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MATHEMATICAL MODEL OF THE KINETICS OF THERMAL DEGRADATION  
OF POLYMERS WITH INTENSIVE HEATING

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A modified equation is proposed to describe the kinetics of the thermal degradation of polymers with allowance for temperature limits for the polymers. A physical interpretation of the model is given.

The need to mathematically model thermal degradation processes arises in the solution of both direct and inverse problems of heat transfer, since the thermophysical characteristics of the materials undergoing degradation are dependent on the completeness of the chemical reactions. It is difficult to perform such modeling because a large number of chemical and physical processes are taking place simultaneously in the material. Thus, if 20 substances are formed as a result of degradation, this corresponds to 20 kinetic equations including 60 parameters. Accompanying the chemical reactions are complex physical processes: mass transfer (diffusive and molar) of the degradation products and their interaction — dissolution, sorption, and desorption, etc. Even for a simple composition during thermal degradation, a complete system of equations describing the transformations in polymers has not yet been solved. Given this situation, the development of simple mathematical models adequate to the physics of the phenomena in question is very important for engineering calculations.

Studies of polymers of different classes by the methods of thermal analysis conducted in a broad temperature range have shown that the regions of thermal degradation of polymers are limited. The upper boundary of the degradation region was first fixed in tests with heating rates of 1-10 deg/sec. Later tests conducted at heating rates up to  $5 \cdot 10^4$  deg/sec confirmed the conclusions made. It was established for linear polymers that thermal degradation is completed upon attainment of a limiting temperature  $T_{mt} = 500-540^\circ\text{C}$ , regardless of the heating rate. The limiting temperatures are higher for cross-linked polymers. Tests with high heating rates were conducted on specimens up to 5-7  $\mu\text{m}$  thick. The particulars of the methods used for tests are described in [1, 2].

In engineering applications, the kinetics of the thermal degradation of high-molecular-weight compounds is usually described by the equation of an  $n$ -th-order chemical reaction

$$d\omega/dt = -k(\omega - \omega_\infty)^n, \quad (1)$$

where it is assumed that

$$k = k_0 \exp(-E/RT). \quad (2)$$

It cannot be expected that system (1)-(2), containing three parameters in all, will adequately characterize the larger number of complex processes that occur in thermal degradation. However, it has been empirically established that this system well reflects the kinetics of the thermal degradation of polymers with a single heating rate. With another heating rate, the parameters  $k_0$ ,  $E$ , and  $n$  turn out to be quite different [3]. Here,  $k_0$  may change by several orders of magnitude when heating rate increases by several factors [3]. A serious

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TABLE 1. Limiting Temperatures of Thermal Degradation of Polymers

Polymer	Gravimetric method		"Replica" method
	$T_i$	$T_f$	$T_{limn}$
Block polystyrene	480	520	525
Shock-resistant polystyrene	470	530	540
Polymethylmethacrylate	450	520	515
Low-density polyethylene	480	500	500
Polyethyleneterephthalate	—	500	490
Colemanite	375	395	400
Ca [B <sub>2</sub> O <sub>4</sub> (OH) <sub>3</sub> ]H <sub>2</sub> O			

Note. The parameters E and  $k_0$  of the polymers studied correspond to the data in [5].

shortcoming of system (1)-(2) is the absence of characteristic temperatures  $T_{mt}$  as a parameter. Also, the system does not consider the appreciable acceleration of thermal degradation as  $T_{mt}$  is approached.

In the theory of absolute reaction rates, each elementary reaction has a rate dependent on temperature in a manner similar to Eq. (2). In accordance with this equation, the maximum  $d\omega/dt$  occurs at the point of inflection of the curve  $k = k(T)$  at the temperature  $T_{trn} = E/2R$ . The activation energy for all of the intermediate stages of thermal degradation of the polymers studied lies within the range 20-60 kcal/mole, which corresponds to a temperature of 5000-15000°C. At the same time, it follows from experiments that degradation of polymers speeds up at considerably lower temperatures. Thus, the limiting temperatures of thermal degradation evidently cannot be explained only by chemical reactions, which makes it necessary to determine the nature of the transformations occurring in physical processes.

The process of thermal degradation is heterogeneous, and the chemical reaction proceeds on the surface of the condensed phase. The generation and removal of degradation products are impeded by the "cage" effect — space-time obstacles to their transport to the surface increase the probability of recombination of dissociation products and macroradicals. An increase in temperature leads to a decrease in viscosity and an increase in the coefficient of diffusion of the degradation products. Here, the rate of gasification increases more rapidly than would follow from Eq. (2), which does not consider the physical properties of the material (viscosity, diffusion coefficient, etc.).

Simultaneously with weakening of the "cage" effect during heating, there is a decrease in surface tension. This intensifies homogeneous nucleation. According to [4], the rate of homogeneous nucleation is equal to

$$J = NB \exp(-W/k_d T). \quad (3)$$

A consequence of an increase in J is an increase in the free surface and an associated increase in the rate of the degradation reaction. Since  $W < E$ , the process begins to intensify at a temperature considerably lower than  $T_{trn}$  — specifically, at the temperature  $W/2k_d$ . Thus, in addition to the heterogeneous nuclei created earlier, an increase in the surface of the bubbles due to homogeneous nucleation is a second component of acceleration of the process of gasification of the polymer and makes it possible to interpret thermal degradation near the temperature  $T_{mt}$  as spinodal decomposition.

However, compared to low-molecular-weight compounds, a polymer has a specific feature — the macromolecules cannot exist in the gaseous state. Upon attainment of the temperature  $T_{mt} = D_m/k_d$  corresponding to the breaking of all intermolecular bonds, the macromolecules turn out to be in an isolated free state. This is preceded by a substantial increase in the volume of the substance. In the isolated state the macromolecules have an excess of free energy G sufficient to shorten the period of their existence before the period of free vibration, and their decomposition is of an explosive nature — as was shown in [5].

The mechanism of degradation of macromolecules in the isolated state was described in [6], which showed the important role of quasiparticles — dilatons — in the loss of stability of vibration of anharmonic oscillators [7]. A significant contribution to acceleration of the dissociation of C-C bonds is made by inertial forces arising in the rotation of kinetic

units. This rotation is unhindered at high temperatures [8]. The values of  $D_m$  for dipole-dipole molecular interaction are about 1620 cal/mole [9], which gives a value of about 500°C for the limiting temperature  $T_{mt}$  for linear polymers. This value agrees well with the experimental data. The above analysis allows us to suggest the following modified equation to describe the rate constants for thermal degradation:

$$k = k_0 \exp \left( -\frac{E}{RT} + \frac{A}{1/T - 1/T_{mt} + a} \right). \quad (4)$$

At moderate temperatures, this equation describes a linear dependence of  $\log k$  on the inverse temperature, while when  $T = T_{mt}$  the function  $k(T)$  approaches a vertical line. When  $T_{mt}$  is reached, the process of thermal degradation is determined by the rate of removal of the products, i.e., it occurs in the diffusive rather than the kinetic region. The parameter  $a$  is introduced to avoid an unlimited increase in the gasification rate at  $T = T_{mt}$ . Table 1 shows some values of  $T_{mt}$  in Eq. (4) determined from experiments in [10] with  $A \cong 10^{-5}$  1/K and  $a \cong 10^{-6}$  1/K.

#### NOTATION

$k_0$ , preexponential multiplier;  $E$ , activation energy;  $R$ , universal gas constant;  $N$ , number of molecules per unit volume,  $m^3$ ;  $B$ , kinetic multiplier,  $B = 10^{10} \text{ sec}^{-1}$ ;  $k_B$ , Boltzmann constant;  $W$ , work of nucleation of the gas phase;  $D_m$ , energy of rupture of intermolecular bonds;  $\omega$ , relative mass of residue,  $\omega = M/M_0$ ;  $\omega_\infty$ , equilibrium value of  $\omega$  at  $t \rightarrow \infty$ ;  $T_i$  and  $T_f$ , limiting initial and final temperatures of thermal degradation under nonisothermal test conditions.

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