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Cure Kinetics of Epoxy Resin Studied by Dynamics and Isothermal DSC Data

Dr. Adnan A. Abdul Razak
Chemical Engineering Department, University of Technology/ Baghdad
Email: adnansss2002@yahoo.com
Dr. Najat j. Saleh
Chemical Engineering Department, University of Technology/ Baghdad
Maryem Emad
Chemical Engineering Department, University of Technology/ Baghdad

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ABSTRACT:

Diglycidyl ether of bisphenol A (DGEBA) epoxy resin was cured with hardeners aliphatic amine triethylenetetramine (TETA). Differential scanning calorimetry (DSC) technique was utilized to study the kinetics of cure of (DGEBA)-(TETA) system, diverse hardener/resin ratios were studied, (5, 13and 20) phr. Isothermal as well as dynamic experiments were carried out of the above mentioned DGEBA/TETA system with three hardener/resin ratios, and cure kinetics were investigated at four temperatures (30, 45, 60 and 80) °C using (DSC) technique. The process of isothermal cure was simulated by the diffusion model (modified Kamal's model and four-parameter autocatalytic model. The obtained outcomes are in good agreement with the experimental results in the early and late cure stages. The events declare that complete cure at 80 °C attains at the stoichiometric ratio (13 phr).

Keywords: Epoxy resin, DGEBA, Cure kinetics, DSC

INTRODUCTION

Epoxy resins are widely used in a several industries. Adhesives, coatings, electronics, and aerospace industries are some of the areas they are used in [1]. The cure kinetics associated with the epoxy resin is very important aspect. With the help of the modeling of cure kinetics, scientists, engineers or process control managers can get valuable information useful for optimizing processing conditions or predicting the thermosetting resins or composites shelf life time. Differential scanning colorimetery (DSC) can be used so that the kinetic parameters are determined by using isothermal and dynamic methods [2].

Analytical expressions to describe cure kinetics are obtained from modeling of phenomenological advance which uses simple procedure and satisfactory accuracy. The mathematical model gives the parameters which agree with experimental data [3]. The cure degree, α, is utilized to reveal the degree of conversion of small molecular weight pre-polymers into high molecular weight cross-linked, having three dimensions

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

construction. α increases with increase in heat given off due to bonds creation and it can be described as follows:

$$\propto = \frac{\Delta H_t}{\Delta H_{total}} \qquad \ldots (1)$$

Where

ΔH_t represents the reaction heat being accumulated up at a particular time t of curing process, and ΔH_{total} represents the total heat which is liberated when the reaction is completed. In case of resins which are uncured $\alpha = 0$ .On the other hand, for resin which is completely cured α equal or less than one.

It is presumed that the curing rate is proportionate to rate of heat generation and the following expression is used to calculate it:

$$\frac{d\propto}{dt} = \frac{1}{\Delta H total}\left(\frac{dH}{dt}\right) \qquad \ldots. (2)$$

To characterize the process of curing, many phenomenological models have been developed to study the system of different resins. The equation of nth order rate represents the simplest one [4]:

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

$$K = A\exp\left(\frac{-\Delta Ea}{RT}\right) \qquad \ldots (4)$$

Where n represents order of reaction, and k is the constant rate of reaction, which is a function of temperature, A represents the pre-exponential constant or Arrhenius frequency factor, ΔE_a is the activation energy, R represents the universal gas constant, and T is the absolute temperature. The model of nth-order kinetics does not explain the autocatalytic property and it gives in advance the rate of maximum reaction at the starting of the curing.

The following equation is used for the systems of autocatalytic thermosetting resin [5]:

$$\frac{d\propto}{dt} = k \propto^m (1-\propto)^n \qquad \ldots (5)$$

Where: m and n represent orders of reaction which are intended by experimental input data. The maximum reaction rate occurs as the reactions proceed as shown by equation (5). This produces a bell shaped curve on plotting rate of reaction against time of an autocatalytic process.

A constant of single rate is used to represent the entire process of curing, by using nth and autocatalytic model; in reality many events may take place at the same time, causing reaction which is very complicated.

Therefore accurate results of modeling can be provided by constants of multiple rates. Kamal's model uses constants of two rates and has been adopted with success to model resins of many types [6]:

$$\frac{d\propto}{dt} = (k_1 + k_2 \propto^m)(1-\propto)^n \qquad \ldots (6)$$

$$k_i = A_i \exp(-\Delta E_i/RT) \; (i = 1, 2) \qquad \ldots (7)$$

There has been wide use of the many mathematical models already described. Nevertheless the extent of being true is restricted to the reactions for bond formation kinetics which is the controlling step during process of curing. Although this usually happens in the advance step, other parameters can participate when reactants are used up and network of cross-linking is created. Therefore, diffusion of species slows down greatly, and controls the rate of curing reaction around the glass transition. Some changes have been done on models of cure kinetics to explain the effect of controlling mechanisms to obtain higher accuracy at later stage of curing.

Species which are represented by equation modified by equation (6) when they added a term to clearly explain the change to diffusion control from kinetics [7], in an autocatalytic isothermal system; the following form represents modified announcement:

$$\frac{d\propto}{dt} = \frac{1}{1+\exp(C(\propto - \propto_c))}(k_1 + k_2 \propto^m)(1-\propto)^n \qquad \ldots (8)$$

Where: c and α_c represent the two temperature dependent practical constants. α_c is termed the cure critical degree.

The form of Kamal's model was modified by Chern and Poehlein to [8]:

$$\frac{d\propto}{dt} = (k_1 + k_2 \propto^m)(\propto_{max} - \propto)^n \qquad \ldots (9)$$

Where α_{max} represents the upper extremely cure degree at a particular temperature because the verification fact was noticed in isothermal cure. The reaction orders, constants m and n are to be determined practically. On the other hand k_1 and k_2 remain as given in equation (7).

The Kamal model which is already modified includes the term α_{max}, because of the verification at the specific temperature thus the changes of fractional transformation will not go beyond the cure degree.

Pusatcioglu et. al., [9] modified Kenny et. al. [10] model to explain effects of diffusion through equation (5) modification:

$$\frac{d\propto}{dt} = K \propto^m (\propto_{max} - \propto)^n \qquad \ldots (10)$$

Where: α_{max} is the last reaction degree carried out by isothermal DSC scans. As the curing temperature increases so that the final degree of reaction increases, due to structural changes which takes place during polymerization reaction consequentially glass transition temperature (T_g) increases. As the rising T_g reaches the temperature of isothermal cure, the movement of molecules is greatly diminished, and the reaction turns into diffusion controlled and be over at the end, it was noted that α_{max} depends linearly on temperature of isothermal cure.

It was found by Michand that the fit of the autocatalytic model is very much improved by use of α_{max} [11].

Liang et. al., [12] utilized the Kamal's model as in equation (5) to produce kinetic models of epoxy resin which are the soy-based .These resins were made of different formulations. The models produced can be easily used in processing of composite.

Hongyang et. al. [13] used two types of hardeners (Jeffamine) to investigate curing kinetics of DGEBA- Epoxy resin. It was found that the activation energy is proportionate to the curing degree of DGEBA- Epoxy resin.

Moreover, differential scanning colorimetery DSC was used to study the kinetics of curing and mechanism of a bisphenyl type epoxy molding compounds with thermal latency organophosphine accents. The results showed that the rate curves are autocatalytic mechanism [14].

This work aims to test current kinetic models. There have been many reports on kinetic models. The first and nth order reaction models can be utilized but their precision is not high. The models of reaction involving complicated autocatalytic are used to get better accuracy, and the results are compared with data obtained from experimental work.

Experiment Work

Materials

This work used diglycidyl ether of bisphenol A epoxy resin type Epikote 828, which was provided by Shell Co. Curing agent (hardener) was Araldite HY 951 (Triethelentetramine TETA) supplied by Ciba Company.

DSC Measurements

The curing kinetics of epoxy resin was studied using DSC Model Pyris 6 DSC from Perkin-Elmer.

Procedure

Curing agent and resin were blended at three ratios a (5) phr, (13 and 20) phr at room temperature.

For isothermal and dynamic DSC scans species (10-20) mg were encapsaled (sealed) in aluminum pans ,then for dynamic scans samples were heated from room temperature up to 250 ºC at a rate of 5ºC/min. ,while for isothermal scan samples measured at four temperatures, 30ºC, 45ºC, 60ºC & 80ºC, respectively. Nitrogen was introduced at a rate of 100 ml/min. Reference was an air (free aluminum pan).

As the recorder signal leveled-off the base line, the reaction was considered to be completed. When the reaction is over, the summation of area below the exothermic curve was determined from the extrapolation of final base line.

Result and Discussion

Dynamic Cure Analysis

The heat liberated detected by DSC in general is proposed to be correlated to the degree of depletion of reactive groups [11].

During the dynamic assessment the specimen was scanned from 30 to 250 ^{o}C at 10 ^{o}C/min rates. From the DSC curve some information could be obtained such as onset temperature of reaction, peak temperature and the values of dH/dt (total heat of reaction) for different resin / hardener ratios of DGEBA/TETA system. These values are shown in Table (1)

It can be seen that the peak temperature (Tp) for 13 phr (which is the stoichiometric ratio) is 99.71 ^{o}C, as anticipated the peak temperature for 20 phr is less due to the reaction is more efficient. As hardener/resin (H/R) ratio increases more amine group is available consequently more cross-linking reaction takes place [15]. On the other hand when (H/R) is 5 phr no significant peak was observed, that is because no appreciable curing occurred [16].

Table (1) :For DGEBA/TETA system , peak temperature and total reaction heat dynamic cure for 13 and 20 phr

Hardener/resin ratio (phr)	Onset temperature (°C)	Peak temperature (°C)	Total reaction heat (J/g)
13	70.96	99.71	201
20	68.15	97.58	240.5

Isothermal DSC Cure Analysis

Figure (1) and figure (2) show the change in curing degree varies with time at different curing temperatures, for DGEBA/TETA system 13 phr and 20 phr (H/R) ratios respectively. It is clearly seen that at a given temperature range from 30-80 ^{o}C the degree of curing increases quickly during the early stage, then it gradually declines, and ultimately reaches a given assessment. This can be attributed to the consequence of reactions of the chain continuation, branching and self- cross-linking of epoxy resin in the process of curing. Consequently these reactions lowered the movement of the reacting molecules and retarded the rate of conversion. The same behavior was mentioned by Cai et. al. in their study on cure kinetic of epoxy resin /elastic amine toughness system [13]. Figure (1) shows that for DGEBA/TETA system when 13 phr H/R ratio is used the value of α= 1 at 80 ^{o}C, final cure degree at 30 ^{o}C, α is close to 0.62.

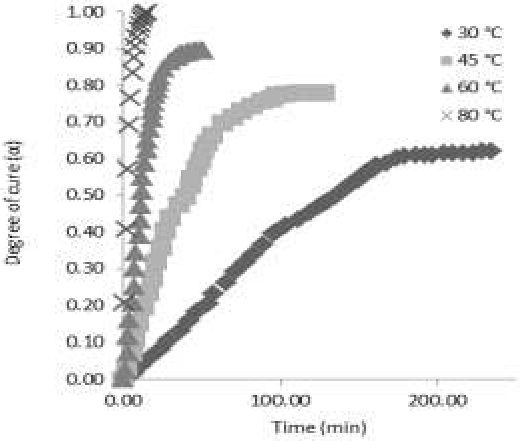


Figure (1) Degree of cure vs. time for 13 phr hardener/resin ratio of GEBA/TETA

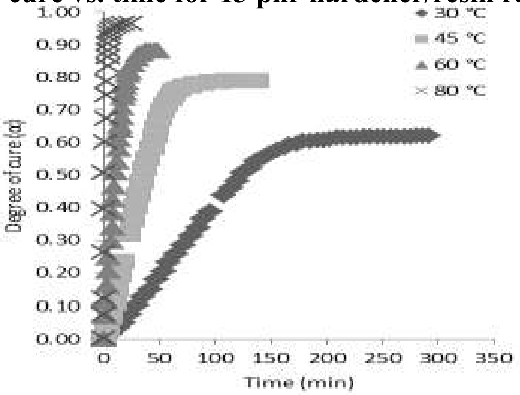
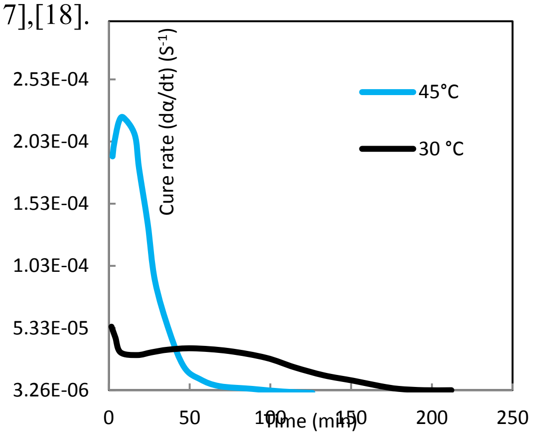


Figure (2) Degree of cure vs. time for 20 phr hardener/resin ratio of DGEBA/TETA system

Figures (3) and Figure (4) show the changes in rate of curing with time at various temperatures ranged from 30 to 80 ^{o}C, for 13 phr H/R ratio and for 20 phr H/R ratios respectively.

It is clearly seen that in the initial steps of cure reaction, the rate of curing at an elevated temperature is quicker than at lower temperature, but in the belated steps, the rate of curing is slump at high curing temperature. This can be highlighting by the fact that reaction is being controlled by diffusion , then the specimen reaches the solid state thus the reacting groups and the product movement is highly diminished and consequently the reaction rate is not controlled by the chemical kinetics but diffusion controlled [12]. Similar behavior was observed by Chean et. al. [14].

It is noticed that the maximum heat release (maximum rate of reaction) takes place in reaction time between 20 and 40% of the sum of reaction time, thus conversion $\alpha \neq 0$. [17],[18].



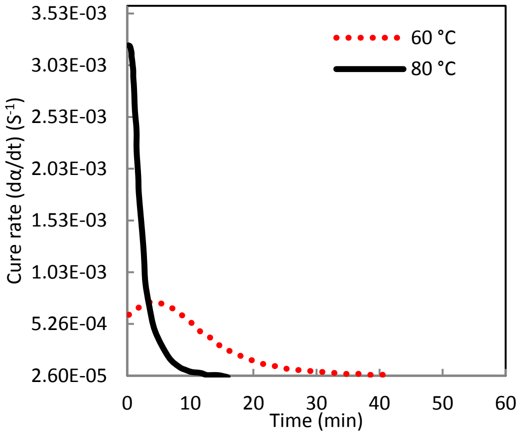


Figure (3) Cure rate vs. time for 13 phr hardener/resin ratio of the DGEBA/TETA system (a) at 30 and 45 °C and (b) at 60 and 80 °C

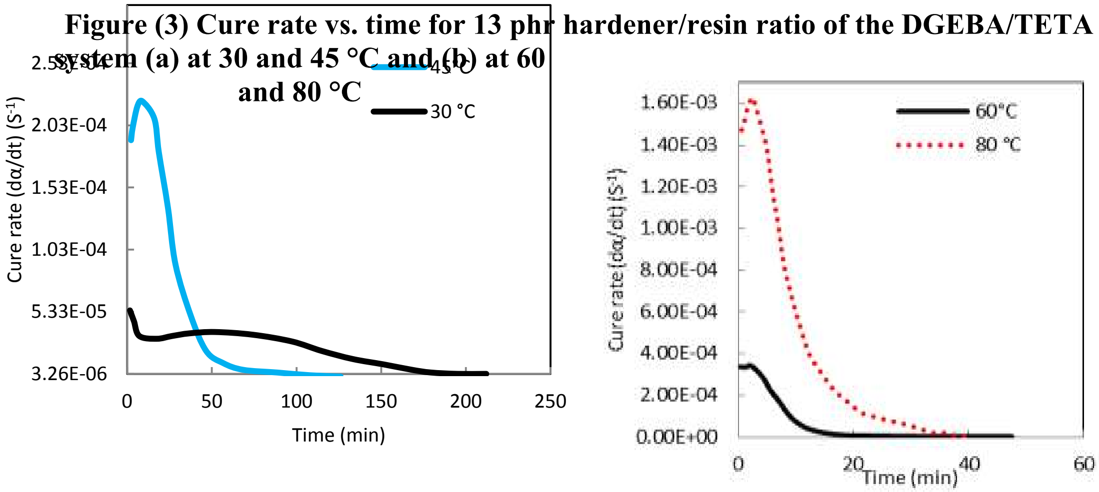
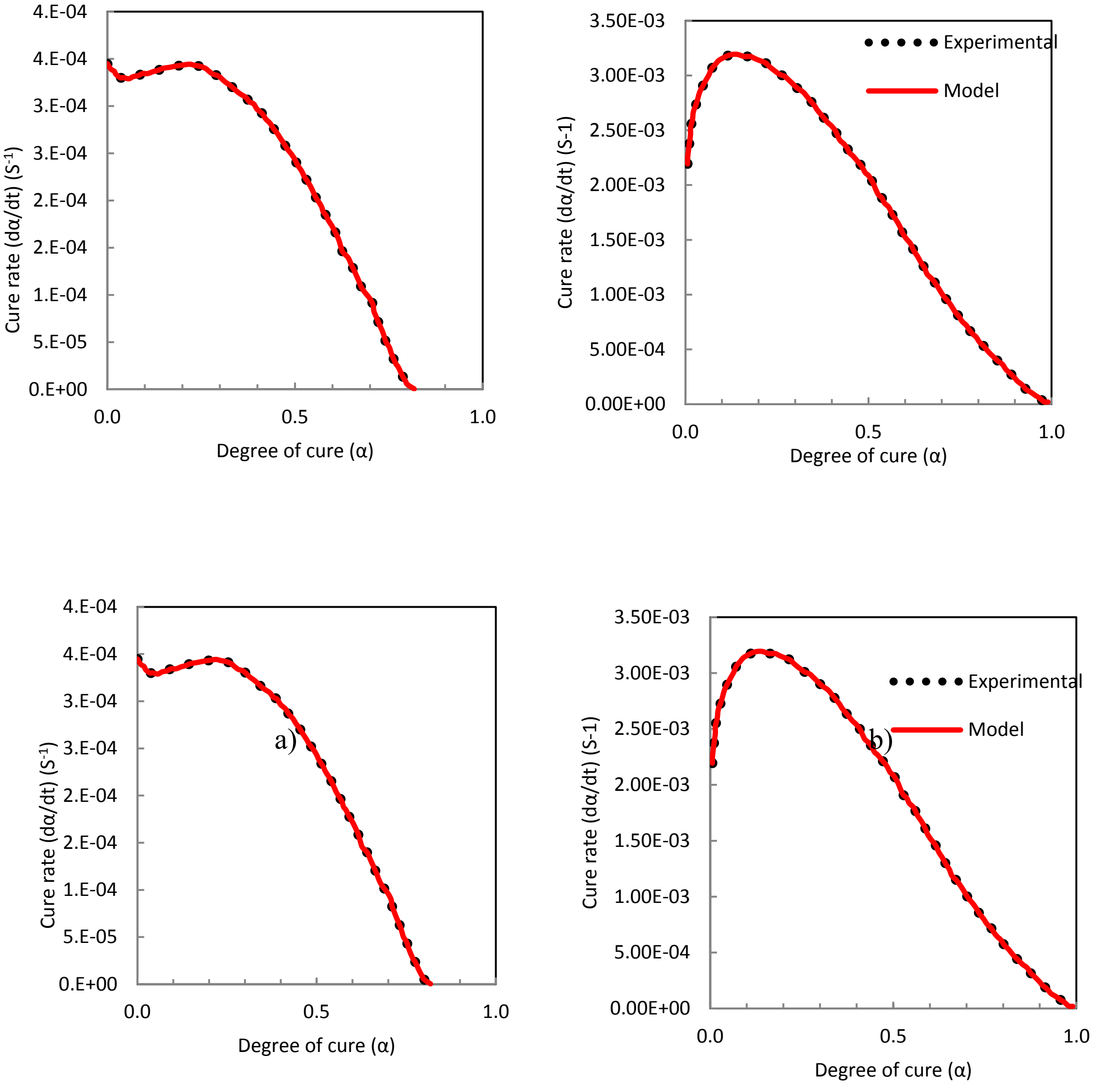


Figure (4) Cure rate vs. time for 20phr hardener/resin ratio of the DGEBA/TETA system (a) at 30 and 45 °C and (b) at 60 and 80 °C

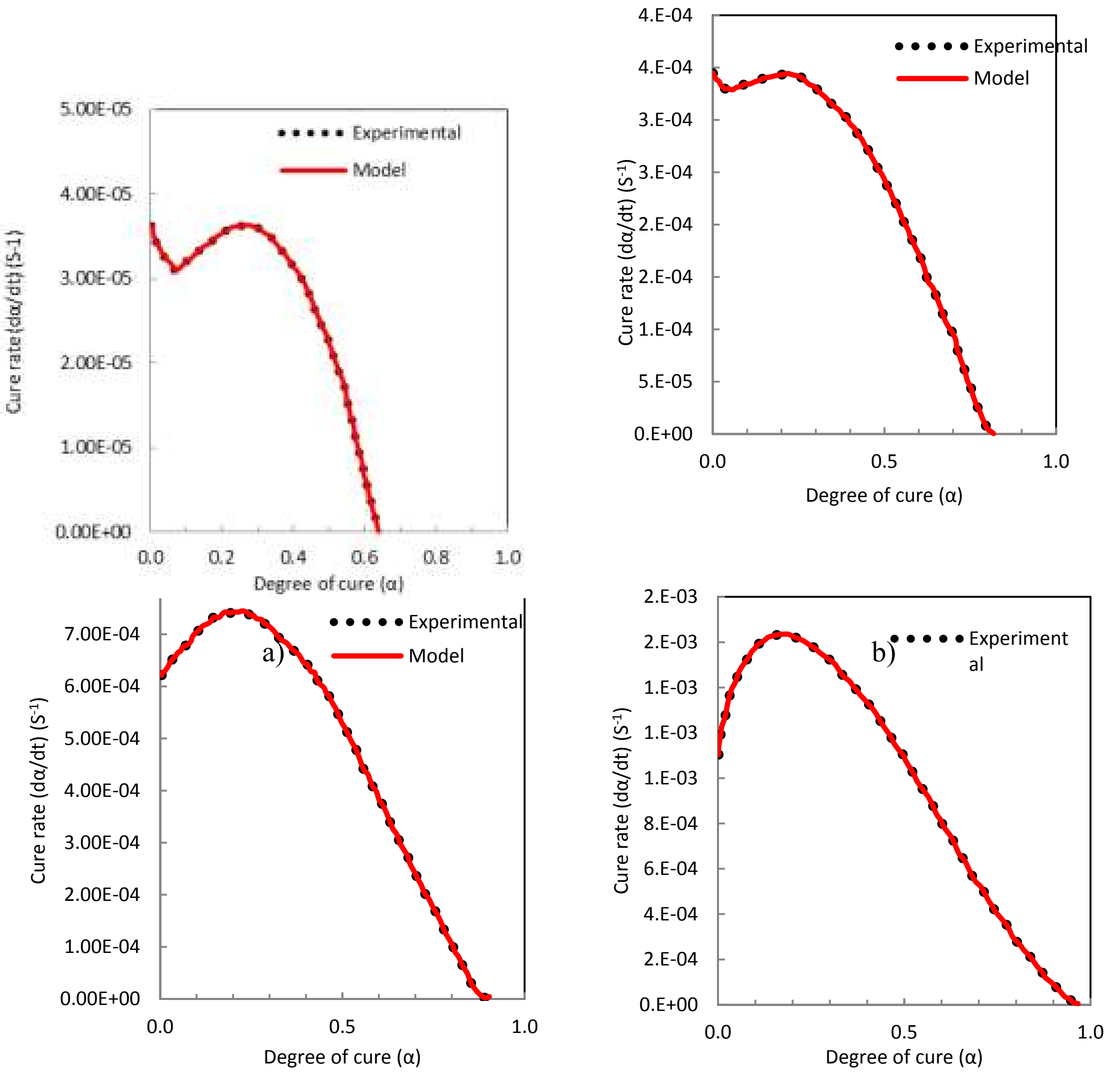
As can be seen in Figures (5) and (6) the maximum rate obtained for 13 and 20 H/R ratio occurs at nearly 30% and 25% of conversion respectively, which means the consumption of 30% and 25% of total sum of epoxy groups has taken place.



c)

d)

Figure (5) Cure rate vs. Degree of cure for 13 phr hardener/resin ratio of DGEBA/TETA system at: (a)30 °C, (b) 45 °C, (c) 60 °C and(d) 80 °C



c) d)

Figure (6) Cure rate vs. Degree of cure for 20 phr hardener/resin ratio of DGEBA/TETA system at: (a)30 °C, (b) 45 °C, (c) 60 °C and (d) 80 °C

It is observed that for 13 and 20 phr H/R ratios of the same system mentioned before, the rate constants k_1 and k_2 and the kinetic exponent n significantly raise as a function of temperature. This may be attributed to a lot character of molecules which accomplished sufficient energy for clash, achieving the reaction activation boundary and, thus enhancing the reaction rate [18],[19].

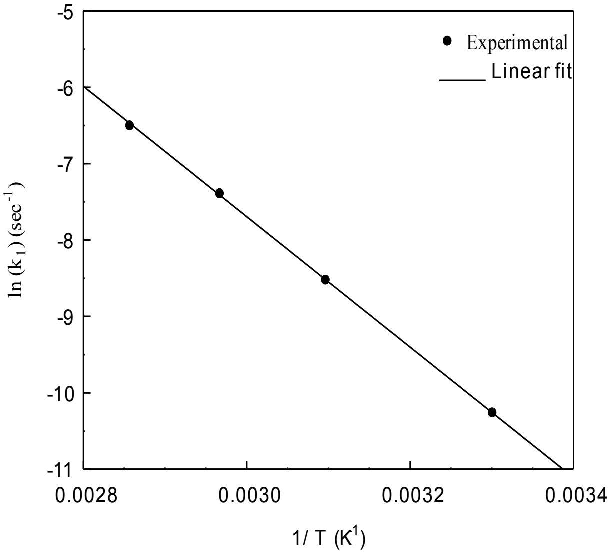
The kinetic exponent m decreases as temperature increases due to superseding of the autocatalytic effect of m [14]. It should be noted that, the sum reaction order (m + n =2) is gained all over the reaction.

The rate constants k_1 and k_2 heighten with the increase of temperature and attend the Arrhenius relationship .The scheme of ln (k1) and ln (k2) vs. 1/T with their linear regression curves are shown in Figures (7) and (8). The pre exponential factors A1 and A2 and activation energies Ea1 and Ea2 can be persistent from the intercepts and slopes of the regression curves, their values are also given in Table (2).

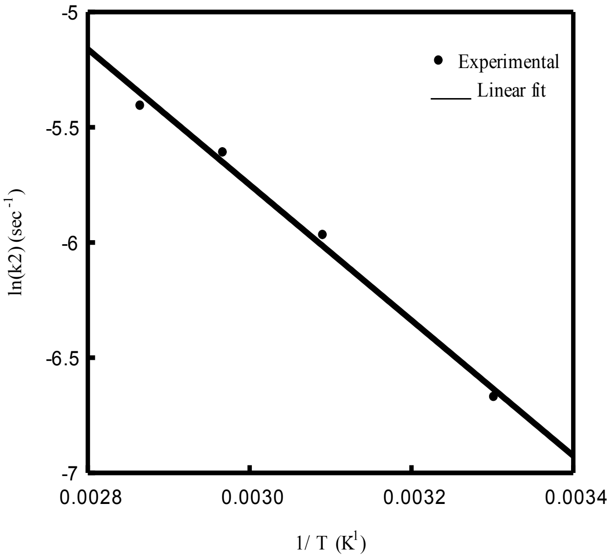
During this examination of 13 and 20 phr H/R ratios of the same system DGEBA/TETA, creation 13 phr appear to give more appropriate end results than the 20 phr, because it offers a elevated cure degree at all the temperatures and achieved the maximum cure degree (α = 1) at 80 °C. Also the activation energies Ea1 and Ea2, 13 phr are less than the 20 phr ratio, which indicates a lesser heating rate is demanded [20].

Table (2): Kinetic parameters of the autocatalytic model for isothermal cure process of 13 phr and 20 phr DGEBA/TETA systems

Systems	Temperature (°C)	k_1(sec^{-1}) ×10^{-3}	k_2(sec^{-1}) × 10^{-3}	m	n	E_{a1} (KJ/mol)	A_1 (sec^{-1})	E_{a2} (KJ/mol)	A_2 (sec^{-1})
13 phr DGEBA/ TETA	30	0.40	1.22	1.325	0.675	55.42	2416	17.85	0.43
	45	2.02	2.51	1.287	0.713				
	60	6.27	3.58	1.277	0.723				
	80	19.4	5.14	1.224	0.776				
20 phr DGEBA/ TETA	30	0.55	1.5	0.566	1.434	67.61	1671	28.43	1.81
	45	1.44	2.04	0.552	1.478				
	60	3.45	2.82	0.446	1.554				
	80	10.32	3.88	0.428	1.572				

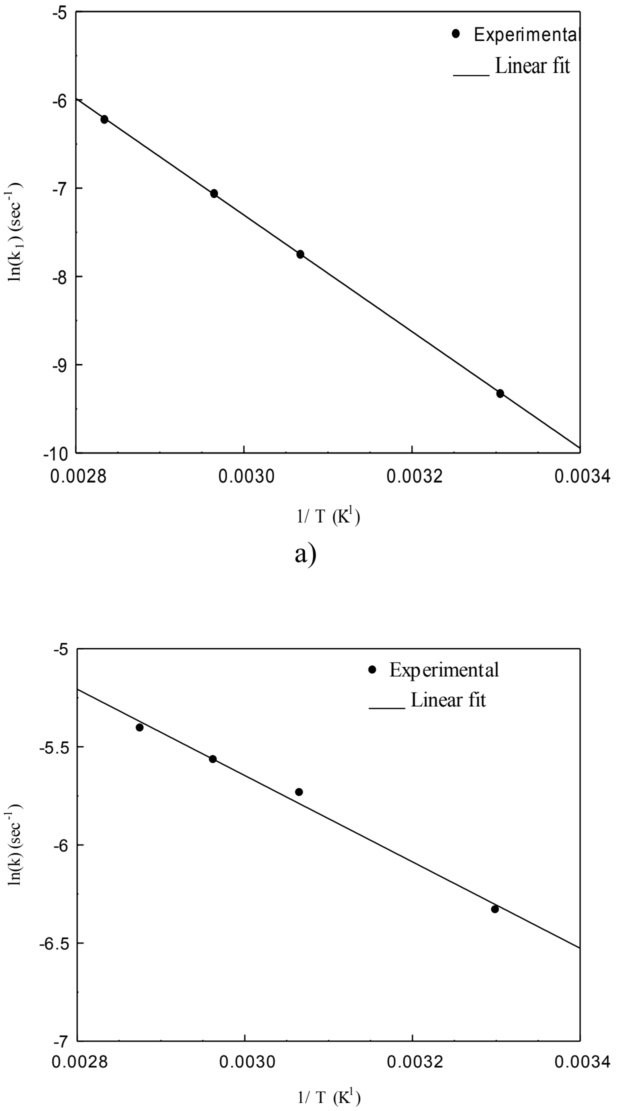


(a)



b)

Figure (7). Rate constant in equation (8) as a function of temperature for 13 phr of DGEBA/TETA system: (a) K_1 and (b) K_2



a)

b)

Figure(8). Rate constant in equation (8) as a function of temperature for 20 phr of DGEBA/TETA system: (a) K_1 and (b) K_2

CONCLUSIONS

1.For DGEBA/TETA system the dynamic DSC computations display that the stoichiometric ratio (13phr) ratio has the highest peak temperature than the above stoichiometric ratio (20 phr) while no peak was detected for under stoichiometric ratio (5 phr).

2. The isothermal DSC estimation broadcast that the complete cure degree is all over at 80 °C for (13 phr), wherever it's ($\alpha = 9.5$) for (20 phr) ratio.

3. For both ratios (13 and 20 phr), the relation between cure rate and cure degree was simulated by the autocatalytic six-parameter model (the modified Kamal's model) containing the diffusion impact. Very good agreement between the simulated finds with the modified model obtained from experimental measurements was reached.
4. The kinetic rate constants k_1 and k_2 and the rate of reaction n enhanced with the increment in cure temperature, while the reaction rate m slumps with temperature, for both the 13 and 20 phr H/R ratios.
5. The activation energies Ea_1 and Ea_2 for the (13 phr) ratio are lesser than the ratio (20 phr) of, which means a lessen heating rate is demanded.

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