# MECHANISM OF FORMATION OF A HIGH-TEMPERATURE ZONE IN THE CASE OF LASER-INDUCED MECHANICAL BREAKDOWN OF TRANSPARENT POLYMERS

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The mechanical breakdown of transparent polymers that have absorbed millisecond laser radiation on inclusions present in the working material is considered. It is shown that the distribution by dimension of absorbing particles in the polymer obeys a cubic law corresponding to the aerosol distribution in the atmosphere. The process by which an inclusion is heated by laser radiation and by which a gas cavity forms around it due to pyrolysis around the material is studied. A mechanism is proposed for light absorption based on carbon black formation from gas-phase hydrocarbons both in the breakdown zone and in the growing macrocrack. The use of macrokinetic parameters of high-temperature pyrolysis for describing laser-induced mechanical breakdown yields satisfactory agreement between the experimental and calculated data.

## INTRODUCTION

The zonal nature of laser-induced mechanical breakdown of transparent dielectrics is due to local light absorption associated with the presence of absorption centers in the raw materials [1-3]. Foreign particles contained in the material may constitute such centers. In particular it has been noted [4] that the presence of such inclusions as carbon black and metallic particles in transparent polymers is associated with the entrapment of atmospheric aerosols in the material in the course of industrial processes. The typical dimensions of the aerosol are about $10^{-5}$-$10^{-3}$ cm [5].

A model has been proposed [6] for the mechanical breakdown process of such transparent polymers as polymethyl methacrylate (PMMA) and polystryrene (PS) due to laser radiation in the visible and near-infrared ranges. This model described mechanical breakdown macrokinetics and takes into account the rupture time of the loaded material. The resulting dependence of the time at which mechanical breakdown begins, i.e., the formation of a macrocrack, on light flux q reasonably corresponds to the experimental dependence. It has been shown [2,7, 8] that the brittle failure process precedes the stage at which the gas cavity filled with polymer decomposition products forms about an absorption inclusion. The experimentally measured cavity temperature is on the order of $2$-$3 \cdot 10^3$°K [9]; its rate of growth according to previous [2] data and averaged over the period of the effect of the threshold flux amounts to $\approx 1$ cm/sec, while the characteristic cavity dimensions are about $10^{-3}$-$10^{-2}$ cm [8].

The high temperature and growth rate of the cavity indicated intensive pyrolysis of the material accompanied by heavy cracking of the decomposition products, since these products did not drain from the thermal effect zone. This is confirmed, for example, by the predominant hydrogen content in the gas fraction of the decomposition products, whose composition is determined by laser irradiation of PMMA powder [10].

The current work is devoted to a study of the process by which a gas cavity forms in a polymer as well as to an investigation of the light absorption mechanism in a high-temperature breakdown zone and of the growing crack.

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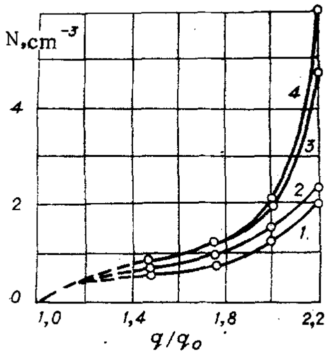

Fig. 1

## 1. Investigation of the Absorption of Laser Radiation on Initial Inclusions

The zonal nature of laser-induced breakdown of polymers implies that the formation of a crack is associated with the presence of an initial absorption center at the given spot. The concentration of given particles on which a crack forms as a given light flux acts on the polymer can be estimated from the final breakdown result by identifying a crack and an inclusion in this way.

For this purpose the dependence of the concentration of inclusions (cracks) on q was experimentally determined. Experiments were carried out on specimens made of PMMA irradiated by freely generated pulses.

The laser ray measured 2.5 cm in diameter and the volume V irradiated was varied by varying the thickness h of the specimens, i.e., these two parameters were made proportional in the experiments ($V \sim h$)

Figure 1 depicts dependences of inclusion concentration N on light flux q [sample thickness h as follows: 4) $h=0.5$; 3) $h=1$; 2) $h=5$; 1) $h=10$ cm$^2$].

A weak variation of N(q) at fluxes slightly exceeding the threshold value* $q_0$ and its sharp increase with increasing q is the most characteristic property of these dependences. This course of N(q) can be qualitatively explained by the fact that breakdowns form on the finest inclusions with increasing light flux, and this determines a substantial increase in concentration, since the number of fine centers is greater than the number of large centers. The value of N increases with decreasing sample thickness or decreasing irradiated volume for given q. This is due to the fact that the relative screening of the cracks in the case of a short optical path of the light beam in the material (thin specimens) is insignificantly small in comparison with specimens possessing a greater length.

To eliminate the influence of screening the curves were extrapolated to low V for fixed q and the dependence $N/N_0(q/q_0)$, characterizing the concentration of inclusions on which cracks form at given fluxes, was constructed. Here $N_0 \approx 0.04$ cm$^{-3}$ was the experimentally determined concentration of the "largest" centers.

The resulting dependence is depicted in Fig. 2 and is described by an exponential function of the form $N/N_0 \sim (q/q_0)^{\alpha}$, while when $q/q_0 \lessdot 2$, $\alpha \approx 3$. An increase in the ratio $q/q_0$ leads to a sharper increase in $N/N_0$.

In order to simplify the analysis of our data we will assume that the most characteristic absorption inclusions, including metallic and carbon black particles, are spherical and that their distribution in the polymer by dimension roughly corresponds to the aerosol distribution in the surrounding air.

Absorption of light by such a particle will heat it, its maximal temperature approaching a stationary value. A stationary temperature is established within time $t_c > r_0^2/3a$, where $r_0$ is particle radius and $a$ is the thermal-conductivity coefficient of the polymer. This coefficient can be estimated as a function of light flux using the equation [11]

$$T = \frac{\sigma_0 q}{4\pi r_0 K}, \tag{1.1}$$

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*The breakdown threshold is understood as the statistically reproducible minimal mean-pulse light flux $q_0$ inducing the formation of a single characteristic crack in the polymer.

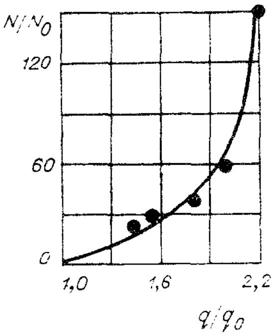

Fig. 2

where $\sigma_0$ is the absorption cross section of light by the particles and K is the thermal-conductivity coefficient of the polymer. The cross section $\sigma_0$ depends on the relation between radiation wavelength $\lambda$ and particle radius [12]:

$$\sigma_0 \approx \begin{cases} \frac{8\pi^2}{\lambda} \operatorname{Im} \frac{1-m^2}{m^2+2} r_0^3 \text{ when } \frac{2\pi r_0}{\lambda} < 1, & (1.2) \\ (1-R_0)\,\pi r_0^2 \text{ when } \frac{2\pi r_0}{\lambda} > 1. & (1.3) \end{cases}$$

The variables m and $\lambda$ in Eqs. (1.2) and (1.3) are the complex index of refraction of the particle substance and the radiation wavelength in the medium, and $R_0$ is the mean reflection coefficient of the particle substance.

Equation (1.3) is valid beginning with $r_0 > 10^{-5}$ cm, i.e., for most typical inclusions. For absorption particles, the value of $\sigma_0$ corresponding to large inclusions is always greater than the value of $\sigma_0$ determined by Eq. (1.2) for fine centers.

Equations (1.2), (1.3), and (1.1) imply that temperature reaches a maximum on large particles at lesser light fluxes, so that a crack forms on the largest inclusions in the polymer under the influence of a threshold flux $q = q_0$.

Since the evaporation temperature of these types of inclusions $T_0$ is about 3-4 $10^{3}$°K, we may use Eqs. (1.1) and (1.3) to estimate the dimensions of the largest particles on which a threshold crack develops.

We obtain $r_0 \approx 10^{-3}$ cm by substituting the value $q_0 \approx 2 \cdot 10^4$ W/cm$^2$ for PMMA and taking into account the fact that $(1-R_0) \approx 1$ for absorbing particles. The time within which temperature becomes stationary on this particle $t_s > 0.3 \cdot 10^{-3}$ sec, i.e., T attains its maximal value $T_0$ at the end of the light pulse, which agrees with the time at which a breakdown forms in the case of threshold fluxes.

Equations (1.1) and (1.3) imply that the light flux q required for heating large inclusions to the evaporation temperature is about $1/r_0$. Then, using the experimental cubic dependence of the concentration of such inclusions on light flux, we obtain

$$N \sim \left(\frac{1}{r_0}\right)^3. \qquad (1.4)$$

Equation (1.4) characterizes the distribution of large absorption centers by dimension in the polymer.

The large-scale branch of the distribution of atmospheric aerosol is described, according to previous [5] data, by an exponential function of the form $N \sim (1/r_0)\,\beta$, where $\beta \approx 2\text{-}5$; $\beta = 3$ for particles with $r_0 > 4 \cdot 10^{-4}$ cm, which coincides with Eq. (1.4).

Thus, the resulting correspondence between aerosol distribution and distribution of inclusions clarifies the experimental results and confirms the hypothesis regarding the way in which absorption centers appear in polymers from an atmospere.

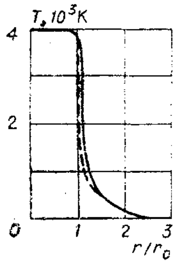

Fig. 3

## 2. High-Temperature Laser-Induced Pyrolysis of Polymers

The absorption of radiation by particles leads to overheating of the surrounding polymer. A solution of the heat-conductivity equation in spherical coordinates yields a temperature distribution in the medium with respect to radius in the form [13]

$$T = \frac{3(1-R_0)qr_0^2}{2C_0\rho_0(r_0+r)ab}\left\{(g-b)^{-1}\Phi^*\left(\frac{r}{2\sqrt{at}}\right)-(g-b)^{-1}\right.$$
$$\times\exp\left[\frac{(g-b)r}{2r_0}-\frac{(g-b)^2at}{4r_0^2}\right]\Phi^*\left[\frac{r}{2\sqrt{at}}+\frac{(g-b)\sqrt{at}}{2r_0}\right]-(g+b)^{-1}\Phi^*$$
$$\left.\times\left(\frac{2}{2\sqrt{at}}\right)+(g+b)^{-1}\exp\left[\frac{(g+b)r}{2r_0}+\frac{(g+b)^2at}{4r_0^2}\right]\Phi^*\left[\frac{r}{2\sqrt{at}}+\frac{(g-b)\sqrt{at}}{2r_0}\right]\right\}, \quad (2.1)$$

where $\Phi^*(y)=\frac{2}{\sqrt{\pi}}\int_0^\infty e^{-y^2}dy$ is an error function.

A calculation was carried out for a carbon black inclusion with typical dimension $r_0=10^{-4}$ cm in PMMA with the following values of the thermophysical parameters occurring in Eq. (2.1); $C_0=0.72$ J/g · °C, particle heat capacity; $\rho_0\approx 2$ g/cm², particle density; C = 1.5 J/g · °C, medium heat capacity; $b=\sqrt{g(g-4)}$, $g=3C/C_0$. A given carbon black particle attains its evaporation temperature, according to Eq. (3.1), for a flux $q=2\cdot 10^6$ W/cm² within time $t\approx 10^{-6}$ sec. The characteristic time for the heat to level off in an inclusion is about $r_0^2/a_0$, where $a_0=1.6$ cm²/sec is the thermal-conductivity coefficient of the particle and is much less than the time for heating to $T_0$. The temperature distribution on an inclusion and in the polymer is depicted in this case by Fig. 3. The ambient temperature reaches 500°K at some distance from the particle, which corresponds to the start of evaporation of the polymer. A gaseous monomer forms about an absorption center, since evaporation of PMMA and PS occurs as a depolymerization reaction until temperatures of about 1000°K [14].

It should be noted that the solution (2.1) is approximate in this case, since it does not take into account phase transition in the medium. However, the latent evaporation heat for PMMA is low ($Q\approx 540$ J/g) and the variation of the phase state (particularly at high temperatures) does not substantially change the nature of the temperature distribution. The broken curve in Fig. 3 corresponds to the approximate temperature distribution, taking into account formation of the gas phase at the front of the thermal wave.

Layers of gas bounding an inclusion were heated to temperatures near the particle temperature. This led to decomposition of the monomer on finer hydrocarbon compounds. For example, cracking of PMMA occurs with the formation of methane, unsaturated hydrocarbons, carbon monoxide, and carbon dioxide; such larger aromatic compounds as benzene and toluene are characteristically found in the gases in the case of PS [14]. We may approximately estimate the time within which the temperature in a cavity of characteristic dimension $r\approx 10^{-3}$ cm levels off by using experimental data on the composition of the decomposition products of laser-irradiatd PMMA [10]. A calculation of the predominance of hydrogen in the gas mixture demonstrates that this time is about $r^2/a^*$, where $a^*\approx 0.6$ cm²/sec is the thermal-conductivity coefficient of the mixture, amounting to about $2\cdot 10^{-6}$ sec.

Consequently, the temperature in the cavity levels off and reaches about $2\text{-}3\cdot 10^3$°K within the period during which several radiation beams act; this value agrees with the experimentally measured value [9]. High-temperature pyrolysis of PMMA and PS is characterized by immediate decomposition of the side branches of the polymer molecule, which are then cracked to acetylene, forming larger hydrocarbon frac-

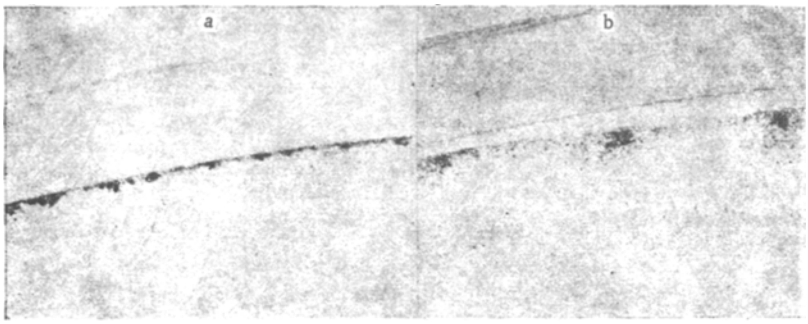

Fig. 4

tions as a result of a series of dehydrogenization reactions [14, 15]. This decomposition process, according to some data [16], occurs with activation energy of 70-80 kcal/mole, i.e., close to the value corresponding to rupture of the C—C bonds ($E_0 = 83$ kcal/mole).

Intensive carbon black formation from gas-phase hydrocarbons begins at a cavity temperature of 2000-3000°K. The amount of carbon black obtained in the course of the decomposition of simple and aromatic hydrocarbons increases in the latter case by a factor of six to seven [17]. This circumstance explains the experimentally observed significantly greater carbon black formation from laser-induced breakdown of PS in comparison with PMMA.

As we already noted, PMMA cracking leads to the formation of gaseous acetylene as a by-product. High-temperature acetylene decay (according to some data [17]) into carbon and hydrogen is accompanied by the formation of spherical carbon black particles with mean radius $\approx 5 \cdot 10^{-6}$ cm. The production of a carbon black particle is characterized by high activation energy and rate of the process: $E_a \approx 150$ kcal/mole and $u \approx 2 \cdot 10^{18}$ sec$^{-1} \cdot$ cm$^{-3}$, respectively. Enlargement of particles due to carbon enrichment as they collide with the gas molecules is accompanied by a rather low activation energy in comparison with $E_a$. That is, every collision event leads to a hydrocarbon decay reaction.

The concentration of carbon black particles sharply grows, and the radiant energy incident on the breakdown zone is completely absorbed within the cavity.

In fact, the energy absorbed by a single particle within time t is given by $q\sigma_0 t$. Since $4/3\pi r^3 ut$ particles form within this time, where $r = 10^{-3}$ cm is the characteristic cavity radius, the total energy absorbed in the breakdown zone is determined by $E = 4/3\pi r^3 ut^2 \sigma_0 q$. We may approximately assume that the light is totally absorbed within the cavity when the energy incident on the zone $\pi r^2 qt \approx E$ or when

$$\frac{4}{3}\pi\sigma_0 rut \approx 1. \qquad (2.2)$$

The absorption cross section $\sigma_0$ for a carbon black particle of radius $5 \cdot 10^{-6}$ cm is $\approx 2.7 \cdot 10^{-11}$ cm$^2$ as calculated using Eq. (1.2), letting $m = 2.5 - i$ [18]. Substitution of the corresponding values in Eq. (2.2) demonstrates that total absorption radiation on carbon black particles will occur within the cavity in $t \approx 5 \cdot 10^{-5}$ sec.

Thus, carbon black formation determines the mechanism by which laser radiation is absorbed in a breakdown zone, since the other polymer decomposition products are transparent within this range of wavelengths. A carbon black particle of characteristic dimension $5 \cdot 10^{-6}$ cm at a temperature of at least $2\text{-}3 \cdot 10^3$°K will be heated by radiation to the evaporation temperature with fluxes $q \geqslant 4 \cdot 10^6$ W/cm$^2$. The hydrocarbon vapor thus formed can serve as a source for nuclei of new carbon black particles. The growth of a nucleus is accompanied by an increase in laser radiation absorption and is limited by heating to the evaporation temperature. Consequently, a dynamic production, consolidation, and evaporation process of the carbon black particles occurs in the cavity. We may assume that all the energy absorbed by a particle is transmitted to the cavity walls and determines the pyrolysis rate for a mean heat rate of about $2 \cdot 10^6$ cm/sec.

Whenever the motion of the decomposition front in the polymer is determined by the thermal conductivity of the medium, we may use an equation obtained by solving the stationary thermal-conductivity problem from a moving boundary on which a chemical reaction occurs, in order to calculate the pyrolysis rate of PMMA [19]:

$$v = \left[ \frac{ak_0RT^2 e^{-\frac{E}{RT}}}{E\,(T + Q/2c)} \right]^{1/2}, \qquad (2.3)$$

where $k_0 \approx 10^{24}$ sec$^{-1}$ is the reaction rate constant corresponding to high-temperature pyrolysis [6, 16], R is the universal gas constant, $T = 2.5 \cdot 10^{3}$°K is the mean experimental cavity temperature, and $E = E_0 + E_a = 233$ kcal/mole is the total activation energy.

The pyrolysis rate $v \approx 0.4$ cm/sec, calculated using Eq. (2.3), also agrees in order of magnitude with the mean experimental cavity growth rate with a threshold light flux. This result indicates that the macrokinetics of laser-induced decomposition is (basically) determined by two successive reactions: decay of the polymer molecule into hydrocarbon compounds as a result of the breaking of the C−C bonds, and the formation from the gas phase of carbon black particles ensuring absorption of light energy in the cavity.

The pyrolysis rate increases at greater light fluxes and is determined by the equation $v \approx q/4\rho(cT + Q)$ in passing to stationary evaporation, without taking into account heat dissipation. A calculation using this equation within the range $q \sim 10^{6}$–$10^{7}$ W/cm$^2$ gave good agreement with experimental data [6]. Such a laser radiation absorption mechanism was realized throughout the entire mechanical breakdown process, i.e., at the stage of development not only of the high-temperature zone, but of the crack itself.

The moment at which the material is wedged is determined by the pressure of the decomposition products in the gas cavity. An increase in volume at the initial stage of formation of the crack leads to a drop of the pressure and of the motion of the gas and carbon black molecules toward its boundaries. Carbon black particles whose concentration is rather high ($\sim 10^{15}$ cm$^{-3}$) even at threshold fluxes (when colliding with the "cold" surface of the crack) induced decomposition of the surrounding polymer. This leads to the formation of new gas zones and a corresponding growth in pressure within the closed volume.

A subsequent increase in crack dimensions also occurs as a result of the pressure and is discontinuous. Each discontinuity may be correlated to a Walner plane corresponding to the position of the crack boundary in front of the discontinuity. The Walner bands lead to a characteristic wavy structure of the crack surface.

Scattering and stopping of carbon black particles at the crack boundaries will lead to their buildup on protrusions concentrically situated on the surface.

Such a distribution of carbon black on the walls is observed microscopically, as depicted in Figs. 4a and b (buildup of carbon black particles on the Walner band on the crack and buildup of carbon black particles at the crack boundary, respectively). The most intensive absorption of radiation and, consequently, decomposition of the polymer will occur along these annular zones. Separate craters measuring 1-50 μ observed on the crack surface under sufficient magnification indicate that polymer pyrolysis occurs at points at which carbon black particles collide with the crack walls.

In conclusion, the authors wish to express their appreciation to Yu. G. Ivanov for assistance in the experiments.

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# ELECTRIC STRENGTH OF SCATTERED DETONATION GASES

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## INTRODUCTION

One of the most important characteristics in schemes used for the formation of high-power pulses of a given shape by means of condensed explosives [1] is the current density that can be attained in the detonation wave. Whenever the electrical conductivity is determined directly by the detonation process, the maximal current density depends on the maximal electric field strength at which breakdown of the detonation gases no longer occurs, i.e., on their electric strength. This magnitude also determines the characteristics of safety detonators operating at high inverse voltages [2]. Prediction of the parameters of detonators maintained at a high voltage requires knowledge of the electric strength of the detonation gases as a function of pressure. This is because the gaps formed as current is switched off are found under conditions characterized by nonstationarily expanding explosion gases, as a result of which their electric strength is time-dependent as a function of pressure. The required parameters of safety detonators can be obtained from a joint solution of the gasdynamic scatter problems for detonation gases and the motion of current-carrying elements and of electric circuit equations if the dependence of electric strength on pressure is known. In the current work, fundamental results are set forth from an experimental study of the electric strength of expanding detonation gases from bulk density PETN and Hexogen charges.

The scheme of a safety detonator with a gap in which the electric strength of detonation gases was studied is depicted in Fig. 1. The safety detonator consists of cylindrical steel electrodes 1 measuring 42 mm in diameter, lateral surface insulators of the electrodes 2, a plastic plug-type fuse 3 with exploding bridgewire 4, a resistance ring made of Plexiglas 5, and a bulk density explosive 6. The Plexiglas resistance range eliminates

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