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Thermal degradation kinetics of epoxy-anhydride resins: II. Influence of a reactive diluent

S. Montserrat*, J. Málek[1], P. Colomer

Laboratori de Termodinàmica ETSEIT, Departament de Màquines i Motors Tèrmics,
Universitat Politècnica de Catalunya, Carrer de Colom 11, E-08222 Terrassa, Barcelona, Spain

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Abstract

The effect of reactive diluent on the thermal degradation kinetics of epoxy-anhydride resins has been studied by thermogravimetry in both isothermal and non-isothermal conditions. It was found that the kinetics of thermal degradation can be described well by a simple reaction order model. The addition of reactive diluent increases the apparent activation energy and the kinetic exponent. A difference was also observed between the set of kinetic parameters obtained by kinetic analysis of isothermal and non-isothermal data. Such behavior indicates a more complex mechanism of thermal degradation of epoxy resin. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal degradation; Kinetics; Epoxy resins

1. Introduction

Thermogravimetric analysis has been a technique widely used to study the thermal stability [1] and compositional analysis [2] of polymeric materials. In particular, the thermal degradation of thermosets is affected by the structure of the resin, the type of curing agents and other additives as accelerator, reactive or not reactive diluents, and filler [3]. Different methods have been proposed to study the kinetics of the thermal degradation either by isothermal or non-isothermal conditions, see [4–6] and references therein. Special interest has received the analysis in non-isothermal conditions [7–11]. Some of these methods have been applied to a thermal degradation of epoxy resins [12,13].

In a previous paper [14], we studied the influence of a silica filler to thermal degradation kinetics of epoxy-anhydride resins in isothermal and non-isothermal conditions using an analysis based on the methodology introduced by Málek [15,16] for analysis of calorimetric data. The main goal of this work is to study the influence of reactive diluent on the kinetics of thermal degradation of an epoxy resin. Reactive diluents are used as additives in epoxy resins in order to reduce the viscosity of the initial mixture and to improve the processability of the resin. With this additive, the properties of both the system during curing and the crosslinked epoxy can be modified [17]. In our epoxy-anhydride system, the addition of a reactive diluent, which is a low-viscosity aliphatic diglycidyl ether, leads to an increase of the exothermic

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*Corresponding author. Tel.: +34-937398123; fax: +34-937398101.

[1] Permanent address: Joint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84, Pardubice 530 09, Czech Republic.

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heat of curing [18] and significantly affects the final structure of the epoxy [19]. In this paper, the effect of the reactive diluent on the kinetic parameters of the thermal degradation of the fully cured epoxy will be shown.

2. Theory

In thermal degradation TG experiments the change of the sample mass is registered as a function of temperature (non-isothermal experiments) or time (isothermal experiments). The fractional extent of reaction is expressed as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}, \tag{1}$$

where m is an actual mass at time t (or at temperature T), m_0 is the initial sample mass and m_∞ is the mass at the end of isothermal or non-isothermal experiment.

The differential kinetic equation for thermal degradation process can be expressed as [4,5]

$$\left(\frac{d\alpha}{dt}\right) = A \cdot e^{-x} f(\alpha), \tag{2}$$

where A is a preexponential factor, $x = E_a/RT$ is the reduced apparent activation energy and $f(\alpha) = (1-\alpha)^n$ is the "reaction order" kinetic model. The mutual correlation of Arrhenius kinetic parameters (apparent activation energy and preexponential factor) does not allow an accurate kinetic analysis to be performed by using only one experimental TG [4,20]. This problem can be solved, calculating the apparent activation energy from several isothermal (or non-isothermal) experiments and by determining the most probable kinetic model as described below.

The apparent activation energy of the decomposition process can be calculated by isoconversional method [20] from the slope of $\ln(d\alpha/dt)$ vs. $1/T$ plot for the same value of α

$$\left[\frac{d\ln(d\alpha/dt)}{d(1/T)}\right]_\alpha = -E_a/R. \tag{3}$$

This procedure can be repeated for various values of α for both isothermal and non-isothermal data. Therefore the method provides a check of invariance of E_a with respect to α in the $0.3<\alpha<0.7$ range, which is one of basic assumptions in kinetic analysis of TG data.

By integration of Eq. (2) in isothermal conditions the following equation is obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \cdot e^{-x} \cdot t. \tag{4}$$

Combining Eqs. (2) and (4) a new function $Z(\alpha)$ can be defined

$$Z(\alpha) = \left(\frac{d\alpha}{dt}\right) \cdot t = f(\alpha) g(\alpha). \tag{5}$$

For practical reasons this function is normalized within the $\langle 0,1 \rangle$ interval. It was shown by Málek [16] that the maximum of this function (usually labeled α_p^∞) depends on the value of the kinetic exponent

$$\alpha_p^\infty = 1 - n^{1/(1-n)} \quad \text{for } n \neq 1, \tag{6a}$$

$$\alpha_p^\infty = 0.632 \quad \text{for } n = 1. \tag{6b}$$

In isothermal conditions, the exponential term in Eq. (2) is constant and the reaction rate ($d\alpha/dt$) is proportional to $f(\alpha)$ function

$$Y(\alpha) = \left(\frac{d\alpha}{dt}\right) \approx f(\alpha). \tag{7}$$

Therefore, if the reaction rate is plotted as a function α its shape corresponds to the $f(\alpha)$ function. It is convenient to normalize the $Y(\alpha)$ plot within $\langle 0,1 \rangle$ interval. If the kinetic model equals to $(1-\alpha)^n$ then the $Y(\alpha)$ function has a maximum at $\alpha_M = 0$ and it can be convex, linear or concave. Convex dependence corresponds to $n<1$, linear dependence to $n = 1$ and concave dependence to $n>1$. Thus, the shape of both $Y(\alpha) = (d\alpha/dt)$ and $Z(\alpha)$ function can be used conveniently for the determination of the kinetic exponent [16]. It is seen that in isothermal conditions the kinetic model can easily be determined by simple transformation of experimental data.

In non-isothermal conditions when the temperature rises at a constant heating rate β, the $g(\alpha)$ function can be expressed as [16]:

$$g(\alpha) = A \cdot e^{-x} \left[\frac{T}{\beta}\pi(x)\right], \tag{8}$$

where $\pi(x)$ is an approximation of the temperature integral. There are various expression of the $\pi(x)$ term in the literature [4]. The rational expression of Senum and Yang [21] gives sufficiently accurate results

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}. \quad (9)$$

Combining Eqs. (2) and (8) we can obtain following expression for the $z(\alpha)$ function in non-isothermal conditions [15]

$$z(\alpha) = \left(\frac{d\alpha}{dt}\right) \cdot \left[\frac{T}{\beta}\pi(x)\right] = f(\alpha) \cdot g(\alpha). \quad (10)$$

Recently it was found [22] that the term in brackets in Eq. (10) is proportional to T^2. Therefore, the expression for the $z(\alpha)$ function can be substantially simplified

$$z(\alpha) \approx \left(\frac{d\alpha}{dt}\right) \cdot T^2. \quad (11)$$

Thus, the $z(\alpha)$ function can be obtained by a very simple transformation of experimental data just by multiplying measured reaction rate ($d\alpha/dt$) by T^2 and then normalizing within the $\langle 0,1 \rangle$ interval. Similarly, like in isothermal conditions this can be done without the knowledge of any kinetic parameter. On the other hand in non-isothermal conditions the reaction rate ($d\alpha/dt$) is not directly proportional to $f(\alpha)$ as the exponential term in Eq. (2) is not constant. However, the shape of $f(\alpha)$ function can be obtained from the $y(\alpha)$ function defined as [15,16]:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \cdot \exp\left(-\frac{E_a}{RT}\right) = A \cdot f(\alpha). \quad (12)$$

This function has the same mathematical properties as discussed above for isothermal conditions. However, as evident from Eq. (12) for calculation of $y(\alpha)$ function it is necessary to know the apparent activation energy in the case of non-isothermal conditions.

3. Experimental

The epoxy resin studied was a commercial epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), namely Araldite F (CIBA-GEIGY), with an epoxy equivalent of 188.3 g/equiv., cured by a cyclic carboxylic anhydride derived from methyl tetrahydrophthalic anhydride (MTHPA) HY905 with an accelerator (AC) that was a tertiary amine DY061. The reactive diluent (RD) was a low-viscosity aliphatic diglycidyl ether Araldite DY026 with an epoxy equivalent weight of 113.8 g/equiv. The epoxy resin, hardener, and the RD were mixed at the composition given in Table 1 and stirred at room temperature for 20 min. Then, the required amount of accelerator was added, mixed for about 20 min, and degassed in a vacuum oven at room temperature for about 15 min.

Table 1
Composition of the epoxy systems in parts by weight and the corresponding glass transition temperature T_g

Sample	DGEBA : MTHPA : RD : AC	T_g (°C)[a]
FRD0	100 : 100 : 0 : 1	101.3
FRD10	100 : 112 : 10 : 1	96.6
FRD30	100 : 136 : 30 : 1	81.5
FRD50	100 : 160 : 50 : 1	74.2

[a] Values from [18].

The thermogravimetric measurements were carried out by a TG-50 thermobalance coupled to a METTLER TA4000 instrument. Non isothermal experiments were performed at heating rates of 2.5, 5, 10, 15 and 20 K/min. In the isothermal experiments, the furnace was heated up to the desired temperature. Then the sample was introduced, and the weight loss measured during times ranging from 5 to 15 h depending on the experiment temperature. In both cases, powdered samples of about 7 mg were used and a nitrogen gas flow of 200 ml/min was permanently applied. Further details of experimental procedure are described elsewhere [14].

4. Results and discussion

The TG curves in non-isothermal conditions were obtained at different heating rates ranging from 2.5 to 20 K/min. These curves can easily be transformed to $\alpha(T)$ plots and then analyzed by isoconversional method as described in Section 2. Fig. 1 shows the apparent activation energy of thermal degradation of the FRD0 and FRD50 samples as a function of fractional conversion. Any point in this figure (corresponding to E_a for constant α) was obtained from the slope of $\ln(d\alpha/dt)$ vs. $1/T$ plot for non-isothermal data. The error limits are specified by bars. As mentioned in Section 2 the apparent activation energy

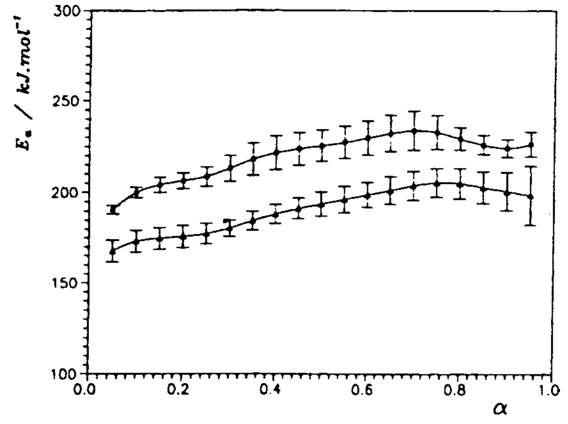

Fig. 1. The apparent activation energy as a function of fractional conversion. The points were calculated from non-isothermal TG data for the FRD0 sample (▲) and the FRD50 sample (■) by the isoconversional method. The lines are drawn as guides for the eye. Error limits are specified by bars.

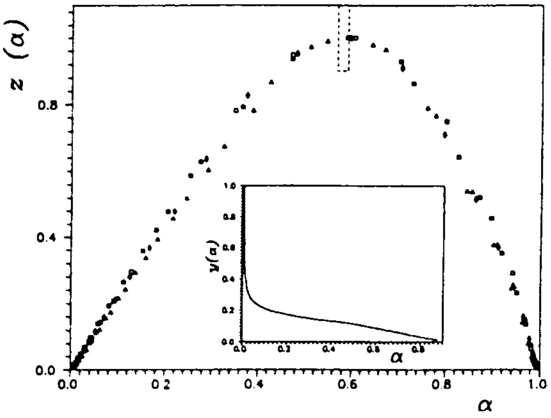

Fig. 2. The $z(\alpha)$ function for the FRD0 sample calculated using Eq. (11) from non-isothermal data: (□) 2.5 K/min; (■) 5 K/min; (△) 10 K/min; (▲) 15 K/min; (◇) 20 K/min. Broken lines correspond to theoretical maximum α_p^∞ calculated using Eq. (6a). The inset shows the $y(\alpha)$ function for the same sample calculated using Eq. (12) from experimental data corresponding to heating rate 10 K/min.

should be invariant with respect to α in the $0.3<\alpha<0.7$ range. In fact the value of E_a increases with the fractional conversion. It should be pointed out that a more pronounced $E_a-\alpha$ plot may be a consequence of more complex mechanism controlling thermal degradation process. An inspection of Fig. 1 shows ca. 12% variation for the FRD0 sample and ca. 9% for the FRD50 sample. These changes are higher than the average error limit which corresponds to ca. 3%. Therefore, average value of apparent activation energy determined in the $0.3<\alpha<0.7$ range is 193±12 kJ/mol for the FRD0 sample and 225±9 kJ/mol for the FRD50 sample.

Figs. 2 and 3 show the $z(\alpha)$ functions for thermal degradation of FRD0 and FRD50 sample, respectively. These functions were obtained from non-isothermal TG data calculated using Eq. (11). The shape of the $z(\alpha)$ functions is practically invariant with respect to temperature ($\alpha_p^\infty < 0.632$) and the $y(\alpha)$ function is concave (see inset of Fig. 2). Therefore, the "reaction order" kinetic model can be used, i.e. $f(\alpha)=(1-\alpha)^n$ where $n>1$. For this model the equation for non-isothermal $\alpha(T)$ curve can be written in the following form:

$$\alpha(T) = 1 - \left[1 - T\left(\frac{\pi(x)}{\beta}\right)(1-n)A\mathrm{e}^{-x}\right]^{1/(1-n)}. \tag{13}$$

The temperature dependence of the reduced activation energy ($x = E_a/RT$) can easily be calculated for average value of apparent activation energy obtained by isoconversional analysis (see above). The values of parameters n and A can be obtained by non-linear regression of experimental data. The average values obtained for FRD samples are shown in Table 2. It is seen that the value of the kinetic exponent as well as

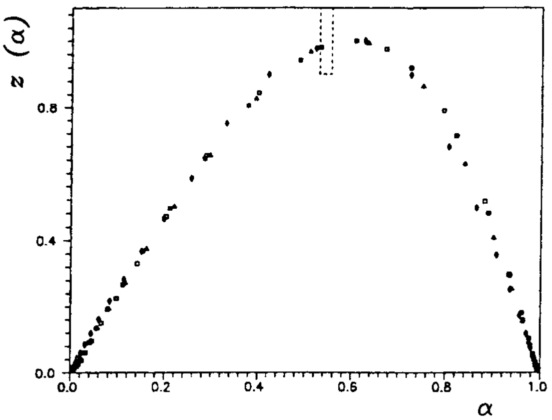

Fig. 3. The $z(\alpha)$ function for the FRD50 sample calculated using Eq. (11) from non-isothermal data: (□) 2.5 K/min; (■) 5 K/min; (▲) 15 K/min; (◇) 20 K/min. Broken lines correspond to theoretical maximum α_p^∞ calculated using Eq. (6a).

Table 2
The average kinetic parameters of thermal degradation of epoxy resins obtained from analysis of non-isothermal data

Sample	E_a/kJ mol^{-1}	n	ln (A/min)
FRD0	193±12	1.33±0.08	33.59±0.06
FRD10	209±18	1.4±0.1	36.4±0.1
FRD30	222±12	1.52±0.09	38.9±0.1
FRD50	225±9	1.6±0.1	39.7±0.1

the E_a increases with RD content. Using the Eq. (6a) the limiting values of α_p^∞ were calculated for the kinetic exponent shown in Table 2 taking into account the error limits. These calculated limiting values agree well with the maxima of experimental $z(\alpha)$ functions as shown in Figs. 2 and 3.

Figs. 4 and 5 show the comparison of experimental data (points) and calculated $\alpha(T)$ plots for the FRD0 and FRD50 sample (full lines). The $\alpha(T)$ curves were calculated using Eq. (13) for the kinetic parameters shown in Table 2. There is quite good agreement between experimental data and the prediction of the model. Some discrepancies are observed only at lower temperatures and slow heating rates for the FRD50 sample.

Thermal degradation in isothermal conditions was studied for the FRD50 sample in the 320°C≤T≤360°C range. These conditions are determined by the possibilities of the TG instrument used as well as by the kinetics of the thermal degradation process of epoxy resins. Outside of specified temperature ranges it is quite difficult to obtain reliable TG data. The thermal degradation is fast at higher temperatures and the initial part of TG curve might be lost during the instrument settling period. In contrast, at lower temperatures the thermal degradation becomes very slow and it is not so easy to determine correctly the relative mass loss corresponding to completely degraded sample.

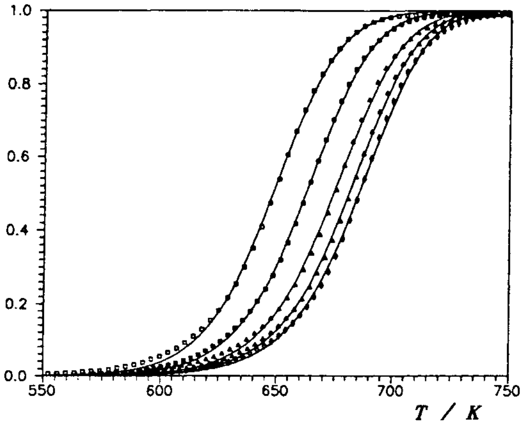

Fig. 4. Non-isothermal TG curves for the FRD0 sample measured at different heating rates: (□) 2.5 K/min; (■) 5 K/min; (△) 10 K/min; (▲) 15 K/min; (◇) 20 K/min. Full lines were calculated using Eq. (13) for the kinetic parameters shown in Table 2.

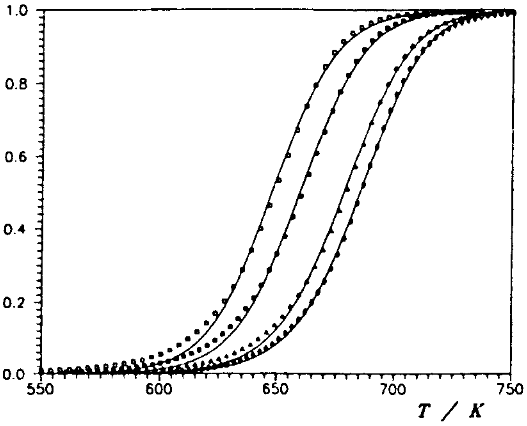

Fig. 5. Non-isothermal TG curves for the FRD50 sample measured at different heating rates: (□) 2.5 K/min; (■) 5 K/min; (▲) 15 K/min; (◇) 20 K/min. Full lines were calculated using Eq. (13) for the kinetic parameters shown in Table 2.

Fig. 6 shows the apparent activation energy of thermal decomposition of the FRD50 sample as a function of fractional conversion. Any point in this figure (corresponding to E_a for constant α) was obtained from the slope of ln(dα/dt) vs. 1/T plot for isothermal data. The value of E_a increases with fractional conversion. An inspection of Fig. 6 reveals ca. 7% variation of the apparent activation energy. These changes are higher than the average error limit which corresponds to ca. 3%. Therefore, average value of E_a determined in the 0.3<α<0.7 range is 157±6 kJ/mol for the thermal degradation of the FRD50 sample in isothermal conditions. This value is about 30% lover than determined from non-isothermal experiments. Such difference is considerably higher than typical uncertainties for this type of analysis of experimental data. It seems that the thermal decomposition of FRD50 sample cannot be described by a unique set of kinetic parameters valid in isothermal and non-isothermal conditions [14,23].

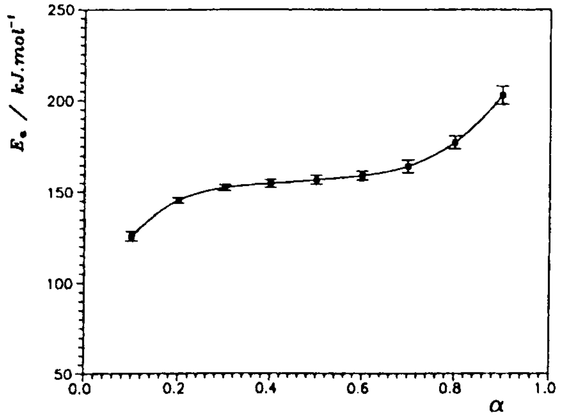

Fig. 6. The apparent activation energy as a function of fractional conversion. The points were calculated from isothermal TG data for the FRD50 sample (■) by the isoconversional method. The line is drawn as guides for the eye. Error limits are specified by bars.

Fig. 7 shows the $Z(\alpha)$ functions for isothermal decomposition of FRD50 sample, calculated using Eq. (5). The shape of the $Z(\alpha)$ functions is practically invariant with respect to temperature ($\alpha_p^\infty \cong 0.632$) and the $Y(\alpha)$ function is nearly linear (see inset of Fig. 7). Therefore, the reaction kinetic model can be used, $f(\alpha)=(1-\alpha)^n$ where $n \cong 1$. For this model the equation for isothermal $\alpha(T)$ curve can be written in the following form:

$$\alpha(t) = 1 - [1 - t(1-n)A\mathrm{e}^{-x}]^{1/(1-n)}. \qquad (14)$$

Table 3
The kinetic parameters for thermal degradation of FRD50 sample obtained by non-linear regression of isothermal data using Eq. (14) and constant value of activation energy (157 kJ/mol)

T (°C)	n	ln (A/min)
360	1.15	26.86
350	1.19	26.86
340	1.28	26.84
330	1.43	26.95
320	1.39	26.92
Average	1.29±0.09	28.89±0.04

The value of the reduced activation energy is constant in isothermal conditions ($x = E_a/RT$) and it can easily be calculated for average value of apparent activation energy obtained by isoconversional analysis. The values of parameters n and A can be obtained by non-linear regression of experimental data. The average values obtained for FRD50 sample are shown in Table 3. The comparison of experimental data (points) and calculated $\alpha(T)$ plots for the FRD50 sample in isothermal conditions (full lines) is shown in Fig. 8. The $\alpha(t)$ curves were calculated using Eq. (14). There is a quite good agreement between experimental data and the prediction of the model. It is evident that the value of kinetic exponent n slightly increases with decreasing temperature. A similar tendency has been

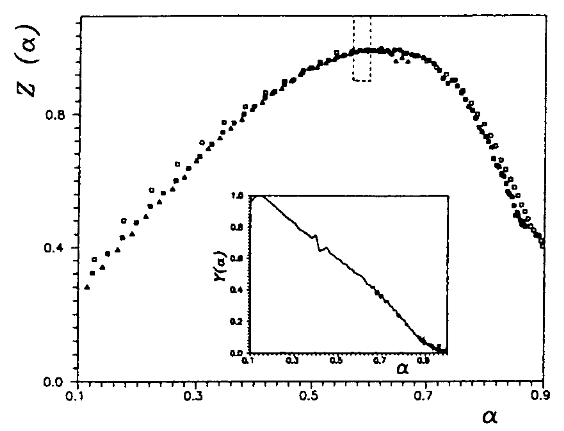

Fig. 7. The $Z(\alpha)$ functions for the FRD50 sample calculated using Eq. (5) from isothermal data: (□) 360°C; (■) 350°C; (△) 340°C. The inset shows the $Y(\alpha)$ function for the same sample ($T = 360$°C) calculated using Eq. (7).

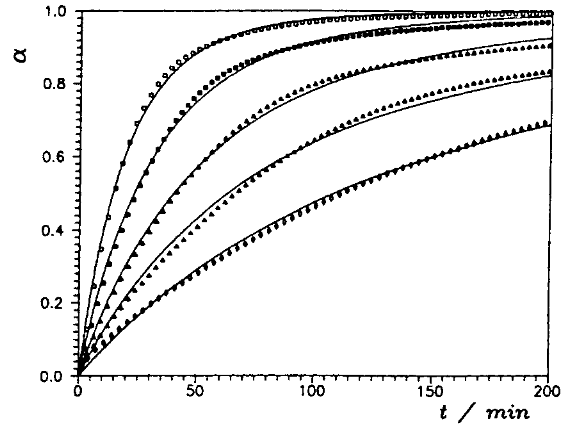

Fig. 8. Isothermal TG curves for the FRD50 sample measured at different temperatures: (□) 380°C; (■) 370°C; (△) 360°C; (▲) 350°C; (◇) 340°C. Full lines were calculated using Eq. (14) for the kinetic parameters shown in Table 3.

observed in the isothermal degradation of an epoxy-anhydride resin between 340°C and 380°C (see Table 2 of [14]). Nevertheless, the average value of n is still considerably lower than obtained from non-isothermal data.

5. Conclusions

The effect of reactive diluent on the thermal degradation kinetics of an epoxy resin has been studied. The kinetics of thermal degradation can be described well by a simple reaction order model. The addition of reactive diluent increases the apparent activation energy and the kinetic exponent. A difference was also observed between the set of kinetic parameters obtained by kinetic analysis of isothermal and non-isothermal data. Such behavior indicates a more complex mechanism of thermal degradation of epoxy resin.

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