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Structural and Functional Properties of Ion Beam Modified Elastomers

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Studies on the use of energetic ion beams for material modification have been initiated originally within the Manhattan project and have been continuously developed since then. The consecutive steps were devoted to the studies of ion implantation into semiconductors, metals, ceramics and, most recently, organic materials. One of the latest areas of applications is modification of elastomers, commonly known as rubbers. In the present paper the results of the studies on structural and functional properties of irradiated elastomers will be presented with the special emphasis on the materials used in aviation and military applications. Among the structural modifications, a massive loss of hydrogen atoms appears as the most peculiar characteristic of irradiated elastomers. Functional properties of irradiated rubbers: microhardness and friction coefficient, will be presented and application potential of the materials discussed.

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1. Introduction

Surface modification of materials appears as the powerful and widely used methodology, as it allows to combine different properties of material bulk and material surface, hence designing of new materials characterized by unique properties. Various techniques are used for this purpose, ion implantation is applied essentially for the modification of metals. Recently, new areas of applications emerge, among them implantation into ceramics and polymers. In the latter case the studies were focused mainly on biomedical applications [1]. Elastomers are traditionally treated by using wet surface chemistry, however, advanced elastomers are hardly susceptible for such a treatment.

Attractive alternative to chemical methods proved to be the use of high-energy ion beams. First, it was found that it is possible to obtain interesting changes in functional properties, mainly the reduction of friction [2, 3]. These results have justified the desirability of undertaking more detailed work on examining the effects of implantation on the structural properties of elastomers and elucidate the observed changes in functional properties. The purpose of this paper is to describe the current state of knowledge about the effects induced by ion implantation in elastomers and identification of the area of its potentially attractive applications.

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2. Structural properties of irradiated elastomers

2.1. Hydrogen release

Hydrogen distribution measurements were made using the resonant nuclear reaction ^{15}N(H, $\alpha\gamma$)^{12}C, excited with ^{15}N nitrogen ions having the energy over 6.385 MeV [4]. This energy corresponds to the resonance, by increasing its value it is possible to sample the concentration of hydrogen at the increasing depths of the sample. The dominant structural effect in the elastomers subjected to the ion bombardment process is a massive loss of hydrogen from the surface layer of material. Figure 1 presents the results of measurements of the hydrogen distribution in the nitrile rubber (NBR) subjected to bombardment with the increasing fluences of helium ions having an energy of 160 keV.

The results indicate that at low fluences (up to 3×10^{14} cm^{-2}) release of hydrogen is negligible, the increase of the irradiation fluence leads to reduction of hydrogen concentration in the surface layer, with the saturation level of about 10 at.%. The next step of the analysis was to determine the so-called kinetics of hydrogen release, i.e. the dependence of concentration on the ion fluence. This relationship is shown for several elastomers in Fig. 2.

The detailed analysis of the mechanism of hydrogen release from the irradiated elastomers has been presented in Ref. [5]. The main conclusion from this analysis is that the hydrogen release process is controlled by the inelastic energy losses due to ion interaction with the target electrons (ionization). Compared to conventional polymers (e.g. polyethylene) the release process is far more

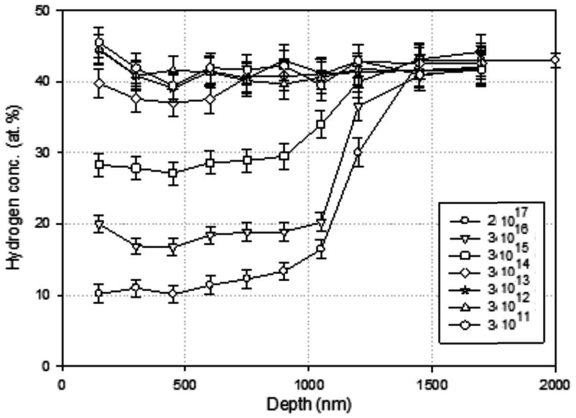

Fig. 1. Depth distribution of hydrogen in NBR samples subjected to irradiation with increasing fluences of helium ions.

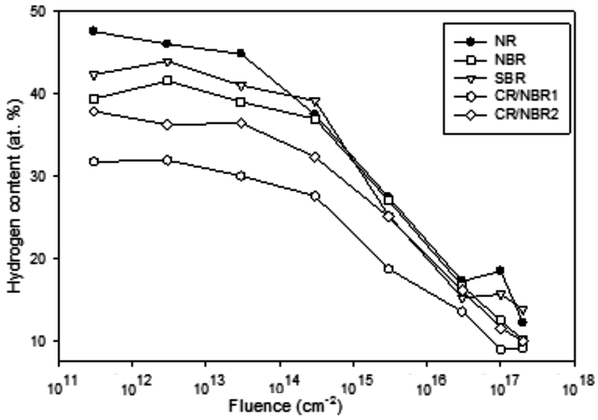

Fig. 2. Kinetics of hydrogen release from various elastomers upon irradiation with increasing fluencies of helium ions.

pronounced, the final concentration of hydrogen is approximately 10 at.%. This is a much lower concentration than in the case of polyethylene, where the final concentration of hydrogen is approximately 40 at.% [6].

2.2. Surface layer oxidation

The release of hydrogen from organic materials often results in the oxidation of the surface layer. This effect may be detrimental for elastomer properties, as it may lead to the loss of elasticity and brittleness of the material. To investigate the oxidation effect the series of measurements of oxygen depth distributions upon irradiation was performed. Measurements were made using the Rutherford backscattering (RBS) technique. An example of oxygen distribution measured for the styrene-butadiene rubber (SBR), measured immediately after irradiation, one and three months after irradiation is shown in Fig. 3. The results indicate that oxidation of the surface layer is limited to the modified layer. The oxidation of the surface layer ends when the oxygen concentration

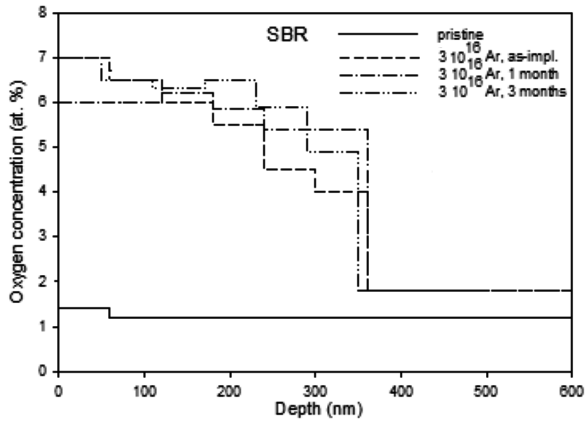

Fig. 3. Oxygen depth distribution profiles in SBR elastomer before irradiation, directly after, one, and three months after irradiation.

reaches approximately 7%, which takes place within approximately one month after the ion bombardment.

2.3. Surface microtopography

Ion bombardment leads to characteristic changes in the surface microtopography of modified elastomers. Typical images obtained by scanning electron microscopy are presented in Fig. 4. These images were made for the SBR rubber samples before the process modification (upper photo) and after helium ion bombardment up to the fluence of 3×10^{16} cm^{-2}. Clearly visible is smoothening and cracking of the surface layer of material. Both of these effects are related to the contraction of the material caused by massive release of hydrogen from the layer subjected to modification.

It is worth noting that despite the clear fracturing observed, the modified layer is characterized by very good adhesion to the substrate. Adhesion tests performed by a scratch test showed no signs of delamination up to the pressures of 5 N. At these pressures the indenter needle penetrates up to a depth of about 0.5 mm, i.e. about 500 times greater than the thickness of the modified layer. Very good adhesion to the surface-modified layer is likely to be due to the fact that the length of the rubber molecules is greater than the range of implanted ions, in consequence, the modified layer remains anchored in the bulk by intact molecules of the rubber. The chemical changes of the surface layer (mainly oxidation) and the formation of cracks on the surface are the main reasons for significant improvement in bonding strength of rubber with various materials; metal and glass composites. This effect has been patented.

3. Functional properties of irradiated elastomers

3.1. Microhardness

Microhardness measurements were performed using the NanoTest 600 device, equipped with a penetrator of

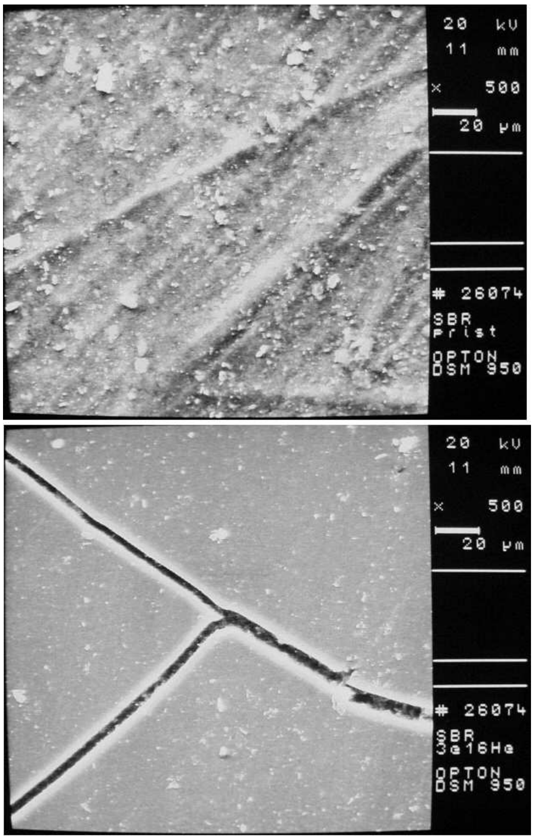

Fig. 4. SEM pictures of SBR rubber before and after irradiation with He ions up to a fluence of 3×10^{16} cm^{-2}.

spherical geometry and radius $R = 5$ mm, at a speed of loading/unloading $\mathrm{d}P/\mathrm{d}t = 0.01$ mN/s at $T = 22 \pm 2\,^{\circ}$C and relative humidity of 60%.

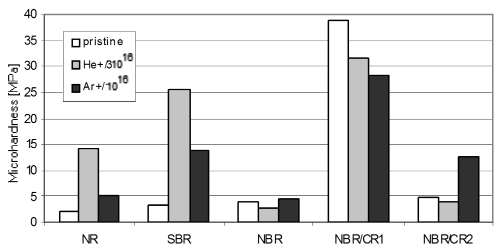

Fig. 5. Microhardness of selected rubbers irradiated with helium or argon ions.

The results of microhardness measurements (Fig. 5) indicate the possibility of obtaining in some cases (natural rubber (NR) or SBR rubber), even a multiple increase in microhardness of the modified layer. The most pronounced hardness increase is observed for helium ions, which undoubtedly is related to both the largest range of these ions (about 1.3 μm, compared to about 0.25 μm to argon) and to the fact that helium ions lose energy mainly by inelastic interactions, which increases the likelihood of cross-linking of the elastomer. In the case of acrylonitrile-butadiene rubber NBR and its mixtures with chloroprene rubber (NBR/CR1 and NBR/CR2) no increase in hardness was obtained, on the contrary, even reduction, which may be caused by the presence in their composition a considerable amount of plasticizer, which "sweats" on the rubber surface under the influence of temperature increase, plasticizing the top material layer.

3.2. Friction coefficient

Measurements of the friction coefficient were made using the Ducom TR28M wear/friction tester working in a ball-surface configuration. A steel ball with a diameter of 12.7 mm was used as a countersample. The results of measurements for the NBR rubber bombarded with the increasing fluences of hydrogen, helium, argon or fluoride ions are shown in Fig. 6.

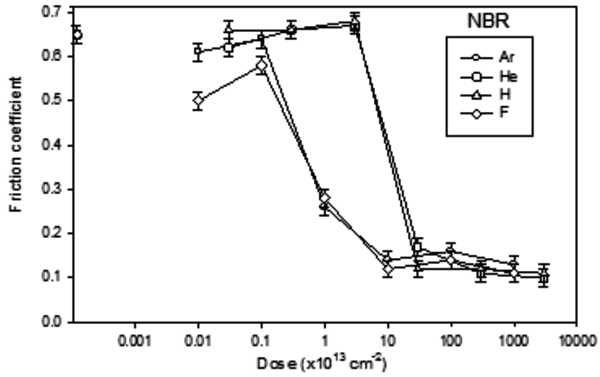

Fig. 6. Friction coefficient measured for NBR rubber irradiated with increasing fluences of H, He, F, or Ar ions.

The results clearly show that ion bombardment leads to drastic reduction of friction forces, which can be sevenfold. The final value of the coefficient of friction is very small and equal to approximately 0.1, regardless of the ion. The results clearly fall into two groups, one for light ions (H or He) and the other for heavy ions (F, Ar). Decrease in the friction coefficient is observed above the fluence 1×10^{14} cm^{-2} for light ions and 3×10^{13} cm^{-2} for heavy ions. An interesting observation is that the decrease in the friction coefficient is observed for fluences for which significant hydrogen release is observed (see Figs. 1 and 2). This result suggests the influence of compositional changes and/or possibly crosslinking on the friction properties of irradiated elastomers.

Similar results were obtained for the other studied elastomers. The summary of the results obtained is shown in Fig. 7.

4. Summary and conclusions

The use of ion beams to modify the surface layer of elastomers leads to interesting effects with significant potential application. The modified layer is characterized by increased hardness, increased wettability, and a really

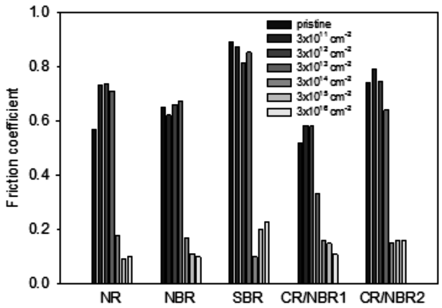

Fig. 7. Friction coefficient measured for NBR rubber irradiated with increasing fluences of helium ions.

low coefficient of friction. The latter effect seems to open up the possibilities of implementing this method, especially in the case of complex elastomers used in military or aerospace industries. Such rubbers in its pristine state are characterized by the high friction coefficient, close to 1. Moreover, these materials are resistant to modification by means of conventional chemical technologies, such as sulfonation or iodination. A significant decrease in the friction coefficient is reached at relatively low fluences of ions resulting in low process costs. As an example in typical industrial applications of an ion implanter built in the NCBJ Świerk, the time needed for implantation into the area of 30 cm $\times$ 50 cm up to a fluence of 1×10^{14} cm^{-2} is about 1 min. It is therefore clear that the main factor determining the costs of implantation modification of elastomer components is the construction of sufficiently efficient manipulators, not the performance of accelerating section of the implanter.

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