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Modification of polyethylene by high energy ion or electron beam — structural, micromechanical and conductivity studies of the surface layer

Summary — Commercial grade polyethylenes: high density (PE-HD) and ultra-high molecular weight one (PE-UHMW) were subjected to the surface modification by electron beam irradiation (0.6—1.5 MeV/50—500 kGy) and ion beam bombardment (He^+ 160 keV/2 · 10^{13}—5 · 10^{16} ions/cm^2; Ar^+ 130 keV/1 · 10^{13}—2 · 10^{16} ions/cm^2). Effects of modifications were studied by spherical nanoindentation and scratch hardness tests. Contrary to electron beam irradiation, the ion beam bombardment, especially of He^+ ions, can significantly increase (up to 3 times) hardness of the surface layer of polyethylene in comparison to the bulk. According to Grazing Incidence X-ray Diffraction (GIXRD) it is associated with an increased degree of crystallinity due to the surface modification. Nuclear Reaction Analysis (NRA) reveals a hydrogen release due to ion bombardment which saturates at the CH atomic composition. It cannot however be associated with cross-polymerization or crosslinking of macromolecules because of some unsaturations being present and a graphite formation. Partially graphitized and/or better organized modified macromolecular chains "rooted" in the polymer substrate explain low friction and wear resistance of ion bombarded polyethylenes. Even high stress crackings are not able to proceed with further delamination of the modified surface layer. Treatment of the material with heavy Ar^+ ions of energy 150—300 keV was combined with an electrical doping by implantation of polyethylene with I^+ ions of energy 150 keV. Apart an increase in hardness, the modification results additionally in a significant reduction of the surface resistivity (more than 20 times), facilitating a removal of static charge.

Key words: polyethylene, ion bombardment, surface layer, modification, degree of crystallinity, hardness, surface resistivity.

MODYFIKACJA POLIETYLENU ZA POMOCĄ WYSOKOENERGETYCZNEJ WIĄZKI JONÓW LUB ELEKTRONÓW — BADANIA STRUKTURY, WŁAŚCIWOŚCI MIKROMECHANICZNYCH I PRZEWODNOŚCI WARSTWY WIERZCHNIEJ

Streszczenie — Próbki handlowych polietylenów: o dużej gęstości (PE-HD) oraz o bardzo wysokim ciężarze cząsteczkowym (PE-UHMW) poddano modyfikacji powierzchniowej metodą naświetlania wiązką elektronów lub bombardowania wiązką jonów (He^+ lub Ar^+). Efekt modyfikacji materiału uzyskany za pomocą nanoindentacji kulistej oceniano na podstawie odporności powierzchni na zarysowanie. W odróżnieniu od efektów naświetlania wiązką elektronów, bombardowanie jonowe, zwłaszcza jonami He^+, może znacznie zwiększyć twardość (nawet do 3 razy) warstwy wierzchniej polietylenu w porównaniu z wnętrzem materiału. Wyniki uzyskane metodą rozpraszania promieniowania rentgenowskiego padającego pod małymi kątami (GIXRD) sugerują, że jest to konsekwencją wzrostu stopnia krystaliczności warstwy wierzchniej polimeru w wyniku modyfikacji. Analiza warstwy wierzchniej metodą reakcji jądrowej (NRA) ujawnia uwalnianie wodoru wywołane bombardowaniem jonowym, które zatrzymuje się na poziomie składu atomowego CH (rys. 4 i 5). Jednakże tego wyniku nie należy traktować jako potwierdzenia polimeryzacji krzyżowej (*cross-polymerization*) lub sieciowania makrocząsteczek polimeru, ponieważ w jego warstwie wierzchniej stwierdzono obecność zarówno wiązań podwójnych jak i grafitu. Obecność częściowo zgrafityzowanych i/lub lepiej zorganizowanych zmodyfikowanych łańcuchów makrocząsteczek, „zakorzenionych" w podłożu polimerowym, wyjaśnia niski współczynnik tarcia i znakomitą odporność na ścieranie bombardowanych jonami polietylenów. Nawet duże obciążenia, powodujące pękanie twardej warstwy wierzchniej, nie

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są w stanie doprowadzić do jej delaminacji. Modyfikowanie materiału za pomocą ciężkich jonów Ar^+ o energii 150—300 keV połączono z elektrycznym domieszkowaniem polietylenu dokonując implantacji warstwy wierzchniej polimeru jonami I^+ o energii 150 keV. W wyniku modyfikacji oprócz wzrostu twardości, uzyskano dodatkowo znaczne obniżenie oporności powierzchniowej (nawet 20-krotne), zapobiegające gromadzeniu się ładunku elektrostatycznego.

Słowa kluczowe: polietylen, bombardowanie jonowe, warstwa wierzchnia, modyfikacja, stopień krystaliczności, twardość, oporność powierzchniowa.

Polyethylene (PE) is one of the most versatile polymers, which properties can be decided already at the stage of synthesis (molecular weight and its distribution, degree and length of branching), or additionally tailored during processing (morphology and degree of crystallinity). However, engineering applications of polyethylene are limited due to its low mechanical durability and wear resistance [1]. Chemical resistance of the polymer makes its chemical modification ineffective, whereas its crosslinking or isothermal solidification are not always advisable because of associated brittleness of the material [2].

The ideal solution would be to limit the modification to the surface layer of polyethylene, leaving its bulk intact and thus preserving overall elasticity. Hard, but thin skin makes the material abrasion resistant, additionally transferring dynamic stresses to the elastic bulk, what protects from cracks formation — initiating the wear [3]. Application of ions or electrons for bombardment of high density (PE-HD) and ultra-high density (PE-UHMW) polyethylene produces significant changes in the surface layer of material in the range of depth not exceeding 1—2 μm [4]. Despite the potential towards polymers the modifications used to be applied so far mainly for metals and ceramics [5]. Works on polymers are numerous [6] but mainly focused on modification of mechanical properties of materials [7—9] and recently biocompatibility [10—12]. One can find only occasional contributions devoted to structural [4, 13—15] and surface engineering aspects of polymer materials [16—19]. The paper presents the spherical nanoindentation data for PE-HD and PE-UHMW subjected to the modifications. Values of hardness, mechanical modulus and scratch resistance, as well as modification of the surface conductivity are correlated with changes of composition and structure of the materials.

EXPERIMENTAL

Materials

Sheets of *ca.* 2 mm thickness made of PE-HD (Lupolen 5231 HX, BASF, Germany) were prepared by press molding between polished metal plates at temp. 195 °C and pressure of 5 MPa and than solidified with air. PE-UHMW samples of similar form (GUR 1020, Ticona, Italy) were kindly provided by Perplas Medical Ltd. (UK).

Table 1. Physical properties of the polymers studied

Material	Producer's characteristics		DSC	
	M_w [a] g/mol	density g/cm^3	T_m [b] °C	X_c [c] wt. %
Lupolen 5231Hx	120 000	0.950	124	64.5
GUR 1020	3 500 000	0.934	117	61.6

[a] M_w — weight average molecular weight.
[b] T_m — melting temperature.
[c] X_c — degree of crystallinity.

Physical properties of both materials given by producers and determined by differential scanning calorimetry (DSC) with rate of heating 10 deg/min are listed in Table 1.

Modification of PE

The surface layer of polymer samples was modified either with beam of electrons or He^+, Ar^+ or I^+ ions. The modification with electron beam was realized using a Van de Graaff accelerator (in the Institute of Nuclear Chemistry and Technology, Poland) whereas a Balzers MPB 202 RP instrument (Liechtenstein) was applied for ion beam bombardment. The following parameters of modification were applied:

— electrons of energy 0.6—1.5 MeV and dose in the range 50—500 kGy,

— He^+ ions of energy 130 keV and a dose in the range: $1 \cdot 10^{14}/cm^2$—$3 \cdot 10^{16}/cm^2$,

— He^+ ions of energy 150 keV and a dose in the range: $3 \cdot 10^{16}/cm^2$—$3 \cdot 10^{17}/cm^2$,

— Ar^+ ions of energy 160 keV and a dose in the range: $1 \cdot 10^{14}/cm^2$—$1 \cdot 10^{16}/cm^2$,

— Ar^+ ions of energy 300 keV and a dose in the range: $3 \cdot 10^{16}/cm^2$—$1 \cdot 10^{17}/cm^2$,

— I^+ ions of energy 150 keV and a dose in the range: $1 \cdot 10^{16}/cm^2$—$1 \cdot 10^{17}/cm^2$.

The energy density of an ion stream was each time maintained below 0.1 μA/cm^2, in order to prevent temperature rise in the surface layer of polymer sample.

Method of testing

Surface characterization of modified samples was made well after modification (3—6 months), so all possible changes caused by surface chemistry were assumed to be finished.

Nuclear reaction analysis (NRA)

Hydrogen concentration was determined by the nuclear reactions method [20]. A sharp resonance of the cross-section at 6.385 MeV was applied for hydrogen depth profiling. Typical value for $^{15}N^{2+}$ ion beam current from a 5 MeV tandem accelerator (the Forschugszentrum Rossendorf, Germany) was about 5 nA. It was focused on a spot of 10 mm^2. γ-rays with the energy of 4.43 MeV were detected by a scintillation detector [4"x4" Na(TI) crystal] located outside the vacuum, about 1.5 cm behind the sample. The incident beam was monitored by the Rutheford Backscattering Signal (RBS) from a beam chopper in front of the sample.

Confocal Raman microscopy

Carbon structures produced by modification were studied using Jobin-Yvon FT-Raman spectrometer T64000 (France), operated with a LEXEL 95 ion laser (514.5 nm Ar line) and equipped with an Olympus BX-10 confocal microscope. Measurements were performed using a 100× (NA 0.90) and a 50× (NA 0.75) microscope objectives. The laser power and the time of sample excitation were adjusted individually in order to obtain the best quality absorption spectra. The spectra were analyzed according to the procedure described elsewhere [4, 21].

Grazing incidence X-rays diffraction (GIXRD)

Experiments were carried out at room temperature using a Seifert URD-6 diffractometer (Germany) equipped with an AMTI DSA 6 attachment (USA). CuK$_{\alpha}$ radiation was used at 30 kV and 10 mA. Monochromatization of a beam was obtained by means of a nickel filter and a pulse-height analyzer. The angle of incidence was fixed to 0.5^{o}, so that the degree of penetration into the sample could be kept constant during measurements. The diffraction scans were collected between 2θ values from 2^{o} to 60^{o} with a step of 0.1^{o}.

Surface conductivity

Surface conductivity measurements were carried out using a typical set containing a Hewlett Packard HP 6186C power supply (USA) and a Brymen BM 811 voltameter and BM 515X amperometer. Two copper electrodes were placed on the surface of PE-UHMW in the distance of 3 mm. Experiments were run for the voltage range 0—300 V.

Spherical nanoindentation

Mechanical properties of the surface layer of polymers were determined using NanoTest 600 instrument (Micro Materials Ltd., UK) [20]. A 5 μm stainless steel spherical indenter penetrated the surface layer of polymers with the loading/unloading rate of dP/dt = 0.02 mN/s, up to the maximum load of P = 1.00 mN. All the experiments were run at room temperature and a 30 s holding period was applied at the maximum load between loading and unloading stages, to minimize the effect of viscoelasticity for the unloading curve. In all tests there was an additional hold at 90 % unloading to assess a thermal drift, which was subsequently subtracted from the force curve.

Scratch testing

Experiments were run using a Revetest instrument (CSEM, Switzerland), operating with a 200 μm Vickers diamond. Test was carried out with loading dP/dt = 100 N/min in the range 0—50 N at the distance of 5 mm. Wear tracks were analyzed with a Leica MZ6 stereoscopic microscope (Switzerland).

RESULTS AND DISCUSSION

Ion bombardment of PE results in a significant surface gradient of mechanical properties, whereas electron beam irradiation brings mainly the moderate bulk effect. Figures 1—3 present micromechanical profiles of the surface layer of PE-HD and PE-UHMW bombarded with He$^+$ and Ar$^+$ ions and electron beams, respectively. It can be associated with different interactions between an energetic beam and a polymer target. Light particles can

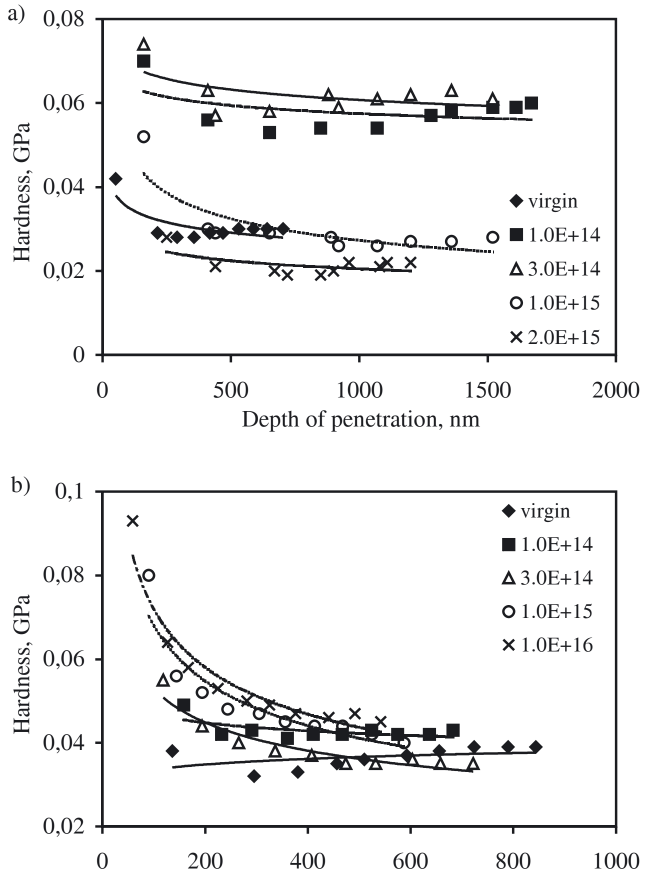


Fig. 1. Micromechanical profiles of the surface layer of polyethylenes bombarded with He$^+$ ions (130 keV): a) PE-HD, b) PE-UHMW

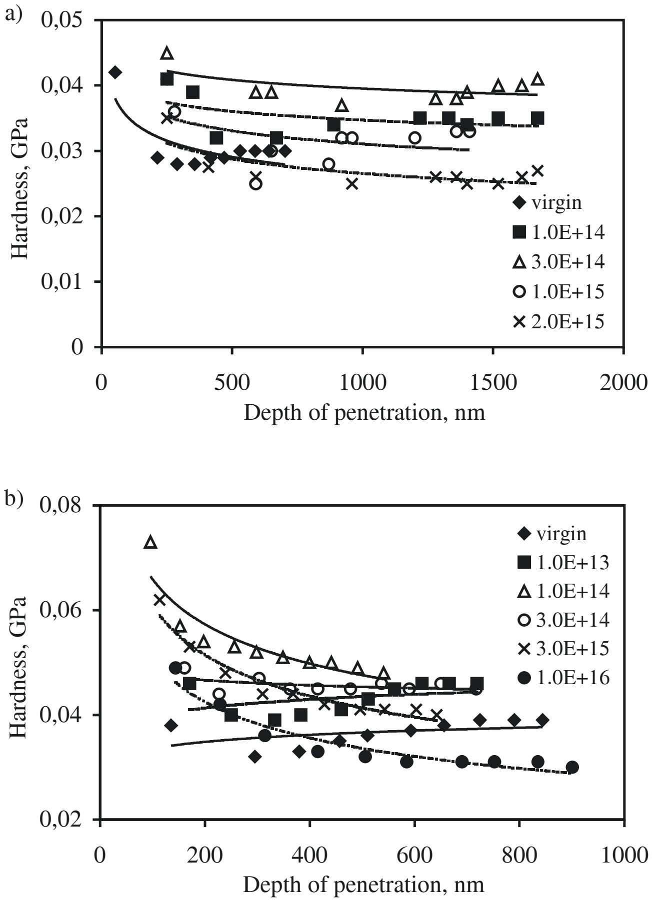
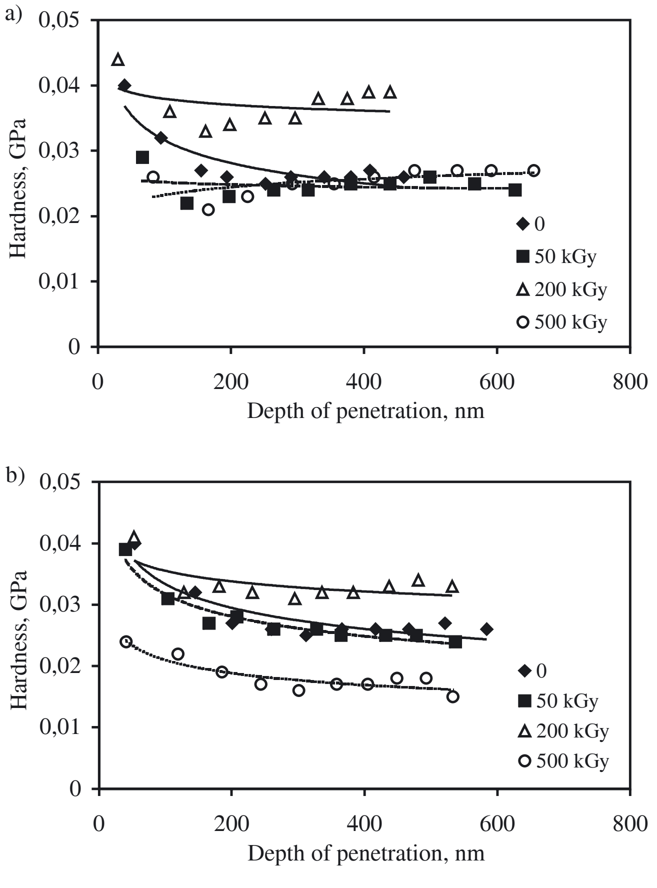


Fig. 2. Micromechanical profiles of the surface layer of polyethylenes bombarded with Ar^+ ions (160 keV): a) PE-HD, b) PE-UHMW



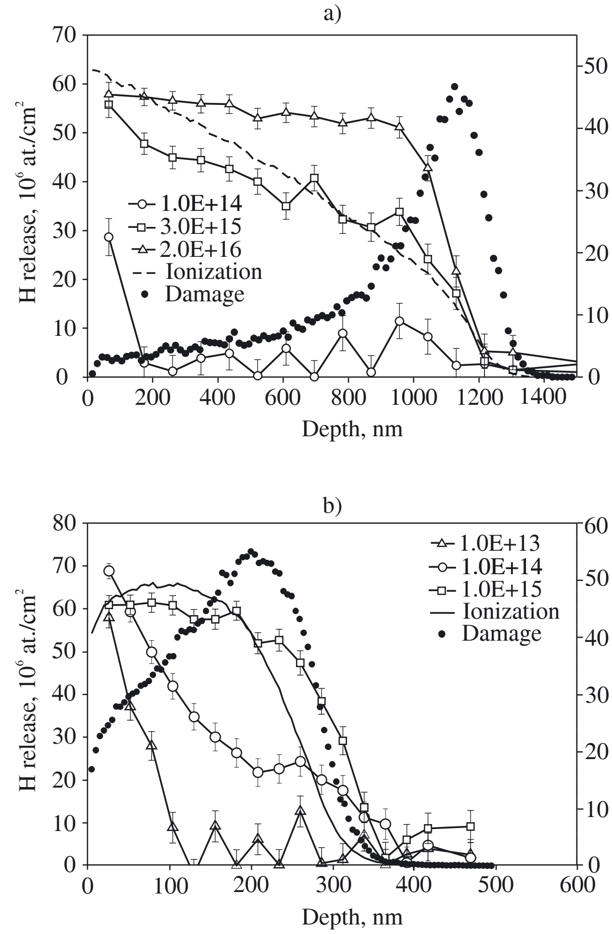


Fig. 4. Hydrogen release from the surface layer and interactions between ion beam and PE-UHMW sample for ion beam: a) He^+, 130 keV, b) Ar^+, 160 keV

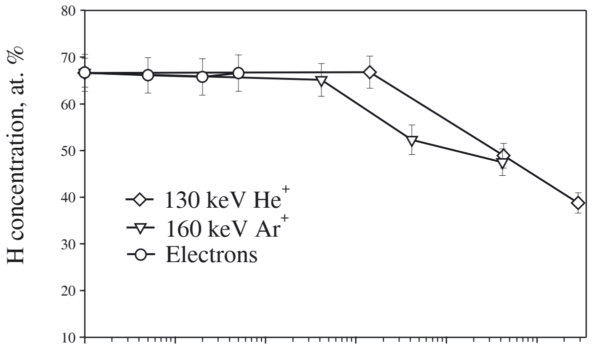


Fig. 5. Hydrogen concentration on the surface layer of polyethylene modified by energetic beams

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Fig. 3. Micromechanical profiles of the surface layer of polyethylenes bombarded with electron beams (1.5 MeV): a) PE-HD, b) PE-UHMW

penetrate deeper, producing mainly ionization, whereas for heavy particles degradation of macromolecules, taking place to shallower depths, is dominating [4]. In the Figure 4 it was shown the hydrogen release from the surface layer of PE-UHMW under the influence of He^+ or Ar^+ ion beams. As it can be seen in Figure 5 ion bombardment, no matter the ion mass, results in dehydrogenation of polyethylene, whereas a release of hydrogen under electron beam is negligible due to very low linear energy transfer (LET). Even the highest dose of electrons (there are limits concerning the time of modification and an increase in temperature) cannot result in dehydrogenation.

Electron beam modification has predominantly a bulk character, what makes it incomparable even to a bombardment with light ions [13]. Additionally, oxidation accompanying the modification is not limited only to the surface layer but, to considerable extent, affects also the bulk of polyethylene [16]. In the light of experimental data obtained we decided to concentrate on ion beam bombardment, resulting in the surface modification of polymers. Micromechanical profiles of the modified materials are reflected by the degree of crystallinity of their surface layer. Data of degree of crystallinity and dimensions of crystallites, calculated from GIXRD spectra are listed in Table 2.

Table 2. Degree of crystallinity and dimensions of crystallites of samples modified by different types and doses of ion beams calculated from GIXRD spectra

Sample	Type and dose of ion beam	Degree of crystallinity vol. %	Dimensions of crystallites, nm	
			$D_{(100)}$	$D_{(200)}$
PE-UHMW/virgin		43.8	20.8	18.1
PE-UHMW	$Ar^+, 1 \cdot 10^{13}$ cm^{-2}	35.5	19.8	19.2
PE-UHMW	$Ar^+, 1 \cdot 10^{14}$ cm^{-2}	42.6	20.4	18.2
PE-UHMW	$Ar^+, 1 \cdot 10^{15}$ cm^{-2}	44.9	20.7	18.3
PE-UHMW	$He^+, 1 \cdot 10^{14}$ cm^{-2}	43.0	19.7	19.0
PE-UHMW	$He^+, 1 \cdot 10^{15}$ cm^{-2}	46.9	20.7	18.8
PE-UHMW	$He^+, 1 \cdot 10^{16}$ cm^{-2}	52.3	21.4	19.5
PE-UHMW	$He^+, 2 \cdot 10^{16}$ cm^{-2}	69.2	23.0	20.0
PE-UHMW	$He^+, 5 \cdot 10^{16}$ cm^{-2}	60.1	22.3	19.7
PE-HD/virgin		46.0	22.1	19.6
PE-HD	$He^+, 1 \cdot 10^{14}$ cm^{-2}	61.7	23.0	20.5
PE-HD	$He^+, 1 \cdot 10^{15}$ cm^{-2}	64.7	22.6	19.9
PE-HD	$He^+, 1 \cdot 10^{16}$ cm^{-2}	67.1	23.0	19.8

With an increase in He^+ ions dose the degree of polymer crystallinity increases, contrary to Ar^+ ions application for which it practically remains constant. The increase however is not monotonous, representing a relation with the maximum. The level of amorphous halo in the spectrum of PE-UHMW bombarded with He^+ ions of the dose $1 \cdot 10^{16}$ $1/cm^2$ is significantly higher in comparison to the spectrum presenting X-rays diffraction for the material modified by $2 \cdot 10^{16}$ $1/cm^2$ ion beam. In turn, crystalline peaks are higher for the latter, what makes a considerable difference in the degree of crystallinity. One can notice also a small increase in crystallites' dimension in the direction perpendicular to (110) planes.

Apart structural changes, also oxidation of the surface layers of polymers and development of the surface geometry [23], accompanying the modification, were detected. The effect observed is durable, pointing at the possibility of hydrophilization of the polyethylene surface. NRA data point at saturation of hydrogen release at the level of CH atomic composition. Formation of diamond like or graphite structures is also confirmed by the Raman spectra presented in Figure 6. The modification takes place for both kinds of ion beam studied and has evidently the surface character. The presence of D and G lines, subscribed to graphite [21] and an appearance of new IR absorption at 1640 cm^{-1} coming from C=C double bonds [24], suggest complex morphology rather than cross-polymerization or crosslinking of macromolecules

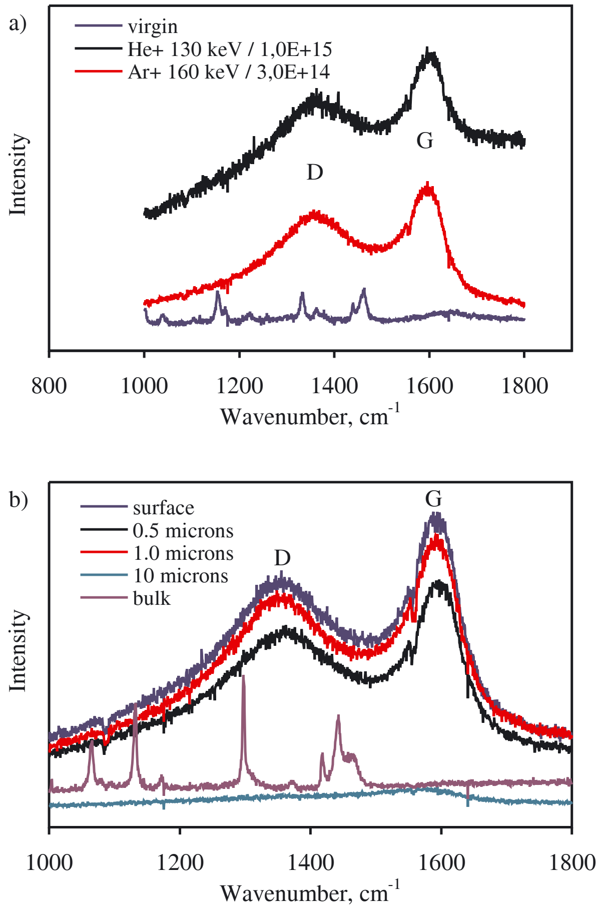

Fig. 6. Raman spectra of the surface layer of polyethylene subjected to ion beam bombardment: a) PE-HD — comparison between treatment with He^+ and Ar^+ ions beams, b) PE-UHMW, He^+ 130 keV/1.0 · 10^{15} cm^{-2} — depth profile

proposed in the subject literature [6]. Infrared spectra did not reveal the absorption at 1684 cm^{-1} originating from trans-vinyl conjugated with carbonyl groups, present in highly oxidized structures formed during electron beam irradiation [24].

The hard "skin" produced on the surface is very thin and is limited by the range of ion beam to several hundred of nm. Even under an extremely hard loading, resulted in plastic deformation of the polymer substrate, no delamination of the modified surface layer during scratch testing has been observed, pointing at potential tribological applications of ion bombarded polyethylene. Figure 7 show microscopic images of a wear track generated by Vickers diamond on unmodified and modified PE-UHMW. The cracks visible on the modified sample are curved in the direction opposite to a movement of the penetrator. The result is not surprising, as may be suggested at first sight. It seems likely that macromolecular chains which start from the subsurface layer of polyethylene, loose hydrogen atoms from their opposite ends due to the modification, what facilitates improvement in the supermolecular organization of the surface layer. "Rooting" of the modified macromolecules secures wear resistance of the material. Even cracking of a hard skin is not able to result in its further delamination, what is demonstrated by the microscopic image of wear track.

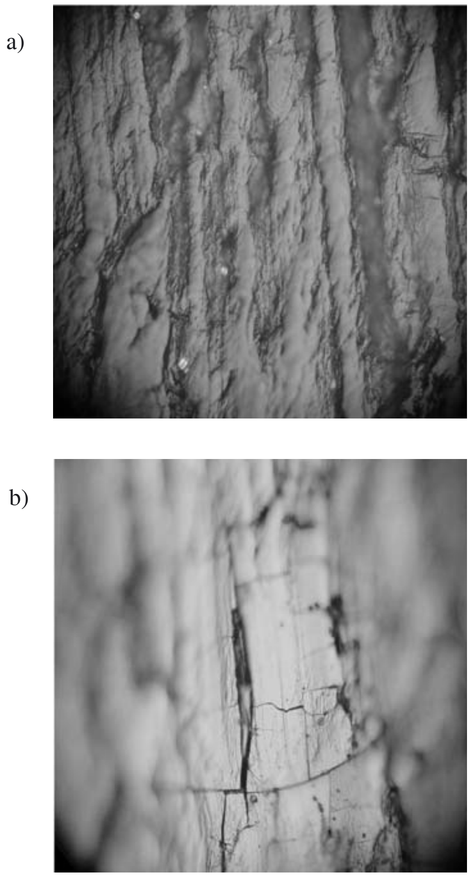

Fig. 7. Microscopic images of wear track generated by a 200 μm Vickers diamond on He^+ ion treated PE-UHMW (end of trace) (a); He^+ ion beam 130 keV/2 · 10^{16} cm^{-2}, (b) and virgin sample

Structural changes of macromolecules have given an impact for studying the surface conductivity of polyethylene. Possibility of charge removing from the surface opens new fields of application of hydrocarbon polymers. Current-voltage characteristics are presented

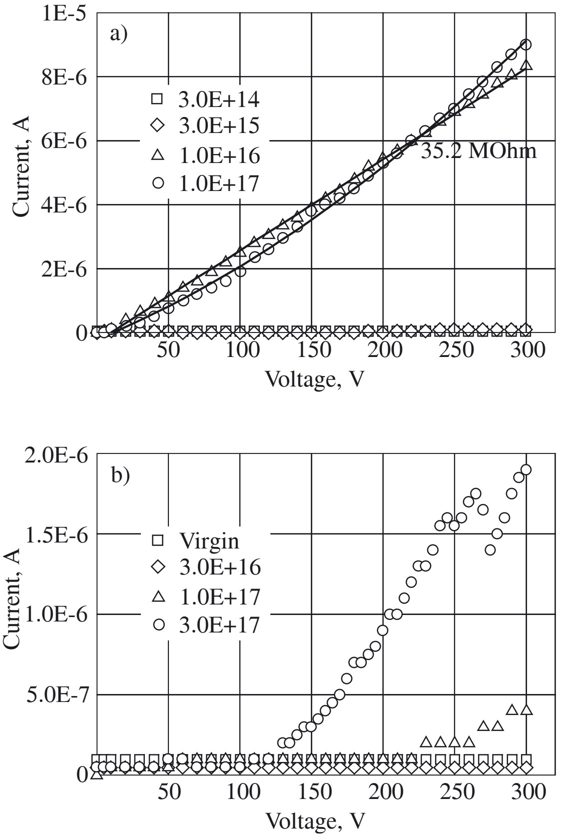

Fig. 8. Current-voltage characteristics of the surface of PE-UHMW irradiated with: a) Ar^+ ions/300 keV, b) He^+ ions/150 keV

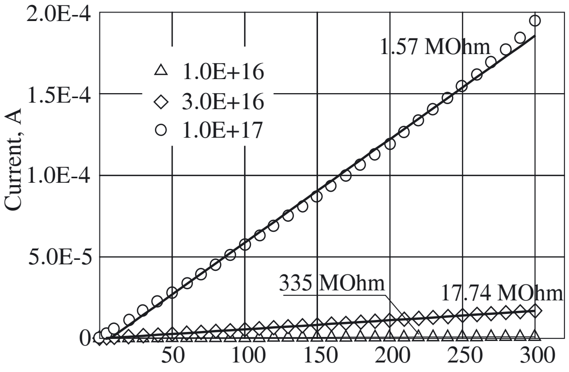

Fig. 9. Current-voltage characteristics of the surface of PE-UHMW irradiated with I^+ ions/150 keV

in Figure 8. Higher voltage and increased ion doses were applied in order to limit the extent of modification to shallow depths and intensify its effects, respectively.

Results obtained indicate on the conductivity threshold of PE-UHMW being the result of ion bombardment. Its critical values are $1 \cdot 10^{16}$ $1/cm^2$ for Ar^+ and $1 \cdot 10^{17}$ $1/cm^2$ for He^+ ions. Contrary to the characteristic for Ar^+, the one for He^+ is not linear — conductivity starts after exceeding some critical voltage what suggests that modified layer is created in the subsurface layer of polyethylene, gradually propagating towards the surface. Following the idea of Shirakawa [25] it has been decided to implant iodine ions to the surface layer of polyethylene.

Linear character of the dependence presented in Fig. 9 made possible to calculate the resistivity of modified materials, which could be reduced up to 1.57 MOhm in comparison to 35.2 MOhm obtained in the case of modification with Ar^+ ion beam. Even taking into consideration a higher defects efficiency of I^+ ions, the influence of addition of the former on polymer conductivity is apparent, opening perspectives for *e.g.* tribological applications and "dust-free" surfaces.

CONCLUSIONS

Based on experimental data the following conclusions can be formulated:

— Contrary to electron irradiation, ion beam bombardment can significantly increase hardness and mechanical modulus of the surface layer of PE-HD and PE-UHMW, preserving their bulk elasticity.

— The effect is mainly attributed to an increase in crystallinity, especially pronounced for the modification of polyethylene with light He^+ ions. The relationship between hardness and ion dose, contrary to Ar^+ beam, is not monotonous for He^+ one, what requires optimization of the modification conditions.

— Ion beam bombardment of polyethylene results in a hydrogen release. The process saturates at CH composition, which however cannot be attributed either to cross-polymerization or crosslinking of macromolecules. The surface layer of modified polyethylene contains both unsaturated bonds and graphite structures.

— Partial graphitization with simultaneous "rooting" of macromolecules in the subsurface layer facilitate tribological applications of ion bombarded polyethylene. Hardening of the thin skin lowers friction. Even its high stress cracking does not result in delamination of the surface layer of the modified material.

— Ion beam treatment improves the surface conductivity of polyethylene. The best results were obtained for I^+ ions, which apart modification of the material play a role of charge carrier.

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