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RATE OF ABLATION WITH DEPOLYMERIZATION

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The rate of ablation is calculated for the case of combined erosion and volatilization due to depolymerization. The parameters of the medium are separated from the properties of the polymer and combined in two complexes whose influence is illustrated by means of nomograms for polymethyl methacrylate. The conclusions are confirmed by the results of tests employing a hypersonic rarefied argon plasma jet.

When heated in a stream of hot gas, polymers undergo ablation. In this process, a viscous layer is retained on the working surface and the temperature may be much higher than the melting point. Therefore, some of the polymer decomposes with the formation of volatiles. We consider the case of depolymerization when the decomposition products consist exclusively of monomers. Polymers with aromatic rings, quaternary carbon atoms, and electrophilic atoms or groups, for example, poly-α-methylstyrene, polymethyl methacrylate, and polytetrafluoroethylene, are prone to such decomposition. Special solutions for the rate of ablation in the case of depolymerization without erosion and erosion without decomposition were proposed in [1, 2]. Our object is to establish the rate of ablation for the general case.

To obtain a solution, it is convenient to use the calculations of [2] with the following modifications:

1. The heat of ablation should also include the energy expended on depolymerization and vaporization of the monomer.

$$F_s = F_m[1 + K(1 - z)(\overline{T}_s - 1)] + zF = F_m\overline{T}_s\tilde{s}, \tag{1}$$

where

$$\tilde{s} = K + \frac{1 - K}{\overline{T}_s} + z\left(K + \frac{\overline{F} - K}{\overline{T}_s}\right).$$

2. Instead of the nominal heat-transfer coefficient α, it is necessary to introduce the effective coefficient α_e, which takes into account the effect of the injection of volatiles into the boundary layer. In calculating the heat load, instead of the temperature drop $T_r - T_s$, we use the enthalpy difference $I_r - I_s$:

$$q = \frac{\alpha_e}{c_p}(I_r - I_s). \tag{2}$$

3. For consistency with the subsequent solution, the temperature gradient in the viscous layer should be taken in accordance with the value at the working surface

$$\overline{T}' = \frac{\rho V F_s}{\lambda T_m}. \tag{3}$$

As a result, we obtain

$$\rho V = \frac{\alpha_e}{c_p}\,\frac{I_r - I_s^+}{F_s}, \tag{4}$$

and the temperature of the working surface, on which the parameters α_e, I_s^+, F_s depend, must satisfy the equation

$$\overline{T}_s\,\frac{\overline{T}_s^{\,n+2} - \overline{T}_s(n + 2) + n + 1}{(n + 2)(n + 1)}\,\tilde{s} = (1 - z)Q_1L_1. \tag{5}$$

Here,

$$L_1 = T_m^{-3} L = \frac{\mu_m}{F_m \rho (T_m \lambda)^2},$$

$$Q_1 = \left(\frac{I_r - I_s^+}{c_p}\right)^3 Q = \frac{(I_r - I_s^+)^3 \alpha_e}{c_p^2 \, \mathrm{Pr}^{0.6} U} \int\limits_0^x \alpha \, dx.$$

If the heat-transfer coefficient does not depend on x, it is more convenient to write

$$Q_1 = q^2 J_1,$$

where

$$J_1 = \frac{I_r - I_s^+}{\mathrm{Pr}^{0.6}} \frac{x}{U}.$$

Although crystalline polymers were considered in [2], relations (4) and (5) can be extended to amorphous or partially crystalline compositions. In this case, the temperature T_m should be understood as the softening point corresponding to a viscosity $\mu = 10^{5.1}$ N · sec/m^2.

To complete the solution, it is necessary to construct an equation for determining the third unknown—the fraction z of depolymerized and vaporized material. We note that, on the one hand, the depolymerization rate ρV_c is related to the total rate of ablation,

$$\rho V_s = z \rho V, \tag{6}$$

and, on the other hand, is determined by the kinetic relations. The reaction develops over the entire heated region and the volume rate has an Arrhenius temperature dependence. Usually, every increase of 10° K in temperature approximately doubles the depolymerization rate. Therefore, the main mass of monomer is formed at $T > T_m$. The chemically active zone may be bounded by a viscous layer of thickness δ. Then, the rate of monomer release per unit surface will be related to the kinetic constants of the volume reaction A and E by the expression

$$\rho V_s = A \delta \int\limits_0^1 \exp\left(-\frac{E}{RT}\right) d\bar{y}. \tag{7}$$

At ordinary values of $\bar{T}_s < 2$, the thickness of the viscous layer (δ) is found from the temperature gradient, which may be assumed constant and equal to

$$\bar{T}' = \frac{\bar{T}_s - 1}{\delta}. \tag{8}$$

However, to evaluate the integral it is more convenient to depart from a linear temperature variation and assume a distribution

$$\frac{T}{T_s} = \left[1 + \left(1 - \frac{T_m}{T_s}\right) \bar{y}\right]^{-1}. \tag{9}$$

If $\bar{T}_s < 2$ the maximum deviation from linearity does not exceed +0.33 and is observed in the least responsible "nonhot" zone $\bar{y} = 1$. From expressions (1), (3), (4), and (6)–(9), we obtain

$$\bar{T}_s^3 \left\{1 - \exp\left[-\frac{\bar{E}}{\bar{T}_s}\left(1 - \frac{1}{\bar{T}_s}\right)\right]\right\} \times$$
$$\times \exp\left(-\frac{\bar{E}}{\bar{T}_s}\right) = \frac{z}{s} q^2 G_1, \tag{10}$$

$$G_1 = \frac{\bar{E}}{A F_m T_m \lambda}.$$

In Eqs. (5) and (10) the complexes L_1 and G_1 depend exclusively on the properties of the polymer, all the external influences are concentrated in the two parameters q and Q_1, and at constant α in q and J_1. The effect of these parameters on the ablation regime is illustrated in Figs. 1 and 2. The graphs were obtained by solving the system of equations (5), (10) for polymethyl methacrylate $(C_5H_8O_2)_p$ with molecular weight $M_n = 1.5 \cdot 10^5$ and the most probable distribution for which the weight-average molecular weight M_w exceeds the number-average M_n by a factor of 2. The density of the polymer was 1190 kg/m^3 and the thermal and viscous properties were: C = 3.7 kJ/kg·deg, $\lambda = 0.19$ W/m·deg, $T_m = 470°$ K, $F_m = 380$ kJ/kg; $\mu_m = 10^{5.1}$ N·sec/m^2, n = 34. The thermal and viscous properties were taken or calculated from the data of [3], the activation energy E = 136 kJ/mole was taken from [4], the frequency factor A = = $2 \cdot 10^{12}$ kg/m^3·sec was calculated from the experimental volatilization rates also presented in [4] for temperatures of 520–620° K in vacuum. The components of the latent heat of volatilization F—the heat of depolymerization $F_1 = 540$ kJ/kg, and the heat of vaporization of methyl methacrylate, $F_2 = 380$ kJ/kg—were taken from [4, 5].

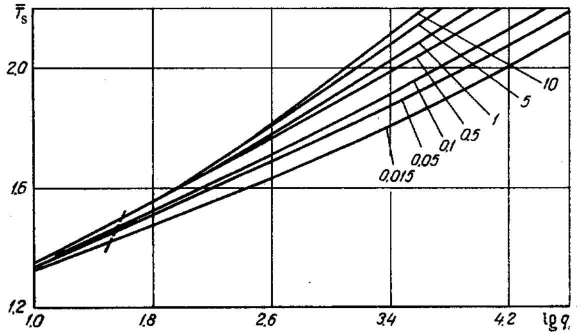

Fig. 1. Effect of heating conditions on the temperature of the working surface of polymethyl methacrylate. The numbers on the curves denote the complex J_1 in kJ·sec/kg. q in kW/m^2.

It is clear from Fig. 1 that increasing the heat load on the polymethyl methacrylate either directly or through the enthalpy in the complex J_1 causes an increase in the temperature of the working surface. Judging from Fig. 2, at large heat-transfer coefficients polymethyl methacrylate undergoes less volatilization, despite the higher temperature. This unexpected behavior is attributable to the spatial character of depolymerization. An increase in the heat-transfer coefficient and the resulting increase in the temperature of the melt lead to a decrease in viscosity with a simultaneous growth of the friction stress at the working surface. For the "weakened" melt there is only one possibility of balancing the stresses—an increase in the velocity gradient due to a thinning of the viscous layer. Hence, the most important zone for depolymerization—the principal source of gas—is reduced, the fraction of material volatilized falls, and a greater proportion is entrained by the flow in the condensed state. In this regime, as noted in [2], an increase in the ropiness of the polymer due to an increase in the molecular weight M_w is especially effective.

To check the solution, polymethyl methacrylate was tested in a rarefied hypersonic stream of argon plasma. The plasma was generated by a dc plasma generator with vortex gas stabilization. The jet flowed through a supersonic nozzle into a vacuum chamber at a pressure of 4 N/m^2. The pressure in the arc chamber was $4 \cdot 10^4$ N/m^2. The Mach number in the jet, calculated from the frozen speed of sound, varied from 2 at the nozzle exit to 25 ahead of the Mach disk. More details concerning the experimental apparatus are given in [6].

In our experiments, the mass-averaged enthalpy of the decelerated plasma, determined from the energy balance, was $1.04 \cdot 10^4$ kJ/kg. At a pressure of $4 \cdot 10^4$ N/m^2 this enthalpy corresponded to an equilibrium temperature of $9.5 \cdot 10^3$ °K. The distance between the Mach disk and the nozzle exit was 20 cm. The diameter of the supersonic zone in the specimen cross section was 16 cm. Argon was used to avoid complicating the analysis by such processes as chemical reactions, dissociation, and molecular vibration and rotation. Gasdynamic, spectroscopic, and acoustic measurements in the jet [6] showed that the flow was near-frozen, the degree of ionization along the jet being almost constant and equal to 0.02.

Cylindrical specimens 20 mm in diameter with a hemispherical nose were mounted on the axis of the jet between the nozzle exit and the Mach disk. By means of a special device the tip of the specimen was kept at a constant distance of 145 mm from the nozzle exit. The heat flow, measured under these conditions by a copper calorimeter in the nose, was 66 kW/m^2. At the surface of the polymethyl methacrylate the heat load was less owing to the injection of volatile depolymerization products. The injection effect was estimated in accordance with [7] as a function of the unknown temperature of the working surface T_s, the results of the computations of q are represented by the dashed line in Fig. 1.

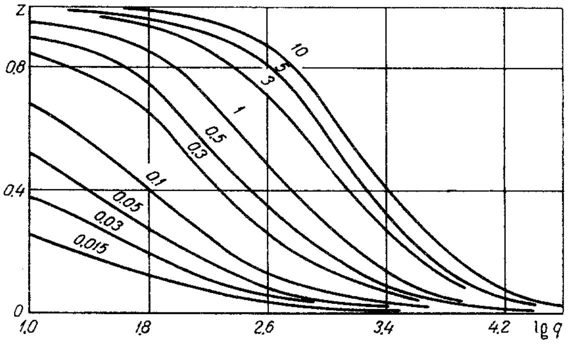

Fig. 2. Effect of heating conditions on the degree of volatilization of polymethyl methacrylate. The numbers on the curves denote the complex J_1 in kJ · sec/kg. q in kW/m^2.

The complex J_1 was found from the following considerations. Using known gasdynamic relations, for the blunt nose we can write

$$J_1 = \frac{I_r - I_s^+}{\mathrm{Pr}^{0.6}} \, \frac{\bar{\rho} r}{U_\infty (2\bar{\rho} - 1)^{0.5}}.$$

For a hypersonic frozen flow, the degree of condensation behind the shock

$$\bar{\rho} = \frac{k+1}{k-1},$$

and the recovery enthalpy

$$I_r \simeq r_r \frac{U_\infty^2}{2}$$

and exceeds by at least several times the enthalpy of the gas I_s^+ at the temperature of the working surface of the polymer. Under these conditions

$$J_1 \simeq 0.36 U_\infty \bar{\rho} r \simeq 0.5 (I_r \bar{\rho})^{0.5} r.$$

For our experiments $I_r = I_m = 1.04 \cdot 10^4$ kJ/kg; $k = 1.67$; $\bar{\rho} = 4$; $r = 10$ mm; $J_1 = 3.16 \cdot 10^{-2}$ kJ · sec/kg. The intersection of the line 0.03 in Fig. 1 and the experimental curve $q = f(T_s)$ determines the temperature of the working surface

$$\bar{T}_s = 1.44, \quad T_s = 1.44 \cdot 470\ ^\circ\mathrm{K} = 677\ ^\circ\mathrm{K}$$

and the true heat load

$$q = 33\ \mathrm{kW/m^2},$$

which in Fig. 2 corresponds to the fraction of unvolatilized material

$$z = 0.26.$$

In this case, in accordance with (1) and (4),

$$F_s = 1150\ \mathrm{kJ/kg}, \quad \rho V = 29\ \mathrm{kg/m^2 \cdot sec}.$$

The regime of erosion with partial volatilization can be visually confirmed—in the tests it can be seen how the viscous mass flows away from the blunt nose, while gas bubbles appear at the working surface. Hence, part of the polymer is converted into spray and the experimental ablation rate is 25% greater than the calculated value.

This analysis does not take into account a number of nonequilibrium processes such as recombination, radiation and nonisothermicity. Electronic heat conduction may play a certain part. However, it is hardly likely that these factors have a decisive influence, since under our conditions the contribution of the ionization energy to the stagnation enthalpy is small, and the degree of ionization is close to the frozen value.

NOTATION

Polymer parameters: T_m is the melting (softening) point; T_s is the temperature of working surface; $\overline{T}_s = T_s/T_m$; F_m is the total heat of fusion; F_s is the heat of ablation; F is the latent heat of volatilization; $\overline{F} = F/F_m$; ρ is the density; λ is the thermal conductivity of the melt; C is the specific heat of the melt at constant pressure; μ_m is the dynamic viscosity at temperature T_m; n is the exponent in the power-law temperature dependence of viscosity; A is the preexponential factor in the temperature dependence of the depolymerization rate; E is the depolymerization activation energy; $\overline{E} = E/RT_m$; z is the mass fraction of volatilized material; ρV is the mass ablation rate. Hot gas parameters: Pr is the Prandtl number; r_r is the recovery coefficient; I_r is the recovery enthalpy; I_s^+ is the enthalpy at temperature T_s; c_p is the specific heat at constant pressure; k is the adiabatic exponent; U is the velocity at the outer edge of the boundary layer; U_∞ is the freestream velocity; α is the heat-transfer coefficient; q is the heat load; x is the longitudinal coordinate; y is the transverse coordinate; δ is the thickness of the viscous layer; $\overline{y} = y/\delta$; r is the radius of the blunt nose; $K = (0.67-0.55)\, CT_m/F_m$, Q, L are parameters from [2].

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