

Multistable thermal decomposition processes are calculated from thermogravimetric experimental data by successive elimination of stages. Results are shown of applying this method to the study of polymer materials.

A constituent part of research pertaining to heat- and mass-transfer processes during interaction of materials and hot gas streams is the study of the kinetics of thermal decomposition processes in composite polymers and their components. Such studies are obviously of not only scientific but also practical value: the data obtained are needed firstly in the search for new materials and secondly for the construction of theoretical models describing the decomposition of these materials in hot gas streams.

In recent years polymer research has been more widely aided by dynamic thermogravimetry, an experimental method based on recording the weight of a material as a function of the temperature (time) while the material is heated in a given medium at a controllable rate. This method yields not only the quantitative characteristics of the thermal decomposition process (temperatures at which the process begins and ends, temperature dependence of the decomposition level, etc.) and their dependence on various factors such as the heating rate and the chemical composition of the ambient medium but also a description of the process in the form of kinetic equations with parameters determined on the basis of experimental data.

It is not very difficult to determine the values of the kinetic parameters for simple single-stage processes where the rate of change of weight can be described by the equation

$$-\frac{dW}{d\tau} = Ze^{-E/RT}W^n, \quad (1)$$

with $W = (w - w_f)/(w_0 - w_f)$ denoting the relative weight of the not yet decomposed active material. Corresponding procedures have been extensively described in [1-4]. Most reliable results are obtained by applying the method of least squares to the logarithmic version of Eq. (1), which is obviously linear with respect to the sought parameters E , n , and $\ln Z$. Integral thermogravimetric S-curves of simple form and single peaks on differential curves correspond to such processes.

A much more difficult problem is determining the values of the kinetic parameters for complex processes which consists of two or more overlapping reactions (stages). Often the multistage character of a process under study is revealed by the intricate form of the thermogravimetric curves, but even when they may be relatively simple in form in cases where the temperature ranges of individual stages overlap appreciably it is not possible to evaluate them by conventional methods.

Therefore, we will analyze the kinetics of the process on the basis of experimental data according to the following procedure. For a preliminary estimate of the process staging and a rough estimate of the effective values of the kinetic parameters we use the characteristics of the maxima on the differential thermogravimetric curves. Differentiating Eq. (1) with respect to time and letting $(d^2W/d\tau^2)_M = 0$ at the point of maximum, then using the Horowitz-Metzger relation [5]

$$W_M = n \frac{1}{1-n}, \quad (2)$$

we obtain an equation which relates the characteristics of the maximum on the differential curve to the kinetic parameters of the process:

$$-\left(\frac{dW}{dT}\right)_M T_M^2 = \frac{E}{R} n^{1-n} = C, \quad (3)$$

where $(dW/dT)_M = (dW/d\tau)_M / (dT/d\tau)$ and C is a constant for a given process. For all independent processes obeying Eq. (1) it is obviously necessary that the experimental curves obtained at various heating rates satisfy condition (3). When this condition is not satisfied, then either the process mechanism does not correspond to Eq. (1) or the process is not a single-stage one.

When condition (3) is satisfied, then the kinetic parameters can be estimated as follows. Writing Eq. (1) in logarithmic form, with relation (2) taken into account, we obtain

$$\ln\left(-\frac{dW}{d\tau}\right)_M = \ln(Zn^{1-n}) - \frac{E}{R} \frac{1}{T_M}, \quad (4)$$

and accordingly find $\ln(Zn^{1-n})$ and E/R on the graph of $\ln(dW/d\tau)_M = f(1/T_M)$. Upon insertion of the value of E/R into Eq. (3), the latter yields the effective order n of the reaction and the parameter $\log Z = \ln(Zn^{1-n}) - \ln(n^{1-n})$.

Thus, after checking for condition (3), one finds the rough values of parameters E , n , and Z without unwieldy calculations. This preliminary estimation of the kinetic parameters greatly facilitates subsequent calculations.

When the estimates indicate that the process is a multistage one, then the analysis is continued more precisely by the method of successive elimination of stages, the basic principles of this method having been outlined in an earlier study [6]. Assuming that individual stages, each of them obeying an equation of the (1) kind, proceed independently of one another so that the resultant rate of change of weight is

$$-\frac{dw}{d\tau} = -\sum_{i=1}^m \frac{dw_i}{d\tau} = \sum_{i=1}^m Z_i' e^{-E_i/RT} w_i^{n_i}, \quad (5)$$

where $Z_i' = Z_i w_{0i}^{1-n_i}$; $\sum_{i=1}^m w_{0i} = w_0 - w_f$, $\sum_{i=1}^m w_i = w - w_f$, and assuming that at some instant of time all reactions except the last one have been completed, we can calculate the kinetic parameters of the m -th stage by any known method from the corresponding segment of the thermogravimetric curves. Then, after determining the initial weight of the material which decomposes during this stage from the integral version of Eq. (1), viz.,

$$I(w) = \frac{Z'E}{BR} p(x), \quad (6)$$

where

$$I(w) = \frac{(w_0 - w_f)^{1-n} - (w - w_f)^{1-n}}{1-n} \text{ when } n \neq 1,$$

$$I(w) = \ln \frac{w_0 - w_f}{w - w_f} \text{ when } n = 1,$$

$$p(x) = \exp(-x) x^{-1} - \int_x^\infty \exp(-x) x^{-1} dx, \quad x = \frac{E}{RT}, \quad B = \frac{dT}{d\tau},$$

and solving the forward problem (calculating the temperature dependence of $w_m(T)$ and $dw_m/d\tau(T)$), we eliminate this stage from further consideration. Now rewriting Eq. (5) as

$$-\frac{d(w-w_m)}{d\tau} = \sum_{i=1}^{m-1} Z_i' e^{-E_i/RT} w_i^{n_i}, \quad (7)$$

we proceed to determine the parameters of the $(m-1)$ -th stage, etc. The result is a mathematical description of thermogravimetric curves corresponding to multistage processes, a description which uses m sets of kinetic parameters and w_{0i} values. The criterion for correctness of these calculations is the agreement between thus calculated and experimentally determined thermogravimetric curves.

The method of successive elimination of stages has been implemented in a comprehensive

program written for a model 15 VSM-5 computer with an external memory and a "Consul" printer. An m-stage process was calculated according to the following procedure:

1. Input of starting data characterizing the conditions and the results of a thermogravimetric experiment (array of $w_i(T)$ values, heating rate, initial and final weight of the specimen).

2. Smoothing the w_i data array by a numerical method [7] according to the expression

$$w_i^* = \sum_{k=i-2}^{i+2} w_k C_k / N.$$

3. Differentiation of the w_i^* data array with respect to T by a numerical method [7] according to the expression

$$w_i^{*'} = \frac{\sum_{k=i-2}^{i+2} w_k^* C_k'}{N' \Delta T}.$$

4. Printing a $T_i, w_i^*, w_i^{*'}$ ($i = 5, \dots, (k - 4)$) table and a $w^{*'}(T)$ graph.

5. Limiting the thermogravimetric curve to a segment for calculating kinetic parameters of just the m-th stage.

6. Determination of E_m, Z_m' , and n_m from the solution to the system of normal equations, and calculation of the rms relative errors

$$\delta_1 = \frac{\delta E_m}{E_m}; \quad \delta_2 = \frac{\delta Z_m'}{Z_m'}; \quad \delta_3 = \frac{\delta n_m}{n_m}.$$

7. Calculation of the mean value w_{0m} from the just found values of the kinetic parameters.

8. Printing $E_m, \delta_1, Z_m', \delta_2, n_m, \delta_3, w_{0m}$.

9. Calculation of the thermogravimetric curves for the m-th stage, and printing a T_i, w_{im}, w_{im}' table.

10. Elimination of the m-th stage: replacement of w_i^* and $w_i^{*'}$ with the differences $w_i^* - w_{im}$ and $w_i^{*' - w_{im}'}$, respectively.

11. Reduction of m by 1 and return to step 4.

Limiting the segments of a $w^{*'}(T)$ curve for calculation of the parameters of individual stages (step 5) can be done either manually or by a program shown schematically in Fig. 1. On the differential curve is selected a segment (points N_i, \dots, N_{i+7} , at least four points) explicitly corresponding to the last stage only, whereupon to this segment are added points "above" and "below" until the relative error associated with even just one parameter begins to increase and thus the weight curve correspondingly departs from Eq. (1).

The calculation ends when the condition $S = \sum_{i=5}^{k-4} (w_i^{*'})^2 < \epsilon$ (ϵ denoting a small number) is satisfied. The last graph printed indicates the deviation of the resultant calculated $w'(T)$ curve from the experimentally determined one.

The experimental part of this study was done with a model TGS-1 Perkin-Elmer (USA) thermogravograph and an MOM system (Hungary) derivatograph. With the TGS-1 instrument it was possible to continuously record the change of weight of a specimen as a function of the temperature (time) over the 20-1000°C range at heating rates from 0.3 to 320°C/min in an active or inert atmosphere, this instrument including a very sensitive balance (up to 20 µg/division of the recorder scale, for a nominal weight of a specimen ranging from 0.5 to 10 mg) and having a short time constant so as to ensure a sufficiently accurate reading of the temperature of a specimen (with the furnace precalibrated against the magnetic transition temperatures of ferromagnetic reference standards).

Both instruments were used for studying the thermal decomposition kinetics in several polymer materials. Here we will report the results of analysis of the thermal decomposition curves for a composite material consisting of a carbon-cloth matrix and a heterocyclic binder, tested in air at a heating rate of 23°C/min. A comminuted specimen of this material weighing 28.05 mg was spread as a thin layer on the surface of a specially adapted platelike platinum crucible of the derivatograph [8].

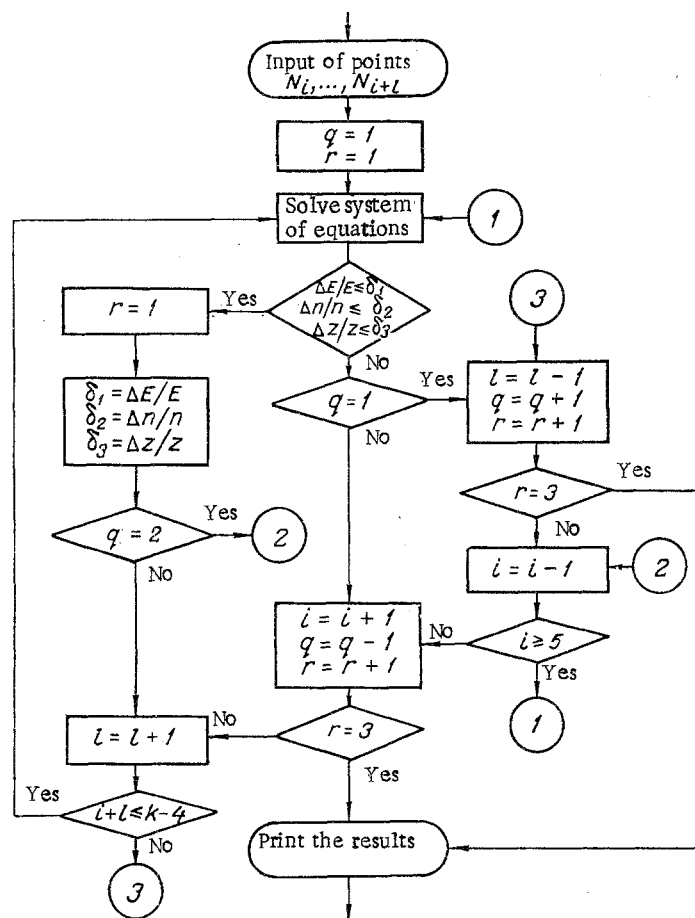


Fig. 1. Schematic block diagram of the program for limiting a segment of a thermogravimetric curve and calculation of the parameters of individual stages.

The experimentally determined curves shown in Fig. 2 have an intricate shape and, obviously, cannot be described by a single set of kinetic parameters. Using the proposed method of calculation, we have successfully identified three independent stages and for each of them determined the kinetic parameters as well as the initial weight. The results of these calculations, including the temperatures corresponding to the maximum rates of change of weight in individual stages, are given in Table 1.

The loss of weight at temperatures from 40 to 300°C, amounting to 1.06 mg (3.8%) and apparently due to removal of moisture from the uncured components, was not included in the calculations.

The graph in Fig. 2 contains calculated curves for each stage as well as the resultant calculated values of w and $dw/d\tau$. The entirely satisfactory agreement between calculated and measured thermogravimetric curves indicates that the given process can be quite accurately described by the kinetic parameters found in this way.

An analysis of the thermogravimetric curves obtained with the TGS-1 instrument for the thermal decomposition of an epoxide binder on an arbor resin base in an argon atmosphere at heating rates of 5, 20, 80, and 160°C/min (Fig. 3) has revealed that this material loses most

TABLE 1. Results of Calculations Pertaining to the Thermal Decomposition Process in the Carbon-Plastic Material

Stage	w_0 , mg(%)	t_{\max} , °C	E , kJ/mole	z , sec ⁻¹	n
1	2,80 (10)	485	41,3	2,7	0,41
2	13,04 (46,5)	615	164,1	5,0·10 ⁷	1,48
3	11,15 (39,7)	700	219,0	5,7·10 ⁸	0,98

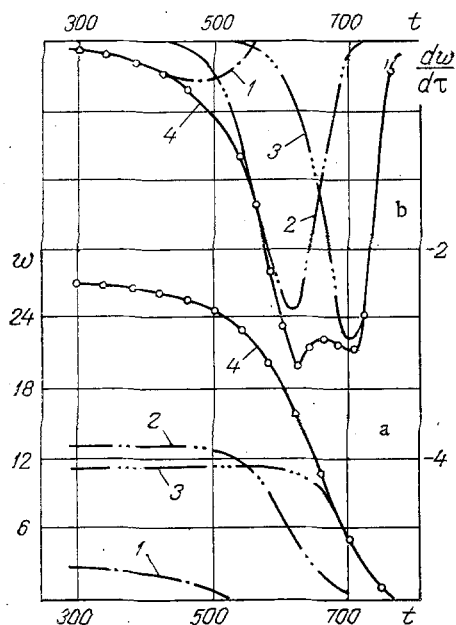


Fig. 2

Fig. 2. Integral (a) and differential (b) thermogravimetric curves for the carbon-plastic material: 1, 2, 3) calculated curves for the first stage, the second stage, and the third stage, respectively; 4) experimentally determined curves; dots indicate the calculated values corresponding to the resultant process; w (mg), dw/dt (mg/min), t ($^{\circ}\text{C}$).

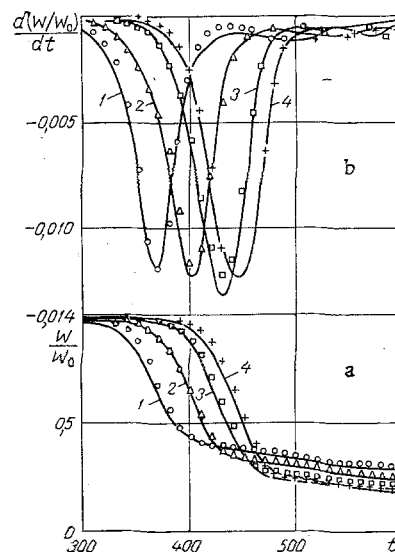


Fig. 3

Fig. 3. Integral (a) and differential (b) thermogravimetric curves for the epoxide binder at heating rates: 1) $5^{\circ}\text{C}/\text{min}$, 2) $20^{\circ}\text{C}/\text{min}$, 3) $80^{\circ}\text{C}/\text{min}$, 4) $160^{\circ}\text{C}/\text{min}$; dots indicate calculated values; $d(W/W_0)/dt$ ($1/^{\circ}\text{C}$).

of its weight, 60-75% of the weight of a specimen depending on the heating rate, within the $300\text{-}500^{\circ}\text{C}$ temperature range. After this process has been completed, loss of weight continues slowly until the temperature reaches $600\text{-}650^{\circ}\text{C}$ and amounts to 5-11% during this stage. Checking for condition (3) within the main peak, with the corresponding change in Δw_f taken into account, has revealed that the quantity $C = (-dw/dT)_{M} T_M^2$ varies appreciably with the heating rate. An attempt to determine the activation energy according to Eq. (4) has, moreover, yielded a negative value for E . This indicates that the process corresponding to the peak on the differential curve cannot be regarded as a single independent reaction which obeys Eq. (1).

An evaluation of the experimentally obtained curves by successive elimination of stages has, after calculation of the slow last stage, revealed a 2-stage nature of the main process and thus produced a mathematical description of the thermogravimetric curves by three sets of kinetic parameters and w_{0i} values. Furthermore, for the purpose of comparison with available published data, approximate resultant values of the kinetic parameters have been obtained pertaining to the indivisible main peak.

In all cases the kinetic parameters found for each stage and the fraction of material participating in it depended on the heating rate. This indicates that the real mechanism of thermal decomposition of this material does not correspond to Eq. (5) and that the method of successive elimination of stages yields in this case only formal values of the kinetic parameters.

The mechanism of thermal decomposition of epoxide resins has not yet been sufficiently well explored, despite the huge number of studies made so far. It is known that this process occurs (at least partially) according to the mechanism of free radicals [9, 10]. During its earlier stages in addition to dehydration, it seems, some role may be played by evaporation of the hardeners and by isomerization with subsequent breakaway of free epoxide groups at $300\text{-}400^{\circ}\text{C}$ [11]. Thus, obviously, the real mechanism of thermal decomposition of an epoxide

TABLE 2. Effective Values of the Kinetic Parameters and Initial Relative Weight for the Second Stage of Thermal Decomposition of an Epoxide Binder, as Functions of the Heating Rate

$B, ^\circ\text{C}/\text{min}$	w_{02}/w_0	$E, \text{kJ}/\text{mole}$	Z, sec^{-1}	n
0	0,706	76,1	$2,8 \cdot 10^9$	1,42
5	0,621	239,5	$2,0 \cdot 10^{17}$	1,74
20	0,557	306,9	$5,8 \cdot 10^{21}$	1,78
80	0,539	327,7	$14,0 \cdot 10^{22}$	1,79
160	0,536	331,3	$2,4 \cdot 10^{23}$	1,79
100000	0,533	335,1	$4,3 \cdot 10^{23}$	1,80

binder is much more complex than that of a process described by Eq. (5). A rather complete description of the entire process is possible, nevertheless, if the dependences of the parameters (found by our method for the individual stages) will be expressed in a quantitative form. With such relations available, one can try to extrapolate given data to other heating rates not included in the experiment.

It has been found through experience with these calculations that it is most expedient in such cases to seek the dependence of w_0 and E on the heating rate in the form

$$Y = g + fh^{-1/B}, \quad (8)$$

where Y denotes $\ln w_0$ or E , where $B = dT/d\tau$, and where g, f, h are empirical constants. An equation of this kind renders a sufficiently accurate description of how the values of w_0 and E change with the heating rate; it also satisfies the constraint that variables w_0 and E reach finite limits as $B \rightarrow 0$ and $B \rightarrow \infty$. Using along with Eq. (8) also the well-known compensatory relation

$$\ln Z = a + bE, \quad (9)$$

which is very accurately satisfied for each stage, despite the inevitable spread of E and $\ln Z$ values obtained for each stage, and furthermore using the empirically established relation between all three parameters

$$E = c + d(n + 1)\ln Z, \quad (10)$$

it is possible to determine the effective values of the kinetic parameters and the initial weight for each stage at any heating rate within the given range under study.

The values of the kinetic parameters and the initial weight obtained for the most sharply distinct stage of thermal decomposition of an epoxide binder at various heating rates are given in Table 2, along with values obtained by extrapolation to a zero heating rate (isothermal process) and to 100,000°C/min.

A comparison of the resultant curves calculated on the basis of empirical relations (8)-(10) for each of the three stages and the curves obtained experimentally indicates that the parameters of the given process are accurately described by these relations within the given range of heating rates. Curves calculated on the basis of analogous relations for the indivisible main peak agree with experimentally obtained curves far less closely.

In the published literature there are given data on the kinetic parameters of thermal decomposition of epoxide resins under various experimental conditions. Values of E range from 109 to 213 kJ/mole and values of n range from 0 to 1.1 [9, 12-14]. In all cases the process has been regarded as a single-stage one which obeys Eq. (1), the last stage being disregarded. These data can be roughly compared with our data in this study pertaining to an indivisible main peak (resultant of first and second stage): $E = 148.6$ - 218.4 kJ/mole and $n = 0.8$ - 1.4 depending on the heating rate. For an epoxide resin cured with maleic anhydride H. S. Anderson [15] quotes $E = 142$ kJ/mole, $n = 1.07$, and $Z = 6.2 \cdot 10^9 \text{ sec}^{-1}$ obtained for $B = 1^\circ\text{C}/\text{min}$ and $w_0 = 10$ mg, which agree closely with our values $E = 148.6$ kJ/mole, $n = 0.8$, and $Z = 4.0 \cdot 10^9 \text{ sec}^{-1}$ for $B = 5^\circ\text{C}/\text{min}$ and $w_0 \approx 1$ mg.

The proposed calculation procedure thus makes it possible to reveal the multistage nature of a process even when individual stages have partially or totally overlapping temperature ranges, to determine the effective values of the kinetic parameters for each stage and the fraction of material participating in it, and to rather completely describe the trends of thermal decomposition processes in materials over a wide range of heating rates.

NOTATION

T, temperature; τ , time; Z, preexponential factor; E, activation energy; n, effective order of a reaction; R, universal gas constant; B, heating rate; W, dimensionless weight; w_0 , w, w_f , initial weight, the weight at any given time, and the final weight; I(w), integral weight function; w^* and $w^{*'}$, smoothing values of weight and of its rate of change; x, a dimensionless parameter; m, number of stages; k, total number of experimental points; C_k and C_k' , numerical coefficients used in smoothing and in differentiation; and α , b, c, d, f, g, empirical constants. Subscripts: M refers to the point at which the rate of change of weight is maximum and l refers to the number of points on a segment selected for evaluation of an individual stage.

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