Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Devi, K. Ambika , Nair, C. P. Reghunadhan , Catherine, K. B. and Ninan, K. N.(2008) 'Triphenyl Phosphine Catalyzed Curing of Diallyl Bisphenol A-Novolac Epoxy Resin System—A Kinetic Study', Journal of Macromolecular Science, Part A, 45: 1, 85 — 92

To link to this Article: DOI: 10.1080/10601320701683389

URL: http://dx.doi.org/10.1080/10601320701683389

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2008) **45**, 85–92

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701683389

Triphenyl Phosphine Catalyzed Curing of Diallyl Bisphenol A-Novolac Epoxy Resin System—A Kinetic Study

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Received May, 2007, Accepted July, 2007

The kinetics of triphenyl phosphine (TPP) catalyzed phenol-epoxy reaction in the 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 for different conversion levels implied that the overall kinetics does not vary much with conversion level. The activation parameters were used to predict the cure profile of the resin under given conditions of temperature and catalyst concentration.

Keywords: phenol-epoxy cure; epoxy resin; differential scanning calorimetry; cure kinetics

1 Introduction

Epoxy resins are the most versatile class of thermosetting matrix resins. However, their limitations, with respect to 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 (1, 2). Phenol-Epoxy thermosets have been evaluated for many applications including void-free composite structures (3). Networks containing high compositions of epoxies cross-linked with phenolic novolacs are used in microelectronics packaging applications (4, 5). However, the low T_g of the phenol-epoxy system could be a limiting factor for its widespread applications. One way to prevent 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 cures 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 (6). 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 (7). Variety of techniques such as Differential Scanning Calorimetry (DSC) (8–11), thermal scanning rheometry (12), dielectric spectroscopy (13), Raman spectroscopy (14), Fourier Transform Infra Red (FTIR) (15–17) etc., have been used to monitor cure reaction of epoxies.

Fernandez et al. (18) studied the cure kinetics of an epoxy matrix based on tetra glycidyl 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 both 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 (19, 20). This activation energy is in close agreement with the value obtained for this matrix in rheological studies (21, 22). The performance of the cured resin depends on the network structure, which in turn depends on its sensitivity to the curing conditions. The multiple chemical reactions between novolac epoxy and curing agents could give rise to a complex kinetic behavior,

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and the physical state of the resin changes with the extent of crosslinking. 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, thermogravimetry (TG) and DSC have outstanding significance in this area, being relatively fast and accurate methods (23). Both non-isothermal and isothermal DSC techniques have been used for the cure kinetic studies of several polymer systems (24). Conversion of data from thermal analysis curves to kinetic parameters, viz. reaction order, energy of activation, pre-exponential factor and rate constants is based on the utilization of classical laws of kinetics. Ghaemy et al. carried out kinetic studies on Nickel(II) complex catalysed epoxy curing using non-isothermal DSC analysis (25).

The most commonly used dynamic methods are the multiple heating rate methods.

In practice, several multiple heating rate methods are generally used. One among them is the maximum reaction rate method proposed by Kissinger (26), which is based on the fact that the exothermic peak temperature varies with the heating rate, and the iso-conversion methods proposed by Flynn and Wall (27), and Ozawa (28) which are based on the attainment of iso-conversion at different temperatures for different heating rates.

The kinetics of biphenyl epoxy-phenol novolac reaction in the presence of TPP has been reported by Han et al. (29, 30) and validated different kinetic models using the non-isothermal DSC data. They developed a kinetic model that could describe and predict the cure reaction of the epoxy resin with different catalyst concentration. A semi-empirical rate law was proposed for this reaction by Biernath et al. (31). Several authors have carried out studies on the reaction between epoxies and phenols in the presence of various catalysts (32, 33). Banthia and McGrath (34) 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. 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 (35, 36).

The curing reaction of novolac epoxy resin and diallyl bisphenol A (DABA) takes place in two steps; phenol-epoxy reaction and allyl polymerization. The evaluation of this resin system at the composite level involves the optimization of the 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. Hence triphenyl phosphine (TPP) was examined as the catalyst.

This paper examines principally the effect of TPP concentration on the kinetic parameters of phenol- epoxy reaction. A comparative evaluation of the kinetic parameters obtained for the phenol-epoxy cure reaction using two 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 under given conditions of temperature and catalyst concentration.

2 Experimental

2.1 Materials

DABA was synthesised in our laboratory by a reported procedure (37). EPN-1139, a novolac epoxy resin having an epoxy value 5.5 equivalents/kg, and a functionality of 3.6, was procured from Hindustan Ciba Geigy, Mumbai and was used as received. TPP (E-Merck, India) was also used as received.

2.2 DSC Analysis

The samples for DSC analysis were prepared by dissolving a weighed amount of TPP in DABA at 90°C and mixing it thoroughly with EPN under ambient conditions. The equivalent ratio of phenol/epoxy was maintained at unity and samples with four catalyst concentrations (0.5, 1.0, 2.0, and 3.0% by weight) were prepared for the study.

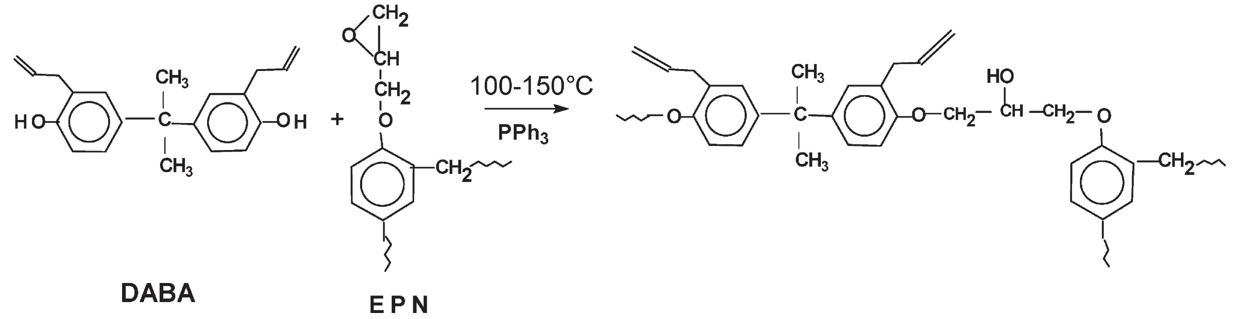
A constant sample mass of 5.0 ± 1.0 mg of the resinous product was used for DSC analysis. Samples were encapsulated in a 40 μl aluminium pan with a pierced lid. Mettler TA 3000 Thermal Analyzer system in conjunction with a TC-10A TA processor and a standard DSC-20 cell was used for all analysis. The DSC experiments were carried out at four heating rates 2, 5, 7 and 10°C/min in a nitrogen atmosphere at a flow rate of 50 ml/min. The peak maximum temperature (T_s), area integration and calculation of fractional conversion (α) were done by TA 72 AT.2 Graphware software.

2.3 Rheological Characterization

The rheological analysis of the phenol-epoxy mix was done with a Reologica Stress Tech Rheometer. The instrument was used in the oscillation mode using a parallel plate assembly (20 mm dia) with a gap of 0.5 mm in a controlled strain mode. The storage shear modulus (G'), loss shear modulus (G'') and complex viscosity (η^*) were measured as a function of temperature.

3 Results and Discussion

The proposed epoxy- phenol reaction scheme of the diallyl bisphenol-novolac epoxy (EP) system in presence of TPP is shown in Scheme 1. The DSC thermograms of the uncatalysed (EP-UC) and catalysed (EP-C) phenol-epoxy cure



DABA **EPN**

Sch. 1. Phenol-epoxy reaction of diallyl bisphenol A and novolac epoxy.

reactions are shown in Figure 1. The neat resin system without catalyst showed a broad exotherm in the temperature range of 130–210°C. The allyl polymerization, which normally occurs at a temperature above 200°C, is not evident in the DSC cure curve. This is because the allyl polymerization is normally a less favored, low enthalpy reaction and goes mostly undetected in DSC. However, it was distinct in the rheogram of the resin on ramping the temperature (Figure 2). The thermal polymerization of allyl groups triggers at temperature above 200°C and extends up to 240°C under dynamic heating conditions as evidenced in a second modulus build-up stage centred around 200°C in the rheogram of the system. The addition of TPP shifted the cure exotherm of phenol-epoxy reaction to lower temperature thus precluding the simultaneous cure of epoxy and allyl groups. The maximum cure temperature (T_s) 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 1. 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 (α) vs. temperature curves plotted from the DSC thermograms showed the effect of heating rate (Figure 3) and catalyst concentration (Figure 4) on the phenol-epoxy reaction, respectively. Figure 4 excludes the temperature conversion profile for the uncatalyzed system as the cure exotherm in this case was more diffused and is apparently incomplete as is evident from the DSC profile in Figure 1. However, its peak maximum was well defined and could be used for a relevant kinetic parameter calculation of a phenol-epoxy reaction in this case (Table 1). The conversion α_T, at temperature T was calculated using the relation:

$$\alpha_T = \Delta H_T / \Delta H \qquad (1)$$

where, ΔH_T is the fractional enthalpy at temperature T and ΔH, the total enthalpy of reaction. Indirectly, these are obtained from the fractional and total areas, respectively under the exothermic peak.

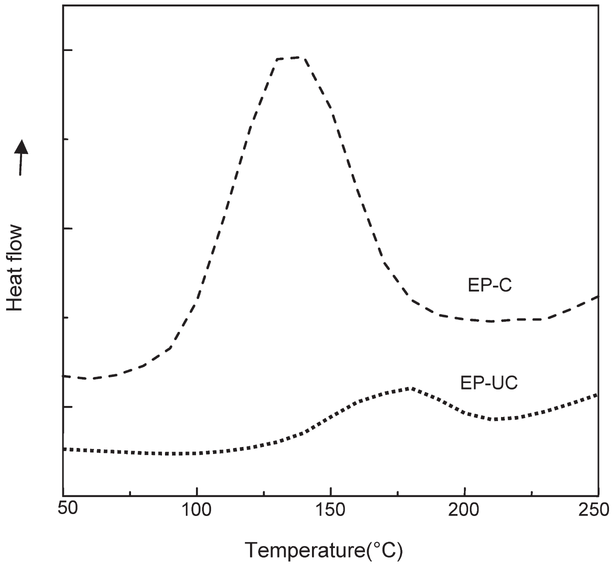


Fig. 1. DSC cure thermograms of catalyzed (EP-C) and uncatalyzed (EP-UC) phenol-epoxy cure reactions (heating rate 5°C/min).

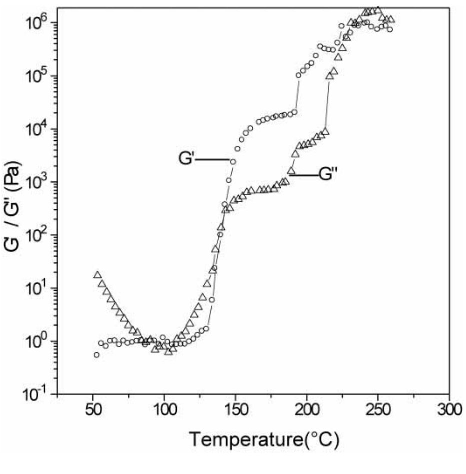


Fig. 2. The non-isothermal rheogram of phenol-epoxy system (0.5 wt.% TPP), heating rate 5°C/min.

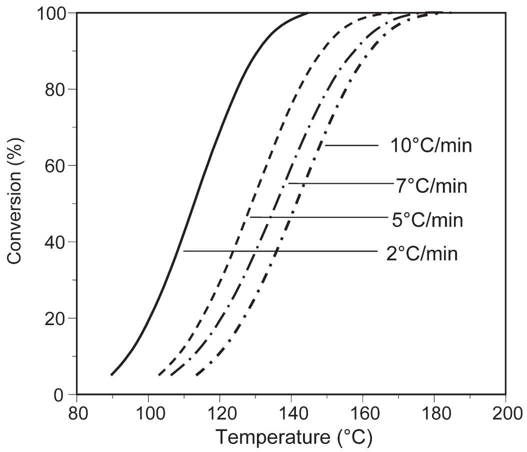


Fig. 3. Effect of heating rate on conversion-temperature profile.

3.1 Calculation of Kinetic Parameters

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 a detectable enthalpy change (38).

3.2 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 Kissinger (39) and Ozawa (28) which are based on the fact that the peak reaction temperature, T_s varies with the heating rate.

The Kissinger method, which assumes that the maximum rate $(d\alpha/dt)$, occurs at the peak temperature, where $d^2\alpha/dt^2 = 0$ can be expressed as:

$$d[\ln(\varphi/T_s^2)]/d(1/T_s) = -E/R \tag{2}$$

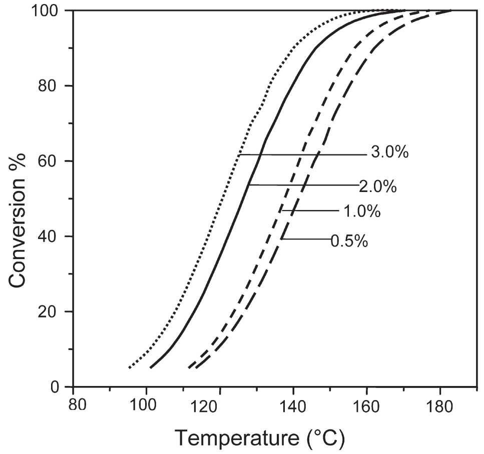


Fig. 4. Effect of catalyst concentration on conversion-temperature profiles.

Table 1. Effect of heating rate and catalyst concentration on peak reaction temperature

	Peak temperature (°C) at different heating rates (Ts)			
TPP (wt.%)	2°C/min	5°C/min	7°C/min	10°C/min
0	169.8	185.6	188.9	199.0
0.5	114.2	129.4	136.4	143.6
1.0	113.9	126.3	133.8	137.8
2.0	102.0	115.8	118.4	125.7
3.0	95.9	109	114.1	120.0

and the final form of the Ozawa equation is given as:

$$2.19d(\log\varphi)/d(1/T_s) = -E/R \tag{3}$$

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

$$A = \varphi(E/RT_s^2)e^{E/RTs} \tag{4}$$

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 the 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 2 and 3 and the Kissinger plots are shown in Figure 5. It is true that in the absence of catalyst, the DSC profile could be influenced by

Table 2. Kinetic parameters (Ozawa method)

TPP (wt.%)	lnA	E_{expt} (kJ/mol)	r	E_{norm} (kJ/mol)	k_{100} $(s^1) \times 10^3$
0	18.5	90.7	0.9922	90.5	0.022
0.5	14.7	67.1	0.9993	80.4	0.77
1	18.8	78.9	0.9959	79.5	1.04
2	19.6	79.3	0.9948	76.9	2.55
3	18.4	74.7	0.9999	75.7	3.38

Table 3. Kinetic parameters (Kissinger method)

TPP (wt.%)	lnA	E_{expt} (kJ/mol)	r	E_{norm} (kJ/mol)	k_{100} $(s^{-1}) \times 10^3$
0	18.9	90.5	0.9972	90.5	0.021
0.5	14.6	66.9	0.9991	78.8	0.94
1	18.8	79.7	0.9952	78.7	1.00
2	19.5	79.5	0.9941	76.1	2.16
3	18.3	74.5	0.9999	74.9	3.27

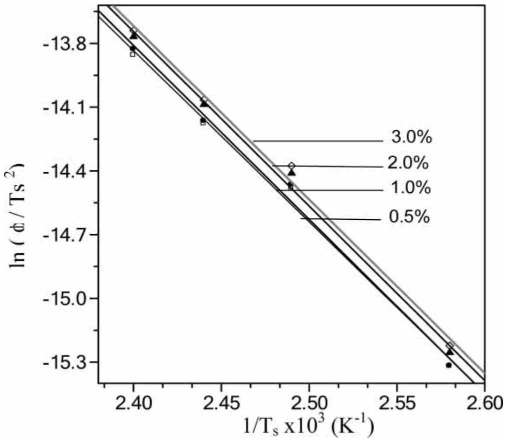


Fig. 5. Kissinger plots for different catalyst concentrations.

the allyl polymerization. As stated earlier, the allyl group polymerization is an unfavored reaction and the associated enthalpy is benign. Hence, the error caused by allyl polymerization in the estimation of E based on the peak maximum is negligible, as the major enthalpy and the peak maxima are derived exclusively from 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. However, the reaction rate calculated at a fixed temperature (100°C) for different catalyst concentrations using Arrhenius equation:

$$k = Ae^{-E/RT} \tag{5}$$

showed an increasing trend with catalyst concentration. From the kinetics point of view, the 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 (40). However, the rate constants at any given temperature showed a systematic decrease with enhancement in catalyst concentration, implying catalysis of the reaction by TPP. Hence, it was appropriate to normalize the E values using the pre-exponential factor computed for the system without catalyst. The normalization was done using the empirical rate constant at an arbitrary temperature of 100°C using the relation:

$$k_{100} = A_{exp}e^{-Eexp/R.373} = A_o e^{-Enorm/R.373} \tag{6}$$

Where, A_{exp} is the experimental pre-exponential factor for an activation energy E_{exp}, A_o is the pre-exponential factor for the uncatalyzed reaction calculated using the relation 4. The normalized E values showed a systematic decreasing trend with an increase in catalyst concentration. The dependences of activation energy and rate constant on the catalyst concentration are given in Tables 2 and 3. The normalized values are useful for comparison only, as these E values could change depending on the temperature at which the rate constants have been considered for normalization.

3.3 *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 the 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 4 and 5. The conversion α_T at temperature T, was computed using Equation 1. The iso-conversional kinetic analysis of the DSC data was adequately interpreted earlier for a model epoxy-amine curing process (41) and it has been found that it is more advantageous than kinetic methods such as ASTM E-698 (42). The activation energy calculated by the ASTM method is based on a single point dependence of E on the degree of conversion α, at $\alpha = \alpha_{max}$ while in the iso-conversional method, the kinetic parameters can be calculated for the complete α

Table 4. Isoconversional kinetic parameters computed by Ozawa method (correlation coefficient > 0.99)

	Kinetic parameters at different catalyst concentrations							
	TPP%							
	0.5		1.0		2.0		3.0	
α	E (kJ/mol)	lnA	E (kJ/mol)	lnA	E (kJ/mol)	lnA	E (kJ/mol)	lnA
0.1	71.9	17.5	81.8	20.8	83.3	22.1	79.1	21.1
0.2	69.9	16.4	80.9	20.1	82.7	21.4	77.4	20.1
0.3	68.8	15.8	79.9	19.4	80.8	20.5	76.9	19.6
0.4	68.1	15.3	79.7	19.1	79.2	19.7	75.7	18.9
0.5	67.4	14.8	79.5	18.7	78.1	21.9	74.3	18.2
0.6	67.1	14.5	80.1	18.7	77.4	18.6	73.6	17.7
0.7	67.0	14.2	81.9	19.0	77.2	18.2	72.8	17.2
0.8	66.4	13.8	83.1	19.0	78.0	18.2	71.8	16.6
0.9	65.3	13.1	87.0	19.8	80.2	18.4	71.3	16.1

Table 5. Isoconversional kinetic parameters computed by Kissinger method (correlation coefficient > 0.99)

	Kinetic constants at different catalyst concentrations							
	TPP%							
	0.5		1.0		2.0		3.0	
α	E (kJ/mol)	lnA	E (kJ/mol)	lnA	E (kJ/mol)	lnA	E (kJ/mol)	lnA
0.1	71.7	17.5	81.6	20.8	83.2	22.1	78.9	21.1
0.2	69.7	16.4	80.7	20.0	82.6	21.4	77.3	20.0
0.3	68.6	15.7	79.7	19.4	80.6	20.4	76.8	19.5
0.4	67.9	15.2	79.5	19.0	79.1	19.6	75.5	18.8
0.5	67.2	14.8	79.3	18.7	77.9	19.0	74.1	18.1
0.6	66.8	14.4	79.9	18.6	77.3	18.5	73.4	17.7
0.7	66.7	14.2	81.7	19.0	77.0	18.2	72.6	17.2
0.8	66.2	13.7	86.8	21.3	77.8	18.1	71.6	16.6
0.9	65.1	13.1	87.0	19.8	80.0	18.8	71.1	16.1

range. The iso-conversional plots (Figure 6) were drawn by plotting ln ф against 1/T for different conversion levels and catalyst concentrations. The activation energy values were computed from the slope of these iso-conversional plots. The activation energy values and its conversion dependency obtained by the two methods were found to be comparable (Tables 4 and 5). These values are also found to be in the range of E values computed by Ozawa and Kissinger methods using the T_s values. At low and high catalyst concentration, the activation energy showed a decreasing trend with conversion. However, this is associated by a proportional increase in pre-exponential factor, rendering the rate constant almost independent of conversion. This variation in E and A is again a consequence of the kinetic compensation effect, where a relation ship exists between A and E (40) as:

$$\ln A = b + cE \tag{7}$$

The plots as per Equation 7 for two catalyst concentrations (0.5% and 3.0%) are shown in Figure 7, the linearity of which confirms the existence of kinetic compensation effect in the present case.

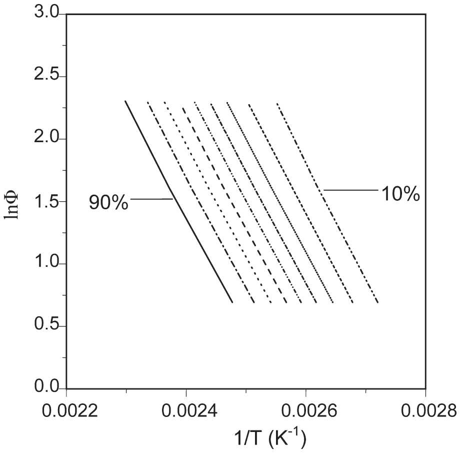


Fig. 6. Isoconversional plots at different conversion levels.

The nearly invariant rate constant (with conversion) implies that the reaction is chemically controlled in the entire conversion range. This is expected since the curing takes place above the T_g of the cured polymer ($T_g \sim 80°C$) (43) where the diffusion effect on kinetics will be negligible.

3.4 *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 other epoxies (44). The normalized E values showed a decreasing trend with catalyst concentration as seen in Figure 8. The addition of 0.5% catalyst resulted in considerable reduction in E value. The rate constant showed a systematic increase with increase in catalyst concentration.

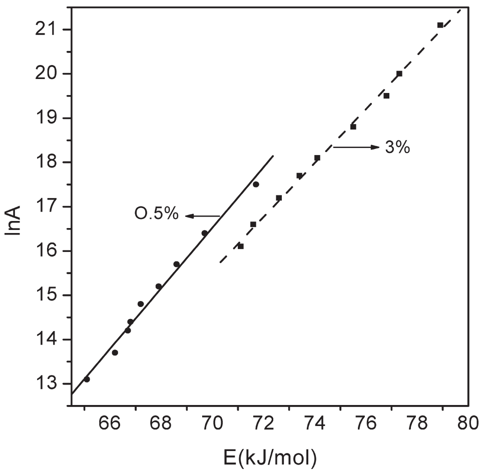


Fig. 7. Kinetic compensation plots for conversion dependency of activation energy for typical catalyst concentrations.

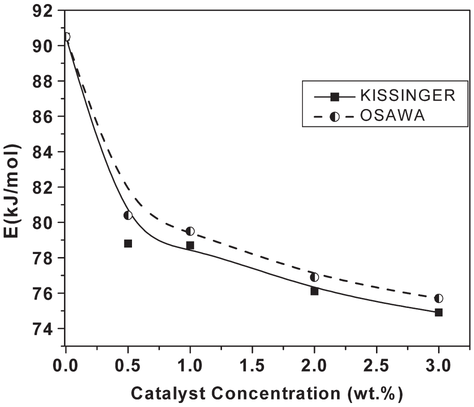


Fig. 8. Effect of catalyst concentration on normalized activation energy obtained by the Ozawa (OZ) and Kissinger (KIS) methods.

3.5 *Kinetic Prediction of Isothermal Cure*

The A and E values are useful for predicting the cure profile of the resin under given conditions of temperature and time. The relationship between A, E, T, time (t) and conversion (α) is derived from the isothermal rate equation for an nth order reaction as:

$$d\alpha/dt = k(1-\alpha)^n = Ae^{-E/RT}(1-\alpha)^n \tag{8}$$

Integration of Equation 8 gives Equation 9 as:

$$\alpha = 1 - \{1 - A(1-n).t.e^{(-E/RT)}\}^{1/1-n} \tag{9}$$

where, n is the order of the reaction which can be found from the temperature integral of Equation 8 given by the Coats-Redfern (C-R) equation (45) for non-iosthermal DSC,

$$\ln[g(\alpha)/T^2] = \ln\{(AR/\phi E)(1-2RT/E)\} - E/RT \tag{10}$$

where $g(\alpha) = \{1-(1-\alpha)^{(1-n)}\}/(1-n)$ and α is the conversion at temperature T in the non-isothermal DSC thermogram.

In fact,

$$\alpha_T = \Delta H_T/\Delta H_M \tag{11}$$

where, ΔH_T is the fractional enthalpy at temperature T and ΔH_M, the total heat of reaction. Indirectly, these are obtained from the fractional and total areas respectively under the thermogram.

The order parameter, n was found by an iteration method from the linear plots of $\ln[g(\alpha)/T^2)]$ vs $1/T$ for different assumed values of n by the C-R method. In the majority of cases, the value of n was found to be very close to 2 for the conversion range from 0.1 to 0.9.

In fact, in many cases of epoxy curing by phenols, a reaction order of two has been reported (46, 47). Hence, for the computation of conversion as per Equation 9, n was taken as 2. The experimental A and E values were considered for the calculation of conversion. The predicted isothermal cure curves at a fixed temperature (100°C) of the resin system for different catalyst concentrations are shown in Figure 9. The data in Figure 9 show that the phenol-epoxy cure reaction stagnates at ~90% conversion at 100°C when the catalyst concentration is 0.5–1.0%. However, a reasonably good conversion is achieved in about two hours for a catalyst concentration exceeding 2% at 100°C. At this temperature, the extent of reaction is negligible (~15%) in the absence of catalyst.

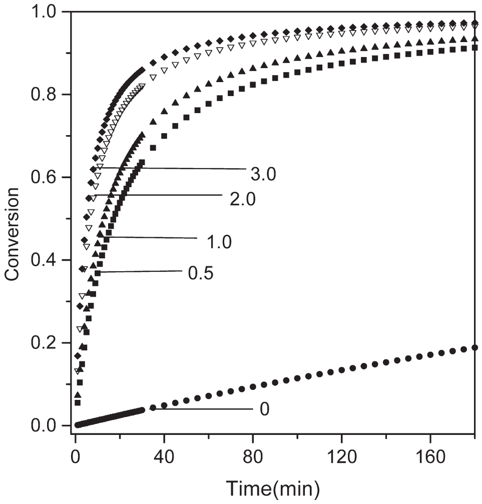


Fig. 9. Isothermal conversion curves for different catalyst concentrations at 100°C.

The time-conversion profiles predicted for the system with 0.5% catalyst concentration at varying temperatures are shown in Figure 10. It is seen that when the temperature exceeds 140°C, full conversion is achievable in about an hour. At this temperature, the extent of allyl polymerization can be expected to be practically zero. Thus, the DABA-EPN cured system with pendant allyl groups can be realized either by increasing the catalyst concentration above 2% and effecting the polymerization at 100°C or by performing the reaction at temperatures exceeding 140°C,

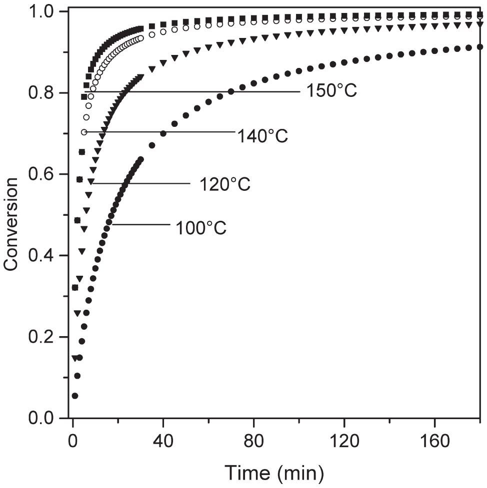


Fig. 10. Predicted isothermal conversion at different temperatures (100–150°C) for 0.5% catalyst concentration.

while maintaining a catalyst concentration of 0.5%. The latter cure protocol was followed for the rest of the studies.

4 Conclusions

The kinetics of triphenyl phosphine (TPP) catalysed phenol-epoxy reaction in the 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 the catalyst concentration. The apparent activation energy values normalized 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 even on 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.

5 References

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