BREAKDOWN OF THERMOPLASTIC MATERIALS UNDER THE SIMULTANEOUS ACTION OF A GAS STREAM AND A HIGH-POWER THERMAL FLUX

N. P. Novikov and A. A. Kholodilov

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An analysis is made of the breakdown of polymethylmethacrylate and polystyrene specimens under the action of a thermal flux and a gas stream. A theoretical interpretation of test results is proposed. A close agreement is found between predicted and measured values.

The breakdown of thermoplastics under the simultaneous action of a thermal flux and a gas stream is of considerable interest. The authors analyze here the case of polymethylmethacrylate (PMMA) and polystyrene (PS) specimens exposed simultaneously to a laminar gas stream and to radiation from a gaseous CO_2 laser. In [1, 2] we studied the breakdown of these polymers under the action of a gaseous CO_2 laser, showing this process to be almost equivalent to a breakdown under a high-power thermal flux. It has also been established in those studies that, inside a specimen near the surface exposed to radiation, breakdown along microstructure boundaries occurs. Fragments of polymer material formed in this manner precipitate into the region covering the specimen, absorb part of the laser radiation, and shield the specimen in breakdown. The difference between the breakdown of PMMA and PS arises from their different microstructures and is reflected, above all, in the respective degree of shielding. It follows from this brief description of the breakdown process that the action of a gas stream will be a compounded one, namely the shielding layer of polymer microparticles will be blown away by it and the thermal flux reaching the specimen breakdown surface will increase on the one hand, while, because of convective cooling on the other hand, the rate of breakdown will decrease in the end. One must also consider the breakdown of a very hot specimen directly in an air stream, as has been noted in [3]. A detailed study of the entire breakdown mechanism is the subject of this article.

Conditions of the Experiment and Test Results

The test apparatus, the dimensions of the specimens, and the gas laser have all been thoroughly described in [1, 2]. The gas stream was produced by discharging nitrogen from a specially designed chamber. Into the chamber was built in a nozzle of such a design as to produce a flat velocity profile across the stream section, and an NaCl window was provided at the opposite end so as to guide the laser radiation through the chamber onto the specimen. The cross section of the gas stream approaching the specimen was 9 mm in diameter, which was more than twice the specimen diameter. In this way, the conditions of the experiment according to the procedure in [1, 2] ensured a uniform and steady process with coaxial heat and gas flows.

The experiment has shown that, under the simultaneous action of a thermal flux and a gas stream, there are changes not only in the quantitative characteristics of the breakdown of the specimen but also in the shape of the broken-down surface. According to our tests, at low values of V the profile of a specimen remains flat or slightly curved but when the gas velocity increases ($V = 270$ cm/sec) a crater forms on the broken-down surface; as W and V increase this crater becomes larger. At high values of V the crater becomes so deep (up to 10 mm) that it resembles the shape of breakdown craters in large specimens [4]. When $W \geq 12$ cal/cm$^2 \cdot$sec, PMMA liquefies at the breakdown surface [1, 2] and in this case the shape of the surface is the same as in the case of PS (described below). Rather than discussing at length the shape

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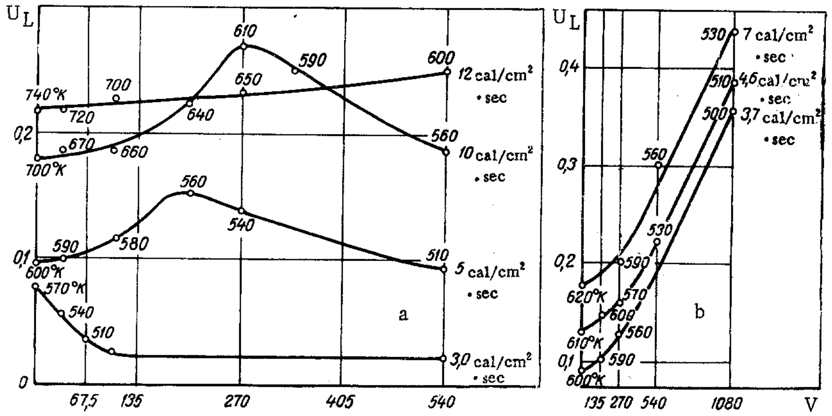

Fig. 1. Linear breakdown rate U_L, mm/sec, under the simultaneous action of a gas stream (V, cm/sec) and a thermal flux: a) for PMMA; b) for PS.

TABLE 1. Eroded Mass, $m \cdot 10^{-2}$ g

W, cal/cm²·sec	V, cm/sec			
	135	270	540	1080
7,0	—	0,7	1,3	2,0
4,6	—	1,0	1,5	4,5
3,7	1,3	1,3	—	7,5

of the breakdown surface – which has to do with the appreciable cooling of the lateral surfaces by the gas stream – we confine this analysis to the quantitative breakdown characteristics, namely its linear rate (U_L) measured by the change in the axial length of a specimen.

In broken-down specimens the surface is determined by their microstructure and by the breakdown process parameters. The surface profile of PS specimens in breakdown is different; its shape is "spherical" regardless of the thermal power and of the gas velocity. The radius of a sphere near the specimen axis, however, depends on W and V: the surface curvature decreases at high blast velocities. As in the case of PMMA, we will confine this analysis to the linear breakdown rate (measured along the specimen axis).

The linear breakdown rate (U_L) of PS specimens has been plotted in Fig. 1b as a function of the blast velocity (V) at various thermal flux levels (W). According to Fig. 1b, this relation is a linear one, except within a narrow range of low velocities. This is essentially due to reaching the "steady state," i.e., a state in which the breakdown processes can be described by some function on the basis of similarity. In the physical sense, the similarity of curves describing this process means that the breakdown is characterized basically by wear of the PS material which the thermal flux has made soft. Reaching the "steady state" signifies, in practical terms, that the gas stream blows away the vapor-mist layer which has formed in front of a specimen [1, 2]. Our whole analysis applies to the test conditions where the heated layer (and, consequently, also the softened layer) is sufficiently deep to avoid erosion by the gas stream. It can easily be predicted that, as the blast velocity increases, at some instant the entire soft layer will be washed away and the curves in Fig. 1b will peak out (when account is also taken of the polymer breakdown caused by the gas stream). The surface temperature of a specimen in breakdown is indicated in Fig. 1b; it decreases as the velocity increases.

As in [1, 2], the specimen temperatures were measured with thermocouples (a thorough description of the procedure was given in [1, 2]). The results have shown that the temperature variation along the specimen axis is the same with or without a gas blast at a given thermal power level (W). On the basis of these curves, a rough estimate of the mass of material eroded by the gas stream can be made. On the curve representing the axial temperature distribution in the unblasted specimen the temperature which corresponds to the surface temperature of the blasted specimen is marked; from there the linear coordinates of the given point inside the unblasted specimen are determined. Then the volume and the mass of the specimen where the temperature has changed from the maximum down to the marked level are found. For rough estimates the mass determined in this manner may be assumed equal to the mass eroded by the stream. In the case of PS, such estimates are valid also because here the shielding vapor-mist layer covering the specimen is thin [1] and the thermal power impinging on it may be assumed equal to that reaching the specimen surface. Such rough estimates are shown in Table 1. According to Table 1, the quantity of eroded specimen material is, at given values of W and V, directly proportional to the blast velocity and, consequently, the curve in Fig. 1b becomes a straight line. Table 1 shows that, as the thermal power is raised, the role of the gas stream in breaking down a specimen diminishes. This is explained by the rate of thermal breakdown, which is high and far above the rate of erosion when the power W is heavy, but low and comparable to the rate of erosion when the power W is light. These rough estimates will surely be corrected by more precise calculations, but the conclusions reached so far concerning the role of a gas stream in the breakdown of PS at various thermal power levels will nevertheless most probably remain valid.

The characteristics of PMMA breakdown are somewhat different. As has been shown in [1, 2], an important factor in the breakdown of PMMA specimens by a high-power thermal flux is the shielding of the specimen by a vapor-mist layer, which in turn is related to the peculiar microstructure of PMMA. The composition and the shielding action of this vapor-mist layer change as the thermal power is raised [1, 2]. The peculiarities of PMMA breakdown under the action of a thermal flux [1, 2] will in many ways determine also the breakdown characteristics of specimens under the action of a gas stream. The linear breakdown rate (U_L) measured along the specimen axis has been plotted in Fig. 1a as a function of the blast velocity (V) at various levels of power W. Temperatures of the breakdown surface are marked on the diagram. Inasmuch as the vapor-mist layer is thin at low W levels (under 5 $\text{cal/cm}^2 \cdot \text{sec}$) [1], its dissipation by the gas stream cannot result in a significant increase of the thermal power reaching the specimen surface. At the same time, more heat is dissipated from the specimen and, in practical terms, this amounts to less thermal power available for breaking down the specimen. This latter circumstance should result in a lower breakdown rate. At a thermal power within $5 < W < 10$ $\text{cal/cm}^2 \cdot \text{sec}$, when the vapor-mist layer becomes heavy [1], the gas stream plays a different role. It blows this layer away from the breakdown surface. The disappearance of such an effective shield causes a larger thermal flux to reach the breakdown surface, which in turn will increase the breakdown rate. According to the estimates in [1], a vapor-mist layer deflects up to 40% of the incident flux ($W = 10$ $\text{cal/cm}^2 \cdot \text{sec}$) and, therefore, a removal of the shielding will increase the breakdown rate by approximately the same amount. Based on the rough estimates of polymer erosion by a gas stream, one can prove that in this case the amount of breakdown is much less due to erosion than due to removal of the shielding. One may assume, accordingly, that removal of the shielding will result in a breakdown rate higher by a factor of 1.5 at a blast velocity $V = 270$ cm/sec. As the blast velocity is increased further, the specimen surface (near the axis) will begin to cool down as in the similar process described previously under low levels of power W. The processes occurring at the lateral specimen surfaces are obviously determined primarily by the heat dissipation into the gas stream, and they will not be discussed here. At high thermal power levels the polymer (PMMA) in the vapor-mist zone near the breakdown surface liquefies, as in the case of the PS material. Under these conditions the breakdown of PMMA specimens is analogous to that of PS specimens (see Fig. 1a) as the profile of the breakdown surface indicates.

Thus, using PMMA and PS as typical examples, we have established experimentally that the breakdown of polymer materials by the simultaneous action of a gas stream and a thermal flux is largely governed by the operating characteristics of both as well as by the microstructure of a given polymer specimen. Moreover, the gas stream may either raise or lower the linear breakdown rate. Tests have also shown that a theoretical interpretation of these processes must take into account the mechanism of thermal breakdown of polymers by a thermal flux with due consideration of the effect of the microstructure.

Discussion of the Test Results

As has been established in the tests, the breakdown process by the simultaneous action of a gas stream and a thermal flux is different for PS and PMMA specimens. For this reason, we decided on a separate theoretical analysis for each of these materials. The breakdown of PS under the action of a gas stream may be treated as an ablation of a liquid polymer layer from the breakdown surface. For such a liquid layer of polymer one can set up a system of equations describing this process [10] (y is the longitudinal coordinate, x is the transverse coordinate):

$$\frac{\partial}{\partial x}(xV_x) + \frac{\partial}{\partial y}(xV_y) = 0, \tag{1}$$

$$\frac{\partial}{\partial y}\left(\mu \frac{\partial V_x}{\partial y}\right) = \frac{dp}{dx}, \tag{2}$$

$$c\rho\left(V_x \frac{\partial T}{\partial x} + V_y \frac{\partial T}{\partial y}\right) = \lambda \frac{\partial^2 T}{\partial y^2} + \alpha W \exp(-\alpha y). \tag{3}$$

Systems (1)-(3) apply to the region around the critical point in the two-dimensional problem. The boundary conditions at the breakdown surface will be

$$-\lambda \frac{\partial T}{\partial x}\bigg|_s - \rho V_x H_s + q_s(T_s) = W, \quad \frac{\partial V_x}{\partial y}\bigg|_s = \frac{1}{\mu(T_s)} F_\tau,$$

and in an unheated specimen

$$T(x, \infty) = T_0, \quad V_x(x, \infty) = 0, \quad \frac{\partial V}{\partial y}\bigg|_{x,\infty} = 0.$$

The following symbols have been used in systems (1)-(3) and in the boundary conditions: V_x and V_y for the components of the velocity at which liquid polymer flows off; μ for the viscosity; ρ for the density; c for the specific heat; p for the pressure; λ for the thermal conductivity; α for the absorptivity; H_s for the enthalpy of evaporation; Q for the energy lost on thermal breakdown of the polymer; F_τ for the skin friction; and $q_s(T_s)$ for the thermal flux from the surface.

In order to solve this problem, it is necessary first to know the distribution of pressure and shearing stresses, which can be found by solving the appropriate problem of a viscous incompressible fluid flowing against the end surface of a cylinder at a Reynolds number Re $\simeq$ 1000. The data needed for this are not available in the published literature, as far as the authors know, and the solution of such a problem is very difficult. For solving systems (1)-(3), therefore, we will make a few simplifications and reduce it to a convenient form. First of all, we note that, according to the results in [5], the shearing stresses are by one order of magnitude smaller than the braking pressure of the gas stream and, therefore, may be disregarded – as has been done in Eq. (2). Secondly, according to [1, 2], most of the products of PS breakdown are other polymers and, therefore, the $q_s(T_s)$ term may be omitted in the boundary condition. It is well known [6] that the viscosity of a molten polymer is a function of three parameters: temperature, shear, and molecular weight. As the shear changes by one order of magnitude, the viscosity changes only by approximately a factor of 2 [6] and, therefore, it is alright to use only one value μ_0 throughout in our estimates. Within small shearing rates (0.1-10 sec^{-1}) the viscosity does not depend on the molecular weight as long as M > 30,000 [6]. The magnitude of shear (τ) in our tests was

$$\frac{\pi d^2}{4} U_L = \pi d \delta U_\parallel, \qquad \tau = \frac{U_\parallel}{\delta} = \frac{U_L d}{4\delta^2}, \tag{4}$$

with d denoting the specimen diameter.

Inserting into (4) the test values for d, U_L, and δ found from the estimates in Table 1, we find that the shear under our test conditions was within that particular range. Inasmuch as the fraction of gaseous products in the molten layer is small [1, 2], one may consider the molecular weight of PS (600,000) to vary only slightly and the condition M > 30,000 to be satisfied. It follows, then, that $\mu = \mu_0 e^{E/RT}$ [6]. Since $\delta \ll d$, systems (1)-(3) can be reduced to the problem of molten polymer flowing off the specimen edge, and this will correspond to the erosion of polymer material by the gas stream. For simplicity, we will consider the two-dimensional problem:

$$\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} = 0, \tag{5}$$

$$\frac{\partial}{\partial y}\left(\mu \frac{\partial V_x}{\partial y}\right) = 0, \tag{6}$$

$$c\rho\left(V_x \frac{\partial T}{\partial x} + V_y \frac{\partial T}{\partial y}\right) = \lambda \frac{\partial^2 T}{\partial y^2} + \alpha W \exp(-\alpha y), \tag{7}$$

with the boundary conditions

$$\rho V_x [c(T_s - T_0) + Q] = W,$$

$$T(x, \infty) = T_0, \quad V_x(x, \infty) = 0, \quad V_y(x, \infty) = 0,$$

$$\frac{\partial V_y}{\partial y} = 0.$$

Even such a simplified problem is difficult to solve. One possible approximate solution is based on a Michelson temperature distribution inside the specimen, which, strictly speaking, corresponds to reality (the test results have been described here and in [1, 2]). For this case the problem reduces to solving systems (5)-(6), with the assumption that the pressure on the surface of liquid polymer is constant and

TABLE 2. Rates of Polystyrene Breakdown in a Gas Stream

W, cal/cm^2· sec	U	V, cm/sec			
		135	270	540	1080
7,0	U_{bd}	—	0,02	0,12	0,25
	U_e	—	0,03	0,12	0,24
4,6	U_{bd}	0,01	0,03	0,09	0,26
	U_e	0,02	0,03	0,09	0,25
3,7	U_{bd}	0,01	0,04	—	0,27
	U_e	0,02	0,04	—	0,27

Note. U_e is the estimated rate; $U_{bd} = U_1 - U_0$; U_1 is the rate with blast; U_0 is the rate without blast.

equal to the braking pressure of the gas stream and that gas friction is negligible. The wear of material is determined by the flow of liquid under the action of external forces. Having solved (5)-(6) and taking into account the mass of polymer flowing off across the specimen axis, we find the rate of breakdown due to erosion:

$$U_e = V\left(\frac{\rho_G a^2 R T_s}{\mu_0 E}\right)^{1/2} \exp\left(-\frac{E}{2RT_s}\right). \tag{8}$$

It has been assumed here that

$$\mu \frac{\partial V_y}{\partial y}\bigg|_{y=0} = \frac{\rho_G V^2}{2}, \tag{9}$$

where ρ_G denotes the gas density and V the gas velocity. Using the values for E and μ_0 from [6], we calculate U_e for various velocities V. The results of these estimates and the test values for U_{bd} are given in Table 2. As can be seen here, even such rough theoretical estimates agree fairly well with the experiment.

We will now analyze the breakdown of PMMA under the simultaneous action of a gas stream and a thermal flux. We consider the two-dimensional problem. For the Stefan flow of a monomer substance off the breakdown surface against a gas (nitrogen) stream we have:

$$\xi_M = -\frac{DM}{RT}\cdot\frac{dP_M}{dx} + V_\xi \frac{MP_M}{RT}, \tag{10}$$

where D denotes the diffusivity; V_ξ denotes the velocity of the Stefan flow, and the x-axis runs along the specimen axis in the direction opposing the gas stream. At x = 0 the flow ξ_M is equal to the mass flow of monomer substance produced by the breakdown and should remain uniform over the thickness. The diffusion of nitrogen at the breakdown surface is equal to zero:

$$\xi_{N_2} = 0 = -\frac{DM}{RT}\cdot\frac{dP_{N_2}}{dx} + V_\xi \frac{M_{N_2} P_{N_2}}{RT}, \tag{11}$$

$$V_\xi = -\frac{D}{P_0 - P_M}\cdot\frac{dP_M}{dx}, \tag{12}$$

because the total pressure $P_0 = P_{N_2} + P_M = \text{const}$. Substituting (12) into (10), we obtain an equation for determining the monomer concentration:

$$\xi_M = -\frac{DM}{RT}\cdot\frac{P_0}{P_0 - P_M}\cdot\frac{dP_M}{dx}. \tag{13}$$

In the boundary layer at $x = \delta_1$ we have $P_M(\delta_1) = 0$, while $P_M(0) = P_s$ and D/T = const at x = 0. Equation (13) is then easily solved as follows:

$$P_M(x) = P_0\left[1 - \exp\left(-\frac{\rho U_L RT(\delta_1 - x)}{DMP_0}\right)\right], \tag{14}$$

$$V_\xi = \frac{\rho U_L RT}{MP_0} = \text{const}. \tag{15}$$

The thickness of the diffusion layer can be found from the expression [7]:

$$\delta_1 = d/\mathrm{Nu}_D, \tag{16}$$

where the Nusselt number Nu is equal to Nu_λ within our range of the Reynolds number and can be calculated. Polymer particles which have formed the vapor-mist layer under the action of a thermal flux are now carried into the diffusion layer in a Stefan flow mode and will be dissipated at the boundary by the external gas stream. We will prove that, under the given conditions, these particles shield the specimen and do not "burnout" completely while remaining in the stream. Namely, knowing the dimension of the diffusion layer δ_1 in (16), one can estimate the shielding effect of the vapor-mist layer. The carry time is

$$\tau_c = \frac{\rho_{so}\Delta^2}{18\mu} \approx 10^{-4}\ \text{sec},$$

with $\mu \simeq 10^{-4}$ g/cm · sec [8] denoting the viscosity of gaseous monomer. The dwell time in the diffusion layer is

$$\tau_d = \frac{\delta_1}{V_\xi} \simeq 10^{-3} \text{ sec.}$$

The burnout time $\tau_b = \Delta l_0 / W \approx 10^{-2}$ sec, $l_0 = 200$ cal/g, $W = 10$ cal/cm^2 · sec, and $\Delta = 5 \cdot 10^{-4}$ cm [1, 2] is the particle dimension. Thus, $\tau_b > \tau_d > \tau_c$ and complete burnout does not occur. As the absorption parameter of the vapor-mist layer we define

$$m_0 = n\delta\rho_{so} \frac{\pi\Delta^3}{6}, \tag{17}$$

where n denotes the concentration of particles in the layer and is found from the condition

$$U_L n_0 = nV_\xi, \tag{18}$$

while n_0 is the concentration of particles in the solid polymer. Inserting (18), (16), and (15) into (17), we obtain

$$m_0 = \frac{dMP_0}{1.3\mathrm{Re}^{0.5} RT} n_0 \frac{\pi\Delta^3}{6}. \tag{19}$$

The energy flux impinging on the breakdown surface is

$$W_s = W \exp(-k_0 m_0) - W_\lambda, \tag{20}$$

where W_λ denotes the thermal flux dissipated at the surface by the external nitrogen blast:

$$W_\lambda = \frac{\lambda}{d} 1.3\mathrm{Re}^{0.5} f(B)(T_s - T_0), \tag{21}$$

B is the parameter of gaseous monomer injection. On the basis of the results in [9], one may assume that $f(B) \approx 1$. We differentiate (20) with respect to Re, taking (21) into account, and then equate the derivative to zero, to find the condition of maximum thermal flux at the breakdown surface – corresponding to the condition of maximum breakdown rate under the simultaneous action of a thermal flux and a gas stream:

$$\mathrm{Re}_{\max} = \frac{W_0 k_0 d^2 M P_0 n_0 \pi\Delta^3}{9.14\lambda R\bar{T}(T_s - T_0)} \exp\left(-\frac{k_0 d M P_0 n_0 \pi\Delta^3}{7.8\mathrm{Re}_{\max}^{0.2} R\bar{T}}\right). \tag{22}$$

Temperature $\bar{T}$ has been assumed equal to the temperature of the blasting stream, inasmuch as the diffusivity of nitrogen is much higher than the diffusivity of the monomer and the penetration of N_2 into the layer covering the specimen determines the change in the temperature distribution in this region, bringing the mean temperature here closer to the nitrogen temperature.

With the value for k_0 from [1], $W = 10$ cal/cm^2 · sec, $P_0 = 1$ atm, $d = 3$ mm, and $T_s = 700$°K, Eq. (22) yields $\mathrm{Re}_{\max} \simeq 100$, which is sufficiently close to the test results shown in Fig. 1a for Re = 500.

Thus, on the basis of the theoretical presentation given here, an analytical solution to the problem concerning the breakdown of polymer materials under the simultaneous action of a gas stream and a high-power thermal flux is possible (if one considers the two-dimensional problem with subsequent simplifications).

LITERATURE CITED

1. N. P. Novikov, V. P. Perminov, and A. A. Kholodilov, Prikl. Mekhan. i Tekh. Fiz. (in press).
2. N. P. Novikov and A. A. Kholodilov, Mekh. Polim., No. 1 (1971).
3. T. von Kármán, From Low-Speed Aerodynamics to Astronautics, Pergamon Press, Oxford–London –New York (1963).
4. D. P. Krindach, N. P. Novikov, and Yu. I. Yudin, Mekh. Polim., No. 2 (1968).
5. I. M. Sibulkin, Mekhanika, No. 3 (1953).
6. E. Bernhardt, Reprocessing Thermoplastic Material [Russian translation], Khimiya, Moscow (1965).
7. D. A. Frank-Kamenetskii, Diffusion and Heat Transmission in Chemical Kinetics [in Russian], Nauka, Moscow (1967).
8. N. B. Vargaftik, Handbook of Thermophysical Properties of Gases and Liquids [in Russian], Fizmatgiz, Moscow (1963).

9. G. Lies, in: Gas Dynamics and Heat Transfer during Chemical Reactions [Russian translation], IL, Moscow (1962).
10. Yu. B. Polezhaev, Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk, Mekhanika i Mashinostroenie, No. 3 (1963).