Activation Energies for the Epoxy System BADGE $n = 0$/m-XDA Obtained Using Data from Thermogravimetric Analysis

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ABSTRACT: In this article we study the kinetics of thermal degradation of the epoxy system BADGE $n = 0$/m-XDA using different kinetic methods with data from thermogravimetric analysis (TGA) in dynamic conditions. Activation energies obtained using different integral methods (Flynn-Wall-Ozawa and Coats-Redfern Methods) are in good agreement with the value obtained using the Kissinger method (204.44 kJ/mol). The solid-state decomposition mechanism followed by this epoxy system is a decelerated R_n type (phase boundary controlled reaction). We have also calculated activation energies using the Van Krevelen and the Horowitz-Metzger methods. These last methods corroborate the decelerated behavior. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 776–782, 2001

Key words: epoxy resins; thermogravimetry; activation energies

INTRODUCTION

Epoxy resin-derived materials play an important role when trying to find suitable materials for many different applications. They offer great versatility, low shrinkage, good chemical resistance, and outstanding adhesion. Epoxy resins also provide low-cost materials. For these reasons, knowledge of the degradation of a thermoset epoxy is very important because it can be used to determine the final properties for the use of a material, such as the upper temperature limit, the mechanism of a solid-state process, and the lifetime.

Many studies of thermogravimetric data have been used for the determination of kinetic parameters. Thermogravimetric analysis (TGA) is a technique widely used because of its simplicity

and the information afforded from a simple thermogram. From thermogravimetric experimental data, using different kinetic methods (differential and integral), parameters such as activation energy, preexponential factor, and reaction order may be obtained. Kinetic analysis is based on collecting thermogravimetric data from a wide range of constant heating rates. A constant heating rate is preferable to an isothermal technique because allows measurements of the details of the reaction both in its initial phases and over the entire range of weight-loss for each experiment.[1]

The main objective of this work is to study the kinetics of thermal degradation for the epoxy system diglycidyl ether of bisphenol A (BADGE $n = 0$)/m-xylylenediamine (m-XDA) using different kinetic methods (differential and integral) in nonisothermal conditions. The variables used are temperatures, heating rates, and conversions. In a previous investigation the kinetics of the cure of this epoxy system[2,3] and the effects of diffusion on

the kinetics[4] have been studied by differential scanning calorimetry.

KINETIC METHODS

The rate of conversion, $d\alpha/dt$, is a linear function of a temperature-dependent rate constant, k, and a temperature-independent function of conversion, α, that is:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

Substituting Arrhenius equation into eq (1), one obtains:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \qquad (2)$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta = dT/dt$, the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating.

Therefore, the reaction rate gives:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \qquad (3)$$

Integration of this equation from an initial temperature, T_0, corresponding to a degree of conversion α_0, to the peak temperature of the derivative thermogravimetric curve (DTG), T_p, where $\alpha = \alpha_p$ gives:[5]

$$g(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T_p} e^{-E/RT} \, dT \qquad (4)$$

It may be reasonable to assume that $\alpha_0 = 0$ for low temperatures, and that there is no reaction occurring between 0 and T_0:

$$g(\alpha) = \int_{0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{0}^{T_p} e^{-E/RT} \, dT \qquad (5)$$

where $g(\alpha)$ is the integral function of conversion.

Table I   Algebraic Expressions for $g(\alpha)$ for the Most Frequently Used Mechanisms of Solid-State Processes[1,6–9]

Symbol	$g(\alpha)$	Solid-State Processes
	Sigmoidal Curves	
A_2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth [Avrami eq (1)]
A_3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth [Avrami eq. (2)]
A_4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth [Avrami eq. (3)]
	Deceleration Curves	
R_1	α	Phase boundary controlled reaction (one-dimensional movement)
R_2	$[1 - \ln(1-\alpha)^{1/2}]$	Phase boundary controlled reaction (Contracting area)
R_3	$[1 - \ln(1-\alpha)^{1/3}]$	Phase boundary controlled reaction (Contracting volume)
D_1	α^2	One-dimensional diffusion
D_2	$(1-\alpha) \cdot \ln(1-\alpha) + \alpha$	Two-dimensional diffusion
D_3	$[1 - (1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$(1 - \frac{2}{3} \cdot \alpha) - (1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling-Brounshtein equation)
F_1	$-\ln(1-\alpha)$	Random Nucleation with one nucleus on the individual particle
F_2	$\dfrac{1}{(1-\alpha)}$	Random nucleation with two nucleus on the individual particle
F_3	$\dfrac{1}{(1-\alpha)^2}$	Random nucleation with two nucleus on the individual particle

In the case of polymers, this integral function, $g(\alpha)$, is either a sigmoidal function or a deceleration function.[1] Table I shows different expressions of $g(\alpha)$ for the different solid state mechanisms.[6–9] These functions were satisfactorily em-
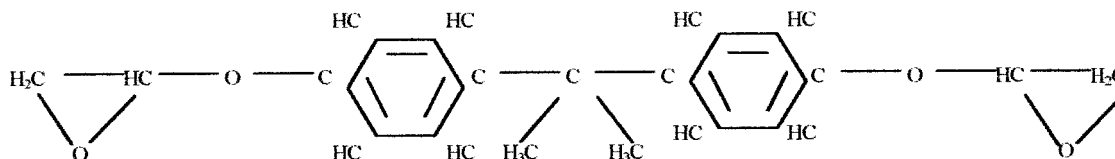
Figure 1   Structure for the diglycidyl ether of bisphenol A (BADGE $n = 0$).

ployed for the estimation of the reaction solid-state mechanism from nonisothermal TG experiments.[7–9]

In this article we used different kinetic methods (differential and integral).

Differential Method

Analysis of the changes in thermogravimetric data brought about by variation of the heating rate, β, are the basis of the most powerful differential methods for the determination of kinetic parameters.

Kissinger's method[10] has been used[7,9,11] to determine the activation energy, E, of solid-state reactions without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln \frac{\beta}{T_{\max}^2} = \left\{ \ln \frac{AR}{E} + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E}{RT_{\max}}$$
$$(6)$$

where β is the heating rate, $T_{\max}$ is the temperature corresponding to the inflection point of the thermodegradation curves that corresponds to the maximum reaction rate, A is the preexponential factor, $\alpha_{\max}$ is the maximum conversion, and n is the reaction order.
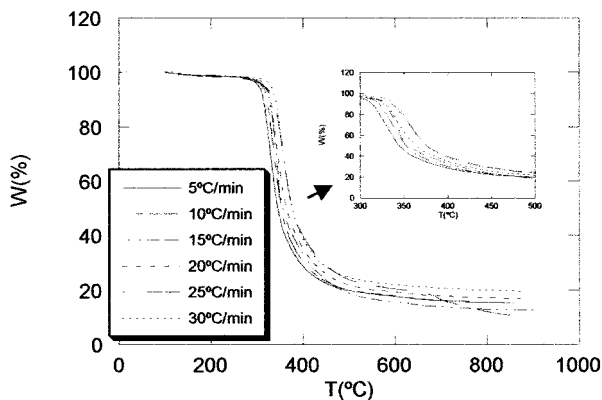
Integral Methods

The integral methods involve an approximate integration of eq (5). Some of these methods used in the present article are:

Flynn-Wall-Ozawa Method[12,13]

Equation (5) is integrated using the Doyle approximation.[14] The result of the integration after taking logarithms is:

$$\log \beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \qquad (7)$$

where β, A, E, and T have the known meanings.

This is one of the integral methods that can determine the activation energy without the knowledge of the reaction order. It is used to determine the activation energy at given values of conversion.

Coats-Redfern Method[15]

Coats-Redfern used an asymptotic approximation for resolution of eq (5). These authors supposed that $\ln\left(1 - \dfrac{2RT}{E}\right) \to 0$ for the Doyle approximation, obtaining in natural logarithmic form:
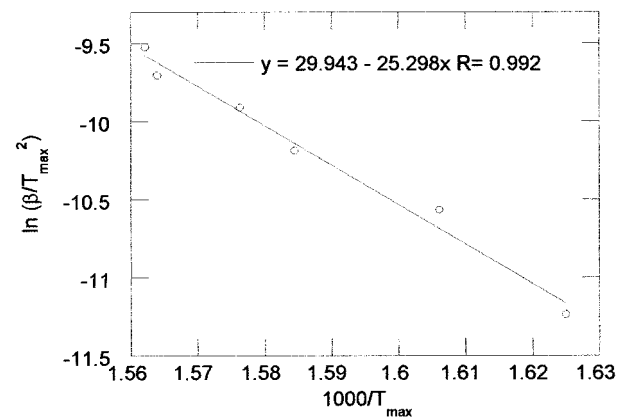

Figure 2   Experimental TG curves at different heating rates.

Figure 3   Kissinger method applied to experimental data at different heating rates.
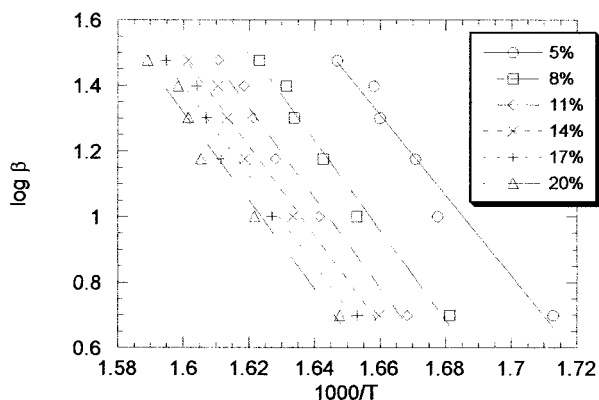
Figure 4 Typical plots of log β vs. $1000/T$ at several conversion values in the range 5–20% in steps of 3%.

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \qquad (8)$$

The different degradation processes $g(\alpha)$ are listed in Table I.

Van Krevelen et al.[16] Method

Van Krevelen et al. made a serious theoretical treatment of thermogravimetric data. These authors approximated the exponential integral to obtain a final equation in logarithmic form:

$$\log[g(\alpha)] = \log B + \left(\frac{E}{RT_r} + 1\right)\log T \qquad (9)$$

where

$$B = \frac{A}{\beta}\left(\frac{E}{RT_r} + 1\right)^{-1}\left(\frac{0.368}{T_r}\right)^{E/RT_r}$$

and T_r is a reference temperature.

Horowitz and Metger[17] Method

Horowith and Metzger simplify the exponential integral using an approximation similar to Van Krevelen et al., defining a characteristic temperature θ, such that $\theta = T - T_r$ where T_r is a reference temperature. Making the approximation:

$$\frac{1}{T} = \frac{1}{T_r + \theta} \cong \frac{1}{T_r} - \frac{\theta}{T_r^2}$$

they finally obtain for $n = 1$,

$$\ln[g(\alpha)] = \frac{E\theta}{RT_r^2} \qquad (10)$$

The Van Krevelen and Horowitz-Metzger methods present the problem of the arbitrary election of the reference temperature. In this study, to obtain reproducible results, the reference temperature was taken as that corresponding to the inflection point in TG curves.

EXPERIMENTAL

Materials

The epoxy resin was a commercial BADGE ($n = 0$) (Fig. 1) (Resin 332, Sigma Chemical Co. St. Louis, MO) with an equivalent molecular weight of 173.6 g/Eq, as determined by wet analysis.[18,19] The curing agent was m-xylylenediamine (m-XDA, Aldrich Chemical Co., Milwaukee, WI).

Sample Preparation

Epoxy resin and curing agent were carefully and homogeneously mixed at a stoichiometric ratio. The mixture is introduced in a cylindrical frame previously waxed to avoid adherence. After 24 h at room temperature, the frames are placed for 2 h in an oven at 120°C. Finally, the samples were cut into 6 mm discs weighing 15–25 mg.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a Thermogravimetric Analyzer (TGA7) from Perkin-Elmer controlled by a computer. This microbalance was calibrated making use of the discontinuous change in the magnetic properties of perkalloy and alumel on heating. The Curie point of every metal was calculated by the microbal-

Table II Activation Energies Obtained Using the Flynn-Wall-Ozawa Method

$\alpha(\%)$	E_a (kJ/mol)	r
5	148.64	0.9908
8	157.00	0.9949
11	188.37	0.9885
14	208.84	0.9950
17	220.92	0.9945
20	229.17	0.9934

Table III   Activation Energies Obtained Using the Coats-Redfern Method for Several Solid-State Processes

Mechanism	E (kJ/mol)	r
	(a) Heating Rate of 5°C/min	
A_2	75.92	0.9948
A_3	48.23	0.9938
A_4	24.96	0.9897
R_1	145.21	0.9968
R_2	149.96	0.9962
R_3	151.56	0.9961
D_1	317.05	0.9973
D_2	323.31	0.9970
D_3	329.75	0.9967
D_4	325.45	0.9969
F_1	163.11	0.9961
F_2	9.587	0.8537
F_3	29.20	0.9276
	(b) Heating Rate of 10°C/min	
A_2	53.02	0.9880
A_3	29.22	0.9825
A_4	17.31	0.9724
R_1	116.34	0.9907
R_2	120.33	0.9910
R_3	121.68	0.9911
D_1	251.06	0.9911
D_2	256.33	0.9920
D_3	261.74	0.9923
D_4	258.13	0.9922
F_1	124.40	0.9912
F_2	1.88	0.4472
F_3	14.63	0.8842
	(c) Heating Rate of 15°C/min	
A_2	90.27	0.9721
A_3	54.03	0.9656
A_4	35.92	0.9569
R_1	186.69	0.9763
R_2	192.76	0.9766
R_3	194.82	0.9766
D_1	391.82	0.9785
D_2	399.82	0.9786
D_3	408.07	0.9786
D_4	402.58	0.9786
F_1	198.97	0.9768
F_2	6.67	0.6757
F_3	31.95	0.9087
	(d) Heating Rate of 20°C/min	
A_2	94.22	0.9928
A_3	56.99	0.9914
A_4	37.87	0.9898
R_1	195.22	0.9949

Table III   *Continued*

Mechanism	E (kJ/mol)	r
R_2	202.49	0.9944
R_3	207.94	0.9942
D_1	412.92	0.9953
D_2	422.48	0.9950
D_3	434.35	0.9946
D_4	427.77	0.9948
F_1	206.91	0.9938
F_2	7.04	0.7742
F_3	32.55	0.9103
	(e) Heating Rate of 25°C/min	
A_2	97.58	0.9923
A_3	58.83	0.9907
A_4	39.55	0.9884
R_1	200.81	0.9949
R_2	207.15	0.9942
R_3	209.30	0.9940
D_1	420.10	0.9953
D_2	428.46	0.9949
D_3	437.06	0.9945
D_4	431.32	0.9948
F_1	213.63	0.9936
F_2	7.725	0.6760
F_3	33.92	0.8955
	(f) Heating Rate of 30°C/min	
A_2	110.11	0.9936
A_3	66.55	0.9924
A_4	45.29	0.9908
R_1	222.52	0.9957
R_2	229.50	0.9951
R_3	231.87	0.9949
D_1	463.52	0.9960
D_2	472.73	0.9957
D_3	482.22	0.9953
D_4	475.90	0.9955
F_1	236.64	0.9946
F_2	10.39	0.7591
F_3	39.27	0.9105

ance, which was calibrated at different heating rates.

The system was operated in the dynamic mode in the temperature range 100–900°C, at different heating rates: 5, 10, 15, 20, 25, and 30°C/min.

All the experiments were carried out under a dry nitrogen atmosphere. The TGA7 analyzer requires two purge lines: one to purge the balance chamber, and a second one to purge the sample-furnace area. After various experiments, it was

Table IV   Activation Energies Obtained Using the Van Krevelen et al. Method for Decelerated R_n Mechanism at Different Heating Rates

Heating Rate (°C/min)	Mechanism	E (kJ/mol)	r
5	R_1	164.76	0.9979
	R_2	169.70	0.9975
	R_3	171.37	0.9973
10	R_1	174.93	0.9929
	R_2	179.46	0.9931
	R_3	180.50	0.9931
15	R_1	205.76	0.9903
	R_2	212.03	0.9904
	R_3	214.14	0.9905
20	R_1	213.17	0.9960
	R_2	220.66	0.9955
	R_3	223.20	0.9954
25	R_1	222.06	0.9951
	R_2	228.65	0.9961
	R_3	230.87	0.9956
30	R_1	243.95	0.9967
30	R_2	251.19	0.9962
	R_3	253.64	0.9960

found that the optimum gas flow rates were: 25 mL/min for the balance purge gas and 35 mL/min for the sample purge gas.

RESULTS AND DISCUSSION

Using Kissinger's method and the experimental data recorded in the TG curves (Fig. 1), the activation energy for the decomposition of the epoxy system was calculated from a straight line fit of a plot of $\ln(\beta/T_{\max}^2)$ vs. $1000/T_{\max}$ (Fig. 2). $T_{\max}$ is the inflection point temperature on the TG curve or the minimum of the derivative of these curves at different heating rates. The value obtained for the activation energy was 204.44 kJ/mol. Compared to the activation energy for similar epoxy systems,[11,20] this value is higher because the beginning of degradation takes place at higher temperatures.

TG curves (Fig. 2) are C type,[1] corresponding to a single-stage decomposition reaction where the decomposition temperatures (initial and final) are well defined.

The activation energies were also determined using the Flynn-Wall-Ozawa method [eq. (7)], from a linear fitting of log β vs. $1000/T$ at different conversions (Fig. 3). Owing to the fact

that this equation was derived using the Doyle approximation, only conversion values in the range of 5–20% can be used. In this study we have used heating rate values of 5, 10, 15, 20, 25, and 30°C/min. Figure 4 shows that the fitted straight lines are nearly parallel, thus indicating the applicability of this method to our system in the conversion range studied.[21–23] Table II shows the activation energies corresponding to the different conversions. From these values a mean value of 192.16 kJ/mol was obtained. Comparing this last value with the activation energy calculated from Kissinger's method a difference of 12.28 kJ/mol was found.

These two methods have the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy. Some authors[4,9,11,20] use the activation energies obtained using these methods to check their thermodegradation mechanism models.

The activation energy corresponding to different $g(\alpha)$ for sigmoidal and decelerated mechanism (Table I) can be obtained at constant heating rates using the equation proposed by Coats and Redfern from a fitting of $\ln \lfloor g(\alpha)/T^2 \rfloor$ vs. $1000/T$ plots. This method was used the same conversion values as those used by the previous method. Tables IIIa–f shows activation energies and correlations for conversions in the range of 5–20% at constant heating rates of 5, 10, 15, 20, 25, and 30°C/min, respectively. Analysis of Tables IIIa–f show that, at heating rate values of 15, 20, and 25°C/min, the activation energies are in good agreement with those obtained using the Kissinger method and the Flynn-Wall-Ozawa method and an R_n-type mechanism. From these tables it can be observed that the better agreement is for the heating rate value 15°C/min at which the activation energy corresponding to R_2 is 192.76 kJ/mol, very close to 192.16 kJ/mol obtained from the Flynn-Wall-Ozawa method. These facts suggest that the solid state thermodegradation mechanism followed by our epoxy system is probably a decelerated (R_n) type.

To corroborate the decelerated behavior, we have calculated activation energies and correlations using Van Krevelen and Horowitz-Metzger methods. For the first method the activation energy is obtained through a linear fitting of log $g(\alpha)$ vs. log T plots . The second method uses a linear fitting of ln $g(\alpha)$ vs. $(T - T_r)$ plots . Table IV shows activation energies and correlation values for the R_n mechanism at different constant heating rates for the Van

Table V Activation Energies Obtained Using the Horowitz-Metzger Method for Decelerated R_n Mechanism at Different Heating Rates

Heating Rate (°C/min)	Mechanism	E (kJ/mol)	r
5	R_1	176.62	0.9983
	R_2	181.76	0.9979
	R_3	183.50	0.9977
10	R_1	179.94	0.9927
	R_2	185.28	0.9929
	R_3	190.74	0.9929
15	R_1	217.23	0.9905
	R_2	223.67	0.9906
	R_3	225.85	0.9913
20	R_1	235.94	0.9955
	R_2	242.77	0.9960
	R_3	245.08	0.9959
25	R_1	266.61	0.9964
	R_2	274.35	0.9959
	R_3	276.97	0.9957
30	R_1	293.01	0.9970
	R_2	301.51	0.9965
	R_3	303.04	0.9964

Krevelen method. Table V shows activation energies and correlation values for the R_n mechanism at different constant heating rates for the Horowitz-Metzger method. Both tables show that the best agreement with Kissinger and Flynn-Wall-Ozawa methods correspond to heating rates of 10°C/min and 15°C/min. These values are also in good agreement with the values obtained using the Coats-Redfern method at heating rates of 15 and 20°C/min. For a similar epoxy system, BADGE n = 0/1, 2 DCH, the solid-state mechanism is a sigmoidal A_n type.[11] This change of the thermodegradation mechanism is produced by the use of a different curing agent. From an energetic point of view, the activation energies for the epoxy system used in this article are higher than for the epoxy system BADGE n = 0/1.2 DCH. This means that the activated complex can be obtained less easily, resulting in a more difficult degradation of the material.

CONCLUSIONS

The thermodegradation mechanism for the epoxy system BADGE n = 0/m-XDA is a decelerated R_n type, that is a solid-state process based in a phase boundary controlled reaction. The activation energies obtained are higher than for similar epoxy systems.[11,20] This indicates that the degradation is more difficult for our epoxy system. At a heating rate of 15°C/min, activation energies are in good agreement for all the integral methods that need the knowledge of the reaction mechanism.

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