Journal of Thermal Analysis, Vol. 28 (1983) 421–430

Special Review

THERMAL DECOMPOSITION OF POLYMERIC MATERIALS:
Characteristics of kinetics at non-isothermal heating

O. F. Shlensky

MENDELEEV INSTITUTE OF CHEMICAL TECHNOLOGY, MOSCOW, U.S.S.R.

(Received June 22, 1983)

General conclusions are made based on the results of experimental and theoretical investigations of the decomposition kinetics of various polymeric materials in a wide range of heating rates. It was found that the decomposition process of the investigated materials proceeds within confined temperature intervals. Kinetic equations are suggested to describe the thermal decomposition processes of polymers and natural coals, based on the characteristic revealed.

Thermal decomposition ranges of polymeric materials

The thermal decomposition kinetics of polymeric materials with different chemical compositions and natural coals have been studied in a wide range of heating rates $b = dT/dt$ by DTA [1–3]. They demonstrated that each material investigated has a characteristic temperature range in which the thermal decomposition process takes place. Figure 1 represents the typical position of TG curve groups in these ranges, and the limits are marked by lines. The lower limit $\omega_\infty(T)$ corresponds to the hypothetical conditions of equilibrium heating. The ordinates of the curve $\omega_\infty(T)$ are determined for each fixed temperature T as the asymptotical limit of $\omega_\infty(T)$:

$$\omega_\infty(T) = \lim_{t \to \infty} \omega(T, t)$$

where ω is the relative mass of sample residue $= M/M_0$ and t is the observation time of the sample at monotonous heating.

The curve $\omega_\infty(T)$ characterizes the observation results at the lowest heating rates allowing to establish the chemical equilibrium between the starting material and the decomposition products. In practice, the points of the lower limit are obtained by means of a series of isothermal studies of the material up to the total stop of mass loss at each given temperature. The characteristic points of the lower limiting curve are the

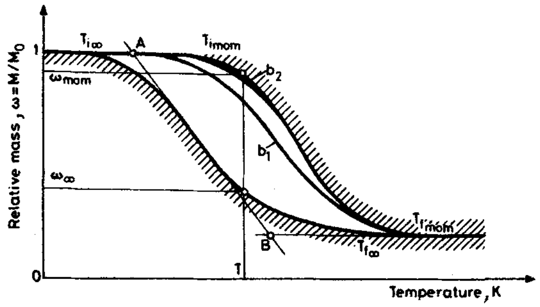

Fig. 1 Characteristic position of TG curves for thermoplastic polymeric materials in the range of their thermal decomposition. Heating rate $b_2 > b_1$. The lines mark the limits of the range

initial temperature $T_{i\infty}$ and the final temperature $T_{f\infty}$ of the decomposition, corresponding to 5% and 95%, respectively of material decomposition, or the points A and B, that is the points of intersection of the tangent to the curve $\omega_\infty(T)$ in the inflexion point.

When heating rate is successively increased, the TG curves will be shifted irregularly towards the right side, they show a tendency to cluster in the vicinity of the other extreme position, that is, of the upper limit $\omega_{\text{mom}}(T)$. Each ordinate of the curve $\omega_{\text{mom}}(T)$, at a fixed temperature T, corresponds to $\omega_{\text{mom}}(T) = \lim\limits_{t\to 0} \omega(T, t)$.

Since time and heating rate are interrelated, the condition $t \to 0$ is equivalent to the condition $b \to \infty$. The ordinates of the curve $\omega_{\text{mom}}(T)$ correspond to the shortest possible, "momentaneous" heating rates. Heating time must, however, be sufficient to establish the temperature in question within the sample, and to remove decomposition products. To accomplish the latter condition -- which is of high importance -- the specimens should have dimensions as small as possible. Details of such experiments are described in [2].

It is equally justified to formulate rules for determining sets of points for the limits of thermal decomposition in another manner. Let us consider the horizontal intersecting line of the groups of curves in Fig. 1 at some fixed value $\omega = \text{const}$. One then obtains the following limit values:

$$T_\infty = \lim_{t\to\infty} T(\omega, t) \quad \text{and} \quad T_{\text{mom}} = \lim_{t\to 0} T(\omega, t)$$

The limit temperatures $T_{i\text{mom}}$ and $T_{f\text{mom}}$ are readily determined graphically. Thus the temperature interval in which thermal decomposition of a given polymeric material takes place is confirmed between the initial temperature $T_{i\infty}$ and the final temperature $T_{f\text{mom}}$ of the decomposition. In the case of natural coals and thermoreactive polymers, intersecting (inversion) of the limiting curves $\omega_\infty(T)$ and $\omega_{\text{mom}}(T)$ was observed.

Figure 2 represents examples of graphically determined limit temperature from the data in [4]. As seen from the figure, the limit temperatures are reached with the polymers in the examples at heating rates as low as 2 . . . 6 degree/s. Other examples of similar determinations are described in the literature [1, 5].

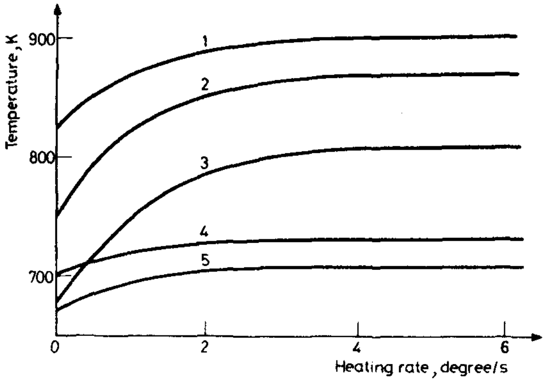

Fig. 2 Characteristic temperatures of thermal decomposition for linear polymers *vs.* heating rate. 1 – $T_{50\%}$ polyamide; 2 – T_f polycarbonate; 3 – T_i polycarbonate; 4 – $T_{50\%}$ polystyrene; 5 – T_i resol (resin DBS-1)

Physical interpretation of the upper temperature limit of thermal decomposition for polymers

Thermoanalytical methods with monotonous heating of the samples allow to determine many characteristic transformation temperatures, in particular melting temperature T_m, caused by stability loss of oscillation in intermolecular bonds. The structure attributed to the macromolecules of polymers is that of linear crystals. When such structures are being heated, stability loss of the vibrations of the covalent bonds between the atoms takes place, till the characteristic decomposition temperature T_d is reached. According to [6], the temperature of stability loss of oscillator vibrations is defined by the following formula:

$$T_d = \frac{h\omega_0}{K \ln \dfrac{A+1}{A-1}}$$

where $A = \dfrac{2\bar{m}\omega_0}{h}\left(\dfrac{\bar{m}\omega_0^2}{2}\right)^2$, $\bar{m}$ is the mass of the atom, ω_0 the angular frequency of the vibration, β the coefficient of anharmonism of the vibration, h is the Planck constant. As demonstrated by the calculations in [7], the values of intense destruction T_d are mainly in the range of 600 . . . 800 K; this is in good agreement with TG data.

The value of T_d is influenced by force interactions [8]. Inertia forces, arising from the rotation of kinetic elements in the chains of flexible macromolecules may affect the temperature T_d in the direction of lowering it [3].

The stability loss of the vibrations of the macromolecules oscillators allows to interprete the thermal destruction of polymers in a metastable, thermodynamically unstable state as a specific phase transition, to be more exact, a chemophase transition, which is irreversible, since simple cooling will normally not result in formation of the initial material from the decomposition products. Since strength of the bonds in the macromolecule is not identical, thermal decomposition of polymers, similar to their melting, will not take place at a strictly defined temperature, but within a certain temperature range, including the temperature T_d.

Within the thermal decomposition temperature range, the decomposition degree, independently of the heating regime, will depend solely on the quantity of energy $E_d = pE_P$ consumed for the dissociation of $(N_0 - N)$ bonds. Hence, for the random decomposition of linear polymers it may be stated [9] that

$$\omega = (1-p)^m(1+mp) \tag{1}$$

where m is the relative length of the volatile fragment of the molecule, $p = E_d/E_p$. E_p is the total energy of depolymerization.

The maximum temperature $T_{f\text{mom}}$ that can be reached by a given polymer is defined by the amount of assimilated (or evolved) energy and corresponds to the temperature of the point of intersection. This temperature may be computed if the phase equation of the material in question is known. According to [10] such temperatures of linear polymers do not exceed 800 . . . 1000 K. In [1, 2] analytical expressions for the limit curves of decomposition are suggested, notably an exponential function of the type

$$\omega_{\text{mom}}(T) = \exp\left[-\frac{(T-T_H)^2}{T_0^2}\right]$$

where T_H, T_0 are parameters, arcotangentoid and some other functions.

Equation (1) and the last equation are not kinetic in themselves, since they do not contain time as variable. However, it appears possible by their utilization to find more accurate kinetic relationships.

Difficulties in describing the kinetics of thermal decomposition of polymers by traditional kinetic equations

S. Madorsky [11] demonstrated by a number of high-accuracy experiments that the traditional kinetic equation of the type

$$\frac{d\omega}{dt} = -k\omega^n \tag{2}$$

is of very restricted value in applications to describe thermal destruction of polymers at $T = \text{const}$. For polymers like polystyrene, styrene copolymers, fluoropolymers, polyacrylates, polyamides, Eq. (2) is valid only in the final stages of thermal decomposition. For non-isothermal heating conditions one has, based on Eq. (2)

$$\frac{d\omega}{dt} = -k\frac{\omega^n}{b} \tag{3}$$

It is usually assumed that $k = k_0 \exp(-E/RT)$. A suitable choice of E, k_0 and n will almost always allow good agreement of the solution of Eq. (3) with one of the experimental TG curves of the polymer in question. It was stated, however, [3, 12] that the values E, k_0 and n chosen for one TG curve will not be fit to describe a TG curve obtained at some other heating rate. A triade of E, k_0 and n values corresponds to each heating rate [4]. Particularly sharp differences are characteristic for thermoactive polymers and natural coals [12]. It is obvious that according to Eq. (3), an increase of the heating rate will lead to a decrease in the derivative $d\omega/dT$; the slope of the tangent in each point of the TG curve should tend towards zero, and at $b \to \infty$ the calculated curves will attain a horizontal position:

$$\lim_{b\to\infty} \frac{d\omega}{dT} \to 0$$

This result is not confirmed by experimental data: experimental TG curves do no surpass the limits of the thermal decomposition range, and do not turn into horizontal lines at any heating rate. Hence, Eq. (3) does not adequately describe the true processes, particularly at high heating rates.

It is the characteristic feature of the thermal decomposition of polymeric materials that in the general case, the kinetics of bond dissociation in the macromolecules $N(t)$ are not in conformity with the kinetics of mass loss $\omega(t)$. Let us demonstrate this by an example. Let us assume that the kinetics of the dissociation of N bonds is described by the differential equation $dN/dt = -kN$. For non-isothermal conditions, integration will yield $\frac{N}{N_0} = \exp\left(-\int_0^t k dt\right)$. If the energy input D is required to split one chemical bond, $p = 1 - \exp\left(-\int_0^t k dt\right)$, since $DN_0 = E_p$. Let us substitute this value of p into Eq. (1):

$$\omega = \left[\exp\left(-\int_0^t k dt\right)\right]^m \left\{1 + m\left[1 - \exp\left(-\int_0^t k dt\right)\right]\right\} \tag{4}$$

The solution given by Eq. (4) essentially differs from the integral of Eq. (2), which, at $n = 1$, is $\omega = \exp\left(-\int_0^t k dt\right)$. All this will allow a more accurate equation describing heat absorption q in the course of thermal decomposition:

$$q = \frac{Q}{N_0} \frac{dN}{dt}$$

where Q is the thermal effect of the reaction. This equation differs from the traditional form $q = Q(d\omega/dt)$. For non-linear (branched, cross-linked) polymers it is a more difficult task to establish the relationship between $\omega(t)$ and $N(t)$; in the majority of cases it can only be solved by computation [13], e.g. by the Monte-Carlo method.

Further difficulties in the description of the kinetics of polymer destruction arise when attempting the analytical expression of temperature dependence $k(T)$. To utilize for this purpose the theory of absolute rate of reaction appears questionable. In this theory, the following fundamental assumptions are utilized:

(i) The reaction proceeds in the gas phase and is homogeneous.

(ii) The initial material is in equilibrium with the activated complex.

(iii) The Maxwell–Boltzmann distribution is valid.

(iv) The process proceeds at $T =$ const., consequently $E =$ const, and $k_0 =$ const.

Regarding polymers, the first assumption is not satisfied, since polymers do not exist in the gas phase. Neither can the second assumption be satisfied, since stability loss of the vibrations close to the temperature T_d involves irreversibility of the destruction of oscillators. The third assumption, in the state of thermodynamic equilibrium, has significance regarding energy distribution between the oscillators in their totality. However, up to the present, no convincing evidence on the validity of Maxwell distribution of velocity in the anharmonic oscillators at temperatures close to the temperature of intense destruction T_d has been reported in the literature. The fourth assumption does not correspond to the condition of monotonous heating accepted in thermogravimetry. The assumptions accepted in the theory of absolute rate of reaction do not allow to explain the existence of the characteristic temperatures T_m and T_d and to calculate their values by this theory. It appears reasonable to apply, in order to obtain kinetic relationships, to Hinshelwood's theory [14], in which the behaviour of the reactant is modelled by a set of 2s oscillators whose energy does not exceed a maximum value ϵ_m. This energy corresponds to the vibration amplitudes of the oscillators at which stability loss of the vibrations proceeds. The rate constant of the dissociation of the system of oscillators will depend on temperature:

$$k = k_0 e^{\theta} (j_{s-1} + j_{s-2} + \ldots + 1) \tag{5}$$

where $j_{s-1} = \theta^{s-1}/(s-1)!, j_{s-2} = \theta^{s-2}/(s-2)! \ldots$ are the terms of the polynomial $\theta = \frac{\epsilon_m}{kT}$.

Only the first factor in Eq. (5) corresponds to the Arrhenius equation. Owing to the factor in brackets, the rate constant k will grow more rapidly with temperature than according to the Arrhenius equation, since in macromolecules, the number s

will increase with temperature rise which results in higher mobility of the kinetic units (atom groups, segments) and simultaneously in lower viscosity of the polymer.

It has been shown that if the particles of the decomposing material having energies $\epsilon \geqslant \epsilon_m$ have the possibility to evaporate without any steric hindrance, e.g. from the surface, then

$$\omega_{\mathrm{mom}}(T) = e^{-\theta} j_{s-1} + j_{s-2} + \ldots + 1).$$

Correspondingly the rate constant of decomposition in the surface layer $k_{\mathrm{surf}} = k_0 \omega_{\mathrm{mom}}(T)$. Under conditions of slow (equilibrium) heating, the energy ϵ_m corresponds to the activation energy of the process, and the decomposition products remain in contact with the surface. To arrive to the rate constant of overall mass loss of the material, one must utilize rather highly developed methods of the kinetics of heterogeneous reactions, for instance the Kekam method [16] and introduce the area of the reacting surface S by the relationship $k = k_{\mathrm{surf}} \omega_{\mathrm{mom}}(T) S$.

It should be noted that increasing intensity of heat transfer to the polymeric material results – in proportion of approaching the limit $\omega_{\mathrm{mom}}(T)$ – in an increase of the area of the reacting surface, since at $t \to 0$ we have $q = Qk_0 \omega_{\mathrm{mom}}(T) S$, increased temperature gradients. Swelling of the sample by turbulent gas evolution, dispersal of the material, i.e. emission of fine particles and droplets of unreacted material may occur. These phenomena largely increase the experimental error and render the exact determination of the limit $\omega_{\mathrm{mom}}(T)$ very difficult.

In polymer melts, where in addition to vibrational freedom, rotational degree of freedom also exists, the expressions for $\omega_{\mathrm{mom}}(T)$ and $k(T)$ are obtained by methods of statistical physics [15]; they have a highly complex structure.

Phenomenological description of the kinetics of the decomposition of polymers at non-isothermal heating

The above analysis demonstrates that an accurate description of the kinetics of non-isothermal destruction of polymers, even when their composition and structure is simple, presents great mathematical difficulties; one gets the impression that the prospects for finding simple solutions, particularly for high heating rate regimes, are little. However, to solve many practical tasks, for instance, to perform thermophysical calculations of temperature fields in coking coals at processing, at the conditions of combustion of polymers, the phenomenological approach in which the physical essence of the phenomena is reflected appears useful. The decisive factor allowing to simplify the description of thermogravimetric curves in a wide range of heating rates and simultaneously introduce a principled means to increase accuracy in processing TG results is to take into account the limits of the range of thermal decomposition and the temperature T_d in establishing kinetic relationships.

The function $\omega_\infty(T)$ is introduced directly into the kinetic equation in the following manner [1]:

$$\frac{d\omega}{dt} = -k[\omega - \omega_\infty(T)]^n \tag{6}$$

The solution of Eq. (6) indicates that at $t \to \infty$, $\omega(T) \to \omega_\infty(T)$ at both isothermal and non-isothermal heating conditions.

The existence of the upper limit may be accounted for both in the structure of the kinetic equation and in the construction of the expression $k(T)$. The first method is based on the formal expression of the function of two variables $\omega(T, t)$ in the form of derivates [1]:

$$d\omega = \frac{\partial\omega}{\partial t}dt + \frac{\partial\omega}{\partial T}dT.$$

To obtain the desired equation, one must substitute the partial derivatives by analytical functions. From Eq. (6) one finds $\partial\omega/\partial t = -k(\omega - \omega_\infty)$. Then $d\omega/dT = -k(\omega - \omega_\infty)^n/b + \partial\omega/\partial T$. Let us establish the meaning of the second term. At increased heating rates b it will become substantially larger than the first term containing the parameter b in the denominator. However, at high heating rates the TG curves will coincide with the upper limit of the thermal decomposition range $\omega_{\mathrm{mom}}(T)$, and hence $\partial\omega/\partial T = \partial\omega_{\mathrm{mom}}/\partial T = \omega'_{\mathrm{mom}}$. The kinetic equation then has the following form:

$$\frac{d\omega}{dt} = -k(\omega - \omega_\infty)^n + \omega'_{\mathrm{mom}}(T) \tag{7}$$

In the particular case when $\omega_\infty = 0$ and $b = 0$, Eq. (7) turns into the traditional kinetic equation Eq. (2). Other variants of taking into account the upper limit in the kinetic equation are suggested in [1], and also the introduction of the function $\omega_{\mathrm{mom}}(T)$ into its solution in the form of initial condition.

For materials whose temperature of intense thermal destruction T_d is readily recorded experimentally, the following expression is proposed for the rate constant of the thermal decomposition process [1]:

$$k = k_0 \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_d}\right)\right] \tag{8}$$

According to Eq. (8), $k = k_0$ at $T = T_d$. For materials in which $\omega_{\mathrm{mom}}(T)$ has no sharp fall close to the temperature T_d, it is preferable to use another variant of the temperature dependence of the rate constant:

$$k = k_0\left(1 + \frac{b}{b_0}\right)\exp\left(-\frac{E}{RT}\right)$$

where b_0 is a parameter; for many polymers $b \approx 1$ K/s.

The equations derived above describe the main characteristic of TG curves for polymeric materials and natural coals, namely their clustering in the vicinity of the upper limit $\omega_{\mathrm{mom}}(T)$ with fairly good accuracy. The questions of utilization in practice of these kinetic equations and their solutions have been reported in detail in [1] and [17].

Conclusion

The traditional kinetic equation for one-stage chemical reactions of order n combined with the Arrhenius law does not allow to obtain an adequate description of the TG curves of polymeric materials and natural coals within a wide range of temperature and heating rate. Accuracy in describing TG results of such materials is largely increased by introducing into their kinetic equations the experimentally found limits of the thermal decomposition range $\omega_\infty(T)$ and $\omega_{\mathrm{mom}}(T)$ and the temperature T_d.

References

1 O. F. Shlensky, Thermal Properties of Glass-Reinforced Plastics, Khimiya, Moscow, 1973 (in Russian).
2 O. F. Shlensky and E. G. Vishnevsky, Dokl. AN SSSR, 246 (1979) 151.
3 O. F. Shlensky et al., Dokl. AN SSSR, 253 (1980) 921.
4 E. N. Zadorina, G. E. Vishnevsky and Yu. V. Zelenev, Vysokomol. Soed. A 23 (1981) 1139.
5 I. N. Sazanov, J. Thermal Anal., 23 (1982) 65.
6 P. Feyman, Statistical Mechanics, Mir, Moscow, 1975 (Russian translation from English).
7 A. A. Askadsky, Chemical Structure and Physical Properties of Polymers, Khimiya, Moscow, 1983 (in Russian).
8 V. A. Gilyarov and V. A. Petrov, Fizika tverdogo tela, 23 (1981) 1569.
9 O. F. Shlensky and E. A. Baranova, Dokl. AN SSSR, 226 (1982) 418.
10 O. F. Shlensky, N. V. Afanasev and T. A. Petrova, Dokl. AN SSSR, 256 (1981) 916.
11 S. Madorsky, Thermal Decomposition of Organic Polymers, Mir, Moscow, 1967 (Russian translation from English).
12 L. N. Aksenov et al., Khimiya twerd. topliva, No. 4, (1981) 88.
13 L. N. Aksenov, A. G. Shashkov and O. F. Shlensky, Inzh. fizichesky zh., XII (1982) 910.
14 E. A. Melvín-Hughes, Physical Chemistry, Vol. I and II, Inostrannaya Literature, Moscow, 1962 (Russian translation from English).
15 O. F. Shlensky and N. N. Ermilova, Dokl. AN SSSR, 261 (1981) 929.
16 J. U. Criado, J. Thermal Anal., 19 (1980) 381.
17 O. F. Shlensky and G. G. Muramov, Dokl. AN SSSR, 263 (1982) 119.

Zusammenfassung — Aus den Resultaten experimenteller und theoretischer Untersuchungen der Zersetzungskinetik verschiedener polymerer Materialien in einem weiten Bereich der Aufheizgeschwindigkeit wurden allgemeine Schlussfolgerungen gezogen. Es wurde festgestellt, dass die Zersetzungsprozesse der untersuchten Materialien innerhalb begrenzter Temperaturintervalle verlaufen. Kinetische Gleichungen zur Beschreibung der thermischen Zersetzungsprozesse von Polymeren und natürlichen Kohlen werden vorgeschlagen, die auf den ermittelten charakteristischen Daten beruhen.

Резюме — Дано обобщение результатов экспериментальных и теоретических исследований кинетики терморазложения ряда полимерных материалов в широком диапазоне скоростей нагрева. Установлено, что процесс терморазложения исследованных веществ протекает в ограниченных температурных интервалах. Предложены кинетические уравнения для описания процессов терморазложения полимеров и природных углей с учетом обнаруженных закономерностей.