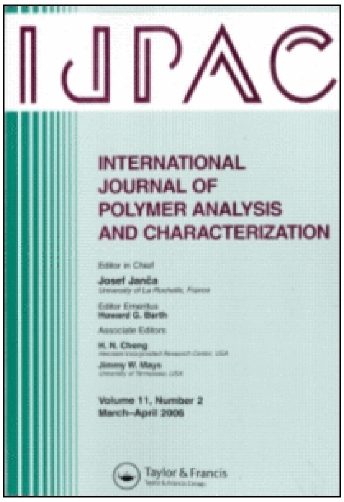

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Kinetic Data and Mechanisms in Diglycidylether Bisphenol A/ Ethylenediamine with Mono- and Bimetallic Fillers from Digitized Thermogravimetric Analysis*

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Kinetic data and mechanisms of the thermal degradation of an epoxy/amine system were investigated by dynamic thermogravimetry in a nitrogen atmosphere over the temperature range 25°C–500°C and at a constant heating rate of 10°C/min. One sample without metallic filler and three composites with 30% of various metallic fillers (Zn, Cu and Zn/Cu alloy) were selected. The thermogravimetric curves were analysed by digital image processing techniques. The kinetic data and the mechanisms were evaluated according to the methods of Freeman and Carroll, Schlömilch, and Krevelen *et al.* The study showed: (a) a high correlation among the kinetic data and also among the reaction mechanisms; (b) a decrease in the activation energy of the thermal degradation of the epoxy/amine materials in the presence of metallic fillers; (c) the material with Zn/Cu alloy had the lowest activation energy in comparison to those of the respective pure metals; and (d) high reproducibility and reliability of the results obtained by the digital technique used.

Keywords: Kinetics; Mechanisms; Epoxy resin; Composite; Thermogravimetry; Digital techniques

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INTRODUCTION

Thermogravimetry (TG) is a thermal analytical technique that measures mass change as a function of temperature or time. It is frequently used to study the primary decomposition reactions of solids, including the thermal decomposition of polymers. The TG curve provides information about the thermal stability of a sample and the different reactions and processes that occur upon heat treatment. Suitable data treatments permit the calculation of kinetic constants useful for engineering purposes.

The determination of kinetic parameters using TG analysis is based on the general equation for reactions in the solid state:[1]

$$d\alpha/dt = k \cdot f(\alpha) \tag{1}$$

where α is the weight, $f(\alpha)$ is a function of α, and k can be considered to be a rate constant.

When pyrolysis takes place under the conditions of thermogravimetric analysis, k will not remain constant and will depend on temperature. The temperature dependence of k is expressed by the Arrhenius equation,

$$k = Z\exp(E/RT) \tag{2}$$

where Z is the frequency factor, E is the activation energy, and R is the gas law constant. Since TG analysis is often carried out at a constant heating rate, $q = dT/dt$.

The analytical form of the function $f(\alpha)$ depends on the mechanism of the thermal decomposition. The simplest form of $f(\alpha)$ is obtained when it is assumed that the rate of conversion is proportional to the concentration of nondegraded or unreacted material, viz.,

$$f(\alpha) = (1 - \alpha)^n \tag{3}$$

where n can be considered an apparent reaction order.

By substitution of $dt = dT/q$ and Equations (2) and (3) into Equation (1), the following is obtained:

$$d\alpha/(1 - \alpha)^n = (Z/q)\exp(E/RT) \cdot dT. \tag{4}$$

For the mathematical treatment of Equation (4) many methods have been used. The methods investigated in the present paper include those by Freeman and Carroll[2], Schlömilch[3], and Krevelen *et al.*[4]

Equation (4) can be integrated to yield a function

$$g(\alpha) = \int_0^\infty \mathrm{d}\alpha/f(\alpha) = (Z/q)\int_0^T \mathrm{e}^{-E/RT}\mathrm{d}T. \qquad (5)$$

The choice of $g(\alpha)$ depends on the object of the kinetic study. In heterogeneous systems it is possible to distinguish three elemental processes: diffusion, nucleation, and reaction at the phase boundary.

Previously, the kinetics of diglycidylether bisphenol A (DGEBA)/ ethylenediamine (ETDA) thermal decomposition using different epoxy/amine molar ratios have been studied by the present authors.[5,6] Moreover, we have recently developed a data processing methodology applicable to TG test curves using a digital image processing technique.[7] In the present paper, an evaluation of the kinetic data and the mechanisms of the thermal decomposition of epoxy/amine systems by digital analysis is presented.

EXPERIMENTAL

The preparation of samples has been described in detail previously.[5] One sample without metallic filler and three composites were prepared. In the composites, both monometallic (Zn and Cu, respectively) and bimetallic fillers (Zn/Cu alloy) were used. In the monometallic composites 30wt% of the filler was used, while in the case of the bimetallic material 15wt% of each of the metals was employed. For all the materials studied a single epoxy/amine molar ratio of 1 : 1.5 was analysed. The thermal treatment was carried out in a 1090 DuPont thermobalance, in a nitrogen atmosphere over the temperature range 25°–500°C and at a constant heating rate of 10°C/min.

The digital image processing was carried out using the following steps:

(*a*) *Scanning the TG curves*: A full-page colour scanner, SCANJET IIC.HP, connected to a personal computer (486DX, 80 MHz, 8 Mbytes of RAM, hard disk drive with 470 Mbytes, SVGA monitor with a video card with 1 Mbyte of memory) was used. Curves were first digitized in a grey scale of 8 bits/pixel, in 3500 × 2500 pixels. A region of interest of 1200 × 1500 pixels was selected.

(*b*) *Outline*: Because of the high resolution obtained during the scanning process (0.424°C/pixel in the X-axis and 0.0082% at the Y-axis), the original traces of the TG curves were interpreted by the computer as a wide band of points; thus, an outline algorithm was developed, which allowed us to choose a single value at the Y-axis for every value of the pixel at the X-axis.

(*c*) *Scaling of the digitized TG curves*: Curves already outlined were scaled so that the size of pixels of the image corresponded to the real dimensions indicated at the X and Y Cartesian axis. Mathematical algorithms were written in the C language as a Windows application, within the Adoculus graphic programming system.

(*d*) *Drawing of the TG curve and selection of optimum interval for the kinetic study*: From the digitized data of temperature (T) and mass (wt%) a new thermogram was drawn. The decomposition rate was calculated from the first derivative of the digitized TG curve. The second derivative allowed us to choose the optimum thermal decomposition interval. This interval occurs in the region where the mass change has a direct relation to the temperature, and it corresponds to the interval between the two maximum values of the second derivative, as shown in Figure 1. For the calculation of the derivatives, the 5-point derivation method was used.[9]

RESULTS AND DISCUSSION

Figure 1 shows the digitized thermograph of the material with a bimetallic filler (DGEBA/ETDA/Zn–Cu). The region of higher loss of mass is between 300°C–400°C approximately, and it corresponds to the optimum thermal decomposition interval. In both digitized and non-digitized thermograph a similar behaviour was observed for the sample without filler and for the samples with monometallic filler. The weight losses observed at ~100°C were attributed to humidity adsorbed by the porous filler, water content in the matrix, and ETDA volatilization (boiling point, 118°C).

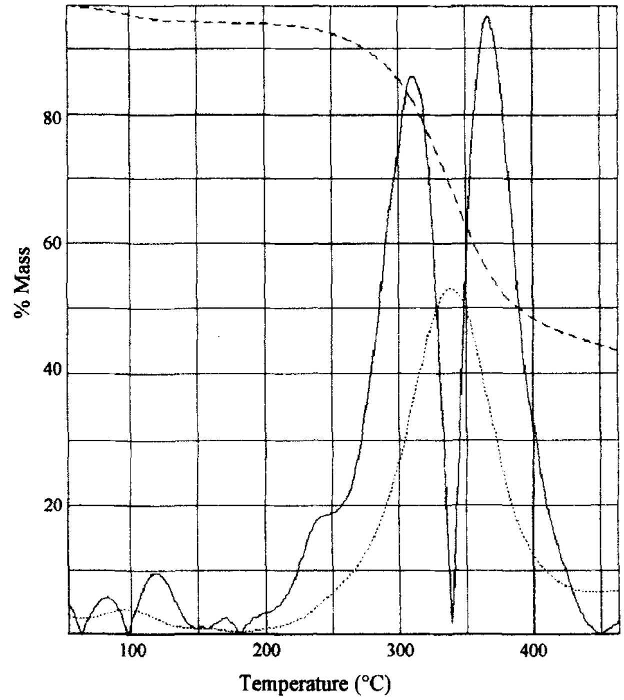

FIGURE 1 Digitized TG curves for DGEBA/ETDA/Zn–Cu: (---) observed curve; (······) first derivative; (—) second derivative.

Table I shows the kinetic parameters calculated from the digitized TG curves. We observe a good correlation among the kinetic data determined according to the three methods employed. Besides, there is evidence of a catalytic effect of the metal on the thermal degradation reaction of the composites, and this effect has a direct relationship with the thermal conductivity of the filler. The material with bimetallic filler shows the largest effect, which corresponds to the highest thermal conductivity expected for metal alloys, in contrast to those of the respective pure metals. This difference can be explained by an increase in the structural heterogeneity of the filler.

Table II summarizes the probable reaction mechanism for each material studied. The same results were observed by both Schlömilch and Krevelen methods. In the selection of the mechanisms an automatic system designed in Mathcad for Windows[10] was used. The

TABLE I Kinetic data of the thermal decomposition of DGEBA/ETDA, with and without fillers, from the digitized TG curves

Method	*Filler*	ΔT*(°C)	E (kcal/mol)	N
Freeman–Carroll			73	
Schlömilch	0	395–427	70	2.2
Krevelen *et al.*			72	
Freeman–Carroll			57	
Schlömilch	Zn	351–398	58	2.6
Krevelen *et al.*			60	
Freeman–Carroll			37	
Schlömilch	Cu	364–415	36	1.8
Krevelen *et al.*			39	
Freeman–Carroll			30	
Schlömilch	Zn/Cu	311–366	27	2.0
Krevelen *et al.*			29	

* ΔT = Optimum thermal degradation interval.

TABLE II Reaction mechanisms for DGEBA/ETDA, with and without fillers

Method	*Filler*	*Function*	*Rate-controlling process*
Schlömilch	0	R3	Phase-boundary reaction, spherical symmetry
Krevelen *et al.*		R3	
Schlömilch	Zn	F1	Random nucleation
Krevelen *et al.*		F1	
Schlömilch	Cu	R2	Phase-boundary reaction, cylindrical symmetry
Krevelen *et al.*		R2	
Schlömilch	Zn/Cu	R2	Phase-boundary reaction, cylindrical symmetry
Krevelen *et al.*		R2	

curves obtained from the evaluation of the employed methods were calculated and recorded directly by the computer. The curve that presented the lowest error was selected as the best fit to the mechanism.

Thirteen kinetic expressions corresponding to the rate controlling process in degradation of solids[11] were evaluated and listed in Table III. The mechanisms investigated were: diffusion (D1, D2, D3, D4), nucleation (F1, A1, A2, A3, A4, A5), and phase boundary (R1, R2, R3). When manual calculations using other methods[8] were applied, it was not possible, in some cases, to decide on the rate-controlling process.

Table IV shows the analysis of the data corresponding to the mechanisms listed in Table III for the thermal degradation of the DGEBA/ETDA/Zn–Cu system. Figures 2 and 3 provide graphical representations of some of the kinetic equations analysed according to

TABLE III Kinetic expressions used in the evaluation

Mechanism	$g(\alpha)$	*Rate-controlling process*
D1	α^2	One-dimensional diffusion
D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion; Jander equation
D4	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion; Ginstling-Brounshtein equation
F1	$-\ln(1-\alpha)$	Random nucleation; one nucleus on each particle
A1	$[-\ln(1-\alpha)]^{1/4}$	Random nucleation; Avrami equation
A2	$[-\ln(1-\alpha)]^{1/2}$	Random nucleation; Avrami equation
A3	$[-\ln(1-\alpha)]^{1/3}$	Random nucleation; Avrami equation
A4	$[-\ln(1-\alpha)]^{3/4}$	Random nucleation; Avrami equation
A5	$[-\ln(1-\alpha)]^{3/4}$	Random nucleation; Avrami equation
R1	α	Phase boundary reaction; one-dimensional
R2	$1-(1-\alpha)^{1/2}$	Phase boundary reaction; two-dimensional
R3	$1-(1-\alpha)^{1/3}$	Phase boundary reaction; three-dimensional

TABLE IV Analysis of the reaction mechanisms for DGEBA/ETDA/Zn–Cu

Process	*Error (Schlömilch)*	*Error (Krevelen)*
D1	1.352	1.176
D2	1.022	0.633
D3	2.482	0.887
D4	0.383	0.223
F1	3.707	1.492
A1	0.906	0.373
A2	1.839	0.746
A3	1.217	0.497
A4	2.773	1.119
A5	2.462	0.995
R1	2.605	0.705
R2	0.364	0.092
R3	1.227	0.444

Schlömilch and Krevelen methods for the DGEBA/ETDA/Zn–Cu material, respectively. In each case, the highest linear correlation corresponds to the phase-boundary controlled process. This result indicates[11] that the surface nucleation takes place extremely rapidly, and the total process is governed by the movement of the resulting interface towards the center. Two-dimensional movement (for a cylinder or a prism) is represented by the R2 function, and a sphere reacting from all surfaces inwards (i.e., three-dimensional movement) by R3.

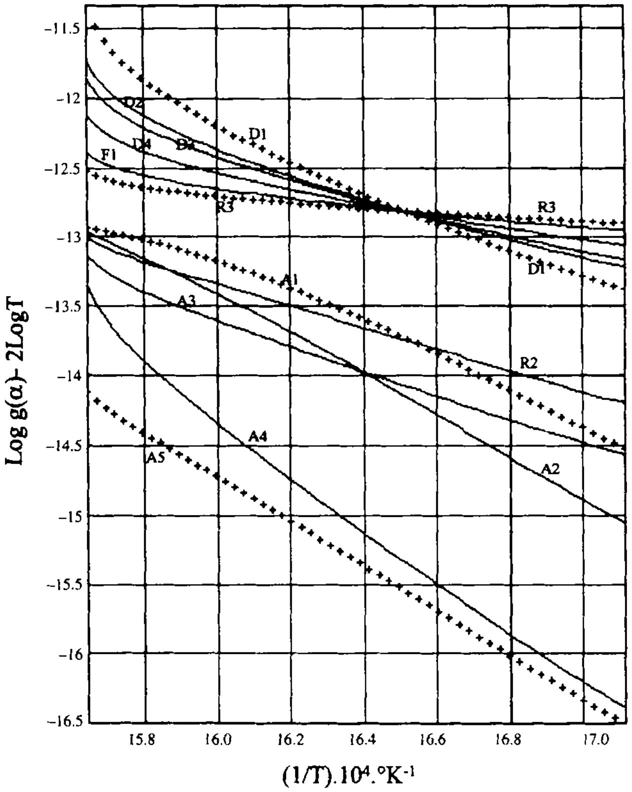

FIGURE 2 Treatment of Schlömilch's equation for DGEBA/ETDA/Zn–Cu using different rate-controlling processes. Crosses are experimental points.

CONCLUSIONS

This study showed a high correlation among the kinetic data and also among the reaction mechanisms determined by the different methods employed. There is also evidence of a catalytic effect of the metallic filler on the thermal degradation of the composite, which bears a direct relationship with the thermal conductivity of the metal. The material with bimetallic filler showed the lowest activation energy and consequently the highest catalytic effect.

The evaluation of the kinetic data using the digital image technique minimized experimental errors. In addition, processing of the TG curves was made almost instantaneously and the reproducibility and

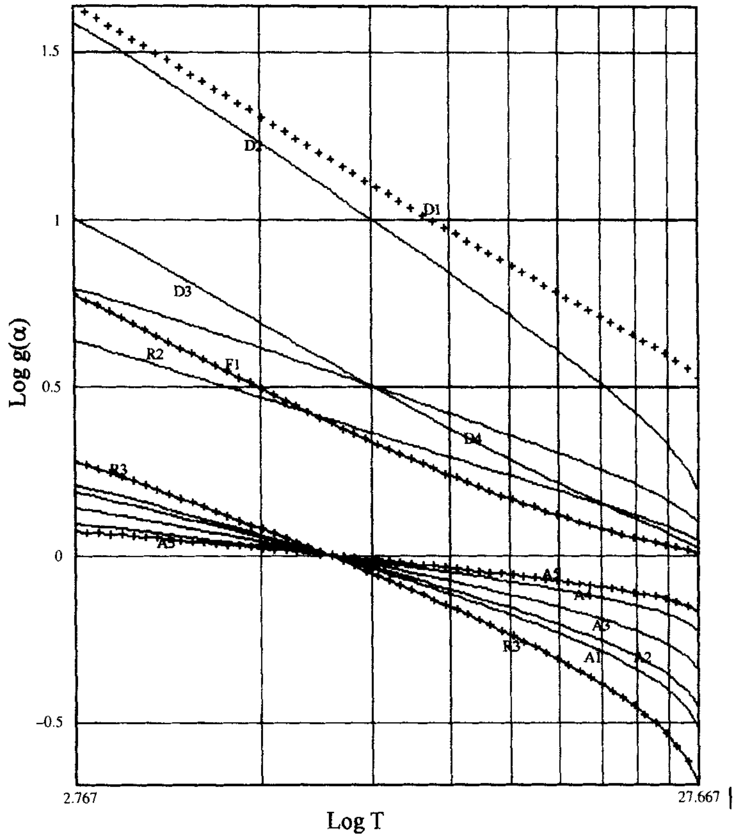

FIGURE 3 Treatment of Krevelen's equation for DGEBA/ETDA/Zn–Cu using different rate-controlling processes. Crosses are experimental points.

reliability of results increased, in contrast to results obtained by manual calculations. The use of the second derivative of the TG curve as a criterion to choose the optimum thermal degradation interval further increased the reproducibility of the results because the kinetic equations are particularly valid for that region of the TG curve.

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