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Structural and functional properties of ion-irradiated graphene-reinforced elastomers

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A B S T R A C T

Since more than half century ion beams are used for modification of functional properties of various materials: after semiconductors, metals and ceramics ion irradiation appeared recently as an interesting method of modification of organic materials, especially for friction and wear properties. Among polymeric materials the newest area of applications of ion beams is their use for modification of elastomers, commonly known as rubbers. Main structural effect caused by heavy ions in polymers is a massive loss of hydrogen from the surface layer, this leads to a smoothening and shrinking of the sample surface. The paper describes the results obtained in several rubbers modified by ion beams. Both, pristine and graphene-reinforced rubber samples were used, graphene doping led to the strengthening of the material bulk whereas ion irradiation allowed for surface property improvement. In the first part of the paper the hydrogen release from irradiated elastomers is shortly presented. Mechanical properties (hardness and friction) are discussed in the second part.

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 answer these needs. A common feature of these materials is relatively low strength and rather high friction coefficient leading to increased wear rate and temperature rise in the contact area. Each of these drawbacks can be improved in a different way. Whereas the strength is related to the bulk properties, so to improve the strength a volume of the elastomer should be modified, the friction is surface-related property. Consequently, to reduce friction only a surface modification is required. In the presented work we used ion irradiation to improve surface properties of elastomers with bulk properties reinforced by adding graphene flakes to a standard rubber filler which is carbon black. The main objective of the present work is to analyse the effects of ion irradiation on structural and mechanical properties of nitrile butadiene rubber (NBR) elastomers: pristine and graphene reinforced. 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 fluences 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, selected information about graphene-doped rubbers in refs. 12–16. Irradiation with ions leads to shrinking and smoothening of the polymer surface layer, what suggests, that the effects obtained may be related to the hydrogen release from the surface layer. Hydrogen release was measured by using Nuclear Reaction Analysis (namely $^{15}N(^{1}H, \alpha\gamma)^{12}C$ reaction induced by ^{15}N ions at 6.385 MeV). Structural properties of virgin and irradiated elastomers was assessed from Scanning Electron Microscopy, whereas the mechanical properties were studied by using nanoindentation (to measure nanohardness) and pin-on-disc friction tests.

2. Experimental

Samples made of several elastomers: natural rubber (NR), butadiene-acrylonitrile rubber (NBR), styrene-butadiene rubber (SBR) as

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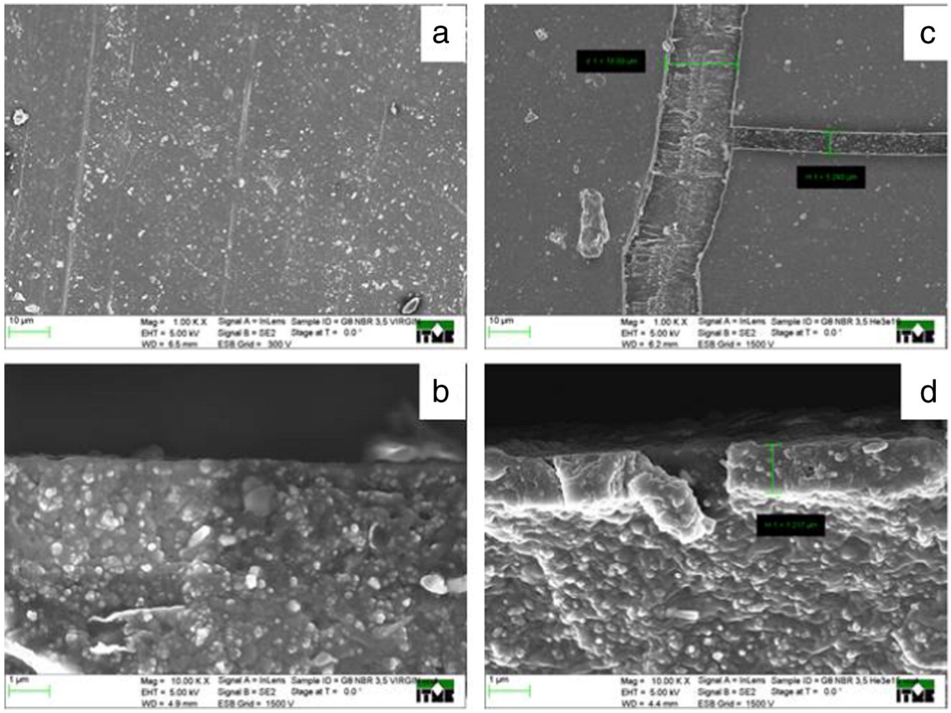

Fig. 1. SEM micrographs showing the plane views (a and c) and cross-sections (b and d) of NBR elastomer before (a, b) and after (c, d) irradiation with He ions (160 keV, 3×10^{15} cm^{-2}).

well as mixtures of chloroprene (CR) and butadiene-acrylonitrile rubber (NBR/CR1 and NBR/CR2) were vulcanized with sulphur system or sulphur system and metal oxides (CR containing mixes). Graphene flakes (reduced graphene oxide, rGO, produced in ITME) were mixed with the elastomer matrix using dry mechanical milling. Synthesis of elastomer matrix and doping with carbon black and graphene flakes were performed in IEPMD. Specimens were steel – moulded to form large plates of one millimeter in thickness. Samples for irradiation experiments having 1 × 2 cm were cut from these plates. Irradiations with different ions (H^+, He^+ and Ar^+) having the energy of 160 keV were performed in wide fluency range from 3×10^{11} cm^{-2} up to 2×10^{17} cm^{-2}. The maximum values of inelastic (Se) and nuclear (Sn) energy losses calculated using a SRIM code [17] 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, corresponding to 0.5 microA/cm^2) to avoid significant temperature rise during irradiation. Typically several samples were mounted together on 10 cm × 10 cm sample holder, ion beam was scanned over the whole target holder and samples were sequentially removed after irradiation to a desired fluence.

Measurements of hydrogen content were made by using a resonant reaction $^{15}N(^1H, \alpha\gamma)^{12}C$ 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 details of the experimental procedure have been described in [18]. Mechanical properties of the irradiated layers were assessed from nanoindentation (hardness) and nanoscratch (adhesion) tests, as well as pin-on-disc test (friction properties).

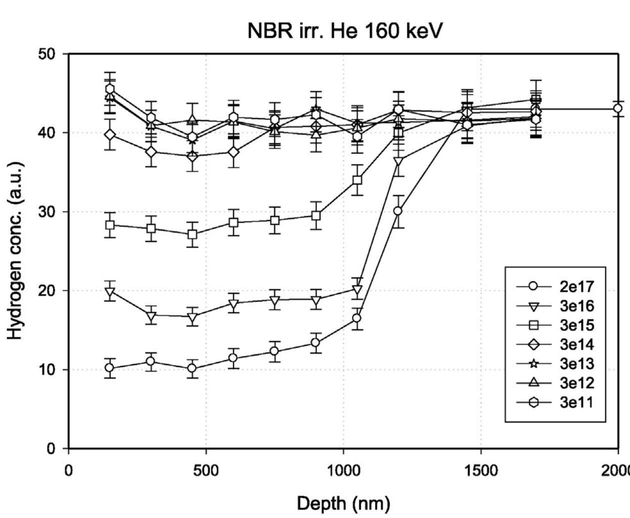

Fig. 2. Hydrogen depth distribution profiles measured for NBR sample irradiated with increasing fluences of 160 keV He^+ ions.

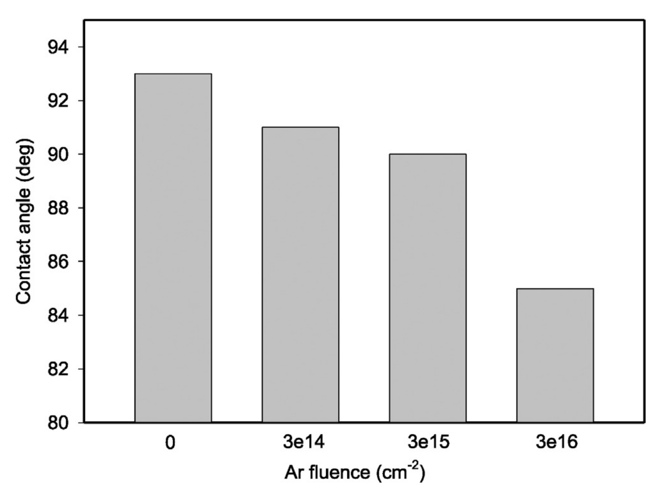

Fig. 3. Water contact angle measured on the surface of Ar-irradiated NBR rubber.