

## Study of the Cure Reaction of Epoxy Resin Diglycidyl Ether of Bisphenol-A (DGEBA) with Meta- Phenylene Diamine

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### ABSTRACT

The cure process of epoxy resin diglycidyl ether of bisphenol-A (DGEBA) with aromatic amine (m-PDA) as curing agent was studied by means of differential scanning calorimetry (DSC) Perkin Elmer Pyris 6, at ratio (15 phr). Isothermal DSC measurements were conducted between 80 and 110 °C, at 10 °C intervals. The maximum degree of cure at isothermal cure temperature 110 °C was 0.9. The isothermal cure process was simulated with Kamal modifier with diffusion model, the model agrees well with the experimental data. For dynamic cure process, the activation energy was determined by two methods. One was based on Kissinger and Ozawa approach, given only one activation energy for the whole curing process. There was a slightly difference between the obtained activation energy and pre-exponential factor, 63.6 and 70.7 kJ mol<sup>-1</sup> respectively. Another method was based on isoconversional, given activation energy at any conversion, and observed the Ea decrease with increment conversion (67-63) KJ/mol.

**Keywords:** Epoxy resin, Cure kinetics, and Differential Scanning Calorimetry.

### دراسة الخواص الحركية لأنضاج راتنجات الايبوكسي مع ثنائي الأمين الفينيلين

#### الخلاصة

تم دراسة حركية الأنضاج ودرجة التحول الزجاجي لنظام راتنج الايبوكسي المحضر من تفاعل (DGEBA) مع الامينات العطرية (m-PDA) عن طريق جهاز المسح التفاضلي (Perkin Elmer Pyris 6) بالأعتماد على نسبة الخلط الوزنية (15:100). فحوصات حركية الأنضاج ودرجة حرارة الانتقال الزجاجي تمت بجهاز المسح التفاضلي وبثبوت درجة الحرارة (isothermal). درجات الفحوصات التي اعتمدت هي (80,90,100,110) °م، كذلك تم محاكات حركية الأنضاج باستخدام موديل كمال المعدل مع عامل الانتشار (diffusion factor)، حيث اظهرت النتائج بان نسبة التحول تزداد بزيادة درجة الحرارة واعلى تحول تم الحصول عليه هو (0.9) عند درجة الحرارة (110) °م، وقد لوحظ أيضا هناك تطابق جيد بين نتائج الفحوصات مع تلك التي تم الحصول عليها من الموديل المفروض. كما ان درجة

حرارة التحول الزجاجي (Tg) تزداد بزيادة درجة التحول. كما ان فحوصات حركية الانضاج تمت بجهاز المسح التفاضلي بطريقة تغير درجات الحرارة (non isothermal), حيث تم حساب طاقة التنشيط بطريقتي (Kissinger) و (Ozawa), حيث اعطت طريقة (Ozawa) قيمة اعلى بقليل من طريقة (Kissinger). كما طبقت طريقة (isoconversional) حيث اعطت مدى من طاقات التنشيط مع التحول. حيث اظهرت تناقص بالطاقة مع زيادة درجة التحول.

## INTRODUCTION

Epoxy resins represent an important class of polymers primarily due to their versatility. High degree of crosslinking and the nature of the interchain bonds give cured epoxies many desirable characteristics. These characteristics include excellent adhesion to many substrates, high strength, chemical resistance, fatigue resistance, corrosion resistance and electrical resistance [1]. Epoxy has the ability to transform its readily liquid (or thermoplastic) state to tough, hard thermoset solids. This hardening is accomplished by the addition of a chemically active reagent known as a curing agent [2]. Optimum performance properties can be obtained by cross-linking the epoxy resins into a three-dimensional and infusible network. The epoxy group, because of its three-membered ring structure, is highly reactive and can be opened up by a variety of nucleophilic and electrophilic reagents, curing agents are either catalytic or coreactive. Catalytic curing agents include Lewis bases, Lewis acids and photo initiated cationic cures. Coreactive curing agents include amines and acid anhydride [3]. In order to optimize the curing cycles for epoxy resin, it is necessary to understand the cure kinetics. Differential scanning calorimetry or DSC is one of the methods used to analyze the cure kinetics, [4]. Multi kinetic models are available to analysis curing kinetic one from models is  $n^{\text{th}}$  order reaction. This model gave a good fit to the experimental data only in a limited range of degree of cure [5]. Another model can be used to describe curing kinetic with more complexity is autocatalytic model [6].

## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

It is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment [4]. The result of a DSC experiment is a curve of heat flow versus temperature or versus time.

The measured heat flow from the thermosetting sample during cure can be used to calculate its degree of cure with the following equation:

$$\alpha(t) = \frac{\int_0^t q dt}{H_{\infty}} \quad (1)$$

Where  $\alpha(t)$  is the degree of cure,  $q$  is the heat released from the sample from time 0 to time  $t$  during cure measured by DSC, and  $H_{\infty}$  is the ultimate heat of reaction obtained by the experiment. Thus, the reaction rate or rate of conversion,  $d\alpha/dt$  is:

$$\frac{d\alpha}{dt} = \frac{dH}{dt} \frac{1}{H_{tot}} \quad (2)$$

Where dH/dt or heat flow represents the rate of heat generated during curing reaction [7].

#### KINETIC MODELS AND EQUATION

Chemical kinetics is the description of conversion of reactants to products [8]. Phenomenological models use properties which are related to the reaction, for example the change in viscosity or shift in glass transition temperature of a growing polymer. These models describe the degree of conversion or percent of cure from uncured to fully cure as a function of time and temperature. Phenomenological models are advantageous because they do not require knowledge of the reaction mechanism, only the changes in properties. As any chemical reaction, the curing reaction will be described by a rate equation, which will relate the rate of the reaction to the rate constant and the consumption of reactants or production of products. In the case of thermoset curing, a generalized rate function utilizing the degree of cure,  $\alpha$ , which is the disappearance of epoxide functional groups or appearance of chemical bonds, with  $(1 - \alpha)$  representing the epoxide group concentration.

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3)$$

This equation describes an nth order equation. However, many thermosetting materials are autocatalytic, so that the product of the reaction serves as an additional catalyst in the reaction, as in the catalyzation of the epoxy-amine system by generated hydroxyl groups. Kinetic modeling of autocatalytic reactions requires an additional term to account for this effect, namely.

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (4)$$

Where  $\alpha m$  represents the catalytic effect of the products of the reaction with an order of  $m$ . It is also apparent, that an nth order reaction is a special case of the autocatalytic reaction where  $m = 0$ . However, the two types are readily differentiated by experimental data. As can be easily predicted from Equation 3, an nth order reaction will exhibit its maximum rate at the beginning of the reaction, whereas the autocatalytic reaction, predicted from Equation 4, will exhibit its maximum rate at some later time during the reaction, typically 20 to 40 % of the reaction [9]. In addition to the time dependence of the rate of conversion, the rate constant,  $k$ , is temperature dependent, usually assumed to follow an Arrhenius relation of the form:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

Where k is the reaction rate constant, A is the pre-exponential function, and  $E_a$  is the activation energy. The initial rate of an autocatalytic reaction is not necessarily zero since the reaction can proceed via alternative paths, especially in the presence of impurities like water and catalyzing ions. Taking this into account, the autocatalytic equation is given as

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (6)$$

Where  $k_1$  is the reaction rate constant at zero time and  $k_2$  is the rate constant of the reaction by traditional pathways. The initial rate constant,  $k_1$ , is easily calculated from the experimental data since it equals the rate at zero conversion. Both m and n are the kinetic exponents of the reaction, and m+n is the overall reaction order. Both kinetic constants,  $k_1$  and  $k_2$  depend on temperature according to Arrhenius law. Such a model has been successfully applied to describe the initial stage of cure of epoxy/diamine systems. Kamal showed that the model was valid only for the initial stage of cure but not for the later stage of cure where the reaction mechanism was diffusion controlled. Kamal with diffusion model can be defined as [10].

$$\frac{d\alpha}{dt} = \frac{1}{(1 + \exp(C(\alpha - \alpha_c)))} (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (7)$$

The term  $1/(1 + \exp(C(\alpha - \alpha_c)))$  is the diffusion factor that includes two constants: C, the diffusion constant, and  $\alpha_c$ , the critical degree of cure.

According to the Kissinger method [11], the activation energy can be obtained from the maximum reaction rate where the exothermal peak appears under a constant heating rate.

$$\ln\left(\frac{\beta_i}{T_{p,i}^2}\right) = \ln(AR/E_a) - \frac{E_a}{RT_{p,i}} \quad (8)$$

Thus, the activation energy  $E_a$  can be obtained from the slope of the plot of  $\ln(\beta/(T_p^2))$  as a function of  $1/T_p$  without a specific assumption of the conversion-dependent function.

Ozawa [12], developed an alternative method to determine the activation energy from  $T_p$ . The equation shows as following

$$\ln(\beta_i) = Const. - 1.052 \frac{E_a}{RT_{p,i}} \quad (9)$$

thus,  $E_a$  can be obtained from the slope of the plot of  $\ln \beta$  as a function of  $1/T_p$ .

Another method for determining  $E_a$  was first developed by Fava [13], named as an isoconversional method. The isoconversional method allows complex processes to be detected by a variation of  $E_a$  with  $\alpha$ . The equation for determining the activation energy is given by.

$$\ln(\beta_i) - \text{Const.} = -1.052 \frac{E_a}{RT_{\alpha,i}} \quad (10)$$

Where  $T_{\alpha,i}$  is the temperature at different conversions at different heating rates.

### PREVIOUS WORK

Hyun Kim and Chul Kim [14], studied the curing reaction of diglycidylether of Bisphenol-A (DGEBA) with triethylene tetramine (TETA) by the differential scanning calorimetry (DSC). They found that the reaction was affected as the vitrification occurred when the glass transition temperature ( $T_G$ ) of the reaction mixture exceeded the curing temperature ( $T_G$  appeared at temperature 15°C higher than the isothermal curing temperature). Barral et. al [15] studied the kinetic of the cure reaction for a system containing a diglycidyl ether of bisphenol-A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) as a curing agent, By employing differential scanning calorimetry (DSC), used an isothermal approach, he have determined the reached conversions at several cure temperatures and the reaction rates. He found that this cure reaction is autocatalytic ( $T_{\text{cure}}$  from 60 to 110 °C). Sbirrazzuoli et. al [16] studied the kinetic of the cure reaction of diglycidyl ether of bisphenol A (DGEBA) with meta phenylene diamine (m-PDA) as a stoichiometric mixture and as a mixture having an excess of amine, by differential scanning calorimetry (DSC) technique at different heating rates, the model-free isoconversional method was used to estimate the activation energy. He found that in the presence of an excess of the amine the curing is controlled by the primary amine reaction as indicated by practically constant effective activation energy, and in the stoichiometric system shows a decreasing dependence of the effective activation energy (decreases to as low as 20 kJ/mol). Macan ET. al [17] studied the kinetic of the cure reaction of epoxy resin based on a diglycidyl ether of Bisphenol A (DGEBA), with poly(oxypropylene) diamine (Jeffamine D230) as a curing agent, was performed by means of differential scanning calorimetry (DSC). Isothermal and dynamic DSC characterizations of stoichiometric (30 phr) and sub-stoichiometric (20 phr) mixtures were performed. He found that cure kinetics of system DGEBA (30 phr), with stoichiometric content of amine, can be successfully described with Kamal model.

The main objective of the present work was to study the kinetics of the curing reaction of DGEBA with aromatic diamine (m-PDA) by isothermal, and dynamic (DSC), at stoichiometry ratio.

## EXPERIMENTAL

### Materials

The studied system is based on commercial epoxy resin (DGEBA), (Shell Co., Epikote 828) with weight per epoxy of 186 g eq<sup>-1</sup>. Meta phenylene diamine (m-PAD), were used as hardeners.

### Techniques

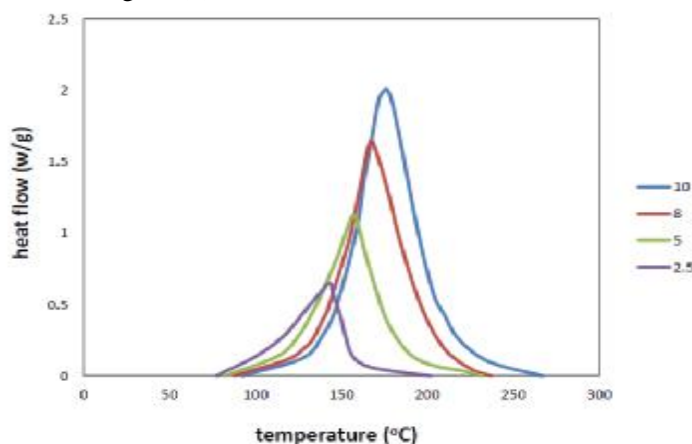
A Perkin-Elmer differential scanning calorimeter (DSC-6) was used to measure the peak area, with (15) phr. Epoxy resin was completely mixed. (3-10) mg of this mixture of DGEBA/m-PDA was put into an aluminum DSC sample pan, separately and covered with aluminum lid.

Dynamic DSC studies of curing reaction of the mixtures were performed from (30-300) °C at different heating rates (2.5, 5, 8, and 10) °C min<sup>-1</sup>. For isothermal experiments, sample performed from (80-110) °C in 10 °C increments.

## RESULT AND DISCUSSION

### Multiple scan rate method

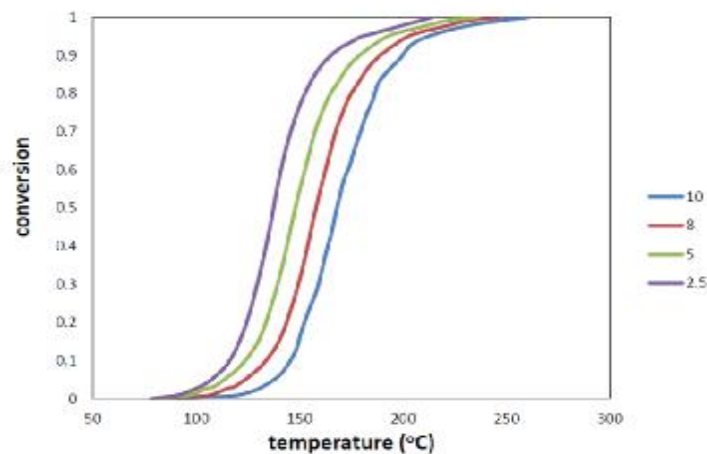
DSC curves of investigated systems obtained at heating rates of (2.5, 5, 8, and 10) °C min<sup>-1</sup> are shown in Figure (1).



**Figure (1) Heat Flow Changes at the Heating Rates of 2.5, 5, 8, and 10 °C/min.**

Which shows the heat flow changes versus the temperature. It is observed the influence of different heating rates on the curing behavior, heating rate increases, the peak exothermic temperature,  $T_p$ , shifts to higher temperature. It is clearly seen from Figure (1), that  $\Delta H_{tot}$  is not constant, with its value decreasing particularly for the high heating rate. The decrease in total reaction enthalpy with increasing heating rates may be attributed to the higher temperature attained in these samples. At higher temperature, unreacted molecules or volatiles could be lost, thus providing a contribution to the total heat flow that is not linked to the curing reaction. In addition, at the fast heat rate, thermal decomposition due to the higher temperature attained in the samples probably interferes with the later stage of cure. These results are in good agreement with Prime [18]. The

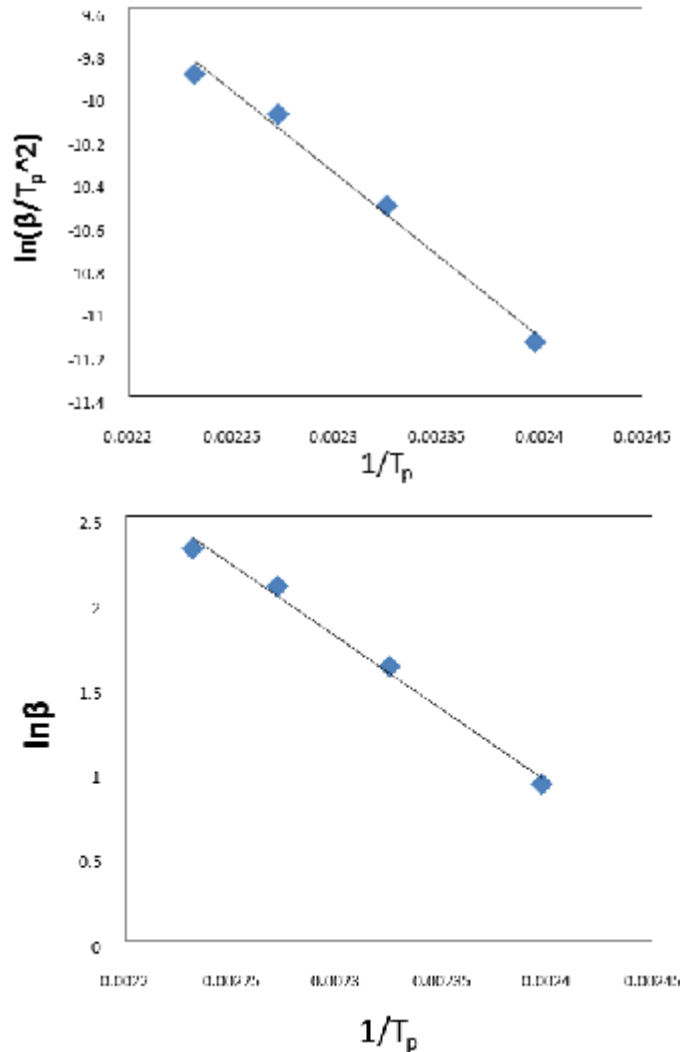
degree of cure ( $\alpha$ ) at each temperature could be calculated. Figure(2) represents conversion versus temperature; shows the variation of the fractional conversion as a function of temperature for the same sample. Due to the shift in  $T_p$ , the activation energy could be calculated by the Kissinger and Ozawa methods. From economy view and final properties rate 2.5 °C/min was selected.



**Figure (2) plot conversion versus temperature for curing epoxy DGEBA with m-phenylene diamine at different rate 2.5, 5, 8, and 10 °C/min.**

According to Kissinger's and Ozawa's method,  $\ln(\beta/T_p^2)$  and  $\ln(\beta)$  were plotted as a function of  $1/T_p$ , respectively. All plots are shown in Figure (3) respectively.

From this Figure, the linear regression fits well for both Kissinger's and Ozawa's analyzed methods with  $R^2$  of 0.99, thus confirming the validity of both methods. From the fitted slope, the activation energy  $E_a$  is calculated. It is found that the values of  $E_a$  calculated from Kissinger's method are slightly lower than those from Ozawa's method. The behavior of this study is in agreement with those of Ghaemy [19]. The Kissinger's and Ozawa's methods have a limitation because they produce a single value of  $E_a$  for the whole process which is a sign of a single-step process. A more complete determination of  $E_a$  at any selected conversion can be calculated by the isoconversional method. In this method, each plot has the same degree of cure. At the different heating rates, the temperature required to achieve the same degree of cure is different.



**Figure (3) Plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  (Kissinger) and  $\ln \beta$  versus  $1/T_p$  (Ozawa) for epoxy DGEBA with m-phenylene diamine**

It increased with the increment of heating rate. At each isoconversional curve, the apparent activation energy  $E_a$  should be constant. The isoconversional plots of the logarithmic heating rate versus the reciprocal of the absolute temperature are shown in Figure (4). For all the isoconversional curves, a good linear relationship is observed between the logarithm heating rate and the reciprocal of the absolute temperature. The apparent activation energy at each degree of cure is calculated from its slope in the isoconversional curve and plotted. Figure (5) illustrates the activation energy versus



conversion. The isoconversional plots helped to understand the details of the curing process. As shown in Figure (5), the apparent activation energy decreased with the increment of degree of cure. The decrease in  $E_a$  is an indication that the rate determining step of curing changes to a process having smaller activation energy. In epoxy curing systems, molecular motion of small molecules (amine and epoxy) is prevented by the growing polymer chains. Once an epoxy curing system has passed the gel point, the small molecules may be trapped within the polymer network and can engage in a chemical reaction only after a series of diffusion jumps [16]. The behavior of this study are in agreement with those of Sbirrazzuoli [16], that the decrease in  $E_a$  is associated with diffusion control, which is caused by a decrease of molecular mobility as the epoxy system approaches the glassy state.

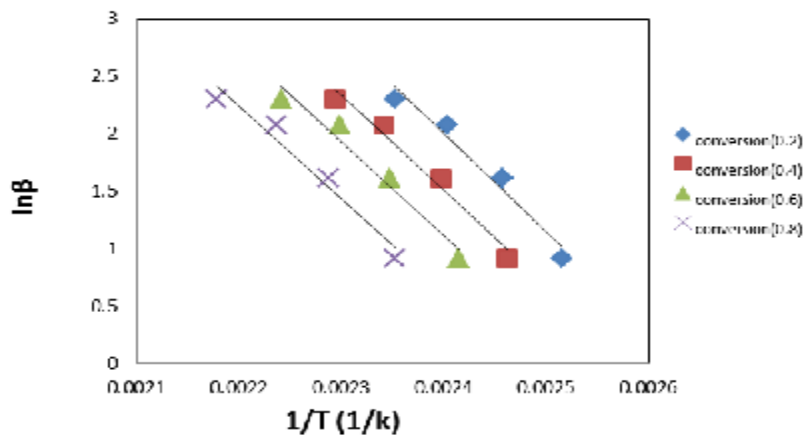


Figure (4) logarithm heating rate vs. Inverse temperature at different conversion.

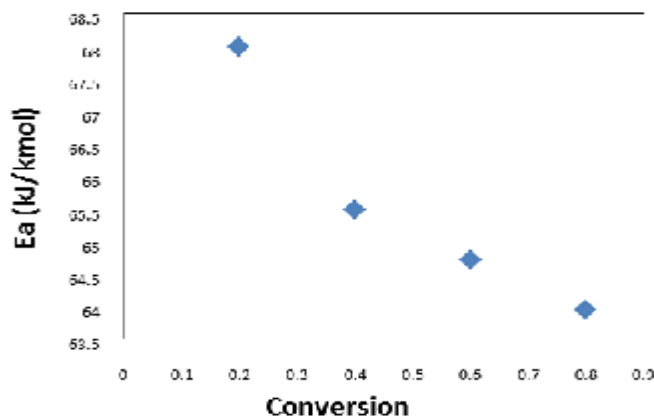


Figure (5) Activation Energy vs. Conversion.

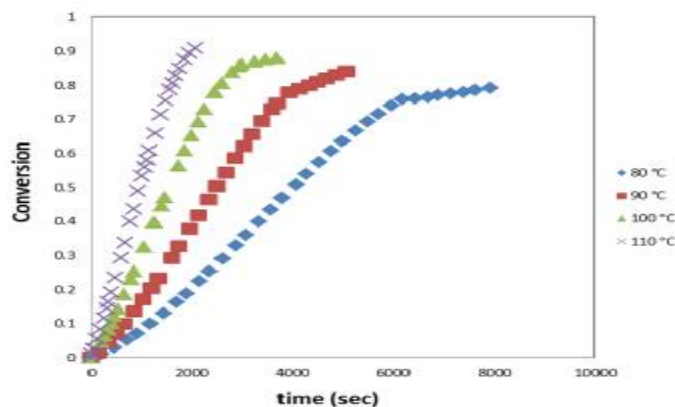
**ISOTHERMAL SCAN RATE METHOD**

To calculate the total heat of reaction generated to reach full conversion  $\Delta H_{tot}$ , DSC dynamic scans at different heating rates were performed, and the total area under each thermogram was determined for all systems. The average values of  $\Delta H_{tot}$  at heating rates from 2.5 to 10 °C/min were used to calculate the fraction of conversion ( $\alpha$ ). Aromatic amine has weaker basicity than aliphatic amine and slowly cures at room temperature due to steric hindrance by the aromatic ring. The curing virtually stops in the B-stage of a linear polymer solid due to the large difference in the reaction of primary and secondary amines. Normally, the curing of aromatic amine requires heating. The first heating is carried out at temperature of approximately 80°C and which agreement with Technical Department [20]. DSC experiments under isothermal conditions for epoxy DGEBA/phenylene diamine at four different curing temperatures yield the heat flow-time curves. The isothermal cure heat is different. Its value increases with the increment of temperature. The calculated cure heat values are listed in Table (1).

**Table (1) Total heat of reaction,  $\Delta H_t$  of DGEBA curing with m-phenylene diamine from isothermal.**

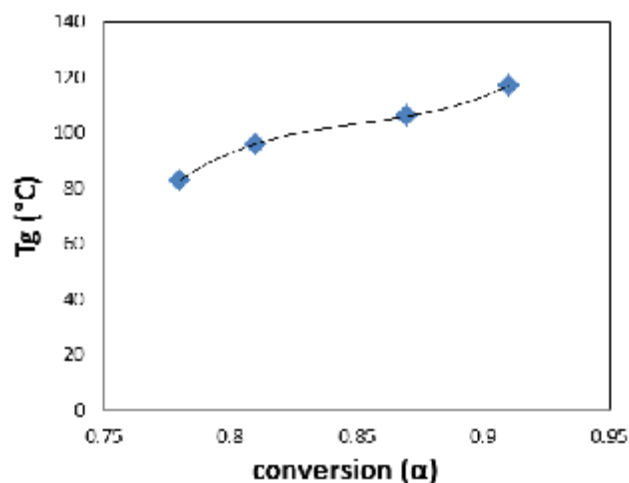
T (°C)	$\Delta H$ (J/g)	$\Delta H$ average
110	507	475
100	493	
90	462	
80	439.5	

The behavior of this study is in agreement with those of Sbirrazzuoli [16]. Typical plots of conversion ( $\alpha$ ) as a function of time of epoxy (DGEBA) curing with phenylene diamine at various temperatures are shown in Figure (6).



**Figure (6) Conversion vs. time at different temperature.**

The curing reaction is thermally catalyzed; the high conversion is attained earlier at a higher temperature of curing. It is also observed from Figure (6), that the time needed to reach the final degree of cure is also much different, depending on the isothermal cure temperature. At the curing temperature  $T_c$  of 80 °C, the complete maximum conversion reached only to a stage of  $(\alpha) = 0.78$ . The glass transition at complete cure  $T_{g\infty}$  determined for the cured system is 83°C.  $T_c$  is lower than  $T_{g\infty}$ , thus cured epoxy is in a glassy state. This behavior is agreement with Hyun Kim and Chul Kim [18]. At  $T_c$  where vitrification set in ( $T_c = T_{g\infty}$ ), there is an overall diffusion control that affects the rate of polymerizations because segmental motions are considerably slowed down [21]. Once the vitrification of the epoxy systems has passed, the reaction is dominated by the diffusion effect. If the cure temperature is too low, then the final conversion never reaches the unity [22]. This is well resolved on the conversion versus time traces in Figure (6). As the curing temperature increases to 90, 100, and 110°C, the complete maximum conversion rises to 0.81, 0.87, and 0.90 respectively. This unique relationship between  $T_{g\infty}$  and conversion is striking because one would expect that different network structures result from cure at different temperatures. The relationship between  $T_{g\infty}$  and conversion are shown in Figure (7).



**Figure (7) Glass transition temperature vs. Conversion from isothermal.**

As the conversions increase the  $T_{g\infty}$  increases, when the crosslinking reaction exhausts all the reactive sites available, the resulting structure is hard (high modulus) and insoluble due to a high degree of interchain bonding [23]. Figure (8) shows the isothermal rate of curing reaction versus time for curing of the epoxy (DGEBA) with aromatic amine at 80, 90, 100, and 110°C respectively. The curves show that the rate of cure increases with increasing curing temperature, as for reactant molecules to react, they need to contact other reactant molecules with enough energy for certain atoms or groups of atoms to come apart and recombine to make the products. When the reactants are heated, the average kinetic energy of the molecules increases. This means that more

molecules are moving faster and hitting each other with more energy. If more molecules hit each other with enough energy to react, then the rate of the reaction increases [2].

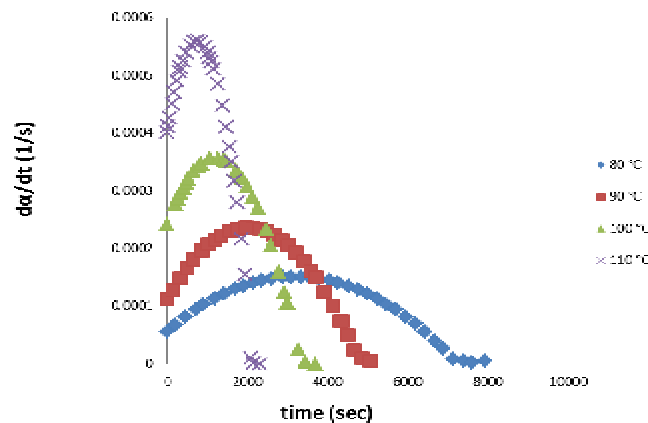


Figure (8) Reaction rate vs. time at different temperature.

The maximum reaction rate at time greater than zero. Thus the  $n^{\text{th}}$ -order curing kinetics become invalid; autocatalytic model is applicable instead. However, the maximum rate is observed at a conversion too low to be autocatalytic reaction because the maximum rate of the autocatalytic reaction usually shows at about 30-40% of reaction [9]. For most systems, the maximum peak value of the rate of reaction is higher and shifted to a shorter period of time as the curing temperature increases. The time at maximum rate of reaction,  $t_p$ , and the maximum rate of reaction,  $r_p$ , at different curing temperatures are shown in Table (2).

Table (2) Time at maximum rate of reaction  $t_p$  and maximum rate of reaction  $r_p$  at different curing temperatures.

T (°C)	$t_p$ (min)	$r_p$ ( $s^{-1}$ )
110	9.9	0.00075
100	17.5	0.00047
90	32	0.00029
80	48.9	0.00018

It is found that changes in  $r_p$  and  $t_p$ , as curing temperature  $T_c$  varies. These are because of the dependence of curing mechanisms on the curing temperature  $T_c$ , and the reaction rate is known as the temperature dependence. Due to the maximum rate of the reaction occurring at time greater than zero, the autocatalytic kinetics, expressed by Kamal with diffusion model were selected to represent the experimental isothermal curing behavior of these epoxy systems. To obtain the parameters of equation (7), several methods have been proposed. In this work,  $K_1$  is first calculated from the intercept of the isothermal thermogram [24], and  $(\alpha_c)$  from experimental data, and then  $K_2$ ,  $m$ , and  $n$  are determined by non-linear estimation. The example of the plot of reaction rate  $d\alpha/dt$  as a function of conversion, and the fitting curve obtained are shown in Figure (9&10).

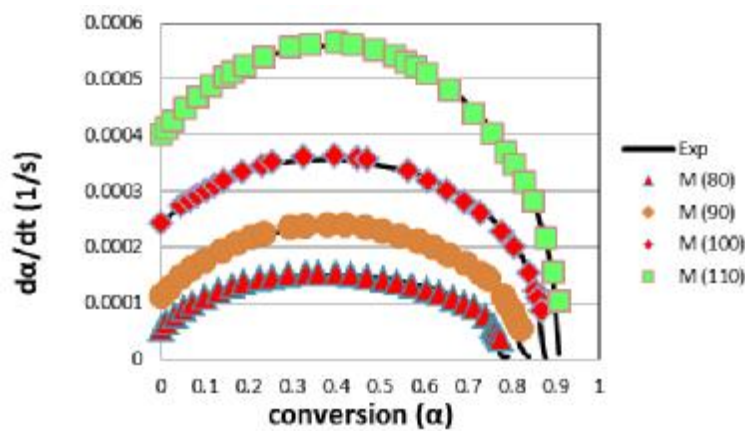


Figure (9) Comparison of experimental data with model predictions: Rate vs. Conversion at different temperatures.

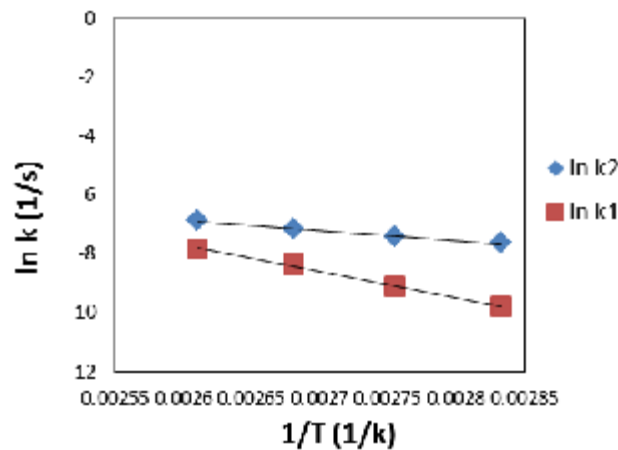


Figure (10) Temperature dependence of rate constant  $k_1$  and  $k_2$ .

It is found that the chosen model shows a good fit with the experimental data. The kinetic parameters  $K_1$ ,  $K_2$ ,  $m$ ,  $n$  and  $m+n$ , obtained for all curing systems as a function of curing temperature, are shown in Table (3). The overall reaction order ( $m+n$ ) is observed to be in the range of 1.73 to 2.05 for all the systems. The temperature dependence of the Arrhenius relationship equation (5) for the rate constants  $k_1$  and  $k_2$ , is shown in Figure (11). The autocatalytic rate constants  $k_1$  and  $k_2$  show a good correlation with temperature. However, the overall tendency is the increasing of  $k_1$  and  $k_2$  as temperature increases. Activation energies  $E_{a1}$  and  $E_{a2}$ , are calculated from the slope of the plot  $\ln k$  as a function of  $1/T$ .

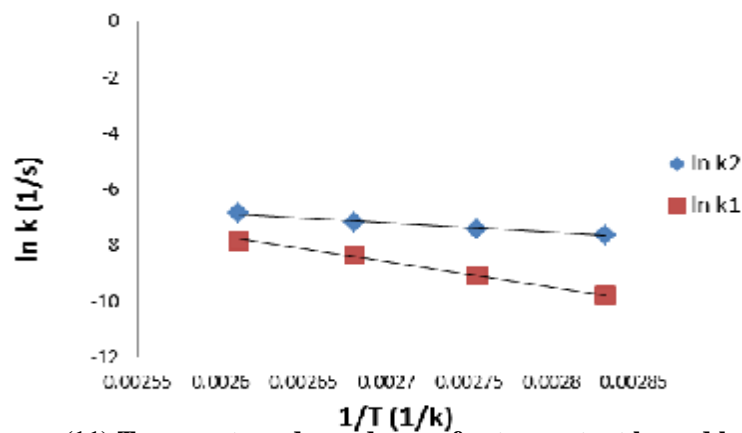


Figure (11) Temperature dependence of rate constant  $k_1$  and  $k_2$ .

Table (3) Kinetic parameters as determined from the autocatalytic kinetic model for epoxy (DGEBA) with m-phenylene diamine at various curing temperatures.

T (°C)	$k_1$ ( $\times 10^5$ s <sup>-1</sup> )	$k_2$ ( $\times 10^4$ s <sup>-1</sup> )	m	n	m+n	c
110	40.09	10.48	0.95	0.78	1.73	50.61
100	24.18	7.69	0.94	0.87	1.81	45.75
90	11.2	6.05	0.85	0.97	1.82	57.99
80	5.6	4.94	0.85	1.2	2.05	61.44
$E_{a1}$ (kJ/mol)		$A_1$ (s <sup>-1</sup> )	$E_{a2}$ (kJ/mol)		$A_2$ (s <sup>-1</sup> )	
75.31		15.877	28.12		1.9347	

## CONCLUSIONS

The isothermal cure reaction heat increases with the increment of cure temperature. The reaction heat of isothermal cure is achieved at 110°C. The maximum degree of cure at isothermal cure temperature 110°C is 0.9. In the earlier stage of the isothermal cure reaction, the cure rate at the higher temperatures is faster than the cure rate at the lower temperatures. The relationship between cure rate and degree of cure was simulated by Kamal with diffusion model. The model can provide a good predication in the large range of experimental data. The kinetic rate constants  $K_1$ ,  $K_2$ , and  $m$  increase with the increment of cure temperature while the orders of reaction  $n$  and  $(m+n)$  decrease. The final  $T_{g\infty}$  was studied by DSC of each curing temperature. The final  $T_{g\infty}$  increase with the increment of degree of cure.

The dynamic DSC provide additional information about the curing process. The cure reaction heats decrease with increment heating rate while the  $T_p$  increase. In the modeling method based on the Kissinger, Ozawa, and isoconversional approach, the obtained activation energy and pre-exponential factor, slightly difference between them. The isoconversional method provide activation energy along for process, and  $E_a$  decrease with increment conversion.

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