DESTRUCTION OF TRANSPARENT DIELECTRICS BY LASER RADIATION

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Destruction of polymer samples (polymethylmethacrylate, polystyrene) by Q-switched laser pulses with intensities below threshold or by picosecond pulses is considered. Sample damage is found to depend on a parameter which takes into account both characteristics of the laser pulse, its energy and intensity. It is shown that there is no principal difference in the nature of the interaction of Q-switched and free-running laser pulses with polymer samples. No nonlinear laser energy absorption effects are observed when passing through the energy threshold value. The light emitted by the sample under action of the laser pulse is studied in detail. It is shown that the emission and temperature heating of microregions that may be related to it cannot explain fissure formation.

THIS paper is concerned with the study of laser radiation damage in blocks of amorphous polymers like polymethylmethacrylate. The basic aim is to determine the reasons for the threshold values of the laser pulses and to establish a damage criterion.

EXPERIMENTAL RESULTS

The experimental arrangement was described earlier[1], so we only indicate here that the experiments were performed with laser pulses of duration 15–20 nsec (at half-power) with energy up to 1 J and wavelength 0.69 or 1.06 μ. In each experiment the parameters of the pulse were monitored. The laser radiation was focused in the samples of polymethylmethacrylate (PMMA), polycarbonate (PC), or polystyrene (PS) by a lens with focal length 35 or 70 mm.

Likhachev et al.[2] introduced the concept of a threshold energy of the laser pulse for the free-running regime. As the threshold giant pulse we shall take the pulse whose action on the sample leads to the occurrence of visible damage with linear dimensions of 50 to 100 μ. Trials showed that the threshold values of the laser pulse depend on the wavelength of the radiation and are: for $\lambda = 0.69$ μm, $J_{p1} = 8.5 \times 10^8$ W/cm^2, $\mathscr{E}_{p1} = 17$ J/cm^2; for $\lambda = 1.06$ μ, $J_{p2} = 0.5 \times 10^8$ W/cm^2, $\mathscr{E}_{p2} = 1$ J/cm^2. Under the action of a series of n pulses with intensity of each J_n below threshold, visible damage is also observed in the samples. In each trial visible damage appears suddenly with the last pulse of the series, and there is a definite relation between the parameters of the pre-threshold pulses of the series and their number. Table I presents the corresponding values of J_n/J_p and n. It turns out that the smaller J_n/J_p, the greater is n and the greater is the total energy of the series of pulses. However, from the experimental data of Table I it follows that there exists a certain damage criterion (in the formation of visible damage) that connects J_n, $\mathscr{E}_n$, and n and remains unchanged for a given wavelength: the ratios $nJ_{n1}\mathscr{E}_{n1}/J_{p1}\mathscr{E}_{p1}$ and $nJ_{n2}^2\mathscr{E}_{n2}/J_{p2}^2\mathscr{E}_{p2}$ extremely close to unity. From this we can say that the criterion for damage at $\lambda = 0.69$ μm is $J_{p1}\mathscr{E}_{p1}$ $= nJ_{n1}\mathscr{E}_{n1} = \text{const}$, and at $\lambda = 1.06$ μm, $J_{p2}^2\mathscr{E}_{n2} = nJ_{n2}^2\mathscr{E}_{n2} = \text{const}$. The numerical value of the damage criterion at $\lambda = 0.69$ μm for nanosecond pulses is 1.4×10^{10} J-W/cm^4.

$\lambda = 0.69\mu$				$\lambda = 1.06\mu$			
$\frac{J_{n1}}{J_{p1}}$	n	$\frac{n\mathscr{E}_{n1}}{\mathscr{E}_{p1}}$	$\frac{nJ_{n1}\mathscr{E}_{n1}}{J_{p1}\mathscr{E}_{p1}}$	$\frac{J_{n2}}{J_{p2}}$	n	$\frac{n\mathscr{E}_{n2}}{\mathscr{E}_{p2}}$	$\frac{nJ_{n2}^2\mathscr{E}_{n2}}{J_{p2}^2\mathscr{E}_{p2}}$
0.25	17	4.3	1.1	0.33	28	9.2	1.0
0.35	10	3.5	1.2	0.44	16	7.0	1.4
0.4	7	2.8	1.1	0.55	6	3.3	1.0
0.5	4	2.0	1.0	0.6	3	1.8	0.7

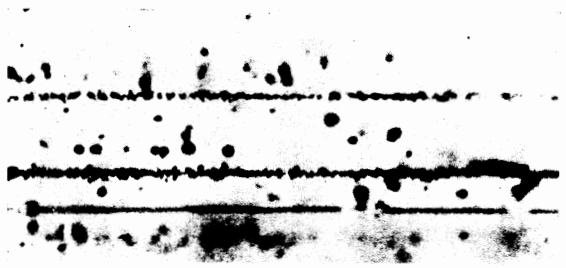

FIG. 1. Damage caused in PMMA by picosecond pulses. Magnification 900X.

In experiments on the action of picosecond laser pulses ($\lambda = 0.69$ μ, $\tau = 5 \times 10^{-11}$ sec, $\mathscr{E} = 0.05$ to 0.1 J) on PMMA samples it was established that visible damage occurs in the samples. The damaged places (shown in Fig. 1) are distributed randomly in the irradiated region or along certain lines (threads); in the latter case their number is 10^4 per centimeter. It was established that the intensity and energy of picosecond pulses leading to visible damage satisfy the value of the damage criterion found for nanosecond pulses, i.e., $J\mathscr{E} \approx 10^{10}$ J-W/cm^4. Thus the damage criterion is identical for pico- and nanosecond pulses and depends only on the radiation wavelength.

A different assumption was made in[3] about the nature of the interaction of a giant laser pulse and a free-

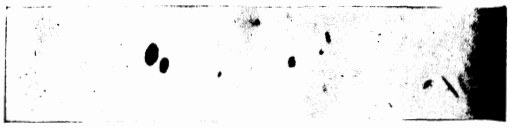

FIG. 2. Disc-shaped damage caused by a giant pulse with $J_{n1} < J_{p1}$. Magnification 50X.

running pulse with a polymer. This assumption was based on the differences in the character of the damage evoked by the two kinds of pulses.

The photograph in Fig. 2 shows the damage in a PS sample due to successive action of a series of sub-threshold giant pulses the number of which exceeded that necessary for the formation of threshold damage. The damage is similar to that caused by a free-running pulse: disc-shaped fractures with their planes oriented at 45 to 90° to the laser beam. The assumption expressed in[3] is therefore inaccurate, and one cannot draw any conclusions about the difference in nature of the interaction of the pulses from the character of the damage without determining the role of the intensity and energy of the pulse.

From our point of view, one needs to seek a single general explanation for the destruction independently of the mode of operation of the laser; damage by a free-running pulse should be treated as the successive action on the sample of a series of peaks (analogous to a series of sub-threshold pulses). It is possible that some of the spikes of a pulse start the cracks and the rest make them grow[1]. By applying our damage criterion to a threshold free-running pulse, we obtain a completely reasonable value for the intensity of the spike, which supports what we said above and shows the universality of the damage criterion. Thus, the damage criterion so established depends only on the wavelength of the laser, not on its mode of operation, and is determined by the number of pulses (or spikes), their intensity and energy.

The experiments which established the damage thresholds of polystyrene (PS) and polycarbonate (PC) showed that the damage criterion found for PMMA is common for these three polymers, though the numerical values differ somewhat. In Table II are the results of these experiments for $\lambda = 0.69\ \mu$. The ratio $nJ_{n1}\mathcal{E}_{n1}/J_{p1}\mathcal{E}_{p1}$ for both materials is also close to unity. For PC damage was recognized as the appearance of black microcavities covered inside by soot and localized by oriented material. The experiments in both cases were carried out at room temperature. The numerical values of the threshold pulses of these materials are different from those found for PMMA: for PS, $J_{p1} = 3.8 \times 10^8$ W/cm^2, $\mathcal{E}_{p1} = 7.6$ J/cm^2; for PC, $J_{p1} = 11.9 \times 10^8$ W/cm^2, $\mathcal{E}_{p1} = 23.8$ J/cm^2, although the value of the criterion remained about the same. Thus, regardless of the polymer material (PMMA, PS, PC) the damage criterion is the same, which indicates the identical character of the process of interaction of the laser radiation with the polymer; the differences in numerical values are due to the different properties of the sample material.

The large number of damaged areas arising under the action of picosecond pulses shows that there is a large number of microdefects ($\sim 10^{12}$ cm^{-3}) that act as nuclei for the formation of damage. This circumstance

Material	J_{n1}/J_{p1}	n	$n\mathcal{E}_{n1}/\mathcal{E}_{p1}$	$n\mathcal{E}_{n1}J_{n1}/\mathcal{E}_{p1}J_{p1}$
PS	0.2	16	3.2	0.6
	0.3	10	3.0	0.9
	0.4	6	2.4	1.0
	0.5	3	1.5	0.8
PC	0.3	11	3.6	1.0
	0.4	15	2.0	0.8
	0.5	5	2.5	1.2

forces us away from the assumption that the damage originates at foreign inclusions, although these can be of some importance. The thermophysical properties, for example, of PMMA and PS are such that for the transformation of the same quantity of each polymer into gas almost the same amount of energy is required, whereas their threshold values differ by a factor of two.

These polymers differ both by their thermophysical characteristics and structure and by their microstructural characteristics. We shall establish that these differences show up in the magnitude of the damage threshold. To this end we changed the microstructure of the PMMA samples by stretching them to produce a strong orientation. In oriented samples the microstructural elements are strongly elongated along the orientation direction and the mechanical strength perpendicular to this direction is about 1.5 times less than in unoriented PMMA; this indicates a decrease in the bonding between the structural elements. The experiments showed that in oriented PMMA the planes of fractures are arranged along the direction of orientation and the threshold value of the laser pulse $\tilde{J}_{p1}$ is less than in unoriented samples J_{p1}; $\tilde{J}_{p1} = 0.63\ J_{p1}$; the damage criterion remained the same. This suggests that the threshold values are determined by the magnitude of the coupling between the structural elements.

In[5,6] it was solidly established that the damaging cracks arise under the action of a gas that is formed at certain points of the irradiated region. The damage criterion, to begin with, indicates that the character of gas formation is non-thermal. To find out whether the destruction was by electrical breakdown, we did some experiments on damage by a laser with plane and circular polarizations. In these experiments the energy and intensity remained constant, but the field changed by a factor of 1.4. The threshold values of the laser pulses remained unchanged. The action on the sample of a dc electric field with $U = 3 \times 10^6$ V/cm at the same time as the laser pulse also did not change the damage threshold, although laser-induced dielectric breakdown frequently occurred. Thus, mechanical destruction of PMMA samples evoked by the action of laser radiation is not caused by an electrical breakdown in the sample induced by the electromagnetic field of the laser radiation.

It is known that under the action of laser radiation the formation of damaging cracks in polymer samples is accompanied by light emission[1,5,6]. Our experiments further showed that the emission is localized in microregions and, judging from the cooling time (decrease of emission intensity), the linear dimensions of the microregions are of the order 0.4 μm ($J \geq J_p$). For $J < J_p$ the intensity of the emission repeats the shape of

the incident pulse, and its maximum value is about an order of magnitude smaller than the maximum intensity under the action of laser pulses with $J \geq J_p$. If a series of pulses with $J_n < J_p$ acts on the sample, then at the moment of damage formation (last pulse of the series) the intensity of the emission increases by an order of magnitude. The intensity of the emission evoked by the action of laser pulses with $J \geq J_p$ has a thermal character ($T = 6500°K$) and is independent of the intensity of the laser pulses in the range $J_p \leq J \leq 3J_p$. The emission ($J > J_p$) arises 10 nsec after the cracks begin to grow and develops "independently"—the maximum intensity does not coincide with the laser pulse maximum. We carefully checked the possibility that the laser caused luminescence in the sample. Experiments showed that at the temperature of liquid nitrogen, where the luminescence spectrum of organic molecules consists of separate bands, the emission spectrum of these microregions was continuous and had a thermal character. It is known that the luminescence radiation of strongly oriented polymers is polarized. The action of a laser on our strongly oriented samples did not produce polarized light from the microregions. We conclude that this light does not come from luminescence of the sample or of impurities in it.

Our results can therefore be summarized as follows:

1. There exist threshold values of the laser pulses (for $\tau \approx 2 \times 10^{-8}$ sec) and a damage criterion, which does not depend on the duration of the pulses but does depend on the wavelength of the light field, with a numerical value that is characteristic of the material of the sample. This criterion indicates that the process responsible for the appearance of damage cracks is nonthermal in character.

2. The mechanical destruction caused by a laser in the free-running regime is similar to that caused by a Q-switched laser, which also indicates that the same process takes place in both cases.

3. The damage is not associated with electrical breakdown in the electromagnetic field of the laser radiation.

4. The light accompanying the appearance of damage is localized in microregions, is thermal in character, is delayed with respect to the beginning of damage development, and is not luminescence.

DISCUSSION

1. **The reason for threshold phenomena.** The damage is determined by two types of processes: physical interaction of radiation with the substance and mechanical development of the damage cracks. We shall show that the threshold values are determined by the mechanical process. We start from the firmly established fact that under the action of laser radiation cracks in amorphous polymers develop under the action of a gas that fills the internal cavity of the crack[5,6]. (We leave aside for now the question of where the gas comes from.) Hence the development of the crack is a purely mechanical problem. It is known that a crack begins to grow when its size is greater than a certain critical value; otherwise there is no danger[8]. It follows that the threshold values of the laser pulse are connected with the condition of formation of embryonic cracks, which with a small excess of the pressure of the gas in them over the critical value begin to develop rapidly (germinate). In this case the crack begins to develop practically from a point and at the initial moment of its birth and advance it must overcome the forces of interaction between the structural elements[7], which is the equivalent of overcoming the theoretical strength σ_t. The birth of a crack is in practice the appearance of a cavity in the sample. Let us determine the minimum critical size beginning with which a crack can germinate under loads equal to σ_t. Griffith's theory[8,9], which gives the dependence between the stress in the crack and its size, can be used here:

$$\sigma_r = K / \sqrt{2r}, \qquad (1)$$

where r is the crack radius, $K = 160$ kg(force)/cm$^{3/2}$ is the cohesion modulus, $\sigma_t = 5000$ kg(force)/cm^2. From (1) we find the critical size of the crack: $r_0 = 5.1$ μm, and the completely definite quantity of gas that is formed is

$$\Delta m \approx 10^{-10}\ g \qquad (\rho = 1.2 g/cm^3).$$

A small excess (over equilibrium) pressure of gas in a crack of critical size causes it to develop, which leads to the formation of certain end-point profile to the crack[9], which, in turn, brings about overstresses around the point. As the crack develops stresses necessary for cleavage of the material will occur near its end (in this case σ_t). Meanwhile, inside the crack the gas pressure will decrease, but the quantity of gas will remain the same. In this case cleavage of the sample occurs on account of overstress at the end of the crack of a certain profile. Considering the problem of the existence of an equilibrium crack with compressive forces at its end[10] equal to σ_t[7] and taking into account that new quantities of gas are not formed, i.e., if the amount of gas Δm remains constant, we find the final dimensions of the equilibrium crack r_f that spontaneously grows from $r_0 = 5.1$ μm. It is $r_f = 51$ μ, and the pressure of the gas inside it is about 50 atm. That is, if in the sample there is formed a sufficient quantity of gas to overcome the theoretical strength in a portion with linear dimension of about 5.1 μ, then with a small excess of pressure this microcrack will grow to a size of 50 to 100 μ. Thus, the condition for the appearance of visible damage cracks ($r = 50$ to 100 μ) is the formation of gas capable of overcoming the bond between the structural elements (theoretical strength) in a portion with $r_0 \simeq 5.1$ μ. This is a mechanical condition and determines the threshold value of the laser pulse.

2. **Physical meaning of the damage criterion.** The principal problem of laser damage of amorphous polymers is to explain the formation of gas. Unfortunately, it is not presently possible to solve this problem completely. However, the damage criterion we have found and the experiments we have done provide some hope for success. The nonlinear dependence of the destruction on the intensity of the laser pulse shows unequivocally that the gas is not formed by a purely thermal process. The damage criterion can be interpreted in the following way. The mechanical requirement that specifies the threshold pulse assumes the formation of a definite

quantity of gas Δm at the time of action of the laser pulse:

$$\Delta m = n\int_0^\tau \dot{m}\,dt, \qquad \begin{cases} n=1 & \text{for} \quad J=J_p, \\ n>1 & \text{for} \quad J<J_p, \end{cases} \tag{2}$$

where $\dot{m}$ is the rate of gas formation, which is in practice determined by the number of polymer molecular bonds ruptured per second. It is complete reasonable to assume that $\dot{m} = f(J)$, so that (2) takes the form

$$\Delta m = n\int_0^\tau f(J)\,dt, \qquad \begin{cases} n=1 & \text{for} \quad J=J_p \\ n>1 & \text{for} \quad J<J_p \end{cases}. \tag{2a}$$

Let us represent

$$f(J) = K_1 J + K_2 J^2 + K_3 J^3 + \ldots, \tag{3}$$

which assumes the possibility of multi-quantum processes of gas formation. In quantum mechanics it is shown that the operation of one multi-quantum process makes the others improbable; this means that in our case f(J) can equal only one of the terms on the right side of (3). In experiments, one of these possibilities will occur. For simplicity, we assume that the laser pulse is rectangular with J = constant; then we obtain alternative equalities:

$$\begin{gathered} \Delta m = nK_1 J\tau = nK_1\mathscr{E}, \qquad \Delta m = nK_2 J^2\tau = nK_2 J\mathscr{E}, \\ \Delta m = nK_3 J^3\tau = nK_3 J^2\mathscr{E}; \\ n = 1 \text{ for } J = J_p,\ n > 1 \text{ for } J < J_p. \end{gathered} \tag{4}$$

As experiment shows, the two last equalities in (4) coincide with the value of the damage criterion for λ = 0.69 and 1.06 μ. Since the experiments showed that the damage is determined in the first place by the intensity of the laser radiation and not by the energy of the pulse, the assumption of multi-quantum processes of gas formation can be considered justified. Thus, from mechanical requirements that determine the development of cracks of critical size, a critical damage condition flows naturally; the rate of formation depends on multi-quantum processes of the interaction of laser radiation with a solid. Since the theory of the interaction of laser radiation with solids is not developed, we are limited to just these assertions, unless we are to make estimates of the probability of multi-quantum processes using the calculations developed for gases.

3. Microregion emission. One of the most significant experimental facts presented above is the independence of the processes of crack formation and the emission from them: the emission begins after the crack has already begun to grow and develops independently. We believe that the microregion emission is dielectric breakdown. The phenomenon of dielectric breakdown by an electric field is well known, but little studied[11]. Two types can be considered—in the field of the light wave in the intact dielectric and in the damaged dielectric, i.e., in the growing crack. Breakdown in dielectrics depends to a large extent on the porosity of the material and foreign inclusions[11]. Theoretical calculations have been made mainly for inclusions or large pores (larger than 10 μ). In the polymers we used there is a large number of micropores with dimensions less than 1 μ, so that existing theory is inapplicable here, although one would suppose that under the action of laser radiation on the polymer samples breakdown will occur in them (or at foreign inclusions). It is not possible to make a theoretical estimate. It is probably this type of breakdown that produces emission in microregions for subthreshold intensities. At the moment of formation of damage cracks in the sample a cavity is formed filled with gas the pressure of which falls with time (as the crack grows). In this case breakdown is possible in this cavity. After 10 nsec (delay time of the thermal emission) the crack has grown by 20—40 μ, and according to the estimates made above, the gas pressure is not more than 100 atm. If the electrical discharge fills the entire cavity, the maximum size of the light-emitting region is 50 to 100 μ, which is the size observed experimentally[1]; the minimum size is about 0.8 μ and will determine the cooling of the discharge-heated gas, which also agrees with experiment. This explanation of the experimental facts cannot be supported by theoretical calculations, since there is as yet no theory of breakdown under the conditions considered here.

4. Further remarks. In determining the critical crack size, we started from the assumption that everywhere at the end of the crack the forces of interaction between the structural elements (taken equal to the theoretical strength) had to be overcome during its development. However, it is possible that a crack will encounter a structural element. Then it is necessary for it either to change direction in accordance with the boundary of the element or to destroy it; otherwise the crack will stop there. At the beginning a crack propagates with supersonic speeds[12] and is associated with a shock wave, which demolishes microstructural formations. Hence localization can occur with a crack of large size when its speed drops and the spherical shock wave has weakened or before it starts.

As was indicated above, when a crack begins to grow and the pressure within it falls, a breakdown is possible in the cavity. This breakdown causes the gas inside the crack to heat up. As a consequence there can be heating and melting of the polymer near a crack, increase of gas pressure, and formation of a bubble inside the sample (such defects were observed in PMMA) or an advance of the crack due to the increase in the pressure of the heated gas. The first case is found when the crack is localized by microstructural elements and is most often seen in experiments with PMMA samples that have large-size microstructures[4]. Advance of the crack due to gas heating is rare in real systems since after formation of the crack profile, which, incidentally, can be hastened by heat, its further development must take place by the moving apart of the opposite walls of the crack, i.e., the crack should evolve according to the usual laws of mechanics[9]. In this case elementary estimates show that heating the gas to 6500° K is insufficient for the walls of the crack to have separated so far as is required by the conditions for the existence of an equilibrium crack with radius r = 50 μ.

From an examination of the condition for the existence of a threshold and a criterion of damage we can find a relation between the macrocharacteristics of the material and the threshold values of the pulse. The quantity of substance converted to gas by a threshold pulse is

$$\Delta m = \rho V = \rho 3.4\frac{K}{E}r_0^{5/2} = 0.6\rho\frac{K^5}{E\sigma_t^5}, \tag{6}$$

where ρ is the density and E is Young's modulus. Using the relation between Δm and the damage criterion, we find

$$\left(\frac{J_p'}{J_p''}\right)^2 = \frac{\rho_1}{\rho_2}\frac{K_1^6}{E_1\sigma_{t1}^5}\frac{E_2\sigma_{t2}^5}{K_2^6} \quad \text{for} \quad \lambda = 0.69\ \mu, \tag{7}$$

$$\left(\frac{J_p'}{J_p''}\right)^3 = \frac{\rho_1}{\rho_2}\frac{K_1^6}{E_1\sigma_{t1}^5}\frac{E_2\sigma_{t2}^5}{K_2^6} \quad \text{for} \quad \lambda = 1.06\ \mu, \tag{8}$$

Substituting the numerical values of K and E for PMMA and PS into Eq. (7), we obtain the value 3, and from experiment the ratio of the threshold values is 2.2. The agreement can be considered satisfactory. Thus, the observed damage criterion serves as a measure of the light resistance of a sample.

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