

## STRUCTURE AND STRENGTH TO LASER DAMAGE IN POLYMERS

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*Hypermolecular structure is studied of polymethylmethacrylate, of a copolymer of methylmethacrylate with methacrylic acid, modified by metal salts of organic and inorganic adds, and certain element-organic compounds. Studies involved electron microscopy. The second harmonic of a Nd:YAG laser was used to test the polymers' laser damage strength (LDS). The efficiency of modifying polymer to improve its LDS is shown to depend strongly on the effect of modifier on the polymer structure, determining conditions of intermolecular interaction. A noticeable increase in LDS is found in those cases when a dense grid of chemical or physical bonds is formed in the polymer, providing most favourable conditions for transfer of energy from vibrationally excited macromolecules to modifier molecules.*

Wide application of transparent polymers to laser optics instead of conventional optical materials (such as crystals and glasses) is strongly restrained by the low resistance of the former to powerful light beams.

The studies of destruction of methacrylic polymers with laser beams revealed a strong effect of low-molecular modifying additions from the class of aliphatic alcohols and ethers, mainly, on these polymers' LDS.<sup>1-3</sup> Following the model proposed in Refs. 1 and 2, its authors explained higher LDS of polymethylmethacrylate modified by low-molecular additives of up to 37% mass to energy transfer from the vibrationally excited macromolecules to molecules of additive (i.e., by vibrational cross relaxation). It is obvious at the same time that adding quite large amounts of substance to a polymer in the process of its synthesis must affect its micro- and hypermolecular structure, the role of the latter in forming LDS of the polymer remaining unexplored yet. In addition, the influence of structural inhomogeneity of a polymer on its LDS was noted in Ref. 4. It is also well known that micromechanics of polymer destruction, i.e., the kinetics of formation and growth of destruction areas, depends on its physical structure.<sup>5</sup>

The present paper attempts to explain the results of studies of LDS of polymethylmethacrylate (PMMA) and of a copolymer of methylmethacrylate (MMA) with methacrylic acid (MAA) using the data on their hypermolecular structure. Salts of organic and inorganic acids of metals, from alkali to rare-earths, were selected as modifiers to these polymers, as well as certain element-organic compounds.

Polymers were modified in the process of their synthesis. In so doing the amounts of modifiers used did not exceed 1% mass, therefore they did not change noticeably viscoelastic properties of polymers. The ratio of MMA to MAA in the process of copolymer synthesis was 9:1. Special diaphragms catching particles in excess of 0.1  $\mu\text{m}$  in size were used to cleanse the initial monomelic compounds from foreign inclusions.

A "Tesla" BS-500 electron microscope was used to study the hypermolecular structure of polymers. The structural relief of sample surface was plasma-etched in a linear high frequency no-electrode discharge. The study further followed the technique of coal-silver replicas.

The second harmonic of an NG:YAG laser ( $\lambda = 532 \text{ nm}$ ,  $t_s = 10 \text{ ns}$ , pulse repetition frequency 125 Hz) was used for LDS tests. Energy density of radiation varied from 0.25 to 1.00  $\text{J}/\text{cm}^2$ . Figure 1 shows the optical diagram of the setup. Laser radiation was focused by lens  $L$  to sample  $S$ , part of the incident radiation sent to beam splitting plates  $BSP1$  and  $BSP2$  to reach the photodetector  $D1$  while the part of radiation passing through the sample went to photodetector  $D2$ . The radiation energy was measured by calorimeter  $C$ . Signals from photodetectors were fed to differential inputs of oscillograph  $OS$ , its line synchronization driven by pulses from the power supply unit  $PSU$  of the laser. Using an optical wedge  $OW$  signals from photodetectors were balanced so as to almost completely extinguish each other on the oscillograph screen in the case there was no breakdown of the sample. The electrical signal from  $D2$  decreased sharply when a breakdown occurred resulting in imbalance, observed as a pulse on the oscillograph screen. Thus the instant of breakdown could be determined and the number of pulses counted to sample destruction at some density of radiation energy. The latter was taken to be the criterion of the polymer LDS.

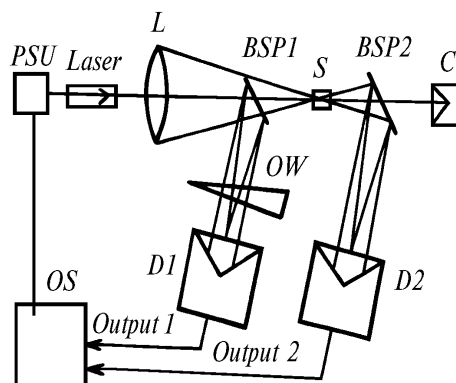


FIG. 1. Optical diagram of the setup for LDS tests.

Modifying MMA by salts of metals a noticeable increase in LDS was only observed when salt cations were certain rare-earth elements. Figure 2 shows the number of

laser pulses endured by a sample at pumping radiation density of  $0.5 \text{ J/cm}^2$  depending on the concentration of modifiers incorporated: cerium nitrate, methacrylate, and erbium carbonate. One may see from that figure that both the nature and concentration of the modifier affect the copolymer. The dependences of copolymer LDS featured extrema, and the maximum increase in copolymer LDS, by a factor of 6–7 was reached at 0.1 – 0.25% mass of Er MAA and  $\text{Er}_2(\text{CO}_3)_3$ .

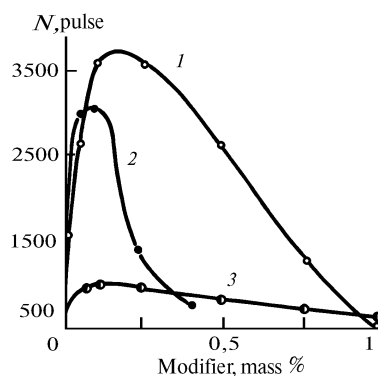


FIG. 2. The number of laser pulses  $N$  endured by the MMA–MAA copolymer at density of radiation energy  $0.5 \text{ J/cm}^2$  vJ concentration of the modifier introduced: 1)  $\text{Er}_2(\text{CO}_3)_3$ , 2) Er MAA, and 3)  $\text{Ce}(\text{NO}_3)_3$ .

As is shown by our investigations LDS of PMMA and of a copolymer of MMA with MAA increased most strongly, that is by a factor of about 30–60, when the derivatives of benzoylthiocyanate and amines were used as modifying additives.

Since all the modifiers strongly enhancing the LDS of polymers include C = O, NH, and OH groups whose vibrational spectra multiple to the spectra of polymer macromolecules, an effective resonance transfer of energy becomes possible from the vibrationally excited macromolecules of polymer to the molecules of modifier, in agreement with concepts developed in Refs. 1 and 2. Such a transfer results in suppression of the mechanical

chemical process of formation of absorbing radicals so that the polymer LDS increases. However, experimental data indicate that certain salts of MAA selected for modifiers, including methacrylates of sodium, barium, and some other metals of valence one and two do not increase the copolymer LDS. Meanwhile the vibrational spectra of their molecules completely overlap the spectrum of macromolecules of the copolymer containing groups of the same MAA. It was thus important to focus on our results on the hypermolecular structure of polymers.

According to images from electronic microscopy of the samples (Fig. 3) a classical globular hypermolecular structure with globules of a rather uniform size is typical for PMMA. The hypermolecular structure of the MMA–MAA copolymer features a biphasic structure, that is, larger close-packed structural elements of hundreds of Angstroms in size are randomly scattered against the background of the globular matrix. That feature is caused by the presence of a grid of carboxyl–carboxylic hydrogen bonds in the copolymer, absent in PMMA. The copolymer LDS was found to be higher than that of PMMA. Copolymer modification by introduction of small amounts of polar salt groups of erbium methacrylate, for example, results in agglomeration of large structural elements, their size reaching thousands of Angstroms, so the number of areas with least orderliness (of "microreactors", see Ref. 5) lowers, the latter serving as centers of copolymer destruction under external forcing.

As compared to the control one, much more macrochains take part in the intermolecular bonds in a modified copolymer (see Fig. 4, showing only three of them to be chemically combined with the modifier). That is so, because a grid of chemical bonds becomes available along with a denser grid of hydrogen bonds then. One arrives at that picture taking into account the capacity of the cation salt group for donor–acceptor interaction with carbonyl oxygen from both the acid and ester groups of the copolymer. Moreover, this cation holds about four molecules of water by complex bonds and is capable of interacting with active groups of the copolymer. Therefore such intermolecular interaction appears stronger than in the copolymer containing methacrylates of metals of valence one and two, that is, the conditions for energy transfer from the vibrationally excited macromolecules of the copolymer to molecules of the modifier become optimal.<sup>6</sup>

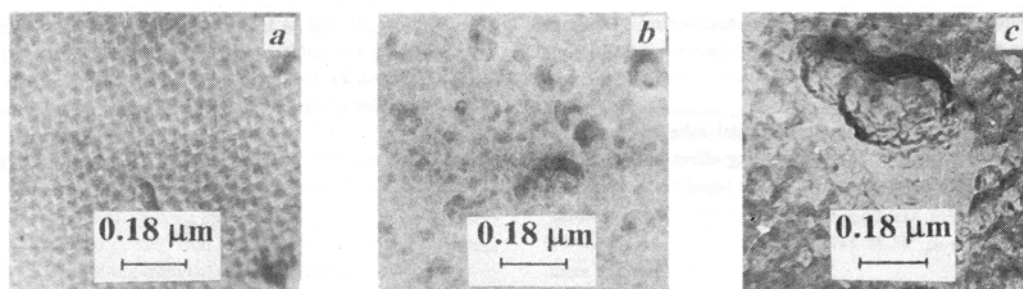


FIG. 3. Electronic microscopy images of hypermolecular structure of polymers, a) PMMA and b) MMA–MAA–ErMAA copolymer.

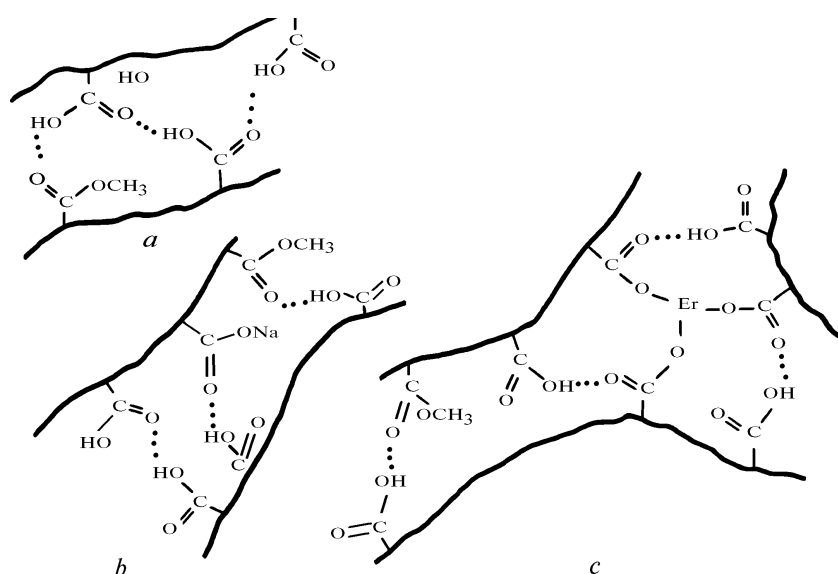


FIG. 4. Intermolecular interaction in copolymers, a) MMA-MAA, b) MMA-MAA-Na MAA, and c) MMA-MAA-Er MAA.

Thus the efficiency of modifying polymer to improve its LDS greatly depends on the effect of the modifier on that polymer structure; that effect controls the conditions for intermolecular interaction.

Judging from similar electronic microscopic images the same picture is observed when the copolymer is modified by erbium carbonate not chemically combined with it, or by elemental organic compounds containing more than three active groups. Instead of a grid of chemical bonds only the highly mobile physical bonds exist in the copolymer then. The enhanced LDS of polyurethanes is also well known to be explained by such a mobile grid of physical bonds. A dense grid of physical bonds is obviously formed when large amounts of low-molecular additives (alcohols and esters) are introduced into PMMA. The latter significantly enhance its LDS, as found elsewhere.<sup>1-3</sup> Such additives act as plastifiers simultaneously, "doctoring" the defects of the PMMA hypermolecular structure and filling up its interstructural areas, such as cracks and micropores, which are most prone to destruction. However, doing so these additives turn the glassy polymer into elastic, and produce considerable operational difficulties along with increasing the polymer hygroscopicity.

Although the low amounts of metal salts and elemental organic compounds have lower stabilizing effect in PMMA and the MMA-MAA copolymer as their

modifiers, they lack the above drawbacks. These are organic glasses which do not feature any enhanced hygroscopicity. Moreover using modifiers chemically combined with a polymer exclude their migration and exudation thus providing for extended operation under harsh operating conditions, including those of deep vacuum, when the rate of exudation of additives is exceptionally high.

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