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An analysis is made of the laws governing the cumulative effect in laser damage to optical materials. A method for studying this effect, based on a statistical approach, is proposed and the main characteristics are introduced to describe laser damage to materials in the multiple-exposure regime. The possible mechanisms of the cumulative effect are discussed. Experimental data are given on laser damage to optical polymer materials and these data demonstrate some of the fundamental laws governing this effect. Using the example of transparent polymers, methods for suppressing the cumulative effect are proposed and put into practice.

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1. INTRODUCTION

It is well known that the strength of optical materials subjected to high-power laser radiation is often considerably lower for multiple interactions than for a single exposure. This fact was established quite a long time ago, although it was not investigated systematically until recently and it was mainly the laws governing laser damage to transparent media in the single-pulse regime which were studied. In view of the practical significance of the laser strength of optical materials in the multiple-exposure regime, it is exceedingly important to investigate the factors which reduce the optical strength.

The most probable among these is the accumulation of microscopic damage from pulse to pulse due to irreversible changes in the matrix surrounding the initiating absorbing defects.[1–4] The dynamics of such changes was studied in various classes of optical materials, by different methods: using the scattering kinetics of the incident radiation and the luminescence accompanying the damage process,[2–11] by the methods of electron[12] and infrared[13] spectroscopy, and by laser calorimetry.[14] Up to the present time, the cumulative effect has been investigated in silicate glasses,[2–4,12,15,16] alkali-halide[6,14] and ferroelectric crystals,[11,17] and in polymers,[5,7–10] it being most striking manifested in the last of these (for intensities below the single-pulse damage threshold by a factor of up to 100). Various mechanisms have been suggested in the literature for the cumulative effect (these will be analyzed below), although on the whole the nature of this effect has been given insufficient study and the dominant mechanisms have not yet been established.

In view of this we shall analyze the fundamental laws governing the cumulative effect, their relationship to the characteristics of laser damage due to a single interaction, and the possible mechanisms of this effect. We shall also report an experimental investigation of the cumulative effect in organic glasses, where it is most strikingly manifested compared with other optical materials.

2. FUNDAMENTAL LAWS GOVERNING THE CUMULATIVE EFFECT

The cumulative effect in optical materials is usually studied as follows. The laser damage threshold of the surface or volume of a specimen due to one pulse is determined. The incident radiation intensity is lowered by a certain factor relative to the threshold and the critical number of laser pulses N_{cr} is found which leads to the appearance of visible macroscopic damage. Experiments show[5] that a considerable spread (by more than a factor of 10) is observed in the values of N_{cr} from point to point in the specimen. This fact demonstrates the statistical nature of the cumulative effect and its description evidently requires the introduction of fundamental concepts and characteristics similar to those employed in statistical analysis of the laser damage by a single exposure. In our view the characteristics which adequately describe this effect are: the critical number of laser pulses $\overline{N}_{cr}(I)$ averaged over a large number of illuminated points, which (for a fixed intensity I) results in macroscopic damage in the specimen; the threshold intensity of laser damage by the Nth laser pulse I_N (Ref. 10) which causes damage in the specimen after a fixed number of pulses N and the probability of such damage $W_N(I)$ equal to the ratio of the number of damaged points in the specimen to the total number of points illuminated with fixed I and N; the damage threshold distribution function for the Nth pulse $f(I_N)$, determined by the ratio of the concentration Δn of defects, for which the threshold of damage by the Nth pulse lies in the interval $(I_N, I_N + \Delta I_N)$, to ΔI_N. The function $f(I_N)$ enables $W_N(I)$ to be calculated from the formula

$$W_N(I) = 1 - \exp\left[-\int dA \int_0^I f(I_N)\, dI_N\right], \qquad (1)$$

where A is illuminated volume or surface of the specimen.

In general, the function $f(I_N)$ depends on the parameters of the incident radiation (wavelength, pulse duration, etc.) and on the characteristics of a specimen (absorption coefficient, size of defects, thermoelastic properties of the surrounding matrix, etc.). In view of the statistical nature of the damage described by the distribution function $f(I_N)$, a dimensional distribution of the thresholds I_N should be observed, and this is confirmed by the results of experiments.[10] One may expect a single-valued correspondence between the dimensional dependence of I_N and the function $W_N(I)$ for damage due to multiple exposure, similar to that in the case of a single pulse. Moreover, in view of the identical nature of

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the processes leading to the damage by single and multiple exposure, a definite relationship can be expected between the damage characteristics in these two cases. This relationship can be described by the evolution of the damage-threshold distribution function for the first pulse $f_0(I_1)$, which is usually introduced when analyzing statistically the laser damage in the single-exposure regime, during successive laser pulses:

$$f_0(I_1) \to f_1(I_1) \to \ldots \to f_{N-2}(I_1) \to f_{N-1}(I_1) \equiv f(I_N)$$
$$\text{or } f_1(I_1) = \hat{A}_1 f_0(I_1), \ldots, f_{N-1}(I_1) = \hat{A}_{N-1} f_{N-2}(I_1)$$
$$\text{and } f_{N-1}(I_1) = \hat{A} f_0(I_1),$$

where $\hat{A} \equiv \hat{A}_{N-1}\hat{A}_{N-2}\ldots\hat{A}_2\hat{A}_1$ is an evolution operator whose form is determined by the specific mechanism of the cumulative effect in a particular material. Generally speaking, the operator $\hat{A}$ is nonlinear, depends on the parameters of the incident radiation (wavelength, pulse duration and shape, etc.) and can be found by solving the inverse problem, i.e., from the experimentally obtained dependences of the damage characteristics in the multiple-exposure regime on the radiation parameters and the characteristics of the specimens.

The evolution of the distribution function can, in principle, either lower the laser strength of a material for multiple exposure, compared with that for single exposure, or raise it (laser polishing or hardening). As a rule, lowering of the damage threshold is observed experimentally for multiple exposure ($I_N < I_1$), although there are reports in the literature[18] of the inverse effect ($I_N > I_1$).

3. POSSIBLE MECHANISMS FOR THE CUMULATIVE EFFECT

Irreversible changes in the matrix responsible for the cumulative effect can occur due to photochemical, thermochemical, and mechanochemical reactions, and to different types of phase transition. The first type of process can be initiated both directly by laser radiation (due to multiphoton absorption) and by emission from strongly heated absorbing defects. Thermochemical and mechanochemical reactions are most probably initiated in the neighborhood of absorbing defects due to the matrix being heated and to the resultant local thermoelastic stresses. Naturally, only those reaction products which absorb the incident laser energy, by a process which is direct (linear) or nonlinear in the laser intensity, can be responsible for the cumulative effect in multiple-exposure laser damage.

The irreversible-change mechanisms mentioned were used by different authors to explain experimental results. Thus, a model discussed in Ref. 19 suggests the accumulation of gaseous products in microcavities (of dimensions $\sim 10^{-4}$ cm) due to multiphoton photochemical reactions, leading to the dissociation of polymer molecules. In this model the macroscopic damage is attributed to the cleaving action of the gases. However, this model does not agree with the available experimental data[10] on laser damage to polymers. These indicate the absence of gaseous products in any appreciable quantities in microscopic damage events having dimensions of $\lesssim 10^{-3}$ cm.

The cumulative effect in silicate glasses was explained in Ref. 33 by assuming a mechanism for the thermal fluctuation decay of the interatomic bonds, stimulated by the laser radiation. However, in this model the microscopic mechanism whereby the electric field of an electromagnetic field acts directly on the interatomic bonds and lowers the activation energy for their rupture remains nuclear.

A mechanism was discussed in Refs. 20–22 for the buildup in polymer materials of strongly absorbing products (such as carbon black), formed around absorbing inclusions. Since the rate constants of the thermochemical reactions depend exponentially on the temperature T as $K_{TC} \propto \exp(-U_0/kT)$, where U_0 is the activation energy usually amounting to 2–3 eV, and only become appreciable at very high temperatures, such a mechanism for the cumulative effect can be observed only within an extremely narrow range of incident radiation intensities.[21] However, the experiments show that in many materials the cumulative effect is observed over a wide range of intensities (up to a factor of 100) below the single-exposure damage threshold. This means that a purely thermochemical mechanism cannot explain the cumulative effect in such materials.

We think that the most probable mechanism for the cumulative effect is associated with mechanochemical reactions[9,23,24] whose rate constants, $K_{MC} \propto \exp[-(U_0 - \gamma\sigma)/kT]$ are substantially higher than K_{TC} due to a lowering of the activation energy by the elastic stresses σ (γ is a structure-sensitive factor). These arise in the neighborhood of absorbing defects when they are heated by laser radiation. The mechanochemical reactions generate excited active particles (radicals, ion radicals, surface and solvated electrons, solitons, etc.) which absorb the laser energy and lead to the development of a chain reaction and to microscopic damage. As a result of such irreversible changes in the matrix, nonlinear absorption appears in successive laser pulses leading eventually to catastrophic damage.

An analysis of the mechanochemical mechanism of the cumulative effect[9,23,24] shows that it must differ strongly for different classes of optical material which are distinguished by their thermoelastic properties (tensile strength, Young's modulus, volume expansion coefficient, etc.) and mechanochemical reaction rate constants. In particular, one can expect substantial differences in the range of intensities ΔI, below the damage threshold of the first pulse, in which the cumulative effect is observed. Indeed, the experiments confirm this expectation. In inorganic glasses the cumulative effect takes place over a small range of ΔI (Refs. 2–4, 12, 13, 15, and 16), whereas in organic glasses (polymers), it is observed over a wide intensity range.[5,7–10,19,20,22] This special feature of polymer materials, distinguishing them from other transparent dielectrics, enables a study to be made of the fundamental laws governing the cumulative effect in this class of materials.

4. CUMULATIVE EFFECT IN TRANSPARENT POLYMERS

The cumulative effect in laser damage to polymer materials was discovered and studied by many investigators.[1,5,7–10,19–24] Here we shall give a number of new results

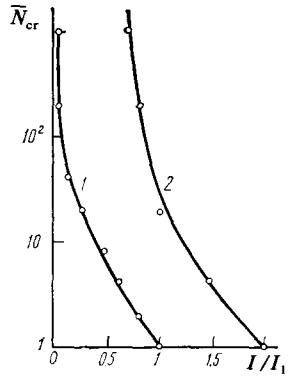

FIG. 1. Dependences of the average number of laser pulses $\bar{N}_{cr}$ after which damage occurs to PMMA (curve 1) and MPMMA (curve 2) on the intensity of incident $\lambda = 0.69\,\mu$ wavelength radiation. The PMMA damage threshold I_1 is taken to be 10 relative units.

which we obtained for polymethylmethacrylate (PMMA) and modified polymethylmethacrylate (MPMMA), used widely in conventional and laser optics, especially for making solid-state dye lasers,[25] bleaching filters,[26] and the optical components for laser ophthalmic instruments.[27]

A strong cumulative effect was observed over a wide intensity range in investigations on specially purefied specimens.[7] For MPMMA this intensity range was a factor of 3, and for PMMA a factor of 30 below the threshold for damage on the first laser pulse (Fig. 1). It can be seen from Fig. 1 that the dependence $\bar{N}_{cr}(I)$ is of an asymptotic nature: $\bar{N}_{cr} \to \infty$ as the intensity goes to $I \to I_{min}$, the values of I_{min} being $I_{min} \approx 0.03 I_1$ for PMMA and $I_{min} \approx 0.3 I_2$ for MPMMA.

We studied the dynamics of the cumulative process using the scattering of the incident laser radiation and the visible and near-ultraviolet luminescence which accompanies the occurrence of damage. Figure 2a shows the dependence of the light-scattering intensity ($\lambda = 0.69\,\mu$) on N for a fixed point in an MPMMA specimen and $I = 0.5 I_1$. It can clearly be seen that the scattering intensity increases monotonically from pulse to pulse up to $N = 20$, whereupon a sharp increase is observed in the scattering intensity and catastrophic damage occurs. There is a similar dependence on N of the luminescence intensity in the visible and near-ultraviolet regions (for $\lambda = 1.06\,\mu$ and a pulse duration $\tau_p = 20$ nsec) with an intensity of $I = 0.5 I_1$ for the same point on a PMMA specimen (Fig. 2b). It was noted in these experiments that the amplitude and temporal profile of the luminescence pulses experienced considerable fluctuations, providing evidence of the random nature of the damage process accompanying laser interaction.

The statistical laws governing laser damage to polymers were studied in terms of the dimensional dependences of the thresholds I_1 and I_{200} for $W_1 = W_{200} = 0.5$, and also the dependences of W_1 and W_{200} on the intensity of the incident radiation. Figure 3 shows these dependences for PMMA acted upon by $\lambda = 1.06\,\mu$ laser pulses. It can be seen that I_1 has a considerably stronger dependence on the diameter d_c of the caustic of the focusing lenses than does I_{200} (Fig. 3a). This characteristic of the dimensional dependences of I_1 and I_{200} correlates with the intensity dependences of the damage probabilities W_1 and W_{200} (Fig. 3b). Indeed, a stronger dependence $I_1(d_c)$ corresponds to a flatter dependence $W_1(I)$ and vice versa. These qualitative laws were confirmed by a detailed analysis of the experimental data obtained on the basis of the statistical laser damage model described by formula (1). In particular, it follows from this analysis that the initial distribution function of the defects initiating damage, $f_0(I_1)$, is transformed in subsequent laser pulses into the functions $f_{N-1}(I_1)$ which have a narrower distribution than $f_0(I_1)$ and are displaced toward lower values of I_1. A determination of the specific form of these functions on the basis of the experimental data enables one to explain the form of the evolution operator $\hat{A}$ which, as shown in Sec. 2, is the fundamental characteristic of the cumulative effect.

In addition to the statistical laws of the cumulative effect described above, we also studied the dependences of the damage threshold I_N on the laser radiation parameters (pulse duration τ_p and wavelength λ) and on the physicomechanical properties of the specimens (temperature, viscoelastic parameters of the matrix, low-molecular impurity content). These investigations showed the existence of the relationship $I_N \tau_p = B\lambda$ (where B is a constant) in the range $\tau_p = 3$–50 nsec and $\lambda = 1.06$–$0.337\,\mu$. Raising the temperature of the PMMA and MPMMA specimens to the glass-transition temperature and introducing plasticizers into the polymers led to a considerable rise (by more than a factor of 10) in their laser strength in the multiple-exposure regime, whereas both of these factors have a relatively weak influence on the single-exposure damage threshold.[5,9,10] The increase in the laser strength was strongly dependent on the type of plasticizer[10] and its molar concentration. These results indicated the suppression of the mechanochemical reactions in the polymer matrix under the action of laser radi-

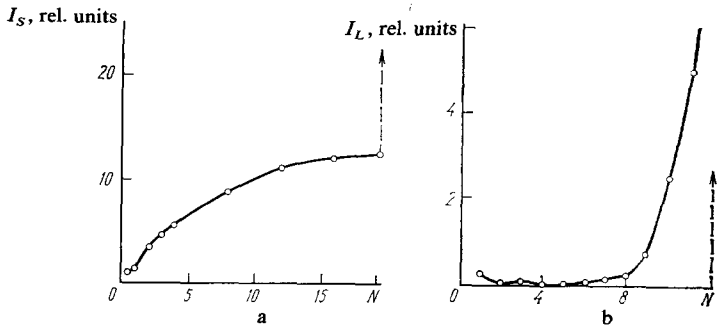

FIG. 2. Dependences of the scattered ruby laser radiation (a) and of the amplitude of luminescence accompanying the development of laser damage (b) on the number of pulses N for damage to develop in MPMMA (a) and for the interaction of $\lambda = 1.06\,\mu$ radiation with PMMA (b).

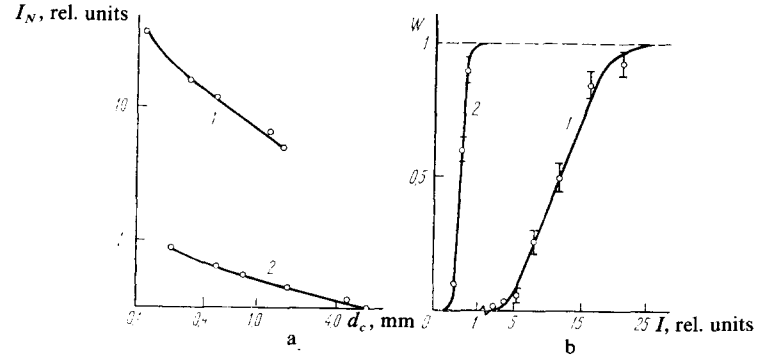

FIG. 3. Dimensional dependences of the thresholds for damage on the first and 200th laser pulses (a) and dependences of the probabilities for damage to occur in the single- (curve 1) and multiple-exposure (curve 2) regimes (b) (beam diameter $d_c = 0.5$ mm) for the interaction of $\lambda = 1.06\,\mu$ radiation with PMMA.

ation owing to quenching of excited active particles arising in the neighborhood of absorbing defects on account of thermoelastic stresses.[9,23,24] One can also expect a similar suppression of the cumulative effect in other optical materials by modifying them structurally and so changing their thermoelastic properties and reducing the rate constants of the mechanochemical reactions.

5. CONCLUSIONS

The method developed for studying the cumulative effect in laser damage is based on a statistical approach, and the basic characteristics introduced to describe damage accompanying multiple exposure enable the laws governing this effect to be investigated in a purposeful manner.

The experimentally established laws governing multiple-exposure damage to polymers, namely a weakening of the dependence of I_N on the dimensions of the illuminated zone compared with the dimensional dependence of I_1 and a narrowing of the dependence of W_N on I compared with the dependence $W_1(I)$, provide evidence of the statistical nature of the cumulative effect. Among the mechanisms for the cumulative effect which were analyzed, the most probable one is that involving the formation of irreversible changes in the material due to mechanochemical reactions.

The investigations performed on laser damage to polymers in the multiple-exposure regime enabled effective methods to be found for suppressing the cumulative effect in these materials (for example, by a carefully planned change in the molecular mass distribution of the macromolecules, or by introducing low-molecular additives to quench the excited active particles and prevent the development of mechanochemical chain reactions). It can be expected that similar methods would be effective for suppressing the cumulative effect in laser damage to other optical materials.

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