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# DETERMINATION OF THE CHARACTERISTICS OF POLYMER DECOMPOSITION USING THE SEMIINFINITE BODY METHOD

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The problem of determining the kinetics of the decomposition and thermophysical properties of polymers from a one-dimensional temperature field is investigated. An analytic solution is obtained under the condition that the rate of decomposition depends strongly on temperature.

Thermal decomposition of polymers is customarily described by some single chemical kinetic equation. The characteristics entering into this equation are, generally speaking, effective (overall) characteristics, and for this reason can depend on the conditions under which the polymer is heated. Usually, decomposition kinetics are determined by thermal analysis methods with their characteristic special heating conditions. The purpose of this paper is to develop a method for determining the decomposition characteristics under conditions when the material being studied is a semiinfinite body, heated on one side. The use of this method is interesting, for example, for obtaining the characteristics of heat-resistant coatings [1]. The conditions for functioning of the coating are similar to those described above, but differ considerably from the conditions realized in thermal analysis.

The starting data for determining the characteristics is the temperature field. For this reason, in order to solve the problem, it is necessary to use the complete system of equations of heat and mass transfer and chemical kinetics, written for the decomposition zone. Then, the thermophysical properties of the material (thermal conductivity and others) are described together with the kinetics as well.

1. We are concerned with one-dimensional heating of a semiinfinite body. The mathematical model of the decomposition of polymer materials is well known [1]. However, it should be noted that Arrhenius' law has, apparently, limited applicability. This is indicated by the existing differences in the kinetic characteristics, obtained under different experimental conditions, their dependence on the heating rate, and other characteristics. For this reason, we will write the kinetic equation in generalized form, taking into account the variability of the decomposition characteristics

$$\partial\varepsilon/\partial\tau = w(\varepsilon,\ T), \tag{1}$$

where $0 < \varepsilon < 1$ is the degree of transformation. The following condition is imposed on the temperature dependence of the decomposition rate $w(\varepsilon,\ T)$

$$\Delta T = \left| w(\varepsilon,\ T) / \left( \frac{\partial w}{\partial T} \right)_{\varepsilon} \right| \ll T. \tag{2}$$

The quantity $\Delta T$ is essentially the characteristic temperature interval in which the decomposition occurs. If $w \sim \exp(-E/RT)$, then (2) gives $E/RT \gg 1$, which is satisfied for most polymers, even taking into account the spread in the data for E.

We will not write out the general equations of heat and mass transfer in the decomposition zone [1], rather we will limit ourselves immediately to approximate equations taking into account the following considerations. Since $\Delta T$, according to (2), is small, the characteristic width of the decomposition zone and the decomposition time $\tau_d$ will also be small. It is then natural to assume that the processes in the decomposition zone are quasistationary and will be described by transfer equations, in which the time derivative $\partial/\partial\tau$ is replaced by $-v(\partial/\partial y)$. The quasistationary equations admit a number of transformations [2-5], lowering their order and reducing the problem to the solution of the heat balance equation

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$$-\lambda(\varepsilon, T)\,\partial T/\partial y = q + \rho v \Delta H \varepsilon. \quad (3)$$

The quantities q and v can be determined from the solution of the heat-conduction problem, in which the decomposition zone is replaced by a front.

Apparently, in order for the conditions of quasistationariness to be satisfied, it is necessary that q and v be changed little over the decomposition time $\tau_d$. The characteristic time over which q and v changed by an amount on the order of their own values is determined from a solution of the heat-conduction equations for the entire heating region and will, apparently, be on the order of $\Delta/v \sim a/v^2$, where $\Delta \sim a/v$ is the depth of heating; $a$ is the coefficient of thermal conductivity. At the same time, $\tau_d \sim \delta_d/v$. But, according to the Fourier law $\delta_d \sim \lambda \Delta T/q$, $\Delta \sim \lambda(T_d - T_0)/q$, where $T_d$ and $T_0$ are the decomposition temperature and the temperature at infinity, respectively. From here, $v\tau_d/\Delta \sim \Delta T/(T_d - T_0) \ll 1$. Thus, for small $\Delta T$, the decomposition can be assumed to quasistationary.* An estimate, which is not presented here, gives for the discarded terms in the transfer equations a quantity on the order of $\Delta T/(T_d - T_0)$.

Further, it is already possible to make a number of simplifications in the quasistationary equations. In particular, we will assume that in the interval $\Delta T$ the heat of decomposition $\Delta H$ is constant, while $\lambda$ depends only on $\varepsilon$. Actually, such an assumption is used in problems with a similar mathematical description in the theory of thermal propagation of a flame (the Zel'dovich—Frank-Kamenetskii method) [2, 3]. However, in application to the problem being examined, it must be checked experimentally, since $\Delta H$ and $\lambda$ are some effective characteristics.

For what follows, it is more convenient to go over in (3) to a time derivative $\partial/\partial\tau$ for fixed stationary coordinate $x = y + \int_0^\tau v\,d\tau$:

$$+\lambda(\varepsilon)\,\partial T/\partial\tau = qv + \rho v^2 \Delta H \varepsilon. \quad (4)$$

Solving (1) and (4) simultaneously, we find $\varepsilon(\tau)$ and $T(\tau)$ at a fixed point in the body. They depend on the coordinate x implicitly through the functions q(x) and v(x), determined, as already noted above, from a solution of the problem with a moving front (for calculation of the characteristic temperature of the front, see, e.g., [1, 5]). Equations (1) and (4) are also starting equations for solving the inverse problem: the determination of the decomposition characteristics $w(\varepsilon, T)$, $\lambda(\varepsilon)$, and $\Delta H$.

2. Let us proceed to the solution of the inverse problem. The starting data are the dependences $T(\tau)$ at different points of the body x, obtained experimentally. The quantities $w(\varepsilon, T)$, $\lambda(\varepsilon)$, and $\Delta H$ must be chosen in such a way that in the time interval $\Delta\tau$, corresponding to decomposition, the function $T(\tau)$ satisfies (1) and (4).†

The quantities q(x) and v(x), entering into (4), are determined beforehand as follows. Evidently, v(x) in the first approximation can be identified with the velocity of displacement $(\partial x/\partial\tau)_T$ of the isotherms with temperatures corresponding to the decomposition process. In the interval $\Delta T$, $(\partial x/\partial\tau)_T$ varies little (on the strength of (2)). The flux q(x) is calculated according to (4) with $\varepsilon = 0$ up to a factor $\lambda(0)$. If, on the other hand, the properties of the starting material (here $\lambda(0)$) are known, which is what is assumed in what follows, then q(x) is known as well.

It is evident from (1) and (4) that the single function $T(x, \tau)$ corresponds to a set of functions $w(\varepsilon, T)$, $\lambda(\varepsilon)$, and $\Delta H$ respectively, i.e., the solution of the problem formulated as above is not unique. For example, given arbitrary $\lambda(\varepsilon)$ and $\Delta H$, we can determine $\varepsilon(\tau, x)$ from (4), and then $w(\varepsilon, T)$ from (1) and (4). It is also possible to give different $w(\varepsilon, T)$, although it is impossible to choose this function arbitrarily (choosing $w(\varepsilon, T)$ arbitrarily, we arrive at the dependence $\partial T/\partial\tau = f(\varepsilon, x)$, which does not reduce in general to the special form (4)).

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*Since it is necessary to have a time on the order of $\tau_d$ to establish the quasistationary process, the quasistationary equations, in particular (3), will be applicable a time $\tau_d$ after the onset of decomposition as well.

†This time interval can be determined as follows. For an appreciable change in $\lambda(\varepsilon)$ and $\rho v \Delta H \gtrsim q$ in the interval $\Delta\tau$, a sharp increase in $|d^2T/d\tau^2|$ will be observed (for $\Delta T \ll T - T_0$) to a magnitude exceeding the value in the starting material by a factor of $N \sim (T - T_0)/\Delta T$. At the end of the decomposition ($\varepsilon \to 1$) $|d^2T/d\tau^2|$, on the contrary, drops sharply.

In order to obtain more complete information concerning the characteristics of decomposition, it is necessary to have as starting data a set of functions T(x, τ) obtained under different conditions of heating of the material (e.g., for different heat fluxes at the surface). In this case, a set of functions q(x) and v(x) is likewise obtained. In the general case, the set of functions T(x, τ), q(x), and v(x) corresponds to a set of functions T(τ, q, v). It is significant that in the interval Δτ, corresponding to decomposition, and in intervals $\Delta q \sim q$ and $\Delta v \sim v$, the functions T(τ, q, v) must be the same (more rigorously, the inverse functions τ(T, q, v) must differ by an additive constant, but this difference can always be eliminated by choosing in an appropriate manner the origin of τ for each function). A small spread is possible due to the approximate nature of Eq. (4). If, on the other hand, the spread is appreciable, then this can indicate either that the conditions for quasistationariness are not satisfied or that the model is inapplicable as a whole.

Of course, within the framework of (1) and (4), it makes sense to analyze only close functions T(τ, q, v), replacing them by some average function.

Let us now show how to determine the unknowns w, λ, and ΔH from T(τ, q, v). For this purpose, we first transform T(τ, q, v). Let us introduce the functions (taking into account (1) and (4))

$$\varphi = \frac{1}{qv}\,\frac{\partial T}{\partial \tau} = \frac{dv + \rho v^2 \Delta H \varepsilon}{qv\lambda(\varepsilon)}, \tag{5}$$

$$\psi = \frac{1}{qv}\,\frac{\partial^2 T}{\partial \tau^2} = \frac{\partial}{\partial \varepsilon}\left(\frac{qv + \rho v^2 \Delta H \varepsilon}{qv\lambda(\varepsilon)}\right) w(\varepsilon, T). \tag{6}$$

Then, we consider $\psi$ as a function of T, v/q, and $\varphi$ and we calculate the integral

$$\xi\left(T, \frac{v}{q}, \varphi\right) = \int\limits_{\varphi_0}^{\varphi} \frac{q\varphi}{\psi\left(T, \dfrac{v}{q}, \varphi\right)},$$

and in addition, the integration is carried out for constant T and v/q, where $\varphi_0$ is an arbitrary number. The inversion $\xi(T, v/q, \varphi)$ gives some function $\varphi(\xi, v/q, T)$. We shall examine its properties. It follows from (5) and (6) that the integral (7) can be represented in the form

$$\xi = \int\limits_{\varepsilon_0}^{\varepsilon} \frac{d\varepsilon}{w(\varepsilon, T)} \tag{8}$$

(integration with T = const, $\varepsilon_0 = \varepsilon(\varphi_0)$). It follows from here that for ε = const and T = const, ξ = const as well. This means that the function $\varphi(v/q)$ for ξ = const and T = const must satisfy (5) (for ε = const) and, in particular, must be linear.

Thus, we arrive at the following algorithm for determining w, λ, and ΔH. From the known function T(τ, q, v), we find the function $\varphi(\xi, v/q, T)$ from Eqs. (5)-(7) and we approximate it for T = const and ξ = const by a linear function. As a result, we obtain λ(ξ, T) and ΔHε/λ = f(ξ, T), and from here λ(ΔHε) and ξ(ΔHε, T) (in addition, the function λ(ΔHε) must not depend on T). Then, differentiating ξ(ΔHε, T) with respect to ΔHε, in accordance with (8), we determine w(ΔHε, T)/ΔH. Then, we establish the region $\varphi(\xi, v/q, T)$, corresponding to ε = 1, i.e., termination of decomposition (see the second footnote). From here we find ΔH and, therefore, λ(ε) and w(ε, T). The last stage is important; in the absence of information concerning T(τ, q, v), for ε = 1, it is impossible to determine the decomposition characteristics uniquely.

The characteristics obtained will be valid for some interval of arguments $\Delta v \sim v$ and $\Delta q \sim q$ of the function T(τ, q, v), which corresponds to an interval of decomposition temperatures of the order of ΔT (2). It is possible to analyze in a similar manner other regions of variation of q and v (but, necessarily, $\Delta q \sim q$ and $\Delta v \sim v$; in the opposite case, it is not possible to neglect the dependences of ΔH and λ on T). In this case, for strongly differing conditions of heating, λ and ΔH can depend strongly on T (since a change in T is appreciable), but if the formulation of the problem (1) and (4) is applicable, then the conditions $\Delta T\left|(\partial\lambda/\partial T)_\varepsilon\right| \ll \lambda$ and $\Delta T(\partial \Delta H/\partial T) \ll \Delta H$ will always be satisfied.

At the same time that w, $\lambda$, and $\Delta H$ are determined, the applicability of the approximations in the formulation of the problem is also checked. Aside from the properties of $T(\tau, q, v)$, already noted above, the fact that linear dependences $\varphi(v/q)$ for constant T and $\xi$ are obtained is important. This follows directly from $(\partial\lambda/\partial T)_\varepsilon = 0$ and $\partial\Delta H/\partial T = 0$ (under the condition, of course, that the decomposition described by (1) is a single-stage process). An additional confirmation is obtaining linear functions $\varphi(v/q)$ for all T with identical $\lambda$ (for $\varepsilon = \text{const}$).

In practice, $\varphi(v/q)$ will be linear only approximately, even if the conditions $(\partial\lambda/\partial T)_\varepsilon = 0$ and $\partial\Delta H/\partial T = 0$ are satisfied exactly, due to the assumption of quasistationariness. Evidently, it is always possible to carry out the calculation to second order, taking into account the nonstationary terms in the energy equation (3) (having the form of some integrals) and calculating them using the functions $\Delta H$, w, and $\lambda$ obtained in the first approximation. However, repeating this procedure is hardly useful, if for no other reason than that the description of a multistage decomposition process by Eq. (1) is in itself an approximation. Introducing a two-stage description of the type

$$\partial\varepsilon_1/\partial\tau = w_1(\varepsilon_1, \varepsilon_2, T);\ \partial\varepsilon_2/\partial\tau = w_2(\varepsilon_1, \varepsilon_2, T)$$

makes the inverse problem not unique; it is possible, given the thermophysical parameters ($\lambda(\varepsilon_1, \varepsilon_2)$, $\Delta H_1$, $\Delta H_2$), to give thereby a definite function $F_1(\varepsilon_1, \varepsilon_2, \tau, v, q) = 0$ following from the energy equation (or equations of the type (4)) and, therefore, $F_2(\partial\varepsilon_1/\partial\tau, \partial\varepsilon_2/\partial\tau, T, v, q) = 0$, and then to choose $w_1$ and $w_2$ from the conditions $\partial F_2/\partial v = 0$ and $\partial F_2/\partial q = 0$. In addition, the expansion of the solutions (1) and (4) in a series in powers of the small parameter $\Delta T/(T_d - T_0)$ is probably asymptotic. This can be shown for some very simple examples, when the system (1) and (4) has an analytic solution [5], which we do not discuss here. For this reason, for processes with $\Delta T/(T_d - T_0) \sim 1$, the method examined above is not applicable.

## NOTATION

$\varepsilon$, degree of transformation; T, temperature; $\tau$, time; x, coordinate; y, stationary coordinate; $\lambda$, coefficient of thermal conductivity; $\rho$, density; $w(\varepsilon, T)$, rate of decomposition; $\Delta H$, heat of decomposition; v, velocity of the decomposition zone; q, heat flux for $\varepsilon = 0$; $\Delta$, depth of heating; $\delta_r$, width of the decomposition zone.

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