THE DEVELOPMENT OF VOLUMETRIC FAILURE IN SILICATE GLASSES AND POLYMERS UNDER THE ACTION OF LASER RADIATION

A. A. Orlov and P. I. Ulyakov

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A investigation was made of volumetric failure in silicate glasses K-8 and F-5 and in polymethylmethacrylate (PMMA), and the energy-time characteristics were recorded for the start of the stage of the formation of damage in these materials due to a laser beam. The article discusses a model of the failure of silicate glasses as a result of the absorption of light at microdefects, as well as a model of the formation of cracks from high-temperature sites in polymers, taking account of the durability of the material. An evaluation is made of the power density q and the energy ε in the proposed mechanisms for the failure of transparent dielectrics.

In a number of articles, for example [1-4], devoted to an investigation of the mechanism of the interaction between laser radiation and optically transparent dielectrics, the threshold parameters for failure have been determined. As the threshold of failure, or the optical strength, there is usually adopted the density of the power $\langle q_0 \rangle$ or the energy $\langle \varepsilon_0 \rangle$ bringing about irreversible changes in the material, recorded visually or optically. In this case, the values of $\langle q_0 \rangle$ and $\langle \varepsilon_0 \rangle$ are averaged over the whole time of a pulse. This type of averaging, while satisfying the requirements of some industrial problems, is not always justified (particularly for millisecond pulses) in an evaluation of the role of one physical process or another in the mechanism of the interaction, since failure of the dielectric begins a very short time after the start of the pulse generation. In addition, the effect of the power and energy of a light pulse on the development of failure remains unexplained.

In the present work a study was made of the role of these characteristics in the process of the volumetric failure of silicate glasses K-8 and F-5 and of polymethylmethacrylate (PMMA), and the threshold values q_0 and ε_0 were determined as a function of the irradiation time. The experimental investigation has made it possible to propose physical models of the initial stage of failure of selected classes of dielectrics.

A schematic diagram of the experimental unit is shown in Fig. 1.

Laser radiation [1] with a wave length $\lambda = 1.06\ \mu$m, operating under spike mode conditions, was focused by lens 2, with a focal length of 120 mm, into the volume of the samples being tested 3, which had linear dimensions of 20-60 mm, considerably exceeding the diameter of the focused spot. The process of failure was recorded by frame-by-frame photography of the focal region, using an SFR-2M camera 4 with a speed up to 125,000 rpm. Illumination was effected using an ISKKh pulse-type lamp 5 through scattering screen 6. The current in the experiment was varied using the calibrated filters 7. Simultaneously with the photography, oscillograph recordings were made of the energy of the laser radiation to measure the energy passing through the sample up to the start of the development of failure. An initiating pulse from the control panel of the SFR, 8, through the separating condenser 9 ignited the source of illumination and, simultaneously, using the ferrite ring 10, connected the three-channel amplifying block 11. This device triggered the oscillograph 12, and ignited the lamps of the pumping laser generator and the spark gap 13, whose luminescence

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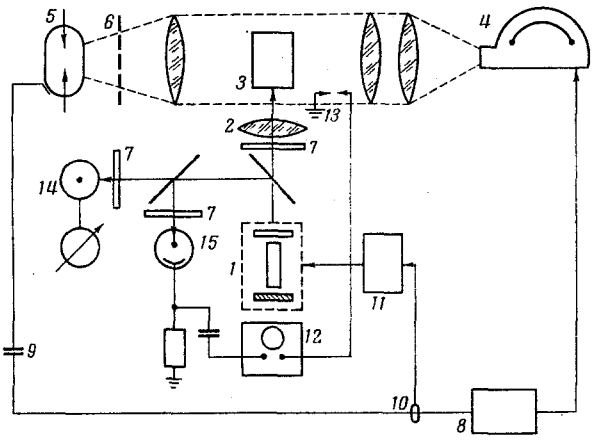

Fig. 1

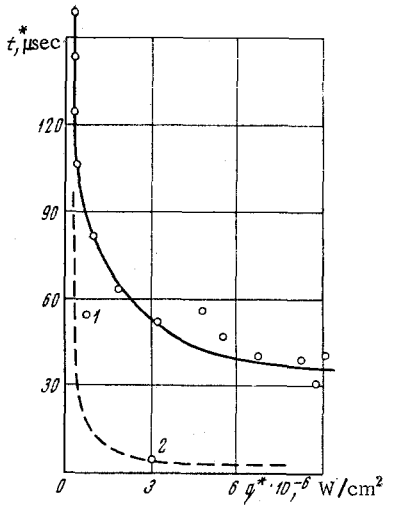

Fig. 2

was photographed simultaneously with the failure process, for time superposition with the oscillogram. Measurement of the energy by calorimeter 14, and recording of the discharge capacitance of the photocurrent of the photoelement 15, were effected by shunting of part of the radiation in each experiment.

Thus, photography was used to determine the time from the flashing of the spark gap (ignition of the laser generator) up to the appearance of failure, while an oscillogram was used to determine the time from ignition up to the start of irradiation. The difference between these times, t*, characterizes the period for the formation of visible damage in the sample, and makes it possible to determine from the oscillogram the energy of the irradiation, E*, after this period. Then, the threshold current density, averaged over the time t*, $q^* = E^*/t^*s$, where s is the area of the focus spot.

Experimental points obtained with the irradiation of PMMA are shown on a curve (Fig. 2). The dotted line shows a plot of a hyperbolic dependence of the type $t_0 = \langle \varepsilon_0 \rangle / q$, under the assumption that the process of failure is determined only by the value of the absorbed energy, and does not depend on the current density. As the quantity $\langle \varepsilon_0 \rangle$ there was taken the threshold energy density, averaged over a whole pulse, and equal to ≈ 15 J/cm^2.

It is evident from the curve that almost all the experimental points lie above the hyperbola $\langle \varepsilon_0 \rangle$ = const. As is shown by investigations of the kinetics of the development of damage in polymers [5], in particular in PMMA [6, 7], in the initial stage there is formed a high-temperature site, in the form of a cavity in the material, filled by decomposition and vaporization products of the polymer. The absorption of radiation at this site leads to an increase of the pressure within it, to an increase of the stresses in the substance surrounding the cavity, and to the subsequent formation of a crack. The process of brittle failure of a polymer, which is brought about by a rise of the pressure in the cavity, is a thermal fluctuation process. However, the time for the development of a crack from the site, or the durability of the material, obeys the dependence [8]

$$\tau = \tau_0 \exp \{\alpha [U_0 - \gamma\sigma (q^*)]\}$$

where $\alpha = R^{-1} (1/T_0 - 1/T_1)$; τ_0, U_0, γ are constants which, for PMMA, have the following values [8, 9]: $10^{-3}T_1^{-1}$ [K^{-1}] = 1.5; U_0 = 57 kcal/mole; γ = 2.6 (kcal · mm^2)/(mole · kg); $\tau_0 = 10^{-13}$ sec; R is the universal gas constant; $T_0 \approx 390$°K is the softening temperature of PMMA. Then

$$t^* = t_0 + \tau = \frac{\langle \varepsilon_0 \rangle}{q^*} + \tau_0 \exp \{\alpha [U_0 - \gamma\sigma (q^*)]\} \qquad (1)$$

The stress σ at the limit of the cavity is proportional to the pressure or to the temperature of the decomposition products, depending on the feed density of the radiation flux. With laser irradiation of a polymer, there is high-temperature linear pyrolysis which, for PMMA, is distinguished by the high rate of the chemical process itself. With an increase in the dimensions of the cavity, there is an increase in the amount of energy absorbed in it, which leads to a rapid rise in the density of the power which brings it about. This is borne out by the fact that with weak radiation fluxes there are individual cavities in the radiation zone after the action of a laser pulse, which are observed under the microscope, but which do not develop into cracks.

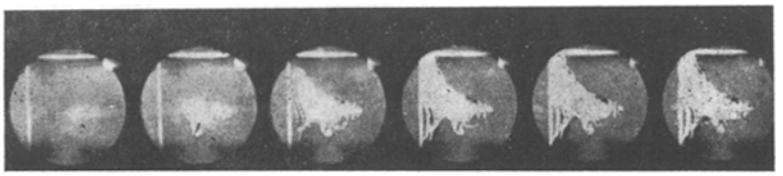

Fig. 3

Let us evaluate the change in the temperature and, correspondingly, of the voltage with the current.

The macrokinetics of the decomposition are characterized by the activation energy E_a in accordance with the exponential formula

$$V = V_0 \exp\{-E_a / RT\}$$

and by the quantity V_0, proportional to the reaction constant K_0, which has an order of the frequency of the vibrations of the molecule equal to 10^{14} sec^{-1}; at high temperatures, the value of K_0 depends strongly on the value of T. In particular, at 750°K, $K_0 \approx 10^{24}$ sec^{-1} and $E_a \approx 70$–80 kcal/mole [10].

This rise in the value of $K_0(T)$ with the temperature can be approximated by a dependence of the form

$$V_0 = V_k \exp\{-E_k / RT\}$$

Then

$$V = V_k \exp\{-(E_a + E_k) / RT\} \tag{2}$$

and the value E_k = 63 kcal/mole is determined from the values of K_0 at 600 and 750°K [10].

On the other hand, from the law of conservation of energy, neglecting the removal of heat and assuming the mean current density to be constant, with the quasi-steady-state development of a spherical site we can determine the radial rate of expansion of the cavity:

$$V \approx q / 4\rho cT \tag{3}$$

where ρ is the density of the material; c is the heat capacity.

With the high-temperature decomposition of PMMA, the value of the specific destruction energy can be neglected in comparison with the value of cT. Then, equating (2) and (3), we obtain a transcendental equation of the form

$$\ln q = \ln 4V_k \rho cT - \frac{E_a + E_k}{RT} \tag{4}$$

The quantity $A = \ln 4V_k \rho cT$ depends only weakly on the temperature; therefore, it can be regarded as constant. Solving Eq. (4) for T, we obtain

$$T = E_a + E_k / R\,(A - \ln q)$$

The value of V_k is determined from (2) by substituting the mean experimental rate of growth of the cavity V ≈ 1 cm/sec [7] near the failure threshold. The weak change of the temperature with the current and its value ~ (2–3) $\cdot 10^3$°K are in good agreement with experimental data on the laser irradiation of PMMA [11].

The stress σ, proportional to the temperature, can be determined as

$$\sigma = \frac{B}{A - \ln q}$$

The constant B for PMMA is determined by the condition that the stress σ attain a value σ_0 at a value of $q = \langle q_0 \rangle$. The value of σ_0 is calculated using the formula for the durability, from the known properties of PMMA [8, 9]. At the limiting temperature of the elastic state T ~ 100–120°C and a duration of a pulse $\approx 2 \cdot 10^{-3}$ sec, the quantity σ_0 attains values of 6 kg/mm^2, which contradicts results obtained with loadings having a duration of ≈ 1 sec [12].

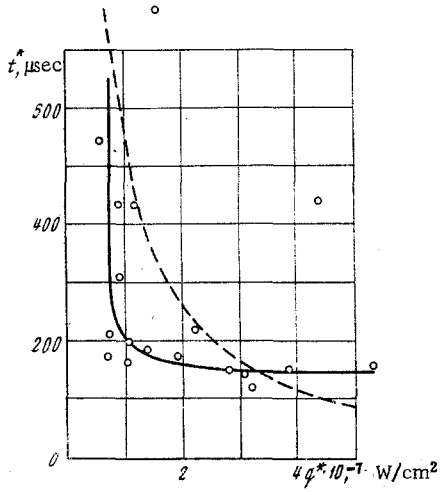

Fig. 4

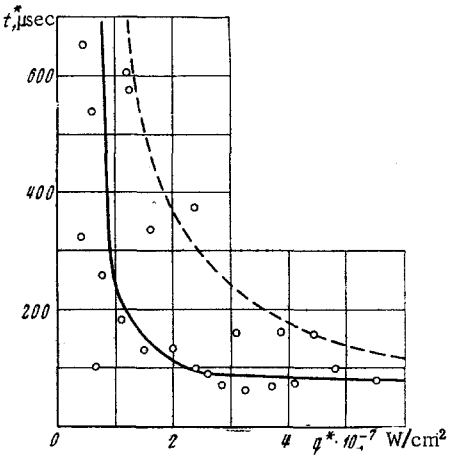

Fig. 5

Then

$$\sigma = \sigma_0 \frac{A - \ln \langle q_0 \rangle}{A - \ln q^*} \tag{5}$$

Thus, substituting (5) into (1), we obtain a connection between the total time of irradiation up to failure of the medium and the mean density of the power

$$t^* = \frac{\langle \varepsilon_0 \rangle}{q^*} + \tau_0 \exp\left\{R^{-1}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)\left(U_0 - \gamma\sigma_0 \frac{A - \ln \langle q_0 \rangle}{A - \ln q^*}\right)\right\} \tag{6}$$

The results of a calculation for PMMA using this formula are shown by the solid line on Fig. 2. The agreement between the calculated and experimental data is completely satisfactory, bearing in mind the averaging of the light flux. In the experiments carried out, the value of q was constant for the first 250 μsec of irradiation.

It is of interest to note that, with a large increase, the form of some of the sites differs from the spherical and has sharply protruding boundaries, at which the stress concentration is considerably higher than the mean value.

In this case, the durability time is found to be small, and the value of t* is close to the value of t_0. Such points are sometimes observed experimentally (points 1 and 2 on the curve) and lie practically on the hyperbolic curve.

In glasses, the appearance of failure has a considerably different character. High-speed photography shows that, within a certain time t* from the start of the irradiation, at the focal region in the glass samples there arises a brightly luminescent zone which, with the passage of time, grows toward the beam. Figure 3 shows a typical moving-picture photo of the failure of glass K-8 (the irradiation is acting from the left, the time of a frame is 16 μsec, the scale is 1 : 2). The longitudinal growth is accompanied by the development of transverse cracks, going away from the zone at different angles. The initial dimension of a longitudinal trace is comparable to the length of the focal region. Depending on the focusing conditions, the failure may reach the leading face of the sample, which is accompanied by intensive splitting off of the face. In the case when the longitudinal trace does not reach the forward boundary, the sample splits along transverse cracks going out toward the lateral surfaces. A study of a failure zone with a large increase shows that it has a form close to cylindrical, and that it is filled inside by sintering particles of the material. In spite of their external similarity, the experimental curves of t* (q*) for PMMA and for glasses have a difference in physical principle. The energy-time characteristics of the failure of silicate glasses are shown on Figs. 4 and 5 for K-8 and F-5, respectively. The solid lines are approximate experimental plots, while the dotted lines, as before, represent the dependence $t_0 = \langle \varepsilon_0 \rangle / q$, plotted from the threshold parameters of these glasses for the period of a whole pulse: for glass K-8, $\langle \varepsilon_0 \rangle \approx 6$ kJ/cm^2; for F-5, $\langle \varepsilon_0 \rangle \approx 11$ kJ/cm^2. Almost all the experimental points on Figs. 4 and 5 lie below the hyperbolic dependence. This means that failure of the glasses starts before the threshold energy density $\langle \varepsilon_0 \rangle$, averaged over the whole time of a pulse, is achieved.

Data on the microstructure of glasses [13, 14] bears witness to the presence of micro- and macrodefects, as well as of impurity levels, which bring about the initial absorption of the radiation. Single-photon ionization of microdefects leads to the appearance of free electrons. Their acceleration in the field of the light wave may bring about the birth of new electrons by the shock ionization of defects with low levels in the forbidden band. For simplification, we shall assume that recombination counterbalances the growth of the number of "single-photon" electrons with the current and of "shock" electrons, with an increase in their concentration. Let single-photon ionization of microdefects of the glass lead to the generation of n_0 free electrons. Their acceleration in the field of the light wave up to the energy

$$E_e(E) \geqslant E_e' = I$$

(E is the intensity of the field; I is the ionization potential of the defect) brings about the shock ionization of part of the defects, i.e., an increase in the concentration n_e. The efficiency of this process is connected with the large content of inherent and impurity defects in the glasses, amounting to 10^{-6}–10^{-3} out of the total number of atoms, i.e., in one measurement, for each 10–100 atoms,* there is, on the average, one defect. In the case under consideration, scattering on the phonons is stronger than the set of energies, and all the energy of the photo- and shock-generated electrons will be given up to the atoms of the substance. The total concentration, n_e, is made up of the concentration of photoelectrons, n_0, and the concentration of electrons, Δn, appearing as the result of the possible ionization of impurity levels, i.e., $n_e = n_0 + \Delta n \eta\,(E_e - E_e')$, where $\eta(E_e - E_e')$ is a Heaviside function.

The probability of shock ionization is proportional to the concentration of photoelectrons, n_0, to their energy, and to the frequency of collisions with defects: $\Delta n \sim n_0 E_e \nu$. In the first approximation, it can be assumed that $E_e \sim E^2 \sim q$. The frequency of collisions with ionizable defects, ν, can increase only with an increase in the value of E_e. A rise in the temperature, bringing about an increase in the frequency of the vibrations of the atoms of the matrix, also leads to an increase in the value of ν.

Approximately, the dependence of the frequency of collisions between a defect and an electron may be assumed to depend only on the energy of the latter

$$\nu \sim v_e \sim \sqrt{E_e} \sim q^{1/2}$$

where v_e is the velocity of an electron.

Then

$$\Delta n \sim n_0 q^{3/2} \eta\,(q - q')$$

where the current density q' corresponds to the energy E_e' and

$$n_e \approx n_0 [1 + \beta q^{3/2} \eta\,(q - q')] \tag{7}$$

where the constant β is a characteristic of the defectivity of the material.

A rise in the concentration n_e leads to a nonlinear reinforcement of the absorption in a small volume, to an increase in its temperature, and, starting at some given moment of time, to vaporization of the substance. A further rapid increase in the temperature and the pressure at the site leads to damage of the material around the site. Thus, the condition for the origin of the site of a source of brittle failure at microdefects of the glass may be characterized by a determined value of the specific enthalpy H, proportional to the absorption energy E_1.

In turn, the energy absorbed after the time t is

$$E_1 \sim q n_e (t - t_1) \geqslant H = \text{const} \tag{8}$$

Here $t_1 = t_1(q)$ is the time starting with which the concentration of electrons set up by the current can ensure an accumulation of heat at the site.

Then, taking account of (7) and (8), the condition for the origin of a site can be written

$$t^* = t_1(q) + \frac{\text{const}}{q^* [1 + \beta (q^*)^{3/2} \eta\,(q^* - q')]} \tag{9}$$

Formula (9) does not take account of the durability of the material since, as the result of a rapid rise in the enthalpy with the current, it becomes small in comparison with the time t^*.

*As in Russian original – Consultants Bureau.

The experimental curves (Figs. 4 and 5) are well described by dependence (9), with the empirical values $q' = 10^7$ W/cm^2, const $= 6 \cdot 10^3$ J/cm^2, which corresponds to the threshold energy density $\langle \varepsilon_0 \rangle$ over a whole pulse, $\beta = 3 \cdot 10^{-10}$ (cm^2/W)$^{3/2}$, $t_1 = 10^{-4}$ sec.

The large scatter of the points on the curves is explained by the strong fluctuations of the local strength of the glass [14]. The qualitative agreement between the approximate dependence (9) and experiment bears witness to the correctness of a site-type model for the appearance of damage in glasses with currents less than 10^{10} W/cm^2, at microdefects due to the absorption of light, appearing as the result of photoshock ionization by electrons.

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