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Thermal mechanisms of laser marking in transparent polymers with light-absorbing microparticles

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ABSTRACT

Interaction of highly viscous polystyrene suspensions of light-absorbing microparticles with pulsed radiation of a Q-switched YAG:Nd^{3+} laser is investigated. Absorption of laser radiation by the suspended microparticles causes thermal decomposition (pyrolysis) of the polymer in the vicinity of the overheated particles. Laser-induced incandescence (LII) of light-absorbing microparticles under irradiation by a sequence of laser pulses is observed. The mechanism of laser marking includes formation of light-absorbing and scattering centers by accumulation of carbonaceous and gaseous products of pyrolysis.

1. Introduction

Investigations of interaction of laser radiation with different materials open new opportunities for science and technology advancements in digital material processing involving microfabrication with surface engraving, volumetric marking, and recording of digital information [1–5]. In transparent polymers, irradiation by powerful pulsed laser radiation produces local darkening of the polymer in the focal spot. Such kind of laser processing is usually named as laser marking. In transparent polymers, laser marking is observed with the use of nanosecond-scale laser pulses with the typical values of average laser power density of 100 MW/cm^2 [1,2]. Physical mechanisms of laser marking in transparent polymers are far from being clear in the details. It is assumed, that laser radiation results in local carbonization of the polymer, and hence black-colored marks can be produced [1–5]. This work aims to shed a bit of light on the physical mechanism of laser mark creation in transparent polymer matrix (polystyrene) doped with a relatively small amount of carbon-based light-absorbing microparticles, which act as nucleation centers for laser-induced marks. As is known, carbon is a widespread light-absorbing material which can be efficiently heated to temperatures of several thousands of Kelvins by nanosecond-scale laser pulses of moderate intensity [6–8]. For example, carbon microparticles in aqueous suspensions (carbon black suspensions) under pulsed excitation by a Q-switched YAG:Nd^{3+} laser with power density of 3–10 MW/cm^2 can be heated to incandescent temperatures, and the appropriate thermal emission of these laser-heated particles is easily observed with a naked eye. This emission is named as laser-induced incandescence (LII) [7–12]. LII is observed in different circumstances of pulsed laser irradiation of various light-absorbing objects: soot particles in flames and exhaust gases [7–11], carbon black suspensions [12], borate glass with light-absorbing inclusions [13], transparent polymers doped with carbon microparticles [14,15], surface layers of carbon-based materials [16]. LII of laser-heated objects provides essential information about the processes that occur in the material under laser irradiation. LII can be used for monitoring of local temperature under laser irradiation. For example, local temperature on the laser-irradiated surface can be estimated by measuring the LII intensity at a fixed wavelength at two values of ambient temperature [16]. It is expected that LII can be of use for monitoring of the laser marking process in transparent polymers.

Concerning laser marking in transparent polymers, polystyrene seems to be a promising material due to its attractive properties, extensive use in industry and ability for laser marking. However,

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with keeping in mind the behavior of light-absorbing microparticle suspensions in transparent polymer matrix under pulsed laser irradiation [14,17], we can expect that the capability of polystyrene for laser marking can be improved by doping this matrix with the appropriate amount of light-absorbing microparticles which can act as nuclei for growth of carbonaceous laser marks. Such approach can be useful for laser marking in bulk polymers. Besides, carbon microparticle suspensions show promise for application of laser-sensitive coatings on the components to be marked.

Another feature of particle-doped transparent polymers is their ability to form microbubbles under pulsed laser irradiation. When the polymer is prepared in the condition with the ability of viscous flow, laser irradiation of this polymer produces microbubbles in the vicinity of overheated carbon microparticles [17]. This circumstance can be useful (at least in principle) for improving the capabilities of laser marking by combination of carbonaceous (black) and bubble-based ("white") marks.

2. Experimental details

In this work, the experiments were carried out using the bulk samples of polystyrene doped with light-absorbing (carbon and carbon-based) microparticles. The samples were prepared by dissolution of solid polystyrene pellets in xylene suspensions of light-absorbing microparticles. Two kinds of light-absorbing microparticles were used. Small (0.1–0.2 μm) carbon particles were generally used in the LII experiments. This kind of microparticles is suitable for laser-induced marking in the volume of transparent polymers. In order to visualize the processes of carbonization and gas release, which accompany pyrolytic decomposition of the polymer matrix under laser pulse action, abrasive powder with larger (5–10 μm) light-absorbing particles was used. The powder consisted of gray particles containing SiC, carbon and other light-absorbing impurities. These microparticles highly absorbed laser radiation that resulted in LII similarly to the case of small carbon microparticles.

The obtained polystyrene-xylene-particle suspension was stirred mechanically until uniform distribution of suspended particles was obtained that was visually monitored by probe laser light scattering. Then, the suspension was kept in an open glass cell in the air at room temperature until its viscosity became similar to the viscosity of epoxy resins at room temperature. Measurements of the suspension viscosity were not performed.

At the stage of preparation of xylene suspensions of light-absorbing microparticles, the concentration of suspended particles was adjusted so that optical transmission of the polystyrene-particle suspension was about 50% at the sample thickness of 1 cm at wavelength of 1064 nm. The estimated value of the concentration of light-absorbing particles was approximately 10^5 mm^{-3}, hence the diameter of the laser beam employed in the experiments (approximately 2.7 mm) was much larger than the distance between neighboring particles. With such arrangement of the experiments, we did not deal with a separate laser-induced point mark, but instead, each laser shot irradiated a large number of particles simultaneously. In such conditions, the cumulative effects of laser-induced micromarks were detected. For example, after laser irradiation, a clearly visible track (darkened trace) was observed in the sample, whereas single point marks were not visible without a microscope.

The prepared samples were irradiated by a Q-switched YAG:Nd^{3+} laser with a wavelength of $\lambda=1064$ nm and pulse duration of $\tau=20$ ns. At this wavelength, the polystyrene is practically transparent, whereas the absorption cross-section of the suspended particles was estimated by the Mie theory as

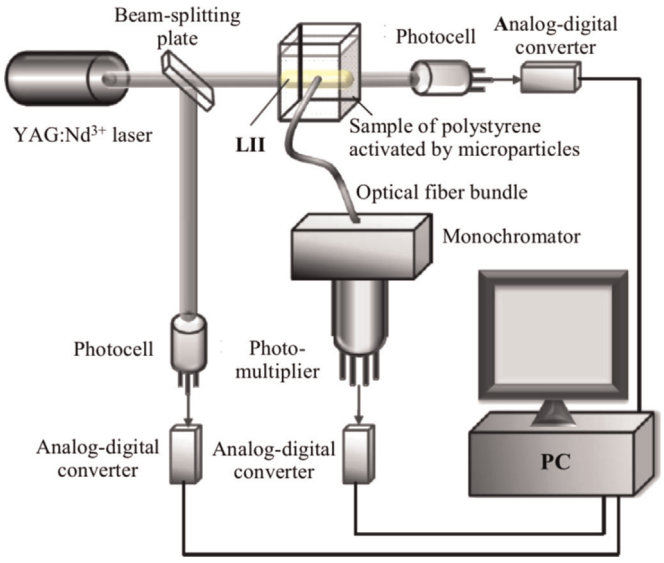

Fig. 1. Experimental setup for LII and optical transmission measurements of light-absorbing microparticle suspensions in polystyrene.

3.6×10^{-10} cm^2, which is high enough for easy overheating of such particles by laser pulses of moderate power density. In the paper, laser power density F was varied within the range of 2–50 MW/cm^2. Such laser excitation level can be considered as moderate one compared with the experiments on laser marking by focused beams in undoped polymers [1,2,5].

The laser power density was monitored before and after passing through the sample cell (Fig. 1), thus the optical transmittance was evaluated. Under pulsed laser irradiation, the samples emitted short pulses of visible radiation (LII), which was monitored at fixed wavelength of 550 nm (through a single grating monochromator). The wavelength of detection of LII is not a critical parameter, it can be chosen practically arbitrary within the range of spectral sensitivity of the photodetector employed. The laser and data acquisition instrumentation operated in a single-pulse mode with the laser pulse repetition rate of approximately 1 pulse per second, hence the accumulation of heat in the irradiated sample was negligible.

3. Results and discussion

First, let us consider the results of the optical transmittance measurement of polystyrene-carbon suspension irradiated by series of laser pulses with variable power density. The range 1 in Fig. 2 ($N=1$–20) corresponds to the relatively low level of laser power density, when laser radiation does not change the properties of the irradiated sample. The range 2 ($N=21$–250) corresponds to the irradiation by high-power laser radiation (Fig. 2). As is seen from Fig. 2, optical transmittance measured with the use of high-power laser radiation is much smaller than the low-signal transmittance. Beside of this, after completion of the high-power laser pulses sequence, the low-signal transmittance of the sample does not restore to its initial value (Fig. 2, range 3, $N=251$–450).

Second, let us analyze the behavior of LII of polystyrene-carbon suspension irradiated by series of laser pulses with high power density ($F=50$ MW/cm^2). Fig. 3 presents the LII intensity (time integral of pulsed LII signal) of polystyrene-carbon suspension as a function of the number of high power laser pulses. Fig. 3 corresponds to the range 2 in Fig. 2. In the case of ranges 1 and 3 (Fig. 2) LII signals are not observed. As is seen from Fig. 3, initial series of laser pulses causes a relatively sharp increase in the integral LII