

Cure Kinetics of a Diglycidyl Ether of Bisphenol A Epoxy Network ($n = 0$) with Isophorone Diamine

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ABSTRACT: The study of the cure reaction of a diglycidyl ether of bisphenol A epoxy network with isophorone diamine is interesting for evaluating the industrial behavior of this material. The total enthalpy of reaction, the glass-transition temperature, and the partial enthalpies at different curing temperatures have been determined with differential scanning calorimetry in dynamic and isothermal modes. With these experimental data, the degree of conversion and the reaction rate have been obtained. A kinetic model introduces the mechanisms

occurring during an epoxy chemical cure reaction. A modification of the kinetic model accounting for the influence of the diffusion of the reactive groups at high conversions is used. A thermodynamic study has allowed the calculation of the enthalpy, entropy, and Gibbs free energy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4169–4173, 2007

Key words: differential scanning calorimetry (DSC); glass transition; kinetics (polym.); resins

INTRODUCTION

The physicochemical properties of polymeric compounds based on structural resin hardeners are mainly determined by the curing conditions. A widely used technique in the study of these systems is differential scanning calorimetry (DSC), which allows the evaluation of the thermal behavior of a material.

An epoxy system based on diglycidyl ether of bisphenol A (number of monomers of the epoxy resin (n) = 0) and isophorone diamine is used in revetments and paints. A good knowledge of its cure kinetics allows us to determine suitable conditions for the structural formation of the material. The purpose of this work is to study the cure kinetics of that epoxy network.

In the first experimental step, the total enthalpy of reaction (ΔH_i) and the glass-transition temperature (T_g) have been determined with DSC in a dynamic mode. In the second experimental step, the partial enthalpy (ΔH^T) values at different curing temperatures have been determined with DSC in an isothermal mode. From these experimental data, the conversions and reaction rates for each curing temperature have been calculated.

These data have allowed us to determine the kinetic coefficients and the global order of the cure reaction with the Sourour and Kamal model,¹ which incorporates simultaneously the n -order and autocatalytic mechanisms. With this model, the constant rates of the two mechanisms and their activation energies have been determined.

Because of the onset of gelation, a gradual decrease in the reaction rate and an increase in the viscosity can be observed, especially at high conversions. Therefore, a modification of the kinetic model proposed by Chern and Polheim^{2–4} has been used to study the diffusion reaction rate. This model is based on free-volume considerations, introducing a diffusion factor into the reaction rate of the system that tends to unity at low conversions at which the reaction is controlled by the chemical kinetics and that tends to zero at high conversions at which the reaction decreases. This seems reasonable because the molecular weight drastically increases the hindrance of the mobility of the reactive groups. This global kinetic model has been used successfully to study the cure kinetics of other epoxy systems.^{3–8}

Finally, a thermodynamic study based on the theory of Eyring⁹ and Evans and Polyani¹⁰ has allowed the calculation of the changes in the enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger), and Gibbs free energy (ΔG^\ddagger) at different curing temperatures during the formation of the activation complex.

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TABLE I
 ΔH^T and α Values at Different Curing Temperatures

Temperature (°C)	50	60	70	80	85	90
ΔH^T (J/g)	444.8	463.3	484.0	501.2	519.5	505.1
α^a	0.8145	0.8484	0.8863	0.9177	0.9513	0.9249

^a $\Delta H^T / \Delta H_t$.

EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A ($n = 0$; resin 332, Sigma Chemical Co., St. Louis, MO) with an equivalent molecular weight of 173.6 g/equiv, as determined by wet analysis.^{11,12} The curing agent was isophorone diamine (Sigma–Aldrich Chemie GmbH, Germany) with an equivalent molecular weight of 170.3 g/equiv.

The epoxy resin and curing agent were homogeneously mixed for 1–1.5 min in a stoichiometric ratio. For the DSC analysis, samples that weighed 3–7 mg were encapsulated in aluminum pans.

Differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC Q100, V6.19 Build 227, TA Instruments, New Castle, DE) was used to obtain all the experimental data. The calorimeter required three calibrations: T_{zero} (calibration without samples) calibration, cell constant calibration, and temperature calibration.¹³ All the experiments were carried out under a dry nitrogen atmosphere.

To determine ΔH_t , a first scan was carried out in a dynamic mode from -30 to 250°C at a constant heating rate of $10^\circ\text{C}/\text{min}$. A second scan from 15 to 250°C at a constant heating rate of $10^\circ\text{C}/\text{min}$ was carried out to determine T_g of the epoxy system.

In the second phase of the experimental investigation, the ΔH^T values were determined with DSC in

an isothermal mode at different curing temperatures close to T_g : 50 , 60 , 70 , 80 , 85 , and 90°C .

RESULTS AND DISCUSSION

The average experimental values obtained from the DSC dynamic experiments for ΔH_t and T_g of the epoxy system are 546 ± 17 J/g and $85 \pm 3^\circ\text{C}$, respectively. These data are in good agreement with those obtained by Núñez et al.¹⁴ for a similar epoxy system.

From the isothermal experiments performed around T_g at the curing temperatures of 50 , 60 , 70 , 80 , 85 , and 90°C , the values of ΔH^T have been determined. From these values, the total degree of conversion (α) of this epoxy system for different curing temperatures can be calculated:

$$\alpha = \frac{\Delta H^T}{\Delta H_t} \quad (1)$$

Table I shows the ΔH^T and α values at different curing temperatures. For this system, the maximum value of α is 95% at 85°C , and for higher temperatures (90°C), α decreases; this justifies the temperature range used in this study for isothermal experiments.

From isothermal calorimetric thermograms, α of this epoxy system for different curing times (time for a percentage of crosslinking $<$ time for the maximum crosslinking) ($t < t_p$) can be calculated:

$$\alpha = \frac{\int_{t_0}^{t < t_p} dH/dt}{\Delta H_t} = \frac{\Delta H}{\Delta H_t} \quad (2)$$

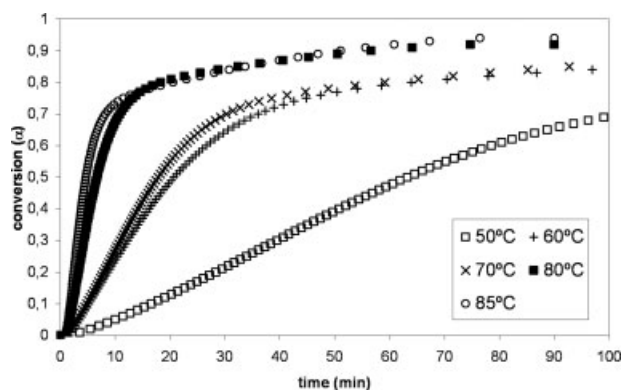


Figure 1 α versus the time at different isothermal temperatures.

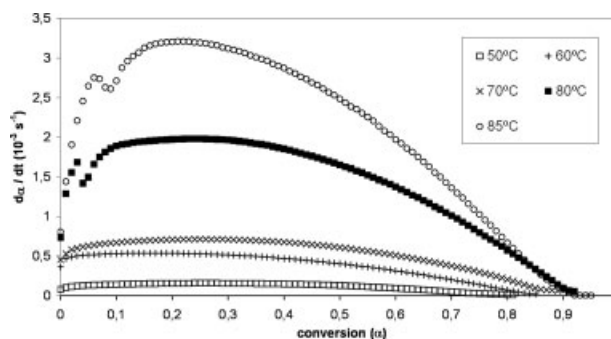


Figure 2 $d\alpha/dt$ versus α at different isothermal temperatures.

TABLE II
Constant Rates and Reaction Orders for the Autocatalyzed and n -Order Mechanisms at Different Curing Temperatures

Temperature (°C)	50	60	70	80	85
k_1 (10^{-4} s^{-1})	0.8	3.7	4.6	7.6	7.7
k_2 (10^{-4} s^{-1})	3.7	6.2	10.4	32.0	72.3
m	0.67	0.44	0.57	0.39	0.46
n	1.35	1.04	0.94	0.95	1.29

where ΔH is the heat that evolves up at a certain time. Figure 1 shows α versus the time at different curing temperatures. The conversion speedily increases with time, reaching a practically constant value. This is due to the increases in the molecular weight with time and due to the higher times hindering the mobility; consequently, crosslinking stops.

From isothermal calorimetric scans, the instantaneous heat flow (dH/dt) and corresponding reaction rate ($d\alpha/dt$) also can be determined:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_t} \quad (3)$$

Figure 2 shows plots of $d\alpha/dt$ versus α at different curing temperatures. $d\alpha/dt$ increases with the temperature.

α and $d\alpha/dt$ for each curing temperature have allowed the determination of the kinetic coefficients and the global order of the cure reaction with the Sourour and Kamal kinetic model,¹ which assumes stoichiometric proportions and equal reactivity for all amine hydrogens:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$

This model expresses the contribution of two mechanisms: the autocatalytic and n -order mechanisms. k_2 and k_1 are the constant rates of the two reactions, and m and n are parameters related to the two reaction orders.

The kinetic model has been used to fit plots of the reaction rates versus the conversion at different curing temperatures. Table II shows the constant rates and reaction orders for the n -order and autocatalytic paths at different curing temperatures. The values listed in this table suggest a value of 2 for the overall reaction order ($m + n$), in good agreement with val-

TABLE III
Activation Energies from the Sourour and Kamal Model

	n -Order mechanism	Autocatalyzed mechanism
Activation energy (kJ/mol)	78.96	56.34

TABLE IV
 α_c and A_1 Values at Different Curing Temperatures

Temperature (°C)	50	60	70	80	85
A_1	18.19	19.62	18.01	17.98	18.95
α_c	0.736	0.771	0.831	0.851	0.846

ues reported by Núñez and coworkers^{3,4} and Zvetkov¹⁵ for similar epoxy systems.

On the basis of Table II, the activation energies corresponding to the n -order and autocatalytic paths have been obtained from an Arrhenius plot of $\ln k$ versus $1000/T$ (where k is the specific reaction rate and T is the absolute temperature), and they are shown in Table III. Similar results for both activation energies were reported by Fraga et al.¹⁶ The values suggest that the autocatalytic mechanism is predominant over the other one.

The cure reaction of an epoxy resin with an amine is controlled by the chemical kinetics. However, the deviations between theoretical and experimental data from a critical conversion (α_c ; typically 58%)¹⁷ are due to a gradual decrease in the reaction and a higher increase in the viscosity. α_c for the formation of the network can be used to calculate the critical fraction free volume at which the cure reaction becomes diffusion-controlled. A semiempirical model based on free-volume considerations, proposed by Chern and Polheim² and used by Cole et al.,⁵ Khanna and Chanda,⁶ and Núñez and coworkers,^{3,4,14} has been used to study the diffusion-controlled reaction rate. In this model, a diffusion factor [$F(\alpha)$] is defined as follows:

$$F(\alpha) = \frac{1}{1 + e^{(A_1(\alpha - \alpha_c))}} \quad (5)$$

where A_1 is an adjustable parameter.

Table IV shows values of A_1 and α_c for different temperatures. The values found for A_1 , around 18, lack a relationship with the temperature, in good

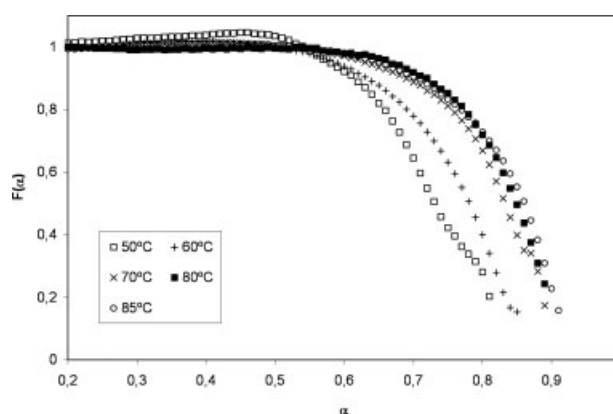


Figure 3 $F(\alpha)$ versus α at different curing temperatures.

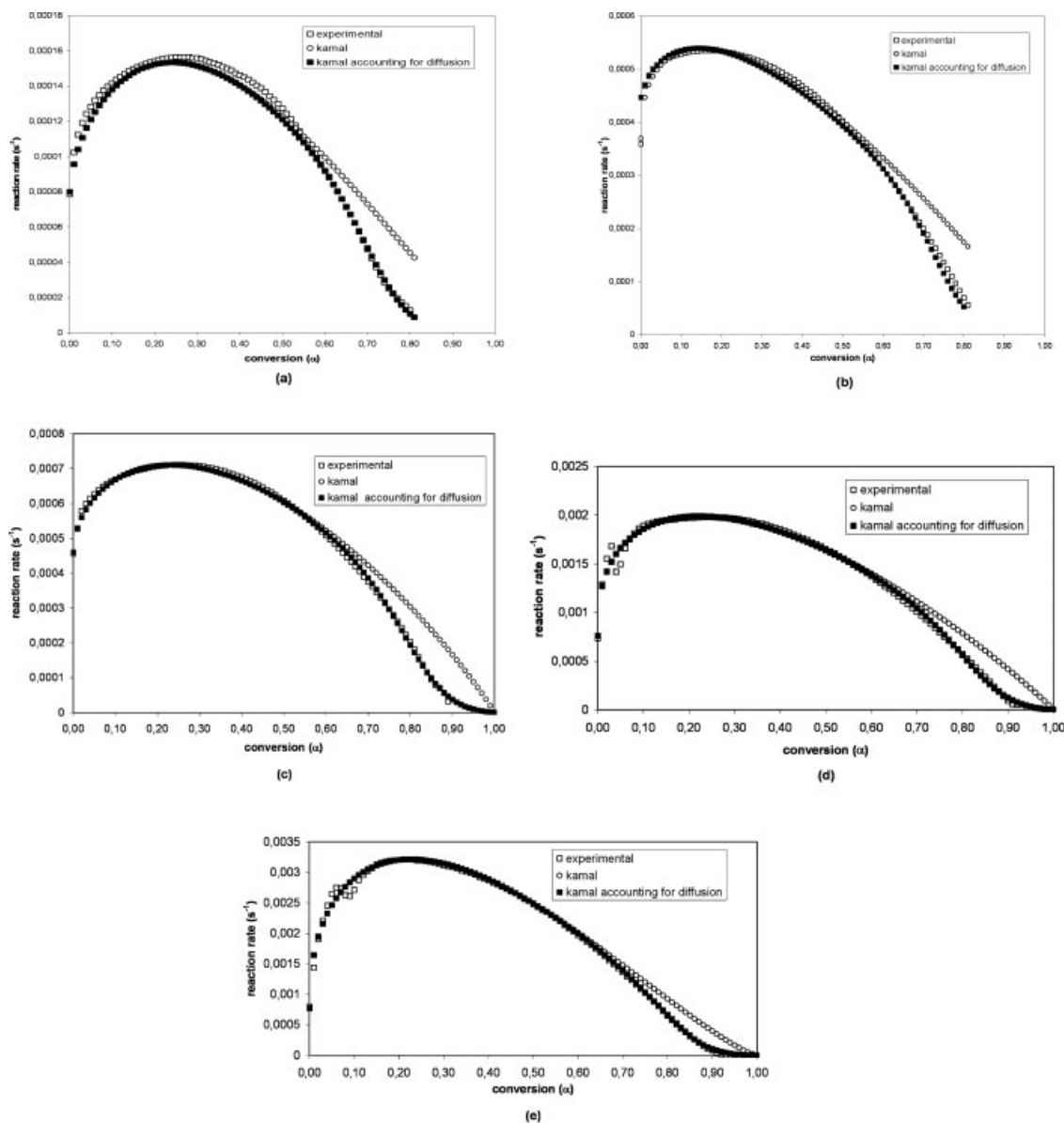


Figure 4 Plots of the reaction rate versus α at (a) 50, (b) 60, (c) 70, (d) 80, and (e) 85°C.

agreement with Chern and Pholein;² nevertheless, similar studies^{3,4} have shown an increase in A_1 with the temperature. α_c increases with the temperature, indicating that diffusion effects appear later.

With $F(\alpha)$, the reaction rate can be expressed in the following form to account for the effects of diffusion:

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

Figure 3 shows the behavior of $F(\alpha)$ versus α at different curing temperatures. When α is smaller than α_c , $F(\alpha)$ tends to unity, and the reaction is controlled by the chemical kinetics. When α becomes greater than α_c , $F(\alpha)$ tends to zero, and the reaction dramatically decreases and finally stops. This decrease is based on

the reaction rate associated with the increase in the onset of diffusion at a high conversion.

Figure 4(a–e) shows the reaction rate versus the conversion at different curing temperatures, and the experimental results are compared with those obtained with the chemical kinetic model and with the kinetic model accounting for diffusion. The agreement is extremely good between the experimental results and kinetic model accounting for diffusion.

TABLE V
 ΔH^\ddagger and ΔS^\ddagger Values for the n -Order and Autocatalyzed Mechanisms

	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol K)
n -Order mechanism	-76.13	-77.81
Autocatalyzed mechanism	-53.52	-155.05

TABLE VI
 ΔG^\ddagger Values Corresponding to the n -Order and Autocatalyzed Mechanisms at Different Curing Temperatures

Temperature (K)	ΔG^\ddagger (kJ/mol)	
	n -Order mechanism	Autocatalyzed mechanism
323.15	-51.25	-3.43
333.15	-50.48	-1.88
343.15	-49.71	-0.33
353.15	-48.94	1.22
358.15	-48.55	1.99

With the theory of Eyring⁹ and Evans and Polyani,¹⁰ state functions ΔS^\ddagger and ΔH^\ddagger can be evaluated with the following equation:¹⁴

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h} e^{\Delta S^\ddagger/R}\right) - \frac{\Delta H^\ddagger}{RT} \quad (7)$$

where k_B is the Boltzmann constant, h is the Planck constant, and R is the gas constant. The linear fitting of the plot of $\ln(k/T)$ versus $(1/T)$ allows us to calculate ΔH^\ddagger and ΔS^\ddagger . Table V shows the values of ΔH^\ddagger and ΔS^\ddagger for the n -order and autocatalytic paths. ΔS^\ddagger is more negative for the autocatalytic mechanism, so the n -order path is dominant for the formation of the epoxy network. This behavior is in good agreement with that obtained by other authors.^{14,18,19}

With these data, it is possible to calculate ΔG^\ddagger for the n -order and autocatalytic paths at different curing temperatures (Table VI). Similar values were determined by Núñez and coworkers^{3,19} for a similar epoxy system. These results suggest that both mechanisms coexist in the initial stage of the activation process at temperatures lower than 70°C. At higher temperatures, from a thermodynamic point of view, the autocatalytic mechanism cannot occur.

CONCLUSIONS

A kinetic model that accounts for diffusion effects has been used. There is a good agreement between the experimental results and the kinetic model accounting for diffusion. A good agreement between the kinetic and thermodynamic data has been found. The ΔG^\ddagger values for the n th-path and autocatalytic mechanisms suggest a trend to the n th-path mechanism with increasing temperature.

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