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The influence of electron beam irradiation, plastic deformation, and re-irradiation on crystallinity degree, mechanical and sclerometric properties of GUR 1050 used for arthroplasty

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ABSTRACT: The article describes the influence of an electron beam irradiation (I), plastic deformation (D), and re-irradiation (R) on the properties of ultrahigh molecular weight polyethylene (GUR 1050). It was found that the modification through irradiation entailed a gradual increase in the degree of crystallinity (after irradiation–I). After plastic deformation and re-irradiation (IDR) the degree of crystallinity decreases which had a direct influence on the mechanical properties. The polymer irradiation only (technique I) resulted in an increase in the maximum stress as compared with the material in the initial state. The application of deformation and re-irradiation (technique IDR) allowed increasing the deformation resistance by more than 40%. Moreover, the irradiation with an electron beam resulted in the increase in hardness (H) and Young's modulus (E) proportionally to the applied irradiation dose and in the reduction of total indentation work (W_{tot}) and its components. After deformation and re-irradiation the polyethylene hardness went down. The application of technique (I) caused an improvement to the material abrasion resistance (reduction of parameter PD–working scratch depth) with the increasing irradiation dose. The introduction of deformation and re-irradiation did not have a material impact on parameter (PD) increasing at the same time elastic properties of UHMWPE (increase in parameter NPS–elastic recovery). Modification IDR has changed the wear mechanism (β) toward ploughing and has increased the abrasion-resistance index (W_β) and also significantly reduced the coefficient of friction (μ) of GUR 1050. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43683.

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INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) is a material of favorable set of such properties as chemical inertness, slide properties, impact strength, and abrasion resistance.[1]

UHMWPE has been used in orthopaedics, as a material for elements of artificial joints. Each year nearly 2 million operations of artificial implants implantation are performed and approx. 90% of endoprostheses contains elements made of UHMWPE. A total endoprostheticplasty of the knee joint (TKA) and of the hip joint (THA) became the main treatment enabling patients a return to a normal life. A sudden increase in the number of primary and revision operations has been witnessed during the last decade. It is anticipated that by 2030, the number of artificial hip joint implantations will increase to 572 thousand, and of knee joints to 3,480,000. According to the NIS organization and to the National Hospital Discharge Survey (NHDS), the percentage of revision operation is now minimum 15%. It is anticipated that during the next decade even more reoperations will occur, which results from the elongation of patients life and from increased accessibility of endoprostheticplasty. Such operations create a huge burden to patients and also to the health care systems. Practically, there is one resolution of the problem–the extension of the implants life, including elements made of polymer plastics.[2–4]

Two trends may be distinguished in activities of leading scientific centres, resulting in increasing the polymers abrasion resistance–as a result of chemical structure changes (e.g., by ions implantation, by chemical methods, by irradiation crosslinking) and as a result of microstructure formation (e.g., through heat, thermo-mechanical treatment, compression under high pressure). There is also a third trend, being a natural combination of the aforementioned two. In this case, the crosslinking by e.g., γ rays or by an electron beam precedes the process of deformation and texturing (at a temperature of 110–200 °C)[5–7] or the irradiation modification is applied after the material deformation.[7] The stress relief annealing is applied at the end of most

of those methods to form the polyethylene structure and properties. It reduces the anisotropy of properties and removing a substantial part of free radicals stabilizes polyethylene from chemical point of view (oxidation resistance).[5–12]

Methods for polymer forming for implants described in the second and third group of methods are relatively complicated, labor consuming, and costly and in addition the ultimate effect depends on the situation of the UHMWPE working surface, type of movement (one- or multidimensional) and on the roughness of the metal counterpartner surface.[13–17]

The aim of the study was polyethylene modification, consisting in orientating, through a lamellar microstructure deformation, of previously irradiation cross-linked polymer and then in the re-irradiation (IDR). The sequence of those three forming actions should ensure improvement to mechanical and sclerometric properties and as a result–to increasing the abrasion resistance.

EXPERIMENTAL

Material

Polymer GUR 1050 (manufactured by Quadrant PHS MediTECH Division Deutschland GmbH) was the tested material, which in the initial state was designed as BZ_{50}. It was supplied in the form of rods, 25 mm in diameter and 1 m in length. In the as-received condition it had a molecular weight of -9.2×10^6, and density = 0.93 g/cm^3. For the tests, ø20 mm cylindrical specimens were prepared, 20 mm in height.

Tests were carried out on deformed specimens of initial material, preliminary irradiated with an electron beam (I_{50}) and re-irradiated with an electron beam after deformation. In the used markings, index 50 corresponds to the tested polymer grade, letters I and D indicate specimens irradiation and deformation, re-irradiation letter–R, while $i = 1$–4 stands for the number of absorbed doses of 26 kGy. The irradiation modification was performed on a linear accelerator Elektronika 10/10 (electrons energy 10 MeV, beam power 10 kW) at room temperature 21 ± 1 °C. The irradiated samples were stabilized by a thermal treatment–samples were immersed in glycerin and heated up to the temperature of 130 °C in 4 h, then annealed at that temperature for next 2 h and allowed to cool down slowly during another 10 h.

Polymer Crystallinity Examination

Examinations of polymer's crystallinity degree in initial state, after electron-beam irradiation and irradiation-deformation-irradiation were performed using the differential scanning calorimetry method (DSC). Samples of approx. 15 mg for the DSC tests were collected from the central part of the cylindrical samples of material. The samples were closed in standard aluminium cells. Thermograms of the examined samples melting were registered during heating at a rate of 10 °C/min from temperature $T = -40$ °C to $T = 180$ °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. The melting temperature was determined on a thermogram for the maximum of an melting endotherm. The degree of crystallinity was calculated from the formula[18]:

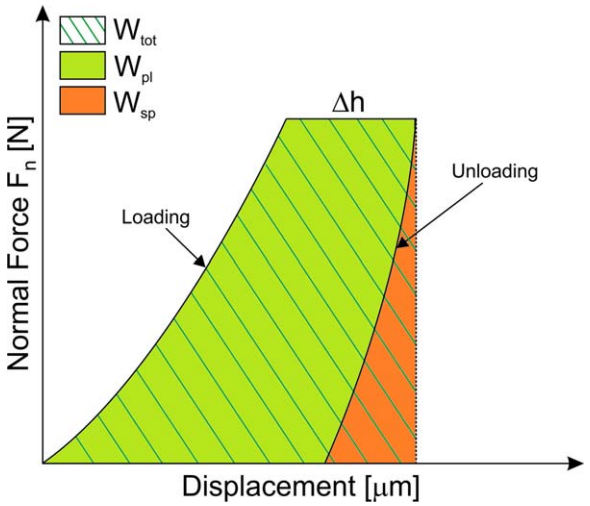

Figure 1. Types of work represented by the areas under the load/load removal curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\chi_C = \frac{\Delta H_m}{\Delta H_c} \cdot 100[\%] \quad (1)$$

where: ΔH_m–the heat of phase transition (i.e., melting) of the investigated polymer sample, determined from a DSC thermogram [J/g]; ΔH_c–the heat of phase transition of completely crystalline polyethylene (empirically determined value amounting to 293 J/g).

Examination of Polymer's Compressive Strength

Uniaxial compression of cylindrical specimens was carried out at room temperature on an Instron 5,985 machine at the crossbeam speed of 5 mm/min. The specimens for compression tests had a diameter of 20 mm and height of 20 mm. As part of each compression test, 5 repetitions were made. In the case of modification technique, IDR deformation $e_f \approx 0.5$ was applied after the preliminary irradiation, resulting in partial orientation of lamellar structure, followed by re-irradiation. Also the influence of applied forming techniques on polyethylene behavior during compression was determined. At the moment of maximum load, the system was unloaded without holding on and the maximum stress was determined $\sigma_{max} = P_{max}/A_0$, ($P_{max}$–the maximum force registered at 50% of specimen dimension change, A_0–the initial cross-section of specimens). Measurements were made at room temperature.

Microindentation Tests

Mechanical properties of polymers were determined using a Micron-Gamma instrument (produced by the Faculty of Aviation, Kiev University of Technology), equipped with an additional self-leveling table. In hardness tests, seven indents were made for each specimen, at randomly selected places. The load by a normal force was consistent with the LD direction of the compressed cylinder axis. A Berkovich penetrator was used in microindentation tests, the load of 1 N, the time of holding under the maximum load −5 sec (Figure 1). A standard Oliver-Phare method[19] was used to determine hardness H and Young's modulus E. After approximation of the unloading curve by means of a second degree polynomial 70% of its scope was

covered by the analysis. Measurement results were averaged for seven indents. A digital record of $P(h)$ graph allowed determining also the indentation work, represented by the area under the loading curve. Figure 1(c) presents areas representing individual types of work: W_{tot}–the work of total deformation, W_{pl}–the work of plastic deformation, and W_{sp}–the work of elastic deformation. Measurements were made at room temperature.

Sclerometry Tests

Sclerometry tests were performed on a Revetest Xpress instrument of the CSM company, using a Rockwell indenter (Y-275, radius of 200 μm). A normal force of 4N was applied during the scratch test and the scratching speed was 5.4 mm/min at the scratch length of approx. 4 mm. The penetration depth under load PD (during a scratch test), after unloading RD (measured after elastic recovery), and the immediate elastic recovery being the PD-RD difference were registered. In the scratch test, three scratches were made on each specimen.

The measurement of the furrow area A and the plastic elevation area B were measured using a Taylor Hobson profilographmeter with the TalyMap Universal software. A section of scratch, 2 × 2 mm in size, was examined preserving the sampling distance of $x = 1$ μm, $y = 2$ μm. To determine the wear resistance coefficient W_{β} the analysis covered $n = 500$ profilograms.

In sclerometric tests of the layer situated on the front surface of cylindrical specimens, the calculations of the abrasive wear resistance coefficient were carried out based on formula.[13,20]

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

where β_i–coefficient of the micromechanism of the abrasive wear determined from,[21,22] A_i, B_i–are the surfaces of the scratch channel and the plastic elevation lips, measured from profilograms of the scratched surface

$$\beta = \frac{1}{n}\sum_{i=1}^{n}\frac{A_i - B_i}{A_i} \quad [-] \tag{3}$$

Tribological properties of polyethylene were determined during scratching (friction coefficient $\mu = F_t/F_n$). Measurements were made at room temperature.

RESULTS AND DISCUSSION

The topological structure of the polymer, including the chains entanglement, has a strong influence on its properties. The chain segments confined by entanglements create a molecular network, in which they fulfil the function of physical cross linkages.[1] Such structure determines the course of many processes and determines polymer properties, e.g., the crystallization process, the deformation resistance, mechanical properties or the abrasion resistance. The irradiation by an electron beam results in crosslinking of the UHMWPE amorphous phase, while the dense and ordered crystalline phase remains practically unchanged.[23] This has a direct influence on material's deformation resistance.

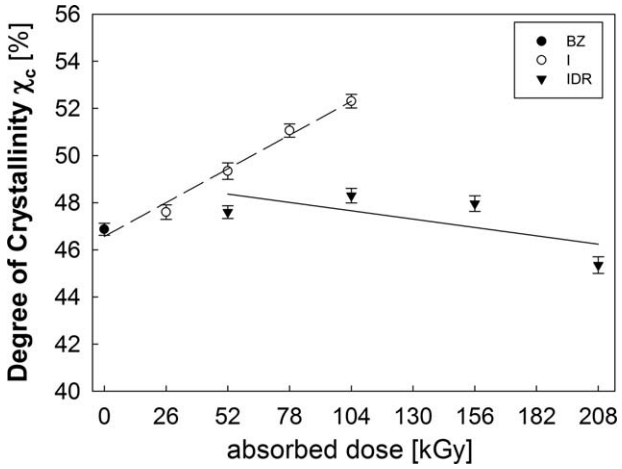

Figure 2. Changes in the crystallinity as a function of electron-beam irradiation absorbed dose.

Changes in the Crystallinity of UHMWPE after Electron Beam Irradiation

DSC studies of UHMWPE irradiated at room temperature showed that the crystallinity degree χ_c determined on this basis increase with radiation absorbed dose from 46.87% (0 kGy) to 52.31% (104 kGy). The analysis of the results of the IDR technology, has shown that plastic deformation with value $e_f \approx 0.5$ applied after first irradiation causes a decrease crystallinity degree, as compared to samples subjected only to irradiation *I*. The decrease in the degree of crystallinity does not prevent re-irradiation performed after compression. A minor decrease may be caused by crystalline phase degradation and/or a certain decrease in the share of the high-molecular fraction under the influence of the applied deformation load. The dependence between the degree of crystallinity, χ_c, of the tested material and the absorbed dose of electron-beam irradiation is presented in Figure 2.

Mechanical Properties of Ultra High Molecular Weight Polyethylene

The compression was carried out till a total cold work $Z_{tot} = 50\%$, and then the system was unloaded without holding under the maximum load. Materials in the initial state (BZ), irradiated by an electron beam (*I*), and shaped by the IDR technique were compared. Figure 3 presents the results.

Approx. 12% increase in the maximum stress σ_{max} for the polyethylene irradiated with a dose of 104 kGy ($N_{50.4}$) was found as against the material in the initial state (BZ_{50}). The application of deformation and re-irradiation increased the deformation resistance by more than 40% (from 68.6 MPa to 114.6 MPa). This effect could have been caused by radiation crosslinking of polyethylene as a result of irradiation and forming by deformation, during which the high-molecular fraction share increases and the originated cross linkages make the main chain stiffer, reducing this way the polymer permanent deformability. In our previous articles, we investigated the effect of deformation applied before and after irradiation on the mechanical and tribological properties of the UHMWPE.[13,15,23,24] In the first place, we found that the specimens deformed before and after

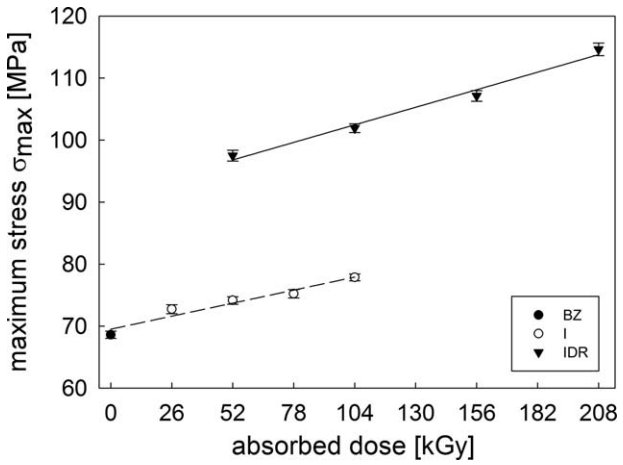

Figure 3. Changes of maximum stress σ_{max} for GUR 1050 polyethylene–initial BZ, irradiated *I* and formed by irradiation-deformation-irradiation IDR as a function of the amount of absorbed electrons dose.

irradiation had lower hardness. We also achieved a decrease in the value of the coefficient of the wear micromechanism, β, compared to the material subjected to irradiation only. A lower value β of the material showed an advantage of the ploughing mechanism, which was a desirable phenomenon. The value of the wear resistance coefficient W_β increased intensively for the sequence with deformation before and, in particular, after irradiation, which reflected the significant reduction of the tribological wear. Long-term tribological studies showed a more than 6 times reduction of the mass wear and a 13 times reduction of the linear wear for the material modified through irradiation and deformation, compared to the unmodified material. For the UHMWPE shaped through deformation followed by irradiation, these values were lower and amounted to a 4 times reduction of the mass wear and an 11 times reduction of the linear wear, respectively. In the discussed article, the simplest and most frequently applied shaping technique (electron-beam irradiation) is compared with a sequential pattern of irradiation–deformation–re-irradiation.

The value of absorbed electron dose and the order of forming actions application in the performed varieties of polymers modification technique affected mechanical properties (hardness *H*, Young's modulus *E*). Obtained relationships are presented in Figure 4.

An increase in hardness and Young's modulus with the growing number of irradiations by an electron beam has been observed for the *I* and IDR technique. Smaller *H* and *E* values for the technique using deformation (IDR) may be noticed when comparing effects of structure reconstruction obtained for the two forming methods. This is an advantage of this method, because as it has been shown in[23] the reduction of UHMWPE hardness results in the limitation of polyethylene machining mechanisms and in the increase in the abrasion resistance. The obtained results show also that the intensity of hardness and Young's modulus increase is maintained with the amount of the absorbed irradiation dose for the polyethylene formed by the IDR technique. A similar course of hardness and Young's modulus

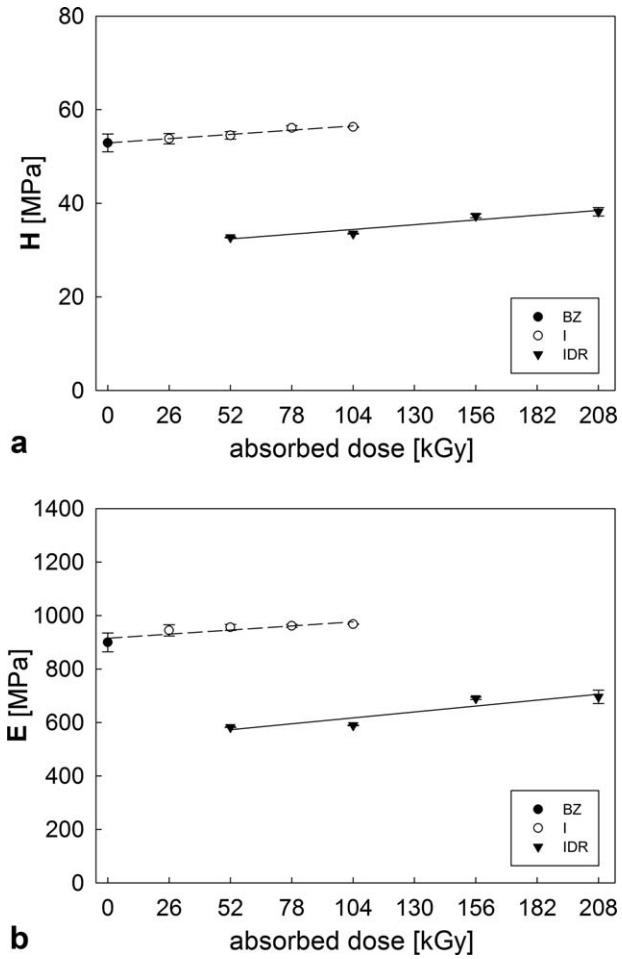

Figure 4. Changes of hardness *H*–(a) and Young's modulus *E*–(b) of GUR 1050 polyethylene in the initial state BZ, after irradiation *I* and after forming by irradiation-deformation-irradiation IDR as a function of the electron irradiation dose.

changes has also been found (Figure 5), common for all forming techniques. This inter-relationship (with correlation $R = 0.996$) of parameters *E, H* could have been determined by eq. (4):

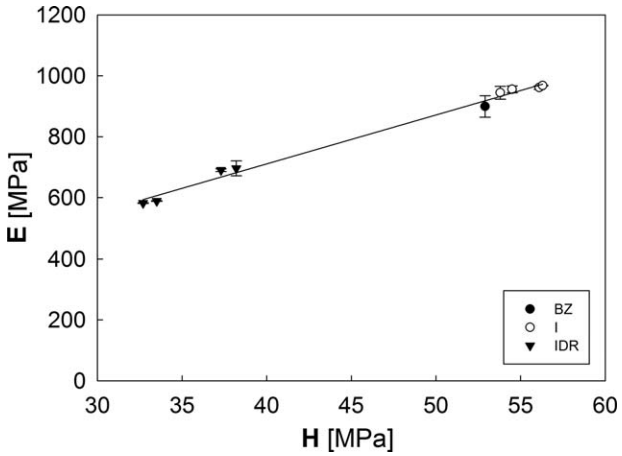

Figure 5. Inter-relationship of Young's modulus and hardness for polymers formed acc. to techniques *I*, IDR and for the initial material BZ.

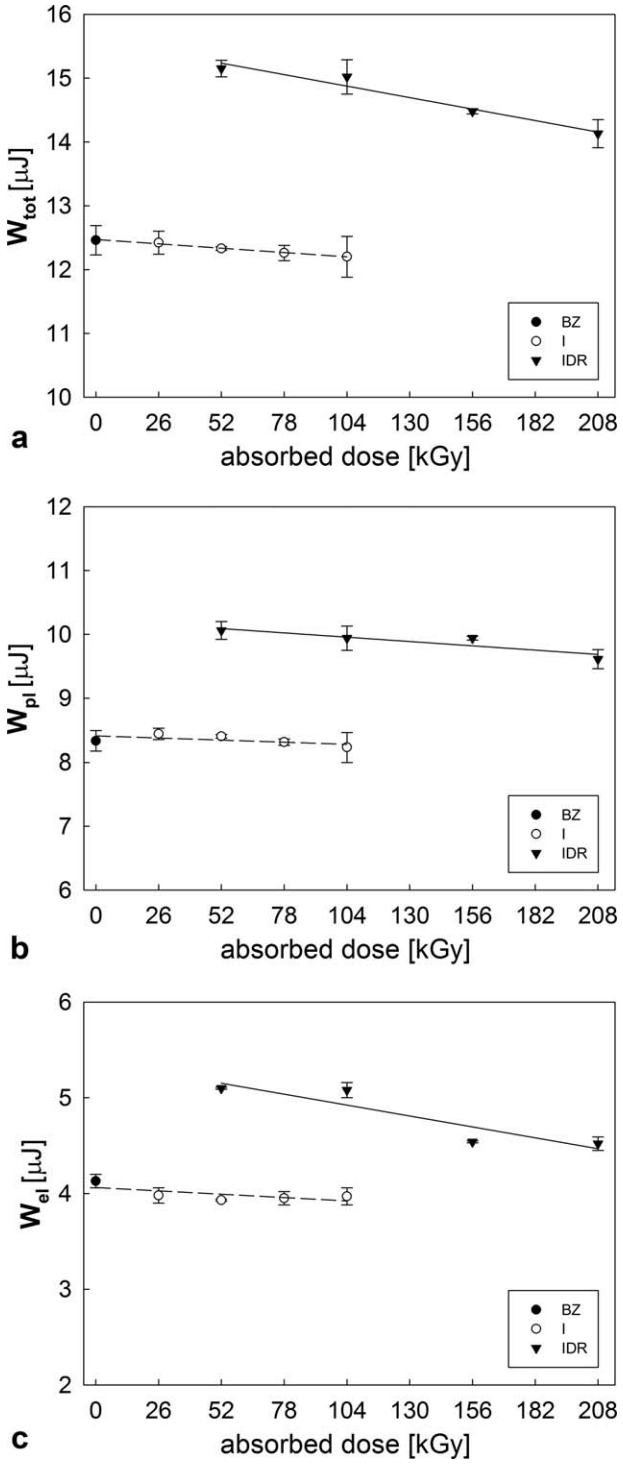

Figure 6. Changes of indentation work for GUR 1050 polyethylene in the initial state and after various forming methods (I, IDR): total indentation work W_{tot}–(a), plastic deformation work W_{pl}–(b), and the elastic recovery work W_{sp}–(c).

$$E = 16.05H + 68.54\,[\mathrm{MPa}] \quad (4)$$

Loading-unloading curves obtained at the hardness measurements allowed determining also the indentation work. This work is related to material's deformation resistance and it is described by such parameters as the indent depth, area, and volume. The total deformation work W_{tot} is the entire area under the loading curve. It is a sum of plastic deformation work W_{pl} and of elastic deformation work W_{sp}.

Based on the obtained results, it is possible to state that for the material subject to forming by irradiation-deformation-irradiation the value of indentation work W_{tot} (and of its components W_{pl} and W_{sp}) increases, which indicates a reduced deformation resistance (Figure 6).

The irradiation by an electron beam has as opposite effect on polymer as compared with deformation–the value of indentation work gets reduced, which means a higher deformation resistance. The case of 2-time and 4-time polyethylene irradiation with the use of deformation $e_f \approx 0.5$ (IDR), when at the same time there is a high value of W_{tot}, W_{pl}, and the highest of W_{sp}, can be considered the most favorable sequence of forming actions.

Sclerometric and Tribological Properties of UHMWPE

The analysis of scratch test parameters PD, RD, NPS has provided a preliminary assessment of UHMWPE forming technique effectiveness. The application of irradiation by an electron beam

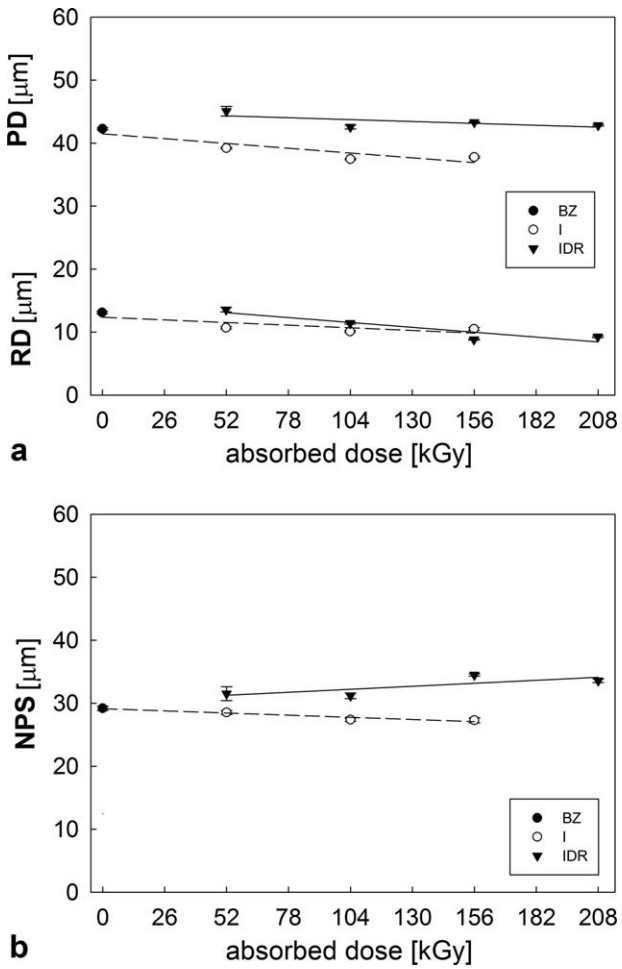

Figure 7. The influence of the forming technique on the abrasion resistance PD, RD–(a) and on elastic properties *NPS* of GUR 1050 polymer–(b).

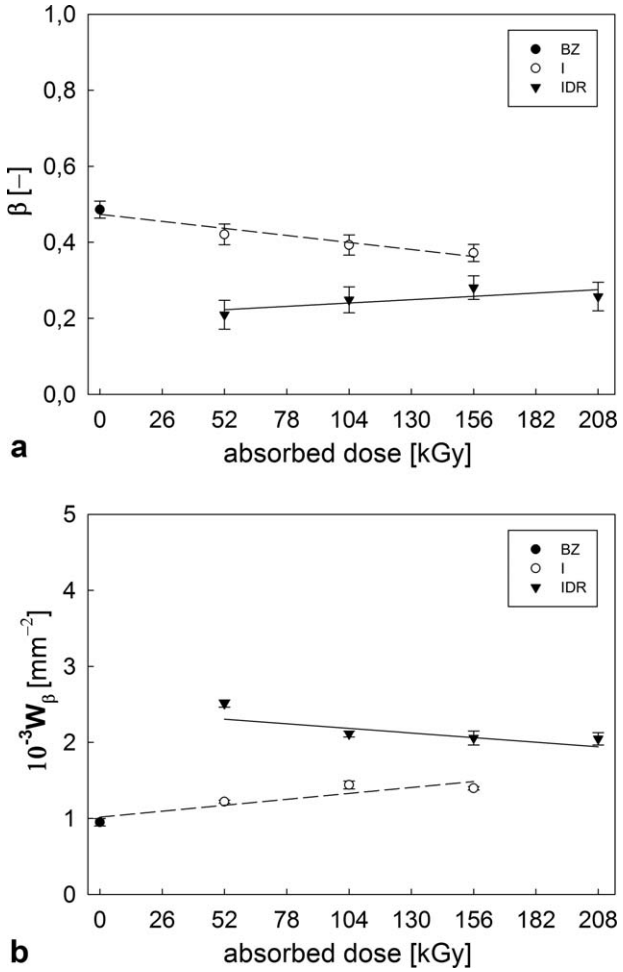

Figure 8. The influence of the forming technique on the GUR 1050 wear micromechanism β–(a), and the abrasion-resistance index W_β–(b).

caused an improvement to the scratch resistance (reduction of parameter PD) with the increasing irradiation dose. This result may be explained by the increase in the crosslinking density and in the crystallinity degree after the irradiation modification.[23]

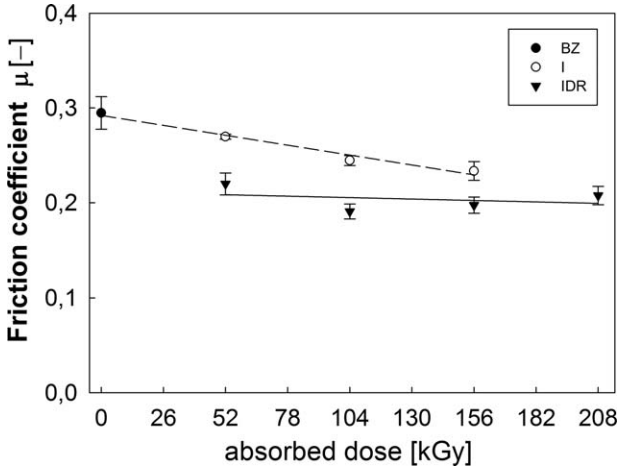

Figure 9. The influence of the forming technique and of the absorbed irradiation dose on the friction coefficient μ of GUR 1050 polymer.

However, it should be noted that the resistance increasing with the irradiation (decline of parameter PD) is accompanied by a small decrease in elastic properties represented by parameter NPS [Figure 7(b)]. Instead, the application of technique IDR results in increasing the GUR 1050 elastic properties at a small increase in the value of parameter PD, which indicates a possibility of material's wear reduction.

The stereometric analysis of material scratches provides more precise information. Parameter β determined on its basis shows, that in the polymer subject to modification by technique IDR the ploughing micromechanism prevails ($\beta \rightarrow 0$), especially in the case of absorbing a summary dose of 52 kGy and 104 kGy [Figure 8(a)].

This means that in the GUR 1050 polyethylene irradiated by an electron beam, subject to plastic deformation and re-irradiation, majority of furrow material is plastically deformed during the scratch test and is uplifted at the edge of the forming scratch. This was proven also by the increase in the abrasion-resistance index W_β [Figure 8(b)]. The obtained results show a possibility of substantial reduction of tribological wear of material after the IDR treatment as against the initial material as well as against material only irradiated by an electron beam. The application of highest irradiation doses results in a small decline of index W_β. Value of W_β is higher than in specimens subject only to radiation crosslinking.

Also the influence of UHMWPE modification technique on the coefficient of friction μ was determined during material's scratch test (Figure 9).

It has been found that in the case of technique *I* there is a nearly 17% reduction of the coefficient of friction as against the initial material; the application of the deformation and irradiation (IDR) results in a 30% reduction of the coefficient of friction (in the case of absorbed dose of 52 and 104 kGy), which may have a direct impact on a large reduction of the wear of endoprostheses acetabulums made of material modified using this technique.

CONCLUSIONS

The obtained test results show a possibility of substantial extension of the working life of endoprostheses acetabulums made of polyethylene modified by the irradiation by an electron beam, deformation and re-irradiation. Changes in the GUR 1050 polymer structure, caused by the application of modification *I* (irradiation by an electron beam) and IDR (irradiation-deformation-irradiation), result in:

1. A significant increase in the crystallinity degree. Irradiation-deformation and re-irradiation causes crystallinity decrease;
2. A 12% increase in the maximum stress σ_{max} in the case of technique *I* and a nearly 40% growth of deformation resistance for technique IDR as compared with the material in the initial state;
3. An increase in hardness *H* and Young's modulus *E* together with the amount of the absorbed irradiation dose; the application of deformation and re-irradiation reduces the value of both parameters;
4. An improvement to material's deformation resistance (decrease of parameter PD) with the increasing irradiation

dose; instead, technique IDR results in improving the elastic properties of GUR 1050 at a small increase in parameter PD caused by the plastic deformation;

5. A change of wear mechanism β toward ploughing and a high increase in the abrasion-resistance index W_β (especially for technique IDR);
6. A decline of the friction coefficient μ by 17% in the case of technique I and by 30% for technique IDR as compared with the initial material.

These changes in the properties of the polyethylene modified by irradiation, deformation and re-irradiation (IDR) indicate reaching the target of the work, which can cause a long life of the polyethylene endoprostheses.

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