

DEGRADATION KINETICS OF AN EPOXY/CYCLOALIPHATIC AMINE RESIN UNDER ISOTHERMAL AND NON-ISOTHERMAL CONDITIONS

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Abstract

A study of an epoxy-cycloaliphatic amine system has been realized using a thermogravimetric technique (TG). Isothermal and non-isothermal (dynamic) methods were employed to determine the kinetic data of this system.

Five methods were used for determining the activation energies of this system in the dynamic heating experiments. In two of them (Flynn-Wall-Ozawa, and Kissinger) it is not necessary to have a prior knowledge of the reaction mechanism of the degradation behaviour for this system. In the other ones (Coats and Redfern, Horowitz and Metzger, and Van Krevelen *et al.*) it is necessary to know this reaction mechanism, besides Criado *et al.* method was used for determining it.

The results have shown that good agreement between the activation energies obtained from all methods can be achieved if it is assumed that the degradation behaviour of this system is of sigmoidal-rate type.

Keywords: activation energies, degradation behaviour, epoxy resin, master curves, TG

Introduction

Research in thermal degradation of epoxy systems is of great interest because this is an outstanding problem in the application of these systems in different types of environment and for the widely usage of these materials as structural adhesives, coatings and as matrices in fiber reinforced composites.

In polymer science thermal methods of analysis have found important applications, among them the determination of kinetic parameters. For this purpose TG is a technique widely used in polymer science because of its simplicity. In TG, the mass of a substance as a function of time and temperature is used to as-

sess the thermal stability and degradation of polymers, which includes the generation of kinetic data such as activation energies. However, there are many proposed methods to determine kinetic parameters [1–3] and the values calculated with these methods depend not only on experimental conditions but also on mathematical treatment on data.

In this paper the thermogravimetric study of the diglycidyl ether of bisphenol A/1,3-bisaminomethylcyclohexane (DGEBA/1,3-BAC) epoxy system was realized using isothermal and non-isothermal (dynamic) methods in order to determine the activation energy of this system. In an isothermal experiment the sample is quickly brought to a predetermined temperature where the thermal analysis instrument monitors the behaviour of the system as a function of time. Non-isothermal methods record the response of the sample as it is scanned, at a constant heating rate.

The aim of this work, that is a part of a larger study on the relationship between structure and physicochemical properties of this system [4–6], is to study the suitability of these methods comparing the values of the kinetic parameters.

Experimental

The epoxy resin used was a commercial diglycidyl ether of bisphenol A (DGEBA), Shell Epikote 828, with mass per epoxy equivalent of 192.2 g eq^{-1} as determined by hydrochlorination [7]. The curing agent was a cycloaliphatic diamine, 1,3-bisaminomethylcyclohexane (1,3-BAC, from Mitsubishi Gas Chem. Co.) with molecular mass of 142.18 and manufacturer purity value of

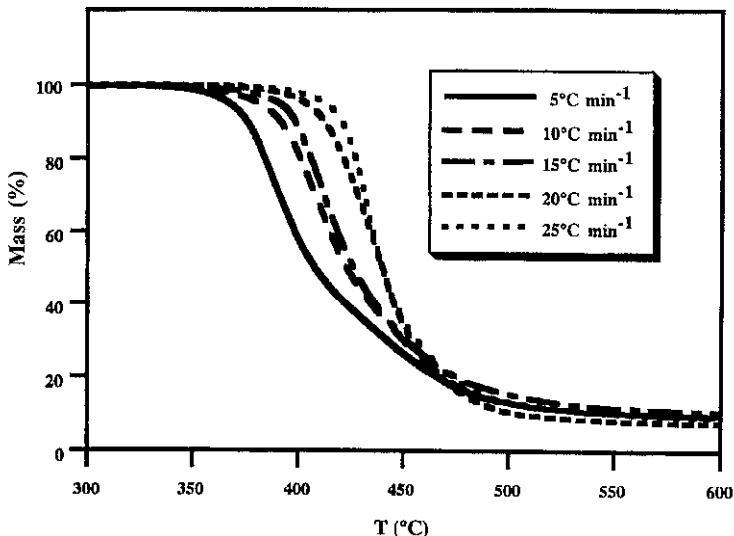


Fig. 1 Thermoanalytical curves of DGEBA/1,3-BAC at 5, 10, 15, 20 and 25°C min⁻¹

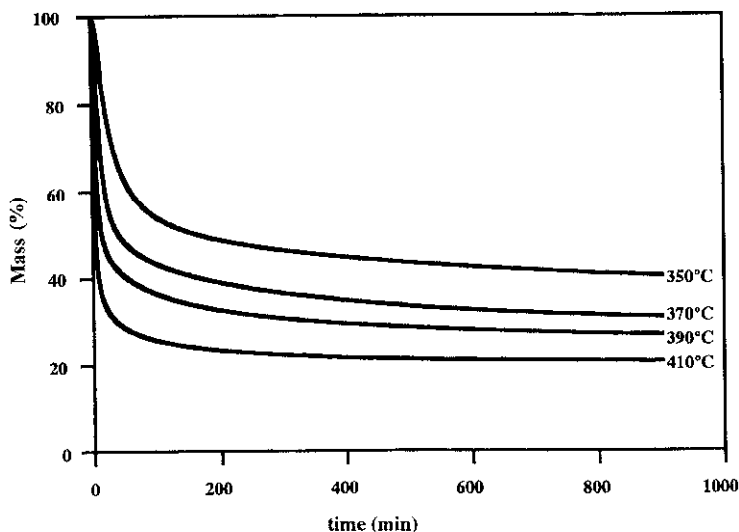


Fig. 2 Isothermal curves of DGEBA/1,3-BAC from 350 to 410°C with a 20°C temperature increment

>95%. The formulation used was 100 g DGEBA to 18.5 g 1,3-BAC. The resin and the hardener were stirred under vacuum at room temperature for 10 min and then poured into a rectangular mold to obtain a homogeneous sheet of the material. The mixture was cured 24 h at room temperature followed by 8 h at 60°C, and then postcured 2 h at 120°C. Small discs about 10 mg mass were cut to use in TG experiments.

Thermogravimetric analysis was performed using a Perkin Elmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor and the conditions were the similar used in other system [8] being the heating rates for dynamic experiments of 5, 10, 15, 20, and 25°C min⁻¹. The Fig. 1 shows these five thermoanalytical curves. For isothermal experiments the temperature was from 350

Table 1 Percentage of the original mass remaining as char for all the isothermal experiments

Temperature/°C	Char residue/%
350	40.375
360	36.030
370	30.940
380	28.655
390	26.895
400	23.950
410	20.755

to 410°C with a 10°C temperature increment and the thermoanalytical curves are shown in the Fig. 2. In all isothermal cases the complete degradation was not reached. The percentage of the original mass remaining as char in each experiment is shown in Table 1.

Results and discussion

Dynamic analysis

Five methods were used for determining the activation energies in the dynamic heating experiments: Kissinger, Flynn-Wall-Ozawa, Coats and Redfern, Horowitz and Metzger, and Van Krevelen *et al.* Most of the methods employed to quantify kinetic parameters require prior knowledge of the reaction mechanism [2, 3], but this information is not always available. Nevertheless there are some methods (Flynn-Wall-Ozawa [9, 10] and Kissinger [11]) that can be used to calculate kinetic parameters, such as activation energy, E , without involving any mechanistic knowledge of the system.

The method established by Flynn-Wall-Ozawa is an integral method for determining the activation energies in the dynamic heating experiments. The activation energy can be obtained from a plot of logarithms of heating rates, q , as a function of the inverse of temperature, $1/T$, for a constant $g(\alpha)$, since the slope of a such line is given by $-0.457 E/R$, where $g(\alpha)$ is the integrated form of the conversion dependence function, $f(\alpha)$. This method applied to experimental data is

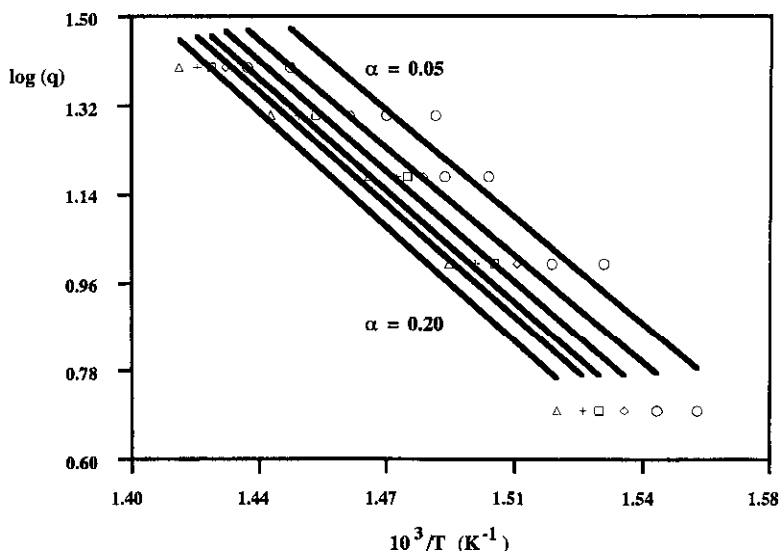


Fig. 3 Flynn-Wall-Ozawa's plot for $\alpha=0.05, 0.075, 0.10, 0.125, 0.15$ and 0.20

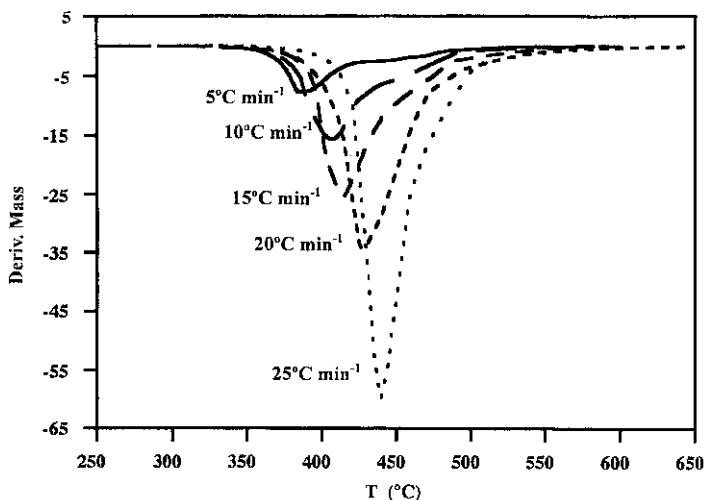


Fig. 4 Derivative curves from dynamic experiments

shown in Fig. 3. The activation energy was calculated from the average value for the different conversions, resulting a value of $E=113.4\pm 3.9$ kJ mol⁻¹.

The Kissinger's method was also applied. According to this method, the activation energy can be obtained from plots of the logarithms of the heating rate vs. the inverse of temperature at the maximum of the reaction rate in constant heating experiments. The Fig. 4 shows the value of the peaks of derivative curves. Criado and Ortega [12] proved that the Kissinger's method is possible to apply without any assumptions, in order to obtain the general expression which can be applied to determine the activation energy. A value of $E=107.4$ kJ mol⁻¹ was obtained with this method in well agreement with the value previously determined.

The Coats and Redfern, Horowitz and Metzger, and Van Krevelen *et al.* methods require the knowledge of the reaction mechanism, and were developed in detail in an earlier work [8].

The results obtained from kinetic analysis of the experimental data in the range of conversion $0.05 < \alpha < 0.20$ by mean of the Coats and Redfern method [13] taking into account different $g(\alpha)$ functions are shown in the Table 2 for the heating rate of 5°C min⁻¹.

Besides the Horowitz and Metzger [14], and Van Krevelen *et al.* [15] methods were analysed for mechanisms of type A_n , in the same range of conversion. A summary of activation energies results for these methods is presented in Table 3.

Comparing these results with those previously obtained by Flynn-Wall-Ozawa, and Kissinger methods, seems that a reasonable agreement between the activation energies obtained from these methods could be achieved if it is assumed that the degradation behaviour of the DGEBA/1,3-BAC system is of sigmoidal-rate type.

Table 2 Activation energies for the different mechanisms by Coats and Redfern's method, for the heating rate of 5°C min⁻¹

Mechanisms	$E/\text{kJ mol}^{-1}$	r
A ₂	143.0	0.995
A ₃	91.7	0.995
A ₄	66.1	0.995
R ₂	261.9	0.997
R ₃	245.6	0.997
D ₂	580.2	0.996
D ₃	592.2	0.996
F ₁	296.7	0.996

Table 3 Activation energies for the A_n mechanisms for the methods of Coats and Redfern, Horowitz and Metzger, and Van Krevelen *et al.*

$q/$ °C min ⁻¹	Coats & Redfern			Horowitz & Metzger			Van Krevelen <i>et al.</i>		
	A ₂	A ₃	A ₄	A ₂	A ₃	A ₄	A ₂	A ₃	A ₄
5	143.0	91.7	66.1	158.4	105.6	79.2	150.6	98.6	72.6
10	124.7	79.5	59.7	142.6	95.1	71.3	133.5	87.1	63.9
15	175.5	113.3	81.7	195.1	130.0	97.5	185.1	121.5	89.7
20	151.3	97.1	72.6	175.6	117.1	87.8	163.1	106.6	93.6
25	191.3	123.7	92.9	214.8	143.2	107.4	202.8	133.2	98.4
$E/\text{kJ mol}^{-1}$	157.1	101.0	74.6	177.3	118.2	88.6	167.0	109.4	83.6

In order to find out the reaction mechanism for the studied system, we have employed reference theoretical master curves. A master plot is a characteristic curve independent of the condition of the measurement. The method used was proposed by Criado *et al.* [16].

Knowing previously the activation energy by some method, in this case with the Flynn-Wall-Ozawa method, where it is not necessary to know the reaction mechanism, and defining the function

$$z(\alpha) = \frac{d\alpha/dt}{q} \pi(x)T \quad (1)$$

where $\pi(x)$ is an approximation of the temperature integral [17] and considering the general kinetic equation $f(\alpha)$ and the integrate form, $g(\alpha)$, is obtained

$$z(\alpha) = f(\alpha)g(\alpha) \quad (2)$$

In this work, the Senum and Yang's approximation for $\pi(x)$ [18] was used, and is

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (3)$$

The master curves of the Eq. (2) can be seen in the Fig. 5, where 'o' represented the experimental points. These points seem to belong at the family of the sigmoidal curves in the range of conversion studied.

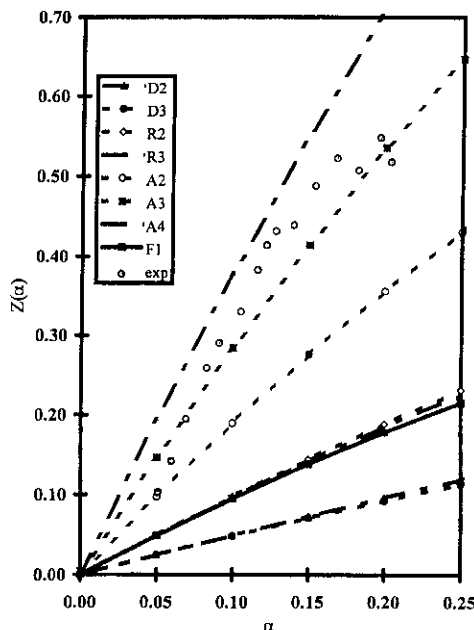


Fig. 5 The master curves $z(\alpha)$ vs. α

Isothermal analysis

From the isothermal experiments and representing conversion vs. time it can be observed a sigmoidal behaviour although it is difficult of distinguishing [19] the specific model, as it is shown in Fig. 6.

In order to determine the activation energy in these experiments [20] the general equation may be written as

$$\ln t = \ln \left[\frac{g(\alpha)}{A} \right] + \frac{E}{RT} \quad (4)$$

According to this expression, the activation energy, E , can be obtained from the slope of $\ln t$ vs. $1/T$ at a constant conversion level. The average value of this

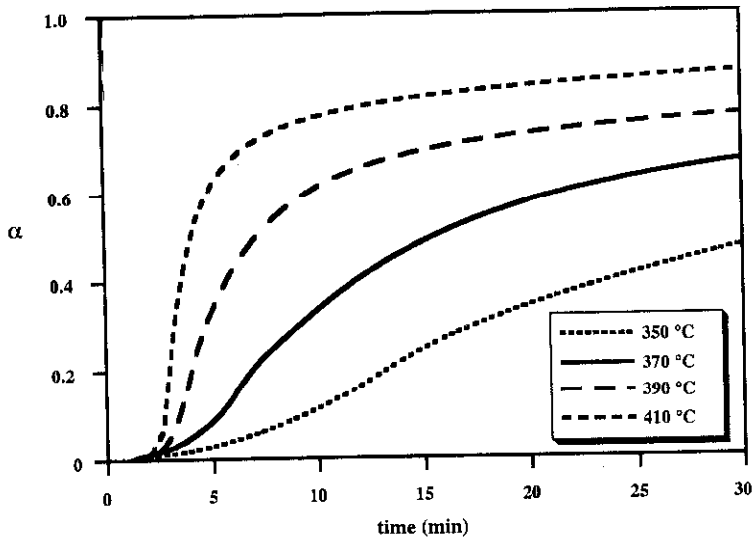


Fig. 6 Plot α vs. t , for isothermal experiments

Table 4 Activation energies obtained from isothermal experiments

Conversion	$E/\text{kJ mol}^{-1}$	r
10	86.6	0.990
15	95.3	0.992
20	99.3	0.995
25	106.4	0.995
30	107.7	0.992
35	114.6	0.992

energy is $E=101.6 \text{ kJ mol}^{-1}$ (Table 4). This result is in agreement with the values obtained from the dynamic methods, and this is an important experimental finding.

Conclusions

In summary, a thermogravimetric study about the degradation behaviour of a DGEBA /1,3-BAC epoxy resin system has been realized using isothermal and non-isothermal methods.

The results obtained show that the different methods used in spite of their differences, afford similar consistent results of activation energies between them as it can be seen in the Table 5. Within the difficulty of establishing the type and the

Table 5 Activation energies for all the studied methods. For the Coats-Redfern, Horowitz-Metzger, and Van Krevelen *et al.* methods the values are referred to the sigmoidal mechanism

Methods	$E/\text{kJ mol}^{-1}$
Flynn-Wall-Ozawa [9]	113.4
Kissinger [11]	107.4
Coats & Redfern [13]	101.0
Horowitz & Metzger [14]	118.2
Van Krevelen <i>et al.</i> [15]	109.4
Isothermal [20]	101.6

mechanism of degradation, it seems that the degradation behaviour for this system is a sigmoidal-rate type.

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