Journal of Thermal Analysis, Vol. 25 (1982) 423—431

DIFFERENCE METHOD OF EVALUATION OF DYNAMIC INTEGRAL THERMOGRAVIMETRIC CURVES IN DECOMPOSITION OF POLYPROPYLENE

J. RYCHLÝ, L. MATISOVÁ-RYCHLÁ and M. VAVREKOVÁ

Polymer Institute of the Slovak Academy of Sciences, 809 34 Bratislava, Czechoslovakia

(Received February 16, 1982)

A new differential method of evaluating integral thermogravimetric records of the formation of volatile products during the degradation of polypropylene in air is presented. The method, applied to 0 – 100% conversion of the polymer to volatile products, may distinguish the initial presence of low molecular compounds in the polymer, as well as changes in the mechanism of degradation of the material.

At the present time a fairly large number of methods exist with which we can evaluate the dynamic integral thermogravimetric (TG) records obtained in the decomposition of various polymers. The most frequently used procedures of Coats – Redfern [1], Horowitz – Metzger [2], Doyle [3], etc. [4 – 6] are more or less exact approximations of the integral

$$I = \int_{T_0}^{T} e^{-E/RT} dT,$$

which stands in the general relation

$$f(w) = \frac{A}{\beta} \int_{T_0}^{T} e^{-E/RT} dT \qquad (1)$$

where the left side is a suitable function of the mass w of the examined polymer, β is the constant rate of heating in deg/min, A is the pre-exponential factor of the Arrhenius dependence of the rate constant k for the release of volatile products at the temperature T, and E is the activation energy of "evaporation" of the material. The aim is usually determination of the activation energy and pre-exponential factor, and subsequent estimation of the mechanism of decomposition of the polymer. The shape of function $f(w)$ can, of course, vary; most frequently it is assumed that the release of volatile products follows the scheme

$$nP \xrightarrow{k} V \qquad (2)$$

where n is the reaction order and k is the rate constant;

$$\text{for } n = 1: f(w) = \ln (w_0/w),$$
$$\text{and for } n \neq 1: f(w) = (w_0^{1-n} - w^{1-n})/(1 - n) \tag{3}$$

where w_0 is the initial weight of sample corresponding to the temperature T_0, and w is the weight of sample at the given temperature T.

Besides the uncertainty in the determination of n, each of the proposed approximations is valid with sufficient exactness only in the given region of the values E, which are, however, "a priori" unknown in the investigation of new materials. In order to reach agreement between theoretical and experimental curves for given E and A, it is necessary to optimize the values n and E, which is mostly impossible without the use of a computer.

In the present paper we describe the procedure of difference approximation which was found suitable for the thermogravimetric study of the degradation of polypropylene in air. The procedure was proposed in connection with research into the flammability of this polymer, and in our experience it is sufficiently sensitive even to the changes of mechanism during degradation, and possibly to the presence of the more volatile additives in the polymer. A necessary feature of the integral TG record for the possibility of determination of the temperature on the temperature axis with a minimum precision of 0.2° is the assumption of the use of integral difference approximation.

Experimental

The changes in weight of samples of polypropylene Tatren TF-411 (the polymer was purified in boiling *n*-heptane), a product of Slovnaft, Bratislava, were measured on Perkin-Elmer TGS-1 thermobalance. Samples with initial weight of 1 – 2 mg were placed on aluminium pans and heated in the given atmosphere at the maximum heating rate, 160 deg/min, to the temperature $T = 470$ K, from which the given rate of heating was applied. The records were followed until practically complete evaporation of the polymer.

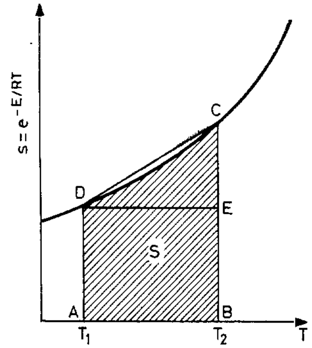
Results and discussion

Integral difference method of evaluation of TG records

If we represent the value of integral I by the area under the curve

$$s = e^{-E/RT} \text{ (see the scheme)} \tag{4}$$

and as long as the values s_1 and s_2 correspond to two different temperatures T_1 and T_2, then the area under the given curve in the interval $\langle T_1, T_2 \rangle$ can be expressed approximatively as the area of the tetragon ABCD as follows:



$$S = \frac{1}{2}(T_2 - T_1) \cdot (e^{-E/RT_1} + e^{-E/RT_2})$$
$$S = \frac{1}{2}(T_2 - T_1)\, e^{-E/RT_1}[1 + e^{-E/R(1/T_2 - 1/T_1)}]. \tag{5}$$

For $n = 1$, this expression simultaneously equals

$$S = \frac{\beta}{A}\left(\ln\frac{w_0}{w_2} - \ln\frac{w_0}{w_1}\right) = \frac{\beta}{A}\ln\frac{w_1}{w_2} \tag{6}$$

where w_1 and w_2 are the mass of the sample at the temperature T_1 and T_2.

In order that the expression

$$\ln\frac{w_1}{w_2} = \frac{1}{2}(T_2 - T_1)\frac{A}{\beta}\, e^{-E/RT_1}\,[1 + e^{-E/R(1/T_2 - 1/T_1)}] \tag{7}$$

can be linearized, it is necessary to choose the temperatures T_1 and T_2 in such a way that the function m

$$m = \frac{1}{T_1} - \frac{1}{T_2}$$

is constant.

It is suitable to change T_1 for example, by 5 or 10° and, for the chosen m, to calculate T_2 as $T_2 = T_1/(1 - mT_1)$. (By the value m we also determine the precision of the approximation.)

After transformation of relation (7) to

$$\ln\frac{\ln(w_1/w_2)}{T_2 - T_1} = -\frac{E}{RT_1} + \ln\frac{A}{2\beta}[1 + e^{Em/R}] \tag{8}$$

which represents a straight line in the coordinates

$$\ln\frac{\ln(w_1/w_2)}{T_2 - T_1} \text{ and } \frac{1}{T_1},$$

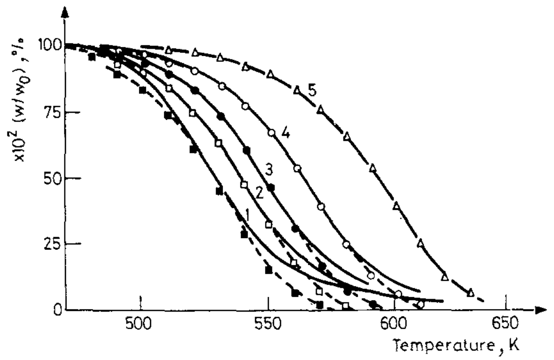


Fig. 1. Course of mass changes of isotactic polypropylene in air at various heating rates in deg/min: 1.25 (1), 2.5 (2), 5 (3), 10 (4), 20 (5). The initial sample weights w_0 are: 1.028 mg (1), 0.954 (2), 1.090 (3), 1.078 (4), 1.060 (5). The points in the individual curves are theoretical values determined from known values of E and A with Simpson's method

we can determine the values E and A from its slope and the intercept. Provided that the left side of Eq. (1) is a general function f(w), the given curve can be linearized in coordinates

$$\ln \frac{f(w_2) - f(w_1)}{T_2 - T_1} \quad vs. \quad \frac{1}{T_1}.$$

Evaluation of the integral TG records in the decomposition of polypropylene

The course of the experimental dependence of the mass of isotactic polypropylene on the temperature in air at various heating rates β is illustrated in Fig. 1. Their linearization in the coordinates of Eq. (8) for heating rates 2.5 and 10°/min is to be seen in Fig. 2. For illustration, we give in Table 1 the values w_1 and w_2 for the

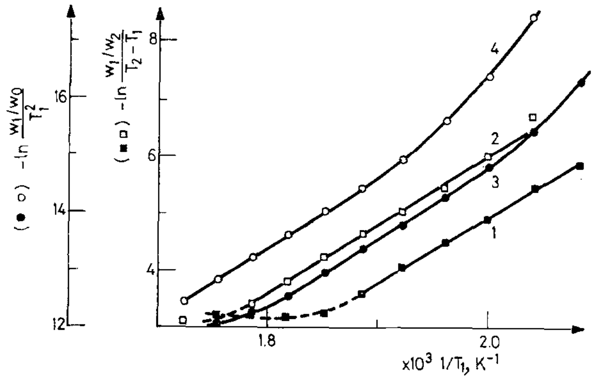


Fig. 2. Linearization of curves (2) and (4) from Fig. 1 with the integral difference method — straight lines 1 and 2 ($n = 1$) — and the Coats—Redfern method — lines 3 and 4 ($n = 1$)

Table 1

Linearization of integral records of mass changes of iPP samples in air at a heating rate of 2.5°/min with the integral difference method (ID) and the Coats—Redfern method (CR)

T_1, K	T_2, K	w_1, mg	w_2, mg	ID $-\ln\frac{\ln(w_1/w_2)}{T_2-T_1}$	CR $-\ln\frac{\ln(w_1/w_0)}{T_1^2}$
480	490	0.9366	0.9105	5.8692	16.3432
490	500.4	0.9105	0.8714	5.4671	15.4539
500	510.9	0.8736	0.8062	4.9108	14.8584
510	521.3	0.8127	0.7149	4.4785	14.2995
520	531.8	0.7279	0.5931	4.0540	13.8152
530	542.2	0.6149	0.4388	3.5879	13.3684
540	552.7	0.4714	0.2888	3.2549	12.9327
550	563.2	0.3257	0.1866	3.1653	12.5479
560	573.7	0.2149	0.1236	3.2094	12.2567
570	584.2	0.1475	0.0823	3.1914	12.0670

$m = (1/480) - (1/490) = 4.2517 \times 10^{-5}\ \mathrm{K}^{-1}$

pairs of temperatures T_1 and T_2 (T_1 chosen, T_2 calculated) for line 1 of Fig. 2 (the value m was chosen in the region of the first observable decrease of polymer mass in such a way that $T_2 - T_1 = 10°$). It may be shown that in the degradation of polypropylene in air the order $n = 1$ is the most suitable. This is also indicated in Fig. 3, where the corresponding functions are plotted for line 2 of Fig. 1, for $n = 0$, $n = 1$ and $n = 2$, respectively.

The values of the approximation of Coats and Redfern for $n = 1$ have a tendency to deviate from linearity in the initial stages and to give higher values of E

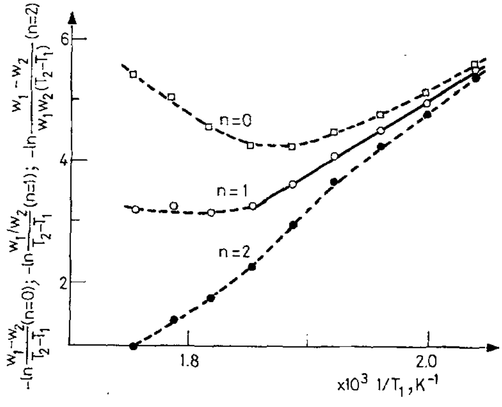


Fig. 3. Rectification of curve (2) from Fig. 1 for reaction orders $n = 0$, $n = 1$, and $n = 2$

(Fig. 2). In the integral difference method the deviation of the experimental points from linearity may be observed only at conversions of the polymer to volatile products in excess of 65%. The lower the heating rate β, the sooner this deviation occurs. At the higher heating rate 20°/min, the corresponding dependence remains linear up to 80–90% conversion.

The observed deviation at the end of the process is evidently caused by partial dissolution of the degradation products in the polymer, and the chemistry of the escape of the volatile products thus begins to coincide with the physical process of "evaporation" of the degradation residues.

By means of the least squares method, the values E and A were determined from the linear parts of the dependences

$$\ln \frac{\ln (w_1/w_2)}{T_2 - T_1} \quad vs. \quad \frac{1}{T_1}$$

for the individual heating rates.

For the known E and A, the values of the integral on the right side of Eq. (1) were calculated by the Simpson method at divisions of 1 degree on the temperature axis and thus theoretical curves of mass changes in the polypropylene samples were reconstructed (points in Fig. 1). It is to be seen again that for the low heating rates the agreement of the theoretical and experimental curves is reached only in the medium parts of the curve. In contrast, at higher rates of heating the agreement is very good.

The values of activation energies E and pre-exponential factors A determined with the integral difference method at various heating rates β for the samples of polypropylene TF-411 are given in Table 2. It is to be seen that the E values show a certain scattering around the average value $E = 101 \pm 6.8$ kJ/mol. Plotting the E values against $\ln A$, we may notice that the increase of $\ln A$ leads simultaneously

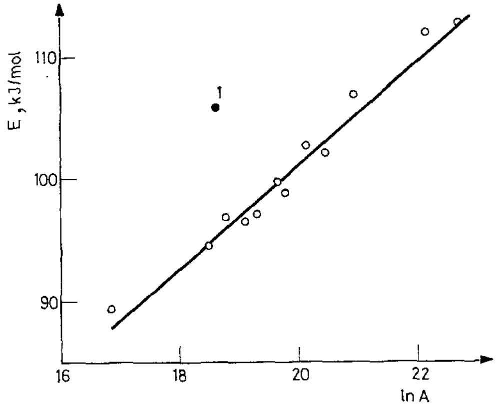


Fig. 4. Compensation of E and $\ln A$ values determined with the integral difference method for degradation of polypropylene in air. (Point 1 corresponds to a roughly fourfold initial weight compared to the other points of the set.)

Table 2

Values of activation energies E and pre-exponential factors A determined with integral difference method of evaluation of dynamic TG records for decomposition of polypropylene in air (the m values determine the scale division on the temperature axis)

Heating rate deg/min	w_0, mg	E, kJ/mol	$A\times 10^{-9}$ min^{-1}	$m\times 10^5$, K^{-1}
1.25	0.992	89.5	0.21	4.2517
1.25	1.028	96.8	1.45	4.0816
2.5	0.954	99.7	3.47	4.2517
2.5	1.024	102.6	5.69	4.2517
5	1.090	102.0	7.85	4.0816
5	0.986	112.6	74.11	4.0816
10	1.040	96.5	2.07	3.9216
10	1.046	94.5	1.08	3.0766
10	1.078	98.7	3.98	4.0816
20	1.010	111.8	43.83	3.7707
40	0.956	106.8	12.61	3.4941
40	4.186	105.6	1.16	3.3670
80	1.042	109.1	11.61	3.1328

to the increase of the E values and vice versa. The sample with an approximately fourfold weight does not correspond to a given compensation. From the compensating straight line for the value $E = 101.7$ kJ/mol, a corresponding pre-exponential factor value of 5.92×10^8 min^{-1} was determined. The first-order rate constant of the release of volatile products in the degradation of polypropylene in air therefore has the form

$$k_{\mathrm{air}} = 5.92\times 10^8\, e^{-101700/RT}\ \mathrm{min}^{-1}. \tag{9}$$

For the decomposition of iPP followed in an atmosphere of technical N_2 (ca. 0.5% O_2), the described method also gives linearization of the course of the mass change of the sample with temperature (Fig. 5) (up to a conversion of 60%). The values of activation energies and pre-exponential factors for two rates of heating are given in Table 3. It may be seen that in an atmosphere with a low concentration of oxygen, both the activation energy and the pre-exponential factor are higher.

Table 3

Values of activation energies E and pre-exponential factors A determined with integral difference method for decomposition of polypropylene in an atmosphere of technical nitrogen

Heating rate deg/min	w_0, mg	E, kJ/mol	A, min^{-1}	$m\times 10^5$, K^{-1}
2.5	1.014	155.6	5.6×10^{12}	3.6284
5	0.960	163.9	8.4×10^{12}	3.3670

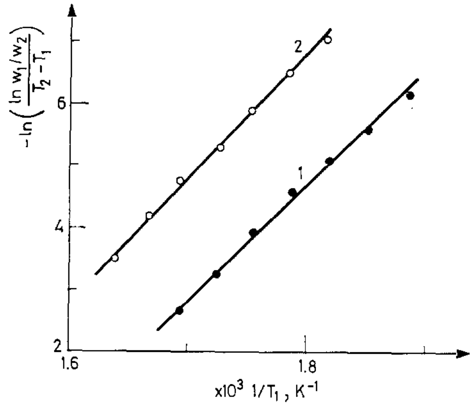


Fig. 5. Integral difference evaluation of decomposition of isotactic polypropylene in technical nitrogen. Heating rates 2.5 (1) and 5 (2) deg/min

It has been stated that the described process of evaluation of TG curves is sensitive not only to the atmosphere in which the degradation preceeds, but also to the presence of low molecular compounds dissolved in the polymer. As a consequence of the greater amount of the products of degradation which dissolve in the polymer, at low heating rates or in isothermal experiments we generally obtain lower activation energy.

The advantage of the integral difference method consists in the ability to distinguish to a certain degree the physical evaporation of low molecular additives from the chemical process of polymer degradation. If the decomposition of iPP is performed in air in the presence of 8% decabromodiphenyloxide, 8% tricresylphosphate and 0.2% ionol, by integral difference evaluation we can observe a break in the corresponding plot, the position of which corresponds to the overall amount of additive in the polymer (Fig. 6). With the Coats—Redfern method for the given experiment we obtain only one straight line (Fig. 6). The values of the activation energies determined from the individual parts of dependence 1 of Fig. 6 are 58.6 and 157.3 kJ/mol the value determined with the Coats—Redfern method is 68.6 kJ/mol. The higher values of E after the "evaporation" of the additive, however, indicate that the additive does not remain chemically inert in the thermooxidation reaction.

In comparison with the other methods of evaluation of integral TG records, the integral difference method renders it possible to change the precision of the choice of m. In the other methods this is possible only by consideration of additional members of the corresponding approximative expression which is accompanied by complications in the linearization of the substantially more complicated function.

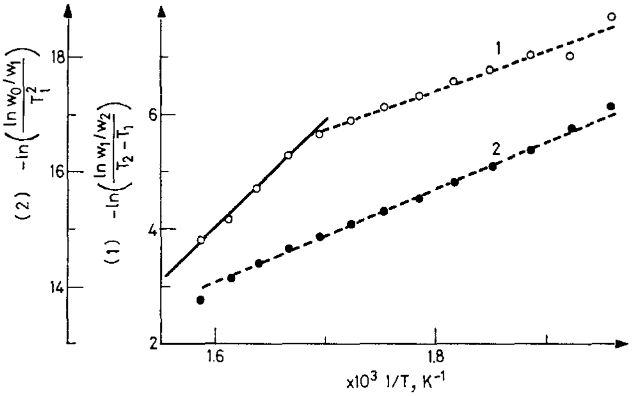


Fig. 6. Comparison of evaluation of decomposition of polypropylene in air in the presence of 8 % tricresyl phosphate and 0.2 % ionol at $\beta = 40$ deg/min, with the integral difference method (line 1) and the Coats—Redfern method (line 2)

References

1. A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
2. H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
3. C. D. Doyle, J. Appl. Pol. Sci., 5 (1961) 285.
4. W. W. Wendlandt, Thermal Methods of Analysis, Sec. Edition, 19, Wiley Interscience Publication, New York, 1974, page 45.
5. J. H. Flynn and L. A. Wall, Journal of Research of NBS, Physics and Chemistry 70 (1966) 487.
6. J. Šesták, Thermochim. Acta, 7 (1973) 447.

Zusammenfassung — Es wird eine neue differentielle Methode zur Auswertung der die Bildung von flüchtigen Produkten während der Zersetzung von Polypropylen in Luft widerspiegelnden integralen thermogravimetrischen Kurven dargelegt. Mit der im Bereich 0—100% Konversion von Polymer zu flüchtigen Produkten anwendbaren Methode können sowohl die Anwesenheit niedermolekularer Verbindungen im Polymer als auch Veränderungen im Abbaumechanismus des Materials erkannt werden.

Резюме — Представлен новый дифференциальный метод вычисления интегральных термогравиметрических данных образования летучих продуктов, образующихся при распаде полипропилена в атмосфере воздуха. Метод, использованный для области 0—100%-ного превращения полимера в летучие продукты, позволяет различать начальное присутствие в полимере низкомолекулярных соединений, а также изменения в механизме распада полимера.