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Laser Ablation of Polytetrafluoroethylene

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Abstract—Anomalous behavior of polytetrafluoroethylene (PTFE) under the action of CO_2 laser radiation in vacuum is discussed. A feature of the ablation process is formation of polymer fibers which quantity depends on the target preliminary treatment and the ablation conditions. Experimental results are set out and possible mechanisms of the polymer fibering are discussed. A conclusion is made concerning two dynamic polymer components differ by the resistance to the laser beam action, appearing in the ablation crater. A method is proposed for producing unique fiber-porous polytetrafluoroethylene materials and other useful products as well as for the polytetrafluoroethylene wastes recycling. The results of industrial application of these new fiber-porous materials are discussed.

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INTRODUCTION

Treatment of polymers with strong energy flows (electron and ion beams, synchrotron and laser radiation, and plasma) induces various physico-chemical processes in the radiation zone depending on the polymer and environment nature and the radiation regime [1–3]. At the thermal, photo and radiation destruction of a polymer are formed many products of different molecular mass that are ejected from the radiation zone forming a crater in the target. In some cases the intense flow of the decomposition products captures and removes from the crater the polymer nano- and microclusters. For denoting such complex process of carrying out a substance under the action of energy flow since recently is used the term “ablation” and the process is classified according to the mode of the acting energetic factor. In this publication we report on the ablation under the action of radiation of a CO_2-laser ($\lambda = 10.6$ μm, $\nu = 943$ cm^{-1}).

Most polymers can be divided into two groups by features of their behavior at the radiation:

(a) the polymers cross-linked and cross-linking under the action of the radiation (polycarbonates, polysulfones, polyimides, aromatic polyamides, etc.);

(b) not crosslinkable polymers (polyolefins, some of fluoropolymers and others).

Note that this classification is not the traditional dividing of polymers to thermoplasts and reactoplasts, because under the critical conditions created at the laser radiation many thermoplasts form a cross-linked molecular structure. The difference between these groups of polymers is that in the radiation zone the first group polymers form two-phase system *solid–gas*, while the group of not crosslinkable polymers affords two-phase system *melt–gas*. This defines both character of the processes and composition of the ablation products.

The ablation flow arising in the initial step of irradiation of the first group polymers consists of the gas and large fragments of macromolecules that by chemical structure are close to the parent polymer [1, 4–6]. At some regimes of radiation appear clusters, that is, the solid particles of the polymer of submicro and micro size.

In the case of not crosslinkable polymers (the second group) the melt formed at overcritical conditions of the laser radiation has too low viscosity, and gas can form bubbles in the melt. When the energy of the gas in a bubble becomes high enough and distance to the target surface is low enough, the gas escapes to the environmental space carrying away particles of the melted polymer. As a result, a flow is formed consisting of gaseous products of destruction of macromolecules, large fragments of molecular chains of biradical type and the melt microdrops.

In the respect of the polymer behavior at the radiation a specific case is polytetrafluoroethylene, that at the action of CO_2-laser in a vacuum does not form a crosslinked molecular structure. At the same time, the melt viscosity in the surface layer of the target is too high and ejection of microdrops to the ablation flow is impossible. In this case an interesting phenomenon can occur: formation at the crater periphery of a crown of long interwoven polymer fibers [1–3, 7]. Such process does not occur at the laser irradiation of any other studied polymer.

In the recent years the interest to the ablation of polymers under the laser radiation has grown being stipulated by the perspective of probable practical application of this method and of the polymeric products that can be obtained. The data accumulated allows to extend scientific view on the physicochemical and thermochemical processes proceeding at the action of radiation on the polymer and on general mechanism of destruction of polymers. This publication is denoted to the studies of ablation of polytetrafluoroethylene using CO_2-laser carried out in the Institute of Mechanics of Metallopolymeric Systems (Gomel, Belarus’) of the Belarus’ National Academy of Sciences since 80th of the last century.

Experimental Study of the Polytetrafluoroethylene Laser Ablation

Devices for the Laser Ablation of Polymers in a Vacuum

In our experiments was used an installation based on an universal vacuum module that provides vacuuming a chamber to the initial pressure at least 2 mPa and supports pressure in the process of ablation at least 100 Pa [2]. Technical versatility of this installation provide focusing and defocusing of the laser beam, additional heating of the polymer sample during radiation, ignition of low- and high-frequency charges in the medium of gaseous products of the polymer decomposition, moving the target relatively to the laser beam, including rotation of the target. Rotation of the sample induces quasi-pulse regime of the action of continuous laser irradiation: each region of the target within the ring defined by the distance between the rotation axis and the ray axis exerts cyclic radiation while the laser radiation and ablation flow remain continuous. For the video registration of the ablation process, inside the chamber near the zone of action of the laser ray on the polymer (ablation crater) is installed miniature digital video camera.

Characteristics of the Initial Step of the Polytetrafluoroethylene Ablation

Polytetrafluoroethylene is quite transparent for the radiation with the wavelength 10.6 μm (Fig. 1).

The CO_2-laser wavelength is shifted by almost 2 μm from the nearest strong absorption peak of this polymer. The main optical phenomenon in the case of polytetrafluoroethylene is radiation scattering by the frontier between crystalline and amorphous zones and between the crystallites differ by orientation. This phenomenon defines principally the transmission of radiation through the polymer. Absorption of the radiation of CO_2-laser occurs mainly in the amorphous areas [8]. At the heating from 300 to 600 K an above the polytetrafluoroethylene extinction coefficient grows 1.4–1.5-fold (depending ion the crystallinity of the initial sample) due to the amorphous material formation [9], and effect of darkening is observed. This thickens the layer that absorbs the laser radiation. For example, while at 300 K occurs loss of 90% of the radiation (absorption and scattering) in the layer 280 μ m thickness (estimation from IR spectra), at 600 K the same occurs at the layer thickness about 80 μm [10] with radiation loss due to absorption only. In the initial step of the irradiation, in the polymer surface layer are formed many localized microareas of energy evolution that coincide with the amorphous areas, and the heat extents over neighboring crystalline areas leading to their heating and melting. Eventually, the radiation is absorbed by all the polymer areas heated above 600 K.

The initial period of the polytetrafluoroethylene ablation at the action of laser radiation passes several steps [10] with the duration depending on the radiation intensity. Initially the target is heated, in some places up to the temperature of red heat (about 1000 K). On the polymer surface can be clearly seen the mode structure of the laser beam (Fig. 2a).

Duration of this step is a few seconds at the radiation of moderate strength 50 W cm^{-2}. The second step with duration 1–2 sec includes formation of gas bubbles and appearance of developed relief of the

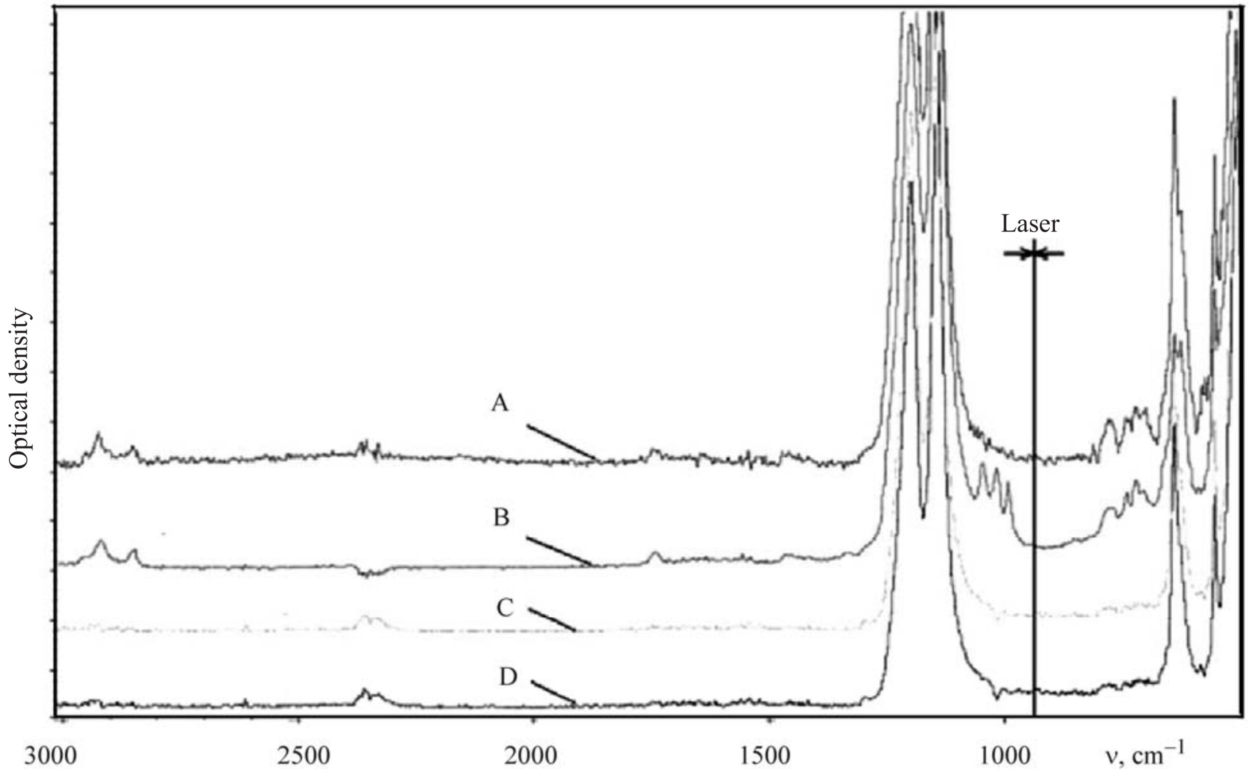

Fig. 1. IR spectra of polytetrafluoroethylene and the products of its laser ablation: (A) fluoroplasrt F-4; (B) fluoroplast F-4M; and (C, D) fibers from F-4 and F-4M, respectively.

surface on the all amorphized surface layer (Fig. 2b): the polytetrafluoroethylene melt foams. In the third step (Fig. 2c) develops the process of local formation of fiber in the points where the irradiation intensity is maximal. The fibers a few hundreds microns length are breaking away and carrying out with the ablation flow from the irradiation zone. In the irradiation zone disappears glow in the visible region that indicates decrease in temperature.

In the fourth step (Fig. 2d), the gas flows from separate microareas are joining and temperature field within the ablation crater are equalized. The net of links between the melt foam cells is disrupted, the most intensively in the center of the crater where the rate of polytetrafluoroethylene decomposition and the rate of gas flow are higher. The fibers lengths increase to the values equal by the order of magnitute to the crater diameter. Stepwise appear the conditions favorable for the fiber breaking away from the layer next after surface in the zones more distant from the crater center. The fibers elongate and achieve the periphery of the irradiation zone, and then being fixed at the crater rim during the whole ablation process they form a peculiar crown (Fig. 2e).

Such a picture is typical for the ablation at the moderate strength of the laser radiation, that corresponds to natural size of laser beam section, by the order of tens and hundreds W cm^{-2}. At the action of the laser beam focused on the formed fiber appears more intense gas flow and the fiber elongating force grows. This force now is higher than the tensile strength of viscous melt even when the fiber is still short. The short fibers are broken away and removed with the gas flow, so the crown does not form. Therefore the fibers obtained at different radiation intensity differ by their appearance (Fig. 3).

The fibers broken away with the flow subside on the surface along the way of their distribution and being in the state of viscous-flow melt form a felt layer fusing together in the points of contact.

After the initial phase of ablationthjat includes the steps described above, in the polymer under irradiation is formed a crater with the surface layer appearing like a cellular net (Fig. 4) from which are pulled the fibers.

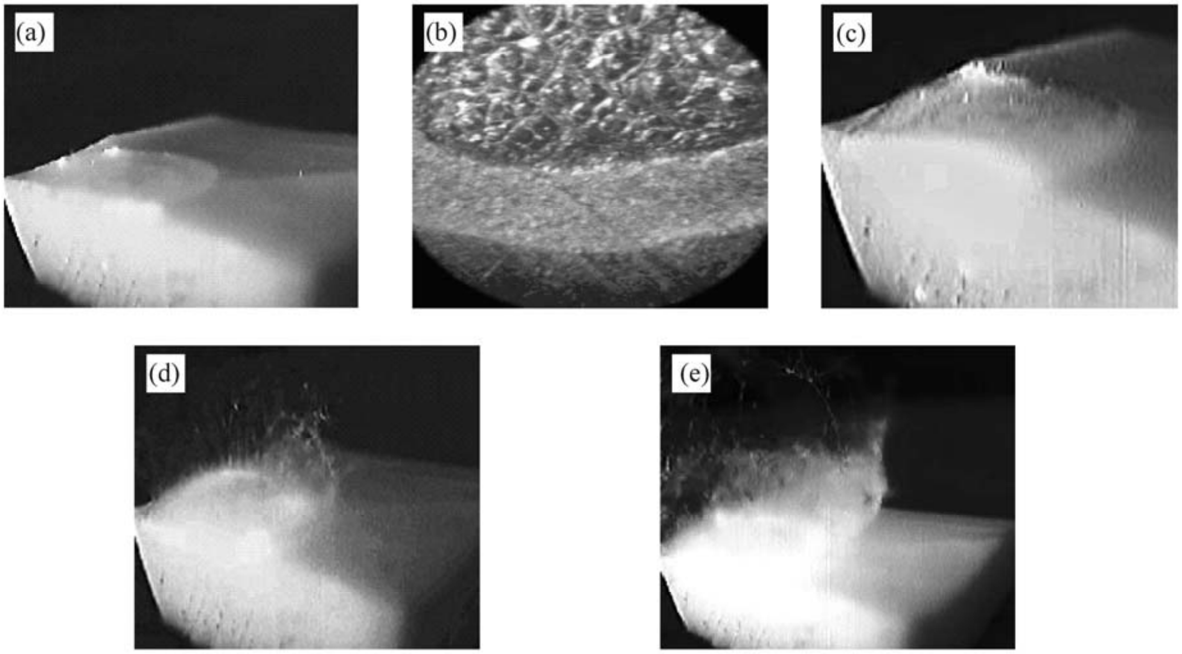

Fig. 2. Photos of polytetrafluoroethylene sample at different steps of laser ablation: (a) end of heating step, after 3 sec of irradiation beginning; (b) formation of bubbles between 3 и 4 s; (c) beginning of fiber grow for 5 s; (d) formation of continuous gas flow during 5.5 s; and (e) formation of crown, during 12 sec. Photos (a), (c) and (d) are registered with digital video camera in the process of ablation; photo (b) view on the surface in optic microscope after stop the process in this step. Laser power 35 W, beam diameter 10 mm.

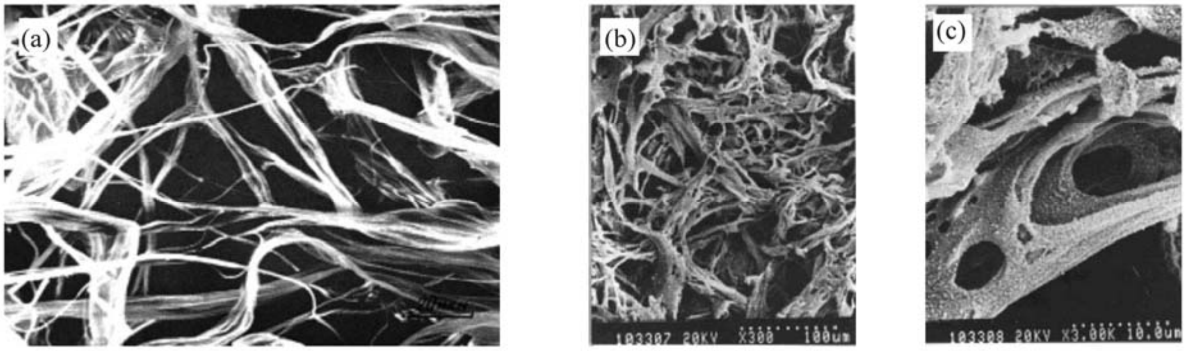

Fig. 3. Polytetrafluoroethylene fibers formed at the irradiation intensity (a) 50 W cm^{-2} and (b, c) 200 W cm^{-2}.

The most unexpected feature of the laser ablation of polytetrafluoroethylene is absolute coinciding of characteristics of the materials of fibers and initial polymer, that is determined by traditional instrumental methods (IR spectroscopy, differential scanning calorimetry, X-ray diffraction an others). The difference has been fixed only by the method of X-ray photoelectron spectroscopy (RFES) (Fig. 5) [11], that characterizes the state of surface layer with the thickness of a few nanometers, that is, occupying 0.2% of the fiber volume or less. It is obvious that would the bulk fiber material had the same structure as is shown in Fig. 5, this should be reflected by IR spectroscopy.

However, at repeated irradiation of the fiber material the ablation picture differs drastically from that observed with the parent polymer. In the irradiation zone are seen bright glowing pints that correspond to the target areas heated above 1000 K, in the products of decomposition there are the fractions

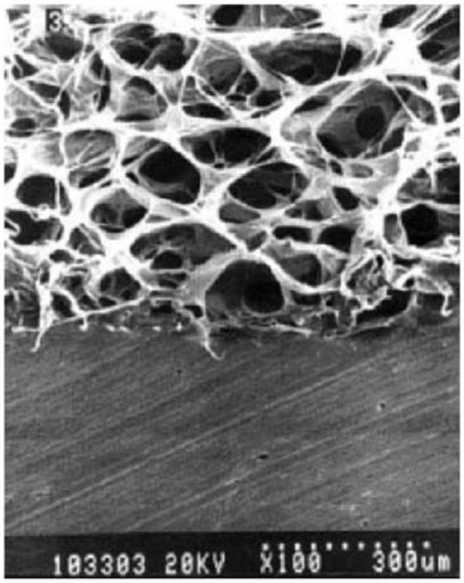

Fig. 4. Section of upper layer of the crater orthogonal to the polymer sample surface.

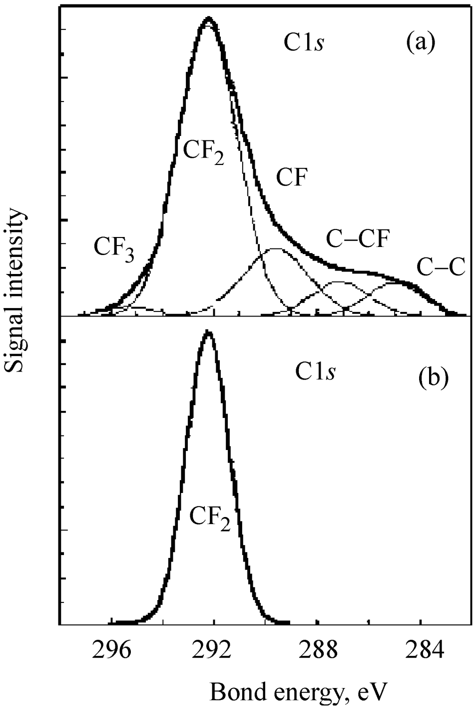

Fig. 5. X-ray photoelectron spectra of (a) polytetrafluoroethylene fiber and (b) of parent polymer.

consisting of heavy fragments of the macromolecular chain that were not observed in the ablation flow of the initial polymer. This fraction is condensed on the solid surfaces as a thin polymeric film. Thus, the mechanism of decomposition of the material of fiber is quite another than at the decomposition of the initial polytetrafluoroethylene. In the base of the differences lie the properties of the products of ablation that are not registered by instrumental methods, but affect considerably the character of laser ablation.

The glowing occurred in the initial step of laser irradiation in the some places of the crater at its formation indicates high temperature of the surface layer. Further, at the stationary ablation this glowing disappears. The registered temperature of the polytetrafluoroethylene sample surface at the continuous action of laser approaches asymptotically the value of 800 K. The experiments showed that the temperature in the crater remains practically the same when the laser beam intensity increases, despite multiple increase in the rate of the target weight loss.

Influence of Conditions of the Laser Irradiation on the Ablation of Polytetrafluoroethylene

The dependence of the process of fiber formation on the pressure is of edge character. At the pressure about 0.6 kPa are formed very short fibers (less than 1 mm) that are distributed by the gas flow over the whole vacuum chamber. The dependence of this edge on the gas medium composition is not found, and the edge is reproduced in residual gases, in argon, in nitrogen and in tetrafluoroethylene. The rate of polytetrafluoroethylene decomposition under these conditions remains practically constant. At elevating the pressure above 20 kPa the decomposition rate falls slightly (by 10–20%). The linear size of the fiber obtained under such pressure falls to the range 1–5 mm. The optimal pressure that provides stable fiber formation and maximal yield of the fiber is 500 Pa and below. At the irradiation in air, in the ablation flow appear glowing torch; the products of laser decomposition burn with evolution of abundant carbon black, and the polymer microparticles do not form in this case.

At the ignition by electric charge, in the gas medium of polytetrafluoroethylene decomposition products the fibers yield initially grows and then stabilizes. When discharge current is high formation of long fibers stops although the rate of the polymer weight loss is not changed.

The principal gaseous product of the polymer decomposition (by the data of mass-spectrometry) is tetrafluoroethylene [5, 12]. The heaver fluorocarbons at the low pressure are formed in trace amount only (les than 1%). The amount of C_3–C_4 fluorocarbons increases at elevating the gas pressure, the most probably due to segondary gas phase reactions of tetrafluooroethylene. Thus, the composition of volatile product of polytetrafluoroethylene decomposition under the action of CO_2-laser corresponds to its low temeperature (800–1000 K) vacuum pyrolysis [13].

In distinct to the treatment by electron beam ablation and ionic spraying [1], at the laser irradiation of polytetrafluoroethylene the polymer film is not formed from the decomposition products that corresponds to the absence in these products of heavy and (or) active fragments of the macromolecules.

Yield of the fiber type products in the initial step is 12–14%, but it grows when the temperature of the preliminary heating of the target is elevated, and at 680 K the yield achieves 24%. The ablation intensity at this temperature grows 3–3.2-fold as compared to the ablation of not heated polymer sample.

Models of the Mechanism of Polytetrafluoroethylene Laser Ablation

Today there is no commonly accepted theory explaining anomalous behavior of polytetrafluoroethylene in the CO_2-laser radiation field. Note that this polymer shows unusual properties, as has been noted by the researchers of different groups [14, 15]. Obviously, the mechanisms inherent in polytetrafluoroethylene defined by its structure and defining its properties are not elucidated completely.

Various models were proposed that in a certain extent explain the observed features of polytetrafluoroethylene ablation [3, 16]. Newly obtained experimental data allowed to ascertain these models and to propose new principles of their creation, and eventually, now is developed a complex model of the processes of polytetrafluoroethylene ablation [8, 11] that includes several submodels [17, 18].

The first component of the model describes the mechanism of transformation of the laser radiation energy into the internal thermal energy of a microheterogenous polymeric structure which components have different optical characteristics. The second submodel explains mechanism of fiber formation under the conditions of laser irradiation.

As is known from the technology of synthetic fiber [19], the ability of a melt to spinning is characterized by the length l of the fiber that can be stretched from the melt without breaking into drops:

$$l = \frac{3\eta}{2\sigma} vd,$$

where η is the melt viscosity; σ is the melt surface tension; v is stretching rate; d is diameter of the fiber.

From this relation follows that with increase in the melt viscosity and stretching rate and with decrease in the melt surface tension the ability to spinning increases.

The polytetrafluoroethylene melt is characterized by a very high viscosity (10^{10}–10^{12} Pa s at 600–660 K [20, 21]) and by exclusively low surface tension (18 N m^{-1}). Hence, polytetrafluoroethylene is a polymer that is the most favorable for the fiber stretching, but only at critical regimes above its decomposition temperature. Both the noted factors are favorable for the obtaining long enough fibers at the drawing, in correspondence with the above relation. Other polymers that are characterized by several orders of magnitude lower η/σ ratio do not capable of the fiber formation. In such cases only one parameter, the stretching rate, can be varied. Higher stretchin rate (by several orders of magnitude) can be achieved only at very intense irradiation, e.g., at the action of extra-short pulses of very high frequency (of course, when at such action leads to appearance of the melt). This is one of the factors contributing to the anomalous ablation of polytetrafluoroethylene.

The third component of the complex model of ablation accounts for the role of defects in the structure of macromolecules in the mechanism of decomposition of the latter. The wave of rapid decomposition into elementary cells propagating along the molecular chain after primary act of its breaking is interrupted when achieves a defect. Therefore the rate of decomposition of the macromolecules possessing defects is lower that of the molecules with perfect structure. The macromolecules with defects are more flexible, and thanks to this becomes possible a reaction of disproportion that also diminishes contribution of the mechanism of chain decomposition. A component containing more flexible macromolecules form the melt used for fiber drawing with lower viscosity. Such quality parameter can be achieved at low concentration of the defects, and therefore they can not be revealed by the method of IR spectroscopy, but are manifested at the repeated ablation of the fiber material: the

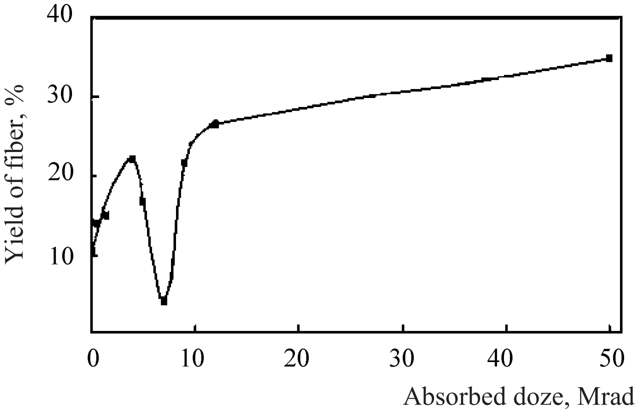

Fig. 6. Dependence of polytetrafluoroethylene fiber yield on the γ-irradiation doze.

ablation flow in this case contains a fraction that is condensed to form a cover which IR spectrum is identical with the spectrum of the parent polytetrafluoroethylene. This fraction is a product of decomposition of macromolecules proceeding at the deceleration of the reaction of chain decomposition.

The fourth component of the considered model describes dynamic process of generation of the molecular defects at the decomposition of polytetrafluoroethylene. Reactions of active gaseous compounds with the polymer molecules lead to the formation of new molecular groups in their chains and of side macroradicals. Such interaction proceeds not only on the surface adjacent to gas phase but also in the boundary layer bulk, to which the active moleculed diffuse.

The role of the defects in the structure of polytetrafluoroethylene macromolecules considered by this model has been verified experimentally: the samples were used containing the defects introduced preliminary by means of γ-irradiation. Fig. 6 depicts a plot of the fiber yield on the doze of the preliminary irradiation .

The complicated character of the plot in the initial step of low doze irradiation shows that thermochemical processes at the laser ablation of the weakly modified polymer is rather complicated, but the general tendency in the changes of the fiber yield at higher irradiaton dozes correspond to the predictions obtained with this model.

In additional experiments were used commercial fluoroplasts F-4M and F-4MB, differ by the presence in their structures of a small amount of perfluoropropylene groups in the ratio one group per 2000 CF_2 links (F-4M) and of perfluoromethyl groups CF_3, about 5 per 100 CF_2 links (F-4MB). At the ablation of the fluoroplast F-4M the yield of fiber was several times higher while in their IR spectra the modifying groups were not registered.

Thus, we conclude that distortion in the regularity of chemical structure of the polytetrafluoroethylene macromolecule that exist in the polymer initially or appears dynamically at the ablation of a polymer with regular structure play the key role. In the second case the modification of chemical structure outrunning its decomposition is defined by the diffusion of the products of surface layer decomposition into the polymer sample bulk.

The carried out investigations do not explain all the observed features of the laser ablation of polytetrafluoroethylene. In part, of interest are radiation and thermochemical processes in the polymer at low doze g-irradiation (in the range up to 7 Mrad). Elucidation of this problem and of other features of the polytetrafluoroethylene ablation requires additional experimental and theoretical investigations.

Practical Application of the Products of Laser Transforming of Polytetrafluoroethylene

On the basis of the effect of laser ablation of polytetrafluoroethylene was developed original technology for producing a fiber–porous material “Grifteks” [22–25] with average fiber diameter 10–15 μm and length 0.2–2 mm. The material porosity is 85–95%. By its chemical properties it corresponds to the parent polytetrafluoroethylene. The material “Grifteks” is hydrophobic, resistant against aggressive liquids and gases and toward UV radiation. By thermal stability it also resembles polytetrafluoroethylene. It is possible to obtain the material “Grifteks” with a high electret charge.

The fiber-porous material “Grifteks” is effective as a filter [26–32]. A series of the filters “Grif” used in various branches of industry has been developed. They can be used for purification of gases from the aerosols including water, oil and acid. They are applied to the purification of compressed air, first of all in the final steps of painting, in bubbling units of halvanic baths, in pneumatic pipe lines, in food industry. The “Grif” filters are perspective for the purification of power transformer oil and diesel fuel. With the usage of the

“Grif” filters are developed the “Grif-brilliant” devices for washing brilliants and “Grif-almaz” for separation of the synthetic diamond products [29, 30]. Application of this material provides 20-fold or even more decrease in exhausting of acids to atmosphere, improves labor conditions, diminishes expenses of exploitation and repairing of auxiliary equipment. The “Grif” filters are effective in the devices for purification of compressed natural gas from condensate at the automobile gas compressor stations and in the systems of preparation of fuel gas for the gas turbine engines [31–32].

Another valuable product obtained at the laser irradiation of polytetrafluoroethylene is a fine disperse powder covering all the internal surfaces of the vacuum chamber during the process. It consists of spherical particles with the size 50–100 nm (Fig. 7) that can also form agglomerates.

Such particles are located also on the fiber surface, therewith their amount grows with the increase in the process duration. Judging from the IR spectra and thermophysical properties, this powder little differ from the parent polytetrafluoroethylene but at the temperature about 590 K it is melted to form a liquid phase. The powder has low bulk density (about 40 g l^{-1}) and is extremely friable. We suggest that this powder is formed at the secondary polymerization of tetrafluoroethylene (the main product of laser decomposition of the polymer) stimulated by the laser radiation. This product is low molecular weight polytetrafluoroethylene, or perfluoriated paraffin.

Combining polytetrafluoroethylene fiber with thermoplasts in composite materials allows to decrease wear of polyamide by an order of magnitude and to avoid seizing details at friction [33, 34]. High porosity and unique properties of the polytetrafluoroethylene fiber make prospective application of such composites in medicine, e.g. as the implants for the soft tissue plasty [35–37], in microwave and piezo technique [38].

Introduction of the laser technology allows utilize side products appearing at producing and exploitation of polytetrafluoroethylene [22, 39]. As known, up to now the problem of wastes treatment and utilization of used details made of this polymer is not solved. Grinding followed by pressing decrease the material quality considerably. The methods of liquidation of polytetrafluoroethylene wastes by means of thermal destruction or action of electron beam afford a wide spectrum of products including quite toxic ones. On the other hand, some of products possess value properties, but the demand does not correspond to the amount of the formed wastes. The laser decomposition of polytetrafluoroethylene wastes allows obtaining new fiber–porous materials and creation of a useful tetrafluoroethylene generator for its further application in the low tonnage chemistry [40].

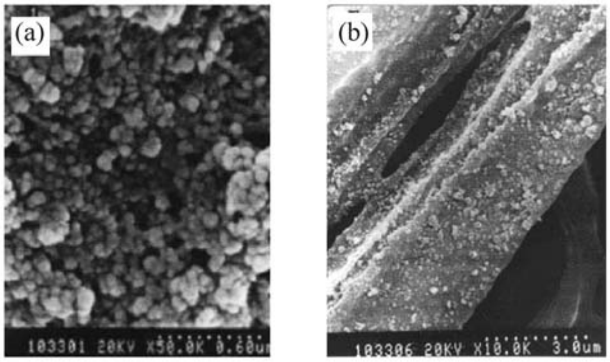

Fig. 7. Fine disperse powder formed at the laser irradiation of polytetrafluoroethylene covering internal surfaces of (a) vacuum chamner and (b) fibers.

CONCLUSIONS

The experimental results and their analysis allow to conclude that formation of fibers at the laser irradiation of polytetrafluoroethylene is defined by the unique combination of various properties of this polymer, including the following:

– existence of two dynamic components formed in polytetrafluoroethylene at the ablation process, of which one has low and stable temperature of decomposition to low molecular weight products in a wide range of intensity of the laser radiation, while another forms under these conditions a melt with the viscosity optimal for stretching the fiber;

– optimal ratio of these components that provides the fiber stretching at the strength of the gas stream;

– low surface tension of the polytetrafluoroethylene melt.

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