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K. M. Dyumaev^a; A. P. Maslyukov^a; G. A. Matyushin^a; V. S. Nechitailo^a; E. P. Ponomarenko^a

^a All-Union Research Institute for Medical Polymers, Moscow, USSR

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On the Mechanism of Laser Destruction of Polymers: Effect of Low-molecular Weight Additives Stemming from Oscillatory Cross Relaxation

K. M. DYUMAEV, A. P. MASLYUKOV, G. A. MATYUSHIN, V. S. NECHITAILO
and E. P. PONOMARENKO

All-Union Research Institute for Medical Polymers, Moscow 117246, Nauchny proezd 10, USSR

The vibrational cross-relaxation mechanism of polymer destruction suppression under laser irradiation are discussed. The experimental data are presented showing the influence of low molecular weight additives on laser damage resistance of optical polymers.

KEY WORDS Laser degradation, polymers, additives

Today it is reliably established that optical polymer breakdown is connected with the absorbing defects that initiate the mechanochemical reactions of formation of absorbing radicals¹ due to laser heating. It has been proved experimentally that the laser polymer strength is tangibly affected by the introduction of low molecular weight additives into the polymer matrix and this influence has a strongly pronounced selectivity.²

Within the mechanism of laser destruction of polymer materials considered in References 1 and 2, the effect of low molecular weight additives is associated with the transfer of oscillatory excitation energy between the polymer macromolecules and the additive molecules (oscillatory cross relaxation). This process of energy transfer should be of a resonance nature, i.e., the efficiency of the oscillatory cross relaxation between the macromolecules and the additive molecules should essentially depend on the overlapping of their oscillatory absorption bands. We may naturally expect that when the oscillatory spectrums of the additive molecules are multiples of the macromolecule spectrum, the effective resonance process of the transfer of the oscillatory excitation energy takes place, the mechanochemical process of formation of absorbing radicals¹ is suppressed and, subsequently, the polymer laser stability significantly increases.

The aim of the present research work is the experimental check of the propounded ideas on the mechanism of laser destruction of polymers.

The investigation is concerned with a widely known polymer, poly(methyl meth-

acrylate), while the low molecular weight additives are chosen from the compounds of the following classes:

—aliphatic alcohols R—OH

where R = —C₂H₅ (1), —C₃H₇ (2), *i*-C₃H₇ (3), —C₄H₉ (4), *i*-C₄H₉ (5), *t*-C₄H₉ (6), —C₆H₁₃ (7), -cyclo C₆H₁₃ (8), —C₇H₁₅ (9), —C₈H₁₇ (10), —C₁₀H₂₁ (11), —CH₂—CHF₂ (12), —CH₂—CF₃ (13);

—halogen-containing hydrocarbons CHX—CHX

where X = —Cl (14), —Br (15);

—aliphatic nitriles C₄H₉CN (16);

—phosphates (CH_nF_m—CH₂—O)₃PO

where $n = 3, m = 0$ (17), $n = 2, m = 1$ (18), $n = 0, m = 3$ (19) which tangibly differ in the oscillating spectrums.

The experiments are performed on samples of polymers having a form of discs, 16 to 20 mm in diameter and 5 to 10 mm thick, obtained by way of block radical polymerization of the initial monomeric compositions with introduced low molecular weight additives under the conditions ensuring the absence of absorbing inclusions, over 0.1 μm in size, in the polymer with subsequent precision machining of the endface surfaces of the discs.³ The content of the residual monomer in the polymers does not exceed 0.1%. The determination of the polymer glass-transition temperature indicates its relatively poor dependence on the additive nature in all cases except trifluoroethanol.¹³ In the latter case, a greater plasticizing effect (as compared with other additives) is observed. The absence of a noticeable dependence of the glass-transition temperature on the nature of the low molecular weight additives means that the samples of polymers containing similar quantities of various additives possess similar viscoelastic properties. This fact is of particular importance in revealing the effect of the additives on polymer laser stability stemming from oscillatory cross relaxation.^{1,2}

The laser irradiation of polymers is carried out at 293 K by means of giant pulses radiated by a neodymium laser ($\lambda = 1.06 \mu\text{m}$). These pulses are focused into the samples with the aid of a lens having focal length $F = 300 \text{ mm}$; the minimum size of the bundle in the field of caustic is $d \cong 1 \text{ mm}$.¹ During the experiments the threshold of N -pulse laser destruction (I_N), which is one of the basic characteristics of the transparent polymer laser stability, is determined at irradiation pulse number $N = 200$ for each point of the sample.^{1,2}

The first series of experiments have made it possible to determine the concentration dependence of the threshold I_N of the polymer samples with aliphatic alcohols (compounds (1)–(11)) distinguished by the length of the hydrocarbon radical and structure introduced as additives. The laser stability of poly(methyl methacrylate) is most strongly increased by introducing aliphatic alcohols with both normal and isomeric structures (Figure 1a) whose oscillatory spectrums are very much alike (Figure 2a). By contrast, introduction of alcohols having a tertiary (6) or cyclic (8) structure into poly(methyl methacrylate) brings about only an insignificant increase in polymer laser stability (compare curves I and II in Figure 1a), which can easily be explained by a substantial difference of the oscillatory spectrums of these compounds from those of the respective normal-structure alcohols (Figure 2a).

In the course of the second series of experiments the investigation has found the

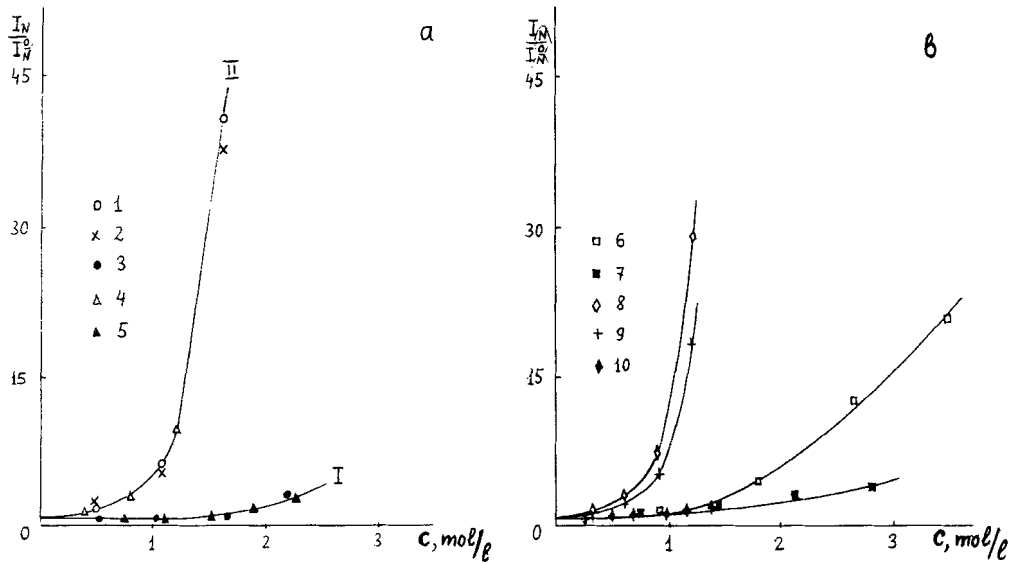


FIGURE 1 Dependence of N -pulse laser damage threshold I_N ($N = 200$) for PMMA with various additives (related to threshold I_N for PMMA) on additive concentration C : (1) C_4H_9OH ; (2) $i-C_4H_9OH$; (3) $t-C_4H_9OH$; (4) $C_6H_{13}OH$; (5) cyclo- $C_6H_{13}OH$; (6) C_2H_5OH ; (7) CF_3CH_2OH ; (8) $(C_2H_5O)_3PO$; (9) $(CH_2FCH_2O)_3PO$; (10) $(CF_3CH_2O)_3PO$.

concentration dependence of threshold I_N of the polymer samples with the low molecular weights additives from the classes of halogen-containing hydrocarbons, aliphatic nitriles, fluoro alcohols, and phosphates. It is established that introduction of fluoroethanol (12) or triethylphosphate (17) leads to a considerable increase in the polymer laser stability, while introduction of trifluoroethanol (13), perfluoro-triethylphosphate (19), ethylene dibromide (15), ethylene dichloride (14), and propyl cyanide (16) has a relatively poor effect on I_N (Figure 1b). These results may also be explained by the differences in the oscillatory spectrums of the compounds above (Figure 2b).

Genuinely, according to the mechanism of laser destruction of polymer materials propounded in References 1 and 2, a low molecular weight additive should significantly increase the polymer laser stability when its oscillatory spectrum is a multiple of the spectrum of macromolecules. Keeping in mind that the mechanochemical process of formation of absorbing radicals in poly(methyl methacrylate) under the action of the laser irradiation is connected with the oscillatory excitation of the carbonyl group (included in the composition of the side chains of the macromolecules and having oscillatory excitation energy $E'_1 = 1730$ to 1740 cm^{-14} for the first level), it can be stated, provided the band with oscillatory excitation energy $E''_1 = 1040$ to 1050 cm^{-1} is found in the oscillatory spectrum of the additive molecules, that this band appears to be a multiple of the carbonyl group spectrum:

$$n_1 E'_1 = n_2 E''_1$$

where $n_1 = 3$ and $n_2 = 5$. In this case, as is obviously seen, the effective resonance

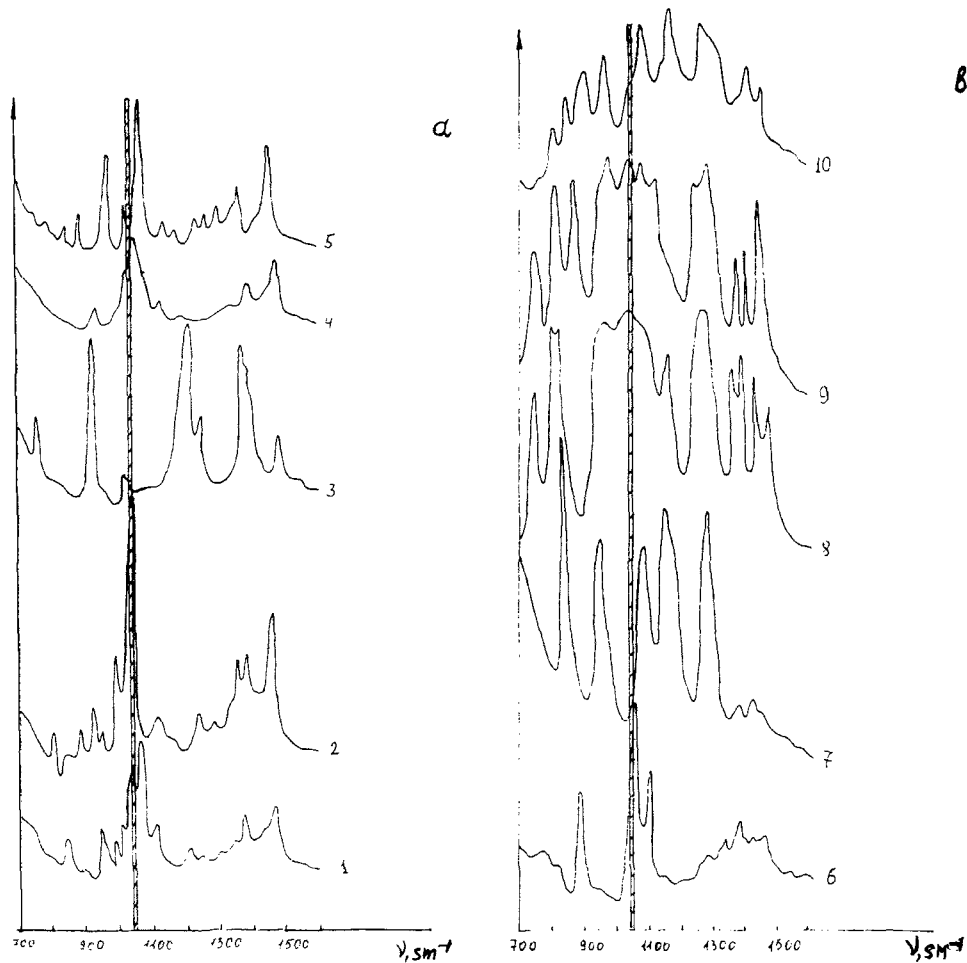


FIGURE 2 Oscillatory spectrums of additives in PMMA: (1) C_2H_5OH ; (2) $i-C_4H_9OH$; (3) $t-C_4H_9OH$; (4) $C_6H_{13}OH$; (5) $cyclo-C_6H_{13}OH$; (6) C_2H_5OH ; (7) CF_3CH_2OH ; (8) $(C_2H_5O)_3PO$; (9) $(CH_2FCH_2O)_3PO$; (10) $(CF_3CH_2O)_3PO$.

process of the oscillatory excitation energy transfer from the macromolecules to the additive molecules should take place and the optical strength of the polymer should significantly increase due to oscillatory cross relaxation.^{1,2}

The additive concentration dependencies of threshold I_N presented in Figure 1 are substantiated within the framework of the developed notions: introduction of ethyl (1), butyl (4), isobutyl (3), and hexyl (7) alcohols, triethylphosphate (17), and fluoroethanol (12) having the absorption band in the oscillatory spectrum with $E_1'' = 1040$ to 1050 cm^{-1} (Figure 2) in poly(methyl methacrylate) results in a considerable increase in polymer laser stability. At the same time, introduction of trifluoroethyl (13), tertiary butyl (6), and cyclohexyl (8) alcohols, as well as perfluorotriethylphosphate (19) in poly(methyl methacrylate) causes only an insignificant increase in polymer optical strength which can easily be explained by the

absence of resonance in the oscillatory spectrums of the carbonyl group of the polymer and the molecules of the additives above.

Within the framework of the developed oscillatory cross relaxation mechanism for suppression of destruction of macromolecules under the action of laser irradiation, a proper explanation is found for the experimental results obtained in Reference 2: water whose molecules are bound with the molecules of other additives (for example, alcohols) by means of hydrogen bonds added even in small quantities (about 1%) greatly affects polymer laser stability. In fact, water molecules bound by means of hydrogen bonds have the oscillation frequency of the OH group ($E_1 = 3460$ to 3480 cm^{-1}) being a multiple of the frequency of the carbonyl group in the macromolecule of poly(methyl methacrylate) ($E'_1 = 1730$ to 1740 cm^{-1}), while free OH groups have the oscillation frequency ($E_1 = 3590$ to 3650 cm^{-1}),⁵ substantially differing from the oscillation frequency of the carbonyl group. Therefore, poor oscillatory cross relaxation that has almost no effect on polymer stability is typical of "free" OH groups, which is proved by the experiment.²

So, the totality of experimental facts pertaining to laser destruction of poly(methyl methacrylate) suggests that introduction of additives effecting oscillatory cross relaxation between macromolecules and additive molecules is an efficient method of increasing polymer stability against powerful light radiation.

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