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Optical transmittance of carbon suspensions in polymer matrixes under powerful pulsed laser irradiation

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Abstract. The effect of optical limiting is investigated in the suspensions of carbon microparticles in aqueous gelatin gel and epoxy resin. Both transient and permanent changes of optical transmittance are observed after the irradiation by a Q-switched YAG:Nd^{3+} laser pulses. The experimental results are explained with taking into account the formation of micro-bubbles filled with water steam and with gaseous products of decomposition of the matrix. In the epoxy resin suspensions, the laser-induced permanent changes of transmittance are caused by pyrolysis of epoxy oligomers in the vicinity of laser-heated carbon particles.

Keywords: carbon suspension, laser heating, optical limiting, polymer matrix.

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1. Introduction

For the last two decades, the interaction of carbon microparticles with high-power pulsed laser radiation has attracted great interest (see, for example, [1-4]). The majority of the publications are devoted to research of carbon suspensions (primarily aqueous) and of soot microparticles in air, which are formed as a result of combustion of organic fuel. The laser-induced behavior of light-absorbing microparticles in solid and high-viscosity matrixes is investigated insufficiently.

The main physical effect of the laser radiation on light-absorbing microparticles in air and in condensed matrixes [5] is their warming up to temperatures of approximately 4000 K. Thermal radiation of laser-heated microparticles is easily observed and is referred to as laser-induced incandescence (LII).

Optical properties of aqueous carbon black suspensions (CBS) under powerful laser excitation are investigated in [6-14]. In CBS, high-intensity nanosecond laser pulses produce not only LII, but also the effect of optical limiting. The basic mechanism of optical limiting in CBS is the self-induced scattering of the laser beam by the micro-bubbles formed around the laser-heated carbon particles. The basic application of the optical limiting effect in CBS is protection of optical devices against casual excess of laser power.

Among other effects that accompany optical limiting and LII in CBS, it is necessary to note the evaporation processes in the microparticle material (carbon). The intense vaporization of carbon is the main factor that limits the particle temperature at a level of approximately 4000 K. Besides, it leads to the reduction of particle size with the increase of laser irradiation dose [14, 15].

In this paper, we present the results of studying the optical transmittance of carbon suspensions in polymer matrixes under powerful pulsed laser irradiation. High viscosity of the matrix essentially reduces the influence of convective streams on the investigated phenomena and allows studying the properties of suspensions depending on the dose of the laser irradiation. Besides, for laser irradiation of non-stirred matrixes, the stable local changes of optical properties are expected. At last, the investigation of laser-induced effects in carbon-doped high-viscosity matrixes can create a bridge for gradual transition from liquids to solids activated by light-absorbing microparticles, which are poorly investigated.

2. Experimental details

In this work, to prepare the suspensions the method of laser ablation [16] was employed. A piece of carbon was submerged into distilled water or epoxy resin and irradiated by a sequence of laser pulses. We used a carbon electrode for spectral analysis as a target and a Q-switched YAG:Nd^{3+} laser (wavelength 1.064 µm, pulse duration about 25 ns) with a 210 mm focusing lens. As a result, carbon suspensions with the average particle diameter of about 130 nm and with approximate particles concentration $8\cdot10^9$ cm^{-3} were obtained. The size of particles in suspensions was controlled by nephelometric measurements using a He-Ne laser (wavelength 0.6328 µm). The average size of the particles was estimated with the Mie scattering theory.

The investigated optical transmittance of the suspensions was measured with the YAG:Nd^{3+} laser (1.064 µm, 25 ns) at two fixed levels of laser intensity: 1.5 and 100 MW/cm^2. The minor laser intensity 1.5 MW/cm^2 does not provide any observable effect on the suspension. The dependence of sample transmittance on the laser irradiation is observed at the intensities above 10-20 MW/cm^2. The major intensity provides clearly visible LII and laser-induced changes in the optical transmittance. The transmittance measured at 1.5 MW/cm^2 hereinafter is referred to as the low-signal transmittance, T_0. The concentration of the investigated suspensions was adjusted for $T_0 \approx 0.6$.

Laser irradiation was performed at 100 MW/cm^2 by a sequence of pulses with the repetition rate of 0.5 to 2 pulses per second. In this paper, the number of laser pulses, *N*, is referred to as the laser irradiation dose.

Relaxation of laser-induced changes in the optical transmittance was investigated by a pump-probe technique. The pumping laser beam (YAG:Nd^{3+} laser, 1.064 µm, 25 ns, 100 MW/cm^2) and the probing laser beam (He-Ne c.w. laser, 0.6328 µm) were crossed in the cell with the suspension investigated. The approximately opposite layout of laser beams was used. A PMT with an analog-digital converter detected the oscillogram of the intensity of probe laser beam transmitted through the cell.

All the measurements were performed at room temperature by using a computer-controlled laser spectrometer.

3. Results and discussion

The transmittance of carbon suspension in gelatin gel at the wavelength 1.064 µm as a function of the laser pulse number, *N*, is presented in Fig. 1. The data were collected at 100 MW/cm^2. The low-signal transmittance measured before laser irradiation is presented as a horizontal solid line in the plot. As seen from Fig. 1, an abrupt decrease of optical transmittance is observed at $N = 1$. It demonstrates the effect of optical limiting in the gelatin gel suspension of carbon microparticles. Further increase of the laser irradiation dose causes gradual increase of the transmittance up to the level exceeding the initial low-signal one. At high doses, the suspension is bleached and the transmittance tends to a limit.

It should be noted that similar effects of optical limiting and bleaching were observed earlier in aqueous CBS [14, 17]. The experimental data presented in Fig. 1 for the gelatin gel suspension can be interpreted using the model proposed in [14,15] for CBS. The effect of optical limiting in both CBS and gelatin gel suspension can be interpreted as laser-induced scattering caused by the formation of bubbles near the laser-heated carbon microparticles. The effect of bleaching of the suspension at high irradiation doses is a consequence of gradual decrease in the particle size due to the vaporization of carbon at temperatures 4000 K and higher.

Thus, the effect of burning out of carbon particles in gelatin gel suspensions makes such suspensions unsuitable for use as optical limiters. Though in aqueous suspensions the effect of burning out the particles is also observed, it can be avoided by pumping the suspension.

The transmittance of carbon suspension in epoxy resin at the wavelength 1.064 µm and the power density 100 MW/cm^2 as a function of the laser pulse number, *N*, is presented in Fig. 2. Here solid and dashed horizontal lines present the low-signal transmittance measured before and after the laser irradiation respectively. As seen from Fig. 2, powerful laser radiation causes significant decrease in the optical transmittance of the epoxy suspension. Unlike gelatin suspensions, epoxy suspensions do not demonstrate bleaching with the increase of laser irradiation dose. The low-signal transmittance of the irradiated epoxy resin suspension (dashed line in Fig. 2) is approximately 25 % decreased as compared with T_0 before irradiation (horizontal solid line in Fig. 2).

The above-considered model of optical limiting in aqueous suspensions does not explain the behavior of optical transmittance of epoxy resin carbon suspension. To interpret the data given in Fig. 2, the following considerations can be applied.

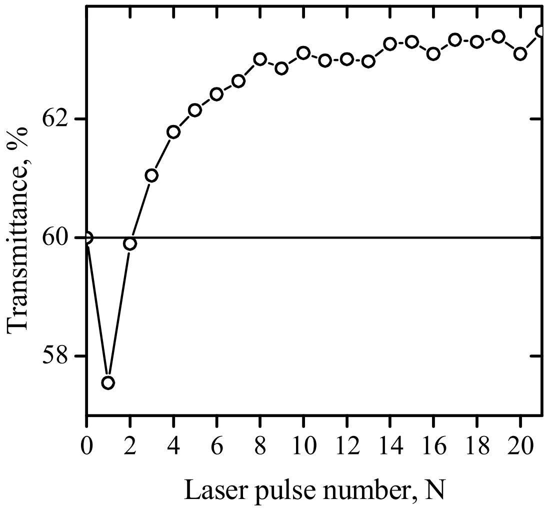

Fig. 1. Optical transmittance of a gelatin gel carbon suspension at 1.064 µm as a function of the laser irradiation dose, *N*. Solid horizontal line presents the low-signal transmittance measured before the laser irradiation.

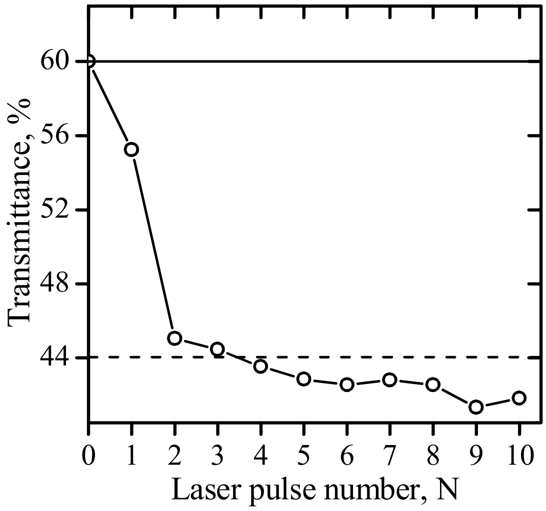

Fig. 2. Optical transmittance of an epoxy resin carbon suspension at 1.064 μm as a function of the laser irradiation dose, *N*. Solid and dashed horizontal lines present the low-signal transmittance measured before and after the laser irradiation, respectively.

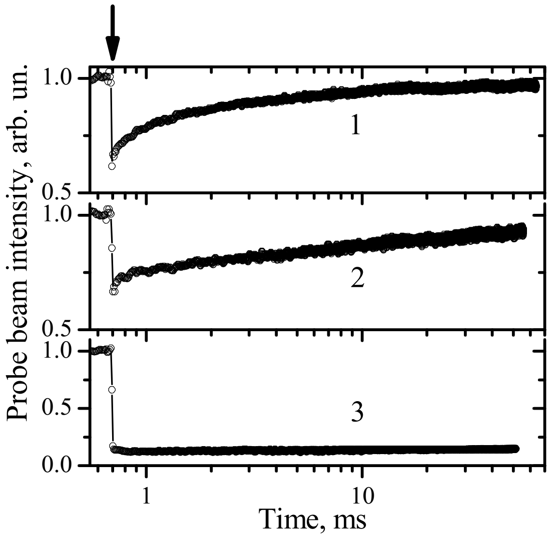

Fig. 3. Oscillograms of the probe laser beam intensity for carbon suspensions in water (*1*), aqueous gelatin gel (*2*) and epoxy resin (*3*).

While in aqueous suspensions the high local temperatures in the vicinity of microparticles cause evaporation of water, in the synthetic resins the main mechanism is the pyrolysis (thermal decomposition) of oligomers around the overheated carbon particle. As known, the products of pyrolysis of epoxy resin are gases (CO_2, CO, H_2, CH_4, etc.) and nonvolatile carbonized products [18, 19]. The carbonized products consist mainly of carbon, and under certain conditions they can form porous structures. The composition and physical properties of the pyrolysis products depend on many factors, including the time and speed of heating as well as the maximal temperature. For laser heating the carbon microparticles suspended in epoxy resin, it is plausible to suggest that the gaseous products of pyrolysis form gas bubbles and the condensed products of pyrolysis form carbonized shells around the particles. Thus, in the irradiated suspension the carbon microparticles are transformed into the complex centers that absorb and scatter laser radiation. As a simplified model, we can imagine such a center as a carbon kernel surrounded with a light-absorbing porous carbonized shell, together with a gas bubble.

According to the proposed model, the effective size of the absorption and scattering centers increases with the laser irradiation dose as the bubbles and carbonized shells grow step by step. As a result, the absorption and scattering cross-sections increase with *N*, and the transmission decreases (see Fig. 2). Besides, the increase of the center's size leads to the increase of its mass and heat capacity, hence the maximal temperature of laser-heated centers decreases with *N*. This circumstance reduces the efficiency of laser-induced pyrolysis, therefore the abrupt drop of optical transmittance transforms into the slow decrease with *N* (see Fig. 2).

As an additional confirmation of the validity of the proposed model, the following results of measurements of the optical transmittance by the pump-probe technique can be considered. Fig. 3 presents the oscillograms of intensity of probe laser beam (wavelength 0.6328 μm) transmitted through the cells with carbon suspensions in various matrixes after irradiation by a single powerful laser pulse (1.064 μm, 25 ns, 100 MW/cm^2). In Fig. 3, the position of the irradiation laser pulse is marked with an arrow. In these experiments, the intensity of probe laser beam is proportional to the optical transmittance of the investigated cell. In Fig. 3, the probe beam intensity before irradiation is set to 1.

As seen from Fig. 3, the high-power laser pulse causes significant abrupt drop of the transmittance in carbon suspensions of all the investigated matrixes. After the laser pulse, the kinetics of relaxation of the transmittance differs significantly in aqueous and non-aqueous suspensions. The transmittance of aqueous CBS and gelatin gel suspensions containing water (curves 1 and 2 in Fig. 3) restores to its initial value in approximately 100 ms, whereas the transmittance of carbon suspension in epoxy resin (curve 3) remains practically unchanged after irradiation by a laser pulse.

Time behavior of the laser-induced transmittance observed in the experiments can be interpreted in accordance with the above-considered models. So, in aqueous suspensions and gelatin gels, laser-heated carbon microparticles produce bubbles filled with water steam and other soluble gases, which are short-lived and disappear in a hundred of milliseconds, both in water and in water-rich gelatin gel. Quite the contrary, in the epoxy resin, the overheated carbon particle produces stable entities of the products of pyrolysis – long-lived bubbles (filled with poorly soluble gases) and carbonized shells. As a result, persistent changes in the optical transmittance are observed in epoxy suspensions.

4. Concluding remarks

In this work, we investigated the processes of optical limiting in carbon suspensions in different matrixes, both aqueous and non-aqueous. The results obtained indicate that the presence of sufficient amount of water in the matrix is a crucial factor that determines behavior of the suspension under irradiation by powerful nanosecond laser pulses. Aqueous content of the matrix provides water steam for filling the bubbles formed near the carbon particles; hence the laser-induced changes in the optical transmittance can be transient or permanent in different matrixes.

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