



This work was carried out in whole or in part within the framework of the NOMATEN Center of Excellence, supported from the European Union Horizon 2020 research and innovation programme (Grant Agreement No. 857470) and from the European Regional Development Fund via the Foundation for Polish Science International Research Agenda PLUS programme (Grant No. MAB PLUS/2018/8).

This is a copy of the publication which appeared in: Surface & Coatings Technology, vol 388 (2020) 125562, published on: 03 March 2020.

DOI: 10.1016/j.surfcoat.2020.125562



Study of the electrical properties of ion irradiated polymer materials

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ARTICLE INFO

Keywords:

Ion irradiation
Polymer insulations
Electrical resistivity

ABSTRACT

The long-term exposure of the cable insulation, which are very often manufactured from polymers, to the standard operational environment conditions in nuclear power plant (NPP), such as radiation, heat and humidity, can cause ageing and degradation of their functional properties. Polymers exposed to such factors as ionizing and gamma radiation, undergo significant structural and functional modifications. In order to simulate NPP conditions, one can perform ion irradiation with different irradiation fluences to test insulation of the materials and determine their resistance to radiation.

It is known that the main effect of radiation is hydrogen release from polymer. This phenomenon leads to the increase of hardness, shrinkage of the material and deterioration of material resistivity. Polymer materials exposed to ionizing radiation become fragile, stiff, prone to fracture and breaking. In the case of cable insulation, one of the most significant problem is the decrease of their electrical resistance.

In this study, structural properties of pristine and irradiated polymer insulation were assessed by Scanning Electron Microscopy (SEM), Raman spectroscopy and resistance measurements. The phase composition was identified by Raman spectroscopy technique. It has been found out that these properties are strongly related to the ion irradiation and structure of the material. Reported findings points to the observation that current-voltage (I-V) characteristics depend from ion irradiation fluence – and material resistivity gradually decreases with the increasing fluence of ions.

1. Introduction

Electrical cables and wires are an integral part of any nuclear power plant (NPP) instrumentation, control and security systems [1–3]. Depending on the installation location and usage; cables have to face variety of environmental factors like high temperature, gamma radiation, humidity, corrosive atmosphere and mechanical stresses [4]. Insulation of the cables is made from various types of polymer materials such as: ethylene-propylene-diene monomer (EPDM) rubber, poly (vinyl chloride), silicone rubber or polyethylene.

It is known that structure of polymer materials change under the influence of radiation and the alterations like chains scission and cross-linking occur. Gamma radiation releases hydrogen and consequently leads to cross-linking of the polymer. It also increases the electrical conductivity and optical density due to cross-linking and creation of double and triple bonds [5]. The second effect is degradation which can be observed by the breakage of polymer macromolecules and molecular weight reduction. If this process prevails, decrease in mechanical

properties, including hardness, is observed. Of course, this phenomenon depends on the structure of the macromolecules. Polyethylene macromolecules break to form macro radicals which react with each other causing cross-linking of the polymer. This is manifested by contraction and hardness increase. In contrary, polypropylene macro radicals do not combine, which result in material degradation. Described phenomena can be clearly see in our studies (see Fig. 3 – plain-view). These phenomena determine the lifetime of the cables, define usually by their insulation resistance [6].

Main structural effect caused by ion irradiation is a massive loss of hydrogen from the modified layer what leads to smoothening of the surface and formation of wrinkles on the surface. This is due to the cross-linking of the polymer under the surface (on the surface we observe oxidation, which causes degradation). The layer under the polymer surface shrinks causing surface wrinkling [7–9]. It is known that polymers subjected to radiation become brittle, stiff, prone to cracks and tears [10,11]. This is extremely important because the cable failure may lead to problems with control of certain sections of the NPP

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<https://doi.org/10.1016/j.surfcoat.2020.125562>

Received 16 November 2019; Received in revised form 11 January 2020; Accepted 2 March 2020

Available online 03 March 2020

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which can be detrimental to the installation.

In order to simulate the impact of gamma radiation, ion irradiation has been used. It is known that ion irradiation of polymeric materials change their chemical and physical properties similarly to the gamma radiation. During the irradiation process, ions penetrate into the polymer, losing their energy due to interaction with the nuclei and electrons of the target material. The ion irradiation also has an impact on the breaking of inter-molecular bonds and creation of free radicals in polymers. During ion irradiation, hydrogen atoms detach from different parts of the polymer material through C–H bond cleavage, form H₂ molecules and migrate from the sample. The maximum penetration depth of an ion impinging into the solid depends on the energy of the ion which dissipates into the bulk of the material, delivering energy to the solid [12].

The characteristic changes depend on polymer macromolecule types which degrade through chain scission mechanism and as a result shorter chains fragments are being created. Macroradicals formed in the process of chain scission can react with each other, resulting in cross-linking of macromolecules. Different effects are observed when the polymer macromolecule scission leads to formation of radicals which are not able to interact with each other. In general the irradiated polymer composition approaches the one of hydrogen-doped carbon, the material is usually stiffer, harder and friction-related deformations are smaller, therefore the friction coefficient is lower.

The structure of NBR macromolecules position them in the group of polymers for which cross-linking reactions prevail over degradation reactions due to ion irradiation. The majority of synthetic rubbers like SBR also belong to this group, especially those from which technical products are made. The natural rubber (NR) behaves in a different way. In this material degradation process is dominant. The structure of the EPDM contains fully saturated bonds in the main chain, additionally double bonds in EPDM are pendant to the main chain. Therefore, these properties make EPDM rubber as crosslinkable polymers under radiation. Finally, ethylene-propylene-diene monomer (EPDM) rubber is one of the fastest growing synthetic rubbers on the market today. It can be widely used in many fields due to its saturated hydrocarbon backbone with the presence of double bonds inside of the chains [13]. Different types of polymers like poly(vinyl chloride) (PVC), ethylene propylene diene-monomer (EPDM) and polytetrafluoroethylene (PTFE) used in nuclear power plant (NPP) were investigated in this work. Special attention has been given to the polymer materials which have never been analyzed, for example acrylonitrile butadiene rubber (NBR), butadiene-styrene rubber (SBR), natural rubber (NR). These polymer materials were produced at Institute of Polymer and Dye Technology of Lodz University of Technology.

The main objective of this work was to better understand behavior of different type of polymers used as a cable insulation in a radiative environment in nuclear power plants (NPP). In addition to that, investigation of the structural and electrical properties changes induced by ion irradiation has been performed. In order to simulate NPP conditions, ion irradiation with different irradiation doses were used. Recent works have illustrated how big the use of polymers at NPP facilities is, and how large are their versatility and ability to change their properties.

It is known that materials working in NPP conditions accumulate damage relatively low. Presented conditions were chosen to create damage equivalent to long-term exposure, so recorded effects are clearly visible. In addition to that, it is worth to mention that ion irradiation does not activate the sample, so material is easy to handle and can be tested by using standard techniques.

Finally, one should clearly explain that polymers, especially elastomers because of their viscoelastic characteristic, in their pure state are excellent electrical insulators, and currently no other material can replace them.

2. Experimental

2.1. Materials

Based on the literature review, selection of six different types of polymers was performed. Three of them polyvinyl chloride (PVC), ethylene propylene diene-monomer (EPDM) and polytetrafluoroethylene (PTFE) were already used in a radiative environment [14,15]. PVC and PTFE were purchased from commercial companies. EPDM, acrylonitrile butadiene rubber (NBR), butadiene-styrene rubber (SBR) and natural rubber (NR) were manufactured by the Institute of Polymer and Dye Technology of Lodz University of Technology. All samples were prepared in the form of 10 cm × 10 cm × 2 mm plates and are listed in Table 1. As the samples were designed to model insulation materials, the filler used in the rubbers (silica) has been used.

The samples were irradiated with He⁺ ions having of 60 keV. In order to estimate the thickness of the modified layer, SRIM calculations were done [16]. The maximum value of inelastic (Se) and nuclear (Sn) energy losses calculated by using SRIM code were Se = 160 eV/nm and Sn = 11 eV/nm for NBR, similar values were obtained for other materials. During the irradiation, the beam power density was maintained below 0.6 W/cm², to avoid sample overheating. In order to control this process, a thermocouple (K-type) as a temperature sensor was used. The samples were irradiated using an XY manipulator, which did not allow the surface to be exposed to long-term exposure of the ion beam, the highest temperature did not exceed 90 °C.

Thickness of the modified by energetic ions layer define as a depth, when energy density lost in inelastic collisions drops to 10% of the maximum value. The results depend on the material used and vary from 550 nm for SBR to 700 nm for EPDM [7]. In order to simulate NPP conditions, the samples were irradiated with different irradiation fluences. Ion beam irradiation was carried out at gas-ion implanter located at National Centre for Nuclear Research. Processes were carried out at room temperature in vacuum (~10⁻⁵ Pa) under the given conditions: accelerating voltage 60 kV, beam current 300 μA, beam diameter 60 mm, beam surface area 300 mm² and current density 10 μA/cm².

In order to determine variation of changes in structural and electrical properties caused by ion irradiation, samples were submitted to 60 keV He⁺ ions in the fluency range from 1 × 10¹⁵ ions/cm² to 1 × 10¹⁷ ions/cm² (1 × 10¹⁵ ions/cm², 3 × 10¹⁵ ions/cm², 1 × 10¹⁶ ions/cm², 3 × 10¹⁶ ions/cm² and 1 × 10¹⁷ ions/cm²). Chosen energy modifies the material from several hundreds of nm up to 1 μm depth, which is sufficient for recording Raman signal without impact of the unmodified bulk material.

Table 1
Compositions of the materials used.

Component	Elastomer			
	NR	SBR	NBR	EPDM
RSS II	100	–	–	–
Ker 1500	–	100	–	–
Perbunan NT 1845	–	–	100	–
Keltan EP G2470	–	–	–	100
ZnO	4	4	4	4
stearin	2	2	2	2
Ultrasil 7000	50	50	50	50
Si 69	3,6	3,6	3,6	3,6
Polyethylene glycol	2	2	2	2
6PPD	2	2	2	2
wax	2	2	2	2
TBBS	1,6	1,6	1,6	1,6
S	1,4	1,4	1,4	1,4

2.2. Methods

2.2.1. Raman spectroscopy

Raman spectra were acquired using a confocal Raman microscope (WITec Alpha 300R, WITec, Germany). The laser operated at an excitation wavelength of 532 nm and power of 2 mW. The Raman signal was collected for 1 s. A CCD detector (thermoelectrically cooled to -60°C) was used to collect Stokes signals under 50 or 100 objective lens (Zeiss) over the wavenumber range from 100 to 3500 cm^{-1} . It is known that by using Raman spectroscopy one can detect mechanisms of vibrations which modifies the polarizability of the molecules. Vibrations of the long polymer chains cause no change in the dipole moment due to cancelling out of adjacent dipoles by repeating units, but change their polarizability. For this reason, polymer backbone structure was analyzed by using this technique. Raman spectroscopy is one of the optical techniques capable to give a quantitative information about molecular orientation in polymers [17].

2.2.2. Electrical measurements

Electrical properties such as insulation resistance, which is one of the most vital parameters for cable insulation functionality, was measured by using Fluke Insulation tester. The surface resistance measurements were carried out accordingly to PN-85 C-04259/01 standard [18]. The analysis was performed by using two concentric electrodes with external diameters of 25 mm and 50 mm. Space between electrodes was 2 mm. Resistance has been measured at the same potential of 1 kV. The pressure of the electrodes on the measured sample was equal to 0.1 MPa. To clean the material surface, alcohol and air drying system were used before each measurement. Each measurement has been repeated 15 times, in order to provide proper data collection.

2.2.3. Scanning Electron Microscopy

The ion-irradiation damage effects in polymers were visualized by means of scanning electron microscopy at low beam acceleration voltages (low-kV SEM). The SEM images of polymers surface were performed by using EVO MA 10 Zeiss device. The SEM images of the freshly-cleaved cross-sections of the specimens were collected with low energy (5 keV) electrons using Auriga Zeiss, equipped with the in-lens secondary electron detector.

3. Results and discussion

Raman spectroscopy was used to determine functional groups of the polymer materials. Fig. 1 presents the most intensive Raman bands - marked with the black arrows. Small band shifts of the certain Raman bands have been denoted in Table 2.

The Raman spectra of commercial PTFE showed (Fig. 1a) evidence of acyl fluoride (COF), CF-CF₂ and COO + X end-groups [19]. After irradiation, no changes in the structure of commercial PTFE, except increase in crystallinity (as evidenced by intensity increase of the signal in the region of 700 cm^{-1}) was observed. One can observe signals characteristic for the CF₂ groups in the positions near 298 cm^{-1} and 390 cm^{-1} , doublet of CF₂ in the positions of $580, 598\text{ cm}^{-1}$, and finally F₂ symmetry triplet of CF₂ in the positions of $1384, 1307$ and 1216 cm^{-1} .

Fig. 1b presents Raman signal recorded in the commercial PVC films. It is known that the PVC material shows a change in the spectrum characteristics which has been observed during irradiation [20]. One can see that all Raman bands present in the pristine sample disappeared after irradiation. At the same time, two bands characteristic for amorphous carbon with sp² hybridization appeared. It seems that even the lowest dose of ions effectively degrades the PVC surface. The most

significant changes in the peak intensity were recorded for the region between 1000 cm^{-1} to 1500 cm^{-1} (see, Fig. 1b). The degradation of PVC by the elimination of HCl and the formation of all-tram polyenes is well known and documented [21]. When the first HCl molecule is eliminated, adjacent HCl molecules are quickly split off which leads to a polyene structure. The Raman spectra of commercial PVC show C-Cl stretching vibrations at 634 cm^{-1} and C-H bending vibration at 1438 cm^{-1} . An intense Raman band located at 2916 cm^{-1} can also be observed. This signal corresponds to stretching vibrations of C-H bonds in the CH₂ structural fragment [22]. Raman spectra of irradiated PVC show two intense Raman bands located at 1377 and 1597 cm^{-1} . These bands appear due to the C-C and C=C stretching vibrations of polyenes and are typical for carbon materials. Raman band located at 1597 cm^{-1} position is characteristic to stretching vibrations of C=C bonds in conjugated aromatic compounds, while the band located at 1377 cm^{-1} is attributed to the defect structure of carbon material [23]. When PVC degrades, hydrochloric acid (HCl) is produced, resulting in the formation of C=C bonds which produce absorption peaks in the Raman spectrum. Even if the concentration of these bonds are very low, they are detectable by Raman spectroscopy, even when the amount of HCl lost is about 0.01% [24,25]. In our case, bands located at 1377 cm^{-1} and 1597 cm^{-1} reflect to PVC degradation. One can see that Raman band scattering is almost identical for all peaks irradiated PVC. However, small band shift after ion irradiation was observed, see Table 2.

Another polymer tested by using Raman spectroscopy technique was EPDM (Fig. 1c). The most intense Raman band was recorded at 1576 cm^{-1} , which is related to the in-plane vibrations of the graphitic wall. As shown in Fig. 1c, two scattering peaks can be observed at each EPDM sample, regardless of the irradiation dose. The band located at 1576 cm^{-1} can be assigned to C=C stretching vibration, while the other one located at 1355 cm^{-1} is assigned to C-H symmetric deformation vibration of methyl group [13]. Recorded Raman bands after ion irradiation appear to be less intense.

Fig. 1d shows Raman signal of NBR sample measured in the pristine state and after irradiation. All signals from C-H bonds located at 2883 cm^{-1} recorded in the pristine NBR disappeared after ion irradiation. Lines obtained from fluence of $1 \times 10^{15}\text{ ions/cm}^2$ are characteristic for fluorescence effect, which is the reason why no band has been recorded. Sample irradiated with a fluence of $3 \times 10^{15}\text{ ions/cm}^2$ shows fluorescence as well. However, Raman bands located at 1350 cm^{-1} and 1583 cm^{-1} positions can be seen. Fluorescence may be related to the color of the sample. As it is well known black color leads to the appearance of this adverse phenomena. The two bands located at 1350 cm^{-1} and 1583 cm^{-1} can be assigned to the C-C and C=C stretching vibrations.

Fluorescence due to impurities has prevented the acquisition of a useful Raman spectrum of NR, see Fig. 1e. Fluorescence is a particular problem in cross-linked materials. This is the main reason why we cannot compare bands from pristine material and material after ion irradiation. The mid-frequency region (1500 to 1000 cm^{-1}) displays the most significant changes [26]. New bands can be seen at 1360 and 1584 cm^{-1} . These positions are characteristic for C-C and C=C bands, respectively.

Most Raman bands of SBR are located in the 1800 – 900 cm^{-1} and 3200 – 2800 cm^{-1} regions [27]. Stretching vibrations of SBR characteristic for C-C and C=C are observed in the region between 1356 and 1580 cm^{-1} , respectively. Also, the bands located at 1356 and 1580 cm^{-1} show a relatively large increase in intensity for fluence of $1 \times 10^{15}\text{ ions/cm}^2$, $3 \times 10^{16}\text{ ions/cm}^2$, $1 \times 10^{17}\text{ ions/cm}^2$. Both symmetric and asymmetric -CH₂ and -CH₃ stretching vibrations typically appear in the 2800 – 3000 cm^{-1} region.

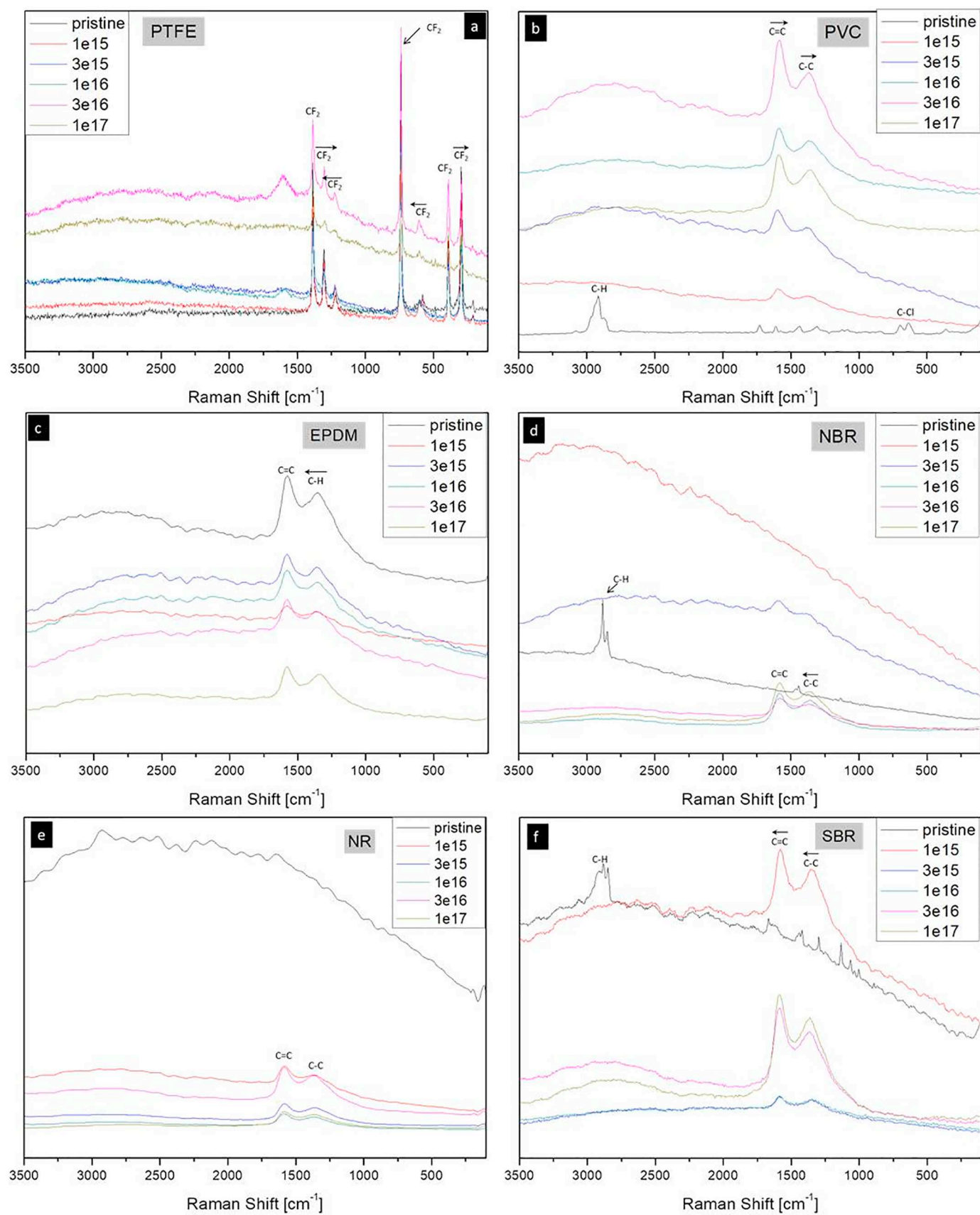


Fig. 1. Raman spectroscopy signal recorded the wavenumber range from 100 to 3500 cm^{-1} (500– 2000 cm^{-1} for EPDM) for pristine and irradiated polymer samples (Panel a. PTFE; panel b. PVC; panel c. EPDM; panel d. NBR; panel e. NR; panel f. SBR).

Table 2
Raman band positions and intensities of pristine and irradiated materials.

Pristine	1×10^{15}	3×10^{15}	1×10^{16}	3×10^{16}	1×10^{17}
PTFE					
298	298	293	293	293	293
390	390	390	390	390	390
580	580	580	606	606	602
739	739	739	739	739	739
1216	1220	1224	1220	1216	1220
1307	1307	1302	1298	1302	1298
1384	1384	1384	1384	1384	1384
PVC					
634	–	–	–	–	–
1438	–	–	–	–	–
2916	–	–	–	–	–
–	1377	1390	1372	1368	1363
–	1597	1597	1584	1584	1588
EPDM					
1355	1359	1359	1359	1359	1340
1576	1580	1580	1580	1576	1576
NBR					
1443	–	–	–	–	–
2883	–	–	–	–	–
–	–	–	1350	1366	1362
–	–	–	1583	1587	1582
NR					
–	1368	1360	1372	1368	1368
–	1584	1584	1584	1584	1584
SBR					
2883	–	–	–	–	–
–	1356	1364	1352	1360	1364
–	1580	1588	1576	1584	1588

Electrical resistance measurements were performed by using Fluke Insulation tester and show that this value decreases with increasing ion irradiation fluence. One can clearly observe that the smallest impact of radiation damage is recorded for EPDM polymers who shows reduction in electrical resistance at 1×10^{17} ions/cm². Conducted measurements clearly show that significant descent of electrical resistance commence at 1×10^{16} ions/cm² for the rest of the specimens. This effect is most likely related to the changes in material stoichiometry caused by a massive hydrogen release, hence to a progressive transformation of polymer into a graphitic structure (Fig. 2).

Presented results confirm the assumption, that EPDM is the most promising polymer material to be used in radiative environment [28]. At the same time, PVC polymer which is known as the most widely used in radiative environment shows the most surprising behavior. According to our measurements, significant reduction in electrical resistance has been observed already at 1×10^{16} ions/cm². On the other hand, NBR elastomer insulation shows the lowest values of electrical resistance.

Finally, SEM plan-view and cross-section micrographs of all studied materials are presented in Fig. 3. The first stage of experiment consisted of He-ion irradiation with 60 keV energy up to the fluence from 1×10^{15} ions/cm² to 1×10^{17} ions/cm². Presented images (see Fig. 3) clearly shows that ion irradiation cause surface shrinkage and crack development on the elastomer surface layer. Surface smoothing is the effect of degradation of macromolecules and the appearance of short chain fragments on the surface which perform function of a grease can be seen. The material becomes more packed and its volume decreases (density increases).

Obtained in the frames of this work results reveal that the EPDM

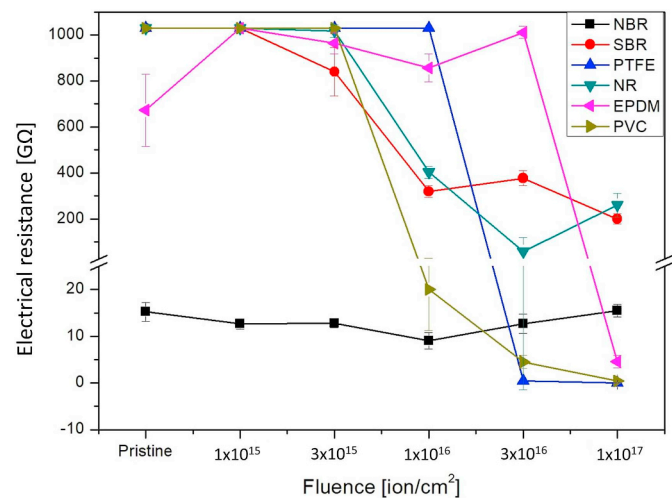


Fig. 2. Surface resistance as the function of ion fluence for all tested materials.

material reveals the highest electrical resistivity. Comparing to other materials EPDM maintains electrical resistance up to the highest irradiation fluence. One can observe two intense Raman bands characteristic for the C–H and C=C stretching vibrations, typical for carbon materials. These bands can be also observed for pristine EPDM and irradiated EPDM specimens. Accordingly, it can be concluded that EPDM does not undergo significant structural changes during the ion implantation process. However, SEM images revealed cracks on the surface of all ion implanted polymers. Presented in this work results suggest that the most commonly used in nuclear power plants PVC material is also the most sensitive to ion irradiation damage.

4. Conclusions

Different types of polymer samples submitted to ion irradiation have been characterized by two different methods in order to investigate structural changes related to radiation damage. Electrical resistance and wear resistance were calculated by electrical measurements and friction tests, respectively. Obtained results can be summarized in the following points:

- in all types of the samples (except EPDM and PTFE), Raman bands recorded in the pristine sample disappeared after ion irradiation.
- two intense Raman bands, characteristic for the C–C and C=C stretching vibrations, typical for carbon materials can be observed in all types of polymer materials, except EPDM and PTFE materials. It can be a matter of temperature in the material, which increases as a result of ion irradiation (PTFE is much more thermally stable than other polymers that have been tested).
- PVC is very sensitive to irradiation damage. Clear difference in morphology between irradiated and pristine materials have been observed.
- A peak shift can identify (at least qualitatively) stress in polymer chains.

In general the best properties were revealed by EPDM samples, which kept its initial resistance to higher irradiation fluences. Further works are in progress to identify material properties that may serve the purpose of early indicator of the insulation property loss.

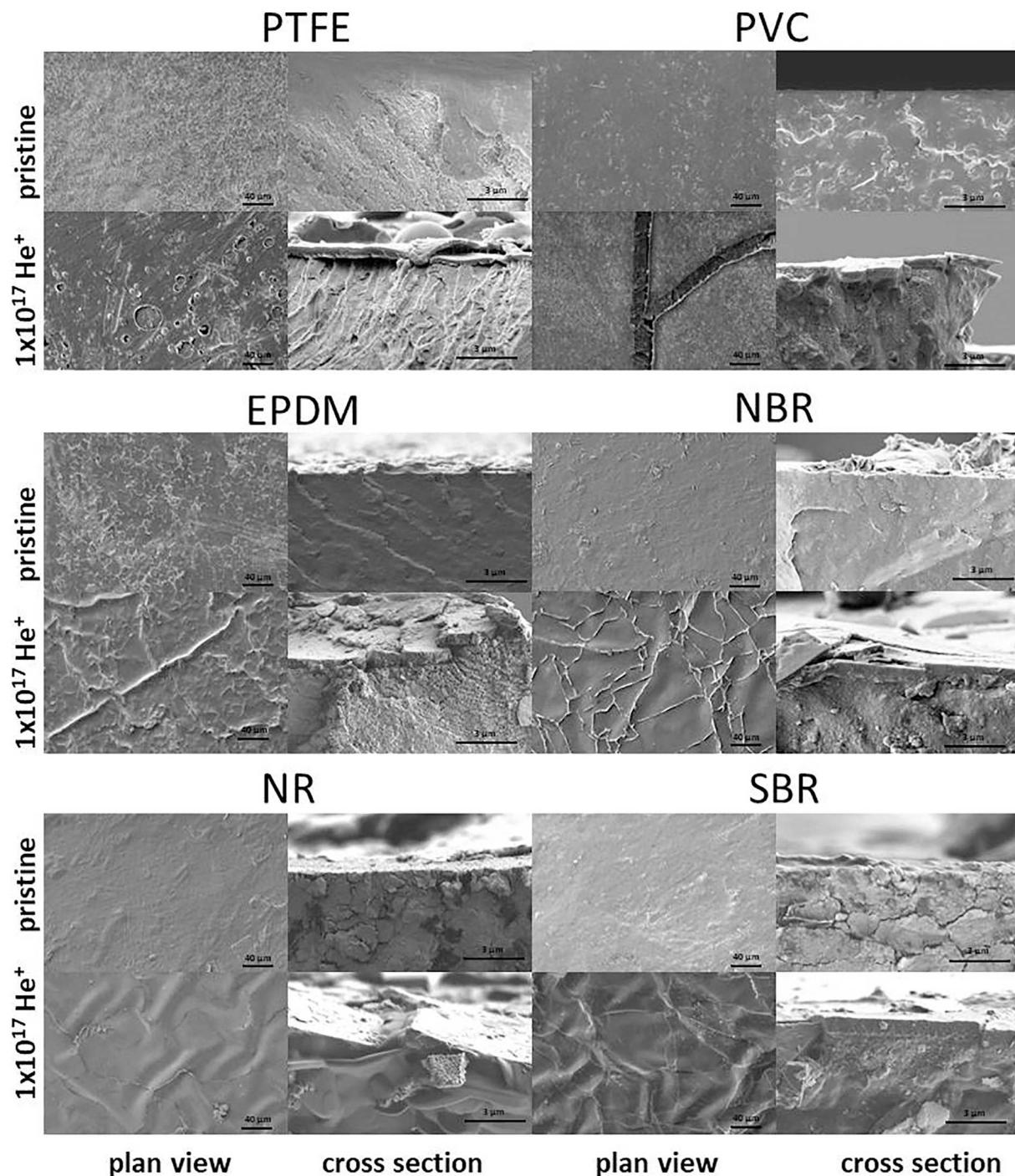


Fig. 3. SEM micrographs showing plan-views and cross-sections of all types of studied polymers before and after irradiation with He⁺ ions.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

CRediT authorship contribution statement

A. Kosińska:Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Project administration.
J. Jagielski:Conceptualization, Methodology, Validation, Writing -

review & editing, Supervision.
M. Wilczopolska:Investigation.
D.M. Bieliński:Resources, Writing - review & editing, Supervision.
M. Okraska:Resources.
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Ł. Kurpaska:Writing - review & editing, Supervision.
K. Nowakowska-Langier:Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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