Resistance of UHMWPE to Plastic Deformation and Wear and the Possibility of Its Enhancement Through Modification by Radiation

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ABSTRACT: The operational durability of a kinematical polymer–metal system, required in many applications, including endoprostheses used for the total knee or hip joint arthoplasty, depends largely on high resistance to wear and permanent deformation of the polymer cup, especially in its near-surface layer, contacting with the metal part. In this study, the wear and deformation resistance of two ultra high molecular weight polyethylene (UHMWPE) grades used in arthoplasty, GUR1020 and GUR1050, as well as the possibilities of its enhancement by radiation treatment were studied in detail. An influence of the molecular characteristic of these grades on functional properties, including permanent plastic deformation, microhardness, elastic mod-

INTRODUCTION

Operational durability of the polymer-metal kinematical systems used in technology and medicine (arthoplasty) depends to a considerable degree on the resistance of polyethylene, which is commonly used for cups in endoprostheses, to the plastic deformation as well as to abrasive and adhesive wear.^{1–3} Many attempts were undertaken in the recent years to improve the wear characteristics of the polymermetal couple including new types of materials, application of anti-wear upper layers and implantation of ions of selected chemical elements on the col-laborating surfaces.^{4–6} However, in about 90% cases of arthoplastic procedures, the conventional and the most cost-effective polyethylene-metal couple is still used. To improve the performance of an artificial joint, two basic approaches have been used: physical modification of the microstructure of polyethylene and modification of its chemical structure. The first takes advantage of plastic deformation inducing molecular orientation of polymer (usually at eleulus, coefficient of the micromechanical wear were studied. The properties of GUR 1050 of higher molecular weight were found advantageous over GUR 1020 grade. It was also confirmed that irradiation with electron beam is an effective method of modification, resulting in an improvement of both resistance to permanent deformation and wear of UHMWPE. It was demonstrated that microhardness, Young's modulus, and wear resistance coefficient increase proportionally to the irradiation dose applied. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polyethylene; UHMWPE; irradiation; deformation; wear; mechanical properties

vated temperature, above 110°C), and is frequently combined with post-deformation crosslinking.⁷⁻¹⁰ In this method, however, the orientation of the working plane of the joint must be precisely adjusted with respect to the direction of the prior deformation. In our previous studies, approximately fivefold reduction of susceptibility to permanent deformation and tribological wear was achieved for the UHMWPE (the Chirulen 1120 grade by Ticona). This effect was achieved by a combined application of relatively small plastic deformation (compression at room temperature to the permanent true strain of $e_f = 0.14$ -0.32) and electron beam irradiation (26 and 52 kGy). The rather small deformation was intended to induce only some subtle morphological changes, too small to destroy the initial isotropic overall structure, rather than heavy orientation of the entire polymer sample. As a result of such treatment, in operational conditions, the thickness of the deformed upper layer of polyethylene reduced, its crystallinity degree and reorientation of the lamellar phase were modified, the degree of structure arrangement increased, and, as a consequence, the operational durability of polymer was improved.¹¹⁻¹³

The progress in physical modification slower than expected led in the last decade once again to an increasing interest of the chemical methods of structure modification, primarily by polymer crosslinking.

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Among three main routes of chemical crosslinking, chemical generation of free radicals, use of silanes and irradiation, the last method is the most important from the practical point of view in manufacturing of artificial joints. It includes the widely used irradiation with the γ radiation and the less frequent electron beam irradiation. The method of crosslinking of UHMWPE together with many side effects assisting irradiation were reviewed by Lewis¹⁴ and by Kurtz.¹⁵ McKellop et al.¹⁶ concluded that for achieving a very good wear resistance of UHMWPE the irradiation dose of 10 Mrad (100 kGy) is usually enough, while higher doses can lead to some deterioration of the properties (e.g., crack resistance) of the material.

Recently, an increasing attention has been paid to more safe and economic irradiation with an electron beam. It was found that application of doses higher than 25 kGy facilitate scission of long chains, spatial rearrangements of the structure, and effective crosslinking of UHMWPE. The higher doses, even up to 150 kGy, when combined with post-irradiation thermal treatment, results in an increased resistance to oxidation, and a considerably enhanced resistance to wear.^{17,18} Premnath and Bellare¹⁹ noted, however, that after electron beam irradiation with the 20-200 kGy dose and subsequent aging of the polymer in air (prolonged storage at room temperature) an increase of the melting temperature and crystallinity proportional to the dose was observed. That increase was as high as 5% immediately after irradiation and grew up to 7-13% after storage of the material at room temperature for 5-29 months. An alteration of the crystalline structure indicated by the increase of crystallinity and melting temperature can result in a substantial decrease of toughness and resistance to brittle fracture. In addition, after the period of approximately 30 months some decrease of the crosslinking degree was also observed.

The literature of the last decade documents, that to increase resistance to wear and aging of UHMWPE, the polyethylene grades of the highest molecular weight, and a balanced proportion of crystalline and amorphous phases had to be used for manufacturing the artificial joints.²⁰⁻²² It was recommended that these guidelines had to met in the production process of the resin, by modification of the molecular weight distribution through a change of the proportion of polyethylene species of different molecular weights. This had to result in conservation of high structural stability as well as improved thermal resistance and resistance to the effect of operational factors.²³ Several years ago, two special medical grades of UHMWPE were introduced into the market by Ticona to increase the life-time of endoprostheses. These grades were GUR 1020 and GUR 1050 with the molecular weight of $5 \cdot 10^6$ and $9.2 \cdot 10^6$ g/mol, respectively. The wide clinical use of endo-

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prostheses with cups produced from GUR 1020 and GUR 1050 grades encouraged us to do a deeper analysis of the properties of these polyethylenes. Two important aspects were targeted:

- Determine the deformation and wear resistance of neat polymers and a possible improvement of these properties by electron beam irradiation (26–104 kGy).
- Determine some parameters of the resistance to deformation, microhardness, and the frictional wear in the near-surface layer of the deformed polymer. This is performed on the basis of microindentation and sclerometric measurements since any direct investigation of the deformed layer during the tribological test would be extremely difficult because of size and geometry limitations.

EXPERIMENTAL PROCEDURE

Two medical grades of UHMWPE: GUR 1020 and GUR 1050, provided by Ticona GmbH (molecular weight of 5×10^6 and 9.2×10^6 g/mol, respectively, density of 0.93 g/cm³) were used in this study. The polymers were provided in the form of rods manufactured by compression molding. Such rods are widely used as a product for endoprosthesis acetabular cups.

The samples of neat GUR 1020 and GUR 1050 (coded BZ₂₀ and BZ₅₀, respectively), samples deformed plastically (coded BZO₂₀, BZO₅₀), irradiated with an electron beam and then deformed $(NO_{20,k}, NO_{50,k})$, and irradiated only $(N_{20,k}, N_{50,k})$ were investigated. The codes BZ, N, and O indicate the initial neat material, irradiated, and deformed samples, respectively. The indices 20 and 50 refer to the tested grades of GUR 1020 and GUR 1050, while k = 1-4 means the multiplication factor of irradiation with a dose of 26 kGy. Electron beam irradiation was performed using a linear accelerator, Elektronika 10/10 (energy of electrons: 10 MeV; beam power: 10 kW). The dose delivered to the sample in a single pass was 26 kGy. Samples were irradiated in one up to four passes, so the total dose was ranged 26-104 kGy. To extinguish all free radicals, left the irradiated samples they 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.

It was assumed that the deformation induced in polyethylene during the operation of a kinematical system can be simulated through the effects of static compression of the polymer samples in a press. Uniaxial compression of cylindrical samples was performed with the Instron 1195 universal testing

The Stress and Strain Range in Compression Experiments Performed						
σ_{tot} (MPa)	Z _{tot} (%)	Z _{ef} (%)	e _f			
50–287	40-80	13–49	0.14-0.66			

TABLE I

machine. The samples were compressed with the rate of 5 mm/min at room temperature. Total compression of Z_t of 40, 50, 60, 70, and 80 % was applied (three samples were prepared for each compression intended). The compression Z_t is defined by:

$$Z_t = \frac{\Delta h}{h_0} \cdot 100\% \quad [\%] \tag{1}$$

where h_o is the initial height of the sample, h_1 is the height of sample under maximum load, and $\Delta h = h_1 - h_0$ is the height reduction due to compression. After reaching the assumed compression, the sample was immediately unloaded. The load P_t corresponding to the applied compression Z_t was recorded and the nominal stress, $\sigma_t = P_t/A_0$ (A_0 is the initial cross-section area of the sample) was calculated.

The unloaded samples were allowed to recover partially the strain in both elastic and inelastic processes. The permanent, effective compression was determined after 10 days of recovery using the following equation (h_f is the final height of the sample):

$$Z_{\rm ef} = \frac{h_0 - h_f}{h_0} \cdot 100\% \quad [\%]$$
 (2)

The effective, permanent plastic strain can be expressed in terms of the true strain (Hencky strain):

$$e_f = \ln \frac{h_0}{h_f} \quad [-] \tag{3}$$

The effective compression Z_{ef} and the plastic true strain e_f are related through the equation:

$$e_f = \ln \frac{100}{100 - Z_{\rm ef}}$$
 [-] (4)

The recovered elastic deformation component Z_{el} was determined as a difference between Z_t and Z_{efr} given by eqs. (1) and (2).

The range of variation of the stress and strain parameters in compression experiments performed in this study is presented in Table I.

For the analyzed set of the compression data, the interdependence of stress σ_t and strain parameters Z_t , Z_{el} , and e_f , was approximated with equations of the linear regression, demonstrating the correlation coefficient $R \ge 0.99$:

$$\sigma_t = \pi \frac{R_e}{2} \left(e^{e_f} \right)^n \quad [\text{MPa}] \tag{6}$$

$$\sigma_t = 5\frac{R_e}{2} + w_{\rm el} \left(e^{Z_{\rm el}}\right)^{0.7}$$
 [MPa] (7)

where:

 R_e the yield stress of the neat polyethylene (R_e = 21 MPa for both GUR 1020 and 1050, according to the manufacturer's data),

 $w (= w_0 + w_k)$ intensity of the stress response on strain: $w_0 = 1.58$ and 1.78 MPa/% for GUR 1020 and 1050, respectively (as estimated for the neat materials BZO₂₀ and BZO₅₀) and $w_k = 0.16\sqrt{k}$ (estimated from the data of the electron-irradiated samples NO_{20.k} and NO_{50.k}),

k (= 1 - 4) the multiplication factor of the electron beam irradiation dose (d = 26 kGy),

 $n \ (= n_0 + n_k)$ the coefficient of increase of the material resistance with increasing true plastic strain $(n_0 = 3 \text{ and } 3.36, \text{ estimated from the data of the neat samples BZO}_{20}$ and BZO₅₀, and $n_k = 0.13\sqrt{k}$, estimated from the data of the electron-irradiated samples, NO_{20.k} and NO_{50.k}),

 $w_{\rm el} \cdot 10^{7}$ intensity of the stress response on the elastic strain: (taken as 1.5 and 2.5 MPa/% for neat sample BZO₅₀ and the irradiated samples NO_{50,k}, respectively, and as 4.5 and 9 for BZO₂₀ and NO_{20,k}, respectively).

Micromechanical and sclerometric properties of the studied polymers were determined with the Micron-Gamma instrument (made at the Technical University of Kiev, Ukraine) equipped with a selfleveling table. In both micro-tests, the load was applied parallel to the loading direction (LD) of the prior compression experiment (which compression simulated the pressure exerted by the endoprosthesis head on the working surface of the polymer cup), i.e., the front surface of the plastically deformed cylindrical sample, which is perpendicular to LD, was directly probed. In the micro-indentation test, a Berkovich penetrator was used. The applied load was 1 N, and the time under maximum load was set to 15 s. To determine the microhardness H and the Young modulus E, the standard Oliver-Pharr method was applied. After approximation of the unloading curve with a 2nd rank polynomial, an upper 70% of the approximated curve was taken for further analysis [cf. Fig. 1(a,b)]. The results were averaged for seven independent micro-indentation tests.

In sclerometric tests, the Berkovich indenter was positioned with the pyramidal chisel tip was pointing toward the direction of the scratch movement. During the scratch test, a normal force of 2.5 N and the speed of 90 μ m/s were applied for a 7-mm long scratch. The scratched channel area *A* and the plastic lips elevation area *B* were measured with the Taylor



Figure 1 Loading/unloading curve as a function of displacement (a), and material deformation during microhardness examination (b) cross-section diagram of a scratch formed during a scratch test (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hobson profilographometer with the TalyMap Universal software [cf. Fig. 1(c)]. A 2 mm × 2 mm section of the scratch was probed, with the sampling distance of $x = 1 \ \mu m$ and $y = 2 \ \mu m$. For the analysis, 500 profilograms were collected and analyzed for each specimen to determine the wear resistance coefficient W_{β} .

The wear of polyethylene was studied only for specimens of not deformed neat and irradiated samples. For every sample, three cylindrical specimens, 5 mm in diameter and 12 mm long, were machined from the 12-mm thick sections of the irradiated rod samples of 25 mm diameter. A disk made from the Vitalium® alloy (60% of cobalt, 20% of chromium, and 5% of molybdenum) was used as a counter-sample. The working surfaces of specimens were prepared according to the ISO 7206-2 standard. The "pin-ondisc" type instrument T-01 (ITeE, Radom, Poland) was used for tribological measurements. The normal stress was set to 2 MPa. The sliding speed in unidirectional rotation of the disk counter-sample was 0.137 m/s, and the total path was 68 km. A very light lubrication with distilled water (0.6 mL/min, $T = 36 \pm 2^{\circ}$ C) was applied. The ambient temperature of 21 \pm 1°C and relative humidity of 50 \pm 5% were maintained during the test. The linear wear Z_l was determined as the difference of the micrometer probe readout prior to and after the wear test (including the cooling period).

The studies of the annihilation of positrons were performed for sample of GUR 1050 polyethylene. The purpose of this study was to find out any trend in variation of the free volume centers (nanovoids), possibly produced in polyethylene by plastic deformation and a combined action of electron irradiation and permanent deformation. It was expected that the tendency found would correspond to the observed changes of mechanical and wear properties, as e.g., *H*, *E*, or W_{β} . For this purpose, the positron lifetime spectroscopy was applied, with the isotope ²² Na in the form of sodium chloride used as the source of positrons. The third constituent of the annihilation spectrum was analyzed, for which, the orthopositronium lifetime is the longest. This constituent is connected with the molecular structure of the polymer to the greatest extent. The Tao-Eldrup formula was used in the calculations,²⁴ calibrated using a number of molecular compounds and liquid.^{24,25} Analysis of the spectra, each of which consisted of ca. 200,0000 acts of annihilation, was performed by means of the LT 9 software.²⁶

RESULTS AND DISCUSSION

The stress–strain relationships found for the samples studied are presented in Figures 2–4. An analysis of changes of strain parameters Z_t , e_f , and Z_{el} related to the maximum compressive stress σ_{tot} based on transformation of eqs. (5)–(7) to the following relations:

$$Z_{\text{tot}} = \frac{1}{0.06} \ln \left[\frac{1}{w} \left(\sigma_{\text{tot}} - \frac{\pi R_e}{2} \right) \right] \quad [\%]$$
 (8)

$$e_f = \frac{1}{n} \ln \left(\frac{2}{\pi R_e} \sigma_{\text{tot}} \right) \quad [-] \tag{9}$$

$$Z_{\rm el} = \frac{1}{0.7} \ln \left[\frac{1}{w_{\rm el}} \left(\sigma_{\rm tot} - 5 \frac{R_{\ell}}{2} \right) \right] \quad [\%] \tag{10}$$

When the compression stress σ_{tot} is small, the difference between strain of neat samples and samples



Figure 2 The dependence of total deformation under load on the nominal compressive stress.

modified by irradiation is hard to notice. However, for larger stress one can easily observe some differences in strain, which suggest that GUR 1020 grade of the lower molecular mass (samples BZO_{20}) is more susceptible to permanent deformation than GUR 1050 (samples BZO_{50}); the strain measures Z_t and e_f are larger, while the elastic strain component Z_{el} is smaller for BZO_{20} than for BZO_{50} (cf. Figs. 2–4).

When comparing the neat and irradiated materials, it can be observed for both polyethylene grades that the radiation modification has reduced their susceptibility to deformation. The reduction of deformation after irradiation is described by coefficients w_k and n_k in eqs. (5), (6) and (8), (9) (cf. Figs. 2 and 3; for clarity of presentation only the data for samples irradiated in four passes, i.e., with the total dose of 104 kGy, are presented). An undesirable effect of irradiation is a slight decrease of elastic deformation, which at stresses of $\sigma_{tot} \geq 100$ MPa decreases Z_{el} by approximately 1%. (cf. Fig. 4).



Figure 3 The dependence of true plastic strain (determined after strain recovery period) on the nominal compressive stress.



Figure 4 The dependence of the elastic strain component (recovered strain) on the nominal compressive stress.

The conclusion drawn from the previous analysis, regarding the protective role of radiation modification against the effects of operational loads, is corroborated by the microhardness behavior (see Fig. 5 and Table II). For both UHMWPE grades studied, the value of microhardness *H* increased along with the multiplication factor *k* of the irradiation dose. Concurrently, a linear decrease of microhardness with an increasing plastic true strain e_f was recorded. The latter was much more intense in the case of the GUR 1020 grade (Fig. 5).

The changes of H with e_f for irradiated samples, shown in Figure 5, can be described with the parameters evaluated on the basis of linear regression analysis of the microhardness variation. The following equation was used for this purpose:

$$H = H_{\rm BZk} - I_H \cdot e_f \quad [MPa] \tag{11}$$

where:

 H_{BZk} microhardness of the sample after k-th electron irradiation,



Figure 5 The dependence of microhardness on the plastic true strain.

TABLE II Parameters of the Eq (11) Describing Microhardness Variation, Derived from the Regression Analysis (R—Correlation Coefficient)

Number of irradiation passes	GUR 1050 ($M_{1050} = 9.2 \times 10^6 \text{ g/mol}$)			GUR 1020 ($M_{1020} = 5 \times 10^6 \text{ g/mol}$)		
K	H _{BZk} (MPa)	I _H (MPa)	R	H _{BZk} (MPa)	I _H (MPa)	R
0	58	21	0.96	63	39	0.90
2	61		0.95	66		0.91
4	64		0.96	70		0.97

 I_H intensity of the microhardness response on the true plastic strain e_f (change of microhardness with an unit increase of the strain).

The results of the regression analysis are presented in the Table II.

In the procedure of estimation of the microhardness variation, both the H values measured for irradiated samples BZ_k , and their standard deviation values taken for the lowest and the highest true strain within the range explored were taken into account. Then, the regression line in the solution presented (parameters shown in Table II) is the center line of the band of standard deviation for the microhardness.

A similar interdependence may be found for the elasticity modulus *E* and the microhardness *H*. This is indicated by the linear correlation of the Young's modulus with microhardness with the correlation ratio of R = 0.96:

$$E = 25H - 350$$
 [MPa] (12)

On the basis of sklerometric studies of the near-surface layer at the front face of cylindrical samples of the deformed material (face perpendicular to the compression direction, LD), the coefficient of the abrasive wear was calculated with the following equation:

$$W_{\beta} = \frac{1}{\frac{1}{n} \sum_{i=1}^{n} (\beta_i A_i)} \quad [mm^{-2}]$$
(13)

where: β_i —coefficient of the micromechanism of the abrasive wear, described by the formula:

$$\beta = \frac{1}{n} \sum_{i=1}^{n} \frac{A_i - B_i}{A_i} \quad [-]$$
 (14)

and A_i , B_i are the surfaces of the scratch channel and the plastic elevation lips, measured from profilograms of the scratched surface.

The variation of W_{β} with e_{fr} shown in Figure 6, was analyzed with the regression analysis, applying the methodology described above for approximation of the microhardness variation and using the following equation

$$10^{-3}W_{\beta} = W_{\beta k} - I_{W_{\beta}} \cdot e_f \quad [\text{mm}^{-2}] \tag{15}$$

where:

 $W_{\beta k}$ —coefficient of the wear resistance of the material after k-th irradiation pass,

 $I_{W\beta}$ —intensity of the wear resistance response on the true plastic strain e_f .

The results of this analysis are presented in the Table III.

Comparing the ratios of the intensities of the response of microhardness and of wear resistance on the plastic true strain (cf. Tables II and III, respectively) and the ratio of the molecular weight of the polymers under study:

$$\frac{M_{1050}}{M_{1020}} = 1.84, \quad \frac{I_{\rm H\ 1020}}{I_{H\ 1050}} = 1.86, \quad \frac{I_{W_{\beta}\ 1020}}{I_{W_{\beta}\ 1050}} = 1.86 \qquad (16)$$

One can find that the value of the product of $M \cdot I_H$ is roughly constant, independent on the molecular weight of both polymers:

$$(M \cdot I)_{1050} \approx (M \cdot I)_{1020} \approx 200 \cdot 10^6$$
 (17)

Similar relation can be found for the product of $M \cdot I_{W\beta}$. The above relations indicate that the larger the molecular weight of the polymer, the lower



Figure 6 The dependence of the wear coefficient on the plastic true strain determined for irradiated samples.

Number of irradiation passes	GUR 1050		GUR 1020			
K	$W_{\beta k} \ (\mathrm{mm}^{-2})$	$IW_{\beta} (mm^{-2})$	R	$W_{\beta k} \ (\mathrm{mm}^{-2})$	$IW_{\beta} (mm^{-2})$	R
0	6	3.5	0.90	6.5	6.5	0.99
2	7		0.90	7.5		0.98
4	8		0.96	8.5		0.93

 TABLE III

 Parameters of the Eq. (15) Describing Variation of the Wear with Plastic True Strain, Derived from the Regression Analysis (R—Correlation Coefficient)

value of the I_H or $I_{W\beta}$ parameter, thus the higher resistance for the plastic deformation and wear.

Figures 5 and 6 together with Tables II and III document a possibility of simultaneous enhancement of several mechanical properties of a polymer (H, E, W_β) proportionally to the dose of electron irradiation. The direct influence of the electron radiation, applied as a sole modification method, is illustrated in Figure 7 presenting the linear wear in unidirectional wear test of radiation modified UHMWPE samples (this type of the wear test is recognized in tribology as the most severe).

The presented results demonstrate that virgin samples of polyethylene of higher molecular weight (GUR 1050) exhibit the higher wear resistance than lower molecular weight GUR 1020. Irradiation of both polymers with the dose of 104 kGy leads to approximately threefold decrease of the wear. This means also about fivefold higher wear resistance than that of the GUR 1120 UHMWPE grade ($M\approx 10^6$ g/mol, samples texturized and additionally modified with γ radiation), tested by Marrs and Barton in unidirectional wear test.⁹

While the studies of the morphology of investigated polymers are still in progress, the observed trends in variation of their mechanical and wear properties were compared with an evolution of free volume centers (i.e., nanoporosity), V_{free} , based on an example of the GUR 1050 grade for which the



Figure 7 The linear wear in a unidirectional motion wear test of samples of irradiated UHMWPE.

positron annihilation studies were performed. The results are presented in Figure 8. In the deformed samples, the nanoporosity increases with an increasing plastic strain. It can be presumed that it is substantiated by the following results of permanent deformation: a reduction of crystallinity and molecular weight, and a considerable increase of the lowmolecular fraction content and hence polydispersity.^{11–13} These changes can lead to worsening of a mutual matching and packing of macromolecules, inducing an increase of the free volume V_{free} . Contrary effects result from irradiation with an electron beam. The content of a low-molecular fraction decreases, the macromolecules, especially the longest, become shorter due to chain scission, which changes the molecular mass distribution and reduces polydispersity. As a consequence of better matching and arrangement of structural elements, the volume of nanovoids $V_{\rm free}$ can be reduced after radiation modification (cf. Fig. 8).

The effect of irradiation and deformation on V_{free} was approximated with a regression equation (the correlation coefficient of R = 0.95):

$$V_{\rm free} = V_{\rm fo} \cdot e^{-0.01 \, k} + 0.01 \, e_f \quad [\rm nm^3] \tag{18}$$

where:

 $V_{\rm fo}$ (= 0.13) the volume of nanovoids in the neat initial material (BZ₅₀),



Figure 8 The dependence of the free volume V_{free} on the plastic true strain and the irradiation dose.

k (= 1-4) multiplication factor of the electronbeam irradiation dose ($d = k \cdot 26$ kGy),

 e_f plastic true strain.

Changes of the polymer structure, including formation of nanovoids (additional free volume created) caused by external stimuli as irradiation and/ or plastic deformation result in modification of the properties of the material, including microhardness and Young modulus (cf. Figs. 9 and 10). These interdependencies can be also approximated with the regression equations given below:

$$H = 300 - 1880 V_{\rm free} \quad [MPa] \tag{19}$$

$$E = 7630 - 50620 V_{\rm free} \quad [MPa] \tag{20}$$

These regression show the correlation ratio of R = 0.94-0.96.

CONCLUSIONS

An analysis of changes in the plastic deformation under the action of stresses induced by operational loads demonstrated that among the polyethylene grades tested, the GUR 1050 grade is characterized by a higher resistance to permanent deformation than GUR 1020. At the same time, it has better elastic properties. The enhancement of resistance to plastic deformation of both materials can be achieved by radiation modification, the efficiency of which is proportional to the dose applied. Irradiation with an electron beam also reduces slightly the susceptibility to the elastic deformation.

Plastic deformation induced by operational loads has a significant effect on worsening properties of the materials analyzed. It was found that the intensity of deformation effects depends on the molecular weight of the polymer. For the GUR 1050, almost



Figure 9 The correlation of the microhardness and the free volume of nanovoids produced by plastic deformation and irradiation.



Figure 10 The correlation of the Young modulus and the free volume of nanovoids produced by plastic deformation and irradiation.

two times lower intensity than for GUR 1020 was observed in the reduction of microhardness, Young modulus, and the abrasive wear resistance coefficient related to an increasing permanent deformation. The enhancement of mechanical properties, especially, the resistance to an abrasive wear of both UHMWPE grades can be achieved through radiation modification, which appears proportional to the irradiation dose applied. The change in the analyzed properties coincides with the direction of evolution of the volume of nanovoids (free volume) due to plastic deformation and electron beam irradiation.

References

- 1. Purski, K.; Górecki, A.; Jabłoński, T. Ortop Traumatol Rehabil 2001, 3, 15.
- Greer, K. W.; Hamilton, J. V. Polyethylene Wear in Orthopedics. Marcel Dekker: New York, 1995.
- 3. Edidin, A. A.; Rimnac, C. M.; Kurtz, S. M. Wear 2001, 250, 152.
- 4. Lancaster, J. G.; Dawson, D.; Isaac, G. H. Proc Inst Mech Eng 1997, 211, 17.
- Wróblewski, B. M.; Siney, P. D.; Dowson, D. J Bone Joint Surg B 1996, 78, 280.
- Gierzyńska-Dolna, M.; Krzesiński, G.; Rajchel, B. Inżynieria Materiałowa 1999, 5, 553.
- Kurtz, S. M.; Mazzucco, D.; Rimnac, C. M.; Schroeder, D. Biomaterials 2006, 27, 24.
- 8. Ohta, M.; Hyon, S. H.; Tsutumi, S. Wear 2003, 255, 1045.
- Marrs, H.; Barton, D.C.; Doyle, C.; Jones, R. A.; Lewis, E. L. V.; Ward, I. M.; Fischer, J. J Mater Sci Mater Med 2001, 12, 621.
- Addiego, F.; Buchheit, O.; Ruch, D.; Ahzi, S.; Dahoun, A. Clin Orthop Relat Res 2011, 469, 2318.
- Maszybrocka, J.; Cybo, J.; Frąckowiak, J. Mater Sci Forum 2006, 513, 75.
- 12. Maszybrocka, J.; Cybo, J.; Cwajna, J. Mater Characterization 2009, 60, 1139.
- 13. Cybo, J.; Duda, P.; Maszybrocka, J. Tribologia 2006, 3, 35.
- 14. Lewis, G. Biomaterials 2001, 22, 371.
- Kurtz, S. M., ed. Compendium of Highly Crosslinked and Thermally Treated UHMWPEs. The UHMWPE Handbook; Elsevier: Amsterdam, 2004.

- McKellop, H.; Shen, F. W.; Lu, B.; Campbell, P.; Salovey, R. J Orthop Res 1999, 17, 157.
- 17. Eddin, A. A.; Jewett, Ch.; Kurtz, S. M. Trans Orthop Res Soc 1999, 45, 101.
- Muratoglu, O. K.; Cook, J. L.; Jasty, M.; Harris, H. W. Trans Orthop Res Soc 1998, 44, 782.
- Premnath, V.; Bellare, A.; Merrill, E. W.; Jasty, M.; Harris, W. H. Polymer 1999, 40, 2215.
- Kurtz, S. M.; Muratoglu, O. K.; Evans, M.; Eddin, A. A. Biomaterials 1999, 20, 1559.
- 21. Eddin, A. A.; Kurtz, S. M. 2000, 1–14. Available at: www. uhmwpe.org.
- 22. Li, S.; Bursein, A. H. J Bone Joint Surg Am 1994, 76, 90.
- Brandon, C. R.; O'Connor, D. O.; Muratoglu, O. K.; Jasty, M.; Ramamurti, B.; Merril, E.; Harris, W. Trans 24 Soc Biomater 1998, 21, 2.
- 24. Eldrup, M.; Lightbody, D.; Sherwood, J. N. Acid Chem Phys 1981, 63, 51.
- 25. Nakanishi, H.; Jean, Y. C. In Schrader, D. M., Jean Y. C., Eds.; Positron and Positronium Chemistry, Elsevier: Amsterdam, 1998.
- 26. Kansy, J. Nucl Instrum Methods A 1996, 374, 235.