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TRIBOLOGICAL PROPERTIES AND TRIBOCHEMICAL CONVERSION OF BIONIC LUBRICANTS BASED ON SODIUM HYALURONATE

WŁAŚCIWOŚCI TRIBOLOGICZNE I KONWERSJA TRIBOCHEMICZNA BIONICZNYCH KOMPOZYCJI SMAROWYCH ZAWIERAJĄCYCH HIALURONIAN SODU

Key words:

bionic lubricants, sodium hyaluronate, anti-wear properties, tribochemical conversion.

Abstract

The aim of the study was to investigate the influence of the sodium hyaluronate in water on the tribological properties of the composition as well as an instrumental analysis of changes in the molecular structure of the bionic lubricant during friction. Tribological tests were carried out using a MCR 102 rheometer in a ball-plate combination made of bearing steel. Based on the recorded friction coefficient values, it was found that a significant improvement in friction conditions may be achieved using a composition containing 0.5% (m / m) of sodium hyaluronate in water. In this case, the value of the friction coefficient can be even below 0.1. This effect was also reflected in the minimization of material losses by about 24% compared to the wear of a friction pair lubricated only with water. During friction, the active component of the lubricant is subjected to tribo-chemical conversion and the resulting products are deposited on the working surfaces of the friction pair. The chemical structure of the resulting products was examined using SEM/EDS, XPS and FTIR. It was found that the active chemical moieties undergoing chemical conversion are the oxygen and nitrogen functional groups present in sodium hyaluronate.

Słowa kluczowe:

bioniczne środki smarowe, hialuronian sodu, właściwości przeciwzużyciowe, konwersja tribochemiczna.

Streszczenie

Celem pracy było zbadanie wpływu stężenia soli sodowej kwasy hialuronowego w wodzie na właściwości tribologiczne kompozycji oraz instrumentalna analiza zmian struktury cząsteczkowej zastosowanego bionicznego środka smarowego przebiegających podczas tarcia. Badania tribologiczne przeprowadzono za pomocą reometru MCR 102 w skojarzeniu typu kula–płytki, wykonanym ze stali łożyskowej. Na podstawie zarejestrowanych przebiegów współczynnika tarcia stwierdzono, iż istotną poprawę warunków tarcia uzyskano w przypadku stosowania kompozycji zawierającej 0,5% (m/m) hialuronianu sodu w wodzie. W tym przypadku wartość współczynnika tarcia może wynosić nawet poniżej 0,1. Efekt ten przekłada się też na minimalizację zużycia materiałowego o około 24% w porównaniu z zużyciem wężła smarowanego jedynie wodą. Podczas tarcia zastosowany aktywny komponent środka smarowego podlega konwersji tribochemicznej, a powstające produkty są depozytowane na roboczych powierzchniach wężła tarcia. Strukturę chemiczną powstających produktów zbadano za pomocą SEM/EDS, XPS oraz FTIR. Stwierdzono, iż aktywnymi ugrupowaniami strukturalnymi podlegającymi konwersji chemicznej są tlenowe i azotowe grupy funkcyjne, obecne w hialuronianie sodu.

INTRODUCTION

The dynamic development of materials engineering, oriented to the production of materials for endoprostheses, generates the need for research in the field of their structural conversion and the potential impact of the emerging products on the endoprostheses. The processes occurring at the interface between the

material of the implant and the body environment have a molecular nature, which is related to the interaction of both water molecules and other substances present in body fluids, e.g., proteins. Thus, the effective substitutes of body fluids are sought, allowing the implementation of model tests simulating the actual conditions of functioning endoprostheses. Therefore, in material tests, various types of liquid agents are used whose chemical

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composition may be similar to natural liquids found in living organisms like chlorides, phosphates, carbonates, sulphates or glucose solutions (e.g., Ringer, Hanks and Cigad, Michaelit fluids and others). One of the simplest formulations is Ringer's fluid, which is an aqueous solution of such salts, e.g., sodium chloride, potassium chloride, and calcium chloride. This type of solution was used as a lubricant in many research works related to the testing of new materials for endoprostheses, both metal alloys as well as plastics [L. 1–6]. It works well in tests of the corrosion resistance of materials for endoprostheses. However, this type of fluid, being a low-viscous Newtonian liquid, does not reflect the rheological phenomena associated with changes in viscoelastic properties during lubrication, and it also does not allow for the investigation of physicochemical interactions with the working surface of the tribological association. Thus, there is no possibility of forming effective lubricating layers in the presence of Ringer's solution, and its role during tribological tests focused mainly on the removal of heat and possible wear products from the friction zone.

Therefore, other compositions are sought with chemical structure and functional properties that allow the modelling of synovial liquid features. The developed direction of these explorations is the development of bionic lubricants, i.e. composed of substances of natural origin or biotechnologically produced, but corresponding to their chemical structure [L. 7, 8]. Among the substances used as ingredients of bionic lubricants are substances present in the natural synovial fluid, mainly chondroitin sulphate and derivatives of hyaluronic acid, optionally with the addition of other components, e.g., cellulose nanofibers [L. 9–18]. Such preparations are used in various types of simulated material tests in which mainly the tribological and anti-corrosive parameters are assessed, without taking into account the structural conversion of the used bionic lubricant and the impact of the resulting products on the condition of the surface layer of cooperating elements of the endoprostheses.

The aim of the study was to investigate the influence of the concentration of sodium salt of hyaluronic acid in water on the tribological properties as well as the instrumental analysis of changes in the molecular structure of the bionic lubricant during friction.

MATERIALS AND METHODS

Research facilities

Bionic lubricant compositions were prepared by dissolving appropriately weighed amounts of sodium hyaluronate in osmotically purified water (conductivity: 0,05 $\mu\text{S}/\text{cm}$). The research involved the use of commercially available (supplied by Ecospa – Warszawa) high molecular weight crystalline sodium hyaluronate (molecular weight 1.0–1.8 MDa). The

structural formula of the sodium hyaluronate molecule is shown in **Figure 1**.

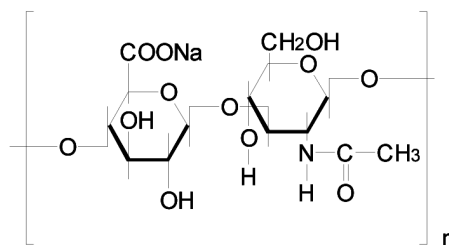


Fig. 1. The structural formula of molecular chains of sodium hyaluronate

Rys. 1. Wzór strukturalny łańcuchów cząsteczkowych hialuronianu sodu

Compositions were prepared with the following concentrations of sodium hyaluronate in water: 0.1% m / m (sample BSS_1), 0.5% m / m (sample BSS_2), and 1.0% m / m (sample BSS_3). The water sample was marked in tests as BSS_0. The obtained compositions had a gel consistency.

Tribological tests and volumetric wear testing

Tribological tests of the prepared compositions were carried out using a rheometer MCR 102 (produced by Anton Paar), equipped with a tribological attachment T-PTD 200 of a ball-plate combination. The components of the test friction pair were made of 100Cr6 bearing steel. The components of the friction pair were prepared for testing by ultrasonic cleaning in acetone, then in water, dried with compressed air and stored in a closed vessel. During tests carried out at 20°C, under the load of 10 N and at 500 rpm, the course of friction coefficient was recorded. After the test, the volumetric wear of the test beads was also evaluated. The Talysurf CCI interferometer microscope from Taylor Hobson was used to study the volumetric wear of the test plates after friction with the evaluated bionic lubricants.

Microscopic examination by SEM / EDS technique

The X-ray scanning electron microscope Hitachi SU-70, equipped with EDS X-ray microanalyser, was used to study X-ray spectra from selected microscopic sites where depositing products of tribochemical conversion of bionic lubricants were expected. The analyses were carried out under the following conditions: magnification $\times 50$, $\times 1000$ and $\times 10000$, acceleration voltage of 15 kV, reception angle 30°, and negative pressure 10–8 Pa. In addition to deposits deposited on the working surfaces of the friction pair, crystalline sodium hyaluronate was tested for comparison purposes. It was suspended in a potassium bromide (KBr) matrix, and then formed in tablets in a special press and directly tested by EDS. KBr tablet studies with occluded crystalline sodium hyaluronate were performed at 250 \times magnification.

FTIR spectral tests using microscope and ATR

The spectrum of the deposit deposited after friction in the presence of aqueous sodium hyaluronate composition was recorded using an FTIR type IRT-5000 microscope (made by Jasco), coupled with an FTIR 6200 spectrometer (Jasco company), in reflection mode. During the spectral measurements, the following parameters were used:

- Spectral range: 4000–750 cm^{-1} ,
- Spectral resolution: 4 cm^{-1} ,
- The number of scans recorded from the background area and the deposit were selected automatically by the software (in this case: 512 scans),
- The type of spectral detector: TGS,
- The dimensions of the microscope aperture: 50x50 μm ,
- Lens type: Cassegrain.

The background spectrum was recorded on the surface outside the trace of friction. The spectrum of the product from various surface areas with the deposit were recorded in the proximity of the friction zone of different microscopic appearance, which was demonstrated in parallel with the results of spectroscopic tests on microscopic images. The FTIR microscopy spectra were digitally processed for removing the carbon dioxide band from 2225 cm^{-1} to 2420 cm^{-1} , smoothing according to the Savitzky-Golay algorithm and normalization of the baseline. The spectrum of crystalline hyaluronic acid was made using FTIR 6200 spectrometer (made by Jasco), equipped with a Pike-type diamond crystal attachment using the ATR technique. The spectrum was

recorded at a resolution of 4 cm^{-1} , in the spectral range 4000–650 cm^{-1} . The resulting spectrum is necessary to compare the molecular structure of the hyaluronic acid used to prepare the bionic lubricant composition with the molecular structures of the friction deposits.

XPS analyses

The analysis was carried out using the PREVAC XPS /ESCA device using an aluminium anode (power 200 W, pass energy 200 eV). The shape of the Gaussian-Lorentzian spectrum included the Shirley background type. Calibration of the energy scale was made for C1s carbon (284.8 eV). The sample was purified using a low energy argon ion beam (1.5 kV) for 30 minutes and then subjected to a 5 kV ion treatment for 5 minutes. The results presented refer to the chemical composition of the outer layer of the sample with a thickness of several nanometres.

RESULTS AND DISCUSSION

Analysis of friction and wear test

During tribological tests of bionic lubricating compositions, the dependence between the friction coefficient and the friction distance were recorded for the lubricated friction pair made of steel. Sample results obtained for the tested tribological systems containing bionic lubricants are shown in **Fig. 2**.

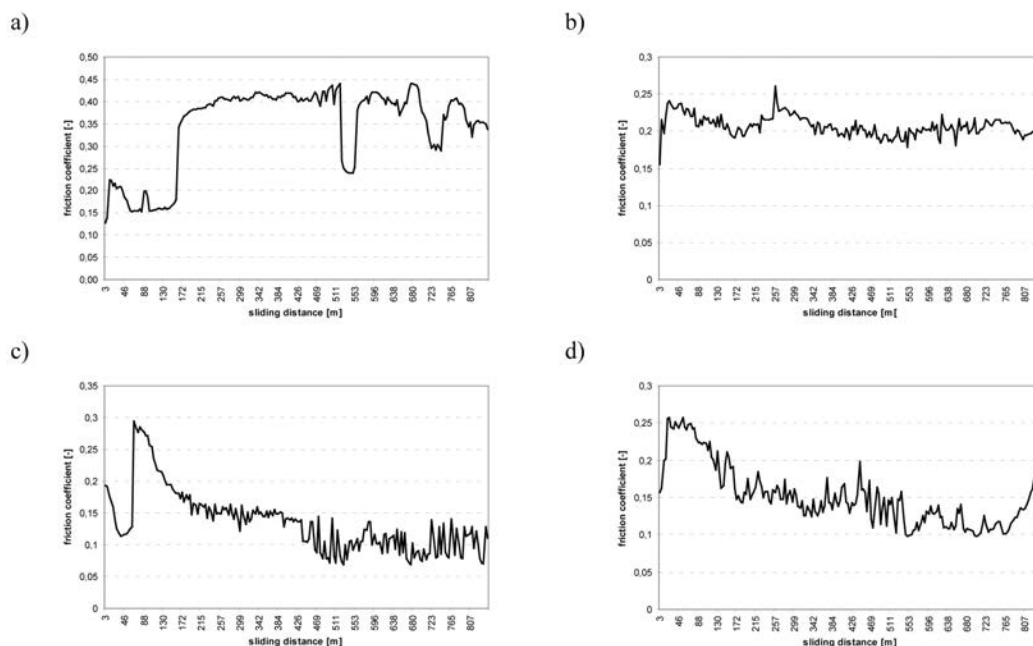


Fig. 2. The characteristics of friction coefficient determined during tribological lubrication tests with: a) pure water, b) 0.1% (m/m) aqueous sodium hyaluronate, c) 0.5% (m/m) aqueous sodium hyaluronate, d) 1.0% (m/m) aqueous sodium hyaluronate

Rys. 2. Charakterystyka współczynnika tarcia wyznaczona podczas testów skojarzenia tribologicznego smarowanego: a) czystą wodą, b) 0,1% (m/m) wodnym roztworem hialuronianu sodu, c) 0,5% (m/m) wodnym roztworem hialuronianu sodu, d) 1,0% (m/m) wodnym roztworem hialuronianu sodu

As a result of lubrication of the friction pair with clean water after the initial period of relatively low friction coefficient at the level of 0.15, there was a significant increase in friction coefficient above 0.35, which was associated with a significant increase in frictional resistance. This effect was most probably associated with the evaporation of water from the friction zone, which resulted in the occurrence of boundary friction or possibly dry friction. The improvement of friction parameters of the friction pair in relation to the combination lubricated with pure water was obtained by introducing a small amount of sodium hyaluronate. Introduction of 0.1% m/m sodium hyaluronate to water caused stable lubrication conditions, where the friction coefficient oscillated around the value of 0.2 during the whole tribological test. A further reduction in the friction coefficient was possible by increasing the concentration of sodium hyaluronate in the aqueous lubricant composition. Tribological tests of compositions with a 0.5% and 1.0% concentration of active substance in water indicated that this type of lubricant allow one to obtain friction coefficients in the tested tribological system even below 0.1. However, it should be noted that better lubricating effects were obtained for compositions with a concentration of 0.5% m/m rather than for a composition containing 1.0% m/m sodium hyaluronate in water. The more concentrated compositions were characterized by a gelatinized consistency and thus non-Newtonian rheological features, which hampered the stability of flow traits in the tribological association [L. 19]. The non-Newtonian properties of the tested compositions caused the fluctuations in the friction coefficient curve depending on the friction path. The reduction of the friction coefficient by the tested bionic lubricants compared to the values recorded for water-lubricated systems was also reflected in the material wear of the friction pair. On the basis of obtained profiles of wear marks, the volumetric wear values of individual plates were calculated. The results are shown in **Table 1**.

The comparison of the obtained values indicates that the introduction of 0.1% (m/m) of sodium hyaluronate (sample BSS_1) reduced the material wear by over 23.6% in comparison to the wear of friction pair lubricated only with water (sample BSS_0). The content of 0.5% (m/m) of sodium hyaluronate in the tested bionic lubricant reduced the wear of the friction pair by 24.1% compared to the control (water) and the composition containing 1% (m/m) of sodium hyaluronate reduced the wear of the test plate by 29%. Observed tribological and anti-wear properties of aqueous sodium hyaluronate compositions may result from both the rheological characteristics of the tested compositions as well as from the dissipation of energy absorbed during the tribochemical conversion of sodium hyaluronate. The evaluation of the directions of the running tribochemical processes were carried out on the basis of spectral studies of the molecular structure of products deposited on the working surfaces of the friction pair.

Table 1. Results of volumetric wear of a test plates during friction in the presence of tested compositions of bionic lubricants

Tabela 1. Zestawienie wyników badań zużycia objętościowego testowej płytki podczas tarcia z udziałem badanych kompozycji bionicznych środków smarowych

| Sample | Volumetric wear [mm ³] |
|--------|------------------------------------|
| BSS_0 | 0.8365×10^{-2} |
| BSS_1 | 0.6389×10^{-2} |
| BSS_2 | 0.6350×10^{-2} |
| BSS_3 | 0.5953×10^{-2} |

Analysis of SEM/EDS results

The components of the friction pair after tribological tests with tested bionic lubricant compositions were subjected to SEM/EDS tests. The images of working surfaces and X-ray analysis were performed in selected areas, both in the friction contact zone and outside it. The obtained test results are shown in **Figs. 3–5**.

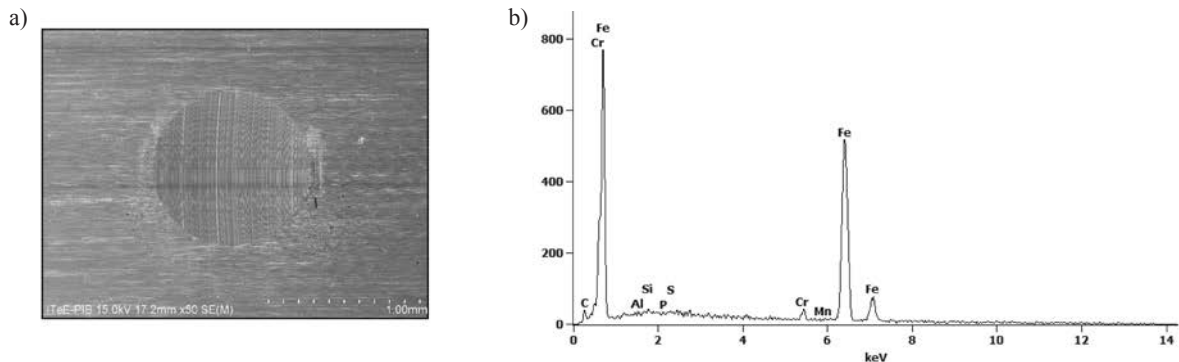


Fig. 3. SEM / EDS data after tribological testing with water as a lubricant (BSS_0): a) microscopic image of the trace of friction (area $\times 50$), b) the spectrum of EDS recorded in the friction trace

Rys. 3. Wyniki badań SEM/EDS próbki po tarcu z udziałem wody jako środka smarowego (BSS_0): a) obraz mikroskopowy śladu tarcia (pow. $\times 50$), b) widmo EDS zarejestrowane w śladzie tarcia

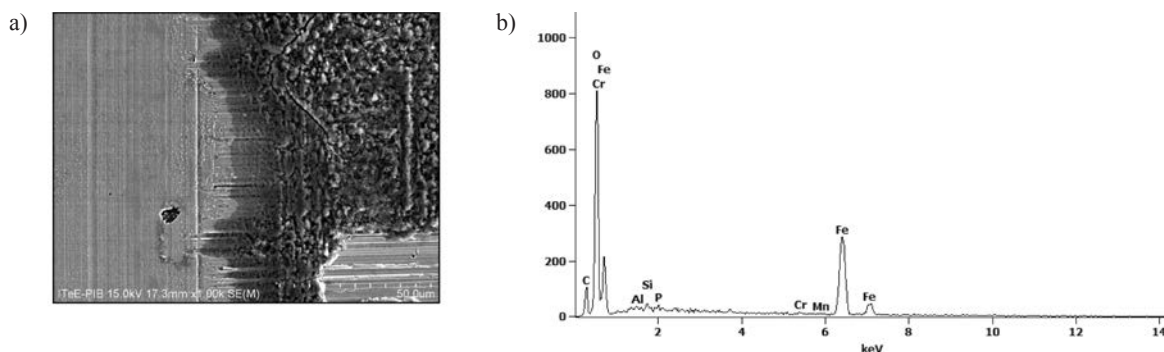


Fig. 4. SEM / EDS results for the sample lubricated with a composition containing 0.1% m / m sodium hyaluronate in water (BSS_1): a) microscope image (magnitude 1000x), b) EDS spectrum recorded from the deposit

Rys. 4. Wyniki badań SEM/EDS próbki po tarciu z udziałem kompozycji zawierającej 0,1% m/m hialuronianu sodu w wodzie jako środka smarowego (BSS_1): a) obraz mikroskopowy (pow. $\times 1000$), b) widmo EDS zarejestrowane z odłożonego depozytu

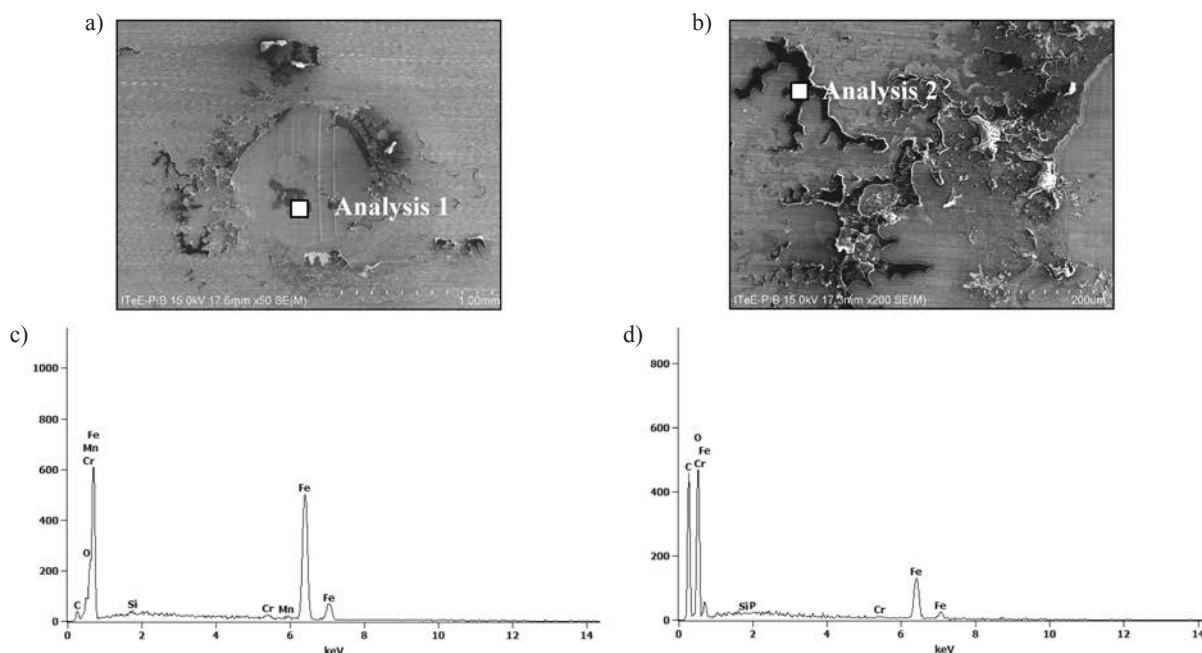


Fig. 5. SEM / EDS results for the sample lubricated with a composition containing 1% m/m sodium hyaluronate in water (BSS_3): a) microscopic image (magnitude 50x) with a marked X-ray analysis site, b) microscopic image (magnitude 200x) with marked place of the X-ray analysis c) EDS spectrum recorded in the trace of friction (analysis 1), d) EDS spectrum recorded from the deposit outside the trace of friction (analysis 2)

Rys. 5. Wyniki badań SEM/EDS próbki po tarciu z udziałem kompozycji zawierającej 1% m/m hialuronianu sodu w wodzie jako środka smarowego (BSS_3): a) obraz mikroskopowy (pow. $\times 50$) z zaznaczonym miejscem analizy rentgenograficznej, b) obraz mikroskopowy (pow. $\times 200$) z zaznaczonym miejscem analizy rentgenograficznej c) widmo EDS zarejestrowane w śladzie tarcia (analiza 1), d) widmo EDS zarejestrowane z odłożonego depozytu poza śladem tarcia (analiza 2)

The assessment of the images indicated that no product is deposited on the working surface during friction with the presence of water as a lubricant. The elemental analysis of the test component lubricated with clean water (BSS_0) shown in **Fig. 3** confirmed the intact chemical composition of the material in the friction zone. However, during friction with the presence of lubricating compositions containing sodium hyaluronate, the author observed a deposition of by-products that were subjected to SEM/EDS and shown in **Figures 4 and 5**.

Analysis of obtained microscopic images and EDS spectra of the products deposited on the working surfaces indicated that, during friction with the sodium hyaluronate-based lubricants, some products were deposited. The amounts of mentioned deposits correlated with the concentration of sodium hyaluronate in water and were located mostly on the fringes. The largest amounts of by-products were deposited during tests with the BSS_3 composition, i.e. the highest content of sodium hyaluronate among the tested compositions. In addition, these deposits formed relatively thick layers, with a cracked texture which visible under the microscope (**Figure 6**).

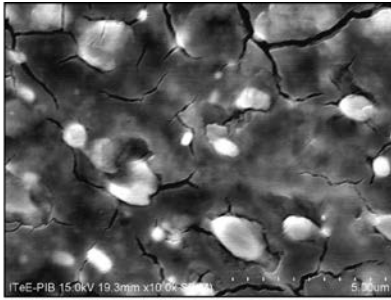


Fig. 6. Texture of the deposit surface (over $\times 10000$) on the test plate lubricated with the composition containing 1% m/m sodium hyaluronate in water

Rys. 6. Tekstura powierzchni depozytu (pow. $\times 10000$) odłożonego na testowej płytce podczas tarcia z udziałem kompozycji zawierającej 1% m/m hialuronianu sodu w wodzie

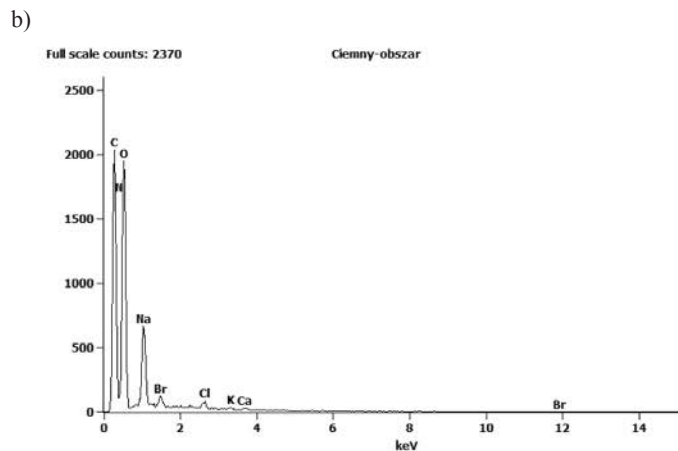
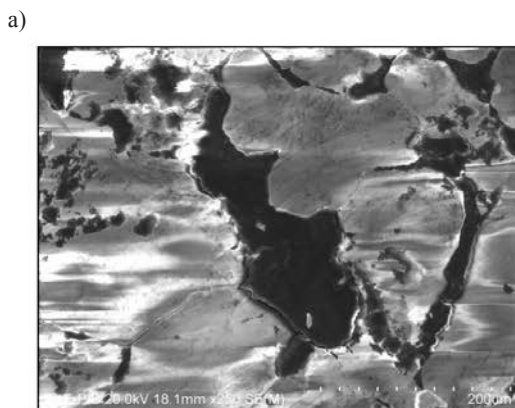


Fig. 7. SEM/EDS images (magnitude $\times 250$) of: (a) the surface of the tablet containing sodium hyaluronate in the KBr matrix and (b) the spectrum recorded from the dark area corresponding to the crystalline sodium hyaluronate placed in the matrix

Rys. 7. Obraz mikroskopowy (pow. $\times 250$): (a) powierzchni tabletki zawierającej hialuronian sodu w matrycy KBr oraz (b) widmo zarejestrowane z obszaru ciemnego, odpowiadającego umieszczonego w matrycy krystalicznemu hialuronianowi sodu, uzyskane techniką SEM/EDS

The resulting spectrum revealed signals of the elements typical for the molecular structure of sodium hyaluronate, as well as signals associated with the tablet matrix (potassium, bromine). The presence of signal of calcium was most likely a result of sample contamination during preparation of tablet. Comparing the results of EDS analysis of the working surfaces of the friction pair and the crystalline sodium hyaluronate, it can be concluded that the deposits resulted from the structural conversion of the applied bionic lubricant. The most plausible mechanism of this phenomenon is related to the conversion of amide structures and oxygenated organic groups, including carboxylate. In addition, aqueous solutions of sodium hyaluronate were present in an ionized form due to the hydrolysis of carboxylate structures. It can also be assumed that the anionic structure derived from the sodium carboxylate

The substances deposited on the test surfaces revealed, in their structure, much higher levels of carbon and oxygen in comparison to the construction material, which was reflected in the elevated signals in the EDS spectra. There were no signals from nitrogen and sodium, which are elements that are present in the molecular structure of sodium hyaluronate. Therefore, for the comparison purposes, SEM/EDS tests of crystalline sodium hyaluronate solidified in a potassium bromide tablet were also performed. These tests verified the correctness of the selected research technique to identify the elemental composition of the deposited products. The obtained microscopic image of the tablet and the sodium hyaluronate spectrum (in the microscopic picture seen as a dark area) are shown in Fig. 7.

is a convenient site for the attachment of iron cations. Thus, the identification of the chemical structure of the deposited product required further spectral tests aimed at the thickest deposits formed during friction in the presence of BSS_3 lubricant.

Analysis of infrared spectra

Representative results of the infrared spectral analyses of deposits on the working surfaces of the friction pair are shown in Fig. 9. The spectrum of the deposit was compared to the spectra of crystalline hyaluronic acid (Fig. 8).

The spectrum of crystalline sodium salt of hyaluronic acid contained typical signals, which are characteristic for oxygenated organic species, including hydroxyl (band at 3413 cm^{-1}), carboxylate (valence

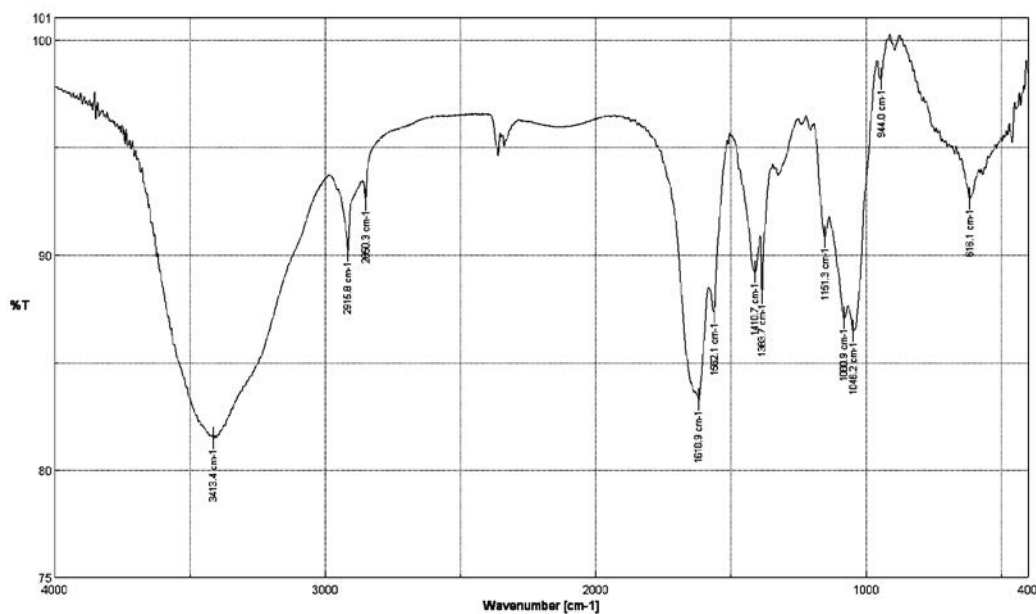


Fig. 8. The FTIR spectrum of the crystalline sodium hyaluronate used for preparation of the bionic lubricant compositions

Rys. 8. Widmo FTIR krystalicznego hialuronianu sodu zastosowanego do przygotowania kompozycji bionicznych środków smarowych

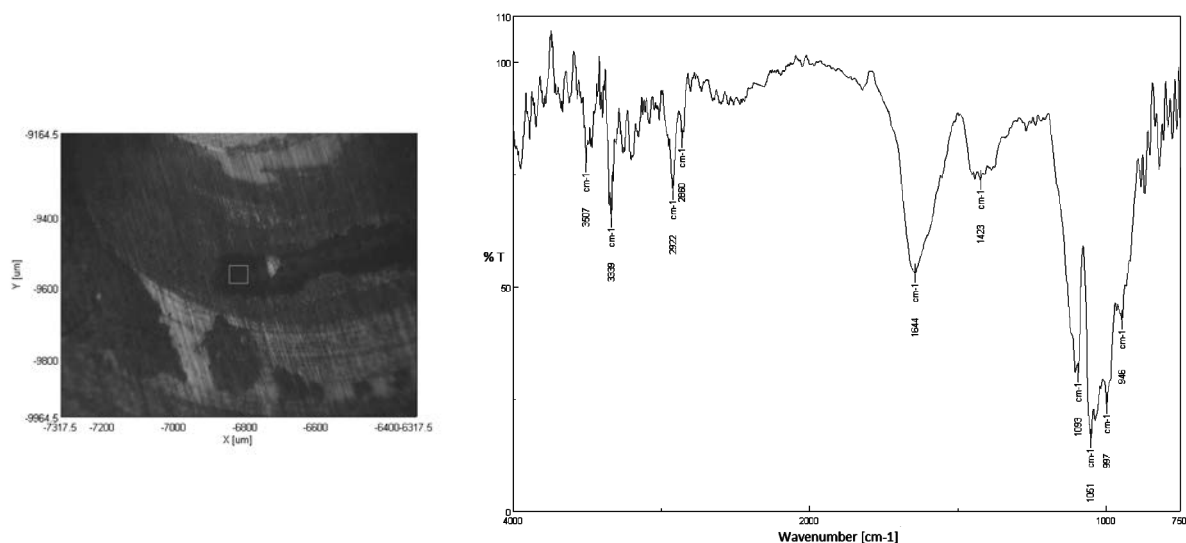


Fig. 9. Microscopic image of the working surface of the tribological association and the spectrum of the deposit formed during lubrication with BSS_3 composition

Rys. 9. Obraz mikroskopii roboczej powierzchni skojarzenia tribologicznego z zaznaczonym miejscem rejestracji widma FTIR oraz zarejestrowane widmo depozytu tribochemicznego powstałego po tarcii z udziałem kompozycji BSS_3

band of asymmetric ionized carboxylate group at wave number 1619 cm^{-1} and symmetrical valence band), and the ionized carboxylate group at a wavenumber of 1410 cm^{-1}). On the other hand, the C-O-C moieties of the glycosidic bonds resulted in a spectral signal located at the wavenumber of 1083 cm^{-1} . Vibrations of bonds coming from the amide group were located in the areas of oscillations of O-H bonds of the hydroxyl group, so

the clear identification of them was impossible. These areas were in the wavelength range $3170\text{--}3100\text{ cm}^{-1}$, (oscillations of N-H bonds in primary amides) as well as bands in the range of $1650\text{--}1620\text{ cm}^{-1}$ related to the combined deformation vibrations of the -NH and -C-H groups. In addition, signals related to the vibrations of carbon-hydrogen bonds in the structures of methyl and methylene groups (bands at 2850 cm^{-1} and 2915 cm^{-1}) as

well as bands from combinational deformations of CN and NH bonds (at 1562 cm^{-1}) were observed.

After tribological tests with an aqueous sodium hyaluronate lubricating composition, the components of the friction pair revealed deposits whose infrared spectrum had a different appearance than that of the crystalline hyaluronic acid. An example IR spectrum recorded from the area marked with a square in the microscopic image is shown in **Fig. 9**.

Analysis of the IR spectrum of the tribochemical transformation products of a bionic lubricant composition revealed the generation of structures containing carbonyl moieties (but in different molecular structures than in the initial sodium hyaluronate). This fact was reflected as the presence of intense overlapping bands with extremes located at the wavenumber of 1644 cm^{-1} . Infrared spectral analyses correlated with EDS spectra suggest that they may be iron carboxylates or intramolecular chelate systems. Deposition of amide structures may also be considered, as seen in the 1423 cm^{-1} bands as well as overlapping signals in the mentioned 1644 cm^{-1}

band. The lack of a separate nitrogen signal in the EDS spectra of tribological deposits was a result of the similar electron energies of the basic spectral line of oxygen, nitrogen, and carbon, which was observed in the EDS spectrum of the sodium hyaluronate shown in **Fig. 12**. Therefore, it was necessary to use a more precise analytical method, arbitrating the problem of depositing nitrogen compounds on working friction surfaces. For this purpose, XPS tests of tribochemical products were performed.

Analysis of the tribochemical deposits with XPS

The XPS tests of deposits on the working surfaces of the friction pair lubricated with the bionic compositions of hyaluronate confirmed the presence of compounds containing nitrogen, oxygen, carbon, and iron in their chemical structure. Exemplary photoelectron spectra of N1s, O1s, C1s, and Fe2p recorded for BSS_3 lubricating composition are shown in **Fig. 10**.

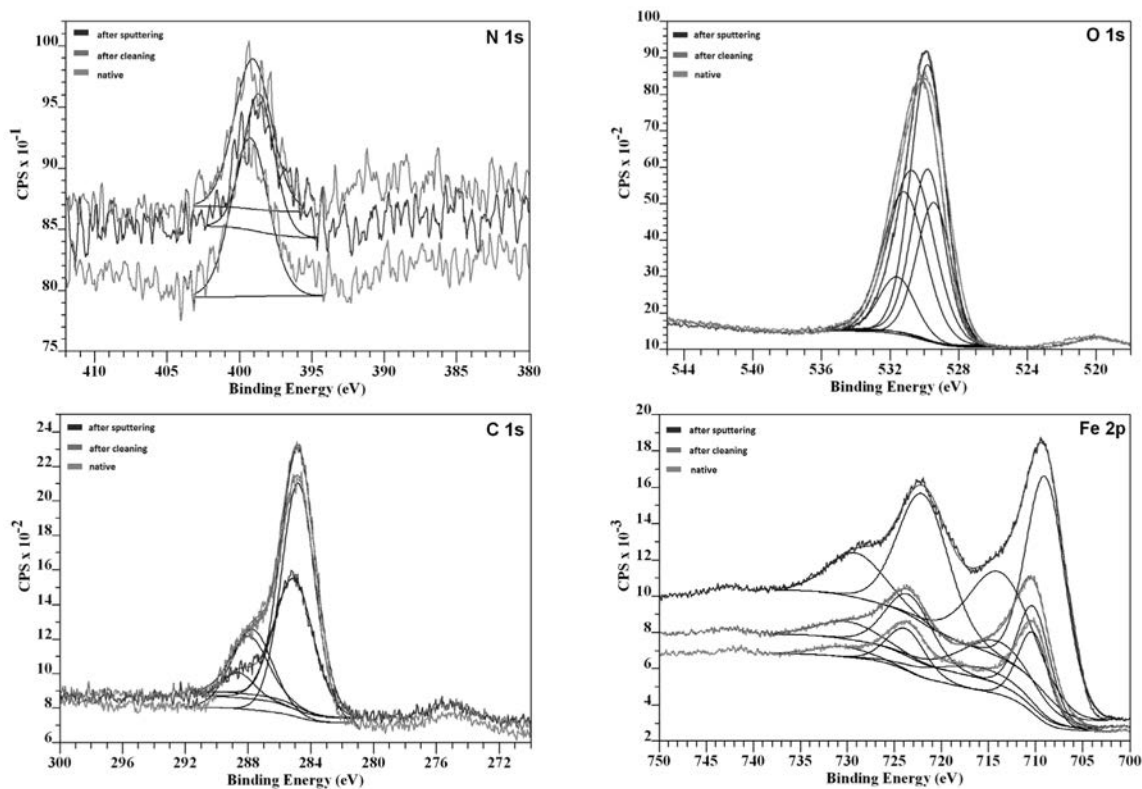


Fig. 10. XPS spectra for the ranges of N 1s, O1s, C1s, and Fe2p recorded for deposits formed during friction with the BSS_3 lubricant

Rys. 10. Widma XPS dla zakresów fotoelektronów N 1s, O1s, C1s i Fe2p zarejestrowane podczas badania depozytu tribologicznego odłożonego na roboczej powierzchni skojarzenia tribologicznego podczas tarcia z udziałem próbki BSS_3

The recorded photoelectron binding energies N1s from the area before and after argon cleaning were 399.28 eV and 399.09 eV , respectively. However, in the deeper layers of the deposit exposed by 5-minute

sputtering with an argon ion beam, the band position shift to 398.67 eV was observed. That may indicate the deposition of nitrogen-containing products with a different chemical structure on the surface than in deeper layers. Detailed analysis of the spectra may

indicate that the 398.67 eV band corresponded to the binding energy of the N1s photoelectron emitted from the carbamate moiety. On the other hand, 399.09 eV and 399.28 eV bands in purified and the tribological deposit spectra without additional surface treatment were associated with the N1s photoelectrons emitted from amid structures. A separate study of the location of

the O1s and C1s photoelectron signals was also required for full understanding. Analysis of obtained spectra of O1s and C1s photoelectrons indicated that there was a shift in the position of the signals after ion purification and 5-minute sputtering of the tested surface with argon ions. The values of recorded binding energies of these photoelectrons are summarized in **Table 2**.

Table 2. Binding energy values for photoelectrons O1s and C1s emitted during the XPS analysis from the native surface, after ion cleaning and after 5-minute sputtering

Tabela 2. Wartości energii wiązania fotoelektronów O1s i C1s emitowanych podczas badania XPS z powierzchni natywnej, po czyszczeniu jonowym i 5-minutowym sputteringu

| Photoelectron type | Binding energy [eV] | | |
|--------------------|---------------------|--------------------|---------------------------|
| | native layer | after ion cleaning | after 5-minute sputtering |
| C1s | 285 | 285 | 285 |
| | 288 | 288 | 289 |
| O1s | 529 | 530 | 530 |
| | 531 | 531 | 532 |

A comparison of the values presented in **Table 2** revealed that the ionic purification of the surface of the deposits did not significantly influence the position of the bands associated with the photoelectron binding energy. In contrast, the removal of a certain layer of material by means of argon (sputtering) revealed a slightly different chemical structure than the surface layer what was proved in some cases by shifts in the position of the photoelectron bands. Analysis of obtained spectra of C1s photoelectrons indicated that, in the native material deposited on the working surfaces of the friction pair, there may be chemical compounds having nitrogen-bound carbonyl groups in their structure (288 eV) and carbon unsaturated group containing a C=C moieties (285 eV). However, in the deeper layers of the deposit, there may be chemical compounds containing the C=O groups present in esters, salts, or chelates (289 eV band), which can be stated as a structural conversion of the initial sodium hyaluronate and the products generated can be directly adhered to the construction material of the friction pair. These by-products deposited on the material are then covered with layers of the initial lubricating substance. These assumptions were confirmed by the analysis of the binding energy of photoelectrons O1s, emitted from the tested deposit (e.g., with an energy of 532 eV). Detection of salts in the deposit layers required a detailed examination of the position of the bands in the XPS spectrum related to the possibility of incorporation of iron to the structure of tribochemical deposits. It should be noted that the initial component of bionic lubricants was the sodium salt of hyaluronic acid; however, the presence of this chemical compound in the aqueous composition resulted in its dissociation. Thus, in solid deposits, a different iron-containing structural

form (e.g., salts or chelates) was expected. Analysis of the binding energy of Fe2p photoelectrons at the level of 709 eV recorded after a 5-minute sputtering of friction deposits indicated a possible combination of iron atoms with carbonyl ligands, which in turn led to the formation of chelates.

CONCLUSIONS

The use of sodium hyaluronate in aqueous lubricating compositions allows for effective reduction of movement resistance, and thus for the reduction of wear of the friction pair. Among the tested compositions, a significant improvement in lubrication was observed for the composition containing 0.5% (m/m) of sodium hyaluronate in water. There is also a possibility of further improvement of tribological indexes along with the increase of the concentration of active substance in water to 1% (m/m). The research on tribochemical deposits (by-products generated during friction with the presence of bio-lubricant) defined the directions of tribochemical transformations of sodium hyaluronate. On the basis of spectral analyses, it was found that the tribochemical transformations involve oxygen functional groups present in the molecular structure of sodium hyaluronate. The conducted research indicated that the complex compounds may be formed from the tribologically converted bio-lubricant and the metal ions released from the friction pair. Nitric moieties, present in sodium hyaluronate, are also involved in the tribochemical conversion, and they may result in the formation of carbamates.

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