Destruction of polymers under the action of laser radiation

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Abstract. Laser ablation is one of the main mechanisms of polymers destruction under the action of laser radiation. In this paper, the basic information on laser ablation of polymers is presented. Under the action of laser radiation on the polymer, processes of thermal, thermo-oxidative, and mechanical degradation occur simultaneously, resulting in the evaporation of macromolecules fragments (up to oligomers), and in some cases, separation of polymer particles and filler by a gas or plasma jet is observed. In addition, a substance ablation is accompanied by a large number of concomitant effects: vapor condensation and liquid phase dispersion.

Introduction

The unique properties of polymers have ensured their widespread use in construction. For example, polymethyl methacrylate is used to produce sheets that replace ordinary silicate glass. Polymethyl methacrylate is used for making door panels and transparent windows in gates. Due to its low specific gravity, resistance to sunlight and ease of processing, polymethyl methacrylate is used as the main material in the construction of visors and transparent balustrades. Sound barriers from PMMA are used to create reflective acoustic baffles along the highways and busy roads.

Obtaining the experimental data on the polymers’ dynamic strength is important for solving many problems in various areas of the national economy. We have investigated the polymers destruction by laser exposure.

The process of a solid destruction, similar to evaporation or sublimation, characterized by the presence of a condensed phase in the destruction products, is called laser ablation.

The energy efficiency of polymeric materials laser ablation depends on the amount of absorbed energy at a certain density. In the infrared, visible and near ultraviolet frequency ranges, radiation absorption is described by the Bouguer-Lambert law:

\[ I(z) = I_0 \eta e^{-\chi z} \]  

where \( I_0 \) — is the intensity of the light beam on the surface; \( \chi \) — is an absorption coefficient; \( z \) — is the coordinate measured into the depth of the material; \( \eta \) — is the coefficient determining the absorbed energy share.

Energy absorbed in the sample layer during \( t \):

\[ E = S \int_0^t I(z) dt = S \eta I_0 e^{-\chi z} t, \]  

where \( S \) is the area of the sample.

[1] Bouguer-Lambert law: \[ \eta = \frac{\ln(I/I_0)}{z} \]

[2] Energy absorbed in the sample layer during \( t \):

\[ E = S \int_0^t I(z) dt = S \eta I_0 e^{-\chi z} t, \]
where $S$ — is the cross-sectional area of the laser beam on the sample surface. The intensity lost in a layer of thickness $z$ is

$$\Delta I = I_0 - I(z) = I_0(1 - \eta)e^{-\chi z}.$$  \hspace{1cm} (3)

Table 1 shows the values of the absorption coefficients $\chi$, obtained by irradiating polymer films with radiation CO$_2$- laser.

Table 1 gives the data indicating that the value of the coefficient $\chi$ significantly depends on the method of obtaining a polymer film.

**Table 1.** The absorption coefficients $\chi$ for laser radiation with a wavelength of 10.6 $\mu$m.

| Polymer           | Method of obtaining       | $\chi_{\text{tr}}$ [cm$^{-1}$] | $\chi_{\text{tr}}$ [cm$^{-1}$] |
|-------------------|---------------------------|---------------------------------|---------------------------------|
|                   | Frequency                 |                                 |                                 |
| Polyethylene      | Extrusion                 | 943                             | 927                             |
|                   |                           | 927                             | 104                             |
| Polypropylene     | Hot pressing              | 37                              | 31                              |
|                   |                           | 31                              | 39                              |
| Polystyrene       | From solution in benzene  | 118                             | 255                             |
|                   |                           | 131                             | 169                             |
| Polystyrene       | Hot pressing              | 112                             | 131                             |
|                   |                           | 347                             | 176                             |
| Polyvinyl chloride| Hot pressing              | 112                             | 131                             |
|                   |                           | 147                             | 176                             |

All polymers, depending on their behavior when irradiated with a laser beam, can be divided into three groups, as it was done in the work [1]:
- polymers that melt and splash (group A);
- polymers that form a coke layer on the surface (group B);
- polymers that turn into a gaseous state without residue (group C).

In some cases, it is necessary to take into account the ignition of polymers, which has an additional destructive effect.

Group B behavior is only polymers characteristic and group A and B behavior is also observed in metals and semiconductors.

Group A includes thermoplastic polymers (polyethylene, polypropylene, polyethylene succinate, nylon, kapron, etc.). Some polymers, such as polystyrene, polymethyl methacrylate, belong to group A - at low radiation power densities, and to group B - at high radiation power densities.

For polystyrene and polymethyl methacrylate, it was found that in the surface layers inside the sample under study, destruction occurs along the supramolecular structures’ boundaries, as a result of which a cloud appears above the surface, shielding the sample by absorbing a part of the radiation and containing solid, liquid and gaseous products, and the composition of the cloud depends on laser beam intensity [1].

Figure 1 shows the destruction zones of the sample along the cross-section perpendicular to the surface: **zone: I** — solid polymer with exponential temperature distribution;
- **II** — the polymer is in a highly elastic state;
- **III** — liquid-like molten polymer (pyrolysis occurs in this area with increasing temperature);
- **IV** — the smallest droplets resulting from the molten polymer crushing;
- **V** — gaseous state of decomposition products.

Zones **IV and V** can be divided only by analyzing the products’ composition in these zones.

Here $T_g$, $T_s$, $T_{dc}$ and $T_d$ — glass transition temperature, softening, decomposition, destruction front (for thermoplastics it does not exceed 773K) respectively.
Figure 1. Schematic representation of the destruction zones of thermoplastics under the influence of infrared laser radiation with a wavelength 10.6 μm.

Figure 1 shows that for the group A polymers it is possible to subdivide the destruction zones and even determine their width. The appearance of rare cross-links in polymers of group A, for example, in radiation-crosslinked polyethylene [2], does not lead to significant deviations in their behavior in a laser beam. The ablation energies of polymers in this group lie within the bounds of the bond strengths GT-GT and are equal approximately 2—3 kJ / g (Table 2).

When exposed to radiation I₁ or I₂ the first-order phase transitions are possible.

**Table 2.** Threshold energy characteristics of the laser radiation effect on some polymers of group A.

| Polymer  | I₁ | I₂ | I₃ | I₄ |
|----------|----|----|----|----|
| Nitron   | 3  | 6  | 18.5 | 25 |
| Lavsan   | 7  | 11 | 17  | 22 |
| Lavsan   | 3  | 5  | 17  | 23 |

I₁-I₄ — are the threshold power densities at which respectively, the rearrangements in the supramolecular structure, softening, destruction process, decay, weight loss due to molecular fragments’ evaporation, etc. start in polymer.

Group B includes aromatic thermosetting polymers (polybenzimidazole, polycyanurates, polyphenylenes, etc.), as well as some thermoplastics capable of crosslinking when heated (polyphenylene oxide, polyphenylquinaxaline, polyarylate, etc.), after which they behave like thermosetting plastics and form a coke layer when heated in a laser beam. After the formation of the secondary structure, such a polymer is no longer able to soften. As the irradiation dose increases, the network structure first becomes denser to the limiting value, and then condensation of aromatic cycles, or dehydrogenation with the formation of multiple bonds, and then aromatic cycles according to the Diels – Alder reaction start, followed by the cycles’ condensation. The result is parquet and graphite-like structures [1, 4].

For the group B polymers when exposed to laser radiation, the zones II, III, IV are either absent, or significantly narrowed and the transition through them temperature occurs in a short time. These
polymers usually do not melt under irradiation (their crosslinking temperature is less than or close to the softening temperature), and along with the formation of a coke layer simultaneously with the processes of destruction and crosslinking, the process of ablation from the surface of oligomeric products is also possible.

The growth rate of the coke layer and its radiation-insulating properties strongly depend on the thermophysical characteristics associated with the morphology and the nature of the coke porosity (pore size, their closedness or openness, etc.), which should be taken into account when measuring ablation resistance. When exposed to laser radiation with an intensity less than 50 W / cm² on polycarbonate and polychlorotrifluoroethylene, a coke layer is formed, but in the second polymer the thickness is stabilized at a value of 0.1 mm, while in the first it grows to 3 mm or more. When the radiation intensity is increased to 200 W / cm² and more, the presence of a coke layer on the surface is not noted, since its formation rate is equal to or less than the ablation rate by sublimation [3].

Table 3. Laser ablation energies for a number of polymers capable of forming secondary polymer structures.

| Polymer          | I, [W/cm²] | Eabl |
|------------------|------------|------|
| Polycarbonate    | 10.5       | 49.0 |
|                  | 21.1       | 10.3 |
|                  | 31.7       | 10.6 |
|                  | 42.3       | 13.6 |
|                  | 55         | 13.3 |
|                  | 58.8       | 12.6 |
| Polynitymid      | 55         | 13.3 |
| Polynithalocyanine| 55        | 37.0 |

The third group B includes polymers that ablate without residue. The mechanism of this process can be depolymerization, complete destruction to gaseous products, or the polymer entrainment in the form of individual chain fragments (oligomers) and their settling on cold surfaces near the site of exposure. Table 4 gives the values of the laser ablation energy Eabl for a number of polymers in this group.

Table 4. Laser ablation energies for a number of group C polymers.

| Polymer                  | I, [W/cm²] | Eabl |
|--------------------------|------------|------|
| Polymethyl methacrylate  | 10.5       | 17.1 |
|                          | 21.1       | 4.8  |
|                          | 31.7       | 4.7  |
|                          | 42.3       | 4.2  |
|                          | 52.8       | 3.3  |
|                          | 55.0       | 3.5  |
| Polystyrene              | 55.0       | 3.9  |
| Poly-α-methylstyrene     | 55.0       | 2.4  |
| Polytetrafluoroethylene  | 55.0       | 3.4  |
| Polytetrafluoroethylene  | 55.0       | 3.8  |

Table 4 data confirm that polymethyl methacrylate and polystyrene belong, apparently, to both group A and group C.

In polymethyl methacrylate, the radiation intensity I less 5-7 W/cm² destruction is not observed at all; at I>7-10 W/cm² the ablation process starts with Eabl>10 kJ / g (the value is overestimated due to additional heat losses for convection and thermal conductivity at long exposure times); further,
the ablation process intensification occurs with a simultaneous decrease in ablation energy to a constant value in the range of 3.3–3.5 kJ / g (see Table 4). Consequently, the mechanism of decomposition of this polymer changes at elevated surface temperatures. In the case of laser ablation at low power densities, decomposition process of polymethyl methacrylate with an activation energy of 92 kJ / mol (decomposition of allyl bonds and depolymerization of radicals) is most likely realized, and with increasing values $I$ till 50-60 W/cm$^2$ in addition, the processes of destruction according to the law of chance and depolymerization of the main polymer chain are additionally initiated, and the dynamic equilibrium is shifted towards the process with a higher activation energy (252 kJ / mol) [4].

Summary
The ablation energy of group C polymers is lower than that of group B polymers. The lowest $E_{abl}$ value is observed in Poly-$\alpha$-methylstyrene, which is due to the occurrence of uncomplicated depolymerization at any values $I$. Close values $E_{abl}$ for other polymers allow us to conclude that the ablation mechanism itself is similar [4]:

- at low and medium power densities, the ablation mechanism of such polymers can include the processes of depolymerization, destruction with the elimination of side substituents, decomposition of the formed fragments, etc.;
- at high power density ($I > 50—60$ W/cm$^2$) the main chain breaks according to the law of chance, followed by partial depolymerization.

References
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