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Structural and chemical changes in He^+ bombarded polymers and related performance properties

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Abstract

The paper presents the effect of He^+ ion irradiation of selected polymeric materials: poly(tetrafloroethylene) (PTFE), poly(vinyl chloride) (PVC), ethylene-propylene-diene monomer rubber (EPDM), nitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR) and natural rubber (NR), on their chemical composition, physical structure and surface topography. The modification was studied by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy and Differential Scanning Calorimetry (DSC). High-energy ion beam leads to the release of significant amounts of hydrogen from the surface layer, making crosslinking increased, what manifests itself by shrinkage of the surface layer, which in turn causes significant stresses, leading to the formation of a crack pattern on the polymer surface. The development of the surface microroughness is combined with its oxidation. Shallow range of the ions makes the modified layer "anchored" in the substrate via bulk macromolecules, assuring its good durability and adhesion to elasto-plastic substrate.

Significant changes in their surface layer, were manifested by the modification of functional properties of the polymers concerning: nanohardness, friction, wear, tensile strength (TS), elongation at break and electrical resistivity. The hardness of the layer subjected to the ion irradiation process increases even up to 10 times. After modification with the ion beam, a significant decrease in frictional forces was also observed, even up to 5-6 times. The microscopic analysis of wear traces confirmed that the wear resistance also significantly increased. However, ion bombardment of polymeric materials caused a reduction in their mechanical strength (despite the range limited to the surface layer of the order of micrometers) and electrical resistance, which has a negative impact on the possibility of using the materials in some applications.

1. INTRODUCTION

1.1. Interactions between energetic ions and polymers

High energy ions penetrating material are losing energy due to interaction with the nuclei and electrons of the target. As a result of ion-atom collisions, atoms can be knocked out of the lattice, while the interaction between ions and electrons results in the excitation or ionization of the atom. The first of these processes is called nuclear stopping (elastic interactions) and the second is called electron stopping (inelastic interactions).

For most of the energies used, the nuclear interaction is small for light ions such as H or He because the Rutherford cross-section and the momentum transfer of low mass atoms are small. In such a case, electronic stopping is dominant and defined by the energy loss function Se (E), which is the average of all energy loss processes for different states of charge. The slowdown can be determined with good accuracy by analytical method using several formulas, the best known of which is the Bethe-Bloch formula [1]. At energies less than about 100 keV, it is difficult to quantify the amount of electron interactions and theoretically determine the electron stopping. Therefore, several semi-empirical formulas have been developed. The model given by Ziegler, Biersack and Littmark (ZBL) is by far the most used today [2]. At the beginning the ion slows down mainly by electron interactions and follows an almost straight path. When the ion slows down sufficiently, collisions with the nuclei become more likely and the nuclear slowing down becomes dominant. When the transfer of energy to the target atom becomes greater than the displacement Energy - Ed, usually around 20 eV, the atoms can be knocked out of the nodal positions, creating a cascade of successive collisions. It should be emphasized that most of the knocked out atoms of the target come from the atom-atom collisions, not the ion-atom, which means that it is the collision cascades that are the main cause of radiation defects created during ion irradiation.

Theoretical and experimental evidences suggest that about half of the energy lost to ionization is caused by ion interactions and the other half by knocked out atoms. [3, 4]. This phenomenon is referred to as the equipartition principle and has been confirmed experimentally [5].

Linear energy transfer, (LET) determines the energy loss per depth, so it is a measure of the energy deposited per unit path length of the ion [6, 7]. In the case of polymeric materials, it is worth identify the volume where energy transfer can initiate chemical reactions. It is the outermost interaction area defined by the chemical radius (r_c). The chemical radius is determined by the rate of reaction of active chemicals such as radicals, cations, anions etc. Since the chemical radius is difficult to measure or calculate, the most common term used is the "effective" radius, which describes the extent to which an energy density or radical concentration is relevant to a given process. Cross-linking, degradation and other chemical reactions take place in the area with an effective radius from the particle trajectory. With the LET increase the deposited energy density increases, as well as the effective radius of interaction. The volume where the interaction caused by the ion penetrating the polymer takes place

can be described as a cylinder with a core with radius r_c (approximate boundary distance of particles where electron excitation initially occurs) and an outer region with radius r_p (the outermost limit of the range of secondary electrons) [8] - Fig. 1.

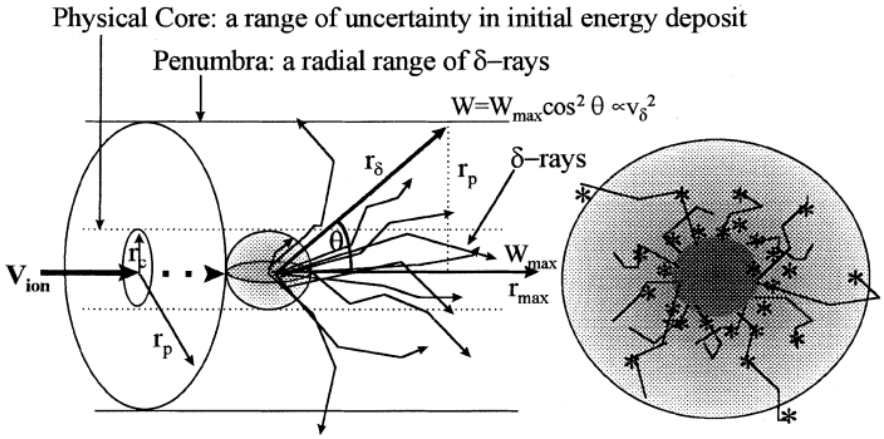


FIG. 1. Scheme of the interactions of a high energy ion beam with polymer target
v_{ion} – ion velocity, r_c – physical radius, r_p – half-shadow radius, W – kinetic energy of ions

The values of r_c and r_p change with the energy of the particle. As LET increases, more radical pairs are formed in the track radius, the traces are joined or overlapped, a high radical concentration gradient is created and therefore the effective radius increases as the distances between the two polymer chains are in the nm range for most polymers. Therefore, two radicals must be in adjacent chains for cross-linking to occur. At the same time, it should be remembered that a significant proportion of the radicals do not contribute to cross-linking due to recombination. The above theory seems to be confirmed by the following experiment, in which to achieve saturation in the polystyrene irradiated with He and Ar, several thousand traces per 1 nm^3 were necessary, which suggests that most of the radicals were neutralized [9].

The intensity of cross-linking processes, i.e. the formation of intermolecular bonds and degradation (breaking the bonds in the main chain and side chains) of the polymer, is determined by many processes. Nuclear collisions cause atomic displacement, which can lead to the degradation of polymer macromolecules. The polymers have a fairly high free volume, often greater than 20%. The atomic density in such a loose system is relatively low compared to metals with a compact structure. Therefore, in polymers, most nuclear displacements occur independently. In nuclear processes, the probability of simultaneously displacement of two atoms from adjacent chains and forming two radical pairs for cross-linking is low. On the other hand, a high electron LET causes the formation of active chemical compounds: cations, anions, radicals as well as free electrons along the polymer chains. Their Coulombic attraction and repulsion causes bond stretching and segmental movement in the polymer chains, which can lead to both bond breaking and cross-linking. As LET increases, the radical density increases and thus the efficiency of the cross-linking process increases, gradually shifting the system from degradation to cross-linking. Cross-linking becomes easier as the distance between the branches in macromolecules approaches 2 nm, which is approximately the intermolecular distance in polymers. Cross-linking occurs when two ions or radicals on adjacent chains interact with each other. Double or triple bonds in macromolecules arise when two adjacent radicals join in the same chain.

It was found that changes in the mechanical, physical and chemical properties of polymers under the influence of radiation are determined by cross-linking and degradation processes that dominate the change in the composition of the material caused by the irradiated ions. Cross-linking increases, while degradation lowers the mechanical strength, although it may also lead to an increase in hardness [10-12]. Usually, as the cross-link density increases polymers become more brittle [13], on the other hand, their

abrasion and scratch resistance increases [14], are more resistant to solvents [6] and barrier properties are better [15]. The formation of cross-links and conjugated double and triple bonds leads to an increase in the electrical conductivity and optical density of polymers [7]. Ion beams can be successfully used to modify such properties of the surface layer of polymeric materials as wettability, hardness and coefficient of friction [16, 17].

1.2. Structural changes in polymers

The main structural effect of the interaction of ion beams with polymers is the removal of hydrogen atoms from the polymer chain by cleaving the C-H bond [18]. This effect releases hydrogen from the material and may contribute to cross-linking [19]. In addition to hydrogen, also molecules are released, which are the product of cleavage of chain side groups and segments from the end of the chain and their reaction products. The process of hydrogen release is very intense and can lead to the loss of up to 50% of hydrogen from the sample, which in the case of polyethylene causes a change in the average composition from CH_2 to CH. The final state of the material can therefore be described as hydrogen-doped carbon. As a result, a thin, carbon-rich layer forms on the surface. This layer is characterized by high hardness (about ten times harder than the starting material), almost 5 times lower coefficient of friction and increased resistance to abrasive wear. The maximum penetration depth of the irradiated ion depends on the type of material, the mass of the ion and the irradiation energy [20, 21].

The way in which the high-energy ion beam affects the structure of polymers depends on the structure of their macromolecules. It can cause macromolecules to break, leading to the formation of shorter radical-terminated fragments. Depending on the structure of the macromolecule, macromolecules either react with each other, causing cross-linking - this is the case, for example, in polyethylene and acrylonitrile-butadiene rubber, or the radicals are not found and the molecular weight of the polymer decreases, which is a sign of its degradation - for example in polypropylene or natural rubber - Fig. 2.

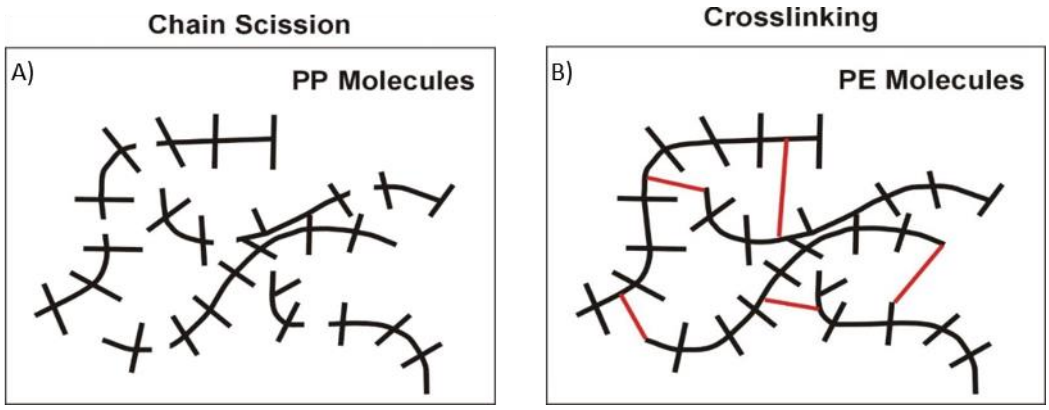


FIG. 2. Mechanisms of macromolecule modification resulting from ion bombardment: degradation (A) and cross-linking (B).

Due to the structure of macromolecules of polyethylene and NBR rubber, they belong to the group of materials for which cross-linking reactions prevail over degradation reactions. This group also includes polystyrene and its derivatives and the vast majority of synthetic rubbers. In the case of rubber, an important role is also played by the content of sulfur, which is part of the cross-linking unit, and soot, used as a reinforcing filler. In the case of polyvinyl chloride (PVC), which is degraded by ion irradiation, both cracking and the formation of double bonds in macromolecules are observed [22]. Energy transfer from high-energy ions to target results in a complex combination of polymer chain cleavage, covalent bond breaking, cross-linking and finally hydrogen release [11, 23-24]. As research shows, the breaking of polymer chains also modifies the molecular weight distribution, which in the case of, for example,

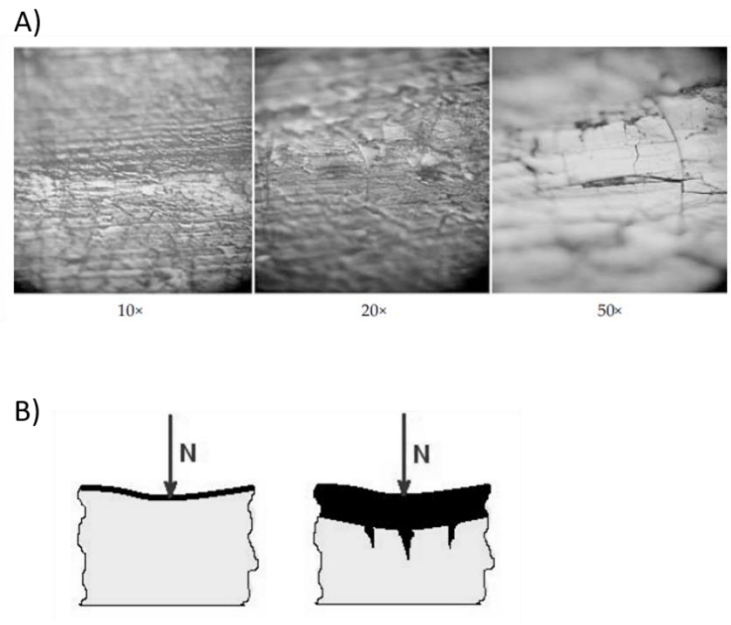
polypropylene, changes the flow characteristics of the polymer. The group of polymers in which the degradation processes dominate the cross-linking processes also includes polymethyl methacrylate (PMMA) [6, 7]. The degradation tendency of PMMA is attributed to the presence of methyl ester groups (CH_3OOC–) attached to the polymer backbone structure [25]. Large side groups limit the mobility of the chain and thus make cross-linking difficult. The literature also provides information on the modification of other physical and chemical properties of various polymers under the influence of ion irradiation, such as, for example, changes in the crystallinity of polyethylene and poly (2,6-dimethylphenyl oxide), wettability of polycarbonate and polymethyl methacrylate, conductivity of polytetrafluoroethylene and polyamide or the solubility of the polysiloxanes [26-31].

Numerous studies have also looked at the effect of ion irradiation on the structure of isotactic polypropylene (iPP), focusing on the type of ions, their fluence and LET [32]. In the infrared spectra of iPP, changes in the intensity of the absorption bands were observed, corresponding to vibrations in the CH_3 and CH_3 groups, and the formation of C = C and C = O bonds. The oxidation effect of the polymer surface layer following ion bombardment was also observed with polytetrafluoroethylene (PTFE). Beams of higher energy ions resulted in the formation of a high density of radicals with longer sequences of conjugated double bonds C = C, which was manifested in a change in the color of the sample and had an influence on the increase of its surface electrical conductivity [33].

Understanding the chemical and structural changes that occur in polymers after irradiation can help in the design of materials with improved properties, resistant to radiation, and even macromolecular structure that enables ion bombardment-induced cross-linking to improve material performance [21].

1.3. Functional changes in polymers

Ion irradiation of a polymer material with a high-energy ion beam changes its chemical and physical properties, as does the interaction of gamma radiation. As a result, ion bombardment can serve as a quick and precisely controlled counterpart of the processes taking place in the material under the influence of ionizing radiation. Ion irradiation makes it possible to modify the properties of only a thin surface layer of the material, on the order of hundreds of nanometers to several micrometers from the surface (comparable to the length of polymer macromolecules)[38] , which allows to create a hard surface layer resistant to abrasion while maintaining the elasto-plastic characteristics of the entire element Fig. 3.



The final fragment of the penetrator needle trace in the scratch test performed on the surface of the PE-UHMW bombarded He^{+}/130 keV/2x10^{16} cm^{-2}. The test was carried out using an indenter with Vickers geometry (ϕ ≈ 200 µm) with a force increasing up to 50 N.

FIG. 3. Diagram illustrating the resistance to delamination of the polymer surface layer modified as a result of bombardment (A), as well as abrasion resistance and fatigue life (B).

Due to the growing use of polymers in radiation environments found in nuclear power plants, spacecraft, high energy particle accelerators and as a shielding material in satellites, the modification of materials by ions is of wide interest. Irradiation can also serve to obtain the desired mechanical or electrical properties of the material's surface layer [35-38]. Much research on the resistance of ion irradiation polymers has been carried out, particularly with respect to ethylene-propylene rubbers (EPM and EPDM), ethylene vinyl acetate (EVA) and cross-linked polyethylene (XLPE) as sheaths for electrical cables that have been tested under various conditions. The obtained results proved that there is a correlation between the electrical and mechanical properties, and the change in the electrical properties measured for polymers operating under ionizing radiation can be used as a marker of their aging. [39-41]. Despite the limitation of the modification range to the surface layer of the material, ion irradiation affects the material breaking strength (TS) and the relative deformation at break (ε_B)[42]. Tensile strength tests show that the measurement of elongation at break is a better indicator of the mechanical properties of a material than its tensile strength. It turned out that the TS value may increase and then decrease with the aging of the material, while ε_B decreases with the progressive aging of the material [43]. For example, for EPDM rubber, the reason why TS increases and then decreases is that this parameter depends on the cross-link density and the number of effective network nodes. Therefore, the mechanical strength of the material, on the one hand, increases with increasing cross-link density, because then the mobility of macromolecules is limited, but on the other hand, it reduces the number of effective network nodes, which leads to a decrease in TS [44]. The results of aging of the cable sheath made of polyethylene under the influence of ion irradiation showed an increase in the density of the material and a decrease in its strain at break. The increase in material density was closely related to its oxidation, which was confirmed by the results of the infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) methods. Oxidation promoted chain breakage in polymers with amorphous structure, which led to a reduction in their breaking strength [45]. The influence of ion bombardment on the oxidation and mechanical properties of PVC was also demonstrated during the aging experiments of polymers [46]. On the other hand, on the basis of studies on the resistance of NBR vulcanizates to aging, caused by irradiation with a high-energy ion beam, it

was found that antioxidants added to the rubber mixture play an important role. By limiting the formation of free radicals during oxidation, they reduce the degree of modification of the material [47], limiting its negative effects. This suggests that FTIR can be used for in situ oxidation measurements to obtain information on the condition of the cable insulation. Mechanical measurements taken on the surface, such as nanoindentation, show a close relationship with the material's strain at break, since cracks are initiated in the surface layer of the material. However, the proposed methods are destructive and involve samples taken from insulation, which requires the cable to be removed from the installation. On the other hand, the optimal inspection method should be quick, convenient to use in any place of the installation and not require taking material from the tested element. One of the methods meeting these conditions could be dielectric (impedance) spectroscopy, which is also a non-destructive and sensitive method showing good correlation with the degree of oxidation of the material. This method can be used as a technique for monitoring the condition of the insulation of cables used in nuclear installation.

The aim of this study is to obtain information on the structural and functional properties of polymers subjected to irradiation with high energy ions, which may be used to develop new polymer materials with a modified technical surface layer for industrial applications. In the work to explain the mechanism of degradation of polymeric materials and elastomers, an accelerated technique based on the use of energetic He + ion beams was used, in which, as in the case of gamma radiation, ionizing interactions dominate.

2. EXPERIMENTAL

2.1. Materials

Six different materials were tested: ethylene-propylene-diene monomer rubber (EPDM), acrylonitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR) and natural rubber (NR), plasticized poly (vinyl chloride) (PVC), polytetrafluoroethylene (PTFE)- Table I.

The rubber mixtures were made at the Institute of Polymer & Dye Technology at the Faculty of Chemistry of the Lodz University of Technology. Polyvinyl chloride was purchased from Anwil S.A. and polytetrafluoroethylene from MPS-MECHANIK.

TABLE I. Composition of the materials tested.

Sample / Components	**NR**	**SBR**	**NBR**	**EPDM**	**PVC**	**PTFE**
NR, RSS II	100	-	-	-	-	-
SBR, Ker 1500	-	100	-	-	-	-
NBR, Perbunan NT 1845	-	-	100	-	-	-
EPDM, Keltan EP G2470	-	-	-	100	-	-
activator, ZnO	4	4	4	4	-	-
stearic acid	2	2	2	2	-	-
silica, Ultrasil 7000	50	50	50	50	-	-
silane, Si 69	3,6	3,6	3,6	3,6	-	-
polyethylene glycol	2	2	2	2	-	-
antiozonant, 6PPD	2	2	2	2	-	-
parafin wax	2	2	2	2	-	-

accelerator, TBBS	1,6	1,6	1,6	1,6	-	-
sulfur, S_8	1,4	1,4	1,4	1,4	-	-
PVC, Polwinit	-	-	-	-	100	
PTFE	-	-	-	-	-	100

2.2. Sample preparation and modification

The materials were exposed to He^+ ions with a beam energy of 60 keV. The irradiation fluence increased from 1×10^{15} to 1×10^{17} cm^{-2}. The total current of the He^+ ion beam was 300 µA, and the current density was dependent on the total area of the exposed sample and did not exceed approx. 1 µA/cm^2. In this case, the power density of the incident beam did not exceed 0.06 W/cm^2, and the sample temperature was not more than 80°C. The maximum values of inelastic (Se) and nuclear (Sn) energy losses calculated using the SRIM code for the above He^+ ion bombardment conditions are: Se = 160eV/nm and Sn = 11eV/nm, in this case ionization dominates the degradation occurring in material. The irradiation was carried out in a gas ion, home-built implanter, which was designed and built at the National Center for Nuclear Research. The use of a home-built implantator allows the implantation of gas ions such as, for example hydrogen, helium or argon. The XY stage, mounted in the implanter's vacuum chamber, made it possible to move the material under the beam and prevent its long-term exposure to the ion beam. Initial tests using beams of hydrogen ions, which are even lighter than helium, indicated the possible influence of irradiated hydrogen atoms, disrupting the analysis of processes related to the release of this element from polymer macromolecules. Helium atoms, which is a noble gas, do not chemically interact with the defective material, and therefore do not affect the reactions that occur under the influence of energy deposition in the polymer.

2.3. Structural analysis

2.3.1. Scanning Electron Microscopy (SEM)

The morphology and microtopography of the surfaces and cross-sections (after cleavage of the samples in liquid nitrogen) of the polymeric materials were examined by scanning electron microscopy (SEM). The samples, previously sputtered with gold, were analyzed with Zeiss Auriga or Hitachi SU 8230 microscopes. In the case of surface testing, low electron energy, typically 5 keV, was used, while for cleaved parts the energy was lowered to 2 keV.

2.3.2. Fourier-transform infrared spectroscopy (FT-IR)

Infrared spectroscopy with Fourier transform (FT-IR) was used to study the effect of He^+ ion beam irradiation of polymer surfaces on chemical and structural changes in their surface layer. FT-IR spectra in the wavenumber range 500-4000 cm^{-1}, averaging the result of 16 scans, were made with a Nicolet 8700 FT-IR Spectrometer.

2.3.3. Raman Spectroscopy

In addition to the infrared spectra, samples of polymeric materials were additionally examined using a confocal Raman microscope WITec Alpha 300R, equipped with a laser source with an excitation wavelength of 532 nm and a power of 2 mW. Raman signal was collected during 1 sec for accumulation. Stokes signals were collected with a CCD detector (cooled to -60°C) under the objective lens (Zeiss) with a magnification of 50 or 100 x in the wavenumber range from 100 to 3500 cm^{-1}.

2.3.4. Differencial Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to analyze changes in phase transition temperatures (glass transition temperature - T_g and melting point - T_m) and the degree of crystallinity of semicrystalline polymeric materials resulting from their bombardment with a He^+ ion beam.

Measurements were made using a Perkin Elmer PYRIS-1 apparatus, in a heating cycle at a rate of 10°C / min, in the temperature range from -50°C to 400°C. The mass of the samples was about 2.5 mg.

2.3.5. Nanoindentation

Nanoindentation was performed at room temperature with a NanoTest Vantage (Micro Materials Ltd.). A Berkovich pyramid-shaped diamond indenter (Synton-MDP) was used for all measurements. The calibrations of the device were performed using an amorphous silica plate as a standard material with specified mechanical properties. Measurements were made at loads ranging from 0.02 - 1 mN, which allowed for making pits from 37 to 935 nm, depending on the material tested and the ion irradiation fluence. Depth was measured as the maximum displacement of the indenter under load. Measurements were made in the load controlled mode (load rise time / load removal time - 5/3 s, stopping time at maximum load - 1 s). The waiting period for the correction was 60 s. This test was repeated 15 times. The nanohardness was determined using the methodology proposed by Oliver and Pharr [48].

2.3.6. Friction and wear measurements

The aim of the tribological tests was to assess the effect of ion irradiation of the surface of polymeric materials with the H^+ ion beam on the nature of friction, the coefficient of friction and their frictional wear. The tests were carried out using a pin-on-disc tribotester with a steel ball with a diameter of mm made of stainless steel, under a load of 10 N. The ball moved along the surface of the tested material with a rotational speed of 43 s^{-1}, along a track with a diameter of 22 mm. The frictional resistances were recorded each time for a period of 10 ks.

2.3.7. Tensile strength (TS)

The static tensile test was performed in accordance with PN-EN ISO 527-1 for plastomers and PN-ISO 37 for elastomers. The determinations were carried out using an Instron 8501 servo-hydraulic testing machine with a 1kN measuring head at 23°C. The head travel speed was dependent on the type of material and was 5 mm/min for PTFE and PVC, and 500 mm/min for EDPM, NBR, NR and SBR. The test specimens were in the shape of paddles, with dimensions strictly defined in the appropriate standard (dimensions of the working part length 25 × width 4 × thickness 1.5 mm).

2.3.8. Electrical resistivity

Surface resistance is one of the most important parameters for the functionality of cable insulation. Measurements were made with a tester Fluke Insulation [49], in accordance with PN-85 C-04259/01 - in a system of two concentric electrodes, with an inner diameter of 25 mm and an outer diameter of 50 mm, respectively. The gap between the electrodes was 2 mm. The resistance was measured at a potential of 1 kV. The electrodes were made in such a way that the pressure on the measured sample was equal to 0.1 MPa. Isopropyl alcohol was used to clean the surface of the material before each measurement. Each measurement was repeated 15 times.

3. Results and discussion

3.1. Surface morphology and microtopography

Irradiation with a high-energy ion beam causes cross-linking of the polymer surface layer. The core of the non-ionized material remains flexible and can stretch the rigid top layer, causing the surface layer to wrinkle and micro-cracks – Fig. 4.

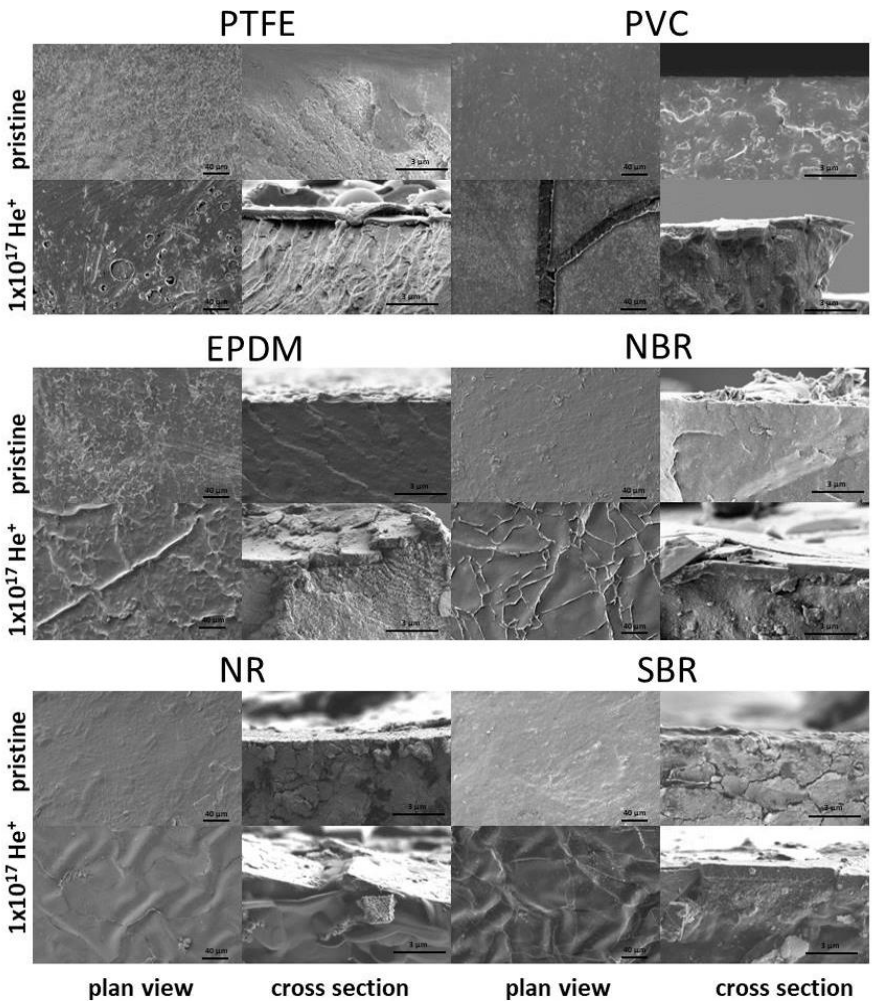


FIG. 4. Images of surface topography and cross-sections of samples of polymeric materials obtained by SEM.

It can be seen that the degree of cross-linking increases with the fluence increase, which causes both the length and width of the cracks to increase. On the surface itself, an oxidation process may additionally take place which causes degradation, sometimes dominating over cross-linking. The cross-sections show clearly the irradiated top layer. You can notice cracks and the interface between irradiated layer and material bulk [50].

3.2. Chemical composition of the surface layer

3.2.1. FT-IR Spectroscopy

The influence of ion iradiation on chemical changes taking place in the surface layer of polymeric materials is presented in Fig. 5.

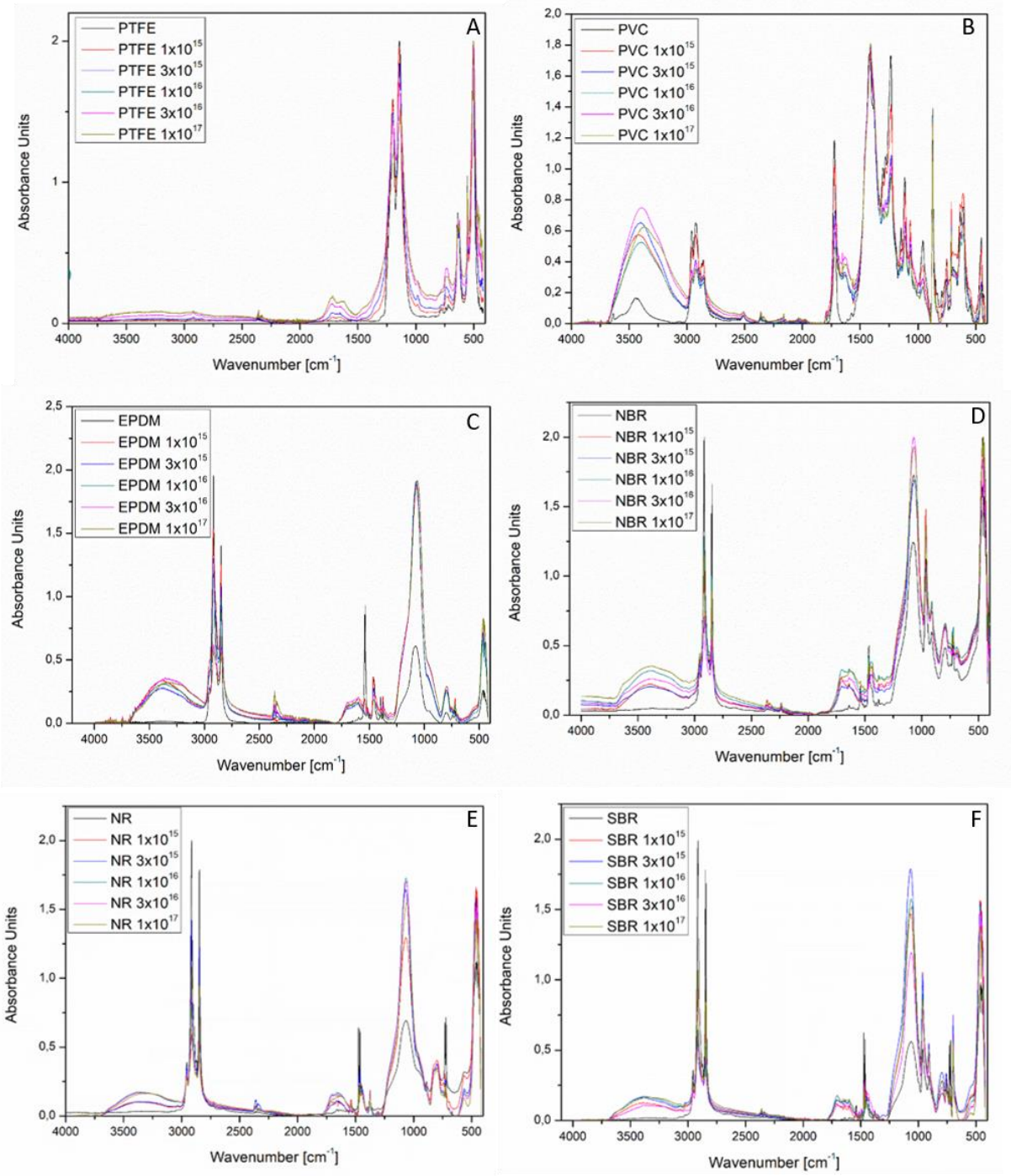


FIG. 5. Influence of He^+ ion bombardment on FT-IR spectra of the polymer materials studied.

The characteristic absorption bands for PTFE, originating from asymmetric and symmetrical stretching vibrations at 1200 and 1142 cm^{-1} wave numbers, respectively, and swaying and stretching vibrations in the CF_2 groups, at 638 and 504 cm^{-1} wave numbers, respectively [51], as a result of ion irradiation decrease its intensity with increasing fluence, which indicates breaking of C-F bonds. The degradation of the material is accompanied by its oxidation, as evidenced by the increase in the absorption bands coming from the hydroxyl groups at the wave number of approx. 3300 cm^{-1} and the carbonyl at 1710 cm^{-1}. There is also a noticeable appearance and gradual increase, along with the ion irradiation fluence

increase, an increase in the absorption bands at 1640 and 938 cm^{-1} wave numbers, derived from vibrations in groups C = C and CF = CF, respectively [52, 53].

The process of polymer degradation by ion bombardment is much more advanced in the case of PVC. The intensity of the absorption bands coming from the C-H vibrations in the methyl and methylene groups (1335, 1425, 2924 and 2958 cm^{-1}) decreases, while the intensity of the absorption peak from the -OH group (approx. 3400 cm^{-1}) clearly increases and new band at 1723 cm^{-1}, coming from vibrations in the C = O group, which confirms the intense oxidation of the material. On the other hand, the disappearance of the absorption peaks at the wave numbers 712 and 635 cm^{-1}, corresponding to the C-Cl bonds, of a oscillation and stretching character, respectively [54] means that PVC also degrades by releasing hydrogen chloride.

On the FT-IR spectrum of EPDM, after ion irradiation, a wide absorption peak in the range of 3000 - 3500 cm^{-1}, coming from hydroxyl and hydroperoxide groups, appears, which together with the strengthening of the absorption band from C-O at the wavenumber of 1077 cm^{-1} indicates the oxidation of the material [55]. The absorption bands at the wavenumbers 2848, 2916 and 1464 cm^{-1}, coming from the CH_2 groups, clearly weakened, while the band at the wavenumber of 1538 cm^{-1} clearly increased and a new band appeared at 1615 cm^{-1}, corresponding to the stretching of the C = C bonds confirming the degradation of polymer macromolecules [56]. The oxidation and degradation of NBR, NR and SBR macromolecules is manifested in the FT-IR spectra of rubbers from the above-mentioned rubbers subjected to high-energy ion irradiation, to an even greater extent than was the case with EPDM-based rubber. The absorption bands mentioned above from oxidation grow more, C-H vibrations in the methylene and methyl groups clearly disappear, while there are additionally peaks originating from C = C vibrations (1600 and 1640 cm^{-1}) [56] and a broad band of absorption in the wavenumber range 1690-1720 cm^{-1} [57], related to carbonyl and carboxyl groups [58]. In the FTIR spectra of NBR and SBR exposed to the high-energy ion beam, the absorption bands remain practically unchanged from the nitrile groups, at the wavenumber of 2240 cm^{-1} and at the wavenumber of 699 cm^{-1}, from the vibrations of the aromatic ring in styrene monomer units, respectively.

3.2.2. Raman Spectroscopy

The influence of ion irradiation on chemical changes in the surface layer of polymeric materials is presented in Fig. 6.

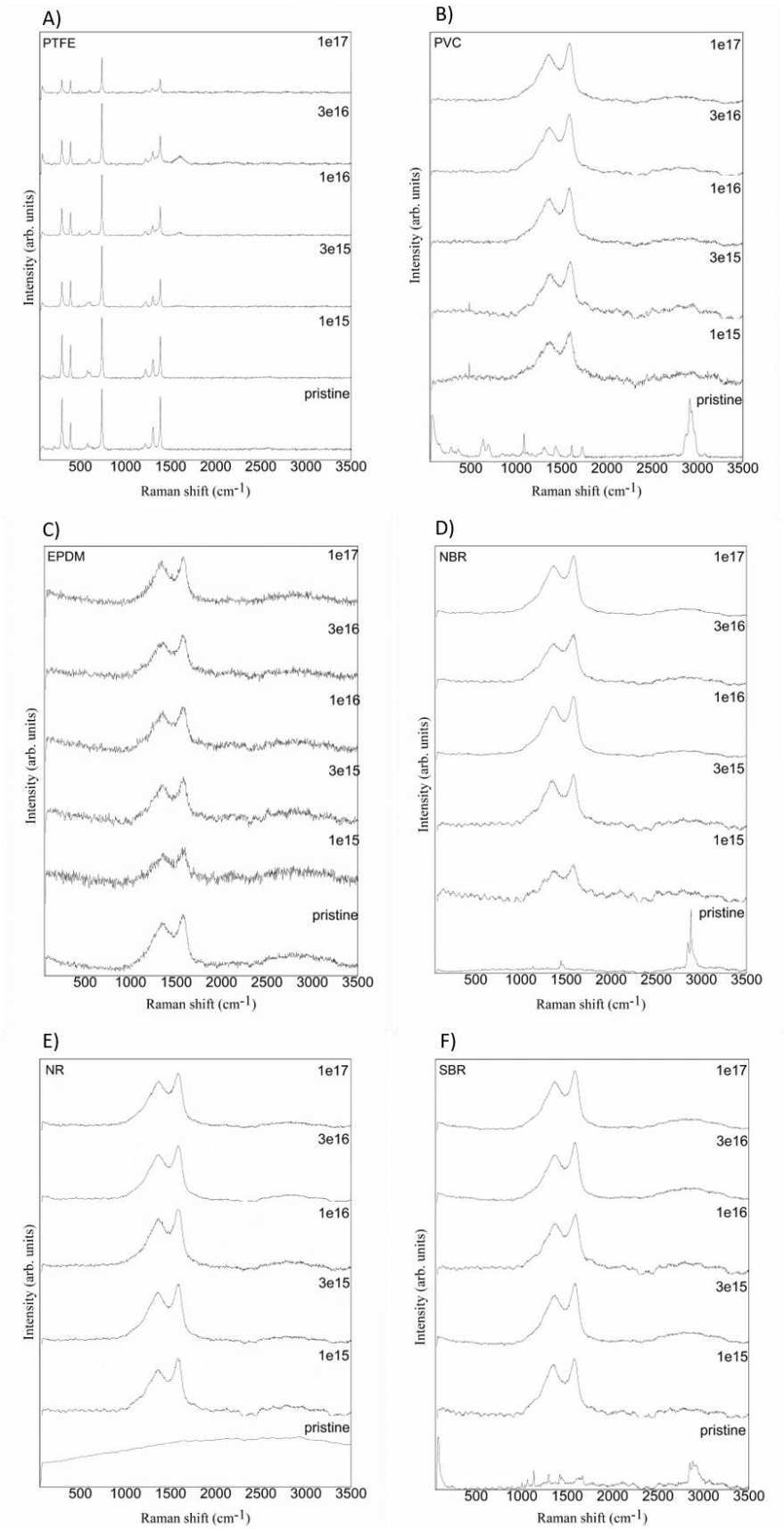


FIG. 6. Influence of He^+ ion bombardment on Raman spectra of the polymer materials studied.

Raman spectra obtained for PTFE treated with a high-energy ion beam indicate the formation of the groups: COF, CF_3 and COOH [59]. For PTFE material after ion irradiation, an increase in crystallinity was observed, as evidenced by an increase in signal intensity in the range of 700 cm^{-1}. The spectrum shows the characteristic peaks of the CF_2 groups at positions near 298 and 390 cm^{-1}, the doublet at positions 580 and 598 cm^{-1} and the CF_2 triplet at positions 1384, 1307 and 1216 cm^{-1}.
Raman spectra of PVC subjected to ion irradiation indicate that even the lowest fluence of ions causes degradation of the polymer surface. All Raman bands present in the initial material disappeared (2916 cm^{-1}, which corresponds to the vibration stretching C-H bonds in the CH_2 groups and 634 cm^{-1}, originating from C-CI vibrations), while bands at 1377 and 1597 cm^{-1} characteristic for amorphous carbon with sp^2 hybridization, appeared [60]. A well-known mechanism for the degradation of PVC is the effect of dehydrohalogenation, which produces a double bond along the backbone of the chain. After the formation of a double bond, the adjacent chlorine atom, assuming the allyl position, is easily detached from the macromolecule. The formation of C = C bonds, even if their concentration is very low, can be detected by Raman spectroscopy [61].
Raman spectra of EPDM samples, regardless of the irradiation fluence, have bands located at 1576 cm^{-1}, derived from C = C stretching vibrations, and 1355 cm^{-1}, which can be attributed to the symmetrical C-H deformation vibration of the methyl group [56, 62]. However, the recorded Raman bands after irradiation with ions seem to be less intense. Even more "sensitive" to ion bombardment is the Raman NBR spectrum. All signals from the C-H bonds located at 2883 cm^{-1} recorded for the starting material disappeared, which can be attributed to the fluorescence effect associated with the color change of the sample. Only when the fluence is increased to $1x10^{16}$ cm^{-2}, Raman bands appear in the spectrum at positions 1350 and 1583 cm^{-1}, which come from vibrations stretching C-C and C = C, respectively. Fluorescence made impossible to obtain the Raman spectrum for NR based rubber. However, after irradiation with the ion beam, similarly to the previous experiments, new bands appear at 1360 and 1584 cm^{-1}, which can be attributed, respectively, to deformations in methylene groups and vibrations of C = C double bonds [63]. In the Raman spectrum of SBR rubber there is a band at 2915 cm^{-1}, indicating the presence of CH_2 groups, which disappears after ion irradiation, while bands appear at 1580 cm^{-1} from stretching of the C = CH groups in the ring of styrene units and at 1356 cm^{-1} from deformation of CH_2 groups in butadiene monomer units [64].

3.3. Phase transitions

Cross-linking and degradation are the main processes influencing the change of the thermal behavior of the tested material. The DSC allowed for the observation of the difference in heat flow in the initial samples and those subjected to ion irradiation, determination of melting points (T_m), glass transition (T_g) and crystallization (T_c) of polymeric materials. The observed changes were not large due to the surface scope of modifications, but their nature is significant from the point of view of the operation of products made of polymers in the temperature field. Ion irradiation caused a slight increase in the melting point of PTFE, denoting a slight increase in the degree of crystallinity of the polymer, most likely due to the degradation and etching of the amorphous phase [65]. The glass transition temperature of PTFE (T_g = - 20 ° C) does not change under the influence of ion bombardment, most probably due to the high degree of crystallinity of the polymer, reaching almost 95%. The situation is different in the case of plasticized PVC, for which the Tg decreased from 93 to 80°C, most probably as a result of the release of the polyester plasticizer from the polymer [66]. Due to the amorphous nature of the rubbers it was only possible to determine changes in the glass transition temperature of the material caused by ion irradiation. In the case of EPDM rubber, a decrease in the glass transition temperature was noted. It is most likely caused by cross-linking induced by ion irradiation and may indicate a decrease in the thermal stability of the rubber after irradiation. The reverse is true for NBR rubber, for which the T_g has increased, most likely due to the presence of a polar nitrile substituent. In the case of rubbers

based on NR and SBR, there was practically no effect of ion irradiation on the glass transition temperature of the rubber. In the latter case, it can be explained by the presence of strong intermolecular interactions (self-induced crystallization) and the presence of aromatic substituents limiting the mobility of macromolecules.

3.4. Mechanical properties

3.4.1. Nanohardness

The primary reaction in polymers and elastomers exposed to radiation is the disruption of atoms or side groups to form radicals, leading to cross-linking which increases the stiffness and hardness of the polymer. At a later stage, the main chain is broken, polymer degradation and deterioration of mechanical properties, including reduction of material hardness. Fig. 7 shows the influence of He^+ ion beam fluence on the nanohardness of polymers studied.

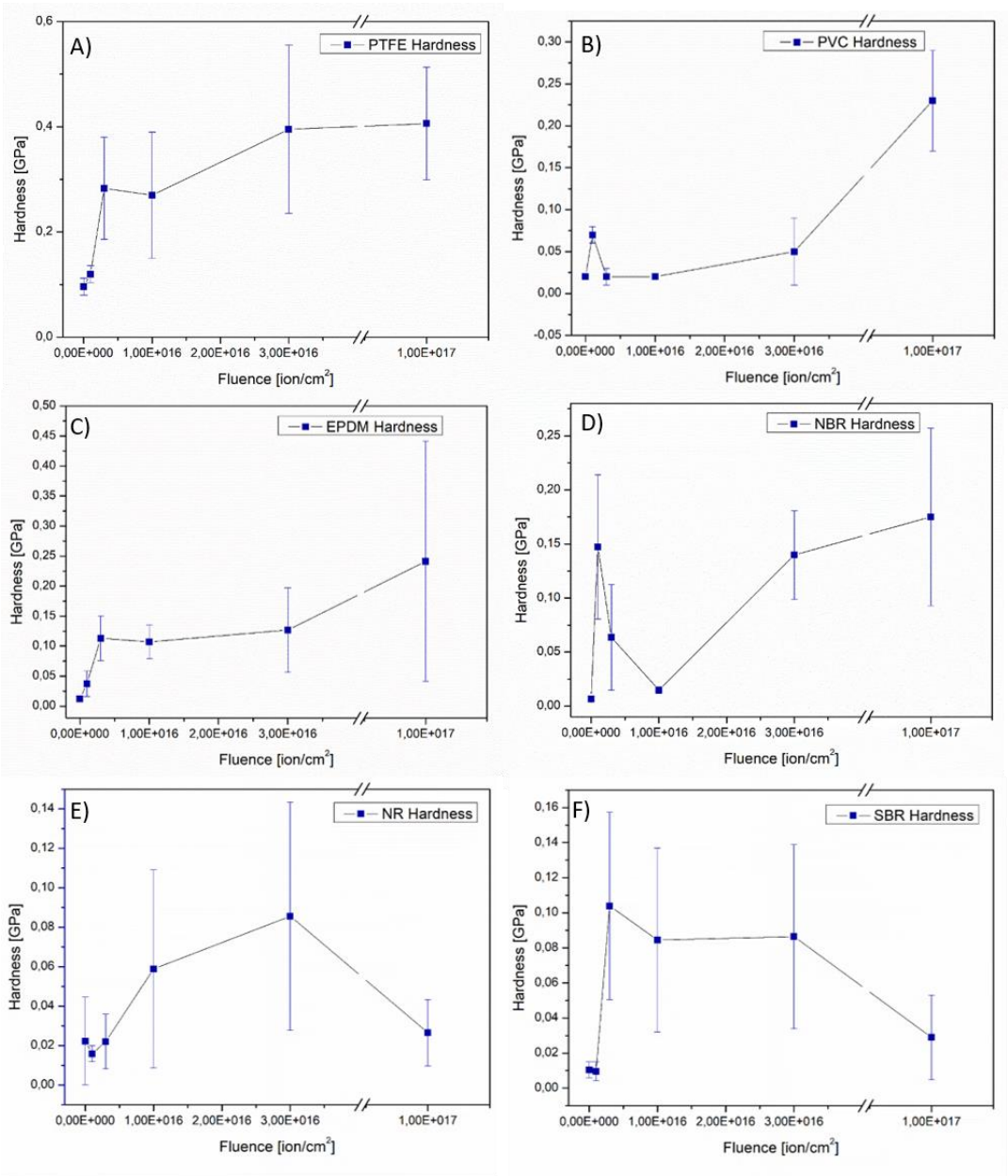


FIG. 7. Influence of the He^+ ion irradiation on polymer surface hardness.

The nanohardness measurements confirm the changes accompanying the fluence increase. The results are characterized by quite large dispersions, which is probably due to the low hardness of the materials, the complex morphology of the surface of the samples and its roughness.
An increase in the ion fluence causes an almost 4-fold increase in PTFE hardness, which should be attributed to the etching of the amorphous phase leading to an increase in the degree of crystallinity of the polymer surface layer (in accordance with the previously presented DSC test results, which showed an increase in T_m). Similar results were obtained by Liu et al. [67]. An even greater effect, manifested by a 10-fold increase in hardness, was achieved in the case of PVC, confirming the removal of the plasticizer and the dominant cross-linking effect. The error bars indicate the dispersion of the nanohardness values for individual measuring points. The reason why error bars show fluctuating values is most likely the high surface roughness and cracks that appear after ion irradiation. These effects explain the fact that the hardness dispersion is the smallest for the pristine sample and increases with the fluence [68]. The greatest changes were observed for EPDM and NBR-based rubbers, where the hardness increased by up to 20 and 26 times, respectively, as a result of the irradiation. Such a large effect can only be attributed to ion bombardment-induced cross-linking, combined with the release of hydrogen from the surface layer, causing the layer composition to evolve towards hydrogen-doped carbon. Differently to the above-mentioned elastomers, NR and SBR rubbers behave. In the case of NR, the hardness of the material initially increases with an increase in the fluence, and then the trend is reversed. SBR reaches its maximum hardness at much smaller fluences, of the order of $3x10^{15}$ cm^{-2}, after which the polymer degradation reactions begin to dominate and its hardness begins to decrease with increasing ion irradiation fluence. The results show that rubber based on NR and SBR show a much greater sensitivity to bombardment with a high-energy ion beam, and the degradation of polymers begins to dominate earlier than for EPDM and NBR materials.

3.4.2. Tensile strength and elongation at break

The results of mechanical tests using the static tensile method (ISO 37) show that the measurement of elongation at break (ε_B) is a better indicator of changes accompanying ion irradiation of polymeric materials than their tensile strength (TS). As Murthy showed [43], the value of TS may increase and then decrease with the progressive aging of the material, while the value of ε_B decreases with the aging time. The tensile curves for polymer samples before and after irradiation up to the highest ion fluence ($1x10^{17}$ cm^{-2}) are presented in Fig. 8.

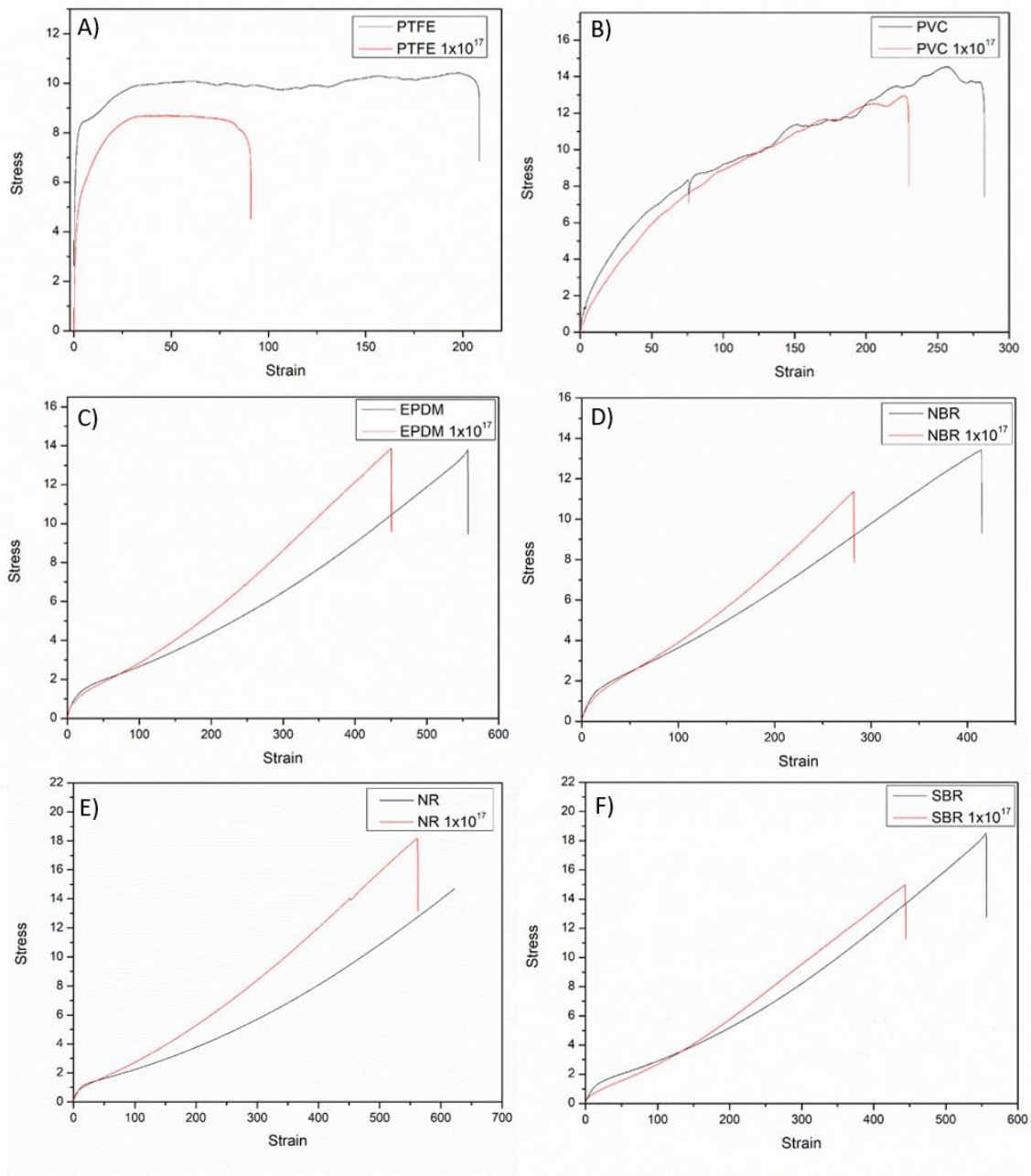


FIG. 8. Influence of He^+ ion fluence on the mechanical characteristic of polymers studied.

Ion irradiation causes a decrease in the tensile mechanical strength of the tested elastomers (PTFE and PVC). The effect is much greater in the case of PTFE, reaching nearly 20%. In the case of elastomers, we observe the opposite effect. In this case, the tensile strength increases with the NR rubber having the greatest effect. Such a behavior may be the result of different mechanisms accompanying the bombardment of a high-energy ion beam of partially crystalline polymers - PTFE or amorphous elastomers. In the first case, we are dealing with the decomposition of the amorphous phase, as a result of which the polymer becomes less resistant to plastic flow and breaks at much lower values of relative deformation. On the other hand, rubber-based rubbers are cross-linked as a result of ion irradiation, which translates into greater strength, which is accompanied by a significant increase in material stiffness at higher deformations (ε_B> 100%, in the case of NR even from 50%). This can be explained based on the relationship between the tensile strength and the cross-link density of the rubber. The processes taking place in the structure of the material under the influence of ion irradiation can be divided into two phases. In the first phase, the tensile strength increased continuously and

reached its maximum value with increasing cross-link density. In the second phase, the tensile strength starts to decrease as the cross-link density increases further. When the cross-link density reaches a critical value, the mobility of the chain segments becomes limited, which causes a stress concentration with a decrease in the effectiveness of the network nodes and consequently leads to a decrease in tensile strength. The stiffness of the polymer does not change much, while the value of the elongation of the material at break decreases quite significantly. As in the case of the tested elastomers, also in this case the course of the stress curve in the function of deformation is viscoelastic. This proves that the small depth at which the changes caused by the action of the ion beam take place, important from the point of view of giving elastomeric materials new functional features [17, 69], allows to maintain the general viscoelastic character of elements.

3.5. Tribological properties

3.5.1. Friction

Earlier tribological tests carried out on elastomers indicate that ion irradiation significantly affects the friction coefficient of these materials [69]. The energetic ions contribute to the reduction of the friction coefficient of the rubber due to the increase in the degree of cross-linking of its surface layer. The hard but thin "skin" on the surface of the elastic core leads to a better distribution of the load, which is spread over the larger area, reducing the deformation of the underlying material, thus reducing the hysteresis component of the friction force, which is dominant in elastomers [70]. This allows for the change of the traditional, volumetric friction mechanism proposed by Moore to the "surface" mechanism by Bowden and Tabor [71] – Fig. 9.

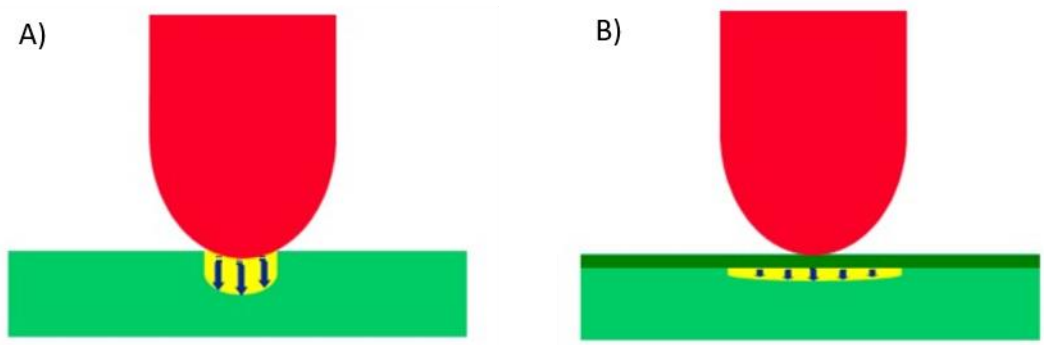


FIG. 9. Scheme of the influence of ion irradiation on the mechanism of friction of elastomers; A) bulk mechanism – Moore; B) surface mechanism – Bowden & Tabor

The friction characteristics for polymer samples before and after ion irradiation (for the highest ion fluences) are presented in Fig. 10.

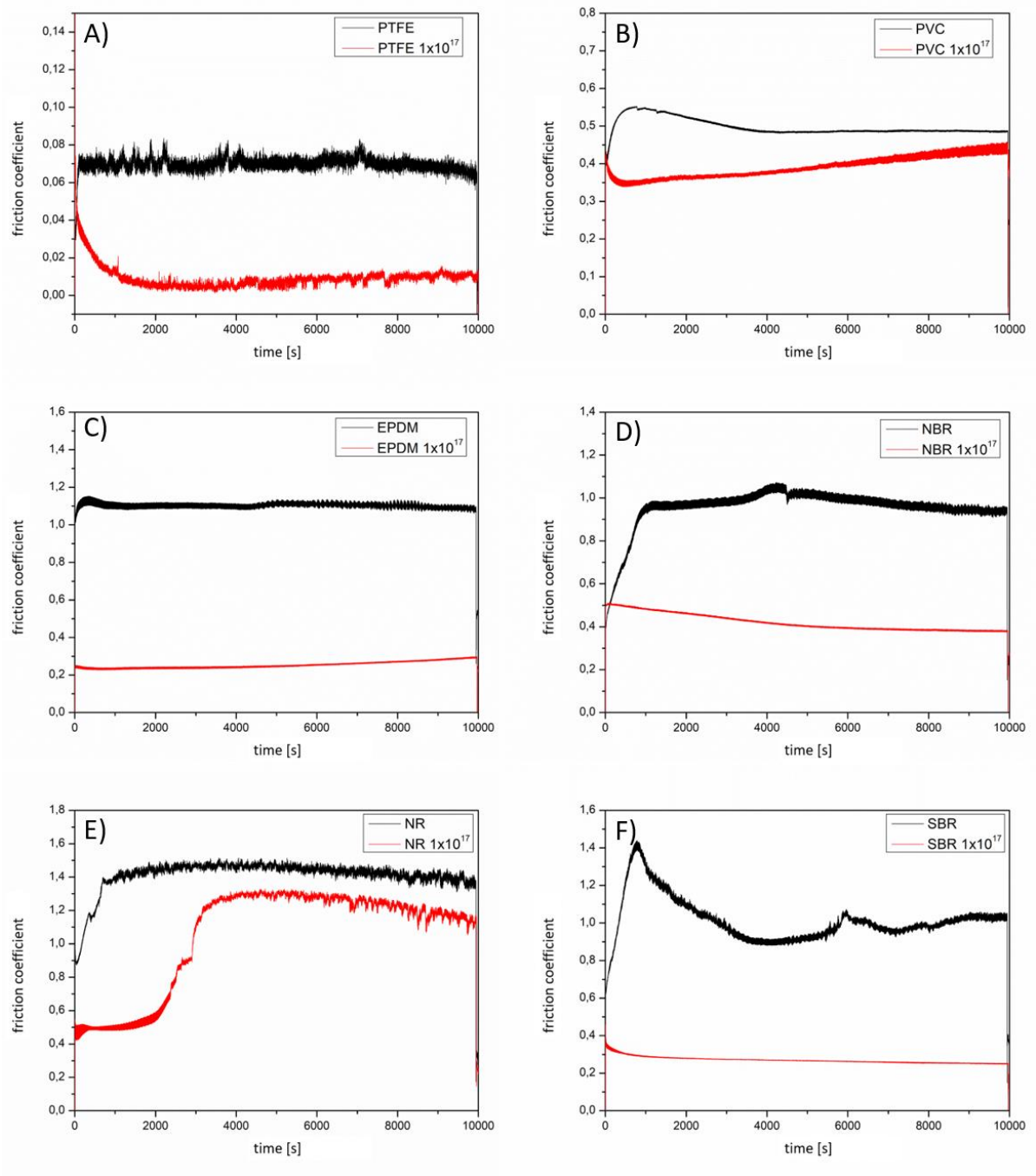


FIG. 10. Influence of He^+ ion beam fluence on the tribological characteristic of polymers studied.

3.5.2. Wear

In the case of the NR elastomer, a decrease in the friction coefficient from 1.4 to 0.5 was observed in the initial phase of the experiment. After approx. 3000 s, however, the friction starts to increase rapidly, which is related to the very high abrasive wear of the material and removal of the modified layer which starts from about 1000 s of the test. This is in line with the results of nanohardness tests: in the case of NR rubber subjected to ion beam irradiation up to a fluence of $1x10^{17}$ cm^{-2}, the hardness of the modified rubber surface layer was the lowest, which explains its highest wear resistance.

In the case of EPDM and NBR rubbers, the thin, stiff layer formed on their surface, which is a consequence of cross-linking the rubber, causes that the frictional wear resistance of materials subjected to ion irradiation increases. The effect can be seen on the example of NBR rubber - Fig. 11.

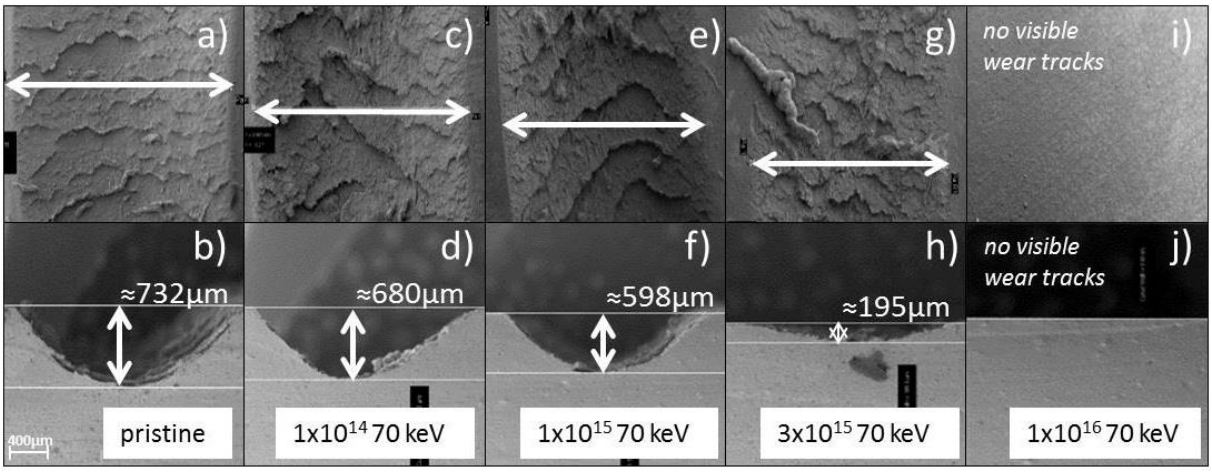


FIG. 11. SEM analysis of wear traces on NBR surface after friction tests (top view and cross-sections).

The images clearly show a decreasing depth of the wear tracks and reduced surface damage as the ion fluence increases. The NBR material irradiated with He^+ ions with the energy of 70 keV and the fluence of 1×10^{16} cm^{-2} shows no visible signs of wear even after the longest 10 000 s friction cycle. Under increasing loads, the rigid layer on the flexible substrate will eventually crack, but nevertheless does not detach from the bulk. This effect is beneficial for applications where it is important not only to reduce friction, but also to increase the wear resistance of the material.

3.6. Surface resistivity

The tested polymeric materials are characterized by various effects of ion irradiation on the amount of electrical resistance - Fig. 12.

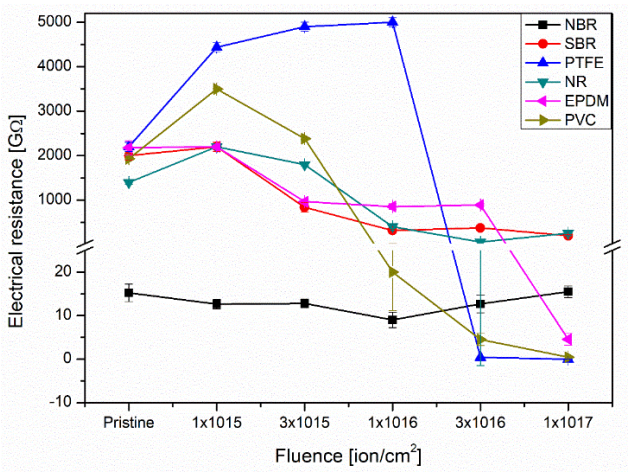


FIG. 12. Influence of He^+ ion fluence on the resistivity of polymers.

For most materials studied, an increase in surface resistance can be observed at the lowest irradiation fluences. This effect can be attributed to the removal of contaminants from the sample surface, such as water or plasticizer particles. Electrical resistance measurements have shown that, for medium and high fluences, resistance decreases with increasing ion fluence. The highest initial resistance was measured for PTFE, but the material is susceptible to sudden and drastic drops in resistance, the final value being 7 MΩ, which is 5 orders lower than the initial value. In the case of PTFE, the resistance increased with the fluence and decreased only for $3x10^{16}$ cm^{-2}. EPDM rubber turned out to be definitely the most resistant to the effects of ion irradiation, for which the resistance value remained at a constant level, showing a reduction in electrical resistance only at the highest fluence - 1×10^{17} cm^{-2}. For the remaining samples, a significant decrease in electrical resistance begins with a fluence of 1 ×

10^{16} cm^{-2}. PVC polymer, known as the most widely used in the radiation environment, shows the lowest resistance value already at $1x10^{16}$ cm^{-2}. The same is true for the NBR rubber sample, except that the NBR resistance value had by far the lowest electrical resistance value among the pristine materials. The effect of the decrease in resistance with the fluence for all materials is most likely related to the changes in the stoichiometry of the materials caused by the massive release of hydrogen, i.e. the progressive transformation of the polymer surface layer into a graphite structure doped with hydrogen.

3. CONCLUSIONS

Ion irradiation of the surface layer of polymeric materials with high-energy ions leads to significant structural changes in their surface layer, manifested by the modification of functional properties.

The SEM images prove that when the ions' fluency increases, the degree of cross-linking increases, which causes the length and width of the resulting cracks to increase. The conclusions based on the SEM images confirm the results obtained during the FTIR and RAMAN studies. In the case of FTIR, the appearance of new bands indicates oxidation of the material during irradiation with ions. The result of oxidation is the formation of new types of chemical groups. The carbonyl band is the characteristic end product of the oxidation reaction. Vibrations of C = O double bonds are observed, which proves that the materials are oxidizing. The band of -OH groups that appear in the materials after irradiation also indicates the degradation of the material. The intensity of the absorption bands increases with increasing ion fluency. The intensity of the bands corresponding to CH2 bonds after irradiation with ions decreases, which indicates their smaller share and also indicates the release of hydrogen atoms from the material.

Ion irradiation leads to the release of significant amounts of hydrogen from the modified layer, for large fluences of ions the final hydrogen concentration is about 10 atomic%, which is about 5 times less than the starting material. Such a significant change in the composition of the material leads to shrinkage of the surface layer, which in turn causes significant stresses, leading to the formation of a crack pattern. However, due to the fact that polymer macromolecules are usually longer than the range of the ions, the surface layer remains “anchored” in the substrate via intact macromolecules, thus obtaining a very good durability and adhesion of the modified layer. It is extremely important that the extent of the modification that occurs as a result of treating the material with a high-energy ion beam is limited only to its surface layer with a depth not larger than few microns, allowing the element made of polymer maintain its elasto-plasticity. The hydrogen release process is usually accompanied by cross-linking of the material in the surface layer, combined with the development and oxidation of its surface. The hardness of the layer subjected to the irradiation process increases significantly, in typical conditions about 10 times (as measured using the nanoindentation method). After modification with the ion beam, a significant decrease in frictional forces is also observed, in typical tribological tests this decrease is 5-6 times, and the value of friction in dry friction and with the use of a steel counter-sample drops from about 0.8 - 1 to 0.1 - 0.2. The microscopic analysis of the signs of wear shows that the wear resistance also increases significantly. The presented research shows, however, that ion bombardment of polymeric materials causes a reduction in their mechanical strength (despite the range limited to the surface layer of the order of micrometers) and electrical resistance, which has a negative impact on the possibility of using the materials as a cover for electrical cables exposed to ionizing radiation, e.g. in nuclear power plants or space applications.

AUTOR’S CONTRIBUTIONS

All authors contributed to this work.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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