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THE EFFECT OF GRAPHENE ADDITIVE ON THE TRIBOLOGICAL PROPERTIES OF BIONIC LUBRICANT COMPOSITIONS TESTED BY THE SRV METHOD

WPŁYW DODATKU GRAFENOWEGO NA WŁAŚCIWOŚCI TRIBOLOGICZNE BIONICZNYCH KOMPOZYCJI SMAROWYCH TESTOWANYCH METODĄ SRV

Key words: bionic lubricants, graphene additives, graphene oxide, anti-wear properties, boundary layer, SRV metod.

Abstract The aim of the study was to investigate the effect of the addition of graphene dispersion on anti-wear properties of bionic lubricant compositions based on aqueous sodium hyaluronate solutions. Tribological tests were carried out using a SRV tester, enabling the tests to be carried out in conditions of linear oscillating movement of the bullet-shield type association in which the ball was made of aluminium oxide and the disc was made of bearing steel 100Cr6. For research, a 0.5% solution of sodium hyaluronate in water (composition BSS2) was chosen, which was the base to which the graphene additive was introduced. During the main stage of work, three lubricant compositions were tested, i.e., as well as BSS2 solution, into which 0.05% m/m or 0.1% m/m graphene oxide was introduced, respectively. The study allowed the observation of a clear anti-wear effect associated with the introduction of graphene preparations into the hyaluronan base, manifested in a change in the trend of the graph of the coefficient of friction over time. In addition, a reduction in the volume wear of friction node components was found. Based on the analysis of tribological research results, it was found that the anti-wear effect of the lubricant on the friction elements of the steel-ceramic material combination increases with increasing the content of the graphene preparation in the lubricant composition.

Słowa kluczowe: bioniczne środki smarowe, dodatki grafenowe, tlenek grafenu, właściwości przeciwzużyciowe, warstwa graniczna, metoda SRV.

Streszczenie Celem pracy było zbadanie wpływu dodatku dyspersji grafenowej na właściwości przeciwzużyciowe bionicznych kompozycji smarowych na bazie wodnych roztworów hialuronianu sodu. Badania tribologiczne przeprowadzono, stosując tester SRV, umożliwiający realizację testów w warunkach liniowego ruchu oscylacyjnego skojarzenia typu kula–tarcza, w którym kula wykonana była z tlenku aluminium, a tarcza ze stali łożyskowej 100Cr6. Do badań wybrano 0,5-procentowy roztwór hialuronianu sodu w wodzie (kompozycja BSS2), stanowiący bazę, do której wprowadzano dodatek grafenowy. Podczas zasadniczego etapu prac testowano trzy kompozycje smarowe, tj., kompozycję BSS2, a także roztwór BSS2, do którego wprowadzono odpowiednio 0,05% m/m lub 0,1% m/m tlenku grafenu. Przeprowadzone badania pozwoliły na zaobserwowanie wyraźnego efektu przeciwzużyciowego związanego z wprowadzeniem preparatów grafenu do bazy wodno-hialuronianowej, przejawiającego się zmianą trendu wykresu zależności współczynnika tarcia w czasie. Ponadto stwierdzono redukcję zużycia objętościowego elementów węzła tarcia. Na podstawie analizy wyników badań tribologicznych stwierdzono, iż efekt przeciwzużyciowego oddziaływania substancji smarowej na elementy trące skojarzenia materiałowego stal–ceramika wzrasta wraz z podwyższaniem zawartości preparatu grafenowego w kompozycji smarowej.

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INTRODUCTION

Bionic lubricants are understood as synthetic preparations with a chemical structure similar to a synovial fluid present in the joints of living organisms **[L. 1, 2]**. Thus, we are talking about substances based on water, which, due to its physicochemical properties, is a medium that effectively dissipates heat, reduces resistance to movement, and also perfectly transmits forces. Among the substances used as components of bionic lubricants, aqueous solutions of substances present in natural synovial fluid, mainly chondroitin sulphate and hyaluronic acid derivatives are used **[L. 3–5]**.

Water consumable fluids are used in some technical applications, e.g., in hydraulic devices, bearings, or as a cooling and lubricating fluid in machining technologies. Water-based lubricants are currently a segment of the range of operating fluids intended for specialized applications where non-flammable properties of the lubricant are necessary or lubricating is subject to plastic components, possibly covered with appropriately selected technological layers **[L. 6–8]**. These types of preparations are characterized by a complex chemical composition, containing a multi-component base and various types of anticorrosive, viscosizing, and tribological properties. Chemical fluid modification products of vegetable oils, the modification products of organosilicon compounds, oligoglycols, as well as adducts of cyanouric acid and melamine are also components of the operating fluids' aqueous bases. In addition, additives improving specific operational properties are introduced, e.g., hexamethylenetetramine as an anti-corrosive additive, polyalkylamides, as viscosifiers, or unsaturated alcohols as anti-wear additives **[L. 9–12]**.

Empirical studies carried out in different research centres indicate a high potential application of graphene as an additive for lubricants based on water. The published results of tribological tests in a bullet-shield combination made of bearing steel indicate that a small amount of graphene addition can significantly reduce the friction coefficient by up to 81.3% and the volume consumption of friction node material by two orders of magnitude, compared to deionized water. The tests were carried out at various loads of the friction node, and, in each case, a clear anti-wear effect of graphene additives was observed. The cited studies used graphene dispersions in water stabilized with the Triton X-100 non-ionic surfactant. The observed effects were attributed to the formation of a protective graphene layer in the frictional contact area, which is favoured by the presence of a surfactant that reduces surface tension at the interface between the friction node material and the lubricant composition. It has also been shown that pure graphene is even more effective than „graphene oxide", while maintaining the same concentration of graphene additive in the aqueous matrix **[L. 13]**. In other tests also carried out in the bullet-shield combination, the ball was made of sintered tungsten carbide and the shield was made of bearing steel, and it also showed the high anti-wear effectiveness of graphene used as an additive to water, associated with the occurrence of a very low coefficient of friction of 0.05 **[L. 14]**. The results of model tests indicate not only a significant reduction in the coefficient of friction and volumetric wear of friction node components as a result of the use of graphene in lubricant compositions, but also confirm the improvement of anticorrosion properties of aqueous lubricants due to the introduction of graphene additives **[L. 15]**.

Previous tribological studies were conducted primarily in bullet-shield model friction nodes in linear sliding friction in which there are relatively mild mechanical forces, allowing the observation of a clear anti-wear effect associated with the presence of graphene in the lubricant composition. The conducted literature research indicates that no research has been conducted in the friction node performing oscillatory motion on a very small path, which is available in the SRV method. Such conditions, due to the high frequency of movement, causing a change in the direction of movement of the cooperating friction node elements relative to each other, affect the removal of any boundary layers and significantly impede their reproduction.

In connection with the above, the aim of the study was to assess the effect of graphene additive on the anti-wear properties of bionic lubricant compositions based on aqueous sodium hyaluronate solutions tested under linear oscillatory motion.

RESEARCH METHODOLOGY

Research objects

The model lubricating compositions were prepared for tribological tests, using the following components: osmotically demineralized water with a conductivity 0.05 μS/cm, commercially available (Ecospa, Warsaw) crystalline high molecular weight sodium hyaluronate (molecular weight 1.0–1.8 MDa), and also a commercial 1% dispersion of „graphene oxide" in water supplied by Nano Carbon (Poland, Warsaw). It should be noted that graphene oxide is the common name for graphene forms having on their surface organo-oxygen functional groups **[L. 16]**.

During preliminary tests, which aimed to assess the effect of sodium hyaluronate concentration on the anti-wear properties of the lubricant composition, solutions of the following concentrations were used:

0.1% (composition BSS1) and 0.5% (composition BSS2). The pure water, designated as BSSO, was used as a reference. Based on these tests, the bionic lubricant base, i.e. the BSS2 composition, which was an aqueous solution of sodium hyaluronate at a concentration of 0.5% m/m, was selected for further testing. An aqueous dispersion of graphene preparation was introduced into this base in such an amount that its content was obtained at the level of 0.05% m/m (composition BSS2_G1) and 0.1% m/m (composition BSS2_G2) in the base lubricant, which was a hyaluronan solution sodium in water.

The tribological tests

The prepared compositions were subjected to tribological tests using a SRV (linear oscillating motion) tester. The tribological tests were performed in the bullet-shield friction combination. The ceramic ball was made of Al_2O_3, while the disc was made of 100Cr6 bearing steel, hardness 60 HRC. The tests were carried out in the following conditions: frequency – 20 Hz, leap – 1 mm, friction node load – 25N, and the test temperature was 25°C. Three parallel tribological tests were performed, during which the friction coefficient was recorded.

The friction surface testing

After the tribological tests were completed, the volumetric wear of the steel disc was determined by means of confocal profilometry, and microscopic and spectral methods of friction surface testing were carried out. Tested discs after tribological tests were washed with osmotically purified water, and after drying, they were stored in closed polyethylene packaging. Traces of friction created on the cooperating elements of tribological association were examined using optical microscopy and scanning electron microscopy coupled with X-ray energy dispersion spectrometry (SEM/EDS). For SEM/EDS tests, a Hitachi SU-70 scanning electron microscope equipped with an EDS X-ray microanalyser was used. The analyses were carried out under the following conditions: accelerating voltage 15 kV, receiving angle 30°, and vacuum 10^{-8} Pa. The mappings of the selected friction trace area were recorded.

The Raman spectrum were recorded at room temperature using an NRS 5100 spectrometer from Jasco (Japan), using 532 nm wavelength laser excitation and an exposure time of 20 seconds. The spectra were recorded in the Raman range from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 2.1 cm^{-1}, using a lens with a magnification of x50 for microscopic measurements. The measurement technique of Raman scattering is particularly useful for studying carbon materials, because the characteristic bands for this type of material, i.e. the D and G bands, change their spectral parameters with the change in the molecular structure of the tested material. The interpretation of the spectrum included the analysis of the location of the D and G bands and the evaluation of the ratio of the intensity (I_D) of the D band to the intensity (I_G) of the G band **[L. 17]**. For calculating the average value of the coefficient, five intensity values of individual bands were used, appearing in spectra recorded at randomly selected places of the analysed area.

RESULTS AND DISCUSSION

The study of the composition without the addition of bionic graphene

The results of preliminary tribological tests of the test compositions without the addition of graphene oxide, the purpose of which was to identify the effect of sodium hyaluronate concentration on the resultant anti-wear effect of the lubricant on the structural elements of the friction node, are shown in **Fig. 1**.

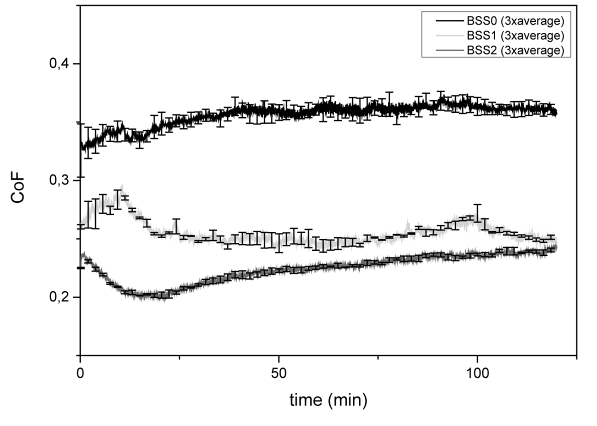

Fig. 1. The dependence of the friction coefficient on the time of the test with the participation of tested bionic lubricant compositions without the addition of graphene oxide

Rys. 1. Zależność współczynnika tarcia od czasu testu z udziałem badanych bionicznych kompozycji smarowych bez dodatku tlenku grafenu

The comparison of the waveforms of the registered dependence of the friction coefficient on the time of the test indicates that the introduction of sodium hyaluronate into the water (compositions BSS1 and BSS2) reduces the friction coefficient, and its value decreases as the concentration of sodium hyaluronate increases in water. Then, profilometric tests of traces of tribological life occurring on steel test discs were carried out, and the obtained profiles are presented in **Fig. 2**.

a) b) c)

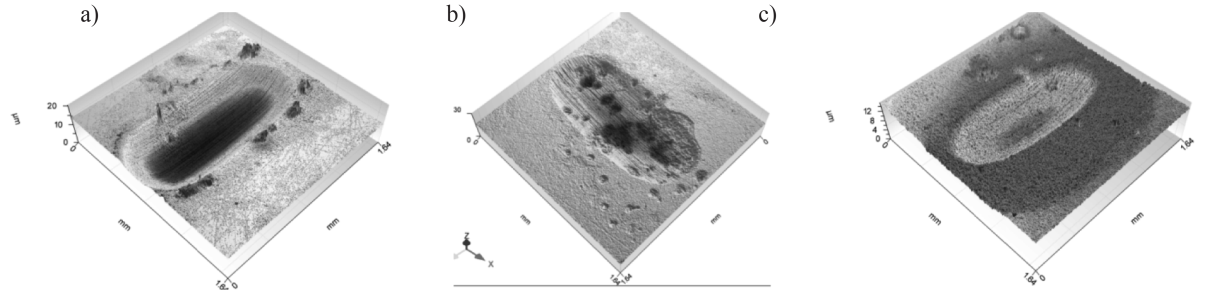

Fig. 2. The profiles of traces of disc wear after SRV tests in the lubricated node: a) water (BSS0), b) 0.1% aqueous sodium hyaluronate solution (BSS1), c) 0.5% aqueous sodium hyaluronate solution (BSS2)

Rys. 2. Profile śladów zużycia tarcz po testach SRV w węźle smarowanym: a) wodą (BSS0), b) 0,1-procentowym wodnym roztworem hialuronianu sodu (BSS1), c) 0,5%-procentowym wodnym roztworem hialuronianu sodu (BSS2)

The volume consumption of the material was then determined on the basis of profilometric measurements, and the obtained results are shown in **Fig. 3**.

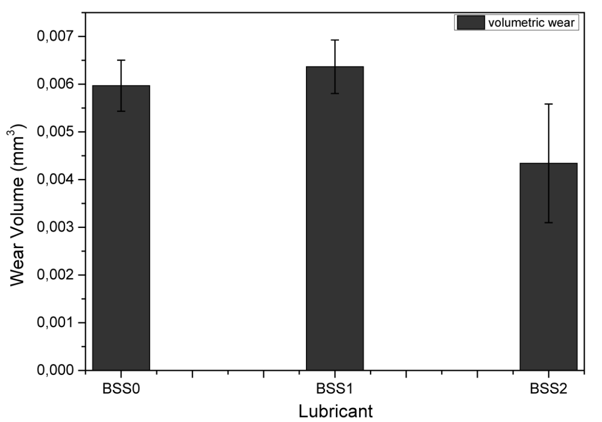

Fig. 3. The comparison of volumetric wear of steel discs after the SRV tribological test in a steel–aluminium oxide material combination, lubricated with water and aqueous solutions of sodium hyaluronate without the addition of grapheme

Rys. 3. Porównanie zużycia objętościowego stalowych tarcz po teście tribologicznym SRV w skojarzeniu materiałowym stal–tlenek aluminium, smarowanym wodą oraz wodnymi roztworami hialuronianu sodu bez dodatku grafenowego

The comparison of the results of material wear of steel discs used during tests indicates that, despite significant improvement in lubricity measured by the friction coefficient, material wear during tribological tests does not change much, especially in the case of testing BSS1 compositions. This is due to the fact that water in combination with hyaluronic acid is a strong oxidant, which results in the formation of corrosive interactions. The corrosion interactions are visible in the sample microscopic images of discs after tribological tests presented in **Fig. 4**.

a)

b)

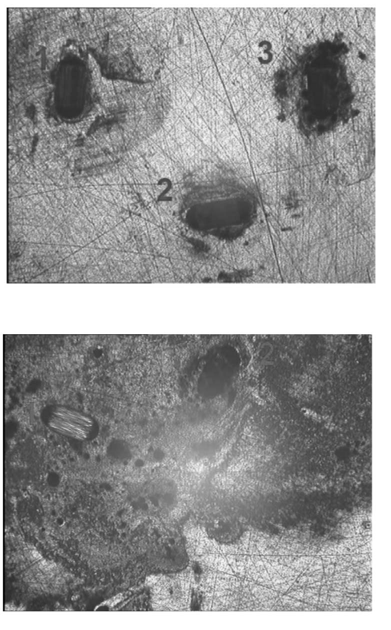

Fig. 4. The microscopic image of the disc surface after tribological tests by the SRV method with the composition of the lubricant: a) BSS0, b) BSS1

Rys. 4. Obraz mikroskopowy powierzchni tarcz po testach tribologicznych metodą SRV z udziałem kompozycji smarowej: a) BSS0, b) BSS1

Traces of friction after individual test runs were marked on the photographs with numbers. The photographs show signs of corrosion on samples that had contact with BSS0 only in the friction area. When observing a surface lubricated with demineralized water, corrosion products are deposited mainly in the friction area. The slight deposit of products is also observed in the immediate vicinity of the friction area, which is also visible on surface topographies registered with the profilometric method. However, when using an aqueous solution of sodium hyaluronate at a concentration of 0.1% m/m, areas with a large amount of deposit are observed, and pitting is observed in the construction material in some places, which is also confirmed by 3D profilometric tests. The deposit formed in the friction area may contain both steel corrosion products as well as tribochemical conversion products of sodium hyaluronate.

The test composition containing added bionic graphene

Averaged waveforms of the coefficient of friction from the test time recorded during tribological tests are presented in **Fig. 5**.

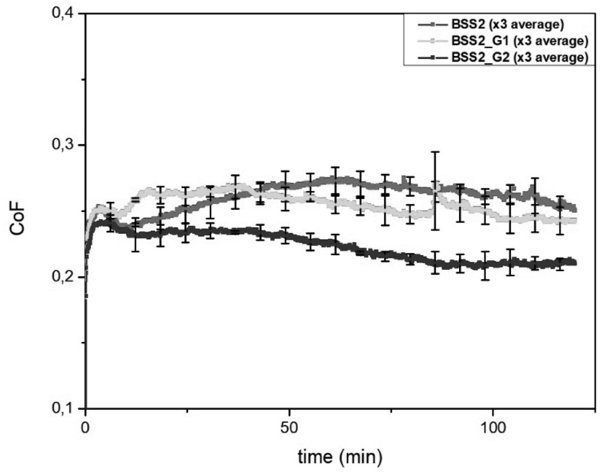

Fig. 5. The dependence of the friction coefficient on the time of the test with the participation of bionic lubricating compositions containing graphene oxide [L. 18]

Rys. 5. Zależność współczynnika tarcia od czasu testu z udziałem badanych bionicznych kompozycji smarowych zawierających tlenek grafenu **[L. 18]**

The course of the curves indicates that, during tests using the BSS2 composition, the values of the friction coefficient in the initial phase of the test systematically increase, and only after about 50 minutes of the test a slight decrease is observed, with characteristic fluctuations. The increase in the coefficient of friction can be associated with the initial evaporation of water from the lubricant composition, and thus the disruption of the lubricant film. After the formation of organic boundary layers from the products of tribochemical conversion of sodium hyaluronate, a reduction of friction resistance is observed. The introduction of the graphene oxide dispersion into the lubricant composition results in a change in the recorded friction coefficient characteristics, already evident with the use of 0.05% (m/m) of the additive. A clear effect of the graphene preparation is observed for the composition containing 0.1% (m/m) of the additive, i.e. the composition designated BSS2_G2. In this case, after a short break-in period of friction node elements, a decreasing trend of the recorded curve is observed until the friction coefficient stabilizes after about 80 minutes of the test. The observed reduction of resistance to movement also reduces the material consumption of the cooperating friction node components, which clearly results from profilometric measurements of the wear of steel discs **(Fig. 6)**.

Based on the obtained profiles of signs of wear of steel discs, the volumetric wear of the construction material was determined, and the results are presented in **Fig. 7**.

Analysis of the results of material wear measurements on steel friction junction elements indicates that an increase in the content of graphene preparation in the bionic lubricant composition reduces friction node wear. This effect is consistent with the reduction of resistance to movement described by the friction coefficient. It is noteworthy that the use of BSS2_G2 composition during tribological tests results in approximately 30% reduction in wear of a steel counter-sample with a simultaneous close to 15% reduction in the friction coefficient in relation to the indicators describing the node lubricated with aqueous sodium

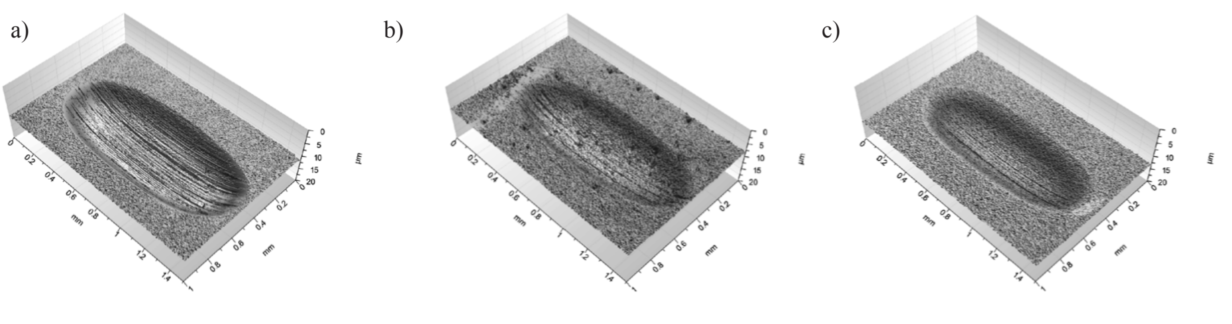

Fig. 6. The profiles of signs of wear of discs after SRV tests in a lubricated node: a) BSS2 composition, b) BSS2_G1 composition, c) BSS2_G2 composition

Rys. 6. Profile śladów zużycia tarcz po testach SRV w węźle smarowanym: a) kompozycją BSS2, b) kompozycją BSS2_G1, c) kompozycją BSS2_G2

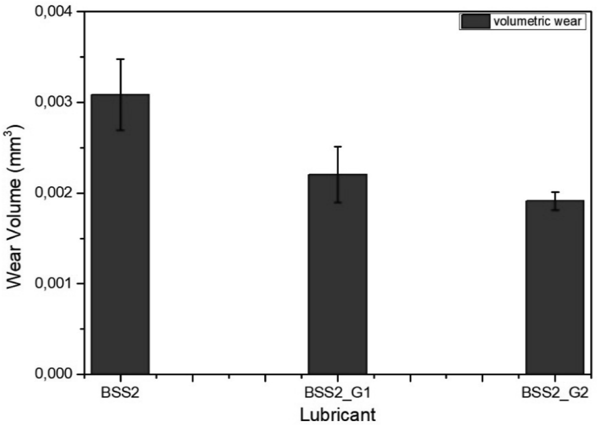

Fig. 7. The comparison of volumetric wear of steel discs after the SRV tribological test in a steel–aluminium oxide material combination, lubricated with a composition of sodium hyaluronate without the addition of graphene oxide (BSS2) and the tested bionic compositions containing the graphene additive [L. 18]

Rys. 7. Porównanie zużycia objętościowego stalowych tarcz po teście tribologicznym SRV w skojarzeniu materiałowym stal–tlenek aluminium, smarowanym kompozycją hialuronianu sodu bez dodatku tlenku grafenu (BSS2) oraz badanymi kompozycjami bionicznymi zawierającymi dodatek grafenowy **[L. 18]**

hyaluronate solution without the addition of graphene oxide. The microscopic images of test ball surfaces obtained by optical technique clearly indicate smaller flaws after friction with the composition containing graphene oxide. Further research was carried out using scanning electron microscopy coupled with X-ray microanalysis (SEM/EDS), allowing the observation of the wear trace texture **(Fig. 8)** and mapping depicting the occurrence of carbon on the surface of the friction trace.

The images of the microstructure of the surface of friction marks on the balls, after tests with the tested bionic lubricant compositions, indicate that the smooth ceramic layer is removed, and consequently, the porous structure of aluminium oxide is exposed. With the increase in the content of graphene additive in the lubricant composition, a smaller wear of the ball made of aluminium oxide is observed. This is associated with better wear protection resulting from the use of a graphene additive.

The positive effect of graphene layers on the reduction of material consumption is observed in SEM images of working test surfaces of discs made of bearing steel, as shown in **Fig. 9**.

Analysis of microscopic images of the friction surfaces of steel discs indicates that the lubricating composition, which is an aqueous solution of sodium

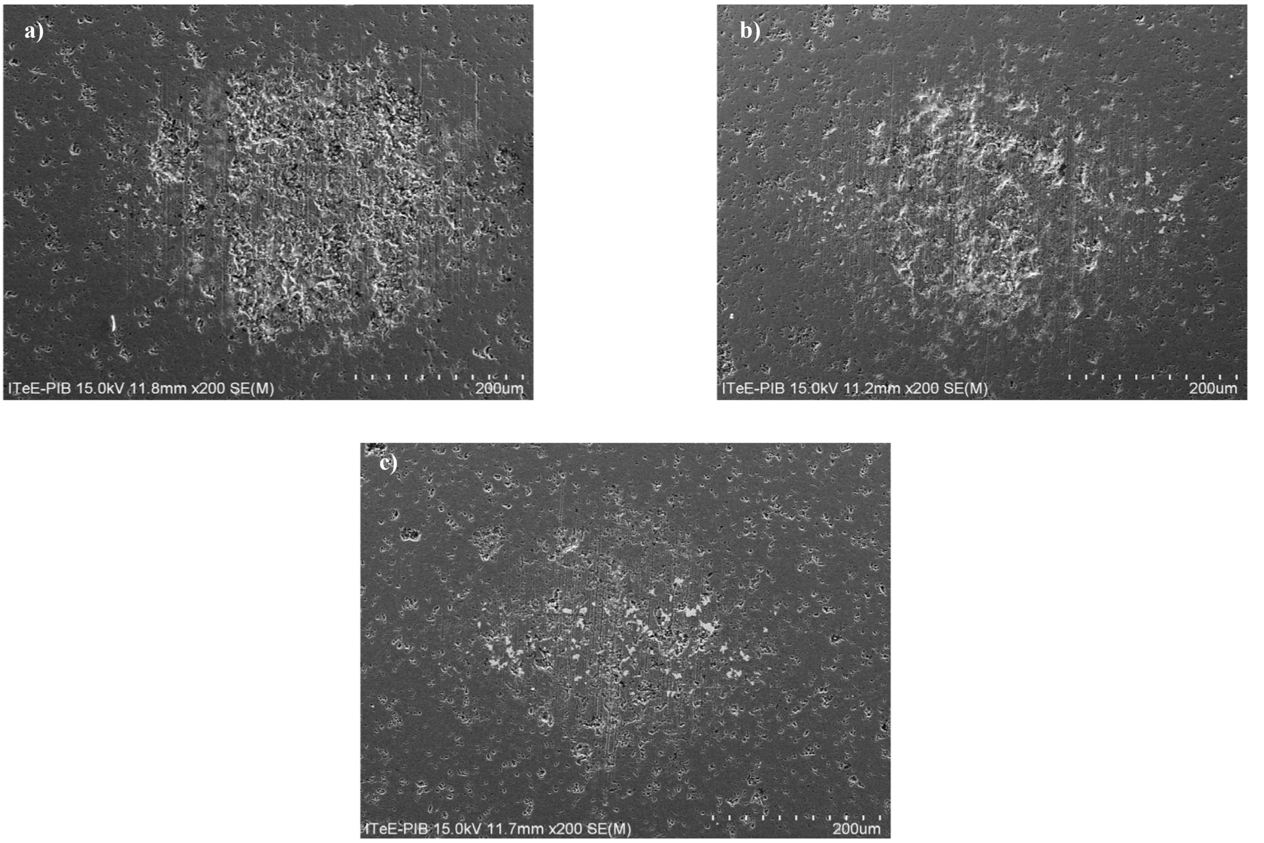

Fig. 8. Photographs obtained using the SEM technique (over 200x), trace of friction balls: a) lubricated with BSS2 composition, b) lubricated with BSS2_G1 composition, c) lubricated with BSS2_G2 composition

Rys. 8. Obrazy uzyskane techniką SEM (pow. 200x), śladu tarcia kulki: a) smarowanej kompozycją BSS2, b) smarowanej kompozycją BSS2_G1, c) smarowanej kompozycją BSS2_G2

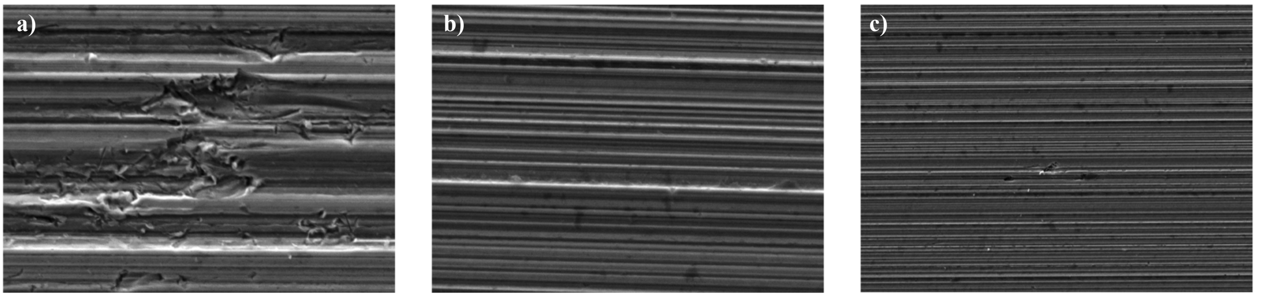

Fig. 9. Microscopic images, taken with the SEM technique (over 3000x), surface of traces friction on test plates made of bearing steel, after tests with the composition of the lubricant: a) BSS2, b) BSS2_G1, c) BSS2_G2 [L. 18]

Rys. 9. Obrazy mikroskopowe, wykonane techniką SEM (pow. 3000x) powierzchni śladów tarcia na płytkach testowych, wykonanych ze stali łożyskowej, po testach z udziałem kompozycji smarowej: a) BSS2, b) BSS2_G1, c) BSS2_G2 **[L. 18]**

hyaluronate, least protects the cooperating surfaces of the friction node against wear. In this case, there may even be material wear occurring in the pitting mechanism, i.e. chipping of the material due to fatigue of the surface layer. However, the introduction of a graphene additive reduces the negative effects of friction. In view of the above, it can be assumed that, in the absence of a graphene preparation in the lubricant composition, the anti-wear effect is associated with the formation of boundary layers arising exclusively from the tribochemical conversion products of sodium hyaluronate. The resulting products are then held on the working surface of the friction node on the basis of chemisorption interactions or the formation of chemical bonds with the substrate and are subject to dynamic processes of cutting and rebuilding the boundary layer. The introduction of graphene oxide into the lubricating composition significantly improves the lubrication conditions while preventing chipping material. In the trace of friction, typical scratches occurring during abrasive wear are observed, while the increase in graphene oxide content in the composition minimizes the negative effects of friction, which is observed as less intense scratches in the trace of friction. These observations correspond to the previously discussed results of volumetric consumption and measurements of the friction coefficient during test runs.

Tests for the presence of carbon in the ball friction on the ball were also carried out using the EDS mapping method. The maps obtained are shown in **Fig. 10**.

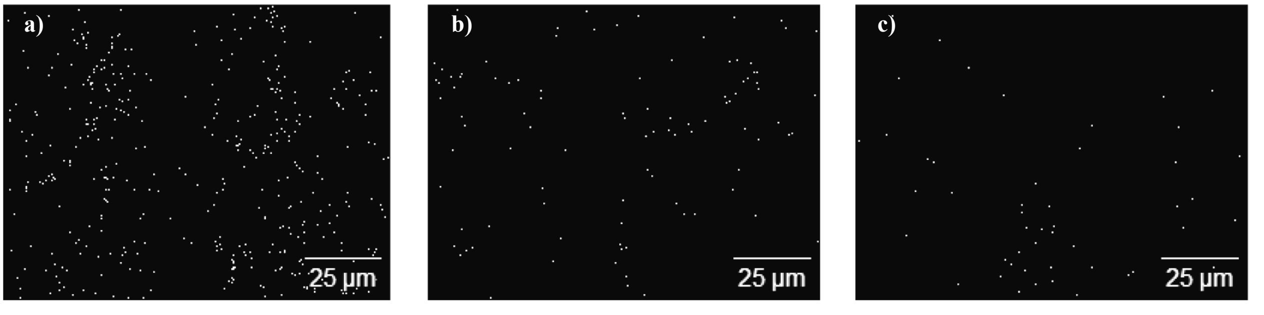

Fig. 10. The maps made using the SEM/EDS technique showing the distribution of carbon in friction traces on alumina balls after tests with lubricant compositions: a) BSS2, b) BSS2_G1, c) BSS2_G2 [L. 18]

Rys. 10. Mapy wykonane techniką SEM/EDS prezentujące dystrybucję węgla w śladach tarcia na kulkach wykonanych z tlenku glinu po testach z udziałem kompozycji smarowych: a) BSS2, b) BSS2_G1, c) BSS2_G2 **[L. 18]**

A comparison of maps of carbon occurrence in the trace of friction on an aluminium oxide ball indicates that the largest amounts of this element are deposited on the lubricated surface during friction with a composition containing only sodium hyaluronate. The presence of carbon on the surface of the trace of friction formed on the dial lubricated with sodium hyaluronate solution may result from the deposit of both graphene preparations as well as substances resulting from the tribochemical conversion of sodium hyaluronate. Depositing products of sodium hyaluronate tribochemical transformations has been demonstrated in previously published papers **[L. 19]**. It is interesting to note that as the amount of graphene preparation, i.e. carbon, increases, the bionic lubricant composition recorded in the bionic lubricant composition is recorded on the surface of the friction trace, while reducing the volume consumption of the friction node material. Thus, it can be assumed that graphene reduces material consumption by creating boundary layers that physically protect against abrasive wear with a minimum of permanently bound products of tribochemical conversion of lubricating fluid components. This type of anti-wear effect may result from the unique characteristics of graphene, in particular, its mechanical parameters and excellent thermal properties, allowing the energy generated during friction to be received **[L. 20]**.

Discussion of the graphene oxide anti-wear mechanism

The confirmation of the depositing of graphene layers on the working surfaces of the friction node are the results of tests using Raman spectrometry at selected points of the friction trace. An example spectrum from a selected area of the friction trace is shown in **Fig. 11**. It should also be noted that, after washing out the test sample on the working surface of the disc, as well as outside the friction trace, deposits are observed in microscopic images, whose spectral analysis indicates the presence of the graphene additive introduced in them. The chemical structure and microscopic appearance of these deposits is different than that occur after applying only sodium hyaluronate solution **(Fig. 4b)**.

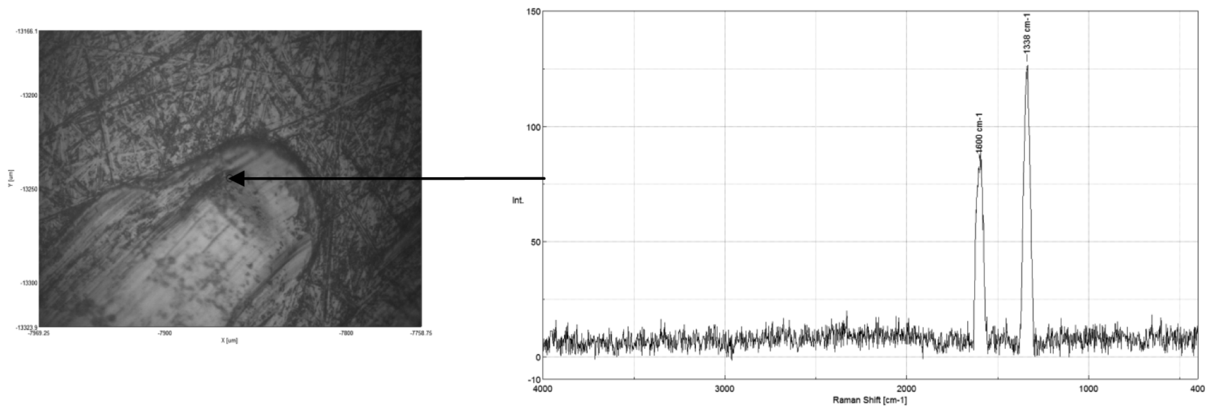

Fig. 11. Raman spectrum and microscopic image of the deposit deposited on the working surface of a steel disc lubricated with BSS2_G2 composition

Rys. 11. Widmo Ramana oraz obraz mikroskopowy depozytu odłożonego na roboczej powierzchni stalowej tarczy smarowanej kompozycją BSS2_G2

The Raman spectrum of the deposits tested contains bands directly related to the vibrations of carbon structures. There are two key bands allowing one to infer their degree of order, i.e. the G band (characterizing regular structures), occurring in the range 1544–1634 cm^{-1} (maximum at 1600 cm^{-1}) and the D band (characterizing amorphous structures) occurring in the range 1300–1392 cm^{-1} (maximum at 1338 cm^{-1}) **[L. 21, 22]**. The recorded spectra have an intense band with the maxima located at a Raman shift of 1600 cm^{-1}, which is derived from vibration stretching carbon bonds with sp^2 hybridization, occurring in the graphene oxide ring structures and is closely related to the occurrence of ordered structure. The next D band, with a Raman shift of approximately 1338 cm^{-1}, characterizes the level of amorphousness of carbon structures.

The obtained spectra was compared with the spectrum registered during the tests, used in the tests of graphene suspension, applied to a steel substrate, which was the same as that used in tribological tests. The recorded spectrum is shown in **Fig. 12**.

The comparison of Raman spectra of deposits in the trace of friction and graphene oxide of the preparation used as an additive to lubricating compositions indicates the identical location of spectral bands. It should also be noted that, as a result of friction the proportions of the intensity of the recorded signals change, i.e. in the spectrum after friction **(Fig. 11)**, the intensity of the D band increases compared to the spectrum of graphene oxide dispersion **(Fig. 12)**. The ratio of the intensity of the D (I_D) band to the intensity of the G (I_G) band was used for the relative assessment of these proportions

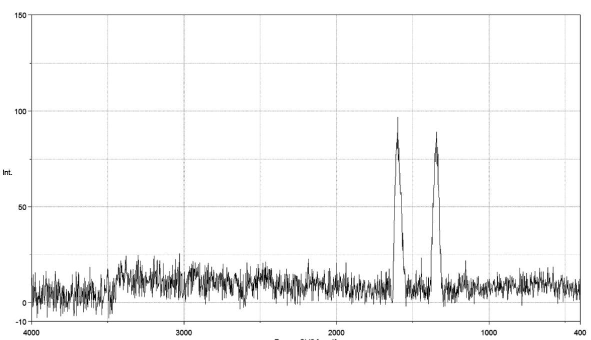

Fig. 12. The Raman spectrum of an aqueous suspension of graphene oxide applied to a steel disc

Rys. 12. Widmo Ramana wodnej zawiesiny tlenku grafenu naniesionej na stalową tarczę

[L. 22]. In the case of the graphene oxide output spectrum, the I_D/I_G ratio was 0.82. In the case of the spectrum of deposits after friction, the average value of this indicator, determined on the basis of recorded spectrum, increased to 1.53. The increase in the value of the determined parameter indicates that, during friction, the quantity of highly ordered graphene structures decreases while the presence of amorphous structures increases. Thus, during friction, the formation of multilayer carbon layers composed of graphene monolayers may occur, which is schematically shown in **Fig. 13**.

The formation of multilayer spatial structures may be favoured by the presence of oxygen functional groups

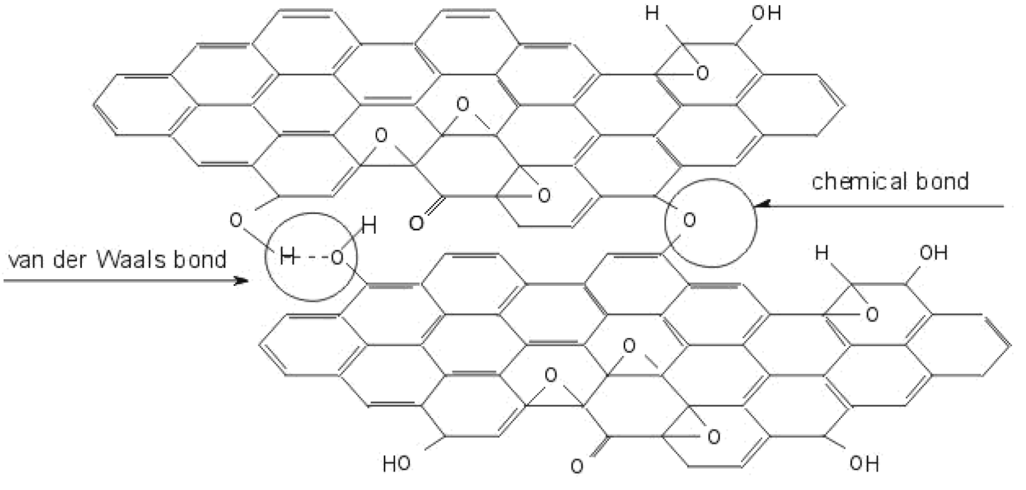

Fig. 13. The diagram of probable chemical interactions occurring during friction, directly between the organo-oxygen groups of graphene layers

Rys. 13. Schemat prawdopodobnych oddziaływań chemicznych występujących podczas tarcia bezpośrednio pomiędzy grupami tlenoorganicznymi warstw grafenowych

in graphene, such as hydroxyl, epoxide, carbonyl, and carboxyl **[L. 16, 23]**. These groups endowed with a partial electrostatic charge can therefore generate van der Waals interactions, and, under favourable energy conditions, also form chemical bonds, forming, for example, ether groups. The van der Waals bonds can also be formed with the participation of water molecules or sodium hyaluronate hydroxyl groups, i.e. substances that are the main components of the lubricant, which build up between the graphene oxide layers. Due to the probabilistic distribution of organo-oxygen functional groups on the graphene surface, which undergo tribochemical reactions, spatial structures with disturbed regularity may arise, which may result from different lengths of formed chemical bonds. However, the formation of multilayer structures with the participation of graphene oxide can affect the effective separation of the cooperating elements of the friction node, and the energy generated in the friction node is used to reallocation the graphene layers, while minimizing the consumption of structural material.

CONCLUSIONS

The conducted research indicates that the introduction of graphene oxide (i.e. graphene with surface oxygen functional groups) for aqueous solutions of sodium hyaluronate improves the tribological properties of lubricants tested by the SRV method in conditions of linear oscillatory motion. As the additive content increases, the material consumption of the friction node decreases. Improvement of the tribological characteristics of bionic lubricating compositions based on aqueous sodium hyaluronate solutions is observed already after introducing into these solutions very small amounts of graphene oxide, at the level of even 0.05% mass. This effect most likely results from the physical separation of the cooperating elements of the friction node by graphene layers, including those creating multilayer spatial systems. The specific physicochemical properties of these layers are responsible for reducing the friction coefficient and reducing the wear of the node's construction materials. In addition, the introduction of graphene oxide into the lubricant composition limited the corrosive effect of an aqueous solution of sodium hyaluronate on steel. This conclusion results directly from the microscopic observation of the disc surface after tests and the analysis of registered profiles, on which no material losses related to the corrosive effects of the lubricant composition were observed.

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