Electron-beam modification of nitrile butadiene rubber in the fore-vacuum pressure range

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Abstract. We have studied the modification of nitrile butadiene rubber surface properties by pulsed and by continuous electron beams generated in inert (argon, helium) and in chemically active (oxygen, nitrogen, air) gas atmosphere in the fore-vacuum range of pressure (~10 Pa). Relative measurements of the wear rate, friction coefficient, and contact (wetting) angle of the sample surfaces before and after beam treatment have been made. We have found that the electron-beam treatment of nitrile butadiene rubber does not result in any significant thermal damage to its surface, and that dependencies of the coefficient of friction and the wear rate on the surface treatment duration have a non-monotonic character. For optimal electron beam treatment conditions, the friction coefficient decreases by a factor of about two.

1. Introduction

Electron-beam modification of dielectric surfaces (ceramic, glass, and polymer) is increasingly used industrially and in medicine [1]. Dielectric surface treatment by electron beams improves the surface sorption, tribological, optical, and conductive properties [2], offering new possibilities for the applications for these materials. Nitrile butadiene rubber (NBR) is used as an oil- and gasoline-resistant material in automotive, oil, electrical, and medical industries [3]. Despite its practical appeal for many applications, surface modification of NBR by plasma or ion beams has been the subject of research in only a few recent publications [4–6]. It is clear, however, that plasma-beam modification of NBR surface properties decreases the coefficient of friction, and hence wear, and will thus considerably prolong the lifetime of NBR products.

For the efficient modification of NBR surfaces, we have used an electron beam in combination with the plasma that the beam generates in its transport in gas at elevated pressure in the fore-vacuum range [7]. Electron-beam modification of NBR, which is an insulating polymer material, requires neutralization of the surface charge built up by the electron beam itself [8]. Further, the treatment must be done under conditions such that the surface temperature does not exceed about 150 °C, when surface degradation and carbidization start to occur. These required conditions can be fully provided by using a forevacuum electron beam source operating at elevated gas pressure in the range 1–100 Pa [9, 10]. At this pressure, ions from the plasma generated in the beam transport region, almost completely compensate the electric charge accumulated on the surface of a non-conducting material. In this way, the electron beam action on the dielectric target is as effective as on metals or other conducting materials [11]. Apart from surface charge neutralization, the beam plasma can also affect the NBR surface modification processes. The required mild conditions of electron-beam action on the NBR surface can
be provided by lowering the power of a continuous electron beam or by operating the source in a repetitively-pulsed mode.

The aim of the work described here was to study the surface modification of nitrile butadiene rubber by an electron beam generated in the fore-vacuum pressure range and the associated beam-produced plasma.

2. Experimental equipment and technique
The NBR surface treatment was performed using two separate experimental installations, one equipped with a forevacuum-pressure plasma-cathode continuous electron beam source based on a hollow-cathode glow discharge [12], and the other facility utilizing repetitively-pulsed beams based on a cathodic arc [13]. These two experimental systems are illustrated schematically in Figures 1 and 2, respectively. The parameters of the two electron beam sources are given in Table 1.

In continuous mode, the electron beam is transported towards the target surface through a drift region filled with the working gas, where a dense beam-plasma is generated. In this way, the NBR sample surface is acted upon both by the electron beam and by charged plasma particles. The samples were placed on a massive grounded metal collector plate, and the surface temperature monitored throughout the processing duration using a Raytek optical pyrometer. Beam parameters (current, energy, and diameter) were selected so that the temperature of the treated surface did not exceed 80 °C.

The pulsed electron beam was generated by a forevacuum-pressure plasma-cathode electron source based on a cathodic arc discharge. The plasma was formed by a pulsed arc discharge, and the beam was extracted by direct current (DC) high voltage power supply from the plasma at constant accelerating voltage $U_a$. The electron source was mounted on a flange of the vacuum chamber, which was evacuated by a forevacuum mechanical pump. The working pressure was controlled by regulating the gas admission rate into the vacuum chamber at a constant pumping rate. The NBR surface was irradiated by a string of pulses, with the number of pulses in a string varied. NBR samples of size $30 \times 40$ mm$^2$ were placed on a special holder, which could be moved by a two-coordinate manipulator. To prevent the
energetic electron beam from striking neighbouring samples while a particular sample was processed, we installed a protective stainless-steel shield with a $60 \times 60 \text{ mm}^2$ aperture aligned with the beam axis. In the pre-experiment set-up period and during sample transfer, the protective shield aperture was closed by a stainless-steel shutter driven by an electric actuator. The treatment process was performed as follows. With the protective shield aperture shut, the beam parameters were tuned. The two-coordinate manipulator then positioned an NBR sample on the beam axis. Then the shield aperture was opened and the sample irradiated by the pulsed electron beam. After irradiation by a specified number of pulses, the aperture was closed and the next sample moved into position and the treatment process repeated.

**Figure 2.** Experimental setup using a repetitively-pulsed electron beam source.

| Table 1. Electron beam source operating parameters. |
|----------------------------------------------------|
| **Mode** | **Continuous** | **Pulsed** |
| Accelerating voltage | 3 kV | 5 kV |
| Beam current | 20 mA | 20 A |
| Beam diameter | 100 mm | 70 mm |
| Beam power | 60 W | - |
| Treatment duration | 100 s, 500 s | - |
| Pulse duration | - | 100 µs |
| Pulse repetition rate | - | 100, 500 pps |
| Beam energy per pulse | - | 10 J |
| Working gas | Ar, N$_2$, H$_2$, O$_2$, Air | Ar, N$_2$, He |
| Residual pressure | 1 Pa | 1 Pa |
| Working pressure | 8 Pa | 8 Pa |
The surface elemental composition of both original NBR samples and those subjected to the electron beam and plasma action was analysed using a Hitachi S3400N SEM coupled with a BrukerX’Flash 5010 energy-dispersive detector. Tribological characteristics were measured using a Pin on Disc and Oscillating TRIBO tester. This instrument makes use of the ball-on-disk method of measurement with a 1 N load on the ball tip. The tip was made of stainless steel 100Cr6. The friction coefficient was determined by measuring deflection of the elastic lever. The wear of the material was determined by measuring the wear track produced during the test. The wear parameter $V$, indicative of the rate of wear, was determined from the formula $V = 2 \cdot \pi \cdot R \cdot A / (F \cdot L)$, where $R$ is the track radius (µm), $A$ the cross-sectional area of the wear scar (µm$^2$), $F$ the applied load (N), and $L$ the distance travelled by the ball (m).

The contact angle was determined using the sessile drop method. The contact angle $\theta$ is a characteristic of the surface wettability. Its value is determined from the equilibrium values of the dimensions that the drop assumes on the three-phase interface line when placed on the solid surface: height $h$ and diameter $d$ of the base of the drop. The contact angle is calculated from the formula [14]

$$\cos(\theta) = \frac{(d/2)^2 - h^2}{(d/2)^2 + h^2}.$$

3. Results and discussion

Figure 3 shows the results of SEM analysis of the NBR sample surfaces before and after treatment by the continuous beam. It can be seen that the rubber surfaces before and after treatment look much the same, implying that beam heating is minimal and does not damage the treated surface.

![Figure 3. Results of SEM analysis of samples before and after electron beam and plasma treatment.](image)
The main elements observed on the sample surface, both before and after processing, are carbon and oxygen, which are constituents of NBR. Also observed are small traces of atomic calcium, potassium, silicon, titanium, zinc, etc., which are used in the NBR curing process. Note that atomic hydrogen was not registered due to specifics of the SEM technique – the analysis can only register elements heavier than boron. One can also see that the proportions of the main elements (oxygen and carbon) change following the beam treatment; this may be the cause of tribological property changes.

The results of measurements of wear rate, coefficient of friction, and contact angle, before and after treatment are listed in Table 2 and shown graphically in Figure 4. The initial values of wear rate, friction coefficient, and contact angle are 3.5 x 10^{-3} mm^3/N·m, 0.62, and 99.5°, respectively.

**Table 2.** Surface parameters of treated samples.

| Treatment duration | Working gas | Rate of wear \( \text{mm}^3/N\cdot m \) | Coefficient of friction | Contact angle, deg. | Rate of wear \( \text{mm}^3/N\cdot m \) | Coefficient of friction | Contact angle, deg. |
|--------------------|-------------|---------------------------------------|------------------------|------------------|---------------------------------------|------------------------|------------------|
| 100 s              | O\(_2\)     | 1.9 x 10^{-3}                         | 0.34                   | 62               | 2.6 x 10^{-3}                         | 0.48                   | 98.5             |
|                    | Ar          | 2.6 x 10^{-3}                         | 0.36                   | 65               | 3.8 x 10^{-3}                         | 0.4                    | 90.5             |
|                    | N\(_2\)     | 2.2 x 10^{-3}                         | 0.34                   | 88               | 3.1 x 10^{-3}                         | 0.37                   | 91.5             |
|                    | H\(_2\)     | 2.5 x 10^{-3}                         | 0.33                   | 93.4             | 3.2 x 10^{-3}                         | 0.47                   | 103.4            |
|                    | Air         | 3.8 x 10^{-3}                         | 0.34                   | 71               | 4.3 x 10^{-3}                         | 0.38                   | 96               |
| 500 s              | O\(_2\)     | 1.9 x 10^{-3}                         | 0.34                   | 62               | 2.6 x 10^{-3}                         | 0.48                   | 98.5             |
|                    | Ar          | 2.6 x 10^{-3}                         | 0.36                   | 65               | 3.8 x 10^{-3}                         | 0.4                    | 90.5             |
|                    | N\(_2\)     | 2.2 x 10^{-3}                         | 0.34                   | 88               | 3.1 x 10^{-3}                         | 0.37                   | 91.5             |
|                    | H\(_2\)     | 2.5 x 10^{-3}                         | 0.33                   | 93.4             | 3.2 x 10^{-3}                         | 0.47                   | 103.4            |
|                    | Air         | 3.8 x 10^{-3}                         | 0.34                   | 71               | 4.3 x 10^{-3}                         | 0.38                   | 96               |

**Figure 4.** Wear rate, coefficient of friction, and contact angle of nitrile butadiene rubber for various working gas species and treatment durations, for continuous mode (a) and pulsed mode (b).
These results show that for short-time action of the electron beam, for both continuous (100 s) and pulsed modes (100 pulses), the coefficient of friction decreases significantly. Except for the sample processed in a helium atmosphere in pulsed mode, the friction coefficient decreases by almost a factor of two compared with its initial value. Note that the decrease of the coefficient of friction for continuous beam treatment is almost the same for all working gases. The lowest values of the coefficient of friction (0.24 and 0.26) were obtained for surfaces processed by the pulsed electron beam in argon and nitrogen (respectively). Longer treatment resulted in lower surface friction except for the sample modified by the pulsed beam in a helium atmosphere.

The surface rate of wear has a similar decreasing trend. For continuous mode, the sample with the lowest wear rate (1.9·10^{-3} mm^3/N·m) was modified in an oxygen atmosphere, and for pulsed mode the lowest value (1.7·10^{-3} mm^3/N·m) was for the sample treated in nitrogen. For the longer treatment times and for all samples, the rates of wear were close to those of the initial samples.

We point out the following:

– There is a strong correlation between treatment time of the NBR surface and the degree by which the coefficient of friction decreases.

– The electron beam action becomes less efficient with increasing treatment duration. This may be connected to adverse effects of surface temperature rise for longer processing time.

– The type of gas has a strong effect on the wear rate: for inert gases (argon and helium) or air, the rubber wear rate is less than for samples processed in nitrogen, oxygen, or hydrogen atmospheres. This effect could be related to the beam-plasma ions, which might initiate processes similar to those that occur in the rubber curing during fabrication; nitrogen, oxygen, and hydrogen are constituents of the acrylonitrile which is added to rubber to improve its surface characteristics.

As seen from the results shown in Table 2 (see also Figure 5), a significant influence on the surface hydrophobic and hydrophilic properties are caused by the short-time action of the continuous electron beam in oxygen, argon, and air.

![Water droplets on initial and modified surfaces of nitrile butadiene rubber.](image)

The lowest contact angle (62 degrees) is found for the sample treated in oxygen. This is due to the formation of oxide functional groups on the surface, which leads to surface hydrophilization [6].

4. Conclusion

Electron-beam treatment of NBR in the forevacuum pressure range significantly modifies the rubber surface characteristics. Following electron-beam processing, the coefficient of friction and the rate of wear decrease, while the effect on contact angle depends on the type of working gas, which is most likely due to the plasma ions produced in the electron beam transport region. The practicality, simplicity, and technological ease of electron-beam irradiation of NBR by forevacuum-pressure plasma-cathode electron beam sources provide an attractive surface modification tool for a wide range of polymer materials.
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References
[1] Clough R L, 2001 Nucl. Instrum. Meth. Phys. Research B. 185 8
[2] Phan L T, Yoon S M, Moon M W 2017 Polymers 9 417
[3] Franta I 1989 Elastomers and rubber compounding materials: manufacture, properties and applications (New York: Elsevier)
[4] Pukhova I V, Kurzina I A, Savkin K P, Laput O A, Oks E M 2017 Nucl. Instrum. Meth. Phys. Research B. 399 28
[5] Shandrikov M V, Artamonov I D, Oks E M, Yushkov G Yu, Zhang B, Bai C, Gao K 2020 Surf. Coat. Tech. 388 125556
[6] Mugica-Vidal R, Mercadal-Guillen J, Sainz-Garcia E, Alba-Elías F 2021 Int. J. Adhes. Adhes. 108 102865.
[7] Uglov V V, Kvasov N T, Petukhov Y A, Koval N N, Ivanov Y F, Teresov A D 2012 J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech. 6 67
[8] Zolotukhin D B, Tyunkov A V, Yushkov Yu G 2017 Appl. Phys. 6 39
[9] Kazakov A V, Medovnik A V, Oks E M 2019 IEEE Trans. Plasma Sci. 47 3579
[10] Tyunkov A V, Burdovitsin V A, Oks E M, Yushkov Yu G, Zolotukhin D B 2019 Vacuum. 163 31
[11] Yushkov Yu G, Oks E M, Tyunkov A V, Zolotukhin D B 2019 Ceram. Int. 45 9782
[12] Burdovitsin V A, Golosov D A, Oks E M, Tyunkov A V, Yushkov Yu G, Zolotukhin D B, Zavadsky S M 2019 Surf. Coat. Tech. 358 726
[13] Burdovitsin V A, Kazakov A V, Medovnik A V, Oks E M 2018 Phys. Plasmas. 25 073109
[14] Adamson A V 1976 Physical chemistry of the surfaces (New York: Wiley)