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Hydrogen release from irradiated elastomers measured by Nuclear Reaction Analysis

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ABSTRACT

Ion irradiation appears as an interesting method of modification of elastomers, especially friction and wear properties. Main structural effect caused by heavy ions is a massive loss of hydrogen from the surface layer leading to its smoothening and shrinking. The paper presents the results of hydrogen release from various elastomers upon irradiation with H^+, He^+ and Ar^+ studied by using Nuclear Reaction Analysis (NRA) method. The analysis of the experimental data indicates that the hydrogen release is controlled by inelastic collisions between ions and target electrons. The last part of the study was focused on preliminary analysis of mechanical properties of irradiated rubbers.

1. Introduction

Advanced elastomers used in sealings of mobile connections must respond to numerous requirements: ability to work in wide temperature range, resistance to various fluids, ageing and oxidation. Several materials were developed to conform these needs. A common feature of these materials is a relatively high friction coefficient leading to an increased wear rate and temperature rise in the contact area. It seems thus obvious, that modification of the surface layer of rubbers may lead to interesting effects having possible industrial applications. Taking into account that ion irradiation has been successively used to reduce friction and wear without affecting bulk properties of various polymers, it seems justified to study the effects of elastomers irradiation on their structural and mechanical properties. Modification of organic materials is interesting from many points of view: wide use of polymers in industry, difficulty with chemical modification of polymer properties and particularly low ion fluencies needed to obtain significant effects are only few of the reasons to study these materials [1]. Ion beams offer the highest attainable densities of energy losses among all radiation techniques (gamma rays, electron and ion beams) [2]. Current reviews describing the state of the knowledge on irradiated polymers can be found in, e.g. Refs. [3–11]. Irradiation with ions leads to shrinking and smoothening of the polymer surface layer, which suggests, that the effects obtained may be related to the hydrogen release from the surface layer. A detailed analysis of hydrogen concentration in irradiated samples is thus required to confirm or reject this assumption. Main experimental problem related to hydrogen measurements is a high susceptibility of organic materials to decompose under an ion beam. This excludes methods such as ERDA, as heavy ions lead to a very fast deterioration of the elastomers. The paper describes the experiments performed by using Nuclear Reaction Analysis (namely $^{15}N(^{1}H,\alpha\gamma)^{12}C$ reaction induced by ^{15}N ions at 6.385 MeV) to measure the amount of hydrogen atoms in several irradiated elastomers. A huge advantage of this reaction is a very low irradiation fluence needed to collect a decent spectrum.

2. Experimental

Samples made of several elastomers: natural rubber (NR), butadiene–acrylonitrile rubber (NBR), styrene–butadiene rubber (SBR) as well as mixtures of chloroprene (CR) and butadiene–acrylonitrile rubber (NBR/CR1 and NBR/CR2) were vulcanized with

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sulfur system or sulfur system and metal oxides (CR containing mixes). Specimens were steel – moulded to form large plates of one millimeter in thickness. Samples for irradiation experiments of $1 \times 2\ cm^2$ were cut from these plates. Irradiations with different ions (H^+, He^+ and Ar^+) of 160 keV energy were performed in wide fluence range from $3 \times 10^{11}\ cm^{-2}$ up to $2 \times 10^{17}\ cm^{-2}$. The maximum values of inelastic (Se) and nuclear (Sn) energy losses calculated using a SRIM code [12] for the above irradiation conditions correspond to: H^+ irradiation – Se = 90 eV/nm and Sn = 1.5 eV/nm, He^+ irradiation – Se = 160 eV/nm and Sn = 11 eV/nm, Ar^+ irradiation – Se = 450 eV/nm and Sn = 350 eV/nm. The beam power density has been kept sufficiently low (below 0.08 W/cm^2) to avoid significant temperature rise during irradiation.

The measurements of hydrogen content were performed by using a resonant reaction $^{15}N(^{1}H, \alpha\gamma)^{12}C$ induced by ^{15}N ions at 6.385 MeV. The emitted γ-rays with the energy of 4.43 MeV were detected by a BGO scintillation detector located outside the vacuum about 1.5 cm behind the sample. The incident beam was monitored by the RBS signal from a beam chopper in front of the sample. The method used is characterized by a relatively narrow resonance (12 keV) making possible depth profiling measurements. Kapton coupons were used as reference samples for calibration of hydrogen content measurements. The details of the experimental procedure have been described in [13]. A tremendous advantage of the method used is a very low fluence of $^{15}N^+$ ions required to perform the measurement. Good quality data were obtained after accumulation of fluencies as low as $6 \times 10^{11}\ cm^{-2}$. Mechanical properties of the irradiated layers were checked by using nanoindentation and nanoscratch tests, as well as friction/wear microprobe.

3. Results and discussion

The typical effects of ion irradiation of elastomer are shown in Fig. 1 presenting the scanning electron microscopy (SEM) images of pristine (a and b) and irradiated NBR samples (c and d). The irradiation has been performed with He^+ ions up to a fluence of $3 \times 10^{16}\ cm^{-2}$. One may note a significant shrinking and smoothening of the surface layer having the thickness of about 1.2 μm. Please note, that smooth surface of the irradiated samples is a mandatory condition for any depth profiling: surface roughening may lead to artificial widening of depth distributions. The thickness of the modified layer corresponds closely to simulations made with a SRIM code [12]. A smooth transition from the irradiated layer to pristine bulk is noteworthy: no delamination of the surface layer was observed in irradiated samples. Additional scratch tests performed with a 0.5 mm ball under loads increasing up to 0.5 N revealed a good adhesion of the modified layer to the substrate.

Verification of the influence of 6.4 MeV nitrogen beam used in analysis on the hydrogen release from elastomers was checked by performing ten consecutive measurements in the same area of the NBR samples (pristine and irradiated with Ar^+ ions up to $1 \times 10^{17}\ cm^{-2}$) and the hydrogen content compared. No changes in hydrogen content were measured in the case of Ar-irradiated sample, whereas a 5% loss in H content was observed for a pristine

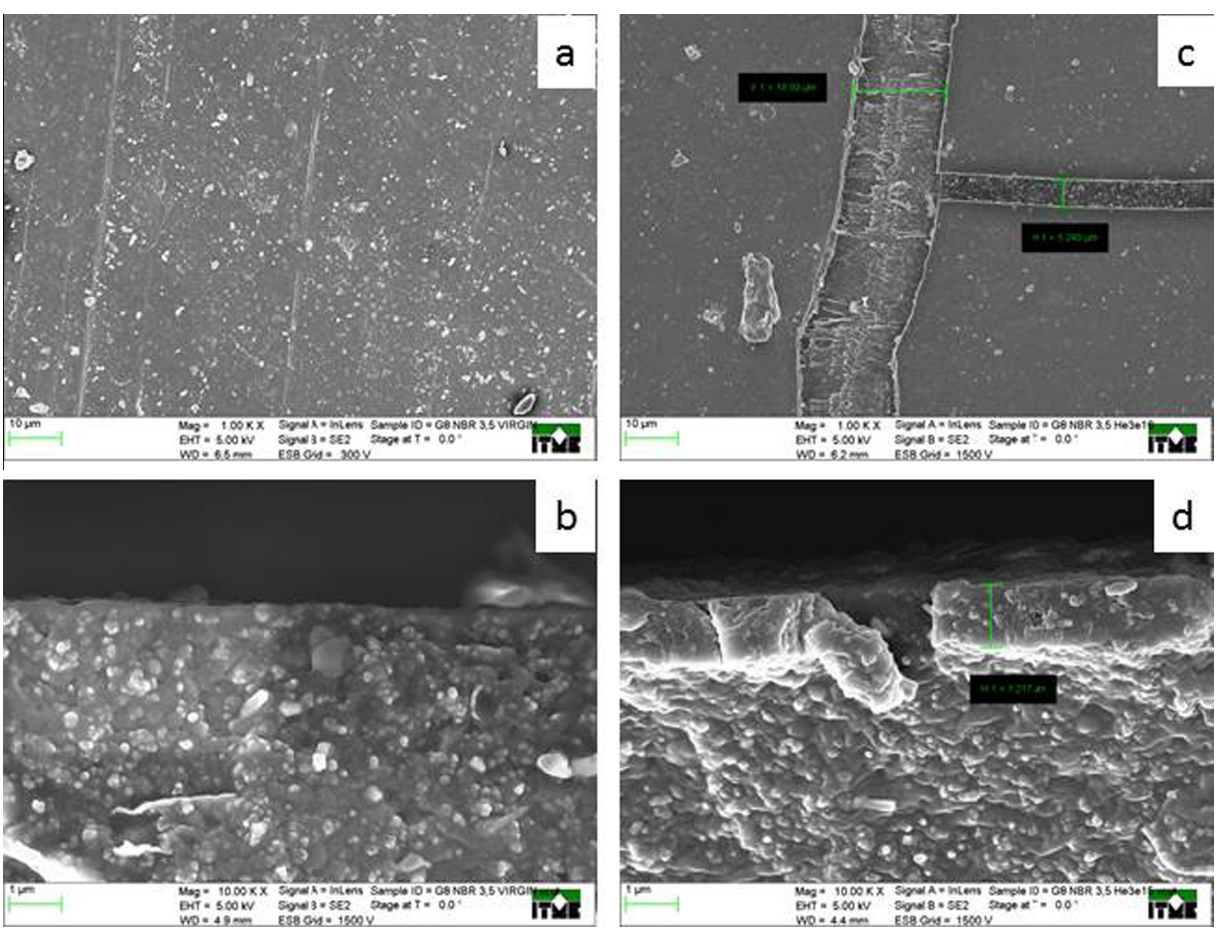

Fig. 1. SEM micrographs showing the plan views (a and c) and cross-sections (b and d) of NBR elastomer before (a and b) and after (c and d) irradiation with He ions. Markers on the micrographs correspond to 10 μm (a and c) and 1 μm (b and d).