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KINETIC FEATURES OF THE LASER ABLATION OF GAMMA-IRRADIATED POLYVINYLIDENE FLUORIDE

S. R. Allayarov,[1,3] L. A. Kalinin,[2] E. M. Tolstopyatov,[2] P. N. Grakovich,[2]
L. F. Ivanov,[2] and D. A. Dixon[3*]

[1]*Institute of Problems of Chemical Physics, Russian Academy of Sciences*
Chernogolovka 142432, Moscow Region, Russia

[2]*V. A. Belyi Metal-Polymer Research Institute, National Academy of Sciences of Belarus*
Gomel 246050, Belarus

[3]*Department of Chemistry*
The University of Alabama
Tuscaloosa, AL 35487-0336, USA

*Corresponding author e-mail: dadixon@as.ua.edu

Abstract

We study the effect of γ-radiation from ^{60}Co on the rate of post-irradiation laser ablation of polyvinylidene fluoride (PVDF). The laser ablation of both the initial and γ-irradiated polymer occurs without an incubation period and does not require time to heat up the polymer target by the laser within the time scale of our measurements. The second feature of the laser ablation of PVDF is an extreme dependence of the ablation rate on the dose of γ-radiation over a wide range (10 kGy − 3.5 MGy) and the appearance of a minimum ablation rate of 0.1 mg/s at a dose 300 kGy. A gradual increase in the dose of γ-irradiation above 300 kGy is accompanied by a rise in the laser ablation rate. At γ-irradiation doses up to 2.3 MGy, the rate of the post-irradiated laser ablation of PVDF reaches 6.5 mg/s, which is equal to the laser ablation rate of non-irradiated PVDF.

Keywords: irradiation, γ-rays of ^{60}Co, IR laser, polyvinylidene fluoride, laser ablation.

1. Introduction

Infrared (IR) radiation and γ-irradiation have different modes of action on macromolecules [1–6]. A clear example of this fact is the process of IR laser ablation of the alternating terpolymer of ethylene, propylene, and carbon monoxide (POK), which was subjected to preliminary γ-irradiation. As a result of its ablation, nanostructured powders are formed with porous layers [3]. We note that the ablation of γ-irradiated POK is still the only method of obtaining coatings with a thickness in the range from tens of nanometers to tens of micrometers. As another example, γ-irradiation of polytetrafluoroethylene (PTFE) significantly increases the yield of laser-modified polymer in the form of fibrous materials [1–3]. This has led to the basis of an industrial process for producing fibrous PTFE materials, "Grifteks," which is chemically similar to native PTFE before processing and is characterized by its hydrophobicity and resistance to aggressive liquids, gases, and UV radiation [2]. The heat resistance of "Grifteks" is close to that of PTFE and it can be used effectively in medical devices and as a filter [7].

Analysis of the available data in the literature about the effect of γ-irradiation followed by IR laser ablation for PTFE [1–3,5] and POK [4] shows that γ-irradiation is useful for optimizing the laser ablation

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process, enabling the production of polymers with specified properties, but may also increase the resistance of the polymer to the IR laser beam. Clearly, further work is needed in order to better understand the influence of γ-irradiation on the laser ablation of various polymers.

Polyvinylidene fluoride (PVDF) is an industrial polymer with high strength, high elasticity, and resistance to abrasive wear. PVDF is easily dissolved in aprotic solvents, and unlike PTFE, is easily processed from the melt at relatively low temperatures [8]. Another feature of PVDF is its high resistance to the effects of ionizing radiation and UV light [8, 9]. Therefore, PVDF is considered to be a useful polymer for applications in the nuclear industry as well as for other new technologies. This potential use has led to an interest in the effects of various types of radiation on the properties of PVDF. Its irradiation with fast electrons and protons [10], an excimer-laser beam [11], or X-rays [12] results in the formation of an unsaturated, partially fluorinated network structure as a result of dehydrofluorination [3, 9], which results in a substantial change in its properties, especially its mechanical and thermal properties. Irradiation of PVDF by γ-rays from ^{60}Co [13] and accelerated MeV protons [14] is accompanied by significant changes in its molecular-topological structure. Despite numerous studies of the radiolysis of PVDF, there is little literature data on the impact of the combined action of different types of radiation, such as γ-radiation and laser radiation, on the polymer. The aim of this work is to evaluate the influence of γ-irradiation on the rate of laser ablation of PVDF.

2. Experimental

Materials. Industrial PVDF of brand “Kynar” was bought from the company “McMaster-Carr Supply Company” (Atlanta, GA, USA) and was used without any further purification.

Laser irradiation. The laser irradiation of PVDF was conducted in the vacuum chamber of a “VUP-4” system, which has been previously described in [1, 15]; the system was additionally equipped with an “LGN-703” gas-phase continuous CO_2 laser (wavelength 10.6 μm, beam diameter at the target surface 9 mm). A vacuum-tight window from a single crystal of NaCl was used to pass the laser beam into the vacuum chamber.

Gamma-irradiation. The irradiation of PVDF samples with ^{60}Co γ-rays was performed in air at room temperature on a “Gammatok-100” source. The dose rate was 0.5 kGy/h.

3. Results and Discussion

Laser ablation of the initial PVDF. During the laser irradiation, heating of the surface layer of the polymer target occurs before the start of thermal polymer decomposition. The latter occurs very fast and the incubation period of ablation of PVDF is not more than 1 s (Fig. 1, curve 1). After 10 to 15 s of laser irradiation, the ablation rate increases with an acceleration of 0.28 mg/s^2. Upon further irradiation, the ablation rate gradually slows down and reaches a constant value equal to 6.5 mg/s after laser irradiation for 15–20 s. The ablation kinetics is determined by the heat transfer from the target zone heated by IR beam into the volume of the polymer target. After the linear velocities of motion of the thermal front and the layer of target with an intense absorption of laser beam coincide, the ablation proceeds to the stationary mode, which happens after 15 to 20 s of laser irradiation.

Laser ablation of the preliminary γ-irradiated PVDF. The curves for the dependence of the ablation speed on the time of the laser irradiation in the samples of PVDF irradiated with γ-ray doses from 10 to

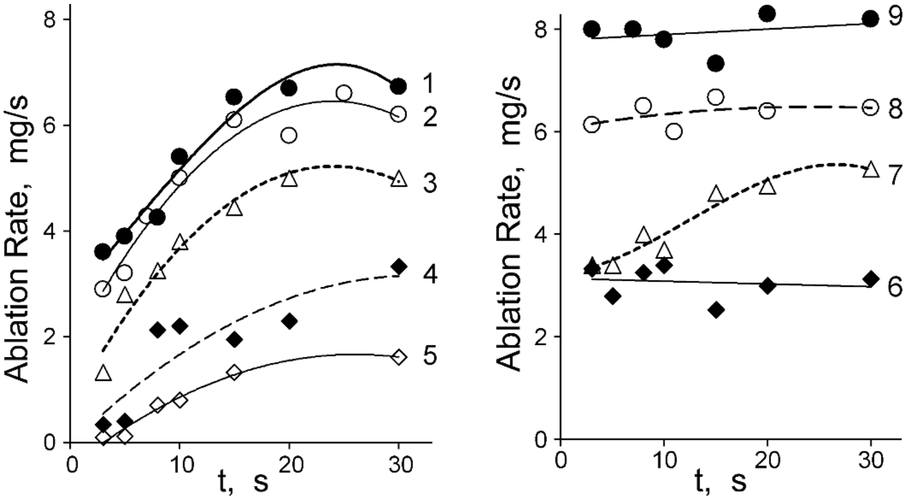

Fig. 1. The dependence of the ablation rate on time of the laser irradiation (1) of the initial PVDF and PVDF irradiated with gamma–rays of dose in kGy: 10 (2), 35 (3), 200 (4), 300 (5), 1000 (6), 2000 (7), 2300 (8), and 3500 (9).

300 kGy have an identical form (Fig. 1, curves 2–6). The curves show an increase in the ablation speed in the initial stages followed by transition to the limiting velocity at 15 to 20 s of ablation.

On curve 4 in Fig. 1 corresponding to a preliminary γ-irradiation dose of 200 kGy, there is considerable scatter of the experimental points, which can be approximated by a flat curve with a smaller acceleration. Perhaps a stationary mode of ablation at such a γ-irradiation dose is achieved by long-time laser exposure, which is beyond the investigated interval of 30 s.

These results allow one to conclude that γ-irradiation of PVDF at doses up to 300 kGy leads to increased stability of the polymer with respect to the action of IR laser irradiation, wherein the ablation rate can be decreased by a factor of 5. Most likely, this is caused by the formation in the polymer of an intermolecular cross-linked structure due to the γ-irradiation. During laser exposure, the cross-linked structure of the macromolecule fragments prevents dissociation into smaller gas-phase species. Thus, there is a complex set of reactions involving the breaking and remaking of chemical bonds, and such processes will have a more complicated dependence of the ablation intensity on temperature and the laser fluence. As a result, breaking n bonds may require n^k times more energy (where $k > 1$) instead of n times. Such a mechanism is consistent with the decrease of a factor of 5 for the ablation rate in the dose range up to 300 kGy.

Increasing doses of preliminary γ-irradiation above 300 kGy changes the trend of increase in the resistance of the polymer to laser radiation in the opposite direction by increasing the ablation rate with increasing the dose (Fig. 1, curves 6–9). Simultaneously the kinetics of ablation changes. This may be due to the fact that the PVDF was greatly degraded under γ-radiation and has a low molecular mass after γ-irradiation. In this case, the evaporation of clusters or molecular fragments during ablation occurs at the lower temperatures present at low laser fluence. Numerical values of the stationary ablation rate in this dosage range are from $\sim$3 mg/s at a dose of 1 MGy (Fig. 1, curve 6) up to $\sim$8 mg/s at a maximum dose of 3.5 MGy (Fig. 1, curve 9). The only exception in this series is a polymer sample irradiated with a dose of γ-radiation of 2 MGy, which has a stationary ablation mode at approximately the same time as the ablation of samples with a low dose of γ-irradiation. The reason for this deviation is unknown. However, the initial and stationary rates of ablation of this sample do show the ablation rate increasing with the dose of ionizing radiation.

The observed nonlinear behavior of the dependence of the ablation rate of PVDF on the dose of preliminary γ-irradiation is clearly illustrated in the curves of dependence of the averaged intensity of ablation in a certain time period (3, 15, and 30 s) of laser irradiation from a dose of γ-irradiation (Fig. 2). The lowest rate of ablation is observed at a dose of 300 kGy. The minimum rate of laser ablation of preliminarily γ-irradiated PVDF upon irradiation with a laser during 3 s is 0.1 mg/s. In the absence of preliminary γ-irradiation of PVDF, the average rate of ablation under the laser beam during 3 s is equal to 3.7 mg/s. After γ-irradiation with a dose of 300 kGy, there is an increase of a factor of approximately 40 of the PVDF resistance to the destructive action of the IR laser beam during the first 3 s.

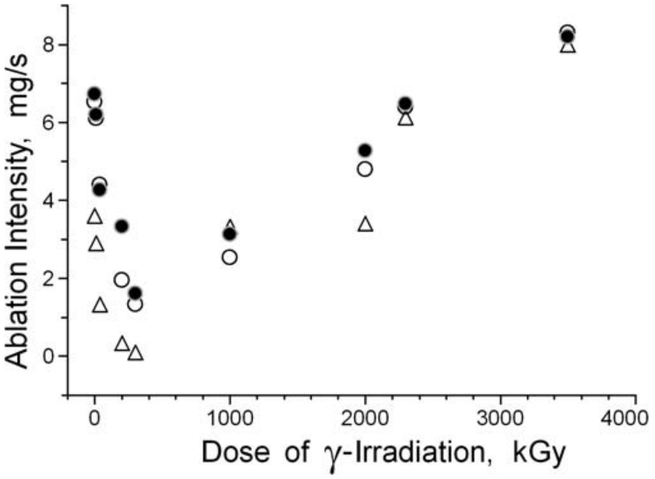

Fig. 2. The dependence of the average laser-ablation intensity during laser ablation of 3 s (△), 15 s (○), and 30 s (●) on dose of preliminary γ-irradiation of PVDF.

The position on the dose scale of the minimum values of the average speed of laser ablation in 15 and 30 s of ablation coincides with the value obtained for ablation in the first 3 s. This suggests the presence of a single mechanism for the joint γ-laser action on PVDF in the initial stage of heating and in the stationary process. The most resistant to IR laser radiation is the PVDF sample pre-treated with a γ-irradiation dose of 300 kGy.

The shape of the initial speed region on the curve of the dependence of laser ablation on the dose of γ-irradiation (Fig. 2) is similar to the curve of dependence of the strength of the same brand of PVDF on the dose of γ-irradiation [16]. In addition, the changes in the strength characteristics of PVDF with the dose of γ-irradiation correlate with the molecular-topological transformations of the polymer irradiated with γ-rays. The observed changes in the molecular–topological and strength properties of the PVDF polymer depend on the dose of γ-irradiation. These changes could be a reason for the decrease in the rate of post-irradiation laser ablation of the polymer for doses of γ-irradiation from 0 to 300 kGy. This is followed by an increase in the rate of ablation for larger doses above 300 kGy. The origin of the extreme dependence of the rate of laser ablation of PVDF on the dose of pre-γ-irradiation of the polymer will be the subject of further research.

4. Summary

A distinctive feature of the laser ablation of PVDF is the extreme nature of the impact of pre-γ-irradiation dose on the rate of the polymer post-radiation ablation. Experiments show that a pre-γ-irradiation dose of 300 kGy increases the resistance of PVDF to the action of IR laser radiation. Under these conditions, a minimum rate of laser ablation is reached. There is then a change in the kinetics of laser ablation from low to high dose preliminary γ-irradiation. A characteristic feature of the kinetics of ablation is a reduction of the output period into the stationary mode of ablation for high doses, which is presumably due to the significant degradation of the polymer, resulting in a change in the molecular structure with the formation of fragments with low molecular weight. It should be noted that the kinetics of laser ablation of γ-irradiated PVDF is significantly different from the kinetics of ablation of polymers such as PTFE [3] and POC [4]. For the latter polymers, preliminary γ-irradiation accelerates their laser ablation process.

Acknowledgments

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