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Thermogravimetric study of the decomposition process of the system BADGE $(n = 0)/1, 2$ DCH

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Abstract

The thermal degradation of the system diglycidyl ether of Bisphenol A (BADGE, $n = 0$) and 1,2 diamine cyclohexane (DCH) was studied by thermogravimetric analysis (TG) in order to determine the actual reaction mechanism (RM) of the decomposition process. Owing to the nature of the problem, the RM cannot be ascertained without knowledge of the activation energy. The activation energy of the solid state process was determined using Kissinger's method, which does not require knowledge of the RM, resulting to be 144.01 kJ/mol. Different integral and differential methods and different RM reported in the literature were used and compared with this value. Also, the experimental results were compared to master plots, in the range of the Doyle approximation. Analysis of experimental results suggests that in the conversion range studied, 5–20%, the actual RM is an A_4 sigmoidal type. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermogravimetry; Activation energy; Reaction mechanisms

1. Introduction

The study of the thermal degradation of a polymer is of major interest since it can, in many cases, determine the upper temperature limit of use for a material. Also, considerable attention has been directed towards the exploitation of thermogravimetric data for the determination of kinetic parameters. For this purpose thermogravimetric analysis (TGA) is a technique widely used because of its simplicity and the information afforded by a simple thermogram.

Many of the methods of kinetic analysis are based on the hypothesis that, from a simple thermogravimetric trace, meaningful values may be obtained for parameters such as activation energy, pre-exponential factor and reaction order. A number of these methods (differential and integral) will be discussed later in this paper.

Many studies designed to evaluate experimental data have employed reference theoretical curves often known as "master plots". In this sense, the master plot can be considered as a characteristic curve, independent of the condition of the measurement, which is easily obtained from experimental data. In this paper we discuss the applicability of the master plots based on the first derivative of the degree of conversion (α) in order to determine the mechanism of a solid state process: nucleation, the growth of the germ, advance of the reaction interface, diffusion of the product, etc.

2. Kinetic methods

Kinetic information can be extracted from dynamic experiments by means of various methods. All kinetic studies assume that the isothermal rate of conversion, $d\alpha/dt$, is a linear function of a temperature-dependent rate constant, k, and a temperature-independent function of the conversion, α, that is:

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

where $f(\alpha)$ depends on the particular decomposition mechanism.

According to Arrhenius,

$$k = A\,e^{-\frac{E}{RT}} \qquad (2)$$

where A, the pre-exponential factor, is assumed to be independent of temperature, E is the activation energy, T the absolute temperature, and R the gas constant.

Combination of Eqs. (1) and (2) gives

$$\frac{d\alpha}{dt} = Af(\alpha)\,e^{-\frac{E}{RT}} \qquad (3)$$

If the sample temperature is changed by a controlled and

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constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, the variation in the degree of conversion can be analysed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the reaction rate may be written as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} = \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{4}$$

A combination of Eqs. (3) and (4) leads to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\,\mathrm{e}^{-\frac{E}{RT}}f(\alpha) \tag{5}$$

Integration of this equation from an initial temperature, T_0, corresponding to a degree of conversion α_0, to the peak temperature, T_p, where $\alpha = \alpha_\mathrm{p}$, gives

$$\int_{\alpha_0}^{\alpha_\mathrm{p}} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_\mathrm{p}} \mathrm{e}^{-\frac{E}{RT}}\,\mathrm{d}T \tag{6}$$

If T_0 is low, it may be reasonably assumed that $\alpha_0 = 0$ and considering that there is no reaction betweeen 0 and T_0[1]:

$$g(\alpha) = \int_0^{\alpha_\mathrm{p}} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T_\mathrm{p}} \mathrm{e}^{-\frac{E}{RT}}\,\mathrm{d}T \tag{7}$$

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

In the case of polymers, the degradation process follows either a sigmoidal function or a deceleration function. Table 1 shows different expressions of $g(\alpha)$ for the different solid state mechanisms [2–4]. These functions were satisfactorily employed in the only known method for the estimation of reaction mechanisms from dynamic TG curves [5].

Table 1
Algebraic expressions for $g(\alpha)$ for the most frequently used mechanisms of solid state processes

Symbol	$g(\alpha)$	Solid state processes
Sigmoidal curves		
A_2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami equation 1)
A_3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami equation 2)
A_4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami equation 3)
Deceleration curves		
R_2	$[1-(1-\alpha)^{1/2}]$	Phase boundary controlled reaction (contracting area)
R_3	$[1-(1-\alpha)^{1/3}]$	Phase boundary controlled reaction (contracting volume)
D_1	α^2	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D_3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling–Brounshtein equation)
F_1	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
F_2	$1/(1-\alpha)$	Random nucleation with two nuclei on the individual particle
F_3	$1/(1-\alpha)^2$	Random nucleation with two nuclei on the individual particle

3. Differential method

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

3.1. Kissinger's method [6]

Kissinger's method has been used in the literature to determine the activation energy of solid state reactions from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments.

The activation energy can be determined by Kissinger's method without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln\left(\frac{\beta}{T_\mathrm{max}^2}\right) = \left\{\ln\frac{A\mathrm{R}}{E} + \ln[n(1-\alpha_\mathrm{max})^{n-1}]\right\} - \frac{E}{\mathrm{R}T_\mathrm{max}} \tag{8}$$

where β is the heating rate, T_max is the temperature corresponding to the inflection point of the thermodegradation curves which corresponds to the maximum reaction rate, A is the pre-exponential factor, α_max is the maximum conversion, and n is the reaction order.

From a plot of $\ln(\beta/T_\mathrm{max}^2)$ versus $1000/T_\mathrm{max}$ and fitting to a straight line, the activation energy E can be calculated from the slope.

4. Integral methods

The integral methods involve an approximate integration of Eq. (7). Some of these methods discussed in this paper are Flynn–Wall–Ozawa, Coats–Redfern, Horowitz–Metzger, and Van Krevelen.

4.1. Flynn–Wall–Ozawa method [7,8]

Eq. (7) is integrated using the Doyle aproximation [9]. The result of the integration after taking logarithms is

$$\log\beta = \log\left[\frac{AE}{g(\alpha)\mathrm{R}}\right] - 2.315 - \frac{0.457\,E}{\mathrm{R}T} \tag{9}$$

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

This is one of the integral methods that can determine the activation energy without a knowledge of reaction order. It is used to determine the activation energy for given values of conversion. The activation energy for different conversion values can be calculated from a $\ln\beta$ versus $1000/T$ plot.

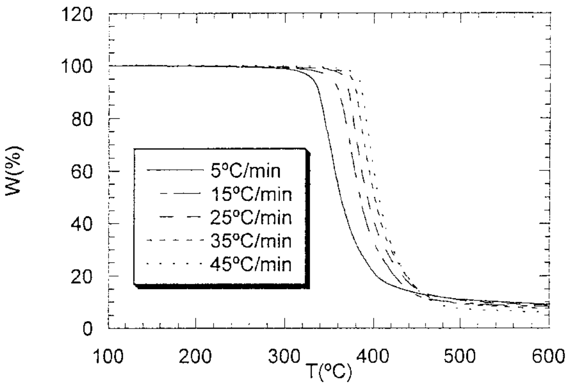

Fig. 1. Experimental TG curves at different heating rates.

4.2. Coats–Redfern method [10]

Coats–Redfern used an asymptotic approximation for the resolution of Eq. (7), obtaining

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{A\mathrm{R}}{\beta E} - \frac{E}{\mathrm{R}T} \tag{10}$$

Activation energy for every degradation process listed in Table 1 can be determined from a plot of $\ln g(\alpha)$ versus $1000/T$.

4.3. Van Krevelen et al. [11] and Horowitz and Metzger [12] methods

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

$$\log g(\alpha) = \log B + \left(\frac{E}{\mathrm{R}T_\mathrm{r}} + 1\right)\log T \tag{11}$$

where

$$B = \frac{A}{\beta}\left(\frac{E}{\mathrm{R}T_\mathrm{r}} + 1\right)^{-1}\left(\frac{0.368}{T_\mathrm{r}}\right)^{\frac{E}{\mathrm{R}T_\mathrm{r}}}$$

and T_r is a reference temperature.

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

$$\frac{1}{T} = \frac{1}{T_\mathrm{r} + \theta} \cong \frac{1}{T_\mathrm{r}} - \frac{\theta}{T_\mathrm{r}^2}$$

they finally obtain for $n = 1$,

$$\ln g(\alpha) = \frac{E\theta}{\mathrm{R}T_\mathrm{r}^2} \tag{12}$$

Both methods present the problem of the arbitrary selection of the reference temperature. In this study, in order to obtain reproducible results, the reference temperature was taken as that corresponding to the maximum temperature rate. In this article we followed Van Krevelen et al. and Horowitz and Metzger's suggestions when they say that the selection of this arbitrary temperature does not affect the integral approximation of the kinetic model.

Using any of these two methods, the activation energy can be determined without the precise knowledge of the thermodegradation kinetics.

4.4. Criado et al. [3] method for determination of reaction mechanism

The activation energy of a solid state reaction can be determined from several non-isothermal measurements, whatever the reaction mechanism. If the value of the activation energy is known the kinetic model of the process can be found in the following way. Criado et al. define the function

$$z(\alpha) = \frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\beta}\pi(x)T \tag{13}$$

where $x = E/\mathrm{R}T$, and $\pi(x)$ is an approximation of the temperature integral which cannot be expressed in a simple analytical form. In this study we used the fourth rational expression of Senum and Young [13], which gives errors lower than $10^{-5}\%$ for $x = 20$.

Combination of Eqs. (1) and (13) yields

$$z(\alpha) = f(\alpha)g(\alpha) \tag{14}$$

This last equation was used to obtain the master curves as a function of the reaction degree corresponding to the different models listed in Table 1.

Plotting the $z(\alpha)$ function calculated using experimental data and Eq. (13), and comparing with the master curves leads to easy and precise determination of the mechanism of a solid state process.

5. Experimental

5.1. Materials

The epoxy resin was a commercial diglycidyl ether of Bisphenol A (BADGE, $n = 0$) (Resin 332, Sigma Chemical Co, San Louis, USA) with an equivalent molecular weight of 173.6 g/eq, as determined by wet analysis [14,15].

Table 2
Inflection point temperature and residue at 800°C at different heating rates

Reaction rate (°C/min)	$T_{\text{inflection point}}$ (°C)	Residue at 800°C W(%)
5	343.76	7.96
15	368.75	6.83
25	376.25	7.58
35	383.75	6.48
45	390.00	5.43

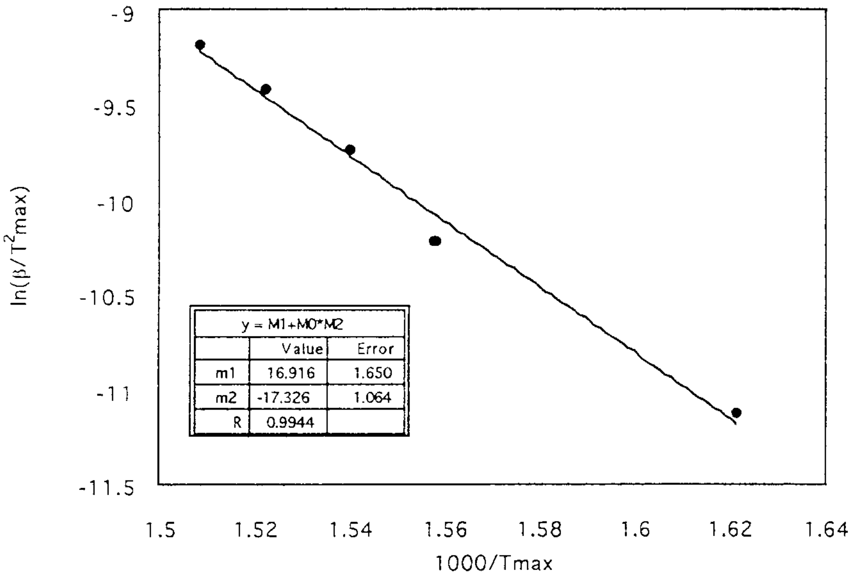

Fig. 2. Kissinger Method applied to experimental data at different heating rates.

The amine was 1,2 diaminecyclohexane (DCH) (Fluka, Switzerland) with an amine hydrogen equivalent weight of 28.5. Both were used as received.

5.2. Sample preparation

Epoxy resin and cure agent were carefully and homogeneously mixed, at stoichiometric ratio, before being introduced in a cylindrical frame.

Curing reaction was programmed according to a TTT diagram described for this material [16]. It consists of two stages: a first step at 23°C for 24 h and a second one in a stove, at 70°C, for 16 h. After curing, the samples were removed from the frame.

For thermogravimetric analysis, the samples were cut in the form of 15–25 mg weight and 6 mm diameter discs.

5.3. Techniques

Thermogravimetric analysis was performed using a TGA7 from Perkin Elmer controlled by a 1020 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 can be calculated and the microbalance 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, 15, 25, 35 and 45°C/min.

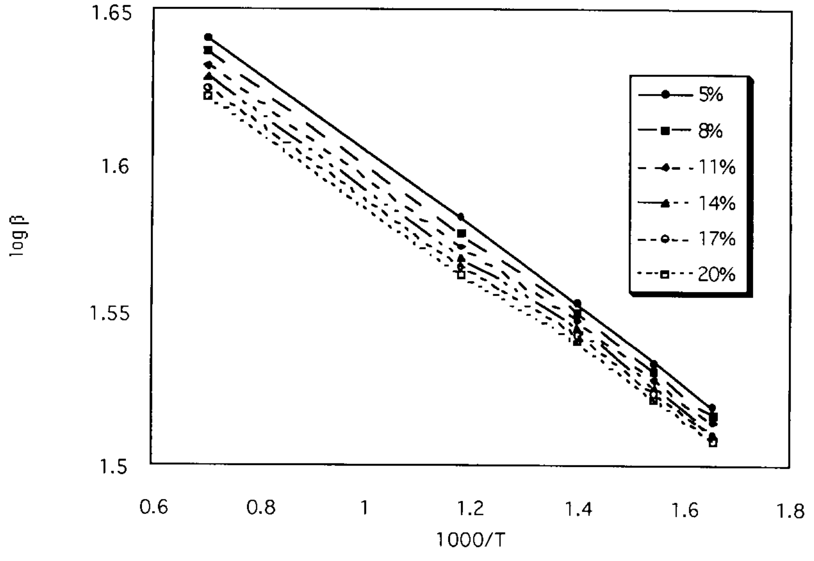

Fig. 3. Typical plots of log β against 1000/T at various conversion values in the range 5–20% in steps of 3%.

Table 3
Activation energies obtained using the Flynn–Wall–Ozawa method

α (%)	E_a (kJ/mol)	R
5	142.89	0.9998
8	145.19	0.9999
11	148.05	0.9997
14	148.65	0.9994
17	152.30	0.9995
20	154.10	0.9994

All the experiments were carried out under a nitrogen atmosphere. The TGA7 analyser requires two purge lines: one to purge the balance chamber and a second one to purge the sample-furnace area. After different tests, it was found that the optimum gas flow rates were

balance purge gas, 25 ml/min; and
sample purge gas, 35 ml/min.

6. Results and discussion

Fig. 1 shows thermal degradation curves corresponding to dynamic experiments carried out at different heating rates: 5, 15, 25, 35 and 45°C/min. These TG curves are C type [2], corresponding to a single-stage decomposition reaction where the procedural decomposition temperatures (initial and final) are well defined.

Inflection point temperature, T_m, and residual mass, W, after complete degradation can be determined from these curves and are shown in Table 2. Analysis of these curves shows that, at 800°C, the residue diminished 2.53% with a 40°C/min increase of heating rate.

Owing to the nature of the epoxy system studied, we have chosen 10°C/min intervals between measurements to avoid the overlapping of inflection point temperatures which occurs when using, as some investigators [17,18] did, 5°C/min intervals. Ma et al. [19] use 10°C/min intervals, and the activation energy increases slightly with increasing heating rate. They use also Kissinger's method for comparison and point out that this method is good when the temperature interval is narrow. They use a 44°C interval while ours is 47°C.

Table 4
Activation energies obtained using the Coats–Redfern method for several solid state processes at a heating rate of 5°C/min

Mechanism	E_a (kJ/mol)	R
A_2	294.41	0.9948
A_3	192.89	0.9946
A_4	142.08	0.9945
R_1	564.99	0.9934
R_2	582.22	0.9942
R_3	588.11	0.9944
D_1	1139.81	0.9936
D_2	1162.96	0.9940
D_3	1186.54	0.9945
D_4	1170.69	0.9942
F_1	598.97	0.9994
F_2	18.78	0.9942
F_3	37.56	0.9942

Table 5
Activation energies obtained using the Coats–Redfern method for several solid state processes at a heating rate of 15°C/min

Mechanism	E_a (kJ/mol)	R
A_2	299.77	0.9975
A_3	196.41	0.9973
A_4	144.42	0.9974
R_1	574.13	0.9967
R_2	591.75	0.9972
R_3	597.59	0.9973
D_1	1158.82	0.9967
D_2	1181.87	0.9971
D_3	1205.61	0.9974
D_4	1189.97	0.9972
F_1	609.67	0.9976
F_2	17.53	0.9903
F_3	35.15	0.9903

Using Eq. (8) and the inflection point temperatures corresponding to the thermograms shown in Fig. 1, the activation energy can be calculated from a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ and fitting to a straight line. Fig. 2 shows the activation energy obtained using this method, which is 144.01 kJ/mol.

The activation energy can also be determined using the method of Flynn–Wall–Ozawa, Eq. (9), from a linear fitting of $\ln \beta$ versus $1000/T$ at different conversions. Owing to the fact that this equation was derived using the Doyle approximation, only conversions values in the range 5–20% can be used. For this study, we have used the conversion values 5, 8, 11, 14, 17 and 20%. Fig. 3 shows that the fitting straight lines are nearly parallel, thus indicating the applicability of this method to our epoxy system in the conversion range studied. This fact suggests that a single reaction mechanism is operative [20,21]. Activation energies corresponding to the different conversions are listed in Table 3. From these values a mean value of 148.59 kJ/mol was found. Table 3

Table 6
Activation energies obtained using the Coats–Redfern method for several solid state processes at a heating rate of 25°C/min

Mechanism	E_a (kJ/mol)	R
A_2	447.26	0.9941
A_3	294.64	0.9939
A_4	218.08	0.9938
R_1	851.38	0.9928
R_2	877.50	0.9935
R_3	886.25	0.9937
D_1	1717.21	0.9929
D_2	1747.64	0.9934
D_3	1783.03	0.9938
D_4	1759.74	0.9935
F_1	905.12	0.9942
F_2	97.23	0.9925
F_3	205.17	0.9933

Table 7
Activation energies obtained using the Coats–Redfern method for several solid state processes at a heating rate of 35°C/min

Mechanism	E_a (kJ/mol)	R
A_2	486.85	0.9922
A_3	320.94	0.9920
A_4	238.25	0.9917
R_1	927.12	0.9907
R_2	955.57	0.9916
R_3	965.21	0.9918
D_1	1864.87	0.9908
D_2	1902.81	0.9914
D_3	1941.47	0.9919
D_4	1915.49	0.9916
F_1	984.59	0.9924
F_2	106.95	0.9951
F_3	224.79	0.9956

Table 9
Activation energies obtained using the Van Krevelen et al. method for sigmoidal processes at different heating rates

Reaction rate (°C/min)		Mechanism		
		A_2	A_3	A_4
5	E_a (kJ/mol)	302.85	200.19	148.86
	R	0.9945	0.9945	0.9945
15	E_a (kJ/mol)	30826	203.71	151.44
	R	0.9974	0.9974	0.9974
25	E_a (kJ/mol)	457.77	300.05	223.69
	R	0.9946	0.9946	0.9946
35	E_a (kJ/mol)	490.91	325.46	242.70
	R	0.9931	0.9931	0.9931
45	E_a (kJ/mol)	550.58	365.25	272.56
	R	0.9914	0.9914	0.9914

also shows that the activation energy corresponding to a 8% conversion is very close to the value obtained using Kissinger's method.

Compared to other methods, these two methods present the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy. Some authors [4,17] used the activation energies obtained using these two methods to check their thermodegradation mechanism models.

Using Eq. (10), proposed by Coats and Redfern, the activation energy for every $g(\alpha)$ function listed in Table 1 can be obtained at constant heating rates from fitting of $\ln(g(\alpha)/T^2)$ versus $1000/T$ plots. For this study we have used the same conversion values as those used in the previous methods. Tables 4–8 show activation energies and correlations for conversions in the range 5–20% at constant heating rate values 5, 15, 25, 35, and 45°C/min, respectively. Analysis of these tables show that, at all the heating rate values, the activation energies in better agreement with that obtained using Kissinger's method correspond to an A_n type mechanism. For comparison, we have chosen Kissinger's method because it is independent of a particular kinetics mechanism. Also, from these tables it can be seen that the optimum heating rate value is 15°C/min, at which the activation energy corresponding to a mechanism A_4 is 144.42 kJ/mol, very close to 144.01 kJ/mol obtained by Kissinger's method. These facts strongly suggest that the solid state thermodegradation mechanism followed by our epoxy system is a sigmoidal (A_n) type. A_3 and A_4 are equally possible. However, an A_4 mechanism needs a lower energy to start, and this energy at lower heating rates, where comparisons are more reliable, are very close to the value obtained by both Kissinger and Flynn–Wall–Ozawa methods, which are independent of any thermodegradation mechanism.

In order to confirm this sigmoidal behaviour, we have calculated activation energies and correlations using the Van Krevelen [11] and Horowith and Metzger [12] models. The Van Krevelen method uses Eq. (11). The activation energy is obtained through a linear fitting of $\log g(\alpha)$ versus $\log T$ plots. Table 9 shows activation energies and correlations values for an A_n mechanism at different constant heating rate values. As can be seen, mechanism A_4, at heating rates 5 and 15°C/min, gives results in better agreement with that obtained using Kissinger's method. At the

Table 8
Activation energies obtained using the Coats–Redfern method for several solid state processes at a heating rate of 45°C/min

Mechanism	E_a (kJ/mol)	R
A_2	536.56	0.9930
A_3	354.15	0.9928
A_4	262.65	0.9927
R_1	1020.26	0.9916
R_2	1051.65	0.9924
R_3	1062.24	0.9926
D_1	2051.78	0.9917
D_2	2092.86	0.9922
D_3	2135.31	0.9927
D_4	2107.36	0.9924
F_1	1083.80	0.9931
F_2	118.42	0.9946
F_3	247.80	0.9950

Table 10
Activation energies obtained using the Horowitz–Metzger method for sigmoidal processes at different heating rates

Reaction rate (°C/min)		Mechanism		
		A_2	A_3	A_4
5	E_a (kJ/mol)	308.67	205.79	154.35
	R	0.9948	0.9948	0.9948
15	E_a (kJ/mol)	315.49	210.34	157.74
	R	0.9975	0.9975	0.9975
25	E_a (kJ/mol)	462.24	308.05	231.12
	R	0.9941	0.9941	0.9941
35	E_a (kJ/mol)	500.95	333.88	250.40
	R	0.9923	0.9923	0.9923
45	E_a (kJ/mol)	552.92	368.74	276.28
	R	0.9928	0.9928	0.9928

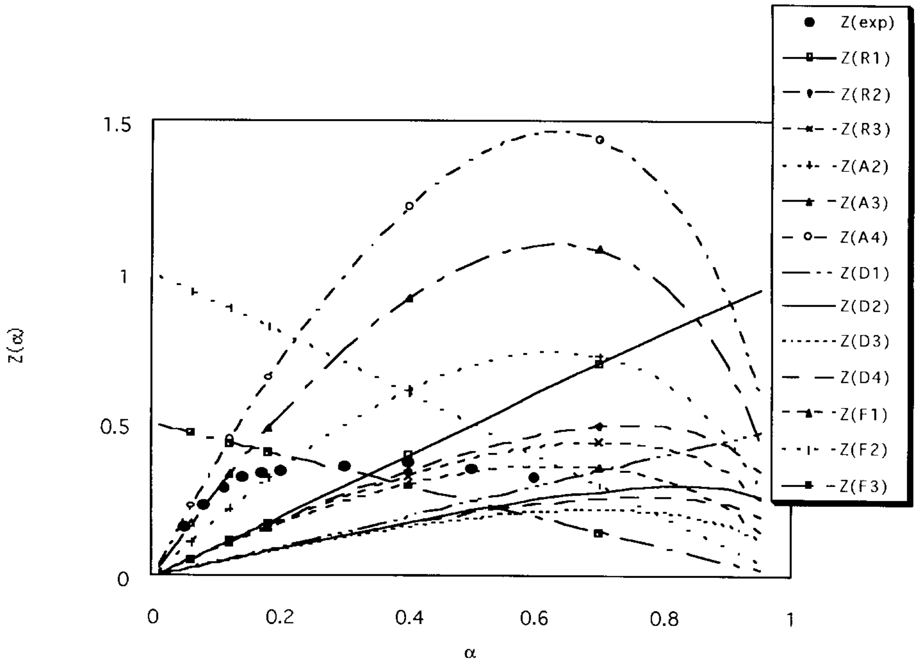

Fig. 4. Master curves Z(α). Experimental data calculated by Eq. (13).

same time, the best correlation (0.9974) is that corresponding to 15°C/min, in good agreement with the value obtained using the Coats–Redfern method.

Table 10 shows activation energies and correlations obtained using sigmoidal mechanisms and the Horowitz and Metzger model, which uses $\ln g(\alpha)$ versus $(T - T_r)$ plots (Eq. (12)). Again the best agreement with Kissinger's method corresponds to a sigmoidal A_4 mechanism and heating rate 5–15°C/min with best correlation (0.9975) at 15°C/min.

To corroborate that our epoxy system follows a sigmoidal thermodegradation mechanism, that is, a nucleation and growth solid state process, we have used the method proposed by Criado et al. [3]. This method employed reference theoretical curves called master plots, which are compared to experimental data.

Experimental results are obtained from Eq. (13) at a heating rate of 15°C/min, which is considered the optimum through studies based on integral methods.

Fig. 4 shows master curve plots $z(\alpha)$ versus α. Because we have used the Doyle approximation, only conversion values in the range 5–20% are considered for discussion. As can be seen in Fig. 4, in this range of conversion experimental results show better agreement with the $z(A_4)$ master curve, which corresponds to a sigmoidal A_4 mechanism. This range of conversion corresponds to the main degradation process.

7. Conclusions

The study of master curves together with interpretation of integral methods, allows confirmation that the epoxy system here studied follows a sigmoidal A_4 thermodegradation mechanism in the conversion range considered. However, at conversions outside the Doyle approximation the identification of our system with a particular degradation mechanism is as yet not fully established.

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