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Zbigniew PAWELEC*, Jarosław MOLENDA, Bernadetta KAŹMIERCZAK*****

THE EFFECT OF THE BIOCARBON TYPE ON THE TRIBOLOGICAL CHARACTERISTICS OF GREASES MANUFACTURED WITH VEGETABLE AND SYNTHETIC BASE OILS

WPŁYW RODZAJU BIOWĘGLA NA CHARAKTERYSTYKI TRIBOLOGICZNE SMARÓW WYTWORZONYCH NA BAZIE OLEJU ROŚLINNEGO I SYNTETYCZNEGO

Key words: greases, biocarbon additives, biocarbon greases, pyrolysis of biomass, anti-wear properties, anti-seize properties, vegetable oil, synthetic oil.

Abstract: The article presents the tribological characteristics of plastic greases in which the dispersing phase was vegetable (rapeseed) oil or synthetic ester oil (Priolube). The lithium stearate was used as a thickener in an amount sufficient to obtain a composition in the second consistency class, and the functional additives were biocarbon produced in the process of pyrolysis of the following plant waste: flax straw, wheat straw, corn leaves and stalks, and cherry stones. The compositions containing 5% m/m of biocarbon were prepared and the influence of the type of biocarbon on the tribological properties of the obtained plastic greases was assessed. The tribological characteristics of the grease compositions were determined using the T-02 tester in accordance with the requirements of the relevant standards. The influence of the applied biocarbon on the anti-wear (G_{oz}) and anti-seize (P_t, p_{oz}) properties of plastic greases made with vegetable and synthetic basis was determined. It was found that some of the biocarbon, especially those derived from the pyrolysis of corn waste, significantly improve the tribological properties of plastic greases, both those based on plant and synthetic sources.

Słowa kluczowe: smary, dodatki biowęglowe, smary biowęglowe, piroliza biomasy, właściwości przeciwzużyciowe, właściwości przeciwzatarciowe, olej roślinny, olej syntetyczny.

Streszczenie: W artykule przedstawiono charakterystyki tribologiczne smarów plastycznych, w których fazą dyspergującą był olej roślinny (rzepakowy) lub syntetyczny olej estrowy (Priolube). Jako zagęszczacz zastosowano stearynian litu w ilości pozwalającej na uzyskanie kompozycji w drugiej klasie konsrystencji, a dodatkami funkcyjnymi były biowęgle wytwarzane w procesie pirolizy następujących odpadów roślinnych: paździerze lniane, słoma pszeniczna, liście i łodygi kukurydzy oraz pestki wiśni. Sporządzono kompozycje zawierające, do których wprowadzano 5% m/m biowęgli i oceniono wpływ rodzaju biowęgla na właściwości tribologiczne otrzymanych smarów plastycznych. Charakterystyki tribologiczne kompozycji smarowych wyznaczono z wykorzystaniem testera T-02 zgodnie z wymaganiami norm przedmiotowych. Określono wpływ zastosowanych biowęgli na właściwości przeciwzużyciowe (Goz) i przeciwzatarciowe (Pt, poz) smarów plastycznych wytworzonych na bazie roślinnej i syntetycznej. Stwierdzono, że niektóre z biowęgli, szczególnie te pochodzące z pirolizy odpadów kukurydzy, zdecydowanie poprawiają właściwości tribologiczne smarów plastycznych zarówno tych na bazie roślinnej, jak i syntetycznej.

* ORCID: 0000-0002-7419-152X. Łukasiewicz Research Network – Institute for Sustainable Technologies, Pułaskiego 6/10 Street, 26-600 Radom, Poland.

** ORCID: 0000-0003-3477-4971. Łukasiewicz Research Network – Institute for Sustainable Technologies, Pułaskiego 6/10 Street, 26-600 Radom, Poland.

*** ORCID: 0000-0002-2712-7330. Łukasiewicz Research Network – Institute for Sustainable Technologies, Pułaskiego 6/10 Street, 26-600 Radom, Poland.

INTRODUCTION

The European Green Deal strategy focuses, inter alia, on a circular economy, one of the key elements of which is the rational management of plant biomass waste. The large amounts of this type of biomass are produced in the agri-food sector. In particular, the following types of waste biomass can be mentioned: fruit stones, husks, bagasse, cereal straw waste, chaff of fibrous plants, algae biomass, and many others. This biomass can be processed into a “biocarbon,” which, according to the definition of the *International Biochar Initiative*, is a fine-grained char with a high organic carbon content and low susceptibility to degradation, and which is obtained by pyrolysis. During the thermal treatment, in an atmosphere of a protective gas that limits the access of oxygen, in addition to the char, products of energetic significance are produced, i.e. oil which is a mixture of liquid hydrocarbons and synthetic gas which is a mixture of gaseous hydrocarbons. The share of biocarbon in the pyrolysis products and its microstructural structure depend on the process parameters, primarily on the process temperature and the residence time at the final temperature **[L. 1–3]**.

During the carbonization of plant biomass, the carbon atoms can be arranged into cyclic structures that form crystalline phases referred to as graphite crystallites. It is this form of carbon that is characterized by a layered structure and shows good lubricating properties; therefore, biocarbon can be used as active components of plastic lubricants **[L. 4–8]**. It should be noted that carbon additives of various structures **[L. 8**, **9]**, especially of fossil origin, are used in graphite greases. The additives introduced into the thickened base oil determine the performance properties of the grease **[L. 9–11]**.

The previous work indicated very good anti-wear and anti-seizing properties of the produced plastic greases based on mineral oil and containing biocarbons from the pyrolysis of vegetable waste as tribological additives **[L. 11]**. Nevertheless, some technical applications require greases to be made of ecological, biodegradable bases, e.g., vegetable or synthetic esters.

In connection with the above, the aim of the study was to assess the effect of the type of biocarbon being a product of the pyrolysis of plant waste from the agri-food industry (flax straw, maize, wheat straw and cherry stones) on the frictional wear characteristics of plastic greases based on vegetable and synthetic oil.

THE RESEARCH OBJECTS

The subjects of the research were plastic grease compositions in which the dispersing phase was vegetable (rapeseed) oil and synthetic Priolube ester oil, and the thickener was lithium stearate in the amount of 10% by weight. The 5% of biocarbon from the pyrolysis of plant waste (flax straw, maize, wheat straw and cherry stones) were added to these compositions as functional additives. The homogenization of the mixture of plastic grease (vegetable or synthetic oil with thickener), to which biocarbon was added, was carried out in a laboratory Z-mixer at room temperature for 30 minutes. In the further part of the article, samples of greases with biocarbons are given names derived from the biomass raw material from which the biocarbon introduced into a given composition was produced. The obtained grease compositions had the second consistency class according to NLGI. The characteristics and production process of biocarbon are presented in detail in **[L. 3]**.

METHODOLOGY OF TRIBOLOGICAL RESEARCH

The T-02 four-ball apparatus was used to determine the tribological properties of the tested grease compositions. During the tests, the limiting load of wear ($G_{oz/40}$), the scuffing load (P_t), and the limiting pressure of seizure (p_{oz}) were determined. The friction node consisted of balls with a diameter of 12.7 mm made of ŁH 15 bearing steel, hardness 60-65HRC. The measurement of the limiting load of wear ($G_{oz/40}$) was made with a friction node load of 392.4 N for the entire duration of the test, i.e. 3600 seconds, and a ball rotational speed of 500 rpm in accordance with the test conditions provided for in WTWT-94 / MPS-025.

The welding load was measured in accordance with the PN-76/C-04147 standard. On the other hand, the measurement of the lubricating properties under scuffing conditions was carried out according to the methodology developed at Ł – ITeE in Radom. The test was performed at a linearly increasing load from 0 to 7200 N during 18 seconds at a spindle speed of 500 rpm and load rise rates 409 N/s. Then, tribological parameters were determined, including scuffing load (P_t), limit load of seizure (P_{oz}), and limit pressure of seizure (p_{oz}). The determination of the limit pressure of seizure, characterizing the anti-seize properties of lubricants, consisted in calculating its value in accordance with the following formula:

$$p_{oz} = 0,52\frac{P_{oz}}{d^2},$$

where P_{oz} – limiting load of seizure, d – diameter of the flaw created on the steel balls used for the test.

An optical microscope was used to determine the size of the trace of surface wear of the test balls. The obtained results were used to determine the size of $G_{oz/40}$ and p_{oz}, i.e. the assessment of anti-wear and anti-seizing properties of plastic greases subjected to tribological tests. The presented results of tests of tribological properties of developed plastic greases were determined based on the results of at least three test runs of the tested material combinations.

RESULTS OF THE RESEARCH

Figures 1 to **5** show examples of the courses of changes in the friction moment in the friction tests of plastic grease compositions based on rapeseed oil containing the tested biocarbon, and **Figures 6** and **7** show the influence of biocarbon on the scuffing load (P_t) and the limiting pressure of seizure (p_{oz}), i.e. parameters describing the tribological properties of the tested lubricants.

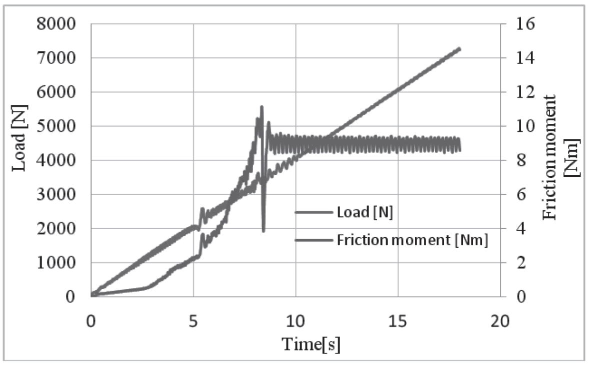

Fig. 1. The course of changes in the frictional moment of the coupling steel – steel lubricated with vegetable-based grease (rapeseed oil) + lithium stearate – initial sample

Rys. 1. Przebieg zmian momentu tarcia skojarzenia stal – stal smarowanego smarem na bazie roślinnej (olej rzepakowy) + stearynian litu – próbka wyjściowa

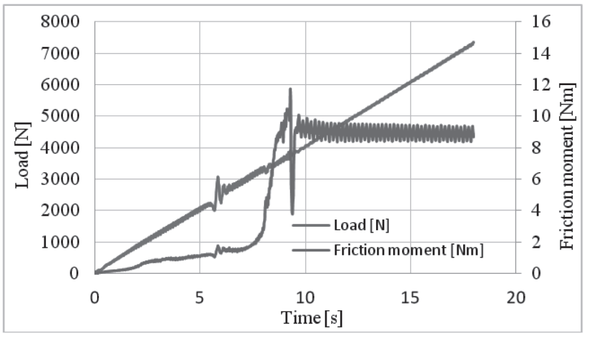

Fig. 2. The course of the frictional moment of the steel-steel coupling, lubricated with a vegetable-based grease (rapeseed oil) with the addition of biocarbon from the pyrolysis of cherry stones

Rys. 2. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem na bazie roślinnej (olej rzepakowy) z dodatkiem biowęgla pochodzącego z pirolizy pestek

The analysis of the data presented in the figures (**Figs. 6** and **7**) suggests that the best anti-seize properties determined by scuffing load (P_t) as well as the limiting load of seizure (p_{oz}) have lubricant compositions containing biocarbon derived from the pyrolysis of cherry stones and biomass from corn maize. For the first biocarbon, P_t increases more than twice as compared to the initial sample, and a greater than 3-fold increase in the scuffing load (P_t) is noted for the lubricant

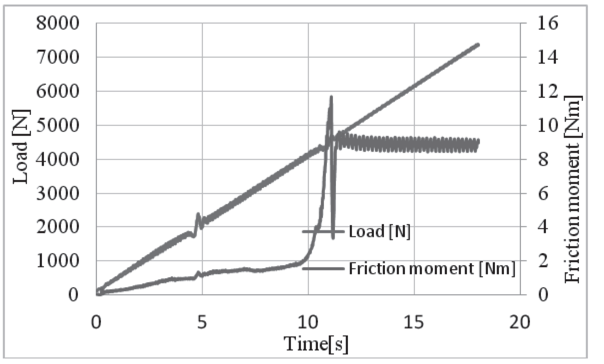

Fig. 3. The course of the frictional moment of the steel-steel coupling lubricated with vegetable-based grease (rapeseed oil) with the addition of biocarbon derived from corn maize pyrolysis

Rys. 3. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem na bazie roślinnej (olej rzepakowy) z dodatkiem biowęgla pochodzącego z pirolizy kukurydzy

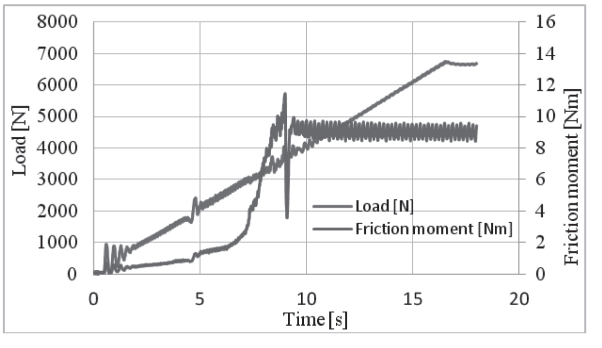

Fig. 4. The course of the frictional moment of the steel-steel coupling lubricated with vegetable-based grease (rapeseed oil) with the addition of biocarbon derived from flax straw wheat pyrolysis

Rys. 4. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem na bazie roślinnej (olej rzepakowy) z dodatkiem biowęgla pochodzącego z pirolizy lnu

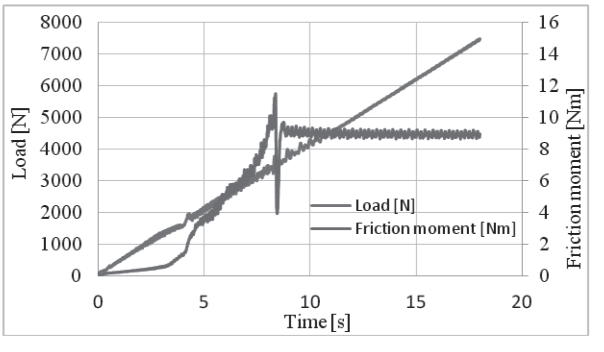

Fig. 5. The course of the moment of friction of the steel-steel coupling, lubricated with vegetable-based grease (rapeseed oil) with the addition of biocarbon from straw pyrolysis

Rys. 5. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem na bazie roślinnej (olej rzepakowy) z dodatkiem biowęgla pochodzącego z pirolizy słomy

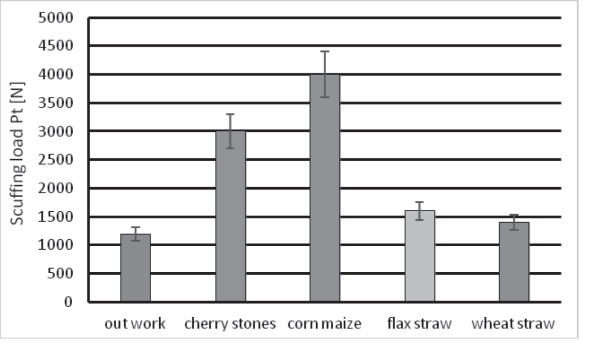

Fig. 6. The influence of biocarbon on the scuffing load (P_t) of plastic lubricants based on vegetable oil

Rys. 6. Wpływ biowęgli na wskaźnik obciążenia zacierającego (P_t) smarów plastycznych na bazie oleju roślinnego

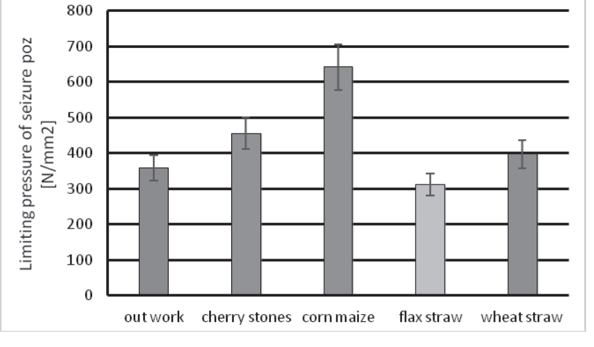

Fig. 7. The influence of biocarbon on the limiting pressure of seizure (p_{oz}) of vegetable oil-based greases

Rys. 7. Wpływ biowęgli na graniczny nacisk zatarcia (p_{oz}) smarów plastycznych na bazie oleju roślinnego

containing biocarbon derived from corn pyrolysis. In both cases, parallel to the increase in the scuffing load (P_t), the limiting load of seizure (p_{oz}) also increases in the case of lubricant with cherry stones biocarbon. The value of this parameter is about 25%, and, in the case of corn biocarbon, it is about 70% higher than for the composition a lubricant containing only rapeseed oil and lithium stearate dispersed therein. The obtained results indicate that, in the case of a plant base, the anti-seize properties of lubricants made with biocarbon are less dependent on the structure of the additives used (stones, porous mass structure, corn fibrous structure), and they result from the possible presence on the surface of these biocarbon on the mechanism of the formation and durability of the lubricating film, delaying the process of seizing and the formation of adhesive grafting.

Figure 8 shows the effect of biocarbon on the anti-wear properties of greases based on vegetable oil.

The data presented in the figure (**Fig. 8**) shows that the majority of biocarbon have a positive effect on the anti-wear properties of lubricant compositions; the wear limit load (Goz) for greases with corn, flax and straw biocarbons increases by about 15–20%. The interesting results were obtained for the lubricant with the participation of biocarbon from the pyrolysis of stones, because its anti-wear properties do not correspond to good anti-seize properties, the limiting load of wear (Goz) is definitely lower than for the lubricant sample without additive and for other samples containing biocarbon. In this case, however, this effect can be related to the structure of biocarbon (powder) as well as the size and duration of the load, which, in the case of wear tests, is about 400 N for a period of 1 hour, which may not contribute to the formation of a lubricating layer effectively separating the mating surfaces of steel balls.

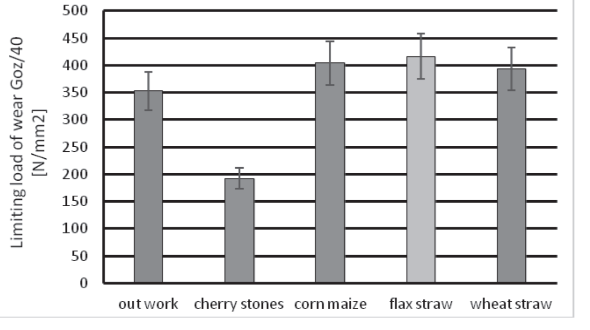

Fig. 8. The influence of biocarbon on the limiting load of wear (G_{oz}) of a vegetable oil-based grease

Rys. 8. Wpływ biowęgli na graniczne obciążenie zużycia (G_{oz}) smaru plastycznego na bazie oleju roślinnego

The further part of the publication presents the results of tribological tests of biocarbon greases based on synthetic oil (Priolube) and lithium stearate. **Figs. 9–13** show examples of the moment of friction changes in the friction tests of plastic grease compositions. **Figures 14** and **15** show the influence of biocarbon on the scuffing load (P_t) and the limiting pressure of seizure p_{oz}. **Figure 16** shows the influence of biocarbon on the anti-wear properties (the limiting load of wear G_{oz}) produced on the basis of synthetic plastic lubricants.

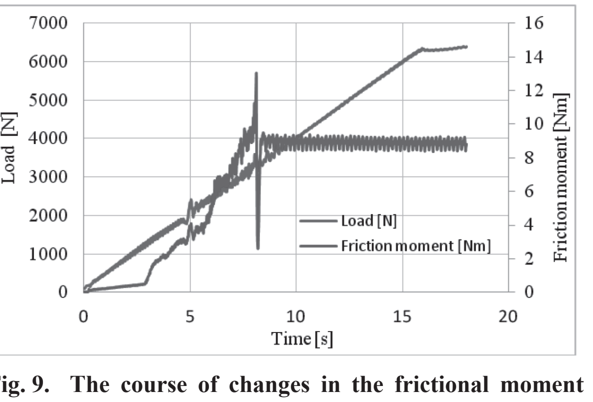

Fig. 9. The course of changes in the frictional moment of the steel-steel coupling, lubricated with plastic grease without additives, based on the synthetic Priolube base

Rys. 9. Przebieg zmian momentu tarcia skojarzenia stal–stal smarowanego smarem plastycznym bez dodatków na bazie syntetycznej Priolube

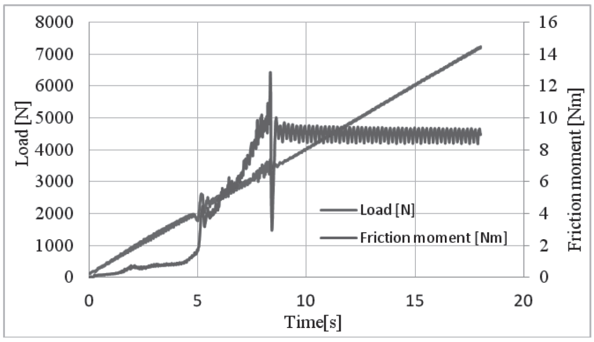

Fig. 10. The course of the friction moment of the steel-steel coupling lubricated with plastic grease based on the synthetic Priolube with the addition of biocarbon derived from the pyrolysis of the stones

Rys. 10. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem plastycznym na bazie syntetycznej Priolube z dodatkiem biowęgla pochodzącego z pirolizy pestek

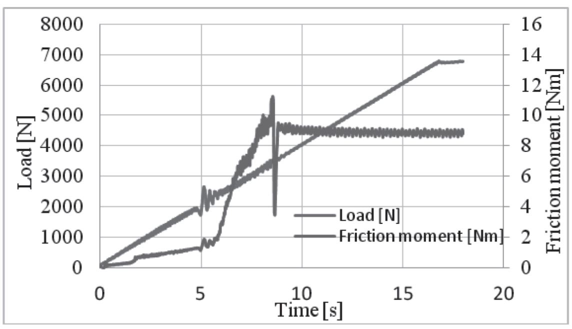

Fig. 11. The course of the frictional moment of the steel-steel coupling lubricated with plastic grease based on the synthetic Priolube with the addition of biocarbon derived from corn maize pyrolysis

Rys. 11. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem plastycznym na bazie syntetycznej Priolube z dodatkiem biowęgla pochodzącego z pirolizy kukurydzy

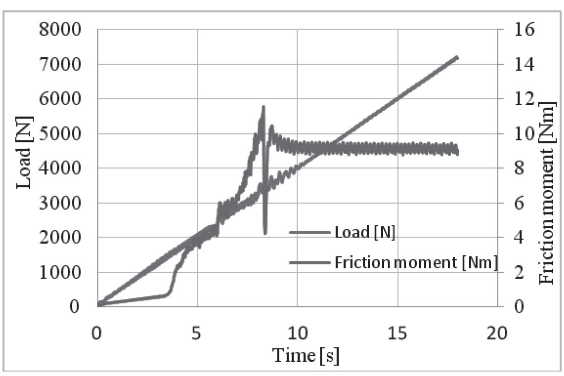

Fig. 12. The course of the frictional moment of the steel-steel coupling, lubricated with plastic grease based on the synthetic Priolube with the addition of biocarbon from flax straw pyrolysis

Rys. 12. Przebieg momentu tarcia skojarzenia stal–stal smarowanego smarem plastycznym na bazie syntetycznej Priolube z dodatkiem biowęgla pochodzącego z pirolizy lnu

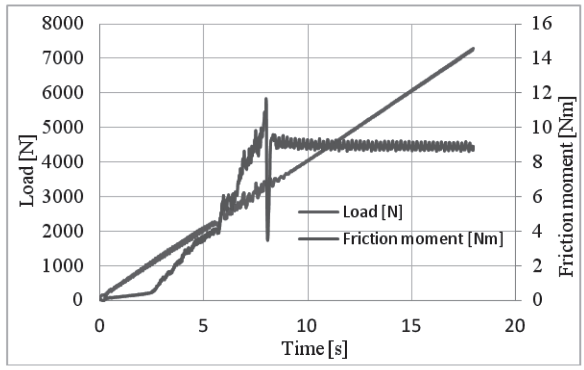

Fig. 13. The course of the frictional moment of the steel-steel coupling, lubricated with plastic grease based on the synthetic Priolube with the addition of biocarbon from wheat straw pyrolysis

Rys. 13. Przebieg momentu tarcia skojarzenia stal stal smarowanego smarem plastycznym na bazie syntetycznej Priolube z dodatkiem biowęgla pochodzącego z pirolizy słomy

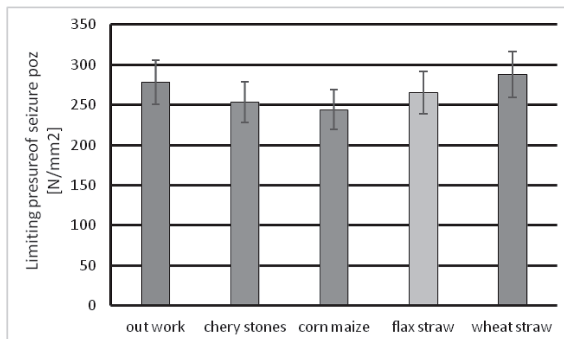

Fig. 14. The influence of biocarbon on the limiting pressure of seizure (p_{oz}) of lubricants based on synthetic Priolube

Rys. 14. Wpływ biowęgli na graniczny nacisk zatarcia (p_{oz}) smarów na bazie syntetycznej Priolube

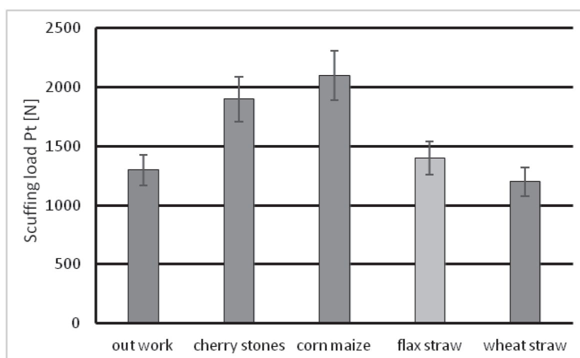

Fig. 15. The influence of biocarbon on the scuffing load (P_t) of lubricants based on synthetic Priolube

Rys. 15. Wpływ biowęgli na obciążenie zacierające (P_t) smarów na bazie syntetycznej Priolube

On the basis of the obtained results of tests of anti-seizing properties of plastic greases based on Priolube synthetic oil containing biocarbon (**Fig. 14**), it can be concluded that their influence on one of the parameters, i.e. the limiting pressure of seizure (p_{oz}), is relatively small. For most of them, we observe a slight reduction of the limiting pressure of seizure. On the other hand, in the case of biocarbon from wheat straw, a slight increase of about 5% of this parameter was noted. The effect of biocarbon on another parameter, which proves the anti-seizing properties of lubricants (the scuffing load P_t), is slightly different, indicating the initiation of the scuffing process. In this case, analogically to vegetable-based greases, we observe about 40% for biocarbon from pyrolysis of stones and over a 50% increase in this parameter for biocarbon from corn pyrolysis. This effect proves that, in both cases, the durability of the lubricating film is much longer and the increase in the moment of friction occurs after a longer period of time and the associated load increase.

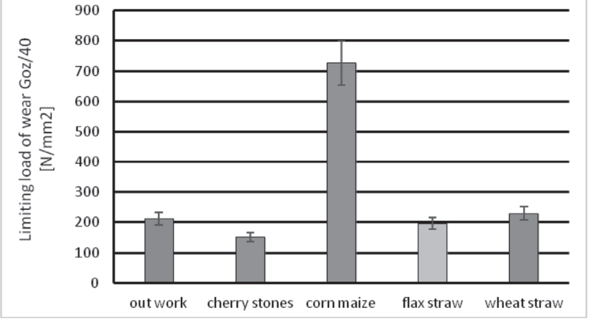

Fig. 16. The influence of biocarbon on the limiting load of wear (G_{oz}) of lubricants based on synthetic Priolube

Rys. 16. Wpływ biowęgli na graniczne obciążenie zużycia (G_{oz}) smarów na bazie syntetycznej Priolube

The very good results, especially in the case of biocarbon from corn waste, were obtained by examining the anti-wear properties of synthetic-based biocarbon greases (**Fig. 16**). The limiting load of wear (G_{oz}) is over three times higher than for the initial sample, which proves the formation of a durable anti-wear lubricant film on the mating surfaces. Probably, in this case, we can deal with the reaction of oxygen functional groups that can be present on the surface of biocarbon with the functional groups of synthetic ester oil (Priolube) and the formation of early oxidation products that improve the anti-wear and anti-seize properties of plastic grease.

Table 1 presents a comparison of the tribological parameters of plastic greases based on vegetable oil and synthetic ester oil.

The table shows the results of tribological parameters of biocarbon grease compositions, showing the best anti-wear and anti-seizing properties among the tested preparations. The comparative analysis of the obtained results shows that, in most cases, the incorporation of biocarbon obtained from corn waste into the lubricant allows for a significant improvement in both anti-wear and anti-seize properties. A deviation from this rule is noticeable in the case of vegetable-based biocarbon grease for which the anti-wear properties determined by G_{oz40} are the best when using biochar obtained from flax straw, and also for synthetic-based plastic grease for which anti-seize properties are the best in in the case of using biocarbon obtained from wheat straw. An interesting observation, however, is that this grease does not have the highest P_t index among the tested compositions. The highest scuffing load (P_t) was recorded when the grease was tested with biocarbon obtained from corn waste. Therefore, it can be assumed that the structure of biocarbon, including its crystallinity and the presence of active functional groups **[L. 12]**, may be responsible for the load at which the lubricant layer separating the cooperating elements of the friction node is degraded.

Table 1. The comparison of the tribological parameters of the tested plastic lubricants

Tabela 1. Porównanie parametrów tribologicznych testowanych smarów plastycznych

A type of biocarbon additive	The tribological parameters of lubricants on selected base oils					
	$G_{oz\ 40}$ [N/mm^2]		p_{oz} [N/mm^2]		P_t [N]	
	Vegetable oil	Synthetic oil	Vegetable oil	Synthetic oil	Vegetable oil	Synthetic oil
without biocarbon	353	212	359	278	1200	1300
Cherry stones	192	151	456	253	3000	1900
Corn maize	404	**726**	**642**	244	**4000**	**2100**
Flax straw	**416**	196	312	265	1600	1400
Wheat straw	393	230	397	**288**	1400	1200

CONCLUSION

Summarizing the work carried out, it can be stated that, regardless of the type of oil base, the product derived from corn pyrolysis significantly improves the anti-wear properties of lubricants (measured by the G_{oz} value), and this biocarbon can be considered as a functional additive to plastic lubricants, improving tribological properties.

Nevertheless, the most effective biocarbon additive improving the anti-wear properties of a vegetable-based grease is a product derived from the pyrolysis of flax straw; however, in this case, the G_{oz40} value is only slightly higher than the value of this parameter determined for the grease with corn waste biocarbon. The biocarbon from corn waste also has a positive effect on the anti-seize properties (measured by the scuffing load – P_t) of both tested plastic greases. On the other hand, the limiting pressure of seizure (p_{oz}) differentiates the tested lubricants. A clear effect of biocarbon from corn waste is observed in the case of a vegetable-based lubricant, and this effect is not observed in the case of a synthetic ester-based lubricant. Due to the different effects of biocarbon interaction, reflected in the tribological characteristics of plastic greases, it is necessary to thoroughly analyse the mechanisms of the interaction of biocarbon in lubricant compositions with the working surfaces of the friction node.

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