obtained for this matrix in rheological studies. The performance of the
cured resin depends on the network structure, which in turn depend on its sensitivity to the curing condition. The multiple chemical reactions between novolac epoxy and curing agents could give rise to a complex kinetic behavior, and the physical state of the resin changes with the extent of cross linking. A comprehensive understanding of the mechanism and kinetics of curing can lead to an optional curing process.

Of the various thermal analysis methods used for kinetic investigations, TG and DSC have outstanding significance in this area, being relatively fast and accurate methods. Conversion of data from thermal analysis curves into kinetic parameters, viz. reaction order, energy of activation, pre-exponential factor and rate constants is based on the utilisation of classical laws of kinetics. Both dynamic and isothermal DSC techniques have been used for the cure kinetic studies of several polymer systems. Yanfang Liu et al carried out kinetic studies on amine cured novolac epoxy resin using dynamic and isothermal DSC analysis.

Differential scanning calorimetry (DSC) is one of the most commonly adopted techniques for the kinetic studies of thermosetting resin systems. The curing kinetics of epoxy resins is generally characterized using DSC in both dynamic and isothermal modes. In practice, several multiple heating rate methods are generally used. A few among them are the maximum reaction rate method proposed by Kissinger, which is based on the fact that the exothermic peak temperature varies with the heating rate, and the iso conversion method proposed by Flynn, Wall and Ozawa, which is based on the attainment of iso conversion at different temperatures for different heating rates.

The kinetics of biphenyl epoxy-phenol novolac reaction in presence of TPP has been reported by Han et al and validated different kinetic models using the non-isothermal DSC data. A semi-empirical rate law was proposed for this reaction by Beneath et al. Several authors have carried out studies on the reaction between epoxies and phenols in presence of various catalysts. Banitha and McGrath proposed a mechanism for the TPP- catalyzed reaction between epoxy resins and phenols and concluded that little or no side reaction of epoxy with secondary hydroxyls takes place. Seung Han et al developed a kinetic model that could describe and predict the cure reaction of the epoxy resin with different catalyst concentration. Han et al reported the curing reactions between biphenyl type epoxy...
resin and three different phenolic functional hardeners in presence of TPP. Detailed studies were also carried out to evaluate the influence of catalyst type on the curing reaction between biphenyl type epoxy and derivatives of phenol novolac\textsuperscript{36,37}.

The thermal curing reaction of novolac epoxy resin and diallyl bisphenol A takes place by phenol-epoxy reaction and allyl polymerisation. The evaluation of this resin system at the composite level involves the optimization of its processing conditions. In order to eliminate the excessive resin bleeding during the composite fabrication, the former reaction is to be initiated at a comparatively lower temperature for which a suitable catalyst is to be used. In the present case triphenyl phosphine (TPP) is used as the catalyst.

This chapter examines principally the effect of catalyst concentration on the kinetic parameters of epoxy-phenol reaction. A comparative evaluation of the kinetic parameters obtained for the phenol-epoxy cure reaction using different kinetic equations—Kissinger & Ozawa—is also made. The iso-conversional kinetic analysis was also done at different conversion levels and at varying catalyst concentrations using Kissinger and Ozawa methods. The activation parameters were used to predict the cure profile of the resin system under given conditions of temperature and catalyst concentration which enable the optimisation of the processing conditions for its composite fabrication.

### 3.2 Preparation and Characterization of Epoxy-Phenol System

#### 3.2.1 Preparation of Epoxy-Phenol System

Weighed quantity of TPP was dissolved in known amount of DABA at 90°C, the temperature was brought down to room temperature and to this; EPN was added so that the equivalent ratio of epoxy/phenol was maintained as unity. The sample was thoroughly mixed and used for cure characterisation. Five similar samples were prepared so that the catalyst concentrations ranged from 0 – 3.0 weight % (0, 0.5, 1.0, 2.0, 3.0).
3.2.2 Thermal Characterisation Using DSC

Properly mixed resin samples were encapsulated in a 40μl aluminium pan with a pierced lid. Mettler TA 3000 Thermal Analyser system in conjunction with a TC-10A TA processor and a standard DSC-20 cell was used for its cure characterisation. The DSC experiments were carried out at four heating rates 2, 5, 7 and 10°C/ min for each catalyst concentration. A constant sample mass of 6±1 mg of the resinous product was used for DSC analysis. The peak maximum temperature (T_m), area integration and calculation of fractional conversion (α) were done by TA 72 AT.2 Graph ware software.

3.3 Results and Discussion

The proposed epoxy-phenol reaction scheme of the novolac epoxy-diallyl bisphenol (EP) system in presence of TPP is shown in Scheme.1. The DSC thermograms of the un catalysed (EP-UC) and catalysed (EP-C) epoxy-phenol cure reactions are shown in Fig.3.1. The neat resin system without catalyst showed a broad exotherm in the temperature range of 130-210°C. The allyl polymerisation which normally occurs at a temperature above 200°C is not evident in the DSC cure curve. This is because the allyl polymerisation is normally a less favoured, low enthalpy reaction and goes mostly undetected in DSC. The thermal polymerisation of allyl groups triggers at temperature above 200°C and extends up to 240°C under dynamic conditions as evidenced in the rheological analysis of the system. This is described in the next chapter and the corresponding rheogram is given in Fig. 4.3 and chapter 4. The addition of TPP shifted cure exotherm of phenol-epoxy reaction to lower temperature thus precluding the simultaneous cure of epoxy and allyl groups.

![Scheme.3.1 The phenol-epoxy reaction of novolac epoxy-diallyl bisphenol system](image)
The maximum cure temperature ($T_m$) for the phenol-epoxy reaction at different heating rates-2, 5, 7 and 10°C/min--and catalyst concentrations -0.5, 1.0, 2.0 and 3.0%--are compiled in Table 3.1.

![DSC cure thermogram showing catalysed (EP-C) and uncatalysed (EP-UC) epoxy-phenol cure reactions (H.R.5°C/min)](image)

The peak reaction temperatures are found to be systematically shifted to the lower temperature side with the increase in catalyst concentration. With the increase in heating rate, the cure exotherms were found to be shifted to higher temperatures and the peak temperature showed a systematic increase. The conversion ($\alpha$) vs. temperature curves plotted from the DSC thermograms showed respectively the effect of heating rate (Fig. 3.2) and catalyst concentration (Fig. 3.3) on the phenol-epoxy reaction. Fig. 3.3 excludes the temperature conversion profile for uncatalysed system as the cure exotherm in this case was more diffused and is apparently incomplete as is evident from the Fig. 3.1. However, its peak maximum was
well defined and could be used for relevant kinetic parameter calculation of phenol-epoxy reaction in this case.

Fig. 3.2 Effect of Heating rate (2-10°C/min) on conversion (0.5% catalyst)

Fig. 3.3 Effect of catalyst concentration (0.5-3.0%) on conversion (H.R.10°C/min.)
The conversion \( \alpha_T \), at temperature \( T \) was calculated using the relation.

\[
\alpha_T = \frac{\Delta H_T}{\Delta H_M}
\]  
(3.1)

Where, \( \Delta H_T \) is the fractional enthalpy at temperature \( T \) and \( \Delta H_M \), the total enthalpy of reaction. Indirectly these are obtained from the fractional and total areas respectively under the exothermic peak.

Table 3.1 Variation of Epoxy-phenol cure temperature \( (T_m) \) with heating rate and catalyst concentration

<table>
<thead>
<tr>
<th>TPP%</th>
<th>Peak temperature ( (T_m \degree C) ) at different heating rates ( (^\circ \text{C}/\text{min}) )</th>
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<td>0.5</td>
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3.3.1 Calculation of Kinetic Parameters

Different methods are used for the computation of kinetic parameters of the cure reaction of similar systems. For the present study, the kinetic parameters for the phenol-epoxy reaction were calculated from non-isothermal DSC data since this technique is versatile for studying the cure reaction of systems associated with considerable enthalpy change.³⁹

3.3.1.1 Kinetic constants by Ozawa and Kissinger methods:

The convenient multiple heating rate methods employed for the computation of kinetic constants of the curing reaction are the maximum reaction rate methods employed by Kissinger⁴⁰ and Ozawa⁴¹ which are based on the fact that the peak reaction temperature, \( T_m \) varies with heating rate.
The Kissinger method which assumes that the maximum $\frac{d\alpha}{dt}$ occurs at the peak temperature, where $\frac{d^2\alpha}{dt^2} = 0$, can be expressed as

$$d \left[ \ln \left( \frac{\phi}{T_m^2} \right) \right] / d \left( \frac{1}{T_m} \right) = - \frac{E}{R} \quad (3.2)$$

and the final form of the Ozawa equation is given as

$$2.19 \frac{d \log \phi}{d \left( \frac{1}{T_m} \right)} = - \frac{E}{R} \quad (3.3)$$

where $T_m$ is the absolute temperature corresponding to the peak temperature in the DSC curve, $\phi$ is the heating rate and $R$ is the gas constant. In Kissinger and Ozawa methods, $E$ values are calculated from the slope of the linear plots of $\ln \left( \frac{\phi}{T_m^2} \right)$ vs. $1/T_m$ and $\log \phi$ vs. $1/T_m$ respectively. The pre-exponential factor is calculated using the equation

$$A = \phi \left( \frac{E}{RT_m^2} \right) e^{E/RT_m} \quad (3.4)$$

For a given catalyst concentration, $A$ is the average of the pre exponential values calculated for the four heating rates. The DSC peak temperatures obtained for phenol-epoxy reaction at different heating rates and catalyst concentrations were used for the computation of activation energy ($E$) and pre exponential factor ($A$). The $E$ and $A$ values computed using the two equations are given in Tables 3.2 & 3.3 and the Kissinger plots are shown in Fig 3.4. It is true that in the absence of catalyst, the DSC profile could be influenced by the allyl polymerisation. As stated earlier, the allyl group polymerisation is an unfavoured reaction and the associated enthalpy is benign. Hence the error in the estimation of $E$ based on the peak maximum is negligible, as the major enthalpy and the peak maxima are derived exclusively by the phenol-epoxy reaction.

The $E$ and $A$ values computed using the two equations were found to be nearly the same but they did not show any systematic trend with catalyst concentration.
Table 3.2. Kinetic parameters (Ozawa method)

<table>
<thead>
<tr>
<th>TPP (wt.%)</th>
<th>lnA</th>
<th>$E_{exp}$ (kJ/mol)</th>
<th>r</th>
<th>$E_{norm}$ (kJ/mol)</th>
<th>$k_{100}$ (s$^{-1}$) x 10$^3$</th>
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<td>0.9922</td>
<td>90.5</td>
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Table 3.3 kinetic parameters (Kissinger method)

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<th>TPP (wt.%)</th>
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<th>$E_{exp}$ (kJ/mol)</th>
<th>r</th>
<th>$E_{norm}$ (kJ/mol)</th>
<th>$k_{100}$ (s$^{-1}$) x 10$^3$</th>
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</thead>
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<td>74.9</td>
<td>3.27</td>
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</table>

However, the reaction rate calculated at a fixed temperature (100 °C) for different catalyst concentrations using the relation,

$$k = A e^{-\frac{E}{RT}}$$  \hspace{1cm} (3.5)

showed an increasing trend with catalyst concentration. From the kinetics point of view, addition of a catalyst should result in a decrease in activation energy, thereby
enhancing the rate constant. The haphazard variation in $E$ could be attributed to experimental factors related to kinetic compensation.\(^{42}\)

Hence these $E$ values were normalised using the pre-exponential factor computed for the system without catalyst. The normalisation was done using the relation

$$
\ln \left( \frac{\phi}{T_n^2} \right) = \ln A - \frac{E}{RT} \times 10^3 (K^{-1})
$$

Fig 3.4 Kissinger plots

Where, $A_\text{ex}$ is the experimental pre exponential factor for an activation energy $E_\text{ex}$, $A_0$ is the pre exponential factor for the un catalysed reaction calculated using the relation 3.4. The normalised $E$ values showed systematic decreasing trend with increase in catalyst concentration. The dependence of activation energy and rate constant on the catalyst concentration is given in Tables 3.2 & 3.3.

3.3.1.2 Kinetic Constants at Different Conversion Levels

The kinetic constants at different conversion levels were computed using the
iso-conversion method, which is based on the fact that the iso-conversion can be reached at different temperatures with different heating rates. The dependency of \( E \) on conversion was separately examined by Kissinger and Ozawa methods. The kinetic constants obtained at different conversion levels from 0.1 to 0.9 and for different catalyst concentrations are given in Tables 3.4 and 3.5. The conversion \( \alpha_T \) at temperature \( T \), was computed using equation (3.1). The conversion dependence of \( E \) was found to be almost independent of catalyst concentration. The activation energy generally showed a decreasing trend with conversion level. The iso-conversional kinetic analysis of the DSC data was adequately interpreted earlier for a model epoxy-amine curing process\(^{43} \) and it has been found that it is more advantageous than numerous kinetic methods such as ASTM E-698-79\(^{44} \). The activation energy calculated by the ASTM method is based on a single point dependence of \( E \) on the degree of conversion \( \alpha \), at \( \alpha = \alpha_{\text{max}} \), while in the iso-conversional method, the kinetic parameters can be calculated for the complete \( \alpha \) range. The iso-conversional plots (Fig. 3.5) were drawn by plotting \( \ln \phi \) against \( 1/T \) for different conversion levels and catalyst concentrations.

![Isoconversional plots](image)

Fig 3.5 Isoconversional plots
Table 3.4 Isoconversional kinetic parameters computed by Ozawa Method

Kinetic constants at different catalyst concentrations

<table>
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<tr>
<th>α</th>
<th>0.5</th>
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<td>lnA</td>
<td>r</td>
<td>E (kJ/mol)</td>
<td>lnA</td>
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Table 3.5 Isoconversional kinetic parameters computed by Kissinger Method.

Kinetic constants at different catalyst concentrations

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<td></td>
<td></td>
<td>71.6</td>
<td>16.6</td>
<td></td>
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</tr>
<tr>
<td>0.9</td>
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<td>65.1</td>
<td>13.1</td>
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<td></td>
<td></td>
<td>71.1</td>
<td>16.1</td>
<td></td>
<td>0.9998</td>
</tr>
</tbody>
</table>
The activation energy values were computed from the slope of these iso-conversional plots. The activation energy values and its conversion dependency obtained by these two methods were found to be comparable (Table-3.4 and 3.5). These values are also found to be in the range of $E$ values computed by Ozawa and Kissinger methods using the $T_m$ values.

3.3.2 Effect of Catalyst Concentration on Reaction Kinetics

The activation energy values obtained using the Kissinger (K) and Ozawa (O) methods were found to be in the range reported for epoxies. The normalised $E$ values showed a decreasing trend with catalyst concentration as seen in Fig.3.6.

The addition of 0.5 % catalyst resulted in considerable reduction in $E$ value. The rate constant showed systematic increase with increase in catalyst concentration.
3.3.3 Kinetic Prediction of Isothermal Cure

The $A$ and $E$ values are useful for predicting the cure profile of the resin under a given conditions of temperature and time. The relationship between $A$, $E$, $T$, time ($t$) and conversion ($\alpha$) is derived from the isothermal rate equation for an $n^{th}$ order reaction as

$$\frac{d\alpha}{dt} = (1 - \alpha)^n = A e^{\frac{E}{RT}} (1 - \alpha)^n \quad (3.7)$$

Integration of equation 3.7 gives equation 3.8 as

$$\alpha = 1 - (1 - \alpha) (1 - n) t e^{\left(\frac{E}{RT}\right)^{1/n}} \quad (3.8)$$

Where, $n$ is the order of the reaction. For bimolecular reactions like phenol-epoxy, the reaction order can be considered as two without any error. In fact in many cases of epoxy curing, the order has been reported as two. Hence for the computation of conversion as per equation 3.8, $n$ value was taken as 2. The predicted isothermal cure curves at a fixed temperature ($100^\circ C$) of the resin system for different catalyst concentrations are given in Fig. 3.7.

![Image of predicted isothermal conversion curves at 100°C at different catalyst concentrations (0 - 2.0 weight %)](image)

Fig. 3.7. Predicted isothermal conversion curves at 100°C at different catalyst concentrations (0 - 2.0 weight %)
The data in Fig. 3.7 shows that the epoxy-phenol cure reaction is practically stagnated at 90% conversion when the catalyst concentration is 0.5 – 1.0%. However, a reasonably good conversion requires a catalyst concentration exceeding 2% at 100°C for a period of minimum two hours. At this temperature the extent of reaction is negligible (~15%) in the absence of catalyst.

The time-conversion profiles predicted for the system with 0.5% catalyst concentration at varying temperatures are shown in Fig. 3.8. It is seen that when the temperature exceeds 140°C, full conversion is achievable in about an hour. At this temperature, the allyl polymerization can be expected to be practically nil. Thus, the DABA-EPN system with pendant allyl groups can be realized either by increasing the catalyst concentration beyond 2% and effecting the polymerization at 100°C or by performing the reaction at temperatures exceeding 140°C while maintaining a catalyst concentration of 0.5%. The latter cure protocol was followed for the rest of the studies.

Fig. 3.8 Predicted isothermal conversion for 0.5 weight% catalyst concentration at different temperatures (100–150°C)
3.4 Conclusions

The kinetics of triphenyl phosphine (TPP) catalysed epoxy – phenol reaction in the reactive blend of 2, 2'-diallyl bisphenol A (DABA) and an epoxy novolac (EPN) was investigated using differential scanning calorimetry (DSC). The kinetic parameters viz. activation energy (E) and the pre exponential factor (A) were calculated by the multiple heating rate methods of Ozawa and Kissinger. The effect of catalyst concentration on the kinetic parameters of the cure reaction was studied and E and A were found to depend on catalyst concentration. The apparent activation energy values normalised to a fixed A value decreased systematically and the corresponding rates of reaction showed an increasing trend with increase in catalyst concentration. The iso-conversional kinetic analysis done for different catalyst concentrations and conversion levels implied that the overall activation energy does not vary much with conversion. The activation parameters were used to predict the cure profile of the resin under given conditions of temperature and catalyst concentration. The predictions confirmed that at lower temperature, complete cure cannot be achieved despite using high catalyst concentration. At temperature exceeding 140°C, a catalyst concentration of 0.5% is adequate to bring about cure completion in about an hour. The predicted isothermal conversion curves enabled the optimization of time- temperature cure schedule of this matrix resin and its composite.

3.5 References

21  SuCC, E. M; Woo, Polymer, 36, 2883 (1995).