MATHEMATICAL MODELING OF THE NONISOTHERMAL DEGRADATION OF HIGH POLYMERS AND NATURAL COALS

L. N. Aksenov, A. G. Shashkov,
and O. F. Shlenskii

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A kinetic equation is proposed to describe the nonisothermal degradation of decomposing materials in a broad range of heating rates with allowance for the coking stage. The physical meaning of the parameters of the proposed equation is demonstrated, and examples of analysis of empirical data using the model are presented.

Analytical description of the thermal degradation of high-molecular-weight compounds in general form is made extremely difficult by the complex character of the simultaneously occurring physicochemical transformations of the original substances and the products of their decomposition, the number of which is very great. Simplified modeling methods are used to solve practical engineering problems. For example, factorial experiment planning and the construction of statistical models are employed in design calculations. However, these methods do not have direct physical significance and are very tentative in nature. It is, therefore, important to construct a physically meaningful mathematical model which considers the basic features of the thermal degradation process and takes in a broader range of temperatures and heating rates than earlier well-known models. Knowing how the physicomechanical and thermophysical properties of decomposing materials depend on the degree of completion of the decomposition process will make it possible to use the model in engineering calculations for heat-protective structures [2] and in fuel processing technology.

An n-th order differential equation of the chemical reaction kinetics is used as the simplest mathematical model of the process of thermal decomposition [2, 3]

$$dC/dt = -kC^n. \tag{1}$$

Accordingly, for nonisothermal heating conditions

$$dC/dT = -kC^n/b. \tag{2}$$

It has been shown experimentally that, at low heating rates and under isothermal conditions, the properties of thermosetting plastics and coals stabilize over time [4]. Figures 1 and 2 show characteristic curves of decomposition of a polymer and coal. These results were obtained on IONKh system thermobalances. Modification of the balances made it possible to expand the range of variation of the heating rates. The test procedure repeated that described earlier in [4, 5]. It was proposed in [6, 7] that the stabilized state be determined by introducing the additional term $C_\infty = C_\infty(T)$ into the kinetic equation:

$$dC/dt = -k(C - C_\infty), \tag{3}$$

$$dC/dT = -k(C - C_\infty)/b. \tag{4}$$

We will show the physical meaning of this parameter. In the thermal degradation of coking materials, simultaneously with purely destructive processes there occur a counter process of recombination of individual bonds and the formation of a solid, nondecomposable residue [1]. The duration of the second process is abbreviated as the heating rate is increased. The rate components of both processes may be considered separately. Meanwhile, the term accounting for the rate of coke formation goes into the right side of the equation with a + sign. Since coke is formed from decomposition products in the solid, liquid, and gas phases (formation of pyrographite), the rate of formation of the nondecomposable residue increases with an increase in

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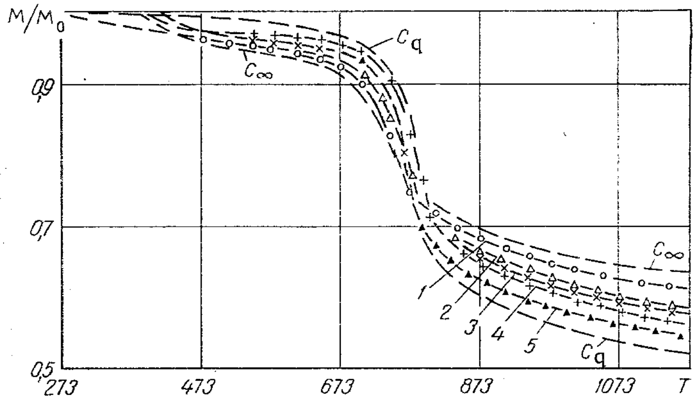

Fig. 1. Change in relative mass of specimens of coal G_6 during nonisothermal decomposition with different heating rates (deg/sec): 1) 0.15; 2) 0.25; 3) 1.17; 4) 2.5; 5) 3.67. T°K.

the degree of decomposition of the original material, i.e., the difference $C_0 - C = 1 - C$. Meanwhile, a substantial component of this process is the reaction involving the formation of the carbon matrix, occurring in the solid phase. Taking this into account, we obtain the kinetics equation with the right side expanded

$$dC/dt = -k_1C^n + k_2(1-C)^m. \tag{5}$$

Establishing the equilibrium of these two processes corresponds to equating the right side of this equation to zero, which means that $k_1C^n = k_2(1 - C)^m$. The solution of the last equation is the equilibrium concentration C_∞. In the special case with n = m = 1, we obtain $C_\infty = k_2/(k_1 + k_2)$, and Eq. (5) becomes Eq. (3). Calculations show that Eqs. (3) and (4) adequately describe the decomposition curves close to the boundary $C_\infty(T)$ [7].

However, Eq. (2) and modified equations (4) and (5) do not permit even qualitative description of the decomposition curves at high heating rates [8]. Moreover, neither these equations nor other kinetic equations in the literature, except for purely empirical equations, make it possible to describe the phenomenon of inversion — crossing of the decomposition curves at high heating rates [6, 9]. An attempt was made to explain the effect of inversion by dispersing test specimens and removing the incomplete combustion products with the flow of gases evolved [6]. However, additional tests conducted with prepulverized specimens (artificial dispersion of the material) showed that the inversion effect is nearly independent of the degree of pulverization and thickness of the specimens.

To adequately describe the kinetic decomposition curves at high heating rates with allowance for inversion, we introduce an additional term into the right side of Eq. (5) which vanishes at low heating rates. We will determine the structure of this new term on the basis of the notion of "weak" bonds, conceived in the thermofluctuation theory of thermal and mechanical degradation [10-12]. The presence of such bonds in macromolecules leads to a substantial reduction in the apparent activation energy of the thermal degradation process in its initial stage [11].

An increase in temperature by the amount $\Delta T = T - T_0$ first primarily intensifies the rupture of the "weak" bonds, and the number of these bonds decreases with time. As a first approximation, we will assume that the rate of loss of such bonds and the corresponding decrease in the mass of the substance is inversely proportional to time and amounts to $k_3(T - T_0)/(t - t_0)$. As $t \to \infty$, this expression tends to zero. In the case of linear heating, $T - T_0 = b(t - t_0)$. Then, after substitution into the right side of Eq. (5) and changeover to the variable T, we obtain

$$dC/dT = -k_1C^n + k_2(1-C)^m + k_3. \tag{6}$$

When n = m = 1, we have the simplified equation

$$dC/dT = -k_1(C - C_\infty)/b + k_3, \tag{7}$$

which was obtained earlier on the basis of somewhat different assumptions [7].

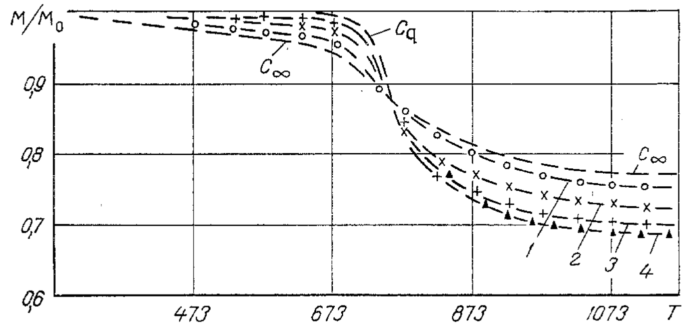

Fig. 2. Change in relative mass of specimens of coal K_2 during nonisothermal decomposition with different heating rates (deg/sec): 1) 0.05 and 0.15; 2) 1.17; 3) 2.5; 4) 3.67; points — experiment; dashes — calculation.

The relation $k_3(T)$ can be determined on the basis of empirical data of high heating rates from the curve of limiting dynamic decomposition $C_q(T)$, since $\lim_{b\to\infty} C(T, t) = C_q(T)$ and $\lim_{b\to\infty} (dC/dT) = d[C_q(T)]/dT = k_3(T)$. The following relation was proposed [13] to analytically describe the relation $C_q(T)$:

$$C_q(T) = \frac{M - M_k}{M_0 - M_k} = \exp\left[-\left(\frac{T - T_0}{T_c}\right)^2\right]. \qquad (8)$$

If $M_k \geqslant C_\infty M_0$, Eq. (7), together with Eq. (8), describes a family of decomposition curves within a broad range of heating rates without their inversion. If $M_k < C_\infty M_0$, then these equations describe the effect of inversion of the decomposition curves. The dashed curves in Figs. 1 and 2 show the results of calculations of the decomposition process on the basis of Eq. (7) with graphical prescription of the functions $C_\infty(T)$ and $C_q(T)$. It is obviously impossible to change beyond the inversion zone from Eq. (7) to the corresponding equation for isothermal heating conditions. Beyond this zone, $C = C_q$, regardless of the heating time, if the boundary of $C_q(T)$ has been reached during the heating.

The physical considerations underlying Eq. (8) pertain to models for several compounds with a low molecular weight [13]. It is necessary to prove the applicability of Eq. (7) on the whole to high-molecular-weight compounds, including coals [1]. For this, we will examine the probable processes of dissociation and recombination of bonds in the macromolecules leading to the formation of removable ("volatile") fragments. Analytical description of such processes in the general case is very difficult in connection with the need to calculate conditional probabilities. We will use the numerical method of random processes (Monte Carlo method). Calculations by this method can be performed on any computer with a random-number block if the structure of the polymer is known. For this, in conformity with the model, we will substitute a sequence of particles joined into a chain for actual macromolecules. Fragments of linear and network structures are shown in Fig. 3 in the form of such models. Each particle of the linear model corresponds to a monomer unit which can be given off in the form of a volatile product, such as C_2F_4 during the decomposition of teflon. All of the bonds in the model are numbered; through (single) numeration is used in the linear model, while binary numbering (along the vertical and horizontal) is employed in the model of a network structure. Each dissociation of a C—C bond, occurring with a supply of energy equal to the dissociation energy D, will be denoted by ~.

The function $C_q(T)$ of each model variant is determined by performing a mathematical experiment involving the following sequence of operations. When the next number is obtained from the random-number generator, the rupture of the bond with this number is noted on the model. This operation is repeated until a so-called "volatile" fragment of the molecule is formed. The length of this fragment, i.e., the number of particles forming it, must be assigned beforehand. In depolymerization, one particle corresponding to the monomer will be contained in the volatile fragments. A volatile fragment will be formed only when all bonds between it and the remainder of the macromolecule have been broken; thus, the formation of a fragment in a linear macromolecule requires the rupture of the bonds on both of its sides, while in the two-dimensional model of a cross linked polymer it is necessary that four bonds be broken. The rupture of six or four bonds is necessary to form a fragment in a three-

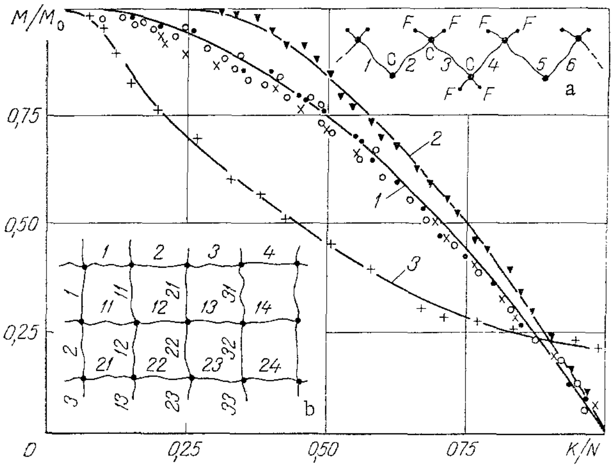

Fig. 3. Results of numerical mathematical modeling of the athermal breakdown of a linear structure (scheme a, curve 1) and a cross-linked structure (scheme b, curve 2) and the thermal breakdown of a linear structure (3).

dimensional structure, depending on the degree of cross-linking. The number of particles in the volatile fragments entered into the counter. After the generation of K numbers and the formation of L fragments, the total loss of mass will be $\overset{L}{\Sigma} M_i$, while the mass of the residue $M = M_0 - \overset{L}{\Sigma} M_i$.

With a repeating random generation of numbers for the dissociated bonds, the number K is increased by unity and any other bonds, such as these closest to the ends of the macromolecule residue, are ruptured. Figure 3 shows the results of calculations of three variants of linear models with $N = 100$ and $M_i = 1$. The ratio K/N has been plotted off the horizontal axis and the quantity $C = M/M_0$ off the vertical. We should note the good reproducibility of the results of the computation in all three variants — the points nearly coincide. The results of the calculation were approximated by the equation of a quadratic parabola: $M/M_0 = 1 - (K/N)^2$. With a linear relationship between the supplied energy KD and the temperature, we accordingly obtain the relation $C_q(T) = 1 - \theta^2$, $0 \leqslant \theta \leqslant 1$.

Calculation of the relation $M/M_0 = f(K/N)$ of the model of the network structure (Fig. 3) showed that an increase in the number of cross-linkings leads to an increase in energy expended on the formation of the first volatile products, i.e., to an increase in the heat resistance of the polymer. Since similar calculations can be performed without significantly more trouble for other polymeric structures (parquet, with three-dimensional cross-linking, heterogeneous, etc.), the proposed method makes it possible to evaluate the effect of features of the structure of the material on its heat resistance T_n.

Using the methods of the theory of probability, it can be shown that, with an arbitrary number n of particles in the one volatile fragment, $M/M_0 = (1 - K/N)^n(1 + nK/N)$. When $n = 1$, $M/M_0 = 1 - (k/N)^2$.

The loss of mass of the models due to other processes is calculated as follows. In accordance with Eq. (1), the frequency of rupture of the bonds is proportional to the number of bonds, with the proportionality factor k. The same sequence of operations is used to model bond dissociation under isothermal conditions except that, with the repeated generation of the number of an earlier-dissociated bond, no note is made of the dissociation of another, different bond. Thus, with an increase in the number of ruptured bonds, the probability (and frequency) of ruptures of the remaining bonds decreases. At the same time, the generation of each random number on a certain scale corresponds to an advance along the scale in time by the amount Δt. The results of the calculations should be represented in the coordinates C, t, where $t = k'\Delta t$. In this computation variant, the amount of energy supplied is related to the number of dissociated bonds k' only, forming the quantity k'D. A change in the size of the interval Δt corresponds to a change in the reaction rate according to Eq. (1): $k\Delta T = -\Delta C/C^n$, where C here is the number of bonds. This makes it possible to graph C as a function of temperature, as well as for nonisothermal conditions. Figure 3 shows the results of modeling of the dissociation of bonds of a linear macromolecule with $N = 100$ and $T = \text{const}$. It is clear that the dissociation process has an initial stage with a slower release of volatile matter. This result corresponds to the delay in the release of volatile matter during the induction period seen experimentally for many polymers [3]. It is important to emphasize that the induction period of the thermal degradation process cannot be described by the simplest equation (1) if we formally substitute the value $C = M/M_0$ into it, as is usually done. The completed analysis shows the reason for such a discrepancy. However, at all subsequent stages of the process, Eq. (1) describes the experimental data at $T = \text{const}$ well.

The two above-examined types of modeling of the thermal degradation process — with and without indication of the rupture of a bond of another number in the case of repeat generation of the number of a dissociated bond — are two extreme possible cases of thermal degradation. Both types are probabilistic in nature and are controlled by the rate of energy delivery to the substance. Using the terminology of polymer mechanics — which also studies such processes — we will call the second of these processes thermal breakdown of the structure, and the first, athermal breakdown. Both processes occur simultaneously in nonisothermal degradation, and the parameter b characterizes their contributions to the total mass loss of the material. The contribution of the athermal process increases with an increase in b, while thermal breakdown predominates with a decrease in heating rate. The thermal process pertains also to the coking process, which is modeled by restoring some of the dissociated bonds in accordance with the law for this case and giving back the restored bond its number. The calculations are complicated considerably if account is taken of the different activation energies of the principal and lateral bonds, different particle sizes, orientation effects, and the consequences of different frequencies of rupture of dissimilar bonds.

However, the uniform-structure models examined are quite informative. The modeling showed that α should be set equal to zero in the expression used earlier [7] for the component rate of athermal breakdown in the form $k_t C$. Then $k_t = k_e$, since the decomposition curve has a nonzero slope at $C_q = 0$ and $dC_q/dT = 0$. The proposed modeling method makes it possible to evaluate energy expenditures during the occurrence of physicochemical decomposition processes and to thus refine the mechanism of these processes. The amount of energy necessary to form monomers from linear macromolecules is related to the temperature of completion of the decomposition process T_h, the specific heat of the material c_p, and the thermal effects of the transformations: $Q : ND = \int_0^{T_h} c_p dT + Q$. The following values of T_h were obtained from this relation for certain linear polymers in depolymerization: polypropylene $T_h = 1040$°K (1000°K), polystyrene $T_h = 650$°K (770°K), polymethyl methacrylate $T_h = 690$°K (550°K), fluoroplastic (Teflon) $T_h = 1070$°K (1000°K). The figures in parentheses indicate experimental values of the same temperature taken from published data [2] obtained with linear heating conditions. The correlation between the experimental and calculated values is satisfactory. The completed calculations make it possible to establish the physical meaning of the parameters of the equations used to describe the relations $C_q(T)$ and $C_\infty(T)$: in Eq. (8), with a prescribed deviation δ from zero of the variable of the corresponding temperature $T(\delta)$, we obtain $T_c = (T_b - T)/\sqrt{\ln \delta}$; the temperature T_h also enters into the expression for θ.

The completed analysis indicates the numerical characteristics of nonisothermal degradation processes subject to empirical determination. This includes the temperature T_b and T_h, the relations $C_q(T)$, and the corresponding temperatures for the material in the stabilized state, as well as the parameters of the relation $k(T)$ or the corresponding function $\int_{T_0}^{T} k(T) dT$, entering into the integrals of the kinetic equations. Use of the relations $C_q(T)$ and $C_\infty(T)$ significantly improves the accuracy of the description of decomposition kinetics at different heating rates compared to Eq. (1), used until now.

NOTATION

b, heating rate; C, coordinate of reaction, concentration; M, M_0, running and initial values of mass of the substance; C_∞, equilibrium value of C(T); n, m, orders of the forward and reverse reactions; M_1, mass of the volatile fragments; k_1, k_2, constants; T_0, initial temperature; T_b, temperature of beginning of decomposition; T_h, temperature of completion of decomposition; D, energy of dissociation of carbon–carbon bond.

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MOLECULAR TRANSFER

V. F. Potemkin

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Universal relations pertaining to molecular transfer of momentum, heat, and mass are derived on the basis of a special mathematical transformation.

Molecular transfer occurs widely in nature as well as in technology and, therefore, knowing the laws which govern it is particularly important. The laws governing the molecular transfer of momentum, heat, and mass cannot be derived through solution of known differential equations, because the system of these equations is generally not a closed one. Relations based on semiempirical theories or on processing of experimental data, on the other hand, contain empirical constants and are not general.

In [1, 2] universal relations for molecular transfer of momentum and heat have been derived with the aid of a special mathematical model. In this study those results will be refined and extended.

The region of molecular transfer will be defined as

$$x_2 \geqslant x \geqslant x_1 \geqslant 0, \quad \delta(x) \geqslant y \geqslant \delta_0(x) > 0, \tag{1}$$

where x is the longitudinal coordinate measurable on the solid surface (wall); y, transverse coordinate measured from the wall; $\delta(x)$, upper limit of this region (e.g., thickness of the turbulent boundary layer); and $\delta_0(x)$, lower limit of this region (thickness of the laminar sublayer).

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