Journal of Thermal Analysis, Vol. 5 (1973) 407–414

KINETIC STUDIES OF MULTI-STEP THERMAL DEGRADATIONS OF COPOLYMERS OR POLYMER MIXTURES*

A. GRÖBLER and T. KADA**

Research Institute for the Plastics Industry, Budapest, Hungary

(Received January 22, 1972)

A kinetic analysis of multi-step thermogravimetric curves was developed for separation of overlapping decomposition steps to determine their individual reaction order, activation energy and weight loss. The method was applied in three instances: (a) separation of evaporation from decomposition for an isobutene-butadiene copolymer; (b) effects of drying conditions on the volatile content of a styrene-indene resin; (c) separation of dehydrochlorination from cyclodecomposition of poly(vinyl chloride).

In polymeric systems, multi-step thermogravimetric curves do not correspond to distinct, well-defined steps, in contrast with most inorganic decompositions. Steps may overlap so that they cannot be treated separately; they are sometimes not even visible directly.

The present kinetic method permits a determination of the actual weight losses in the individual decomposition steps and a detection of possibly latent steps, together with an estimation of the individual activation energies.

Kinetic procedure

Instantaneous decomposition rate constants can be determined from thermogravimetric curves by the following equation [1]:

$$k = -\frac{1}{w_r^n}\frac{\mathrm{d}w}{\mathrm{d}t} \tag{1}$$

where w_r is the residual weight for the particular decomposition step and $\frac{\mathrm{d}w}{\mathrm{d}t}$ the decomposition rate at the momentary temperature. Both are obtained directly from the thermogravimetric measurement while the order of reaction (n) is unknown and must be determined separately.

The present procedure is initiated with the last decomposition step, proceeding from the highest temperature toward the lower ones.

---

* Paper presented at the International Symposium on Macromolecular Chemistry, Budapest, 1969.

** Present address: Research Institute for Mining, Budapest, Hungary.

Determination of the reaction order

The orders of reaction of the individual steps are determined in three ways:

(*a*) According to Horowitz and Metzger [2], the ratio of the residual weight to the total weight loss in the particular step, w_r/w_0, at the moment of the maximum decomposition rate, is correlated with the order of reaction as indicated in Table 1. A graphical plot of this correlation gives a very simple tool for estimating the order of reaction.

Table 1

Relation between the order of reaction and the weight fraction at maximum reaction rate

n	w_r/w_0
0	0.000
1/2	0.250
1	0.368
3/2	0.444
2	0.500
3	0.576
4	0.630
5	0.669

(*b*) Kissinger's method [3] is based on the asymmetry of the derivative thermogravimetric (DTG) curve. Instead of the very complicated calculation, a graphical method is suggested from the DTG curve, drawing the inflexion tangent of the peak defining its asymmetry factor: a/b (Fig. 1). For the order of reaction:

$$n^2 = 1.59 \frac{a}{b} \tag{2}$$

(*c*) The method of Freeman and Carroll [4] is more exact but much more complicated. Their linearized equation is:

$$\frac{\Delta \ln \frac{\mathrm{d}w}{\mathrm{d}t}}{\Delta \ln w_r} = n - \frac{E}{R} \frac{\Delta \frac{1}{T}}{\Delta \ln w_r} \tag{3}$$

where $E =$ activation energy,
$R =$ the gas constant.

When the measured values are plotted according to this equation, the order of decomposition is obtained from the intercept. In addition, activation energy can be calculated from the slope.

In spite of its complexity, this procedure is necessary in cases of strong overlapping, since the n value is estimated from the ultimate stage of the last decomposition step by application of Eq. (3).

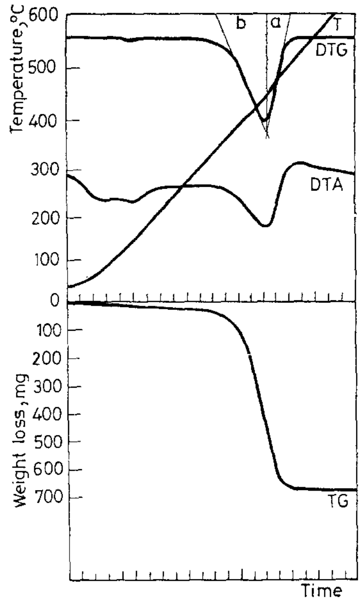

Fig. 1. TG, DTG and DTA curves of an isobutene-butadiene copolymer

Kinetic treatment of the individual decomposition steps

Using the order of reaction, rate constants are calculated in steps of 10 or 20°, downward from the highest one, according to Eq. (1), and plotted against reciprocal temperature (Fig. 2). This plot is linear at higher temperatures, but diverges at lower ones due to the presence of the previous decomposition step.

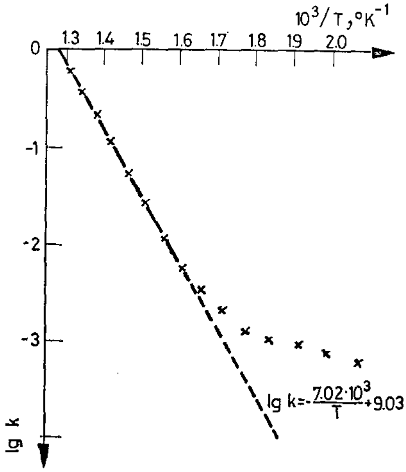

Fig. 2. Arrhenius plot of decomposition rate constants of an isobutene-butadiene copolymer

The equation of the straight line (Arrhenius equation) for the linear range is determined by the least squares method. It is extrapolated to calculate the pure rate constants and decomposition rates of the steps below the measured ones. Thus, an individual thermogravimetric curve can be constructed for the last decomposition step. The differences between the measured and calculated weights result in a thermogravimetric curve without the separated last step.

The whole procedure is then repeated, through the next preceding step, successively for the total thermogravimetric trace.

Experimental

Thermogravimetric measurements were carried out with a derivatograph (Paulik–Paulik–Erdey system, MOM Hungarian Optical Works, Budapest). The temperature was programmed linearly and thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analytical (DTA) curves were recorded simultaneously.

Samples could be held in the apparatus by a series of plates in place of the crucible, permitting a higher amount of material (about 0.5 – 0.7 g) to be spread out with great surface area, thereby eliminating the majority of the errors of diffusion. Alumina was used as inert material under the same conditions.

Before measurements, the sample chamber was flushed overnight with argon. Samples were heated at a rate of about 3° min^{-1}.

Since the calculated thermogravimetric curves accumulated all the errors involved in the kinetic procedure besides the instrumental errors of the measurement, the low-temperature section of the curve was sometimes recorded at increased sensitivity of the thermobalance and the thermocouples. In these cases, weight losses in the low-temperature steps were determined more correctly even if the activation energies calculated from the estimated Arrhenius plots might be erroneous.

Applications

1. *An isobutene-butadiene copolymer* of unknown structure (polymerized from the C_4-fraction of a naphtha pyrolysate) was used as a model for the present method because of its simple decomposition pattern (Fig. 1).

The reaction order of the main decomposition step determined by methods (*a*), (*b*) and (*c*) was 0.96, 0.83 and 1.06, respectively. Thus the order of reaction was regarded as unity. The activation energy was 32.1 $\mathrm{kcal.mole}^{-1}$ from the Arrhenius plot, and 34.2 $\mathrm{kcal.mole}^{-1}$ by the method of Freeman and Carroll using Eq. (3). The weight loss in this step was 96.5% of the total weight.

The initial weight loss of 3.5% was analyzed on the basis of a thermogravimetric curve at increased sensitivity. It proved to be a uniform step; its first-order Arrhenius plot was linear throughout with an activation energy of about 8 kcal.mole^{-1}. This suggests that this weight loss may be evaporation rather than chemical decomposition.

2. *A styrene-indene resin* also polymerized from a naphtha pyrolysate could not be dried to steady weight after polymerization. It was assumed that the de-

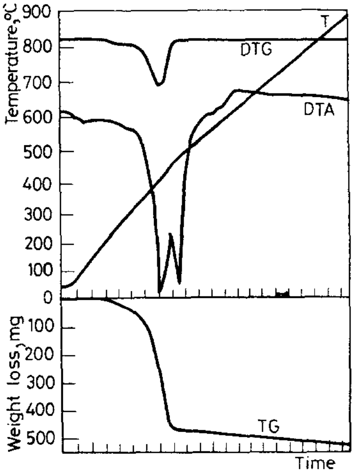

Fig. 3. TG, DTG and DTA curves of a styrene-indene resin

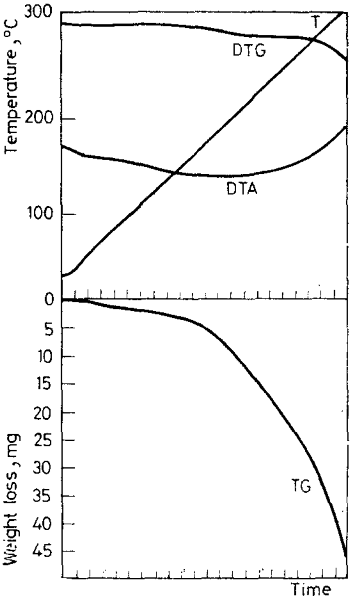

Fig. 4. High-sensitivity thermal curves of the initial part of decomposition of a styrene-indene resin

composition started before the unreacted hydrocarbons had got away. The thermogravimetric trace is really quite diffuse (Fig. 3). The kinetic analysis resulted in three steps. After the main decomposition had been treated, the first part was analyzed by thermal curves of higher sensitivity (Fig. 4).

Effects of drying on weight losses in the individual steps are shown in Table 2. Drying was carried out in a vacuum oven at 20 torr.

Table 2

Effects of drying conditions on the decomposition steps of a styrene-indene resin

Drying		Weight loss, %		
Temperature, °C	Time, h	Step 1	Step 2	Step 3
154	2.5	1.3	15.4	83.3
205	1.25	1.1	10.6	88.2
210	2.5	1.9	4.4	93.6

It is apparent that with increasing severity of drying, the second step decreases while the first step is constant within the range of the experimental errors. This leads to the conclusion that, besides the residual solvent, a less stable fraction exists in the original resin which decomposes in the course of drying. As drying is interrupted, a part of the decomposition products is frozen into the resin and

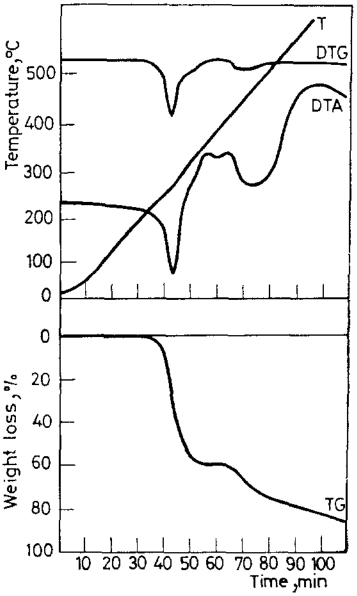

Fig. 5. TG, DTG and DTA curves of poly(vinyl chloride)

appears as solvent in the thermogravimetric curve. This may be the reason of the consistency of the first step. It is also supported by the fact that the activation energies of steps 2 and 3 are similar (about 18 and 22 kcal.mole^{-1}, respectively).

3. *Poly(vinyl chloride)* shows a very characteristic thermogravimetric curve [5]. During its dehydrochlorination (step 1), however, some benzene and other hydrocarbons appear in the escaping HCl [6], especially above 250°. This is due to a cyclodegradation of the conjugated polyene chains resulting from the dehydrochlorination. These consecutive reactions really make the first decomposition step non-uniform. The DTG curve of Fig. 5 shows a secondary step overlapping with the main dehydrochlorination.

The present kinetic method is capable of separating the individual processes. The order of the main decomposition as determined by methods (*b*) and (*a*) was 1.4 and 1.5, respectively. A reaction order of 3/2 is in accord with the dehydrochlorination mechanism suggested by Stromberg et al. [6]. The same order was used for the second step too since its determinations led to inconsistent results and a first order Arrhenius plot was not linear, suggesting a reaction order higher than unity. 22% of the weight loss was accounted for in the second step, and thus 78% of the escaping material was assumed to be HCl. The analytical data of Stromberg et al. [6] supported this result.

Conclusion

The present method of kinetic calculations is capable of separation and characterization of overlapping decomposition steps in thermogravimetric measurements. Order of reaction, activation energy and separate thermogravimetric curve can be obtained for the individual steps.

The calculation is tiresome but regular and periodical, and thus it can easily be computerized including the evaluation of TG and DTG curves.

References

1. A. E. Newkirk, Anal. Chem., 32 (1960) 1558.
2. H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
3. H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
4. E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
5. E. A. Boettner, G. Ball and B. Weiss, J. Appl. Polymer Sci., 13 (1969) 377.
6. R. R. Stromberg, S. Strauss and B. G. Achhammer, J. Polymer Sci., 35 (1959) 355.

Résumé — On a mis au point une méthode d'analyse cinétique des courbes thermogravimétriques en plusieurs termes pour séparer les étapes de décomposition qui se chevauchent et déterminer pour chacune d'elles l'ordre de réaction, l'énergie d'activation et la perte de poids. On a utilisé cette méthode dans trois cas: a) pour distinguer l'évaporation de la décomposition du copolymère isobutène-butadiène, b) pour étudier l'influence des conditions de séchage sur la teneur en substances volatiles d'une résine styrène-indène, c) pour distinguer la déchlorhydratation du chlorure de polyvinyle de la décomposition du cycle.

ZUSAMMENFASSUNG — Eine kinetische Analyse von mehrstufigen thermogravimetrischen Kurven wurde entwickelt, um überlappende Zersetzungsstufen zu trennen, ihre individuellen Reaktionsordnungen, Aktivierungsenergien und Gewichtsverluste zu bestimmen. Die Methode wurde in drei Fällen eingesetzt: (a) Trennung der Verdampfung des Isobuten-Butadien-Kopolymers von der Zersetzung; (b) die Wirkung der Trocknungsbedingungen auf den Gehalt an flüchtigen Substanzen eines Styrol-Inden-Harzes; (c) Trennung der Dehydrochlorierung des Poly-Vinylchlorids von der Ringspaltung.

Резюме — Проведен кинетический анализ многоступенчатых термогравиметрических кривых с целью разделения перекрытых ступеней распада, определения порядка отдельных реакций, энергии активации и потери веса. Метод был использован в трех случаях: (а) разделение стадий испарения и распада для сополимера изобутен-бутадиен; (б) влияние условий сушки на содержание летучих при термораспаде сополимера стирол-инден; (с) разделение дегидрохлорирования и циклораспада поливинилхлорида.