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Functional characteristics of ion-irradiated elastomers used as insulation materials: Comparison between mechanical and electrical properties

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ABSTRACT

The main aim of this work is to get a deeper insight into the problem of insulation properties of materials exposed to radiative environment, namely to compare hardness and electrical resistivity in selected polymers which may be used as electric insulations. The long term objective of the work is to develop a method that can be used for a fast screening of insulation properties without disconnecting the cables from the installation. It is believed that hardness measurements can provide an indication of the insulation resistance, and can hence allow for fast checking of the safety of the electrical installation. A short discussion of the structural effects caused by irradiation with energetic light ions (modeling ionizing radiation) is followed by the analysis of mechanical and electrical characteristics of irradiated polymers aiming at searching for the correlation between these two properties. The results obtained show that hardness may serve the purpose of an indicator of early stages of electrical insulation deterioration in polymers and elastomers.

1. Introduction

Ion irradiation constitutes an interesting and elegant tool for modification of surface properties of practically any solid material. This method is clean, reliable, can be conducted at any temperature, and its parameters are independently controlled, making this technique particularly well suited for advanced modification of surface properties of solids [1]. Having been used initially in semiconductor technology, ion-beam based methods are now widely applied for modifications of metals, ceramics and, most recently, organic materials. Both doping and controlled energy deposition (damaging or ion beam mixing), may be used to induce changes in material structure and functional properties.

Several studies of the effects caused by ion beams in polymers have led to an understanding of the basic structural changes related to ion irradiation in polymers [2–7]. In general, irradiation results in a massive release of hydrogen from polymers, leading to the formation of a much harder carbon-rich surface layer, characterized by lower friction coefficient and higher wear resistance than the pristine material. On the other hand, carbonization of the surface layer may lead to a decrease in electrical resistance which may be beneficial (e.g. due to the reduction of electrostatic charge build-up) or harmful (when electrical insulation is needed). Interesting peculiarities of ion irradiation when compared to other radiation-based methods of polymer modification are: (i) the highest linear density of deposited energy [3] and (ii) exceptionally low irradiation fluences needed to obtain significant effects [2].

In the case of polymers, the structural effects of ion beam interaction with the material are dominated by massive hydrogen release [8–11]. This process is controlled by inelastic energy losses (ionization) [8] and leads to substantial structural modifications, such as shrinking and flattening of the surface layer, changes in composition and in the dominant type of chemical bonds. Typical changes induced by irradiation in elastomers are visualized in Fig. 1 for nitrile-butadiene rubber (NBR) irradiated with He ions. One may note the formation of cracks on the sample surface caused by substantial shrinking of the layer, these cracks may be beneficial in mechanical applications as they may serve as lubricant reservoirs. The final composition of the irradiated layer is close to CH_1 (in case of polyethylenes, the initial composition being close to CH_2) and the chemical bonds are dominated by SP3 ones. In the case of irradiated elastomers, the final concentration of carbon atoms is obviously higher because of the presence of carbon black used as a filler in these materials. Both the densification and changes in polymer composition caused by the hydrogen release lead to a significant increase of the surface layer hardness, up to a factor 10 [12,13]. The hardness increase makes irradiated elastomers much more

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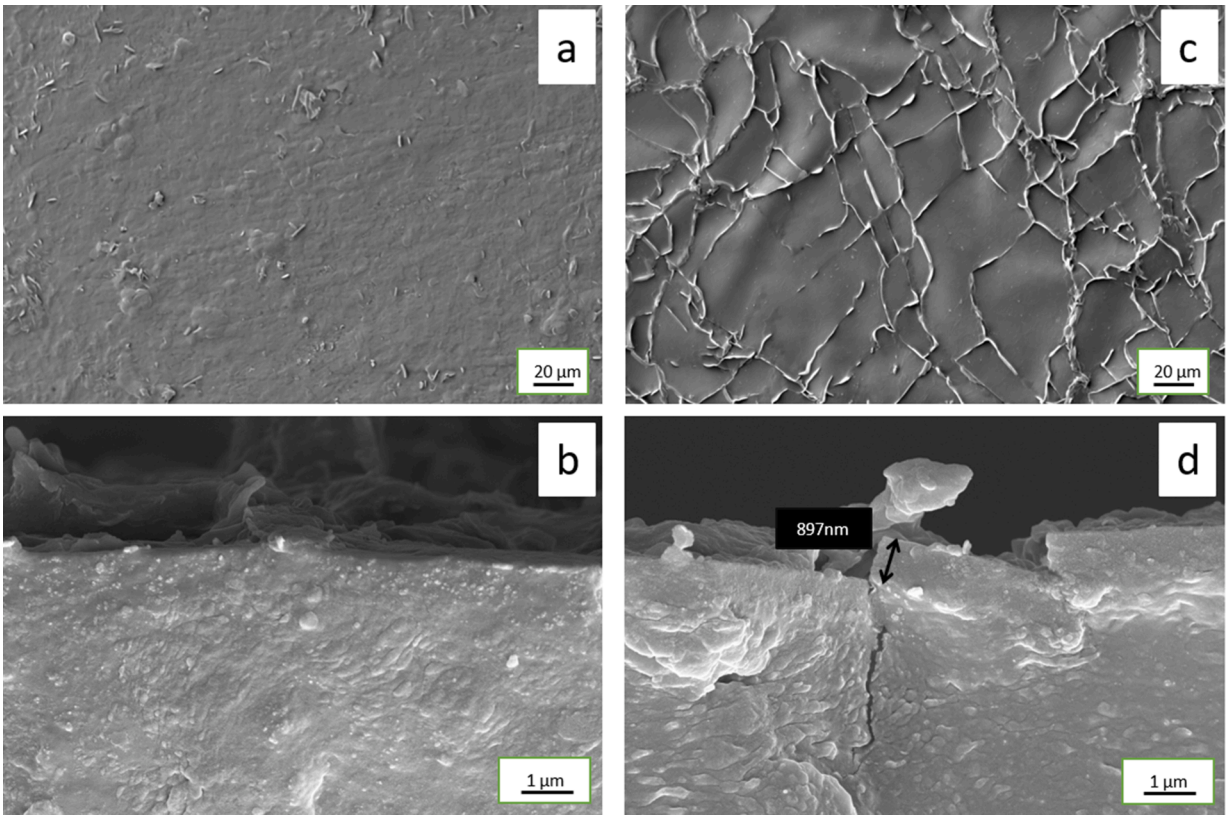

Fig. 1. SEM micrographs showing plan views (a and c) and cross-sections (b and d) of NBR elastomer before (a, b) and after (c, d) irradiation with He ions.

wear resistant. The reduction in wear resistance is difficult to quantify, as in our experiments, the depths of wear tracks on the surface of irradiated NBR were practically impossible to measure, whereas on pristine samples the wear tracks extended up to 700 µm in depth [12,13].

The main objective of the current work is to deepen the knowledge of functional properties of irradiated polymers, with a special emphasis on materials used as electrical insulation in nuclear installations, to better understand their behavior in a radiative environment and to identify useful methods for the analysis of electrical cable condition in nuclear installations. The work is focused on the correlation between electrical and mechanical properties of irradiated polymers (mainly rubbers) to check whether hardness measurements may be used as a non-destructive method of evaluation of electrical properties.

2. Experimental details/procedure?

The selected materials (Nitrile Butadiene Rubber NBR, Ethylene Propylene Diene Monomer EPDM and Polytetrafluoroethylene PTFE) were prepared in form of 10 cm × 10 cm × 2 mm plates. The materials used in experiments are either commonly used as insulation (EPDM and PTFE) or serve the purpose of a rubber insulation model (NBR). EPDM is a highly elastic cross-linked elastomer having good resistance on environmental solicitations. PTFE is a synthetic polymer, where hydrogen is replaced by fluorine. Considering that the main effect of irradiation on a polymer structure is a massive loss of hydrogen atoms, the absence of hydrogen in PTFE material may result in a higher resistance to structural degradation. Finally, NBR is used as a rubber insulation model, and it is one of the elastomers in which the effects of irradiation were most intensively/extensively studied. Therefore, the use of NBR allows one to compare the results of the current work with previous studies. As the samples were designed to model insulation materials, the filler used in rubbers was silica, as opposed to carbon black? (no carbon black has been used). The samples were irradiated by using Helium ions at a fixed energy of 60 keV using a custom-made ion implanter. The projected ranges of 60 keV He ions were calculated using SRIM code [14], the results depended slightly on the material used and varied from 520 nm for PTFE to 605 for EPDM through 580 nm for NBR. However, these values are rather inaccurate, mainly because of changes in the structure and composition of irradiated organic materials (e.g. a massive hydrogen loss), the effects of which are not taken into account by the SRIM code. Samples were irradiated up to increasing fluences in the range from $1x10^{15}$ cm^{-2} to $1x10^{17}$ cm^{-2}. Beam current density was kept sufficiently low (about 1 $\mu A/cm^2$) to ensure that the sample temperature during irradiation did not exceeded 50 °C. Process uniformity was ensured by X-Y mechanical scanning.

After irradiation the surface resistivity was measured according to the PN-85 C-04259/01 standard [15]. The method consists in the use of two concentric electrodes having external diameters of 5 and 2.5 cm with the gap between them equal to 2 mm. Resistivity was measured at the same potential of 1 kV. The pressure on the measured sample was equal to 0.1 MPa. Care was taken to clean the material surface in water and alcohol, and to carefully dry it before measurements. Each sample was measured in five places: at corners and in the centre of the plate.

After resistivity measurements the surface hardness was measured by using nanoindentation method. Nanoindentation was performed on a Micro Materials Ltd system at room temperature. For all measurements, a diamond Berkovich-shaped indenter (Synton-MDP) was used. Measurements were performed using loads from 0,02 mN up to 0,07 mN, which provided indentation depths from 37 nm to 935 nm (depending on the material and irradiation fluence). Indentation depths were measured as a maximum displacement of the indenter during loading. As the measurements were performed in fixed maximum load regime the increase in hardness led to a decrease of the maximum indentation depths. Each measurement was repeated at least 15 times with 40 µm spacing. The indents were made using load-controlled mode (loading/unloading time – 5/3 s, dwell time at maximum load – 1 s). The dwell period for drift correction was set as 60 s. Prior to all

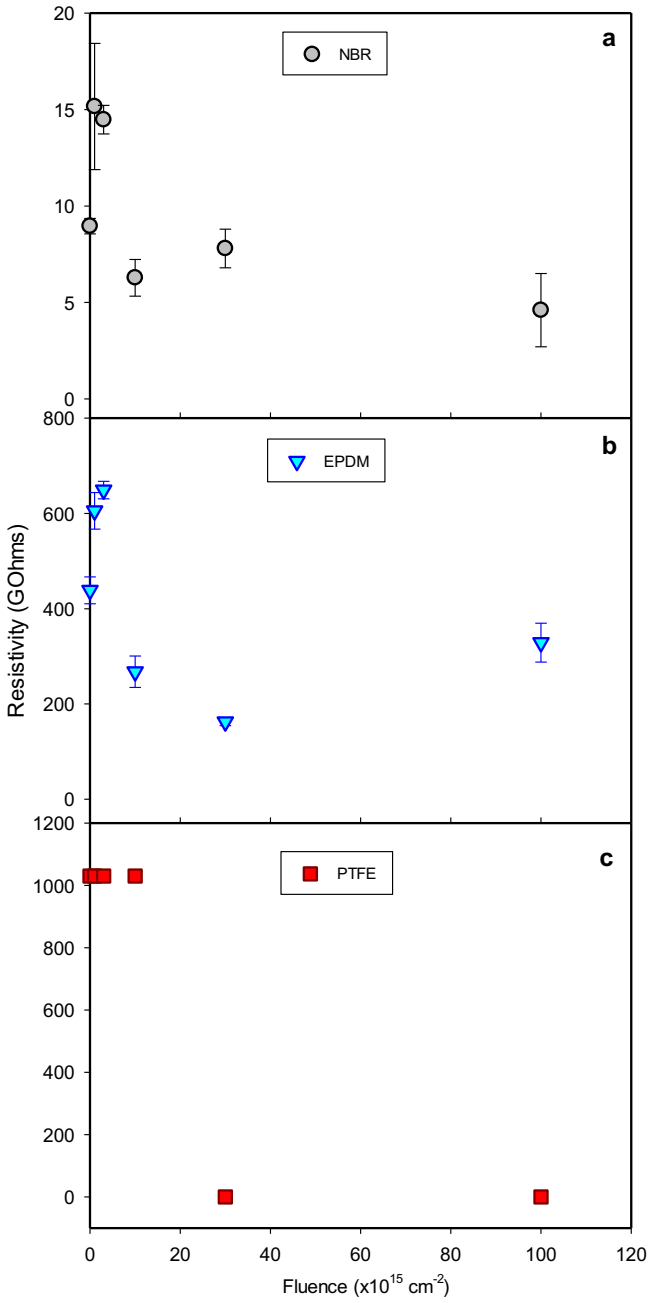

Fig. 2. Nanohardness of irradiated materials; NBR (a), EPDM (b) and PTFE (c).

experiments, an indenter area function of the indenter tip was calculated. Calibrations were performed using fused silica as a standard material with defined mechanical properties. This test was repeated 15 times for 1 mN in order to obtain reasonable statistics and determine the exact area function of the indenter tip under the applied load. Loading-unloading curves were fitted using a standard Oliver-Pharr method [16]. The results presented in this work are for 0.05 mN only, lower loads often led to huge variation in the results, whereas higher loads meant larger penetration depths, which may influence the hardness measurements due to the interaction with the unmodified sample bulk. Indentation depths at 0.05 mN load for all samples ranged from 76 nm to 516 nm, and were thus always smaller than the thickness of the modified layer.

3. Results and discussion

The results of nanohardness measurements are shown at Fig. 2 presenting the changes of nanohardness with the irradiation fluence. The results are characterized by rather large dispersions, which is likely due to the low hardness of the materials, the complex surface morphology and surface roughness. It should be recalled once again that in samples used in the experiments silica filler was used instead of carbon black, as the samples were designed to mimic materials used for electrical insulation. This leads to lower hardness of the rubbers. Another possible reason of experimental errors in nanohardness measurements is related to surface morphology of the samples. Organic materials usually are not as smooth as, e.g. semiconductor wafers, moreover, after irradiation the surface layer is susceptible to shrinking, what leads to the formation of cracks (see Fig. 1). Both of these reasons lead to increased surface roughness, hence also to larger experimental errors in nanoindentation measurements. In order to reduce these effects the measurements were repeated 15 times to increase the credibility of the results. Nevertheless, one can note a general trend in the results obtained: a significant increase in hardness of the surface layer with the irradiation fluence. The average values of the hardness increase by a factor of 4 in the case of PTFE or by a factor of 15–20 in case of EPDM and NBR. One should note that in real applications the radiation will modify the whole volume of the material, not only its thin surface layer. It will thus be possible to use higher forces, hence larger penetration depths, which should lead to the reduction of the experimental errors. The hardness increases vary depending on material and irradiation fluence. The most pronounced changes were observed for NBR (pristine material 0.0065 GPa, after 1×10^{17} cm^{-2} 0.175 GPa, i.e. 26 times increase) and EPDM (pristine material 0.012 GPa, after 1×10^{17} cm^{-2} 0.241 GPa, i.e. 20 times increase) whereas for PTFE the increase was only 4 times (from 0.096 GPa for pristine and 0.406 GPa for 1×10^{17} cm^{-2} irradiated sample).

The next set of measurements was aimed at the analysis of surface resistivity changes. The results are shown in Fig. 3, which contains the changes in surface resistivity with the irradiation fluence. Please note that the highest resistivity that can be measured with our tester (Fluke) was 1030 GΩ, which explains why the first results for PTFE are identical. This only means that the surface resistivity was equal to or higher than 1030 GΩ. Each of the tested materials revealed different behaviors of electrical resistivity. In some cases (NBR, EPDM) one can even observe an increase of surface resistivity for the lowest irradiation fluences. This effect can likely be attributed to the removal of surface contamination from the sample surface: for instance adsorbed water or plastifier molecules. NBR is characterized by the lowest resistivity in a pristine state (about 9 GΩ), this value drops down to about 5 GΩ for the highest irradiation fluence. Pristine EPDM shows much higher resistivity (~440 GΩ), the final value is about 350 GΩ. The highest resistivity in a pristine state has been measured for PTFE (above 1030 GΩ), but this material is prone to sudden and drastic decreases in resistivity: the final values are 7 MΩ only, i.e. 5 orders of magnitude lower.

The main results coming from the presented work are summarized in Fig. 4 which shows the comparison of relative changes in resistivity with relative changes in hardness. The values collected for all studied samples are normalized to plot them in a single figure. The subjectively chosen limit for safe operation of insulation materials was 60% of their initial resistivity. One may note that insulation materials lose their properties when hardness increases above a given threshold, here arbitrarily set at 40% of maximum hardness. When reaching 80% of the highest hardness all materials studied lost their insulation properties. It may be concluded, that the changes in electrical resistivity are closely correlated with changes of the hardness. Hardness measurements may thus serve as an indicator of deterioration of insulation capabilities of organic materials used as insulators.

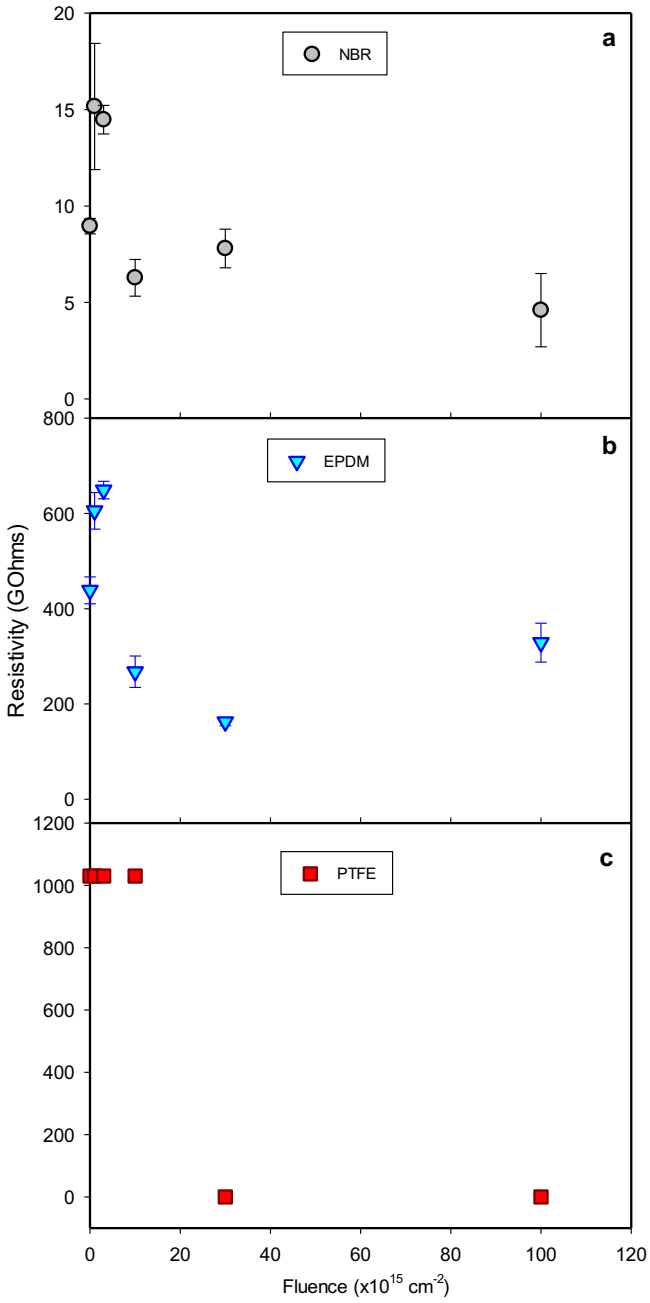

Fig. 3. Surface resistivity of irradiated materials; NBR (a), EPDM (b) and PTFE (c).

4. Conclusions

The results presented in this work point to the evident correlation between electrical resistivity and hardness of the polymer materials exposed to ionizing radiation. It seems that hardness measurements may serve the purpose of an early indicator of deterioration of electrical properties of polymers (mainly rubbers) used as insulation in nuclear installations or in any other equipment working in a radiative environment (such as accelerators, Roentgen diffraction devices, etc.). The huge advantage of using hardness testers to evaluate the state of electrical insulation is the fact that measurements can be performed without disconnecting the cable from the installation, hence without a need to stop the operation of the equipment.

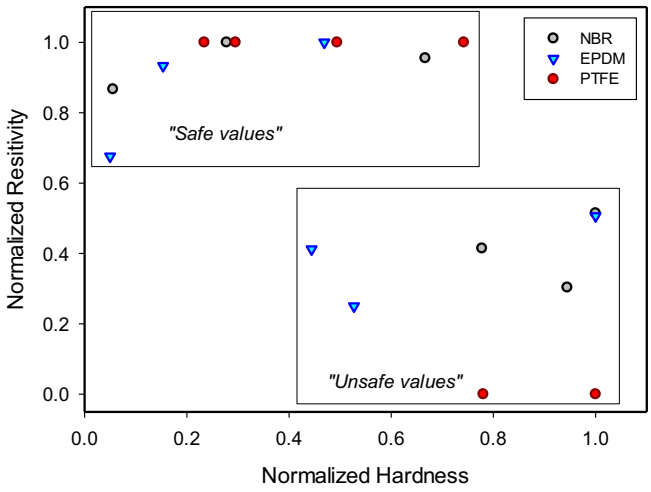

Fig. 4. Comparison of relative changes in nanohardness and resistivity.

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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