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THERMAL DESTRUCION OF POLYMERS IN NONSTEADY HEATING IN A STREAM OF HOT GAS

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The method of laser probing was applied in determining the characteristics of thermal destruction in dependence on the heating rate and the magnitude of the heat flux, and a method was suggested for calculating the kinetic parameters of the reaction of thermal dissociation of polymers.

The application of polymer materials in industry entails ever more stringent requirements concerning the durability of these materials under the effect of intense thermal fluxes. One of the principal requirements is increased heat resistance of polymers; when they are used as structural materials, it is possible to reduce the weight of industrial installations and special structures per unit power [1].

Thermal destruction of polymers is at present investigated by methods of thermogravimetry and of differential thermal analysis involving heating rates not exceeding 10°K/sec [2, 3]. The low rates of change of temperature in linear programmed heating are used because it is necessary to heat the test specimens uniformly throughout their bulk. Under real operating conditions, where the heating rates attain tens or even hundreds of degrees per second, the temperature distribution over the section of the specimen is important, and the method of determining the thermokinetic characteristics used in thermogravimetry are inapplicable. In addition, the recorded parameters (e.g., the temperature and the time of onset of thermal destruction) are substantially affected by the temperature of the gas stream T_e, the heat transfer coefficient α, and the heating rate dT_w/dt. For that reason the properties of polymers have to be studied under conditions that are close to the operating conditions of heat insulating materials [4]; this makes it possible to obtain reliable data on the kinetics of the investigated processes.

1. Method of Carrying Out the Experiment. One of the methods of investigating the thermal destruction of polymers and of composites based on them during rapid heating is the method

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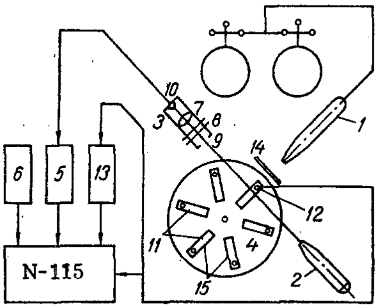

Fig. 1

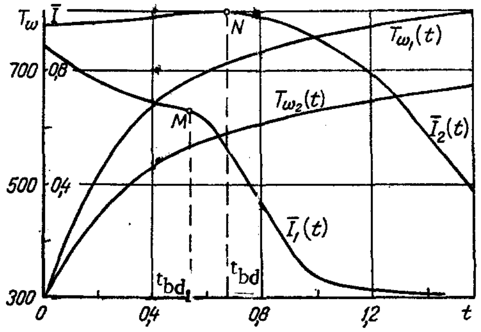

Fig. 2

Fig. 1. Schematic diagram of the experimental installation.

Fig. 2. Oscillogram of the record of the surface temperature T_w (°K) and of the intensity $\bar{I}$ in dependence on the time t (sec) during heating of specimens of EB (curves $T_{w_1}(t)$ and $\bar{I}_1(t)$) and of PMMA (curves $T_{w_2}(t)$ and $\bar{I}_2(t)$) in a gas stream.

of laser probing [5, 6] based on the registration of the changes in optical properties of the surface of the material undergoing destruction while interacting with a heated gas stream.

The laboratory installation whose schematic diagram is shown in Fig. 1 consists of the gas burner 1, the laser 2 (LG-78), the optical system 3, the device for gripping the specimens 4, the amplifier 5, the constant frequency generator 6 (GZ-36), and the recording apparatus. The optical system 3 contains the objective lens 7, the light filters 8, the optical slit 9, the photodiode (FD-6G) 10. The device for gripping the specimens 4 is a stainless steel disk with 300 mm diameter, 20 mm thick; on its upper face six rectangular slits 15 are cut out; they are 20 × 100 mm in size, 10 mm deep, and they serve for gripping the specimens. The disk is made in the form of a cooling radiator: on its lower face channels with 5 × 5 mm section are machined. Cooling of the disk makes it possible to maintain the temperature of the measuring block constant, and thus to ensure equal conditions in parallel experiments. The specimens 11 are plates 20 × 100 × 8 mm in size, and on their surface strip CA (Chromel–Alumel) thermocouples 12, ~50 μm thick, were attached. The light-beam oscillograph N-115 recorded the surface temperature $T_w(t)$, the intensity $\bar{I}(t)$ of the laser radiation reflected from the surface of the specimen, the heating rate dT_w/dt with the aid of the differential device 13. The error of determining $T_w(t)$ in the temperature range up to the onset of thermal destruction is ~1-3% [6].

The experiment is carried out in the following way. The gas burner 1 is set to the working regime, a specimen is mounted opposite the burner, and the optical system 3 is adjusted. The beam from laser 2, directed at the surface of the specimen at a small angle ~2-4° [5], is reflected from the surface, passes through the optical slit 9, the light filter 8, and is focused by the objective lens 7 onto the screen of the photodetector 10 which emits an electric signal proportional to the intensity of the reflected radiation. The specimens are annealed in the burner flame whose temperature was varied in the range 700-3000°K. Each time a specimen has been annealed, the baffle 14 is closed, and the next specimen is set opposite the burner. The position of the specimens is fixed automatically by a special indexing device.

2. Experimental Results.

The nature of the change of $\bar{I}(t)$ and $T_w(t)$ for epoxy binder (EB) and polymethyl metacrylate (PMMA) is shown in Fig. 2.

For EB the instant of beginning thermal dissociation t_{bd} is characterized by the fact that the curve of the intensity $\bar{I}(t)$ has a point of inflection M. In fact, when the temperature $T_w(t)$ increases, the intensity of the radiation reflected by the surface decreases because of the defocusing of the optical system in consequence of the thermal expansion of the specimen. When $t > t_{bd}$, destructive transformations set in on the surface of the investigated material, as a result the optical properties of the surface change and $\bar{I}(t)$ abruptly decreases, forming the point of inflection M [6].

When in materials the process of thermal dissociation is preceded by the appearance of a molten film on the surface, then the behavior of the curve of intensity $\bar{I}(t)$ is characterized by the existence of a maximum (point N) which testifies to the appearance of liquid phase.

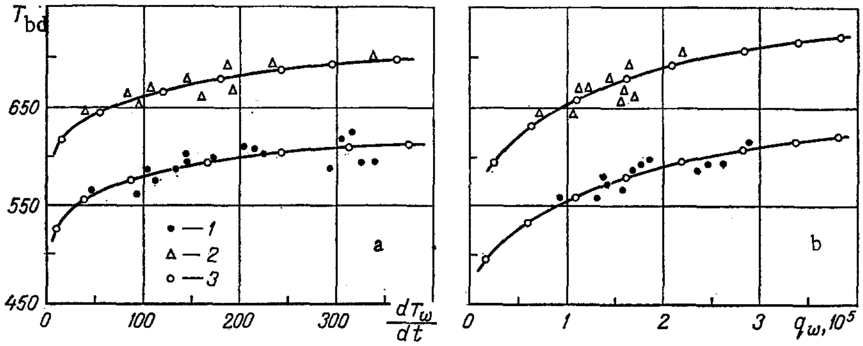

Fig. 3. Experimental dependences of the temperature of the onset of thermal destruction T_{bd} (°K) on the heating rate dT_w/dt (°K/sec) (a) and on the heat flux $q_w = \alpha(T_e - T_{bd})$ (W/m²) (b): 1) PMMA; 2) EB; 3) calculation.

The reflecting properties of the surface are thereby improved. When destructive changes in the molten polymer appear, the reflection coefficient decreases, and the intensity of the reflected radiation decreases. Such a regime of destruction is typical of thermoplastic polymers, e.g., PMMA. In that case the instant of the beginning dissociation t_{bd} is determined at the point where the intensity of the reflected radiation has the highest value.

The results of the experiments (Fig. 3) show that the rate of change of T_{bd} with increasing dT_w/dt is nonidentical for each of the materials. This has to do with the different mechanisms and kinetic characteristics of thermal destruction.

3. Determination of the Thermokinetic Constants. The problem of thermal destruction of polymer materials under conditions of convective heating can be mathematically described by the equation of energy in a solid [4]

$$\rho_s c_{ps} \frac{\partial T_s}{\partial t} = \lambda_s \frac{\partial^2 T_s}{\partial y^2} - \varphi(\eta) Q k_0 \exp\left(-\frac{E}{RT_s}\right) \tag{1}$$

with the initial and boundary conditions:

$$t = 0,\ T_s = T_{si};\ y = \infty,\ \frac{\partial T_s}{\partial y} = 0,\ T_s = T_{si};$$
$$y = 0,\ -\lambda_s \frac{\partial T_s}{\partial y} = (\alpha - \Delta\alpha)(T_e - T_w). \tag{2}$$

An approximate analytical solution of the problem (1)-(2) was obtained in [7] by the method of integral thermal balance [8] with constant coefficients of transfer. It was assumed that in the vicinity of the temperature of the onset of dissociation T_{bd} the function $\varphi(\eta) \to 1$ and $\Delta\alpha \to 0$, and the temperature profile in the solid was specified in the form

$$T_s(y,\ t) = T_{si} + (T_w - T_{si})[1 - y/\delta_T(t)]^m, \tag{3}$$

where $\delta_T(t)$ is the thickness of the thermal layer.

When $m \geq 1$, the solution of the problem (1)-(2) may be written in the following manner [7, 13]:

$$B \frac{dT_w}{dt} = m\lambda_s \frac{RT_{bd}^2}{E} Q k_0 \exp\left(-\frac{E}{RT_{bd}}\right), \tag{4}$$

where

$$B = \frac{\dfrac{\alpha^2 (T_e - T_{bd})^2}{dT_w/dt} - \dfrac{m}{m+1} \dfrac{T_{bd} - T_{si}}{T_e - T_{bd}} (2T_e - T_{bd} - T_{si}) \lambda_s \rho_s c_{ps}}{\theta_{si}\left[1 - 0{,}72 \dfrac{m}{m+1} \theta_{si} + \dfrac{2m^2}{2m^2 + 3m + 1} \theta_{si}^2\right]}, \tag{5}$$

$$\theta_{si} = (T_{bd} - T_{si}) E / RT_{bd}^2.$$

TABLE 1. Degrees of Approximation of m in Dependence on the Dimensionless Parameter u

u	0,1	0,2	0,3	0,4	0,5
m	3,408	3,198	3,022	2,874	2,747
u	0,6	0,7	0,8	0,9	1,0
m	2,640	2,547	2,467	2,397	2,336
u	1,1	1,2	1,3	1,4	1,5
m	2,283	2,236	2,195	2,159	2,126
u	1,6	1,7	1,8	1,9	2,0
m	2,098	2,073	2,044	2,031	2,012

It should be noted that the order of approximation of m has to be chosen in each actual case from the condition of the best approximation to the real temperature profile in the solid at the instant of onset of thermal dissociation.

To obtain the conditions of choosing m, we put Q = 0 in (4). The analytical solution of problem (1)-(2) in that case has the form (y = 0) [9]:

$$\theta = \frac{T_w - T_{si}}{T_e - T_{si}} = 1 - (1 - \operatorname{erf} u)\exp u^2, \tag{6}$$

where

$$u = \alpha\sqrt{a_s t}/\lambda_s,\quad \operatorname{erf} u = \frac{2}{\sqrt{\pi}}\int_0^u \exp(-x^2)\,dx.$$

Making (4) and (6) compatible according to the parameter $\varphi = \frac{dT_w}{dt}\,\frac{t_{bd}}{T_{bd} - T_{si}}$, we obtain

$$m = \frac{(1-\theta)^3}{\theta(2-\theta)\left(\frac{1}{u\sqrt{\pi}} + \theta - 1\right) - (1-\theta)^3}. \tag{7}$$

Table 1 presents the degrees of approximation of m in dependence on the dimensionless parameter $u = \alpha\sqrt{a_s t}/\lambda_s$. For determining the heat transfer coefficient α, the following expression may be used:

$$\alpha = \frac{\lambda_s}{n\sqrt{a_s}} \sum_{i=1}^{n} \frac{F(\varphi_i)}{\sqrt{t_i}} \sqrt{\frac{(1+2\varphi_i)\exp(1-\varphi_i^2)}{3\pi\varphi_i(1-\varphi_i^2)}}\ln\frac{1}{2\varphi_i}, \tag{8}$$

where

$$F(\varphi_i) = 1 + \frac{1 + 2\sin\left[\left(\varphi_i - \frac{3}{4}\pi\right)\left(\frac{\pi}{2} + 5\right)\right]}{100},\quad i = 1,\ 2,\ \ldots,\ n,$$

which approximates for $0 < t_i < t_{bd}$ the exact solution with an error not exceeding ~1%. When α is known, the gas temperature T_e is determined directly from (6).

Thus, when we know the thermophysical characteristics of polymers, the conditions of heat exchange, and the experimental dependences $T_{bd} = f(dT_w/dt)$, we can determine the kinetic parameters of the reaction of thermal dissociation with the aid of the solution of (4) taking (5) and (6) into account. When we find the logarithm of (4) with a view to (5), we obtain

$$\frac{1}{T_{bd}} = A - \frac{R}{E}\ln\frac{dT_w}{dt}, \tag{9}$$

where

$$A = \frac{R}{E}\ln\frac{m\lambda_s R T_{bd}^2}{BE} Q k_0. \tag{10}$$

It was shown in [13] that when the process of thermal destruction occurs within the limits of one structural subsystem, then A is constant within a broad range of changes of the input parameters. This makes it possible to determine E and Qk_0 directly from expressions (9) and (10).

TABLE 2. Initial Data for Calculating E and Qk_0

Polymer	T_{bd}, °K	$\frac{dT_w}{dt}$, $\frac{°K}{sec}$	α, W/(m²·°K)	T_e, °K	m
PMMA	560,0	46,7	185,1	1062,3	3,115
	576,8	90,7	203,4	1273,2	3,240
	578,9	100,4	106,7	1833,9	3,441
	584,1	133,3	396,6	1006,3	3,029
	610,2	320,3	188,8	2093,7	3,514
EB	649,4	37,3	111,2	1290,9	2,839
	663,1	79,9	240,3	1122,0	2,613
	666,9	98,7	131,8	1543,0	2,730
	676,6	141,8	162,8	1552,9	2,961
	706,7	318,5	195,5	1822,6	3,020

To confirm the correctness of applying the suggested calculation method, we chose PMMA (λ_s = 0.176 W/m•°K, c_{ps} = 1605 J/kg•°K, ρ_s = 1200 kg/m³) whose kinetic parameters of thermal destruction are known and presented in [10, 11] for the temperature range up to ~620°K. Modeling was carried out according to the criterion of chemokinetic similarity [12] — the Arrhenius number Arr = E/RT_* (T_* is the characteristic temperature). For this purpose the range of change of the characteristic temperature, which was T_{bd}, was chosen such that the condition Arr = idem was fulfilled. With the aid of the obtained experimental data (Fig. 3, Table 2) and by the suggested method we found E and Qk_0 for PMMA: E = 110 ± 11 kJ/mole; $Qk_0 = 0.18 \cdot 10^{16 \pm 1}$ J/m³•sec; these agree well with the known values, and consequently the condition Arr = idem is fulfilled. This permits the conclusion that the method of experimentally determining the characteristics of thermal destruction and the method of calculating the kinetic constants may be used for investigating a broad class of polymer and composite materials during rapid heating in a gas stream. Specifically, for EB (λ_s = 0.150 W/m•°K, c_{ps} = 1000 J/kg•°K, ρ_s = 1200 kg/m³) the following values of E and Qk_0 were found from the data of Fig. 3 and Table 2: E = 145 ± 14 kJ/mole; $Qk_0 = 1.95 \cdot 10^{16 \pm 1}$ J/m³•sec.

NOTATION

t, Time; y, coordinate; T_s, temperature; λ_s, thermal conductivity; ρ_s, density; c_{ps}, heat capacity; a_s, thermal diffusivity; E, activation energy; Q, thermal effect; k_0, preexponent of the reaction of thermal destruction; $\varphi(\eta)$, function; η, degree of chemical conversion; α, $\Delta\alpha$, heat-transfer coefficient and correction for the injection of the dissociation products into the boundary layer, respectively; T_{si}, initial temperature; T_w, surface temperature; R, universal gas constant.

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HEATING OF DISPERSE POLYMER MATERIALS IN GAS-THERMAL SPRAYING

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The article presents the results of a comparison of the effectiveness of heating disperse polymers in gas-flame and in plasma streams.

A disperse polymer, fed into the jet of a gas-flame or plasma stream, is heated and sprayed onto the surface of the substrate in the molten state or in a state close to that [1, 2]. The degree of fusion of the material of the particles and the intensity of their interaction with the substrate depend on the intensity of the heat and mass transfer of the particles and of the stream. Experiments [1] showed that the number of particles per unit volume of the jet is also of importance.

Although approaches vary as regards the behavior of the particles in gas-thermal spraying because the entire complex of processes is very complicated, it is nevertheless generally accepted that the particle size and the properties of the material and the parameters of the hot stream have to be taken into account [1-3]. In most cases there is not heat exchange between the particle surface and the hot stream at the initial state of heating. It is usually assumed that the maximum temperature on the particle surface is established instantaneously, and that it remains unchanged during the entire period of the particle being in the stream [3]. Such an approach yields an approximate estimate of the size of the particles which are molten during the time they are situated in the hot medium. However, there are data [2] indicating that the heating of disperse materials is determined in particular by the intensity of the heat exchange of the particles with the gas stream impinging on them. In plasma spraying an important part is additionally played by the radiant heat flux coming from the heat source.

A typical diagram of the gas-thermal jet according to data of [1] is shown in Fig. 1; its analysis shows that the hot gas jet usually has the form of a truncated circular cone of length L with the bases F_1 and F_S ($F_1 \ll F_S$).

With a gas-flame jet the temperature on the axis of the stream at the burner attains 2800°K, then the temperature rapidly drops, and at a distance of 100 mm it amounts to about 800°K. In a plasma jet the temperature at the nozzle edge is estimated to be 20,000°K, and at a distance of 100 mm of the order of 1100-1200°K; the maximum temperature of an electric arc attains 32,000°K [1]. The rapid drop of the temperature of the stream with increasing distance from the nozzle edge is due to the supply of compressed gas and the intense ejection of atmospheric air into the jet. The air content in the plasma jet at a distance of 100 mm from the nozzle edge is up to 90%. The particles in gas-thermal spraying move at speeds of 50-150 m/sec in the plasma jet and with 20-50 m/sec in the gas-flame jet [2].

Neglecting the radial and longitudinal nonuniformity of the gas-thermal stream, the space–time pulsations of the heating zone, the ablation of the material of the particles, and the physicochemical processes of thermal and thermooxidation destruction of the polymers in order to simplify the theoretical model, we will examine the uniform heating of a spherical particle with radius r_p moving in a medium with approximately constant temperature T_m at speed v_p during time τ_{th} at approximately constant heat flux density $q = q_c + q_r$, where q_c is the

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