# Application of ion bombardment to modify tribological properties of elastomers[*)]

**Dariusz M. Bieliński[1),2),**)], Urszula Ostaszewska[2)], Jacek Jagielski[3),4)]**

DOI: dx.doi.org/10.14314/polimery.2014.416

**Abstract**: In the paper effects of surface modification of various elastomers upon irradiation with $H^+$, $He^+$, $F^+$ or $Ar^+$ ions are presented. Changes to chemical composition and physical structure of rubber macromolecules are discussed in terms of influence of the treatment on modification of surface layer of the elastomers. Hydrogen release induced graphitization together with post-treatment oxidation of rubber macromolecules increase surface wettability of the materials, facilitating lowering of „wet" friction. Free radicals being created due to interactions between energetic ions and macromolecules produce additional crosslinking, which manifests itself by increased hardness of the elastomers. Modification of mechanical properties of the surface layer changes mechanism of elastomer friction from the bulk to the surface one, what results in significant reduction of friction. Despite crosslinking induced shrinkage of the surface layer, which results in its micro-cracking, ion beam treated elastomers showed to be wear resistant due to the lack of delamination under stress. Interesting results were obtained for heavy $Ar^+$ ions surface etched butadiene-acrylonitrile rubber/multiwalled carbon nanotube (NBR/MWCNT) composites. Nanotube agglomerates created from rubber substrate resulted in „island" morphology, significantly reducing friction of the material.

**Keywords**: ion bombardment, rubber, elastomers, surface modification, friction, frictional wear.

## Zastosowanie bombardowania jonowego do modyfikacji właściwości tribologicznych elastomerów

**Streszczenie**: W artykule przedstawiono wpływ modyfikacji powierzchni różnego rodzaju elastomerów za pomocą wysokoenergetycznej wiązki jonów: $H^+$, $He^+$, $F^+$ lub $Ar^+$ na ich morfologię, charakterystykę mechaniczną i energię powierzchniową oraz właściwości tribologiczne. Dobór jonów był podyktowany chęcią sprawdzenia, jak na efekty modyfikacji wpływa ich masa i reaktywność chemiczna. Porównano także właściwości zmodyfikowanej w następstwie bombardowania jonowego warstwy wierzchniej elastomerów w zależności od składu wulkanizatów (rys. 1—3). Stwierdzono, że efekty modyfikacji są widoczne również w przypadku elastomerów specjalnego przeznaczenia, odpornych na konwencjonalną, „mokrą" modyfikację chemiczną za pomocą chlorowania lub sulfonowania (rys. 4). Uwalnianie wodoru powodujące grafityzację oraz utlenianie zachodzące w wyniku kontaktu z powietrzem, sprzyjają obniżeniu współczynnika tarcia elastomerów modyfikowanych „na mokro". Wolne rodniki, powstające w następstwie oddziaływania pomiędzy wysokoenergetycznymi jonami a makrocząsteczkami, prowadzą do wzrostu gęstości ich usieciowania, które przejawia się większą twardością warstwy wierzchniej elastomerów (rys. 1). Modyfikacja właściwości mechanicznych tej warstwy zmienia mechanizm tarcia elastomerów z objętościowego na powierzchniowy (rys. 5), czego skutkiem jest znaczące obniżenie oporów tarcia. Pomimo skurczu (wywołanego sieciowaniem) materiału, który doprowadził do pojawienia się spękań na jego powierzchni (rys. 2), praktycznie nie zaobserwowano zużycia ściernego elastomerów poddanych bombardowaniu jonowemu. Tak znaczny wzrost odporności elastomerów na zużycie ścierne przypisuje się brakowi występowania delaminacji zmodyfikowanej warstwy wierzchniej poddanej działaniu naprężeń w strefie kontaktu ciernego. Interesujące wyniki uzyskano w odniesieniu do kompozy-

---

[1)] Institute for Engineering of Polymer Materials and Dyes, Division of Elastomers and Rubber Technology, Harcerska 30, 05-820 Piastów, Poland.

[2)] Łódź University of Technology, Institute of Polymer and Dye Technology, Stefanowskiego 12/16, 90-924 Łódź, Poland.

[3)] Institute of Electronic Materials Technology, Wólczyńska 133, 01-199 Warsaw, Poland.

[4)] National Centre for Nuclear Research, Andrzej Soltan 7, 05-400 Otwock, Świerk, Poland.

[*)] Material contained in this article was presented on the Conference „Pomerania — Plast 2013", 4—7 June 2013, Międzyzdroje, Poland.

[**)] Corresponding author; e-mail: d.bielinski@ipgum.pl

tów elastomerowych zawierających wielościenne nanorurki węglowe. Ich wulkanizaty poddane działaniu wiązki ciężkich jonów $Ar^+$, która trawi elastomerową matrycę, uzyskują „wyspową" morfologię powierzchni (rys. 6), co prowadzi do znacznego obniżenia oporów tarcia materiału (rys. 7).

**Słowa kluczowe**: bombardowanie jonowe, guma, elastomery, modyfikacja powierzchni, tarcie, zużycie cierne.

So far, ion irradiation has been applied mainly for modification of metals and ceramics [1]. Recent works on its effects on polymers are devoted mainly to plastomers [2], whereas papers on ion beam treatment of elastomers are mostly associated with medical applications [3, 4]. Despite the fact that influence of high energy ions on composition and structure of semicrystalline engineered polymers seems to be well established [5], knowledge on effects possible to obtain for amorphous elastomers still remains unexplored. Ion beam treatment seems to be a very promising technique, especially for elastomers, because of the extent of modification is limited to the top surface layer of materials, not exceeding a couple of micrometers, leaving overall elasticity of rubber parts intact. From our recent work it follows, that interactions between the ion beam and rubber macromolecules seem to be mainly of energetic character [6]. As a result hydrogen release takes place, which initiates further modification of rubber [7, 8]. Depending on its macromolecular structure, graphitization can be preferably accompanied either by degradation or crosslinking. The former produces free radicals, as a result of chain scission, which readily attract oxygen and modify surface polarity of elastomers. The latter makes their surface layer shrunk, what results in micro-cracking and development of surface geometry, which together with an increased hardness can modify frictional contact area.

The paper discusses chemical modification (oxidation and graphitization), crosslinking and degradation of rubber macromolecules under ion beam treatment in terms of related changes to surface wettability, morphology as well as mechanical properties of the surface layer and associated tribological properties of elastomers.

## EXPERIMENTAL PART

### Materials

Conventional vulcanizates based on: natural (NR), styrene-butadiene (SBR), acrylonitrile-butadiene rubber (NBR) or its mixes with chloroprene rubber (CR), filled with carbon black were studied. The composition of these vulcanizates is given in Table 1. Special purpose elastomers: ester based thermoplastic polyurethane (TPE-U, Estane® 5703, Lubrizol), polyolefin based thermoplastic vulcanizate (TPE-O, Santoprene™, Exxon Mobil), silicone rubber based on Silastic 25160 compound (MPQ, Dow Corning), chloroprene (CR, rubber based on Neoprene GW filled with 50 phr of carbon black, DuPont) and hydrogenated acrylonitrile-butadiene rubber based on Therban® 4307 filled with 50 phr of carbon black (HNBR, Lanxess) were also tested. Samples of these materials were subjected to irradiation by ions of various mass and chemical reactivity: $H^+$, $He^+$, $F^+$ or $Ar^+$. The treatment was realized using a laboratory Balzers MPB 202 RP implanter (Liechtenstein), operating with ion beams of energy 130—160 keV and fluency ranging from $10^{11}$ to $10^{16}$ 1/cm$^2$. Current beam density did not exceed 0.1 μA/cm$^2$, what prevented the surface of elastomers from excessive heating.

**Table 1. Composition (expressed in phr) of the rubber vulcanizates studied**

| Components | Rubber vulcanizate | | | | |
|---|---|---|---|---|---|
| | NR | SBR | NBR | NBR/ CR1 | NBR/ CR2 |
| Natural rubber | 100 | — | — | — | — |
| Styrene-butadiene rubber | — | 100 | — | — | — |
| Acrylonitrile-butadiene rubber | — | — | 100 | 50 | 60 |
| Chloroprene rubber | — | — | — | 50 | 40 |
| Carbon black | 40 | 50 | 80 | 130 | 100 |
| Curing system | 8 | 6 | 9 | 11 | 10.5 |

Sulfur vulcanizates of acrylonitrile-butadiene rubber filled with 1—5 phr of multiwalled carbon nanotubes (NBR/MWCNT) were also subjected to $Ar^+$ and $He^+$ ion beam etching. The way of NBR/MWCNT preparation was described previously [9].

### Methods of testing

Graphitization and oxidation of the surface layer of elastomers, produced by the treatment, were evaluated from FT-IR spectra (Bio-Rad FTS 175 C, equipped with a Harrick Split-Pea IRS attachment). Progress of the modification was monitored by changes of IR spectra of surface layer of the materials in regions: 2800—3000 cm$^{-1}$ (related to absorption of $-CH_2-$ and $-CH_3$ groups) and 1650—1750 cm$^{-1}$ (reflecting the presence of -COOH and >C=O groups, respectively).

The influence of the modification on surface cracking and etching of elastomers was documented by scanning electron microscopy (OPTON DSM-950, USA), operating under low vacuum at the magnification of 50—2000 times.

Wettability of the materials surface before and after ion beam treatment was estimated from contact angle

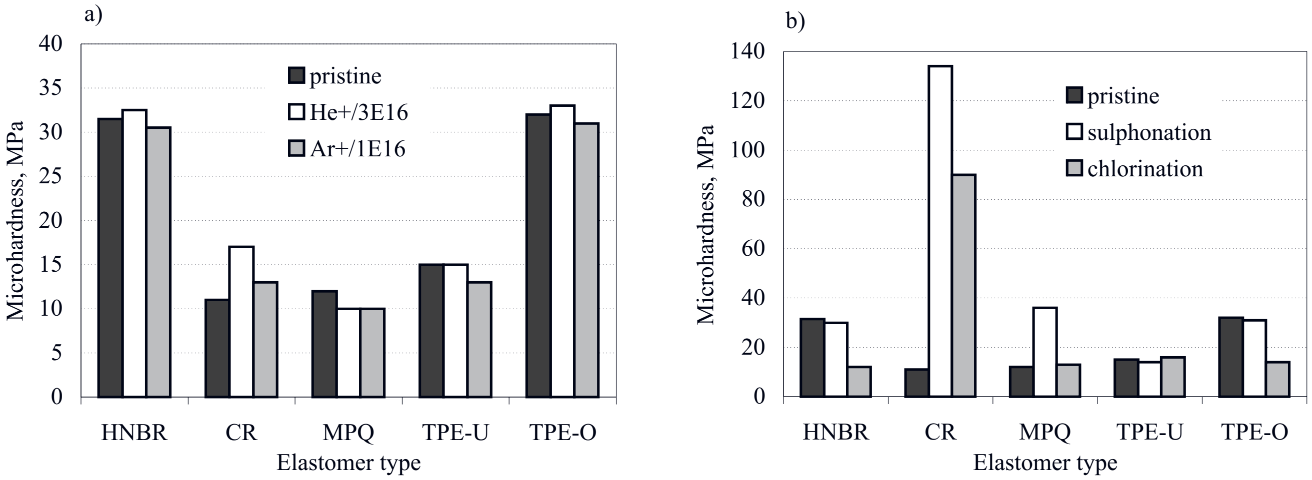

**Fig. 1. Influence of ion beam treatment (a) and conventional „wet" chemical modification (b) on microhardness of special purpose elastomers**

values, determined with a Krüss EasyDrop tensiometer (Germany), whereas changes to microhardness of the surface layer was determined by spherical nanoindentation (MML NanoTest 600, UK) [10]. Increase in microhardness can be subscribed to additional crosslinking of the elastomers studied [11].

The influence of ion bombardment on friction was studied with a Ducom TR-28M microtribometer (India), operating with a 12.7 mm stainless steel ball, normally loaded to 10 N and sliding over surface of the elastomer with the speed of 0.01 m/s. Friction force was taken as the average value of experimental data collected during 20 min of reciprocating test with frequency of 1 Hz. The coefficient of friction was calculated by dividing the friction force by the normal load.

## RESULTS AND DISCUSSION

The interactions between high energy ions and target materials are mainly of physical character [6]. Chemical doping of the surface layer of elastomers, contrary to semiconductive materials, is of no importance. It means that energy projection and penetration depth depends on ion mass [12]. Heavy ions cause mainly chain scission — producing macroradicals, whereas for light ions bombardment the mechanism of ionization dominates — manifesting itself by hydrogen release. Changes to characteristic regions in FT-IR spectra of rubber vulcanizates subjected to ion irradiation demonstrate mainly progress in graphitization of their surface layer [2]. Vulcanizates of NBR and its mixture with chloroprene rubber (NBR/CR in weight proportion of 50/50) seem to be the most resistant to carbonization among the elastomers studied. For the former (NBR vulcanizates), it can be explained by the presence of acrylonitrile monomer units, being more stable towards carbonization than linear monomer units of butadiene. For the latter (CR vulcanizates), higher resistance to carbonization can be subscribed to higher energy of C-Cl than C-H chemical bonds present in the rubber macromolecules [13], and the shielding effect produced by big chlorine atoms. Oxidation is almost not visible in FT-IR spectra of the rubber vulcanizates, probably due to shallow depth of the modification (not exceeding a couple of microns). Weak absorption band of hydroxyl

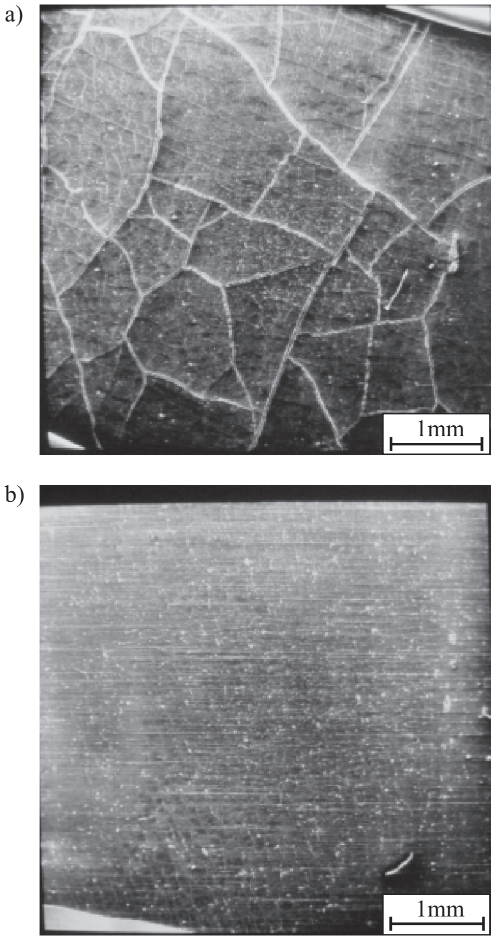

**Fig. 2. Changes in the surface morphology of vulcanizates based on natural rubber (NR) subjected to ion beam treatment: a) He$^+$/3 · 10$^{16}$ cm$^{-2}$/130 keV, b) Ar$^+$/1 · 10$^{16}$ cm$^{-2}$/130 keV**

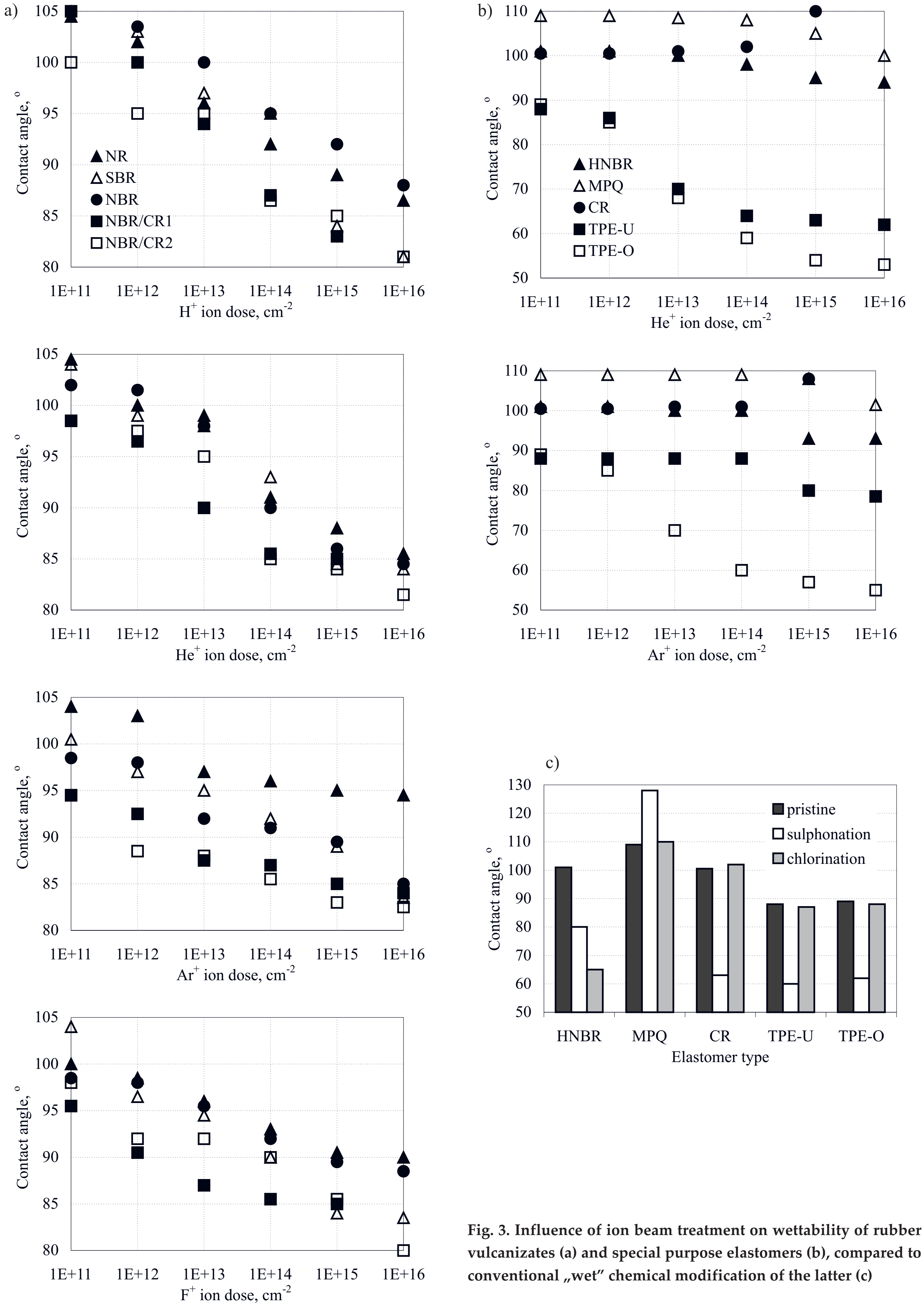

**Fig. 3. Influence of ion beam treatment on wettability of rubber vulcanizates (a) and special purpose elastomers (b), compared to conventional „wet" chemical modification of the latter (c)**

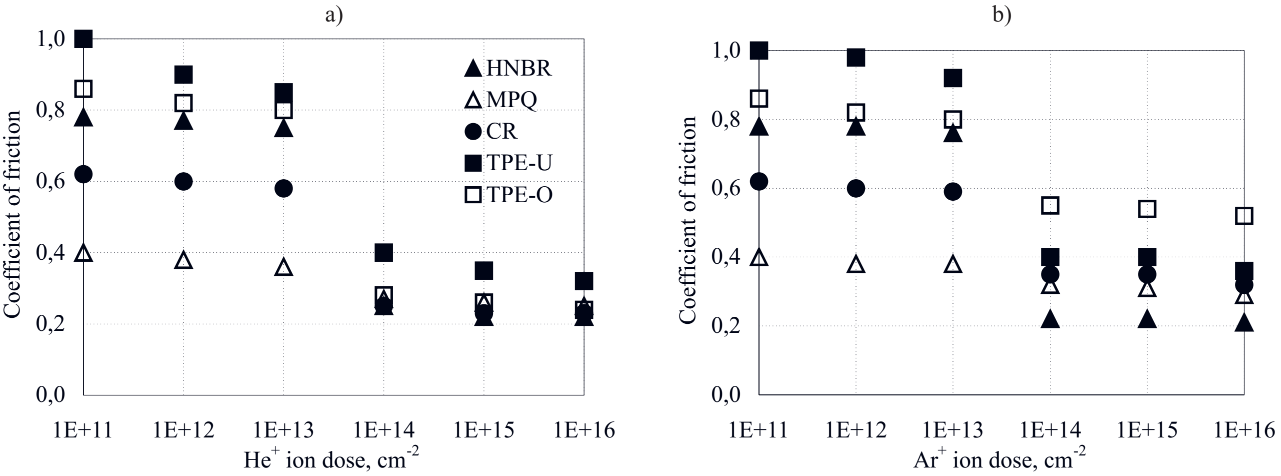

**Fig. 4. Influence of He⁺ (a) or Ar⁺ (b) ion beam treatment on coefficient of friction of special purpose elastomers**

groups at 3400 $cm^{-1}$ appears only in the case of NBR and NBR/CR vulcanizates.

Depending on the molecular structure of rubber, its macromolecules subjected to ion beam treatment exhibit dominating tendency either to degradation (NR, CR) or to crosslinking (SBR, NBR) [7]. The influence of ion beam treatment and conventional „wet" chemical modification on microhardness of special purpose elastomers is shown in Fig. 1. The effect is visible even for these special purpose elastomers, which are resistant to conventional „wet" treatment, realized by chlorination or sulfonation.

Free radicals, present in the surface layer of elastomers, can also react readily with atmospheric oxygen, additionally modifying chemically the materials. Our previous studies using Rutheford back scattering (RBS) spectroscopy, confirmed on oxidation of the rubber vulcanizates [8], which was hardly detected by FT-IR. Crosslinking of macromolecules makes the surface layer shrunk, what results in its cracking, finally increasing surface microroughness. The effect is most visible for SBR vulcanizates, resembling broken ice pieces on water surface [7], whereas for NR ones more fine crack pattern is produced — Fig. 2.

However, the geometrical effect is masked by surface oxidation, which decides finally on increased wettability of the elastomers studied with increasing ion dose, regardless of the kind of ions being applied — Fig. 3a. The modification is an alternative to conventional „wet" treatment, which does not work in the case of chemically resistant, special purpose elastomers — Fig. 3b.

Increased wettability facilitates lowering of friction in the micro-scale, which is governed by adhesion. According to hypothesis proposed by Borutto [14], humidity wetting of polymer surface results in perfect lubrication of a polymer-metal friction couple.

The above reported structural and chemical changes modify mechanical and tribological properties of elastomers also in the macro-scale [15, 16]. Application of ion beam treatment significantly reduces friction, what has been demonstrated in our previous papers [2, 7, 8]. It works also for special purpose elastomers, for which conventional „wet" treatment is ineffective [8], what becomes important for demanding aerospace and automotive applications. Modification of friction can be obtained for any kinds of ions used for bombardment, but its effectiveness depends on the ion dose, what is shown in Fig. 4.

The effect is of 0—1 character, becoming significant to the ion dose exceeding $10^{14}$ 1/$cm^2$, regardless of the kind of rubber irradiated or ion being applied. The persistence of the coefficient of friction at the low level is most likely

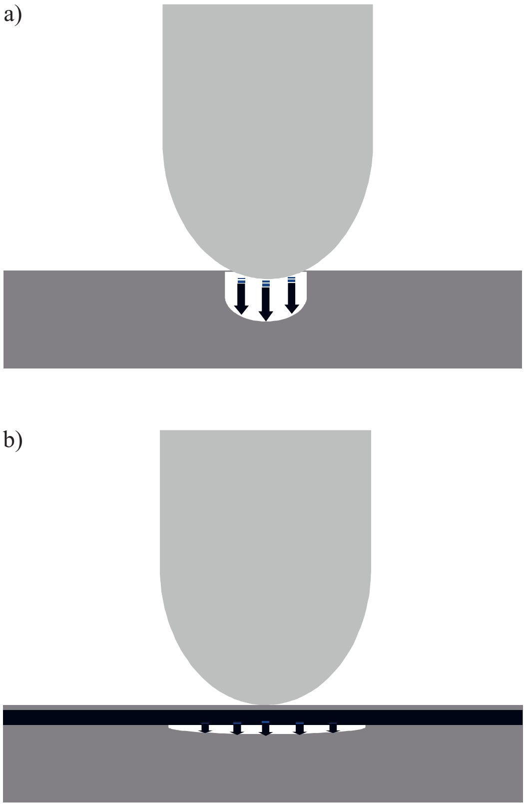

**Fig. 5. Proposed influence of ion beam treatment on elastomer friction: change from the mechanism by Moore (a) to the mechanism by Bowden and Tabor (b)**

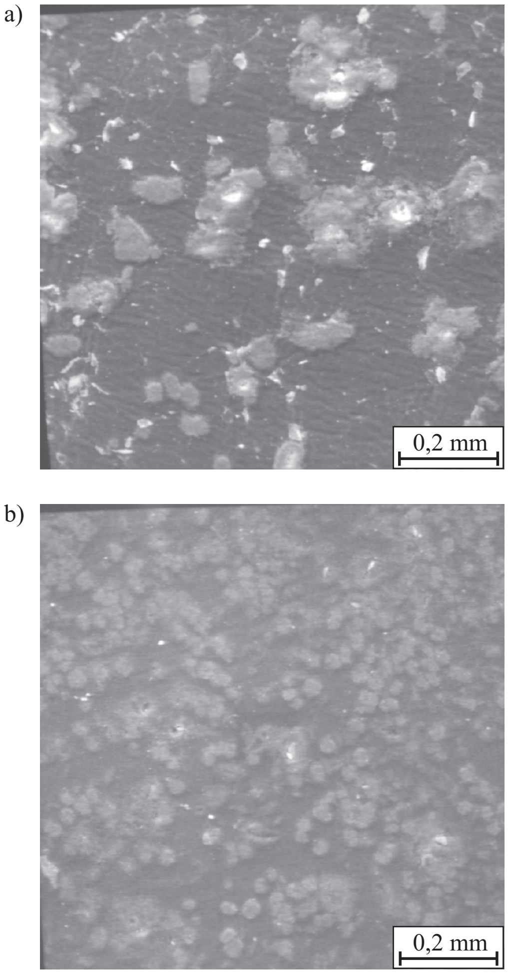

**Fig. 6. Surface morphology of NBR/MWCNT composite (according to [9]): a) containing 3 phr of MWCNT subjected to Ar$^+$ ion etching. 1 · 10$^{14}$ cm$^{-2}$/130 keV, b) containing 5 phr of MWCNT subjected to Ar$^+$ ion etching 1 · 10$^{14}$ cm$^{-2}$/160 keV**

to be associated with a graphitized layer being created on the elastomer surface exposed to higher ion beam doses. The reduction can be subscribed to changes in the mechanism of friction from the bulk — proposed by Moore [17, 18] to the surface sensitive one — described by Bowden and Tabor [19, 20], shown in Fig. 5.

Dissipation of energy prevails over its accumulation for elastomers with hard but very thin surface „skin", produced by ion bombardment, contrary to pristine ones, for which accumulation of energy, due to hysteresis of the materials, is dominating [17]. The effect of treatment is durable, despite presented above surface cracking of elastomers. Delamination wear, characteristic for conventional chemical modification of polymers can be avoided, due to very shallow extent of changes, limited to chain ends in the upper layer, whereas their opposite ends remain firmly anchored in the subsurface layer [2]. Contrary to hard „skin", hard, but thick surface layer produced by chemical treatment of elastomers, cannot cooperate well with elastic bulk of the materials under dynamic conditions accompanying friction, leading to significantly higher frictional wear.

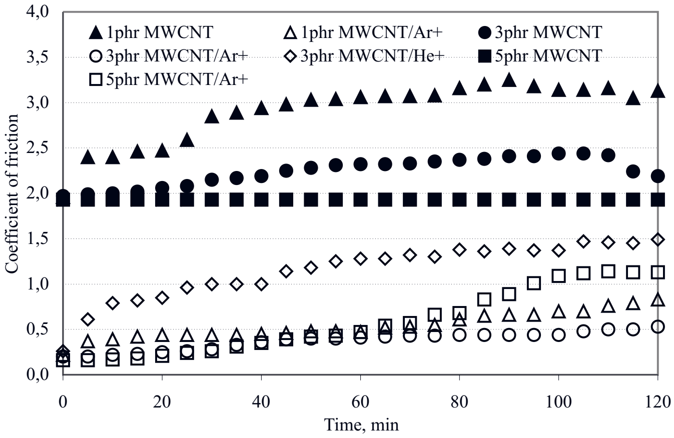

**Fig. 7. Influence of Ar$^+$ ion bombardment on the friction coefficient of NBR/MWCNT composites (according to [9])**

Apart from the discussed above changes to the mechanism of friction, lower friction of elastomers can also originate from decreasing the real area of tribological contact, as a result of increased surface microroughness and/or graphitization. Such a possibility is demonstrated by the surface morphology, shown in Fig. 6, and changes in the friction coefficient presented in Fig. 7 for butadiene-acrylonitrile rubber/multiwalled carbon nanotubes composites (NBR/MWCNT), subjected to ion beam etching with He$^+$ ions.

Irradiation of the composite surface with heavy Ar$^+$ ions reveals big agglomerates of carbon nanotubes protruding from elastomer surface. Such „sliding islands" morphology of the surface facilitates the fulfillment of both the above mentioned low friction criteria.

## CONCLUSIONS

From the results presented it follows, that high energy ion beam irradiation of elastomers offers a lot of interesting possibilities to modify their functional properties. Apart from increased wettability and development of the contact surface — which can also enhance adhesion in joints with metals and other polymers [21], a significant decrease in the friction coefficient and reduction of wear of the materials can be obtained. Low friction coefficient and low wear susceptibility can be maintained under unstable friction conditions, taking place at the beginning or at the end of machine operation (lubrication is not efficient at this time), or even when the lubrication system fails. In conclusion, application of right ion beam treatment produces structural and chemical changes to rubber macromolecules and is able to modify the elastomers in order to meet their engineering and/or functional requirements. The modification works also for special purpose elastomers, hardly modifiable using conventional chemical „wet" treatment like chlorination or sulfonation. It is of great importance, that the modification is limited to the top surface, leaving bulk of the material intact and thus preserving high elasticity of elastomers.

## REFERENCES

[1] Bieliński D.M., Jagielski J., Lipiński P., Pieczyńska D., et al.: *AIP Conf. Proc. Ser.* **2009**, *1099*, 357, http://dx.doi.org/10.1063/1.3/20050

[2] Pieczyńska D., Ostaszewska U., Jagielski J., Bieliński D.M.: *Polimery* **2011**, *56*, 439.

[3] Guzman A.M., Carlson J.D., Bares J.E., Ronko P.P.: *Nucl. Instrum. Methods, Phys. Res., Sect. B* **1985**, *7/8*, 507.

[4] Kondyurin A., Bilek M.: „Ion Beam Treatment of Polymers. Application Aspects from Medicine to Space", Elsevier, Amsterdam 2008, p. 317.

[5] Dong H., Bell T.: *Surf. Coat. Technol.* **1999**, *111*, 29.

[6] Jagielski J., Grambole D., Jóźwik I., Bieliński D.M., et al.: *Mater. Chem. Phys.* **2011**, *127*, 342, DOI: 1016/j.matchemphys.2011.02.015

[7] Ostaszewska U., Pankiewicz D., Bieliński D.M., Jagielski J.: *Polimery* **2012**, *57*, 40.

[8] Bieliński D.M., Pieczyńska D., Ostaszewska U., Jagielski J.: *Nucl. Instrum. Methods, Phys. Res., Sect. B* **2012**, *282*, 141, DOI: 10.1016/j.nimb.2011.08.068

[9] Bieliński D.M., Dobrowolski O., Lesiakowski R.: *Tribologia* **2009**, *223*, 21.

[10] http://micromaterials.net/NanoTest.asp (accessed October 28, 2013).

[11] Bieliński D.M.: *Current Trends Polym. Sci.* **2004**, *9*, 33.

[12] Lee E.H.: *Nucl. Instrum. Methods, Phys. Res., Sect. B* **1999**, *151*, 29.

[13] Pauling L.: *J. Am. Chem. Soc.* **1932**, *54*, 988.

[14] Borutto A., Crivellone C., Marani F.: *Wear* **1998**, *222*, 57.

[15] Bieliński D.M., Jagielski J., Pankiewicz D.: *Gummi Fasern Kunstst.* **2009**, *62*, 201.

[16] *Pat. PL* 207 440 (2012).

[17] Moore D.: „Friction and Lubrication of Elastomers", Pergamon Press, Oxford — New York — Toronto — Sydney — Braunschweig, 1972, p. 288.

[18] Persson B.N.J.: *Surf. Sci.* **1998**, *401*, 445.

[19] Bowden F.P., Tabor D.: „Friction. An Introduction to Tribology" (Polish translation), WNT, Warsaw 1980, p. 167.

[20] Rymuza Z.: in „Surface Modification and Mechanisms. Friction, Stress and Reaction Engineering" (Eds Totten G.E., Liang H.), Marcel Dekker, New York 2004, p. 99.

[21] *Pol. Pat. Appl.* P-392 815 (2010).

---

# MIĘDZYNARODOWA KONFERENCJA
# „SILESIAN MEETINGS ON POLYMER MATERIALS" POLYMAT60
## Zabrze, 30 czerwca—1 lipca 2014 r.

**Organizator**: Centrum Materiałów Polimerowych i Węglowych PAN w Zabrzu

Konferencja organizowana pod auspicjami Europejskiej Federacji Polimerów (EPF), we współpracy z siecią Central and East European Polymer Network (CEEPN) oraz z Oddziałem Gliwickim i Opolskim Polskiego Towarzystwa Chemicznego, jest poświęcona 60. rocznicy utworzenia Centrum Materiałów Polimerowych i Węglowych PAN w Zabrzu.

Konferencja kontynuuje tradycje międzynarodowych spotkań naukowych: Gliwickiego Seminarium Polimerowego GSP oraz konferencji „Polimery nad Odrą" POLYOR2011.

**Przewodniczący konferencji**: prof. dr hab. Andrzej Dworak

**Tematyka konferencji**:
- Nanostrukturalne systemy polimerowe
- Polimery funkcjonalne oraz nanokompozyty polimerowe
- Biodegradowalne materiały polimerowe przyjazne dla środowiska
- Polimery do zastosowań w medycynie

Program konferencji obejmuje: referaty plenarne, komunikaty oraz sesję posterową.

Zaproszenie do wygłoszenia wykładów przyjęli m.in.: prof. Klaus Müllen (Mainz), prof. Emo Chiellini (Piza), prof. Brigitte Voit (Drezno), prof. Bernd Bruchmann (Ludwigshafen), prof. Gerhart Braunegg (Graz), prof. Wim Hennink (Utrecht), prof. Jose M. Kenny (Terni), prof. Helmut Schlaad (Poczdam), prof. Mariastella Scandola (Bologna).

Wybrane referaty zostaną opublikowane w czasopiśmie „Polimery".

**Patronat medialny**: czasopismo „Polimery".

**Terminy**:

Zgłoszenie udziału w konferencji — do 30 kwietnia 2014 r. Przesłanie tekstów wystąpień do publikacji — do 21 czerwca 2014 r.

**Opłaty konferencyjne**: pełna opłata — 400 zł, opłata dla studentów i doktorantów — 250 zł

Opłata obejmuje materiały konferencyjne, 2 obiady oraz kolację konferencyjną.

Opłatę należy przekazać **do 6 czerwca 2014 r.**, na konto BANK PKO SA O/Zabrze, Pl. Warszawski 9, 41-800 Zabrze, IBAN: PL 40 1240 4227 1111 0000 4848 8035 z dopiskiem POLYMAT60 i z nazwiskiem uczestnika.

**Miejsce konferencji** — Hotel Diament, Zabrze ul. Cisowa 4.

Zapraszamy do udziału firmy zainteresowane wystawą promocyjną związaną z tematyką konferencji.

**Sekretariat konferencji**: dr inż. Agnieszka Kowalczuk, tel.: +48 32 271 60 77 wew. 765, fax: +48 32 231 28 31,
e-mail: polymat60@cmpw-pan.edu.pl

**www.cmpw-pan.edu.pl/polymat60**