DETERMINING THE KINETIC PARAMETERS OF A THERMAL-DECOMPOSITION PROCESS BY SOLVING THE INVERSE PROBLEM

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We examine the problems of mathematical description and determination of the kinetic parameters applicable to the process of destroying the binder in the high-temperature heating of a glass-reinforced plastic.

A number of references [1-3] have been devoted to the investigation of the thermal destruction of polymers; a characteristic feature of these references is the chemical approach and qualitative nature of the results derived. The quantitative data found in certain of these references are, for the most part, inadequate to describe the kinetics of the destruction, and in a number of cases they are contradictory [4, 5]. Moreover, it should be noted that the destruction of the polymers in a glass-reinforced plastic, because of the specific and nonhomogeneous structure of the material, and because of certain technological and similar factors, may differ from the destruction of pure polymers. Therefore, the destruction of polymers under conditions close to operational must be investigated.

The thermal destruction of polymers is a complex multistage chemical process in which the original high-molecular substance is converged to gas form, as well as into liquid and solid products of decomposition. According to the results derived in [6, 7], the kinetics of complex chemical reactions can be described approximately by a summary kinetic equation compiled for some determining (and, if possible, easily controlled) parameter. Here we must insist that the change in the chosen parameter be associated with the completion of the highest possible number of elementary reactions and that it uniquely define the remaining characteristics of the process of interest to us (the yield of products of decomposition, the absorption of heat, etc.).

Weight serves as a parameter for the thermal destruction of polymers or, if the weight is referred to the initial volume of the test object, then it is the apparent density of the solid phase that serves as the parameter.

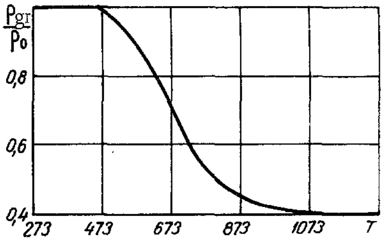

Fig. 1. Thermogravimetric curve for the decomposition of the binder used in AG-4S glass-reinforced plastic, with stepwise heating of the specimen.

The summary kinetic equation for this quantity [5] can be written in the form

$$\frac{d\rho}{d\tau} = -B\rho_0\left(\frac{\rho-\rho_c}{\rho_0}\right)^n \exp\left(-\frac{\Delta E}{RT}\right), \qquad (1)$$

where ρ_0 and ρ_c are, respectively, the density of the polymer and the density of the coke residue; ρ is the density of the solid phase in the destruction process; T is the absolute temperature; R is the universal gas constant; B, n, and ΔE are the generalized kinetic parameters of the process (the coefficient of the reaction rate, the order of the reaction, and the activation energy, respectively), which in the general case depend on the temperature and the degree of polymer decomposition $\varepsilon = (\rho_0 - \rho)/(\rho_0 - \rho_c)$.

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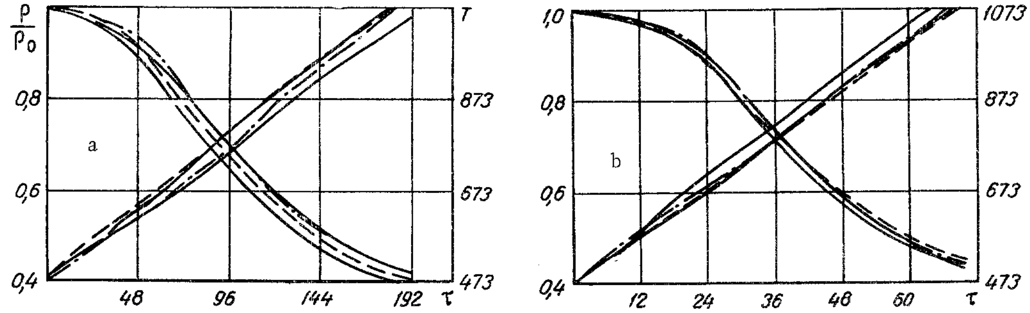

Fig. 2. Variation in the density and temperature of AG-4S glass-reinforced plastic specimens at a heating rate b = 3 deg/sec (a) and b ≈ 10 deg/sec (b).

Equation (1) provides a good description for the destruction process at thermal impact loads with a high temperature level [5].

For heating in the range below 1000°K and with an arbitrary law governing variation in $T(\tau)$ we must take into consideration the relationship between the depth of polymer decomposition and the temperature characterized by the thermogravimetric decomposition curve. The generalized summary kinetic equation of destruction, in which consideration is given to the above relationship, assumes the form

$$\frac{d\rho}{d\tau} = -B\rho_0\left(\frac{\rho-\rho_{\text{gr}}}{\rho_0}\right)^n \exp\left(-\frac{\Delta E}{RT}\right), \tag{2}$$

where ρ_{gr} is the gravimetric density of the polymer at the temperature T.

Equation (2) gives a good description of the polymer destruction for any heating regimes.

The parameters B, n, and ΔE in this equation must be determined experimentally. The usual methods of thermal analysis are not suitable for this purpose, since they are based on an experimental study of the process being investigated under specific conditions and they are also based on the subsequent extrapolation of the derived values of B, n, and ΔE for other regimes and conditions of the process.

Equation (2) is an approximate mathematical model of the destruction process, and the indicated extrapolation may therefore lead to substantial errors. To provide for the best description of the actual process, the parameters of the approximate models must be determined on the basis of the experimental data obtained from an investigation of the process under conditions close to the operational mode.

The above formulation of the problem leads to the task of determining the coefficients in the equation describing the process on the basis of the known experimental data relating to the functions of state for the system being investigated; here, because of measurement errors and errors in interpretation, as well as because of the approximate nature of the process model employed, these data are not exact solutions of the equations taken. The determination of the model parameters under these conditions is possible only in the sense of seeking those coefficients which provide for the best approximation of the entire existing set of experimental data. The approximation described in this case enables us to estimate the degree of correspondence between the chosen model and the actual process.

Let us assume that a polymer specimen of volume V with an initial weight $\omega_0 = \rho_0 V$ is subject to nonsteady high-temperature heating. The temperature distribution $T(p, \tau)$ in the specimen and the change in the weight $\omega^{(\exp)}(\tau)$ of the specimen are measured during the heating process.

If we assume that the destruction of the polymer is described by (2), to calculate the weight of the specimen under consideration we derive the expression

$$\omega(\tau) = \omega_0 - \iiint\limits_V \int\limits_0^\tau B\rho_0\left(\frac{\rho-\rho_{\text{gr}}}{\rho_0}\right)^n \exp\left(-\frac{\Delta E}{RT(p,\tau)}\right) d\tau dV. \tag{3}$$

The kinetic parameters of the destruction process, i.e., B, n, and ΔE, can then be determined from the conditions for the best description of the experimental curve for $\omega^{(\exp)}(\tau)$ by (3). The criterion indicating the satisfaction of this condition may be the magnitude of the mean square deviation in the measured values of the function $\omega(\tau)$ from those calculated with (3). Mathematically, the problem of determining B, n, and ΔE

TABLE 1. Determination of the Kinetic Parameters for the Process of Binder Destruction in the Glass-Reinforced AG-4S Plastic

$p=k$		0	1	2	3
$\ln B=\sum_{j=0}^{k} a_j \varepsilon^j$	a_0	—3,0.73	15,48	24,57	27,25
	a_1	—	—5,12	—2,581	—1,59
	a_2	—	—	—4,531	—6,36
	a_3	—	—	—	1,381
n		0,822	0,8088	0,4287	0,5069
$\frac{\Delta E}{R}=\sum_{s=0}^{p}\frac{d'_s}{T^s}$, °K	d'_0	507,3	19420	35581	43868
	$d'_1\cdot 10^{-3}$	—	—4835	—13578	—22144
	$d'_2\cdot 10^{-5}$	—	—	16436	53668
	$d'_3\cdot 10^{-7}$	—	—	—	—60632
δ, %		5,04	2,004	1,929	1,917
$(\delta_i)_{\max}$, %		8,56	3,12	3,03	3,0
$\frac{\Delta E}{R}$ (500°K), °K		507,3	9756	14999	16.196
$\frac{\Delta E}{R}$ (1000°K), °K		507,3	14591	23647	26485

is written in the form

$$\delta^2=\frac{1}{\bar{t}}\int_0^{\bar{t}}\left[\omega(\tau)-\omega^{(\mathrm{exp})}(\tau)\right]^2 d\tau=\min, \tag{4}$$

where $\bar{t}$ is the duration of the experiment.

To eliminate random measurement errors and to encompass the entire range of conditions of interest to us with respect to the progress of the destruction process, in the determination of B, n, and ΔE we must use the results from the series of experiments performed under various conditions. With simultaneous processing of the results from the series consisting of m experiments, we find that (4) is transformed to

$$\delta^2=\frac{1}{m}\sum_{i=1}^{m}\frac{1}{\bar{t}_i}\int_0^{\bar{t}_i}\left[\omega_i(\tau)-\omega_i^{(\mathrm{exp})}(\tau)\right]^2 d\tau=\min. \tag{5}$$

Minimization of (5) with respect to the parameters B, n, and ΔE allows us to determine the magnitudes of the latter. When B, n, and ΔE are functions of the independent variables T and ε of the process, the representation of these in the form of corresponding series in these variables also reduces the problem to the minimization of (5) with respect to a finite number of parameters (the coefficients of these series).

The problem of determing B, n, and ΔE is substantially simplified if the temperature distribution $T(p, \tau) = T(\tau)$ in the specimen is uniform, which can be ensured in the case of sufficiently thin specimens. In this case

$$\frac{\rho^{(\mathrm{exp})}(\tau)}{\rho_0}=\frac{\omega^{(\mathrm{exp})}(\tau)}{\omega_0},$$

and, having calculated the derivative $d\rho^{(\mathrm{exp})}(\tau)/d\tau$, we can determine B, n, and ΔE from the condition of best approximation of $d\rho^{(\mathrm{exp})}(\tau)/d\tau$ by (2). It becomes possible to reduce the problem of minimization to a linear problem. Having presented B in the form of $B = \exp b$ and assuming b, n, and ΔE to be algebraic functions of T and ε, i.e.,

$$b=\sum_j a_j\varepsilon^j;\quad n=\sum_r\sum_l c_{rl}T^r\varepsilon^l;\quad \Delta E=\sum_s\sum_q d_{sq}T^s\varepsilon^q,\quad s\neq 1,$$

from the condition of minimization for the coefficients a_j, c_{rl}, and d_{sq} of the functional

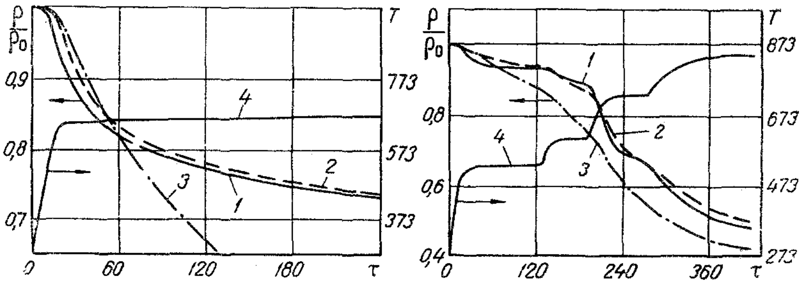

Fig. 3. Comparison of experimental and theoretical curves for $\rho(\tau)$ for various laws governing the heating of glass-reinforced AG-4S plastic specimens: 1) experimental curves for specimen weight loss; 2 and 3) calculation of weight loss according to Eqs. (2) and (1), respectively; 4) law governing the heating of the specimens.

$$\Delta^2=\frac{1}{m}\sum_{i=1}^{m}\frac{1}{\bar{t}_i}\int_0^{\bar{t}_i}\left[\ln\frac{d\rho_i^{(\mathrm{exp})}(\tau)}{d\tau}+n\ln\frac{\rho_i-\rho_{\mathrm{gr}}}{\rho_0}+b-\frac{\Delta E}{RT_i}\right]^2 d\tau \tag{6}$$

we obtain a system of linear equations whose solution determines the values of a_j, c_{rl}, and d_{sq} and, consequently, the functions B(ε), n(ε, T), and ΔE(ε, T).

In calculating $d\rho_i^{(\mathrm{exp})}(\tau)/d\tau$ we should bear in mind that the functions $\rho_i^{(\mathrm{exp})}(\tau)$, because of the measurement and interpretation errors, are random and the usual formulas of numerical differentiation may therefore lead to substantial errors.

With the method of least squares we can smooth the random errors and obtain rather exact values for the derivative of the empirical function

$$\frac{d\rho^{(\mathrm{exp})}(\tau)}{d\tau}=\frac{1}{10\Delta\tau}\left[-2\rho^{(\mathrm{exp})}(\tau-2\Delta\tau)-\rho^{(\mathrm{exp})}(\tau-\Delta\tau)+\rho^{(\mathrm{exp})}(\tau+\Delta\tau)+2\rho^{(\mathrm{exp})}(\tau+2\Delta\tau)\right],$$

where $\Delta\tau$ is the differentiation interval.

The thermal destruction of the binder in high-temperature heating was studied experimentally on glass-reinforced AG-4S plastic specimens with dimensions of 20 × 20 × 0.5 mm. The heating was accomplished in an argon medium on an IMASh-11 installation [8], which provides for unilateral programmed heating. The heating regime is controlled on the basis of the readings from a Chromel–Alumel microthermocouple attached to the specimen surface; the junction of the microthermocouple had been rolled to a thickness of 0.05 mm. The thermocouple junction was attached to the specimen surface with VK-6 heat-resistant glue and covered with a siliceous fabric cover with dimensions of 3 × 4 mm and a thickness of 0.025 mm. The temperature was recorded on the graph paper of an automatic PS1-01 potentiometer.

Special high-sensitivity (up to 0.5 mg) heat-sensitive scales were designed and fabricated for the automatic recording of changes in specimen weight. An electronic–mechanical (mechanotronic) pickup sensitive to small displacements and forces [9] was used as the sensing element. The readings of the heat-sensitive scales were recorded on the tape of an automatic ÉPP-09 potentiometer. Small weights were used to indicate the base markings on this same tape to permit interpretation of the instrument readings. Prior to attachment of the thermocouple junction and subsequent to the tests, the specimens were weighed on an analytical balance to verify the readings of the heat-sensitive scale. In the final weighing the thermocouple and the cover with the glue were carefully removed from the surface of the object being tested. Subsequent roasting for 3 h in air at a temperature of 1073°K enabled us to determine the weight content of the binder in the specimen.

To remove the adsorbed moisture directly prior to the test, the specimen was kept for 10 min at a temperature of 393°K.

Figure 1 shows the thermogravimetric decomposition curve for the binder for the case of stepwise heating of the specimen s (in steps of 50°K), being held at each temperature to the point at which there is no further weight loss. The magnitude of the coke residue at a temperature of 1173°K, equal to ρ_c/ρ_0 = 0.398 (0.4, 0.404, 0.33, 0.4, 0.393, 0.41), proved in this case to be close to the data of [10], where ρ_c/ρ_0 = 0.385

was found as a result of holding such a resin in a porcelain crucible with a cover for 10 min at a temperature of 1173°K.

To study the kinetics of the destruction process, we performed the experiments at constant heating rates of $b \approx 1, 3, 5$ deg/sec. Such regimes are rather close to the operational and make it possible to encompass a very broad range of variation in the variables T and ε. Preliminary experimental investigations and rough estimates showed that the temperature difference across the thickness of the specimen is rather small (not exceeding 10-15°K) and that the heating of the specimen can be regarded as uniform.

Figure 2 shows the curves for $\rho^{(\mathrm{exp})}(\tau)/\rho_0$ and $T(\tau)$, obtained in the heating of the specimens at rates of 3 and 10 deg/sec. Similar curves were obtained for other heating regimes.

The results of each of the 16 tests were processed in accordance with the above-described method. Here it is assumed that

$$b = \sum_{j=0}^{k} a_j \varepsilon^j; \quad n = \mathrm{const}; \quad \Delta E = \sum_{s=0}^{p} d_s \frac{1}{T^s}. \tag{7}$$

The approximation polynomials were assumed to be of the successive degrees p = k = 0, 1, 2, 3. The calculations were performed on an M-20 digital computer. The resulting values for the coefficients a_j, $d_s' = d_s/R$ and n are given in Table 1. Here we also find the magnitude of the mean δ and of the maximum $(\delta_i)_{\max}$ square deviations for the processed series of curves.

It follows from an analysis of these results that the kinetic parameters of the process involved in the destruction of the AG-4S binder are determined by solution of (6) and (7) when p = k = 1, i.e.,

$$B = \exp(15.48 - 5.12\varepsilon); \; n = 0.8088; \; \frac{\Delta E}{R} = 19426 - 48350 \left(\frac{100}{T}\right). \tag{8}$$

The use of higher approximations is not advisable and is incorrect, since the approximation accuracy obtained for p = k = 1 with the experimental data on $\rho^{(\mathrm{exp})}(\tau)$ are within the limits of measurement error and a further increase in p and k results in no significant improvement.

To verify these assumptions and the derived data pertaining to the kinetics of the polymer-destruction process and, in particular, the destruction of the AG-4S binder, we performed additional studies of the destruction under the conditions of complex heating regimes. Figure 3 shows the experimental (curve 1) and theoretical (curves 2 and 3) relationships for the change in the density of the AG-4S binder with a change in the specimen temperature according to the law specified by curve 4. The theoretical curves 2 have been derived from the use of (2) and (8) for the kinetic parameters, while curves 3 have been derived through the use of (1) and the values of B, n, and ΔE, also determined according to the above method on the basis of the $\rho^{(\mathrm{exp})}(\tau)$ data for constant heating rates $b \approx 1, 3, 5, 10$ deg/sec.

We see good agreement in the above graphs between the theoretical (curves 2) and experimental values of $\rho(\tau)$, even in the case of complex heating regimes.

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