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Radiation-chemical modification of PTFE in the presence of graphite

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ABSTRACT: PTFE with a 15% addition of graphite was subjected to irradiation using an electron beam of 10 MeV energy with absorbed doses of 26, 52, 78, 104, and 156 kGy. The effect of electron-beam irradiation on the mechanical, sclerometic, and tribological properties, the crystallinity degree, and the morphology of the polymer surface was examined. It was found that the modification through irradiation entailed a gradual increase in the degree of crystallinity, which had a direct influence on the mechanical properties. An increase in the hardness, Young's modulus, and compressive strength of the polymer irradiated with an electron beam was also demonstrated. The electron-beam irradiation reduced the value of components of the work-of-indentation, showing the growing resistance to deformation. An analysis of the scratch test parameters showed a reduced depth of penetration of the indenter into the material, proportionally to the irradiation value, at relatively constant values of the scratch depth after scratching load removal. A stereometric analysis of the scratch traces on the material allowed to determine coefficients of the wear micromechanism, β, and resistance to wear, W_β. It was found that after irradiation (especially with a dose of 4×26 kGy), a significant quantity of the material showed traces of ploughing, which meant a positive effect on the wear mechanism. The value of the wear resistance coefficient W_β for PTFE subjected to the absorbed irradiation dose increased intensively, which portended a significant reduction of the tribological wear compared to the nonirradiated material. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42348.

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INTRODUCTION

Polytetrafluoroethylene (PTFE) belongs to the group of highly efficient thermoplastic materials and has a number of valuable properties.[1–5] It is characterized by the best thermal resistance among plastic materials used for technical purposes. The highest temperature of its short-term usage is *ca* 300°C, while in the case of long-term usage, it is approximately 260°C. PTFE also has very high chemical resistance. It is insoluble in all known solvents (below 300°C) and resistant to atmospheric conditions. In addition, PTFE has a low friction coefficient (compared to other plastics), as well as perfect insulating power and the lowest dielectric coefficient. A high density of 2.2 g/cm^3 is its another characteristic feature. A 15% graphite addition reduces the friction coefficient, improves rigidity and mechanical strength, and, to a lower degree, improves the resistance to abrasive wear. PTFE without any additives is characterized by a very high wear rate.[6] It is possible to decrease the wear rate of the elements of bearings made of PTFE by three orders of magnitude, by adding different fillers.[7,8] Electron-beam[9,10] or gamma-beam irradiation[4] also contributes to reducing the wear of pure PTFE in a pair with a smooth counterpartner.

The research carried out by Briscoe *et al.*[11] showed that irradiation of PTFE with a gamma beam resulted in a number of considerable changes in the morphology, which have an effect on related properties. The irradiation with a 50 kGy dose contributes to the formation of stable secondary free radicals in freshly irradiated samples. The irradiation with an electron beam, in turn, leads to the formation of acid fluoride groups which easily hydrolyze to acid carboxylic groups in the presence of atmospheric humidity. These groups reduce a high resistance of PTFE to water and oil, which facilitates homogeneous bonding with other materials.[12] The wear resistance of PTFE after irradiation approaches the values obtained when using fillers. The free radicals formed during irradiation may react with one another and create cross-linking bonds between the chains; the irradiation also causes breakage of polymer chains. Descriptions of such reactions, including the types of free radicals participating in the cross-linking, are presented in the articles.[13,14]

Many research groups have focused attention on examining the optimal temperature, dose, and effects of high-energy radiation on PTFE. This study also shows that the electron-beam irradiation at room temperature causes the destruction of the PTFE polymer chains. Cross-linking of the polymer only occurs during irradiation at a temperature closer to the melting point of PTFE.[15–19] The mechanisms that occur in polytetrafluorethylene during high-energy irradiation are described in detail by Khatipov *et al.*[17] The authors demonstrated that the main primary products of polytetrafluoroethylene exposure to ionizing radiation are terminal (CF2—CF2—) and middle (—CF2—CF—CF2—) fluoroalkyl macroradicals resulting from detachment of fluorine atoms and polymer main-chain scission. The yields of terminal to middle radicals for radiation modification in a vacuum at room temperature are in a ratio close to 1 : 10, and the total radiation-chemical yield is 0.07–0.25 (1/100 eV). In the presence of molecular oxygen, the dominating process is formation of terminal (—CF2—CFOO·) and middle (—CF2—CFOO—CF2—) peroxide macroradicals with a ratio close to 1 : 1 of yields and the total yield of 0.12–0.22. The author also demonstrated that at room temperature, fluoroalkyl and peroxide radicals in the polytetrafluoroethylene chain have very long lifetimes and that radiation exposure of polytetrafluoroethylene at high temperatures (above 100°C) causes accumulation of terminal trifluoromethyl and carbonyl groups, as well as of individual terminal and middle double bonds. It was also shown that only near the melting point of the polymer, the low-molecular-weight free radicals CnF $2n+1$ whose recombination with macroradicals yields chain branchings and side branches.[16]

Literature shows that the irradiation does not affect the thermal stability, chemical inertness, electrical property, high weather resistance, water proof, oil proof, high flame resistance but improves properties such as high abrasion resistance, better creep resistance, high radiation resistance, possibility for modification, better processability and provides full control over the properties of adhesive strength, abrasion strength, and mechanical properties.[17] In the case of PTFE, an increase in the wear resistance after irradiation at room temperature[18–20] has also been observed.

Due to the limited availability of electron radiation sources of energy in the order of MeV necessary to penetrate PTFE to a depth of several centimeters, a majority of the available research results refer to the influence of gamma radiation.[20] A major part of the research is also conducted for PTFE without filler additives. The purpose of this study was to investigate the effect of irradiation with an electron beam of energy of 10 MeV on mechanical, sclerometic, and tribological properties of PTFE with a 15% graphite addition.

EXPERIMENTAL

Materials

Research was carried out on commercially available PTFE with a 15% graphite addition (Tarflen® S) in the form of ϕ20 rods, from which 20 mm high cylindrical samples were cut out. The material is produced from a powder mixture with a density of 2.12–2.20 kg/dm^3. The material in its initial condition was marked as BZ_{15}. The irradiated samples were designated as ($N_{15.i}$). The index 15 meant the graphite content, the letter N showed the electron-beam irradiation, and $i=1$–6 referred to the multiplication factor of the irradiation with an absorbed dose of 26 kGy. The modification through radiation was performed using a linear accelerator Elektronika 10/10 (energy of electrons: 10 MeV; beam power: 10 kW) at room temperature 21 ± 1°C. The irradiated samples were stabilized through oxidation by means of thermal processing in a vacuum: heating to a temperature of 200°C for 4 h, soaking for 2 h, and cooling down to ambient temperature for 10 h. Next, all the samples were vacuum wrapped.

Examination of Polymer's Crystallinity Degree

Examinations of polymer's crystallinity degree in initial state and after electron-beam irradiation were performed using the differential scanning calorimetry (DSC) method. Samples of approximately 15 mg for the DSC tests were collected from the central part of the material. The samples were closed in standard aluminum cells. Thermograms of the examined samples melting were registered during heating at a rate of 10°C/min from temperature $T=-40$°C to $T=400$°C using a dynamic differential calorimeter, Mettler-Toledo DSC 1. During the test, dry nitrogen was flowing through the measuring chamber at a rate of 2 mL/min.

Examination of Polymer's Compressive Strength

The effect of electron-beam irradiation on the compressive strength of PTFE was examined using a universal strength testing machine, Instron 5985, at the cross-bar speed of 5 mm/min. Measurements were made at room temperature.

Microindentation Tests

Microindentation tests were performed with the use of a Micron-Gamma machine (manufactured by the Aviation Faculty, Technical University of Kiev) equipped with an additional self-leveling table. The normal force load was consistent with the direction LD of the compressed cylinder. A Berkovich penetrator was used, with indenter load of 1 N, and load time under maximum pressure of 15 s [Figure 1(a,b)]. The hardness, H, and the elasticity modulus, E, were determined with the standard Oliver–Pharr method.[21] After approximation of the load removal curve with the second-degree polynomial, 70% of its scope was covered by the analysis. The measurement results were averaged for 7 indentations. A digital record of the $P(h)$ graph also allowed the determination of the work of indentation represented by the area under the load curve. Figure 1(c) shows the areas representing the particular types of work: W_{tot} is the work of total deformation, W_{pl} is the work of plastic deformation, and W_{sp} is the work of elastic deformation.

Sclerometry Tests

Sclerometry tests were performed with the Revetest Xpress device of CSM, using the Berkovich indenter (Y-275, 200 μm radius). During the scratch tests, a normal force of 4 N and scratching speed of 5.4 mm/min were applied for a scratch around 4 mm long. The following parameters were recorded: the penetration depth under load (PD) and after load removal (RD) and the immediate elastic recovery (NPS) being the difference of PD–RD.

The measurement of the furrow area A and the plastic elevation area B was taken by means of a Taylor Hobson profilographometer with the TalyMap Universal software. A scratch area of 2 × 2 mm was investigated, maintaining a sampling distance of $x=1$ μm, $y=2$ μm. In order to determine the wear resistance

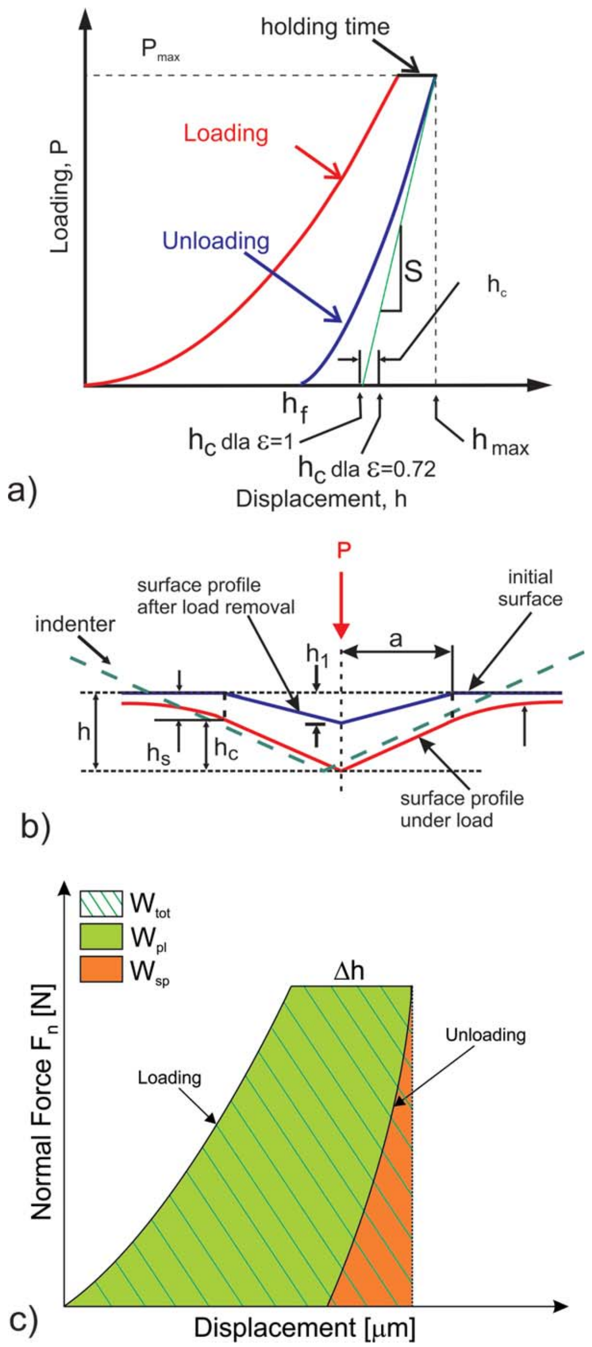

Figure 1. (a) Loading/unloading curve as a function of displacement, (b) material deformation during microhardness examination, and (c) types of work represented by the areas under the load/load removal curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coefficient of the polymers, W_β, 500 profilograms were analyzed. Calculations of the abrasive wear resistance coefficient were made in accordance with the formula:[22,23]

$$W_\beta=\frac{1}{\frac{1}{n}\sum_{i=1}^{n}(\beta_i A_i)} \qquad [\mathrm{mm}^{-2}] \tag{1}$$

where β_i is the coefficient of the micromechanism of the abrasive wear determined from Refs. 24, 25, A_i, B_i are the surfaces of the scratch channel and the plastic elevation lips, measured from profilograms of the scratched surface.

$$\beta=\frac{1}{n}\sum_{i=1}^{n}\frac{A_i-B_i}{A_i} \qquad [-] \tag{2}$$

Examination of PTFE Wear Properties

The tests of PTFE abrasive wear were made for the initial polymer and for the irradiated polymer. In each case, 3 samples were prepared (with $\phi 5$ shanks) by cutting them out from cylinders into which the irradiated PTFE rods were divided. Discs of titanium grade 2 and steel 1H18N9T were used as counter-specimens. The surfaces of interacting elements were prepared so as to obtain roughness in the order of $R_a = 0.2$; this enabled a thin film of PTFE, whose task was to reduce friction, to be deposited during friction. For tribological tests, a pin-on-disc testing stand T-01 (manufactured by ITeE Radom, Poland) was used. The tests were carried out under dry friction conditions. The pressure in the friction couple was 1 MPa. The sliding speed in a one-way rotary motion was 0.1 m/s at a friction distance of 1000 m. Ambient conditions: temperature of 21 ± 1°C, and humidity of 50 ± 5%, complied with the recommendations of VAMAS.[26] The linear wear Z_l was determined as a difference between the indications of the micrometric sensor before and after the test (and after the cooling stage). The friction coefficient was determined as a quotient of the normal force applied, F_n (20 N), and the recorded friction force, F_t.

RESULTS AND DISCUSSION

Changes in the Crystallinity of PTFE After Electron-Beam Irradiation

DSC studies of PTFE irradiated at room temperature showed that the melting temperature T_m of the samples shifts to a higher temperature with the absorbed dose of 26–156 kGy [Figure 2(a,b)]. A similar correlation occurs for the crystallization enthalpy, ΔH_m increases with all doses from 31.04 to 51.39 J/g [Figure 2(c)]. Consequently, the melting heat ΔH_m and the crystallinity degree X_c determined on this basis increase with radiation:[27]

$$X_C=\frac{\Delta H_m}{\Delta H_c}\cdot 100 \qquad [\%] \tag{3}$$

where ΔH_m is the heat of phase transition (i.e., melting) of the investigated polymer sample, determined from a DSC thermogram [J/g]; ΔH_c is the heat of phase transition of completely crystalline polytetrafluoroethylene (empirically determined value amounting to 82 J/g).

The dependence between the degree of crystallinity, X_c, of the tested material and the multiplicity of electron-beam irradiation is presented in Figure 2(d). A high increase in the degree of crystallinity can be noticed (from 37% for the initial samples to more than 62% for the sampled irradiated with a 156 kGy dose). On this basis, it can be assumed that, from the PTFE's functional properties point of view, the effect of the increase in crystallinity will be a direct influence on the polymer's mechanical properties and wear resistance. The cause of the increase in the degree of crystallinity can be associated with the destruction of polymer chains as a major radiation chemical process.

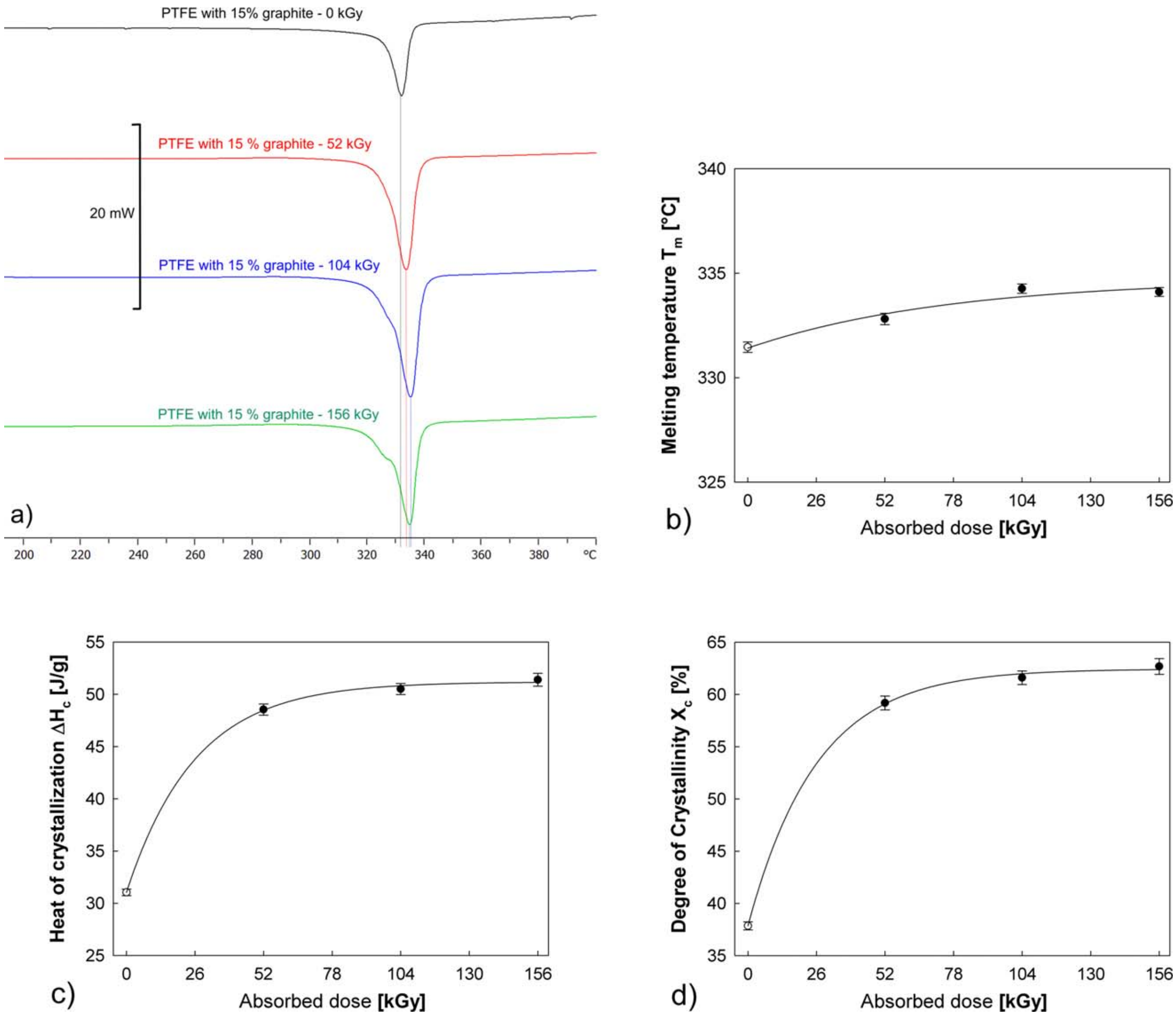

Figure 2. (a) DSC thermograms of PTFE with a 15 % graphite addition. Changes in the (b) melting point temperature, (c) crystallization enthalpy, and (d) crystallinity as a function of electron-beam irradiation absorbed dose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Similar conclusions were published in the article.[19] T_m of γ-ray irradiated XPTFE(XPTFE500) increases with increasing dose, which indicates the macromolecular chain scission of XPTFE by γ-irradiation in the air at room temperature. ΔH_m of irradiated XPTFE500 also increases with dose due to the degradation of XPTFE.

Mechanical Properties of PTFE

Changes in the hardness and Young's modulus of PTFE with a 15% graphite addition induced by electron-beam irradiation are the consequences of the increase in the crystallinity. The course of these changes is presented in Figure 3. The radiation modification of PTFE protects it from the effects of operational loads. The absorption of dose of 104–156 kGy increases the polymer hardness with a simultaneous increase in the Young's modulus of the polymer [Figure 3(a,b)]. It should be noted that at lower absorbed doses of 26–78 kGy, a slight decrease in hardness was observed, as found out after the tribological tests had no effect on reducing the wear of the irradiated PTFE.

In accordance with the micromechanical testing methodology, the indentation process parameters were recorded during the measurement of hardness. The value of the indentation work results from the material's resistance to deformation which determines the depth, surface, and volume of the impression. The measure of the total indentation work (the work of complete deformation, W_{tot}) is the area under the load curve. W_{tot} is the sum of the work of plastic deformation, W_{pl}, and of the work of elastic deformation, W_{el}. Calculations of the respective areas were performed in the Matlab program according to the authors' own script. An analysis of Figure 4 showed that the electron-beam irradiation of polytetrafluoroethylene reduced the value of the indentation work, W_{tot} (and its constituents, W_{pl} and W_{el}), which reflected the increase in hardness as the multiplicity of irradiation increased [Figure 3(a)]. Therefore, the

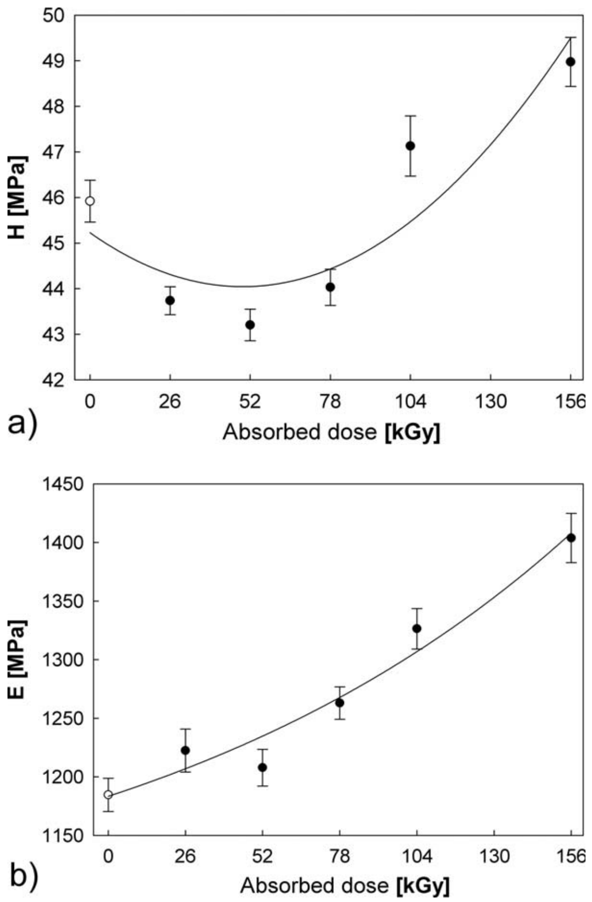

Figure 3. Changes in (a) hardness and (b) Young's modulus as a function of electron-beam irradiation absorbed dose.

work of indentation can be the measure of material's deformability.

The irradiation of the material with an electron beam had an effect also on its compressive strength (Figure 5). R_c increased intensively, especially for the initial absorbed doses of 26 and 52 kGy, and next it stabilized achieving the highest value of 27 MPa for the absorbed dose of 104 kGy. The basic sample, which was not subject to cross-linking, did not fracture.

The Influence of Irradiation on Scratch Test Parameters of PTFE

The influence of irradiation on the scratch test parameters is shown in Figure 6. An improvement in the material's wear resistance (decrease of the PD parameter) with a growing irradiation dose is clearly visible. An increase in the abrasive wear of PTFE as an effect of electron-beam irradiation was also observed in studies.[9,10] This effect may be explained by the increasing crystallinity as a consequence of the modification through radiation. It is worth pointing out, however, that the increasing resistance of PTFE was accompanied with a reduction of the elastic properties represented by parameter NPS [Figure 6(b)].

Parameter β, determined based on a stereometric analysis of scratch traces [Figure 7(a)], shows that a component of the ploughing micromechanism ($\beta \rightarrow 0$) predominated in the polymer subject to electron-beam irradiation. This means that a larger part of the irradiated material (in particular, with the absorbed dose of 104 kGy), underwent plastic deformation during the scratch test and was elevated on the edge of the scratch formed. The abrasive wear resistance ratio, W_β [Figure 7(b)], increased for the absorbed doses of 26–104 kGy, while the 156 kGy dose caused an intensive reduction of this ratio value, which meant that such a dose led to degradation of the material.

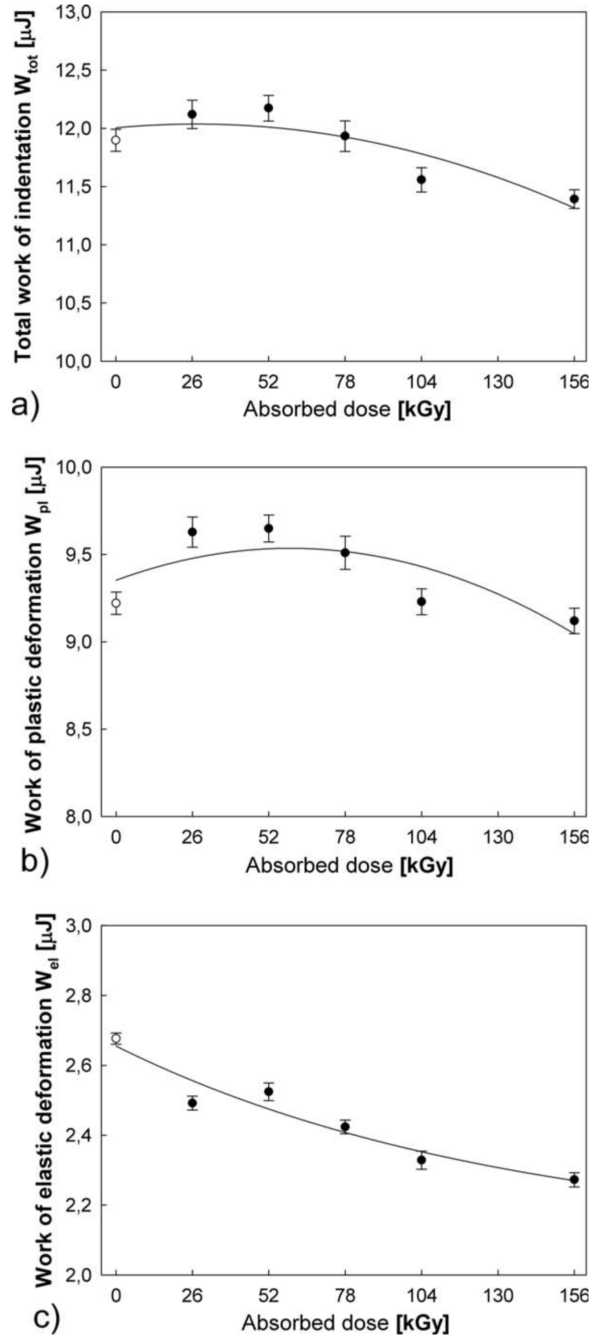

Figure 4. Changes in the work of indentation of PTFE subjected to electron-beam irradiation absorbed dose: (a) the total work of indentation—W_{tot}, (b) the work of plastic deformation—W_{pl}, and (c) the work of elastic recovery—W_{el}.

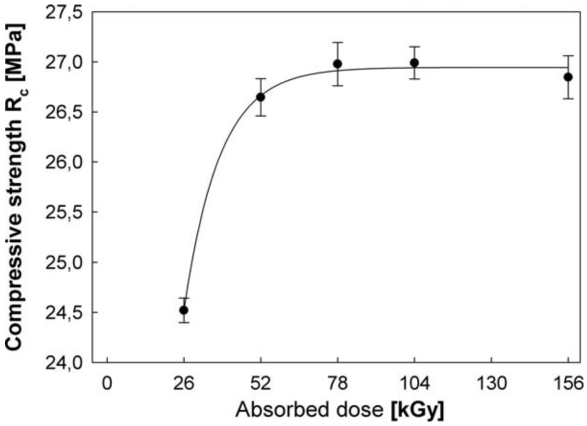

Figure 5. Compressive strength of PTFE subjected to electron-beam irradiation absorbed dose.

The Influence of Irradiation on the Wear of PTFE

A direct effect of modification through irradiation on a reduction of PTFE wear is presented in Figure 8, which shows a linear wear in a unidirectional motion. It can be seen that the irradiation with a 104 kGy absorbed dose caused more than a three times reduction of wear in the case of PTFE's work with a steel counterpartner (stabilized friction coefficient

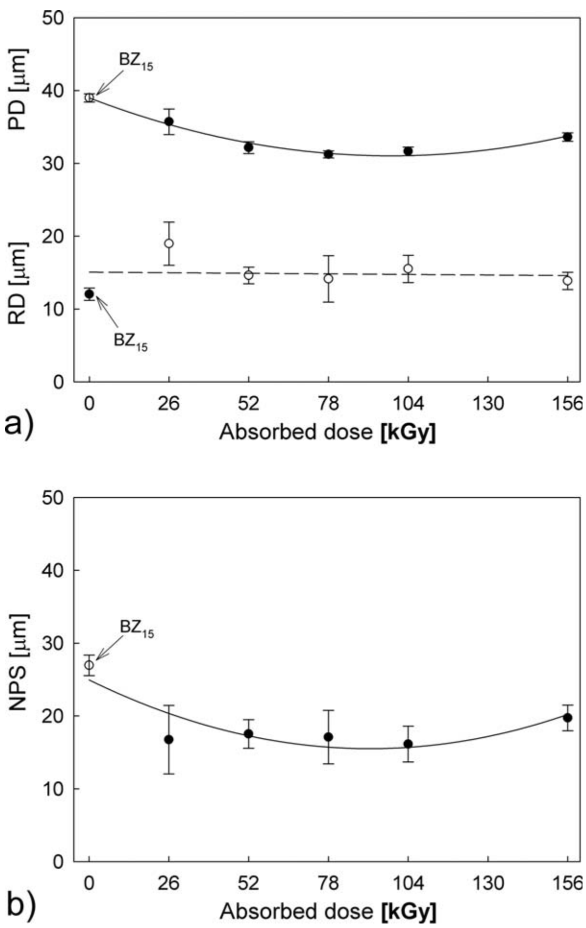

Figure 6. The effect of electron-beam irradiation absorbed dose on the (a) wear resistance PD, RD and (b) elastic properties NPS of the polymer.

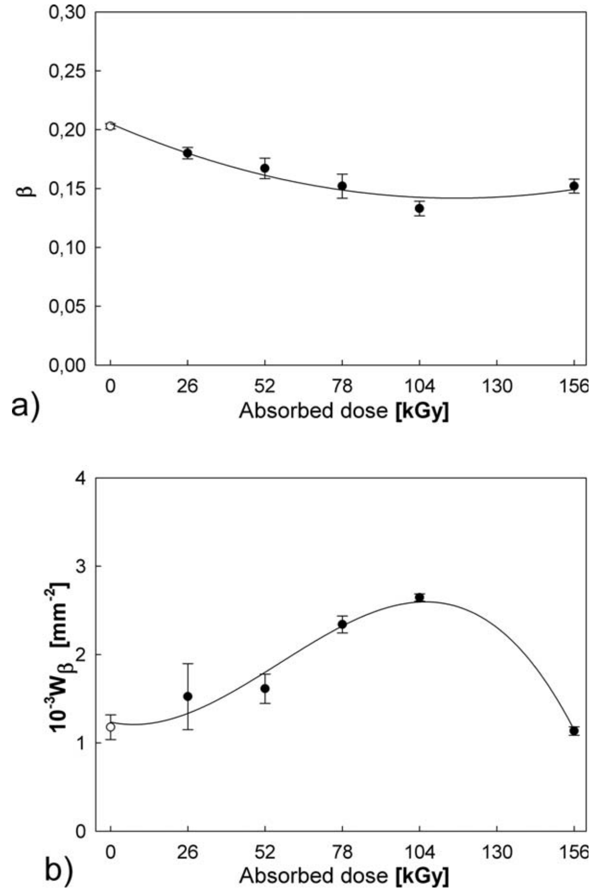

Figure 7. The effect of electron-beam irradiation absorbed dose on (a) the coefficient of micromechanism of the PTFE abrasive wear—β and (b) the abrasive wear coefficient—W_β.

$\mu = 0.1671 \pm 0.007$) and more than a five times reduction of the linear wear during the work with titanium ($\mu = 0.1554 \pm 0.006$).

An evaluation of the work surface of the material before and after electron-beam irradiation was made using profilographometric tests (Figure 9). Convexities and concavities, arranged as

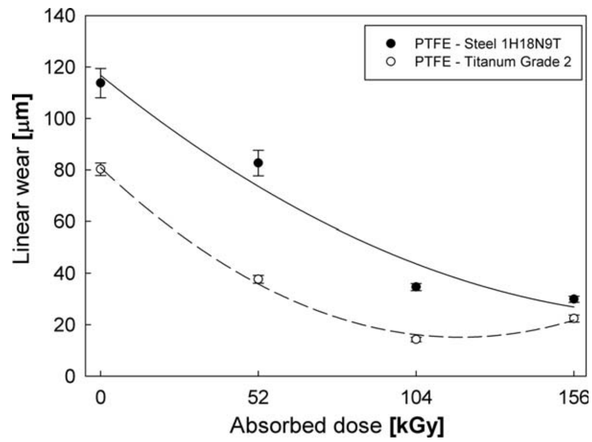

Figure 8. The linear wear in a unidirectional motion wear of irradiated PTFE samples, a disk made of steel and titanium was used as a countersample.

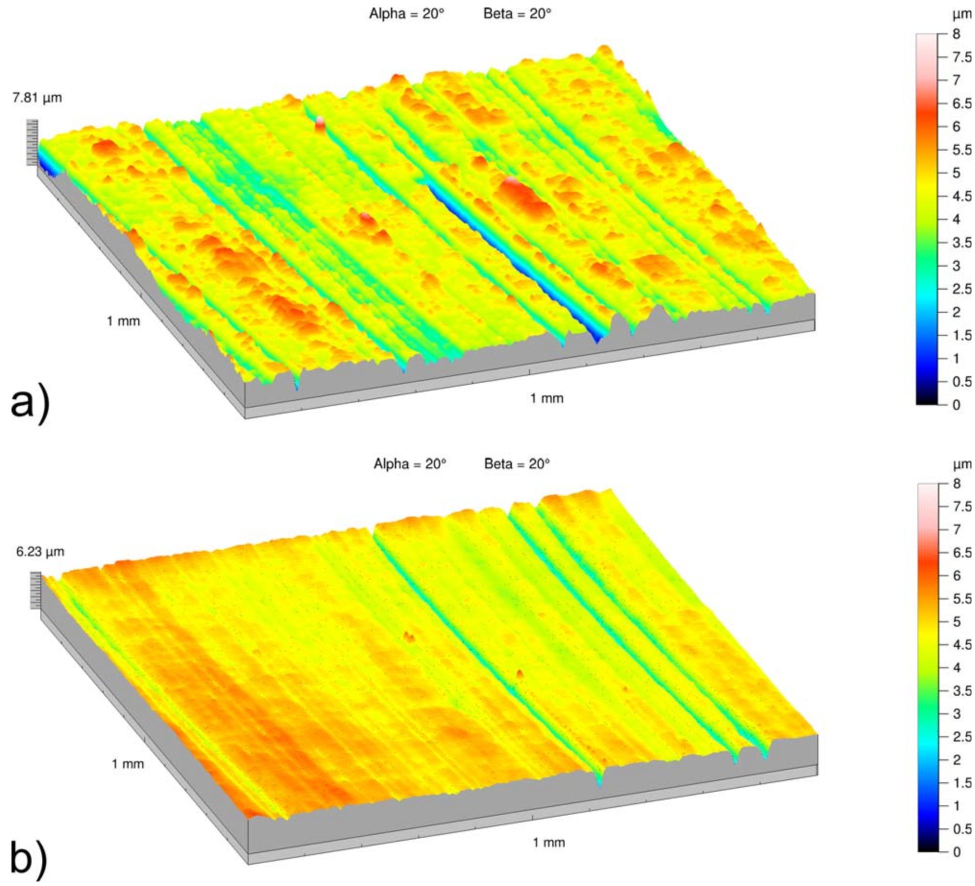

Figure 9. Stereometric structure of the friction surface of (a) the basic PTFE with a 15% graphite addition and (b) the PTFE with the absorbed dose of 156 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bands oriented along the motion direction, can be seen on the friction surface. During the work of the material, the surface was becoming smooth, with smoothness increasing with a higher irradiation absorbed dose. Such a surface morphology indicates the occurrence of lower and lower plastic deformation during the tribological process, as well as a reduced transport of the material from the surface.

CONCLUSIONS

- Destruction of polymer chains is a major radiation chemical process after electron-beam irradiation of polytetrafluoroethylene with a 15% graphite addition.
- Electron-beam irradiation of PTFE with a graphite addition induces a significant increase in the crystallinity degree.
- An increase in crystallinity contributes to an increase in the compressive strength, Young's modulus, and hardness at higher doses determined by means of microindentation.
- The results of the microtests showed a reduced deformability, a change of mechanism β in the ploughing direction, and an increased resistance to abrasive wear, W_β, as a result of irradiation of the material.
- Tribological tests of PTFE showed an approximately 3 times reduction of the linear wear in the case of the irradiated PTFE's work with austenitic steel, and an approximately 5 times wear reduction during its work with titanium.
- Irradiation of PTFE with a dose of 156 kGy causes its degradation which manifests itself through a high hardness, a reduction of the resistance ratio W_β, and an increase in the linear wear.
- Modification of PTFE through its irradiation with an electron beam may contribute to extending the life cycle of this material, e.g., in sliding components which work under heavy load conditions and do not require lubricating.

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