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The evaluation of kinetic parameters from thermogravimetric data: comparison between established methods and the general analytical equation

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Abstract

This paper presents a methodology for the study of thermal decomposition kinetics of polymeric materials by means of dynamic thermogravimetry (linear temperature increase). We have developed a general analytical solution relating conversion to temperature by means of integral procedures. This equation is a recurrent series providing a rigorous method to determine kinetic parameters such as activation energy and frequency factor. We have also conducted an extensive review of the different computing methods available in the literature leading to the determination of the kinetic parameters of thermal decomposition reactions. We have compared the results obtained by using the general analytical solution with those evaluated by means of established methods which were classified into three categories: integral, differential and special methods. Finally we have analyzed the accuracy of the computing methods by considering the simplifications inherent in each of them.

LIST OF SYMBOLS

A	pre-exponential or frequency factor ($g^{1-n}\ s^{-1}$)
A^*	modified pre-exponential factor (s^{-1})
d^2f/dT^2	second conversion derivative (K^{-2})
df/dT	first conversion derivative (K^{-1})
E	activation energy ($kJ\ mol^{-1}$)
f	conversion
K	constant obtained by linear regression (method of Reich and Stivala)
n	reaction order
R	gas constant ($8.315\ J\ mol^{-1}\ K^{-1}$)
t	time (s)

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T	temperature (K)
w	weight of solids at a time t (g)
w_0	initial weight of solids (g)
w_r	residual weight of solids (char remaining at the end of thermal decomposition) (g)

Greek letters

β	heating rate ($\mathrm{K\,s^{-1}}$)
ε	relative error (%)

Subscript

m	conditions at maximum rate of decomposition

INTRODUCTION

Dynamic thermogravimetry (with linear temperature increase) is widely used as a tool to study the degradation of different polymeric materials, to elucidate the order of reaction and also to estimate other kinetic parameters such as the activation energy, the frequency factor and the rate of decomposition [1]. The greater precision of experimental values obtained from TG in comparison with DTA and DSC is attributable to the accuracy in the measurement of mass [2].

The advantages of determining kinetic parameters by non-isothermal methods rather than by conventional isothermal studies are as follows.

(1) The kinetics can be established over an entire temperature range in a continuous manner.

(2) It is possible to obtain a lot of information with a single sample, i.e. thermal parameters such as the temperature at maximum decomposition rate, characteristic temperatures, and kinetic parameters.

(3) The determination of kinetic and thermal parameters using a single sample removes problems arising from different samples, i.e. sample-to-sample error is avoided.

(4) When a sample undergoes considerable reaction in being raised to the required temperature, the results obtained by isothermal methods are questionable because some degradation may occur during the pre-heating period, particularly when the temperature of onset of reaction is considerably lower than the temperature of the isothermal trials.

It was pointed out that the calculated values of the Arrhenius doublet, i.e. activation energy and frequency factor, especially for non-isothermal heterogeneous processes, have only limited validity and cannot be utilized for pin-pointing the rate-controlling mechanism solely on the basis of the values evaluated. It is known that the degradation of a polymer is a very intricate phenomenon composed of various elementary reactions that are difficult to analyze separately and whose quantitative contributions to the global degradation process are virtually impossible to evaluate. For these reasons, even if the overall process has no real significance with regard to the reaction mechanism, it is useful as a means of quantifying the rate of reaction and for design purposes. Mathematical modelling of thermal decomposition reactions helps in understanding the process being studied, in checking the validity of assumptions and in deducing quantitative conclusions therefrom. The latter is essential to achieve engineering calculations leading to the determination of the reactor size.

Concerning the activation energy of the reaction, the literature mentions great variations for a given polymeric material. These differences depend on several factors.

(1) Preparation method of the polymer, i.e. anionic, thermal or other type of polymer preparation, and lattice defects, weak links and impurities [3].

(2) Molecular weight of the polymer [4–7].

(3) Experimental techniques and operating conditions, i.e. sample mass, sample particle size, heating rate, mass flow and type of gas, and thermal contact between sample and sample holder [2, 8].

The mathematical treatment of kinetic equations makes use of one of the following methods: a) integral; b) differential; c) approximate or special. It has been found that these methods do not reproduce the values of activation energy and reaction order when the same data are taken for computation [9, 10].

The goal of this paper is to present a methodology for the study of thermal decomposition kinetics which comply with the following requirements (the mathematical procedure presented in this paper will be applied to the thermal decomposition of anionic polystyrene).

(1) Development of a general analytical solution by means of integral procedures.

(2) Revision of the different methods available: integral, differential and special methods.

(3) Fitting of experimental data by linear regression in order to determine the kinetic parameters by using the general analytical solution presented in this paper, and comparing them to those obtained with other methods reported in the literature.

THEORETICAL CONSIDERATIONS

The rate of weight loss in the process of thermal decomposition depends on weight and temperature according to the equation [11]

$$-\frac{\mathrm{d}w}{\mathrm{d}t}=g(w)k(T)q(w,\ T) \qquad (1)$$

Many heterogeneous decomposition reactions of solids are described by the model of pseudo-homogeneous kinetics. Therefore

$$g(w)=\left(\frac{w-w_r}{w_0-w_r}\right)^n \tag{2}$$

According to Altorfer [12], some conditions have to be fulfilled to enable an ideal course of reaction as represented by the n-order reaction kinetics, i.e. a well-defined, homogeneous sample temperature with no reverse reaction. The latter implies negligible partial pressure of the decomposition gas. Therefore, a continuous flow of gas is recommended in order to evacuate volatilization products as they are formed.

The variation of the constant rate with the temperature is generally accepted to be of the Arrhenius type, because this relationship dominates physical and chemical phenomena

$$k(T)=A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

The cross term $q(w, T)$ takes into account the interactions between the weight and the reaction temperature. These interactions arise from different factors: i) variation of residual weight with operating conditions; ii) variation of kinetic parameters with conversion in the case of competitive reactions; iii) modifications of the sample physical properties during the decomposition. Because it is very difficult to obtain an equation considering all these factors, and in order to facilitate further derivation, the term $q(w, T)$ is generally assumed equal to unity.

Dynamic thermogravimetry is often carried out at constant heating rate. In such a case

$$T=T_0+\beta t \tag{4}$$

Therefore

$$\beta=\frac{\mathrm{d}T}{\mathrm{d}t} \tag{5}$$

Taking into account the relationship between weight and conversion as well as previous considerations

$$\int_0^f \frac{\mathrm{d}f}{(1-f)^n}=\frac{A^*}{\beta}\int_{T_0(f=0)}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{6}$$

where

$$f=\frac{w_0-w}{w_0-w_r} \tag{7}$$

$$A^*=Aw_0^{n-1} \tag{8}$$

Several expansions and semi-empirical approximations have been suggested [13] for the temperature-containing integral: the asymptotic expansion, the van Krevelen et al. approximation, Doyle's approximation, etc. Other authors have stated that the kinetic analysis of dynamic thermogravimetry leads inescapably to integral equations which require numerical solution [14]. Moreover, Coats and Redfern [15] reported that the temperature-containing integral has no exact solution; therefore they used an approximation. However, the integral does have a primitive analytical solution. Making the substitution $z = -E/(RT)$ and after a few consecutive integrations by parts, it is possible to reach a recurrent series. The general solution is

$$-\ln(1-f) = \frac{A^*E}{\beta R}\left[\exp\left(-\frac{E}{RT}\right)\right]\sum_{i=1}^{\infty}(-1)^{i+1}i!\left(\frac{RT}{E}\right)^{i+1} \qquad n = 1 \qquad (9a)$$

$$\frac{1-(1-f)^{1-n}}{1-n} = \frac{A^*E}{\beta R}\left[\exp\left(-\frac{E}{RT}\right)\right]\sum_{i=1}^{\infty}(-1)^{i+1}i!\left(\frac{RT}{E}\right)^{i+1} \qquad n \neq 1 \qquad (9b)$$

When the sum is truncated at the second term ($i = 2$), the kinetic equation developed by Coats and Redfern [15] may be found. Their simplification is quite satisfactory when the thermal energy (RT) is significantly less than the activation energy. This case is often found for the thermal decomposition of solids. However, if RT tends to E, i.e. low activation barrier and/or high temperature, it is necessary to take a greater number of terms in the general analytical solution.

Conversion can be singled out from eqns (9a) and (9b), whereas first and second conversion derivatives follow readily from eqn. (6)

$$f = 1 - \exp\left(-\frac{A^*RT^2}{\beta E}\left[\exp\left(-\frac{E}{RT}\right)\right] \times \sum_{i=1}^{\infty}(-1)^{i+1}i!\left(\frac{RT}{E}\right)^{i-1}\right) \qquad n = 1 \qquad (10a)$$

$$f = 1 - \left[1-(1-n)\frac{A^*RT^2}{\beta E}\left[\exp\left(-\frac{E}{RT}\right)\right] \times \sum_{i=1}^{\infty}(-1)^{i+1}\left(\frac{RT}{E}\right)^{i-1}\right]^{1/(1-n)} \qquad n \neq 1 \qquad (10b)$$

$$\frac{\mathrm{d}f}{\mathrm{d}T} = \frac{A^*}{\beta}\left[\exp\left(-\frac{E}{RT}\right)\right](1-f)^n \qquad \forall n \qquad (11)$$

$$\frac{\mathrm{d}^2f}{\mathrm{d}T^2} = \frac{\mathrm{d}f}{\mathrm{d}T}\left(\frac{E}{RT^2} - \frac{n}{(1-f)}\frac{\mathrm{d}f}{\mathrm{d}T}\right) \qquad \forall n \qquad (12)$$

Because the maximum rate of decomposition is reached when $\mathrm{d}^2f/\mathrm{d}T^2 =$

0, the activation energy can be evaluated from eqn. (12)

$$E = nRT_m^2 \frac{\left(\frac{\mathrm{d}f}{\mathrm{d}T}\right)_m}{(1-f_\mathrm{m})} \qquad \forall n \qquad (13)$$

However, the values of temperature, conversion and first conversion

TABLE 1

Summary of integral methods

INTEGRAL METHODS		Eq.
Analytical solution	$\ln\left[\frac{1-(1-f)^{1-n}}{(1-n)T^2\sum_{i=1}^{\infty}(-1)^{i+1}i!\left(\frac{RT}{E}\right)^{i-1}}\right] = \ln\left(\frac{A^* R}{\beta E}\right) - \frac{E}{R}\frac{1}{T};\ n \neq 1$ $\ln\left[\frac{-\ln(1-f)}{T^2\sum_{i=1}^{\infty}(-1)^{i+1}i!\left(\frac{RT}{E}\right)^{i-1}}\right] = \ln\left(\frac{A^* R}{\beta E}\right) - \frac{E}{R}\frac{1}{T};\ n = 1$	**(14)**
van Krevelen et al. (1951)	$\ln\left[\frac{1-(1-f)^{1-n}}{1-n}\right] = \ln\left[\frac{A^*}{\beta}\left(\frac{0.368}{T_m}\right)^{E/RT_m}\frac{1}{\frac{E}{RT_m}+1}\right] + \left(\frac{E}{RT_m}+1\right)\ln T;\ n \neq 1$ $\ln[-\ln(1-f)] = \ln\left[\frac{A^*}{\beta}\left(\frac{0.368}{T_m}\right)^{E/RT_m}\frac{1}{\frac{E}{RT_m}+1}\right] + \left(\frac{E}{RT_m}+1\right)\ln T;\ n = 1$	**(15)**
Kissinger (1957)	$\ln\left[\frac{\beta}{T_m^2}\frac{1}{n(1-f_m)^{n-1}}\right] = \ln\left(\frac{A^* R}{E}\right) - \frac{E}{R}\frac{1}{T_m};\ n \neq 1$ $\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{A^* R}{E}\right) - \frac{E}{R}\frac{1}{T_m};\ n = 1$	**(16)**
Horowitz & Metzger (1963)	$\ln\left[\frac{1-(1-f)^{1-n}}{1-n}\right] = \frac{E}{RT_s^2}\theta;\ n \neq 1$ $\ln[-\ln(1-f)] = \frac{E}{RT_s^2}\theta;\ n = 1$ where: $\theta = T - T_s$ (T_s is T at which $f = \left(1 - \frac{1}{e}\right)$ for $n = 1$ and $T_s = T_m$ for $n \neq 1$) $A = \frac{\beta E}{RT_s^2}\exp\left(\frac{E}{RT_s}\right)$	**(17)**
Coats & Redfern (1965) (zero-order reaction)	$\ln\left[\frac{f}{T^2\left(1-\frac{2RT}{E}\right)}\right] = \ln\left(\frac{A^* R}{\beta E}\right) - \frac{E}{R}\frac{1}{T}$ $\ln\left[\frac{f}{T^2}\right] = \ln\left(\frac{A^* R}{\beta E}\right) - \frac{E}{R}\frac{1}{T}$; (when $RT << E$)	**(18)**

TABLE 2

Summary of differential methods

DIFFERENTIAL METHODS		Eq.
Classical	$\ln\left[\frac{\left(\frac{df}{dT}\right)}{(1-f)^n}\right] = \ln\left(\frac{A^*}{\beta}\right) - \frac{E}{R}\frac{1}{T}$	(19)
Multiple linear regression (MLR)	$\ln\left(\frac{df}{dT}\right) = \ln\left(\frac{A^*}{\beta}\right) + n\ln(1-f) - \frac{E}{R}\frac{1}{T}$	(20)
Freeman & Carroll (1958)	$\frac{\Delta\ln\left(\frac{df}{dT}\right)}{\Delta\ln(1-f)} = n - \frac{E}{R}\frac{\Delta\left(\frac{1}{T}\right)}{\Delta\ln(1-f)}$	(21)
Vachusca & Voboril (1971)	$\frac{T^2\left(\frac{d^2f}{dT^2}\right)}{\left(\frac{df}{dT}\right)} = \frac{E}{R} - n\frac{T^2\left(\frac{df}{dT}\right)}{(1-f)}$	(22)

derivative at maximum rate of decomposition are not generally known and must be estimated graphically from TG data. Thus, eqn. (13) is useful to obtain an approximate value of the activation energy. This estimate can also serve as the initial value in iterative calculations leading to the determination of activation energy through the general analytical solution.

We have made an exhaustive revision of the different methods reported in the literature. Tables 1–3 summarize integral [16–19], differential [20, 21] and special methods [22–25], respectively. Special methods are those that cannot be classified as integral or differential methods, and they are generally based on particular couples of experimental data or they need data previously evaluated from graphical plots. The equations shown in these tables are in the form used for regression analysis. When applying integral methods, the values of order of reaction have to be assumed ($n = 0$, 1/2, 1, 3/2, 2). The best order is chosen by means of analysis of variance (ANOVA).

EXPERIMENTAL

Samples were obtained from Scientific Polymer Products (anionic preparation and polydispersity below 1.06). The substance used in this study was a white powder having a molecular weight of $M_w = 7800\ \mathrm{g\ mol^{-1}}$. The thermal decomposition of the polystyrene samples was carried out in a thermal analyzer (Netzsch, Gerätebau Model STA 409). The operating conditions were the following: heating rate, 0.50–11.50 K min^{-1} and sample weight, 6.0–6.7 mg. Degradations were conducted at atmospheric pressure and gases produced by decomposition were swept out by a flow of air at 100 ml min^{-1}.

TABLE 3

Summary of special methods

SPECIAL METHODS		Eq.
Reich (1964)	$E = \dfrac{R \ln\left[\dfrac{\beta_2}{\beta_1}\left(\dfrac{T_1}{T_2}\right)^2\right]}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$ T_1 and T_2 are measured at the same conversion value	**(23)**
Friedman (1969)	$n = \dfrac{\ln \dfrac{(df/dT)_m}{(df/dT)}}{\dfrac{T_m (T_m - T)\left(\dfrac{df}{dT}\right)_m}{T(1 - f_m)} - \ln\left(\dfrac{1-f}{1-f_m}\right)}$ $\dfrac{E}{R} = \dfrac{n T_m^2 \left(\dfrac{df}{dT}\right)_m}{1 - f_m}$ $A = \dfrac{\beta\left(\dfrac{df}{dT}\right)_m}{(1 - f_m)^n} \exp\left(\dfrac{E}{R T_m}\right)$	**(24)**
Reich & Stivala (1978)	$\ln\left[\dfrac{1 - (1 - f_1)^{1-n}}{1 - (1 - f_2)^{1-n}}\left(\dfrac{T_2}{T_1}\right)^2\right] = \dfrac{E}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right);\ n \neq 1$ $\ln\left[\dfrac{\ln(1 - f_1)}{\ln(1 - f_2)}\left(\dfrac{T_2}{T_1}\right)^2\right] = \dfrac{E}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right);\ n = 1$ $A = \dfrac{\beta E K}{(1 - n) R};\ n \neq 1$ where ln K is the intercept of the line $\ln\left[\dfrac{1 - (1 - f)^{1-n}}{T^2}\right]$ vs $\dfrac{1}{T}$	**(25)**
Popescu & Segal (1983)	$E = R \dfrac{T_{oi} T_{oj}}{T_{oj} - T_{oi}} \ln\left[\left(\dfrac{\Delta T_i}{\Delta T_j}\right)^2 \dfrac{\beta_j}{\beta_i}\right]$ $\Delta T = T_1 - T_o$ T_O and T_1 are characteristic temperatures $n = \dfrac{E}{R}\left(\dfrac{T_1 - T_m}{T_m^2}\right)$ $A = \dfrac{\beta E}{R (\Delta T)^2} \exp\left(\dfrac{E}{R T_o}\right)$	**(26)**

RESULTS AND DISCUSSION

We have analyzed the effect of truncating, at various levels, the series

$$S = \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i-1} \tag{14}$$

When the series is truncated at $i = 1$, the sum becomes equal to 1 and when truncated at $i = 2$ the sum is then equal to $S = 1 - 2RT/E$. It should be noted that this case corresponds to the equation proposed by Coats and Redfern (1964) [15]. In order to study the effect of truncation ($i = 1$ or $i = 2$), the relative error due to this approximation was calculated according to the equation

$$\varepsilon\,(\%) = \frac{S\,(i=\infty) - S\,(i=1 \text{ or } i=2)}{S\,(i=\infty)}\,100 \qquad (15)$$

As expected, the relative error is much greater when we truncate at $i = 1$ than for $i = 2$ (Fig. 1). Furthermore, we note an increase in the relative error when the temperature increases or when the activation energy decreases. This means that when thermal energy (RT) becomes important compared to the activation energy (E), the error due to the truncation

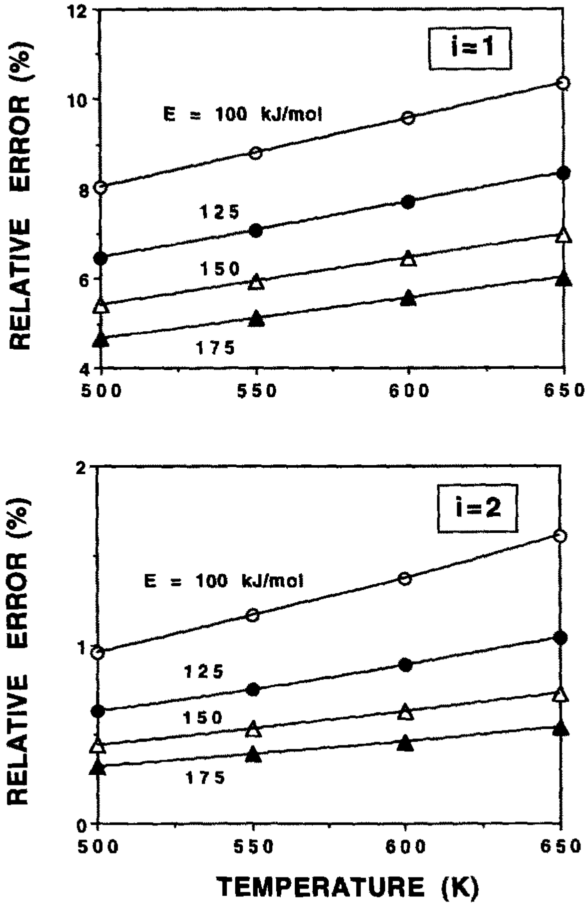

Fig. 1. Variation of relative errors with temperature for various arbitrary activation energies when truncating, at the first ($i = 1$) or second ($i = 2$) terms, the series $\sum_{i=1}^{\infty} (-1)^{i+1} i!\,(RT/E)^{i-1}$.

TABLE 4

Comparison of kinetic parameters obtained by means of the general analytical equation and various representative methods

		REACTION ORDER	ACTIVATION ENERGY (kJ/mol)	PRE-EXPONENTIAL FACTOR (s^{-1})	CONVERSION RANGE	REGRESSION		PROCEDURAL FACTORS
						NO. OF POINTS	r^2	
INTEGRAL METHODS	ANALYTICAL SOLUTION i = 1 i = 2 i —> ∞	1 (best value according to ANOVA)	 129.9 ± 0.3 130.3 ± 0.3 130.1 ± 0.3	 2.16×10^8 2.52×10^8 2.42×10^8	0.025 - 0.85	22	 0.999 0.999 0.999	$w_o = 6.2$ mg β = 1.0 K/min
	van Krevelen et al. (1951)	1 (assumed)	140.4 ± 0.4	2.01×10^9	0.025 - 0.85	22	0.999	$w_o = 6.2$ mg β = 1.0 K/min
	Kissinger (1957)	1 (assumed)	102.4 ± 11.9	1.63×10^{10}	$f_m = 0.606$	4	0.991	$w_o = 6.0 - 6.7$ mg β = 0.5 - 11.5 K/min
	Horowitz& Metzger (1963)	1 (assumed)	151.6 ± 0.7	2.07×10^{10}	0.025 - 0.85	22	0.998	$w_o = 6.2$ mg β = 1.0 K/min
	Coats & Redfern (1965)	0 (mathematical condition)	121.7 ± 2.0	3.01×10^7	0.025 - 0.32	9	0.997	$w_o = 6.2$ mg β = 1.0 K/min
DIFFERENTIAL METHODS	Classical	1 (assumed)	125.6 ± 1.3	9.38×10^7	0.04 - 0.83	21	0.990	$w_o = 6.2$ mg β = = 1.0 K/min
	Multiple linear regression	1.09 ± 0.04	131.4 ± 2.9	3.34×10^8	0.04 - 0.83	21	0.972	$w_o = 6.2$ mg β = 1.0 K/min
	Freeman & Carroll (1958)	1.26 ± 0.15	142.8 ± 5.2	——	0.04 - 0.83	19	0.914	$w_o = 6.2$ mg β = 1.0 K/min
	Vachusca & Voboril (1971)	1.22 ± 0.10	141.8 ± 10.4	——	0.06 - 0.78	19	0.690	$w_o = 6.2$ mg β = 1.0 K/min
SPECIAL METHODS	Reich (1964)	no reaction order is required	106.4 ± 19.7	——	$f_m = 0.606$	6	No regression	$w_o = 6.0 - 6.7$ mg β = 0.5 - 11.5 K/min
	Friedman (1969)	1.01 ± 0.08	139.9 ± 11.2	1.79×10^9	0.04 - 0.53	13	No regression	$w_o = 6.2$ mg β = 1.0 K/min
	Reich & Stivala (1978)	0.96 ± 0.15	128.0 ± 4.4	1.62×10^8	0.09 - 0.81	3 straight lines with 6 pts each	1.000 0.997 0.980	$w_o = 6.2$ mg β = 1.0 K/min
	Popescu & Segal (1983)	0.81 ± 0.02	105.2 ± 19.4	$(5.12 \pm 0.52) \times 10^8$	conversion within ΔT	6	No regression	$w_o = 6.0 - 6.7$ mg β = 0.5 - 11.5 K/min

becomes quite significant. However, this error is not nearly of the same magnitude when we determine actication energy, as evidenced in Table 4. It is apparent that for the thermal decomposition of polystyrene, at the indicated operating conditions, truncation at $i = 2$ is entirely justified. Care must however be taken when thermal decomposition is performed at high temperatures and/or subjected to low activation barrier. It is important to note that only first-order kinetics have been considered. Reproducibility trials have shown that the maximum error committed between two thermograms is less than 0.5%.

Figure 2 illustrates the thermal finger-prints of polystyrene. The conversion curves as well as the two conversion derivatives were obtained from eqns. (10a), (11) and (12) by using the kinetic parameters previously estimated. The conversion experimental data fit perfectly to the theoretical curve. However, a certain disparity becomes visible for the first conversion derivative and it is much more significant for the second conversion derivative. Similar disparities have been previously reported by Carrasco [26] for the thermal decomposition of calcium oxalate monohydrate. These findings indicate that the application of computing methods based on derivatives (especially the second derivative) can generate imprecise kinetic parameters, as will be discussed later.

Table 4 summarizes the results obtained by using the general analytical solution and some representative methods reported in the literature. Confidence intervals were calculated at 95% confidence level.

The application of the general analytical solution resulted in the following kinetic parameters for the thermal decomposition of polystyrene: $E = 130.1 \pm 0.3$ kJ mol^{-1} and $A^* = 2.42 \times 10^8$ s^{-1}. When truncating the series at $i = 2$, the relative errors involved were as low as 0.1% for the activation energy and 4% for the pre-exponential factor.

The method of van Krevelen et al. involves two important approximations.

(1) T_m (temperature at maximum rate of decomposition) must be evaluated by a graphical procedure from the $\Delta f/\Delta T$ versus T plot before applying regression analysis. It was demonstrated that the value of the activation energy could be influenced by T_m, if the latter is not adequately chosen.

(2) The authors approximate the exponential integral by making the substitution

$$\exp\left(-\frac{E}{RT}\right) \approx \left(0.368\frac{T}{T_m}\right)^{E/RT_m} \tag{16}$$

This is almost true when the reaction proceeds entirely in the range $0.9T_m < T < 1.1T_m$.

Figure 3 shows the relative error made when applying this approximation. It is clear that the validity of this assumption is not correct at low

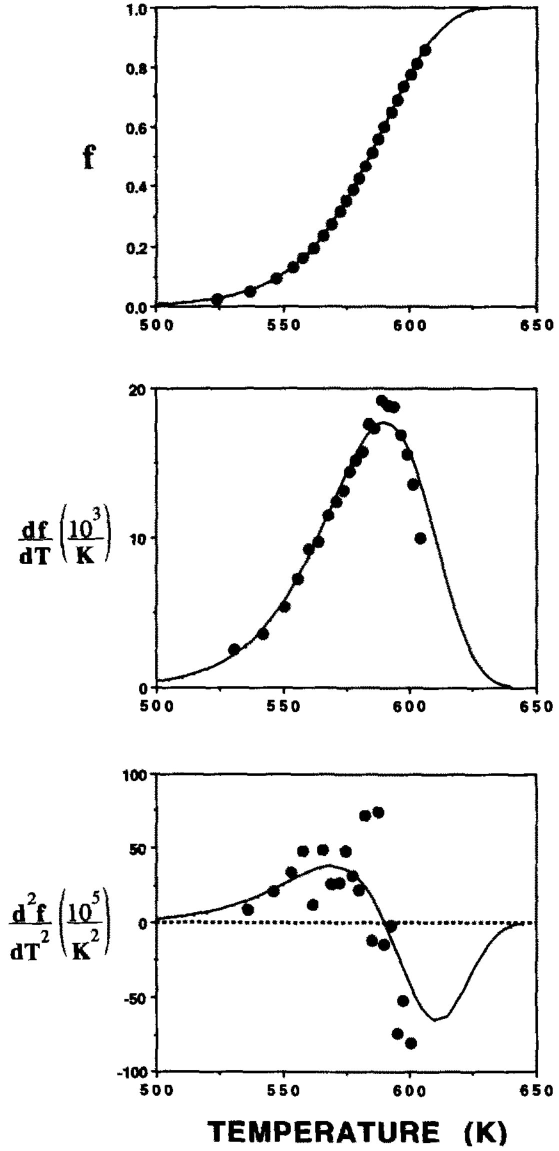

Fig. 2. Variation of conversion, first conversion derivative and second conversion derivative as a function of temperature. Curves were obtained from eqns. (10a), (11) and (12) by taking the kinetic parameters previously evaluated by regression analysis.

temperatures. These reasons can explain why the activation energy obtained is 8% higher than that calculated by using the analytical solution.

The Kissinger method is based on the mathematical condition $d^2f/dT^2 = 0$, i.e. conditions giving a maximum rate of decomposition. The equation developed by Kissinger is exact. However, it is necessary to perform various TG experiments at different heating rates. In order to

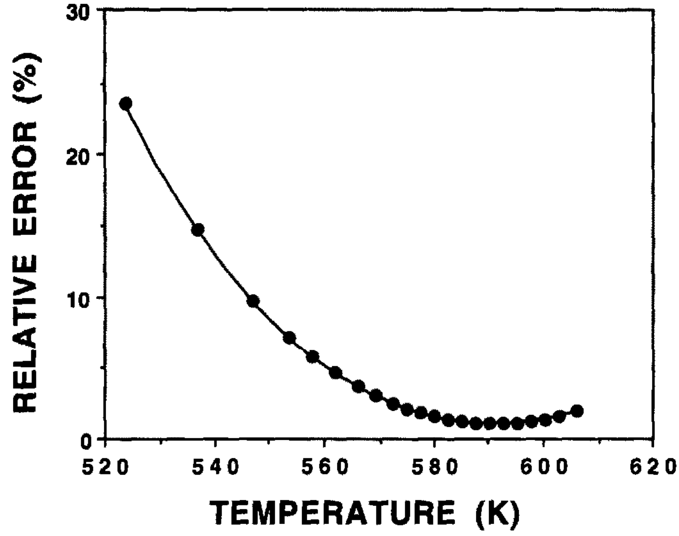

Fig. 3. Variation of relative errors as a function of temperature when considering the approximation, as proposed by van Krevelen et al. $\exp(-E/RT) = (0.368T/T_m)^{E/RT_m}$.

minimize heat transfer and mass transfer limitations, we performed TG runs with approximately the same sample weight (6.0–6.7 mg). The heating rates used were 0.5, 1.0, 5.4 and 11.5 K min^{-1}. Kissinger's method is based on T_m values, which must be calculated from graphical plots before applying regression analysis. Moreover, because T_m is the independent variable, this can introduce additional errors as compared to the van Krevelen et al. method. Furthermore, the Kissinger method can be applied only if the reaction mechanism remains unchanged when modifying the heating rate. The activation energy obtained by the Kissinger method is 20% lower than that calculated by the general analytical solution. On the other hand, the confidence interval (11.9 kJ mol^{-1}) is quite high, probably due to the uncertainty in calculating the T_m values from graphical plots.

Horowitz and Metzger derived an approximate integral method similar to, but even simpler than, that proposed by van Krevelen et al. Moreover, they stated that in many cases it is possible to determine the reaction order virtually by inspection of the conversion value at the maximum rate of decomposition: f_m is equal to 1, 0.75, 0.632, 0.556 and 0.5 for $n = 0$, 1/2, 1, 3/2 and 2 respectively. Again, this method is subject to intrinsic errors due to the graphical evaluation of T_s. The activation energy calculated by the method of Horowitz and Metzger is 16% higher than that obtained by the general analytical solution. However, accuracy is satisfactory as shown by the narrow confidence interval (0.7 kJ mol^{-1}).

Coats and Redfern expanded (before integrating) the conversion-containing integral term (eqn. (6)) in a series and they stated that quadratic and high-order terms may be neglected at low conversion. The mathematical assumption corresponds to a zero-order reaction. The activation energy obtained by the method of Coats and Redfern is only 6% lower than that evaluated by the general analytical solution for $n = 1$, thus indicating that at low conversion levels, there is no significant difference between zero-order and first-order kinetics.

Differential methods are based on either the first or the second conversion derivative. The classical differential method requires the assumption of reaction order before applying simple linear regression analysis. However, it is possible to determine the reaction order from the differential equation by separating the independent variables into two terms, one containing a function of conversion ($\ln(1-f)$) and the other a function of temperature ($1/T$) (see Table 2 and eqn. (20)). It is then possible to apply a multiple linear regression analysis, where the slope of the conversion-containing term yields the reaction order. We obtained a reaction order of 1.09 for the thermal decomposition of polystyrene which is quite close to that found by ANOVA (first-order kinetics) when using the general analytical solution. The activation energies estimated by the classical and multiple linear regression (MLR) differential methods were very close to that obtained by the general analytical solution, but the confidence intervals were much larger.

The Freeman and Carroll, and Vachusca and Voboril methods have the advantage that they calculate the reaction order, unlike the integral methods. Both methods yielded approximately the same reaction order as well as similar activation energies, the latter being approximately 10% greater than that obtained by the general analytical solution. The confidence interval as well as the regression coefficient indicate that both of these methods possess imprecisions. The Freeman and Carroll method, based on the first conversion derivative, revealed that 91% of the experimental points can be explained by the correlation; the activation energy had a confidence interval of ±5.2 kJ mol^{-1}. However, the Vachusca and Voboril method gave a poor data fitting: only 69% of the experimental points could be explained by the correlation, which is unacceptable. The confidence interval for the activation energy was as high as 10 kJ mol^{-1}. The imprecision of these two methods is, no doubt, because both first and second conversion derivatives are calculated from differences between two discrete experimental points. Neither differential method allows for the calculation of the pre-exponential factor from the regression equation. Figure 4 provides a comparison between experimental data and predicted values. The latter were evaluated by means of mathematical equations resulting from the general analytical solution (eqns. (10a), (11) and (12)). The kinetic parameters used are those previously obtained by linear regression. It is obvious that experimental conversion and predicted conversion are in very good agreement because

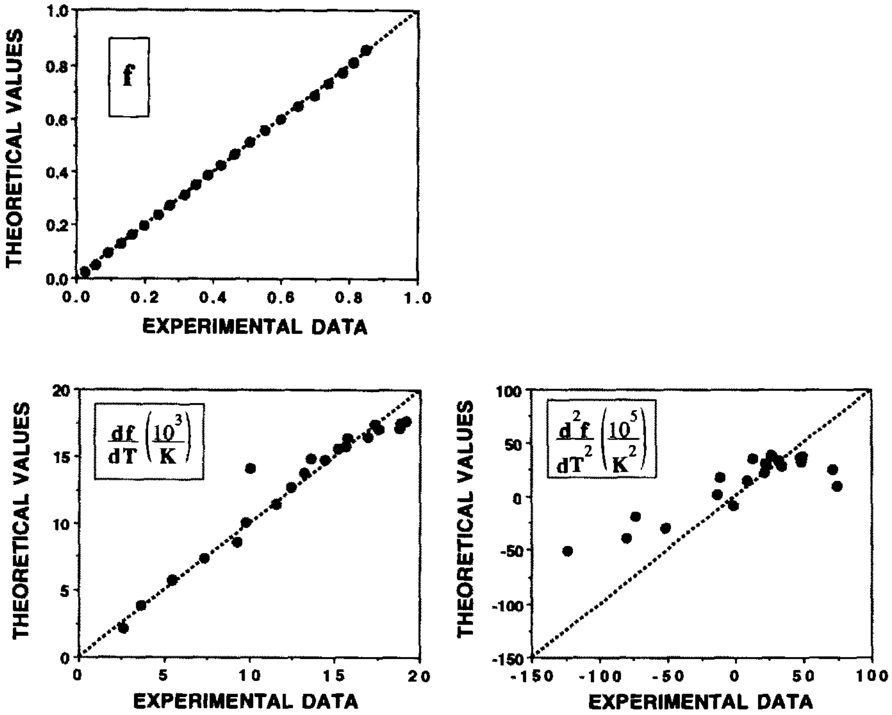

Fig. 4. Comparison between predicted values and experimental data for conversion, first conversion derivative and second conversion derivative. Predicted values were calculated from eqns. (10a), (11) and (12) by taking the kinetic parameters previously evaluated by regression analysis.

points fall on the diagonal line. The first conversion derivative graph shows, however, that there exists some divergence between theoretical results and experimental data. This can be caused by the approximation made when the derivative is calculated by difference between two adjacent experimental points, i.e. $\mathrm{d}f/\mathrm{d}T \approx \Delta f/\Delta T$. The divergence is, however, enormous when comparing theoretical results and experimental data for the second conversion derivative. We believe that this is due to the incorrect computing of experimental second-conversion derivatives, which have to be calculated by means of the approximation $\mathrm{d}^2f/\mathrm{d}T^2 = \Delta^2 f/\Delta T^2$. This divergence can explain the low accuracy of methods based on second conversion derivatives such as the Vachusca and Voboril method.

The special methods were classified as a separate category because the determination of the kinetic parameters is obtained from two experimental points. This operation was repeated on several occasions using different sets of two points, in order to obtain an average value of the kinetic parameters.

The Reich method requires only two points in order to determine the activation energy $((\beta_1, T_1), (\beta_2, T_2))$ where TG curves are obtained for different heating rates; T_1 and T_2 are measured at the same conversion value. This method presents the following advantages: (i) no prior knowledge of the reaction order is necessary; (ii) it consumes relatively little time; (iii) no curve fitting or laborious plots are required. However, this method is very subjective because the evaluation of the activation energy is achieved for a fixed conversion level. Furthermore, if the reaction mechanism varies with different heating rates, then the calculated activation energy will be completely false. In order to calculate the activation energy according to Reich's method, we chose as conversion value, the conversion at the maximum rate of decomposition because it is approximately constant ($f_m = 0.606$) for the various heating rates investigated (0.5, 1.0, 5.4 and 11.5 K min^{-1}). The calculated activation energy was 18% less than that obtained using the general analytical solution. The confidence interval for the activation energy (≈20 kJ mol^{-1}) was too high to be acceptable.

The Friedman method is based on two experimental points at the same heating rate. One of these points corresponds to the maximum rate of decomposition (T_m, f_m and $(\mathrm{d}f/\mathrm{d}T)_m$), a condition which must be evaluated from graphical drawings. The reaction order is calculated by averaging the different n's obtained at each temperature of the TG curve. Once n is calculated, the computation of E and A^* follows readily. This method is very sensitive to parameters at maximum rates of decomposition. Values of f and T had to be taken at conversions lower than f_m because the reaction order calculated with values near the maximum rate of decomposition conditions were often meaningless. However, when conversion was taken at values higher than f_m, n increased continuously. Despite the restrictions and limitations of Friedman's method, the activation energy calculated in this way is close (7% higher) to that calculated using the general analytical solution. However, the confidence interval is relatively high (11 kJ mol^{-1}).

Reich and Stivala proposed their method as follows: values of activation energy, corresponding to various arbitrarily selected values of n, are calculated for each of two given pairs of f and T. The resulting arbitrary values of E are plotted versus the corresponding n values, and the region bounded by intersecting curves is used to estimate simultaneously the actual values of E and n. We have slightly modified the solution method. For each pair of conversion values, we have correlated, through linear regression, the activation energy as a function of the reaction order. The equations obtained were

$$E\ (\text{kJ mol}^{-1}) = 116.1 + 13.0n \quad (f = 0.09 \text{ and } 0.27)$$

$$E\ (\text{kJ mol}^{-1}) = 97.6 + 31.1n \quad (f = 0.27 \text{ and } 0.46)$$

$$E\ (\text{kJ mol}^{-1}) = 37.6 + 96.6n \quad (f = 0.70 \text{ and } 0.81)$$

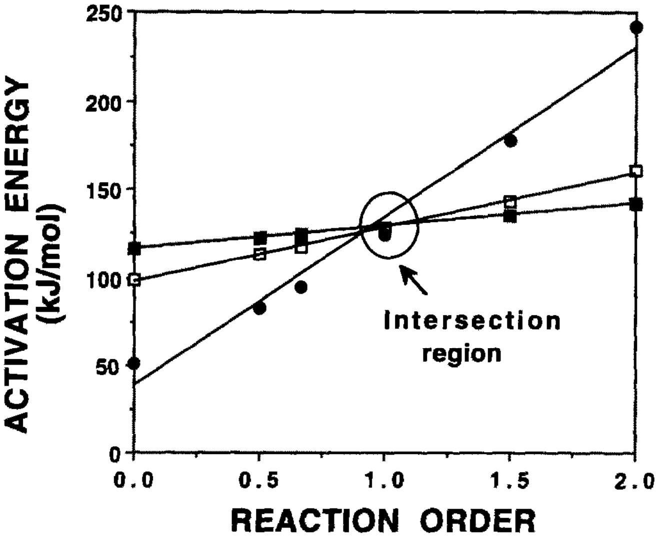

Fig. 5. Graphical method used by Reich and Stivala to calculate simultaneously the activation energy and reaction order.

Using two equations simultaneously, it is possible to obtain three sets of values for *E* and *n*, which permit of the calculation of an average value for *E* and *n* as well as the confidence interval, which was impossible using the graphical method. As shown in Fig. 5 (original graphical method proposed by Reich and Stivala), the intersection region provides a reaction order close to 1, which corresponds to the value obtained by solving the equation system (0.96 ± 0.15). This value is similar to that found by ANOVA when using the general analytical solution. The activation energy obtained by the Reich and Stivala method is only 2% lower than that corresponding to the general analytical solution.

The method of Popescu and Segal is based on two sets of experimental data at different heating rates. Moreover, this method requires the previous determination of temperature at the maximum rate of decomposition as well as two characteristic temperatures. The equation proposed by Popescu and Segal is based on the mathematical assumption $df/dT \approx$ constant. This is physically impossible because the first conversion derivative varies with temperature (or conversion). Thus, we believe that this hypothesis is seriously questionable. Moreover, this method is only valid when kinetic parameters are not affected by temperature. The application of the method of Popescu and Segal to our TG data led to an activation energy 20% lower than that obtained by the general analytical solution and the confidence interval was too large to be acceptable (± 19 kJ mol^{-1}).

Figure 6 summarizes the values of activation energy obtained (including the confidence interval) by the general analytical solution as well as by the

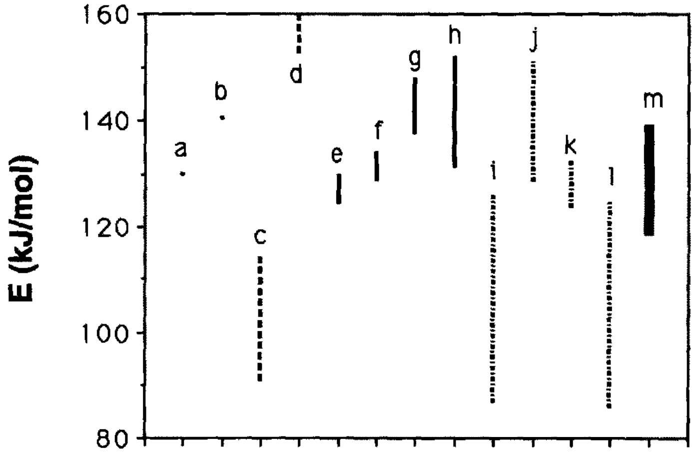

Fig. 6. Confidence intervals for activation energy by using various computing methods. Integral methods: a, general analytical solution; b, van Krevelen et al. (1951); c, Kissinger (1957); d, Horowitz and Metzger (1963). Differential methods: e, classical differential method; f, multiple linear regression differential method; g, Freeman and Carroll (1958); h, Vachusca and Voboril (1972). Special methods: i, Reich (1964); j, Friedman (1969); k, Reich and Stivala (1978); l, Popescu and Segal (1983). All methods: m, average of the 12 previous methods.

various representative computational methods reported in the literature. This graphic allows us to make the following affirmations.

(1) The activation energy calculated varies considerably depending on the calculation method used.

(2) None of the types of method (integral, differential or special) defines a specific zone for the activation energy values. Specifically, integral or special methods give values for activation energies which may be sometimes low and sometimes high, in both cases.

(3) Special methods are generally not accurate, i.e. they have too large a confidence interval.

(4) The most accurate methods, i.e. those having the narrowest confidence interval, are the general analytical solution, the van Krevelen et al. method, the classical differential method and the multiple linear regression (MLR) differential method.

Line m is the mean activation energy obtained by averaging the mean activation energies calculated by using the twelve methods considered in this work. This value is quite close to that found using the general analytical solution. However, the confidence interval is larger because of the significant differences between the values obtained with the different computation methods.

CONCLUSIONS

Dynamic thermogravimetry, with linear temperature increase, is a useful tool to study the degradation of polymeric materials, to elucidate the reaction order and also to evaluate other kinetic parameters such as activation energy and frequency factor. Even if the overall process has no real significance with regard to the reaction mechanism, the apparent kinetic parameters, i.e. the Arrhenius doublet, are useful as a means of quantifying the rate of reaction and for design purposes.

This paper shows that it is possible to develop a general analytical solution, providing a relationship between conversion and temperature for thermal decomposition reactions carried out by means of dynamic thermogravimetry. This analytical solution was obtained by integrating the rate equation by parts, resulting in a recurrent series.

The application of the general analytical solution resulted in the following kinetic parameters for the thermal decomposition of polystyrene: $E = 130.1 \pm 0.3$ kJ mol^{-1} and $A^* = 2.42 \times 10^8$ s^{-1}. When truncating the series at $i = 2$, the relative errors involved were as low as 0.1% for the activation energy and 4% for the pre-exponential factor. Because the thermal energy (RT) is not significant as compared to the activation energy, the truncation is entirely justified.

The determination of kinetic parameters can be achieved by means of established methods. We made an exhaustive revision of these methods, which can be classified into three categories. We analyzed the results obtained by using the following methods: (1) integral methods: analytical solution (this work), van Krevelen et al. (1951), Kissinger (1957), Horowitz and Metzger (1963) and Coats and Redfern (1965); (2) differential methods: classical, multiple linear regression, Freeman and Carroll (1958) and Vachusca and Voboril (1971); (3) special methods: Reich (1964), Friedman (1969), Reich and Stivala (1978) and Popescu and Segal (1983). Linear regression analysis was used to evaluate mean values of kinetic parameters as well as their confidence intervals. The activation energy calculated by using these different methods varied considerably: 102–152 kJ mol^{-1} (integral methods), 126–143 kJ mol^{-1} (differential methods) and 106–140 kJ mol^{-1} (special methods). The accuracy was also variable depending on the method used. For integral and differential methods, the confidence intervals were lower than about 10 kJ mol^{-1}. The most accurate methods, i.e. those having the narrowest confidence interval, were the general analytical solution, the van Krevelen et al. method, the classical differential method and the multiple linear regression differential method. In general, special methods cannot be considered accurate because the confidence interval was often between 10 and 20 kJ mol^{-1}. It is clear that the accuracy of the computing methods as well as the values of the kinetic parameters calculated may be explained by considering the simplifications inherent in each of these methods in comparison with the general analytical solution.

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