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ANALYSIS OF THE INFLUENCE OF HEXAGONAL BORON NITRIDE ON TRIBOLOGICAL PROPERTIES OF GREASE

ANALIZA WPŁYWU HEKSAGONALNEGO AZOTKU BORU NA WŁAŚCIWOŚCI TRIBOLOGICZNE SMARU PLASTYCZNEGO

Key words: tribology, greases, hexagonal boron nitride, nano additives, lubricity properties.

Abstract: The article discusses the problem of using hexagonal boron nitride (h-BN) as a grease additive. The literature on the subject was analysed in terms of greases into which hexagonal boron nitride was added. Particular attention was paid to the nano h-BN, due to the topicality of this topic and the potential of nano-additives to lubricants noted in published scientific studies. It was found that in order to indicate the regularities describing the tribological interaction of hexagonal boron nitride, detailed studies and an analysis of its properties are required. The important factors determining the application of this additive include particle size distribution, morphology, specific surface area, and porosity. The mentioned properties were determined for four samples of hexagonal boron nitride, which were also objects of tribological experiments. For this purpose, a scanning electron microscope (SEM) and XRD method were used, and low-temperature adsorption isotherms were determined. The research on the influence of h-BN on the lubricity properties of lithium grease was carried out on a four-ball apparatus. Possible mechanisms of interaction of different types of h-BN in the friction zone were identified using the information collected on their important properties. Based on the results of the research, it was found that the use of nano h-BN in the discussed context seems promising.

Słowa kluczowe: tribologia, smary plastyczne, heksagonalny azotek boru, nanododatki, właściwości smarnościowe.

Streszczenie: W artykule podjęto problematykę zastosowania heksagonalnego azotku boru (h-BN) jako dodatku do smarów plastycznych. Przeprowadzono analizę literatury tematu pod kątem smarów plastycznych, do których wprowadzano heksagonalny azotek boru. Szczególną uwagę zwrócono na nanodmianę h-BN, z uwagi na aktualność tej tematyki i odnotowywany w opublikowanych badaniach naukowych potencjał nanododatków do środków smarnych. Stwierdzono, że aby wskazać prawidłowości opisujące tribologiczne oddziaływanie heksagonalnego azotku boru wymagane są szczegółowe badania i analiza jego właściwości. Do istotnych czynników determinujących opisywane zastosowanie tego dodatku zaliczono: rozkład rozmiarów jego cząstek, ich morfologię, powierzchnię właściwą, a także porowatość. Wymienione właściwości określono dla czterech próbek heksagonalnego azotku boru, które były jednocześnie obiektami eksperymentów tribologicznych. Wykorzystano w tym celu skaningowy mikroskop elektronowy (SEM), metodę dyfrakcji rentgenowskiej (XRD) oraz wyznaczono niskotemperaturowe izotermy adsorpcji. Badania wpływu h-BN na właściwości smarnościowe litowego smaru plastycznego przeprowadzono na aparacie czterokulowym. Zidentyfikowano możliwe mechanizmy oddziaływania różnych typów h-BN w strefie tarcia, wykorzystując przy tym zgromadzone informacje dotyczące ich istotnych właściwości. Na podstawie wyników przeprowadzonych badań stwierdzono, że zastosowanie nano h-BN w omawianym kontekście wydaje się perspektywiczne.

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INTRODUCTION

Greases are one of the basic groups of lubricants. They are used to lubricate numerous friction nodes operating at various loads, sliding speeds or at low or high temperatures. This fact determines the constant search for solutions to obtain greases, ensuring adequate lubrication efficiency. The directions of development of these lubricants, in addition to operational factors, also depend on legal and environmental conditions **[L. 1]**. One of the possible actions to obtain lubricants meeting the requirements mentioned above is the application of appropriate additives. An important material group is solid lubricants, namely molybdenum disulphide, graphite or hexagonal boron nitride. The structure and physicochemical characteristics determine very good lubricating properties of this type of material **[L. 2–5]**.

An additive whose operation was analysed in this publication is hexagonal boron nitride (h-BN or α-BN). Due to its lamellar structure, it is classified as an anisotropic material. Within each plate, molecules (atoms) are bound by strong covalent bonds, while between adjacent layers, there are weak intermolecular interactions in the form of Wan der Waals forces. This enables easy interlayer sliding – the atomic layers arrange themselves parallel to the direction of sliding motion and then shear relatively easily, which translates into low internal friction resistance. Apart from the crystal structure, this material, as a potential grease additive, has many favourable properties, such as high mechanical strength, good thermal conductivity, and excellent chemical and thermal stability **[L. 6, 7]**. Hexagonal boron nitride is also non-toxic and environmentally friendly **[L. 8]**.

In the literature, there are works whose authors used hexagonal boron nitride as a grease additive. These publications are listed in **Table 1**, pointing out each of them, the research object, the research method used by the authors, and the result of the research. Particular attention was paid to the information contained in these publications on the properties of h-BN samples used by the researchers.

Based on the information presented in **Table 1**, the four-ball apparatus is the most frequently used method to evaluate the tribological properties of greases containing h-BN. Rare among the analysed publications are tribological tests conducted for the same samples under different friction conditions and various types of tribotesters. The authors chose different concentrations and granulation of h-BN. Most often, this additive is introduced into lithium greases. The result of the vast majority of tests is positive – the application of hexagonal boron nitride enables the improvement of the tribological properties of greases.

In articles **[L. 2, 19]** published in the last few years, scientists take up the topic of hexagonal nano-boron nitride. The authors of the article **[L. 20]**, listing the measures and technologies for reducing friction and wear, drew attention to the issue of nano additives to lubricants, pointing to them as one of the areas of development of modern tribology. Due to their properties, nanomaterials can be an alternative to additives used so far **[L. 20–24]**. The main advantage of nanoparticles in the discussion context is their small size, allowing easy friction area access **[L. 2, 21, 25]**. Nanoparticles are also able to initiate the surface repair effect, filling defects in the material formed on the rubbing surfaces and thus preventing their excessive wear **[L. 26]**. Moreover, they can enter into tribochemical reactions with other components of greases and surface wear products, which also contributes to their effective operation **[L. 2, 25, 27]**.

Notably, most of the publications cited in **Table 1** lack a comprehensive description of the additive used. Insufficient knowledge about the properties of the type of hexagonal boron nitride applied undoubtedly hinders the interpretation of the obtained results of tribological tests and the formulation of theses concerning its impact on tribological systems. Therefore, it seems necessary to accurately identify the properties of hexagonal boron nitride, which is important from the point of view of lubrication. These can include, among others, the type of additive particles, their size and the concentration used **[L. 28–30]**. The morphology of these particles also seems to be important. Literature reports indicate that rounded particles give better tribological effects in the form of lower values of the friction coefficient and lower wear than particles with sharp edges **[L. 25, 31]**. In the case of powdered materials, such as hexagonal boron nitride, the specific surface is an important property determining its physicochemical properties **[L. 32]**. It depends, inter alia, on the porosity of the particles. The article's authors **[L. 19]** formulate the thesis according to which the large specific surface area and the developed pore

Table 1. List of publications related to the application of h-BN as an additive to greases
Tabela 1. Zestawienie publikacji związanych z zastosowaniem h-BN jako dodatku do smarów plastycznych

Reference	Research object	Characteristic of h-BN	Methods and results of tribological research
[L. 6, 9, 10]	Lithium grease with 3%, 5% or 10% h-BN (by wt.)	Particle size distribution, SEM imaging	Research on a four-ball apparatus. Improvement of lubricating properties after adding 3% and 5% h-BN to the base grease in relation to the reference sample.
[L. 6, 11, 12]	ŁT-43 grease with the addition of 2% h-BN (by wt.) and lithium base grease with 5% h-BN (by wt.). Ball bearings: ŁT-43 grease with an addition of 2% h-BN (by wt.)	Particle size distribution, SEM imaging	Analysis of resistance to motion on a stand for examining resistance to motion in ball bearings. The beneficial effect of h-BN on the tribological properties of greases when the rolling bearing operates at low loads and revolutions. For high-speed bearings, the best results when added to the reference grease ŁT-43 2% h-BN. Ball bearings: reduced resistance to movement and extended braking time for grease with h-BN
[L. 6, 13, 14]	Two types of h-BN were added to the machine grease in concentrations 5% and 10% (by wt.)	Size of h-BN particles	Assessment of antifretting properties on a vibrating stand with a ball on a flat system and a stand with a roller-sleeve junction. Vibration stand: adding h-BN to grease improved its anti-fretting properties. Stand with a roller-sleeve junction: improved anti-fretting properties, better in case of 10% h-BN. In both studies, no significant effect of h-BN granulation was found.
[L. 15]	Low-temperature grease to which 2%, 4% and 8% h-BN has been added	Imaging of particle	Research on a four-ball apparatus. Deterioration of anti-seize properties and anti-wear as a result of the addition h-BN for grease.
[L. 16]	Lithium grease with 4% h-BN	–	Measurement of the moment of friction between the spherical surfaces of the tie rod pin and its seat. 27… .50% reduction in frictional resistance compared to the lithium base grease after adding h-BN.
[L. 17]	Lithium grease containing 1%, 3%, 9% h-BN (by wt.)	Size of h-BN particles	Research on a four-ball apparatus. Due to the welding point, wear limiting capacity load and wear index, the best was considered concentration 1%.
[L. 18]	Lithium grease with h-BN in concentrations of 5%, 10% and 20%	Size of h-BN particles, SEM imaging, XRD crystal structure determination	Research on reciprocating sliding motion using a ball-on-flat contact. Greases with h-BN can replace the composition with the addition of graphite in the process of forming aluminium sheets. To ensure good lubrication conditions and better surface quality, a minimum of 20% h-BN with granulation above 5 µm.
[L. 2]	Lithium grease with nano h-BN in concentrations of 0.5%, 0.67%, 1.33%, 1.5% and 2% (by wt.)	Size of h-BN particles, SEM imaging, XRD crystal structure determination	Research on the ball-on-disc tribometer. As a result of the use of 2% h-BN, the friction coefficient was 46% lower than with the base grease lubrication. This concentration was considered the best in the context of improving the tested tribological properties.
[L. 19]	Lithium grease with nano h-BN in concentrations of 0.15%, 0.30%, 0.45%, 0.60%, 0.75% and 0.90% (by wt.)	Particle size distribution, specific surface area, SEM and AFM imaging, XRD crystal structure determination, h-BN spectra obtained by Raman spectroscopy and Infrared Fourier spectroscopy	Research on a four-ball apparatus. The grease containing 0.60% was characterised by the lowest value of the coefficient of friction h-BN. Its use also resulted in the best protection of rubbing surfaces.

structure may increase the degree of bonding of lubricant particles and h-BN particles. The porous structure determines, among others, the materials' mechanical and thermal properties and adsorption capacity. The standard parameters describing the porous structure include specific surface area, total pore volume and pore size distribution, which are most often determined based on low-temperature adsorption isotherms **[L. 33, 34]**.

The motivation for the research conducted for this article was the fact that the literature on the subject lacks publications that would include the impact of various types of h-BN (including nano h-BN) on the tribological properties of a specific grease. Without such a direct comparison, it is difficult to determine the validity of using a nano-variety of this material. The research topic was also justified by the desire to disseminate information about the need for a detailed description of the additive used among interested recipients. According to the authors, such studies are relatively rare in the literature and enable a reliable assessment of the analysed material system for perspective lubrication applications.

This article aims to determine the effect of four types of hexagonal boron nitride on the lubricity properties of lithium base grease. Tribological tests were carried out on a four-ball apparatus. Also, experiments were performed, allowing for a detailed characterisation of the h-BN samples used. The scheme of the research procedure is presented in **Figure 1**.

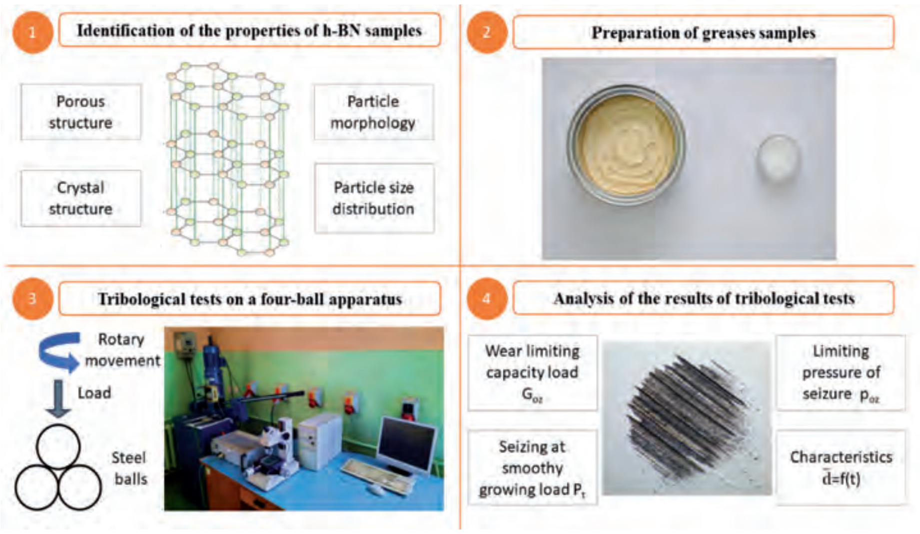

Fig. 1. Scheme of the research procedure
Rys. 1. Schemat postępowania badawczego

EXPERIMENTAL OBJECTS AND METHODS

Hexagonal boron nitride samples

Four types of hexagonal boron nitride samples were used in the research work. For each of them, experiments were carried out, including:

- Determination of the crystal structure of h-BN samples by X-ray diffraction (XRD);
- Imaging of h-BN particles using a scanning electron microscope (SEM) and determining the size distribution of these particles using an image analysis method;
- Determination of the BET specific surface area, total pore volume and pore size distribution based on obtained low-temperature adsorption isotherms.

Figure 2a shows the diffractograms obtained for the tested samples using the XRD method. Hexagonal boron nitride was identified in each of them. Among the samples, two crystallographic systems typical for hexagonal boron nitride were detected, designated as $P6_3/mmc$ and R3m. Differences in the intensity at individual values of the angle between the incident beam and the reflected and different widths of the diffraction peaks indicate differences in the shape and size of the particles of samples of the analysed material. Along with the reduction of the particle size, the widening of the diffraction peaks and the reduction of the radiation intensity were noted – the smaller the crystals, the more radiation is scattered without complying with Bragg's law. Confirmation of the differences in the particle morphology of the h-BN samples is the particle size distributions obtained by the image analysis method, which are shown in **Figure 2b [L. 35]**.

The process of making these histograms began with taking pictures of hexagonal boron nitride particles using a scanning electron microscope. The surface area of each of the imaged particles was calculated. Then, it was assumed that this area is equal to the area of a circle with a specific diameter d. The obtained values of such diameters were presented in the form of a histogram. They were the basis for calculating the arithmetic mean particle size D. Assuming that the diameter of the circle d is the diameter of the sphere. The volume of each of such spheres was calculated, and the equivalent diameter D_{50} was determined, for which smaller and larger grains constitute half of the total volume of a specific hexagonal boron nitride sample. The h-BN 4 sample contained the largest particles. Similar particle size values were recorded for the h-BN 2 and h-BN 3 samples. The smallest particles were identified for the h-BN 1 sample. **Figure 3** shows pictures taken with a scanning electron microscope. The difference in the shape of the particles is visible and confirms the observations from the analysis of the results of X-ray diffraction tests. The grain shape for all samples was non-isometric. For samples h-BN 2, h-BN 3 and h-BN 4, lamellar-shaped were recorded **[L. 35]**.

Figure 4a shows the experimental nitrogen adsorption isotherms obtained for hexagonal boron nitride samples. Using the method presented in the publication **[L. 36]**, the total pore volume was calculated based on a single isotherm point. The next step shows the adsorption isotherms in the BET equation coordinates in the range of 0.05… 0.25 relative pressure (**Fig. 4b**). By the BET method **[L. 37]**, the specific surface area for each sample of the analysed material was calculated. The h-BN 4 sample was characterised by the smallest specific surface area and the total pore volume. The h-BN 1 and h-BN 3 samples turned out to be similar in terms of the values of both parameters. The highest specific surface area and total pore volume were recorded for the h-BN 2 sample. The similarity of the samples of the additive in terms of the values of the parameters describing the particle porosity (especially h-BN 1 and h-BN 3) and the particle size (especially h-BN 2 and h-BN 3) and their dissimilarity in relation to the h-BN 4 sample, may have an influence on the results of tribological tests. Low-temperature adsorption isotherms are

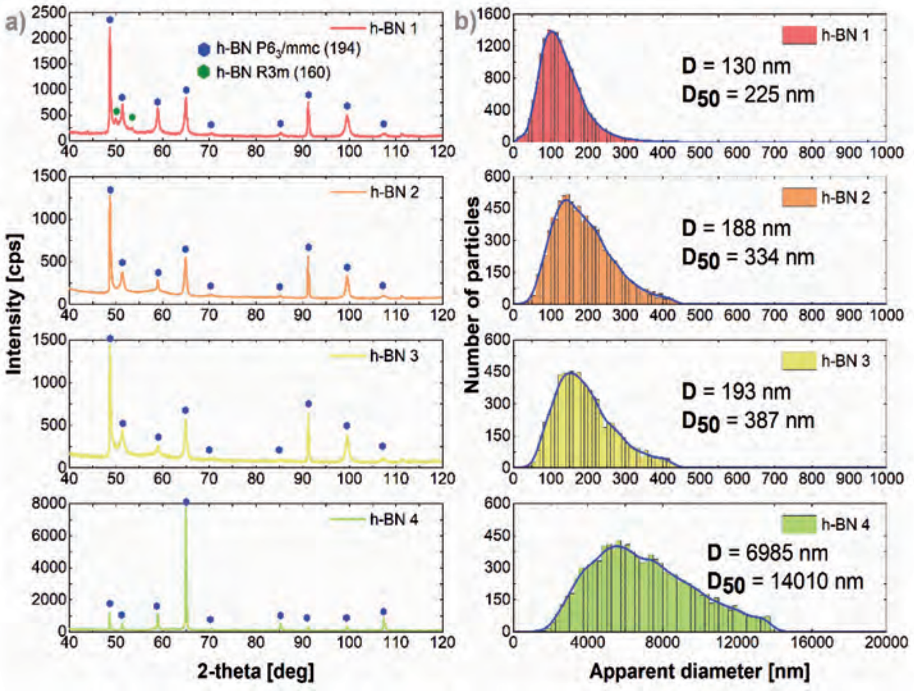

Fig. 2. XRD patterns (a) and particle size distributions (b) of h-BN samples. Adapted from [L. 35]
Rys. 2. Dyfraktogramy (a) oraz rozkłady rozmiarów cząstek (b) próbek h-BN. Zaadaptowano z **[L. 35]**

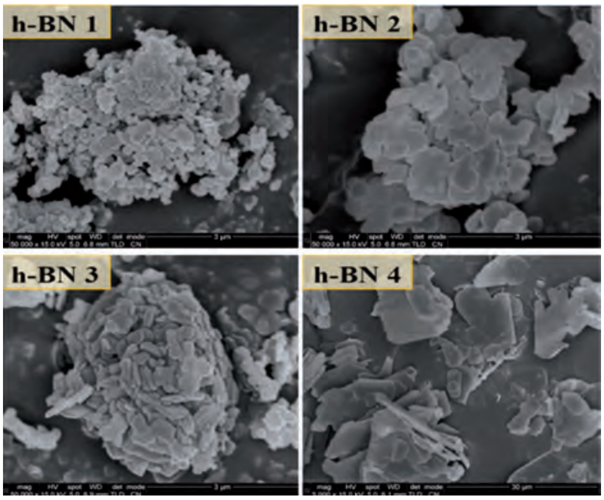

Fig. 3. SEM images of h-BN samples. Adapted from [L. 35]

Rys. 3. Obrazy SEM poszczególnych próbek h-BN. Zaadaptowano z **[L. 35]**

also commonly used to determine porous materials' pore size distribution (PSD). The total adsorption in pores of strictly defined sizes is then represented by the general integral equation of adsorption **[L. 34]**. The pore size distribution functions, shown in **Figure 4c**, were determined using the non-local density functional theory method (2D-NLDFT) for carbon slit-shaped pores under the assumption of energetic heterogeneity and geometrical corrugation of the pore walls **[L. 38]**. All samples of hexagonal boron nitride were observed to show heterogeneous pores, mainly in the mesopore region. The predominant sizes of the mesopores were around 4 nm and 23 nm. The h-BN 1 sample can be classified as nanoporous materials because of pores with sizes included in this category **[L. 35]**.

Table 2 summarises the values of parameters characterising the size and porous structure of the analysed samples of hexagonal boron nitride.

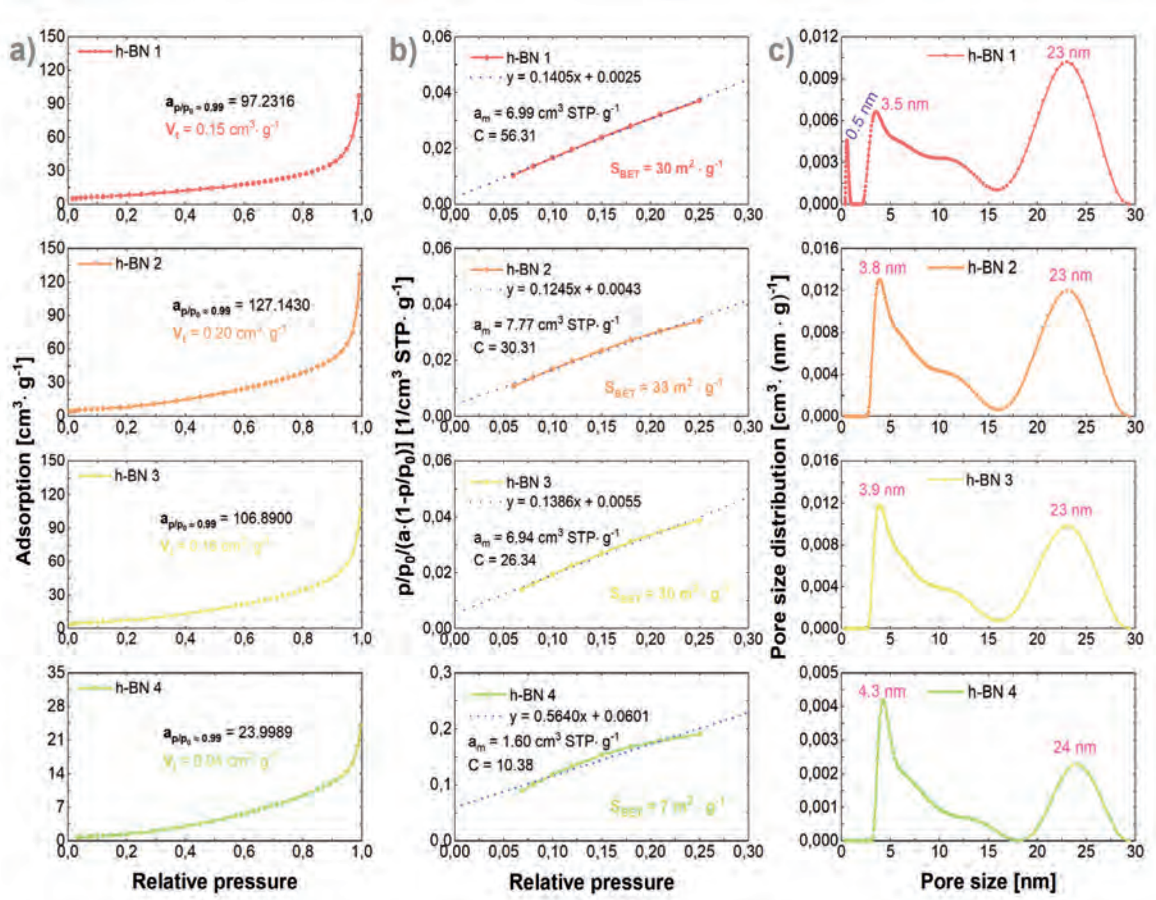

Fig. 4. Nitrogen adsorption isotherms (a), nitrogen adsorption isotherms in BET equation coordinates and pore size distribution functions (c) for h-BN samples. Adapted from [L. 35]

Rys. 4. Doświadczalne izotermy adsorpcji azotu (a), izotermy we współrzędnych równania BET (b) oraz funkcje rozkładu rozmiarów porów dla próbek h-BN. Zaadaptowano z **[L. 35]**

Table 2. Values of parameters characterising the properties of h-BN samples. Adapted from [L. 35]
Tabela 2. Wartości parametrów charakteryzujących właściwości próbek h-BN. Zaadaptowano z **[L. 35]**

Sample	Arithmetic mean particle size D [nm]	Diameter of particles D_{50} [nm]	Specific surface area S_{BET} [$m^2 \cdot g^{-1}$]	Total pore volume V_t [$cm^3 \cdot g^{-1}$]
h-BN 1	130	225	30	0.15
h-BN 2	188	334	33	0.20
h-BN 3	193	387	30	0.16
h-BN 4	6985	14010	7	0.04

Base grease and experimental samples

For the research, a synthetic base of grease was used, with a thickener in the form of complex lithium soaps. This base did not contain any additives, and a dropping point of over 200°C characterised it. Based on the value of the number of penetrations in the range 310÷340 [10^{-1} mm], it was classified as consistency number 1 according to the NLGI (National Lubricating Grease Institute) classification. As additives to the indicated grease, four samples of hexagonal boron nitride were applied in mass concentrations of 5% and 10%. The concentrations were adopted based on the research results **[L. 6]**. Designations and descriptions of lubricants are given in **Table 3**.

Table 3. List of samples subjected to tests with their designations in the article
Tabela 3. Zestawienie próbek poddanych badaniom wraz z ich oznaczeniami w artykule

Sample	The concentration of h-BN [%]	Designation
Lithium grease	0	S 0
Lithium grease + h-BN 1	5	A 5
	10	A 10
Lithium grease + h-BN 2	5	B 5
	10	B 10
Lithium grease + h-BN 3	5	C 5
	10	C 10
Lithium grease + h-BN 4	5	D 5
	10	D 10

Methodology of tribological research

The research for this publication was carried out on a standard T-02 four-ball apparatus manufactured by the Institute for Sustainable Technologies (Radom, Poland). In the model tribological node of the four-ball apparatus, four spheres arranged in the form of a regular tetrahedron were used, so the applied load was distributed into three equal forces acting in the area of the point of contact of the upper sphere with the three lower balls. The balls were made of 100 Cr6 bearing steel (AISI 52100 – EN 10027), with a hardness of 62÷64 HRC and a diameter of ½ inch, i.e., 12.7 mm. As a result of the rotational movement of the upper ball, sliding friction was realised in the presence of the tested lubricant. The basis for determining the value of most of the selected lubricity parameters was the average diameter of the wear scars calculated based on the diameters of the scars formed on three lower, stationary balls, which are part of the friction junction of the four-ball apparatus. The following parameters characterising the lubricity properties of the assessed lubricants were determined: seizing at smoothy growing load P_t, wear limiting capacity load G_{oz}, limiting pressure of seizure p_{oz} and the characteristics of $\bar{d} = f(t)$, where it is the test time under a specific load.

Seizing at a smoothy growing load P_t is the smallest load at which a significant increase in resistance will occur in the tribological node, signalling the breaking of the lubricating film **[L. 39]**. During this test, the load increased continuously from the value of 0 N to the load, causing a marked increase in frictional resistance in the node of the four-ball apparatus at a speed of 408.8 N/s. The rotation speed of the upper ball was 500 rpm. The test result was the characteristic of the frictional moment as a function of time. Based on this characteristic, the moment when the lubricating film was broken, resulting in a sudden increase in resistance in the friction node of the four-ball apparatus, was indicated. Then, the value of the seizing load Pt was determined based on the equation:

$$P_t = t \cdot 408.8\ [N], \tag{1}$$

where:
t – time when there was a sudden increase in resistance in the friction node [s],
408.8 – the value of the speed of load growth during the test [N / s].

Wear limiting capacity load G_{oz} is a parameter characterising the anti-wear properties of the lubricant, reflecting unit pressures in the friction node of the four-ball apparatus **[L. 39]**. The tests were carried out at the upper ball speed of 500 rpm, for 60 s and with a load of 1471.5 N. The value of this parameter was calculated based on the normative equation:

$$G_{oz} = 0.52 \cdot \frac{P}{d^2}, [\frac{N}{mm^2}], \tag{2}$$

where:
0.52 – coefficient resulting from the distribution of forces in the friction node of the four-ball apparatus (regular tetrahedron),
P – applied load [N],
d – mean diameter of the wear scars on the balls [mm].

The test conditions for determining the limiting pressure of seizure p_{oz} were similar to those for which the P_t parameter was determined. The applied load also increased continuously at a speed of 408.8 N/s; however, it increased up to the maximum value of P_{max} = 7845.3 N, at which the four-ball apparatus turned off spontaneously. The p_{oz} parameter, like the wear limiting capacity load G_{oz}, reflects the surface pressures in the friction node of the four-ball apparatus; therefore, its value was determined by the equation:

$$p_{oz} = 0.52 \cdot \frac{P_{max}}{d^2}, [\frac{N}{mm^2}], \tag{3}$$

where:
0.52 – coefficient resulting from the distribution of forces in the friction node of the four-ball apparatus (regular tetrahedron),
P_{max} – maximum value of the applied load (at which the device was turned off spontaneously) [N],
d – mean diameter of the wear scars on the balls [mm].

The methodology used for determining limiting pressure of seizure p_{oz} was modelled on the publications **[L. 40, 41]**, with the difference that for each of the tests, the maximum value of the load P_{max} that could be obtained on a four-ball apparatus was assumed.

The characteristic of the mean diameter of the wear scars as a function of time $\overline{d} = f(t)$ was determined under the load of 317.8 N, while the rotational speed was 1450 rpm. Based on the research carried out earlier, it was concluded that such a load would not cause sudden increases in the frictional resistance in the friction node of the four-ball apparatus, resulting in an increase in the average diameters of the wear scars during the tests, indicative of the breaking of the lubricating film. Avoiding such abrupt changes made it possible to use the obtained characteristics to assess the anti-wear properties of the tested substances.

RESULTS OF TRIBOLOGICAL TESTS AND DISCUSSION

The results of determining the parameters characterising the lubricity properties of the prepared samples of greases are shown in **Figure 5**.

The analysis of the wear limiting capacity load G_{oz} (**Fig. 5a**) shows that the anti-wear properties improved after adding hexagonal boron nitride to the base grease – regardless of its granulation and concentration. The increase in the value of this parameter was 19.9÷48.8% compared to the base sample. Regardless of granulation, samples containing 5% h-BN were characterised by lower values of the wear limiting capacity load G_{oz} than the samples with the addition of 10% h-BN. During

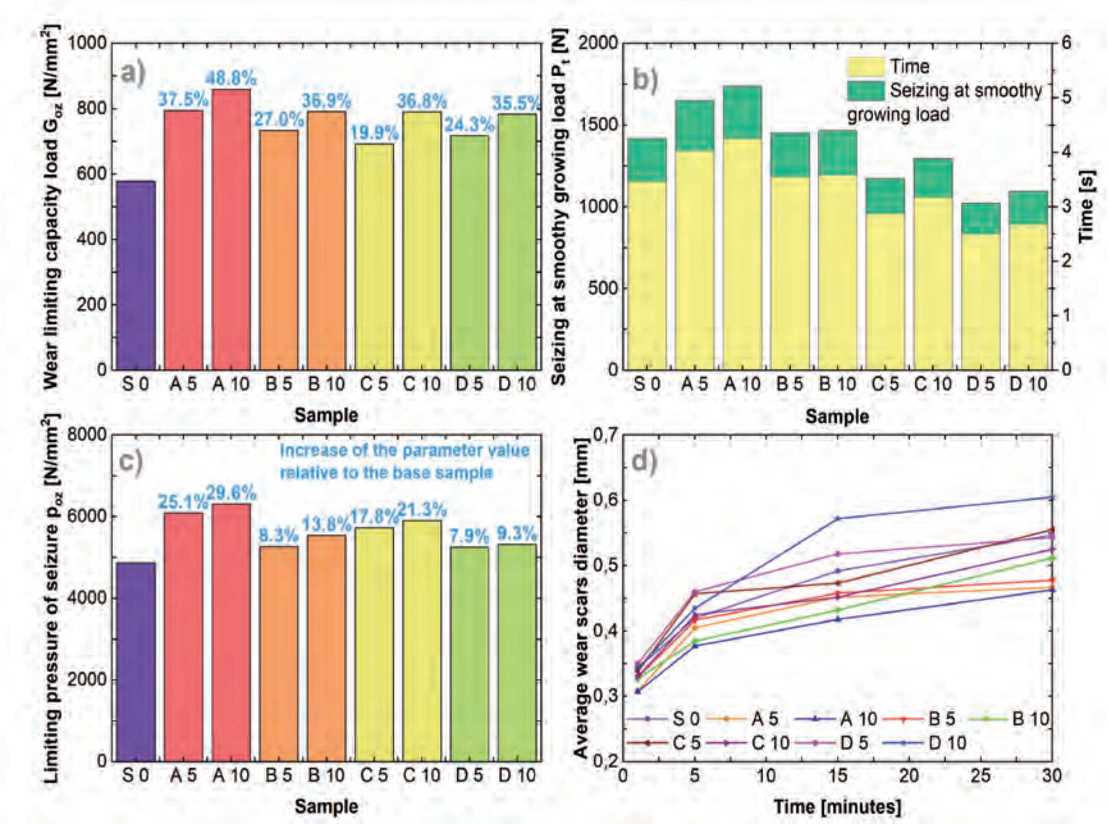

Fig. 5. Test results for the lubricity properties of greases: a) wear limiting capacity load G_{oz}, b) seizing at smoothy growing load P_t, c) limiting pressure of seizure p_{oz}, d) characteristics $\overline{d} = f(t)$

Rys. 5. Wyniki badań właściwości smarnościowych próbek smarów plastycznych: a) graniczne obciążenie zużycia G_{oz}, b) obciążenie zacierające, c) graniczny nacisk zatarcia p_{oz}, d) charakterystyki $\overline{d} = f(t)$

these one-minute tests, carried out under constant load, the greater number of particles dispersed in the base grease made it possible to produce a more durable lubricating film. The best effects were recorded for samples A 5 and A 10 containing the addition of h-BN 1.

Improvement in lubricity properties, assessed based on the obtained values of the seizing at smoothy growing load P_t (**Fig. 5b**), was not observed after adding h-BN 3 and h-BN 4 to the base grease, regardless of the concentration. A slight increase in this parameter's value was noted after using h-BN 2. The introduction of the h-BN 1 additive to the base grease gave the best results. It can be stated with a high degree of certainty that as the load continued to increase during the test, smaller h-BN particles penetrated more easily into the friction zone and contributed to forming a more durable lubricating layer. In the case of a sample with the smallest granulation (h-BN 1), an important role should also be attributed to the concentration of the additive. Its greater amount (greater number of nanoparticles in the friction zone) in the lubricant used resulted in better improvement effects on the discussed tribological criterion. A sudden increase in frictional resistance in the node of the four-ball apparatus, resulting in increased wear of the balls, took place 2.50÷4.25 s from the start of the test (**Fig. 5b**). After this time, stabilisation of frictional resistance was observed, resulting from the decrease in pressure in the contact zones and probably from the action of h-BN, easily penetrating there with the lubricant. This is confirmed by the obtained results of limiting pressure of seizure p_{oz} (**Fig. 5c**). An increase in the value of this parameter, indicating an improvement in the lubricity properties of the composition, was recorded for each of the samples containing the additive and it amounted to 7.9÷29.6%. The best improvement results were obtained again for samples A 5 and A 10. It is worth mentioning that after exceeding the moment determining the value of the seizing at smoothy growing load P_t, when increased ball wear occurred, larger h-BN particles could also penetrate the friction area, contributing to the stabilisation process and reducing wear. Such a course of the process seems to be confirmed by the p_{oz} values obtained for compositions containing the addition of h-BN 2, h-BN 3 and h-BN 4.

The characteristics of the average diameter of wear scars as a function of time $\overline{d} = f(t)$, shown in **Figure 5d**, allowed us to confirm the conclusions drawn from the analysis of other parameters. The best results were obtained when 10% h-BN 1 was added to the base grease. The combination of the developed porous structure and the smaller particle size of this sample suggests that they can flow more easily into the friction zone together with the lubricant, forming lamellar anti-wear films. Therefore, as the granulation of the additive increases, the values of the mean diameter of the wear scar as a function of time increase. It can also be assumed that an important role in such relatively long-term tests is played by the repair mechanism noted in the literature for nanoparticles, which is very possible in the case of h-BN. This type of action of nano-additives is based on the fact that they penetrate the local gaps formed on the friction surface due to the wear process. As a result, they form a lubricating layer on the surface of such micro-cracks, preventing their further wear. This effect is confirmed by the values of the mean diameters of the wear scars obtained for the A 10 sample for the tests lasting 15 and 30 minutes.

The results of tribological tests show the influence of hexagonal boron nitride's properties on lithium grease's lubricity properties. The least effective turned out to be the use of h-BN 4, i.e., the additive with the largest particle size and the smallest specific surface area and total pore volume. Samples with a much more developed porous structure and smaller particles showed a better effect on the tribological interaction of greases. This fact confirms the observation noted during the analysis of the properties of h-BN samples.

CONCLUSIONS

As a result of the analysis of the research concerning the properties of individual types of hexagonal boron nitride samples and the tribological tests carried out on a four-ball apparatus, the following conclusions were formulated:

1. Recognition of hexagonal boron nitride properties is an important research stage in implementing this material as an additive to lubricants. Such a procedure explains the differences in the results of tribological tests, which are related to the differences in the size, shape and porosity of h-BN particles. Moreover, it makes it possible to identify the mechanisms of the additive's influence in the friction node.
2. The best lubrication efficiency assessed based on the adopted set of lubricity criteria, was achieved by introducing 10% of the base grease h-BN 1. Therefore, the use of hexagonal boron nano-nitride seems to be prospective due to its properties that allow better cooperation of this type of particle in a tribological system compared to larger particle sizes.
3. Each hexagonal boron nitride type used in the present research allowed for improvement, especially the anti-wear properties of lithium plastic grease. From among the two analysed concentrations, better tribological effects were obtained for 10% h-BN.
4. By taking into account the adopted lubricity parameters, the worst effects were noted for the samples with h-BN 4 introduced. It can be concluded that the addition of samples h-BN 2 and h-BN 3 gave similar tribological effects, better than h-BN 4.

It is necessary to confirm the conclusions of this article; there is further research on a larger scale, with other greases, on various tribotesters with different model friction nodes and inputs. Such research is currently carried out at the Military University of Technology in Warsaw.

REFERENCES

1. Shankar S.: Emerging trends in the Industrial Greases Market, Journal of Business Chemistry, 11, 3, 2014, pp. 143–149.
2. Yan C., Zeng Q., Hao Y., Xu Y., Zhou M.: Friction-induced hardening behaviors and tribological properties of 60NiTi alloy lubricated by lithium grease containing nano-BN and MoS_2, Tribology Transactions, 62, 5, 2019, pp. 812–820.
3. Krawiec S.: Kompozycje smarów plastycznych i stałych w procesie tarcia stalowych węzłów maszyn, Oficyna Wydawnicza Politechniki Wrocławskie, Wrocław 2011, pp. 57–64.
4. Sahoo R.R., Biswas S.K.: Effect of Layered MoS_2 Nanoparticles on the Frictional Behavior and Microstructure of Lubricating Greases, Tribology Letters, 53, 1, 2014, pp. 157–171.
5. Kimura Y., Wakabayashi T., Okada K., Wada T., Nishikawa H.: Boron nitride as a lubricant additive, Wear, 232, 1999, pp. 199–206.
6. Kałdoński T.: Tribologiczne zastosowania azotku boru, Wojskowa Akademia Techniczna, Warszawa, 2006, 11–13, pp. 78–79.
7. Shatansky D.V., Firestein K.L., Golberg D.V.: Fabrication and application of BN nanoparticles, nanosheets and their nanohybrids, Nanoscale, 10, 2018, pp. 17477–17493.
8. Wang J., Ma F., Sun M.: Graphene, hexagonal boron nitride, and their heterostructures: properties and applications, RSC Advances, 27, 2017.
9. Kałdoński T.: Wpływ azotku boru na właściwości użytkowe smarów plastycznych do łożysk ślizgowych, Materiały VIII Kongresu Eksploatacji Urządzeń Technicznych, Krynica Górska, Polska, 23–26 września 1997.
10. Kałdoński T.: Wpływ rodzaju smaru plastycznego i azotku boru na proces samosmarowania łożyska porowatego, Materiały VIII Kongresu Eksploatacji Urządzeń Technicznych, Krynica Górska, Polska, 23–26 września 1997.
11. Kałdoński T., Krzemiński K.: Zastosowanie azotku boru jako dodatku do smaru plastycznego wypełniającego łożysko toczne, Materiały VIII Kongresu Eksploatacji Urządzeń Technicznych, Krynica Górska, Polska, 23–26 września 1997.
12. Kałdoński T.: Badania i technologia optymalnego stosowania azotku boru α-BN jako dodatku smarnościowego w sprzęcie wojskowym, Sprawozdanie z realizacji projektu badawczego PB 0T 00A 014 08, WAT, Warszawa, 1998.
13. Kałdoński T., Nosal S., Zwierzycki W.: Wpływ zawartości azotku boru produkcji WAT na właściwości antyfrettingowe substancji smarujących, Materiały IV Konferencji Poltrib'97, Białobrzegi, Polska, 10–12 czerwca 1997.
14. Pawlak Z., Kałdoński T., Lisewski M., Urbaniak W., Oloyede A.: The Effect of Hexagonal Boron Nitride Additive on the Effectiveness of Grease-Based Lubrication of a Steel Surface, Industrial Lubrication and Tribology, 64(2), 2012, 84–89.
15. Bajer J., Wpływ dodatku smarnego na charakterystyki tribologiczne niskotemperaturowego smaru plastycznego, Tribologia, 2006, 6, 67–80
16. Józwiak P., Siczek K., Badania wpływu obecności azotku boru w smarze na opory ruchu sworznia drążka kierowniczego, Archiwum Motoryzacji, 2012, 58, pp. 123–137.
17. Krawiec M., Leśniewski T., Badanie efektywności smarowania litowego smaru plastycznego napełnionego azotkiem boru, Górnictwo Odkrywkowe, 2013, 54, pp. 82–86.
18. Podgornik B., Kosec T., Kocijan A., Donik Č.: Tribological behaviour and lubrication performance of hexagonal boron nitride (h-BN) as a replacement for graphite in aluminium forming, Tribology International, 81, 2015, pp. 267–275.
19. Wang T., Li Z., Li J., He Q.: Impact of Boron Nitride Nanoparticles on the Wear Property of Lithium Base Grease, Journal of Materials Engineering and Performance, 29(8), 2020, 4991–5000
20. Holmberg K., Erdemir A.: Influence of tribology on global energy consumption, costs and emissions, Friction, 5, 2017, pp. 263–284.
21. Dassenoy F.: Nanoparticles as Additives for the Development of High Performance and Environmentally Friendly Engine Lubricants, Tribology Online, 14, 5, 2019, pp. 237–253.

22. Gulzar M., Masjuki H.H., Kalam M.A., Varman M., Zulkifli N.W.M., Mufti R.A., Zahid R.: Tribological performance of nanoparticles as lubricating oil additives, Journal Nanoparticle Research 18, 8, 223, 2016, pp. 1–25.
23. Rawat S.S., Harsha A.P.: Current and future trends in grease lubrication. In: Katiyar J., Bhattacharya S., Patel V., Kumar V. (eds): Automotive Tribology. Energy, Environment and Sustainability, Springer, Singapore, 2019, pp. 147–182.
24. Spikes H.: Friction modifier additives, Tribology Letters, 60, 5, 2015, pp. 1–26.
25. Hu E.Z., Xu Y., Hu K.H., Hu X.G.: Tribological properties of 3 types of MoS_2 additives in different base grease, Lubrication Science, 29, 8, 2017, pp. 541–555.
26. Wu H., Li X., He X., Lu J., Wang L., Zhou B., Dong G.: An investigation on the lubrication mechanism of MoS_2 nanoparticles in unidirectional and reciprocating sliding point contact: The flow pattern effect around contact area, Tribology International, 122, 2018, pp. 38–45.
27. Rapoport L., Feldman Y., Homyonfer M., Cohen H., Sloan J., Hutchison J.L.: Inorganic fullerene-like material as additives to lubricants: structure–function relationship, Wear 225–229, 2, 1999, pp. 975–982.
28. Hisakado T., Tsukizoe T., Yoshikawa H.: Lubrication Mechanism of Solid Lubricants in Oils, Journal of Tribology, 1983, 105, pp. 245–252.
29. Chinas-Castillo F., Spikes H.A.: Mechanism of Action of Colloidal Solid Dispersions, Journal of Tribology, 2003, 125, pp. 552–557.
30. Bondarev A., Kovalskii A., Firestein K., Loginov P., Sidorenko D., Shvindina, N., Sukhorukova I., Shtansky D.: Hollow spherical and nanosheet-base BN nanoparticles as perspective additives to oil lubricants: Correlation between large-scale friction behavior and in situ TEM compression testing, Ceramics International, 2018, 44, pp. 6801–6809.
31. Bagi S.D., Aswath P.B.: Role of MoS_2 Morphology on Wear and Friction under Spectrum Loading Conditions, Lubrication Science 2015, 27, 7.
32. Chkhartishvili L.: Correlation between Surface Specific Area and Particles Average Size: Hexagonal Boron Nitride Nano-Powders, Nano Studies 2012, 6 (1), pp. 65–76.
33. Van der Voort P., Leus K., De Canck E.: Introduction to porous materials, Wiley, 2019.
34. Thommes M., Kaneko K., Neimark A.V., Oliver J.P., Rodriguez-Reinoso F., Rouquerol, Sing K.S.W.: Pure and Applied Chemistry, 87, 9–10, 2015, pp. 1051–1069.
35. Senyk S., Chodkiewicz A., Gocman K., Szczęśniak B., Kałdoński T.: Hexagonal Nano and Micro Boron Nitride: Properties and Lubrication Applications, Materials 2022, 15, 955.
36. Gregg S.J., Sing K.S.W., Salzberg, H.W.: Adsorption Surface Area, and Porosity, Journal of The Electrochemical Society, 1967, 114, 279C.
37. Brunauer S., Emmett P.H., Teller E.: Adsorption of Gases in Multimolecular Layers, Journal of the American Chemical Society, 60, pp. 309–319.
38. Jagiello J., Olivier J.P.: 2D-NLDFT Adsorption Models for Carbon Slit-Shaped Pores with Surface Energetical Heterogeneity and Geometrical Corrugation, Carbon 2013, 55, pp. 70–80.
39. Norma PN-76/C-04147 – Przetwory naftowe. Badanie własności smarowych olejów i smarów, 1976 .
40. Tuszyński W.: Badanie przeciwzużyciowych oddziaływań środków smarowych (rozprawa doktorska), Wojskowy Instytut Techniki Pancernej i Samochodowej, Sulejówek, 1999.
41. Szczerek M., Tuszyński W.: Badania tribologiczne. Zacieranie, Wydawnictwo Instytutu Technologii Eksploatacji, Radom, 2000, pp. 79-81.