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THE INFLUENCE OF BIOCARBON ADDITIVES ON GREASE FUNCTIONALITY

WPŁYW DODATKÓW BIOWĘGLOWYCH NA WŁAŚCIWOŚCI FUNKCJONALNE SMARÓW PLASTYCZNYCH

Key words: plastic greases, graphite greases, biocarbon greases, biomass pyrolysis, biocarbon additives, tribological properties.

Abstract: The article presents the results of tests on tribological and physicochemical properties of plastic greases, in which the dispersing phase was highly refined mineral oil and the dispersed phase (thickener) lithium stearate. The functional additives were biocarbon, which were obtained in the pyrolysis process of waste of natural origin, i.e. stems with corn leaves, wheat straw, flax straw, and cherry stones. The compositions containing 5% m/m biocarbon were prepared. Their evaluated on the functional properties of plastic greases was assessed. Tribological characteristics of the greases compositions were determined using the T-02 tester in accordance with the requirements of the subject standards. The effect of biocarbon used on anti-wear (G_{oz}) and anti-seizing (P_t, p_{oz}) plastic greases was determined. An assessment was also made of the effect of plant biocarbon on changes in basic physicochemical properties of the composition of plastic greases, i.e. penetration, dropping temperature, and thermo-oxidative stability. It was found that some of the biocarbon significantly improve the tribological properties of plastic greases without significantly affecting the change of key physicochemical parameters. The most beneficial impact of the tested additives on the operational properties of plastic greases was observed when using biocarbon from wheat straw. In some cases, a lower oxidative resistance of biocarbon grease is observed compared to grease without the addition of biocarbon.

Słowa kluczowe: smary plastyczne, smary grafitowe, smary biowęglowe, piroliza biomasy, dodatki biowęglowe, właściwości tribologiczne.

Streszczenie: W artykule przedstawiono wyniki badań właściwości tribologicznych i fizykochemicznych smarów plastycznych, w których fazą dyspergującą był wysokorafinowany olej mineralny, a fazą zdyspergowaną (zagęszczaczem) stearynian litu, dodatkami funkcyjnymi były biowęgle otrzymane w procesie pirolizy odpadów pochodzenia naturalnego tj. łodyg wraz z liśćmi kukurydzy, słomy pszenicznej, paździerzy lnianych i pestek wiśni. Sporządzono kompozycje zawierające 5% m/m biowęgli i oceniono ich wpływ na właściwości funkcjonalne 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 (G_{oz}) i przeciwzatarciowe (P_t, p_{oz}) opracowanych smarów plastycznych. Dokonano także oceny wpływu biowęgli pochodzenia roślinnego na zmiany podstawowych właściwości fizykochemicznych kompozycji smarów plastycznych, tj. penentrację, temperaturę kroplenia i stabilność termooksydacyjną. Stwierdzono, że niektóre z biowęgli zdecydowanie poprawiają właściwości tribologiczne smarów plastycznych, nie wpływając istotnie na zmianę kluczowych parametrów fizykochemicznych. Najkorzystniejszy wpływ badanych dodatków na właściwości eksploatacyjne smarów plastycznych zaobserwowano w przypadku zastosowania biowegli ze słomy pszenicznej. W niektórych przypadkach obserwuje się niższą odporność oksydacyjną smarów biowęglowych w porównaniu ze smarem bez dodatku biowęgla.

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INTRODUCTION

Plastic greases are a specialized group of lubricants used in cases where there is a need for good sealing of the friction node against water and mechanical impurities, as well as the requirement of good adhesion to metal surfaces. The range of use of greases is wide and includes both rolling and plain bearings (the main group of greases), unsealed gears, joints, and other friction surfaces. Greases are applied to friction centres operating in various conditions and a wide range of quality parameters: in high and low temperatures, high rotational speeds, and variable loads **[L. 1–4]**.

The basic characteristics of greases resulting from their plastic character are consistency, the temperature limit of the plastic state – "the dropping point of grease," structural stability, and mechanical stability. In addition to the above, the main properties of plastic greases from the point of view of operating conditions play an important role such as water resistance, oxidation resistance, the ability to protect against corrosion, as well as anti-wear and anti-seizing properties. These properties are improved by incorporating improvers. Graphite greases are a special group in which graphite in combination with molybdenum disulphide is used as a tribological additive **[L. 5–8]**. For example, Polish graphite grease contains 10% coarse graphite **[L. 6]**. It is a substance with anisotropic consistency. The existing theories of friction of this type of substance explain their behaviour in tribological systems. In the explanations proposed by various authors, the main role is assigned to structural factors. Their lubricating properties are associated with the characteristic layered structure of the crystal lattice where the carbon atoms arranged in the layer are bound together by strong bonds and significantly smaller Van der Waals forces act between the carbon atoms located in the adjacent layers. Many authors consider that this is excessive simplification and the argument against such explanation of the lubricating properties of layered materials is the fact that some materials, such as mica, talc, and titanium disulphide, are characterized by high friction coefficient despite the layered structure. In addition, substances such as graphite or boron nitride in the air, which is the friction environment, have low values of the coefficient of friction, while in the vacuum the value of the coefficient of friction increases significantly. Based on the above considerations, it can be suggested that in friction processes with solid greases such as graphite, sorption phenomena are important because, in the air environment, there is sorption of gases and water vapour on their surfaces; whereas, in a vacuum of such processes, there is no value in the friction coefficient, e.g., graphite is more than twice as large **[L. 5, 9]**. Literature reports as well as previous experience in shaping the chemical structure of biocarbon has prompted the authors to carry out research related to the use of biocarbon from the pyrolysis of plant waste as tribological additives, which are characterized by good adsorption properties.

The aim of the study was to examine the impact of biocarbon additives obtained in the process of pyrolysis of plant waste on the operational properties of plastic greases, with particular regard to tribological properties.

RESEARCH OBJECTS

The biocarbon additives were obtained in the pyrolysis process, which was carried out in an atmosphere of protective gas (carbon dioxide) at a flow of 5 L/min. As a result of waste heat treatment, the biomass was carbonized. The comparison of the waste microstructure before and after the pyrolysis process obtained by means of a scanning electron microscope (over 500x) is shown in **Figs. 1–4 [L. 10]**.

a) b)

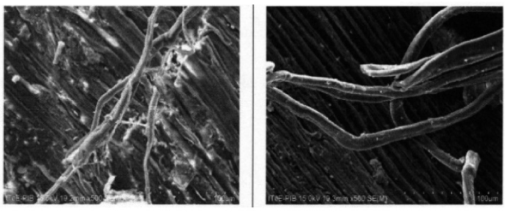

Fig. 1. The picture of the microstructure of flax straw: a) before pyrolysis, b) after pyrolysis

Rys. 1. Obraz mikrostruktury paździerzy lnianych: a) przed pirolizą, b) po pirolizie

a) b)

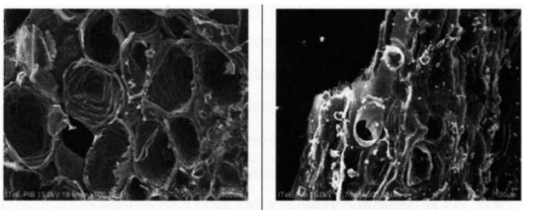

Fig. 2. The picture of the microstructure of corn maize: a) before pyrolysis, b) after pyrolysis

Rys. 2. Obraz mikrostruktury kukurydzy: a) przed pirolizą, b) po pirolizie

a) b)

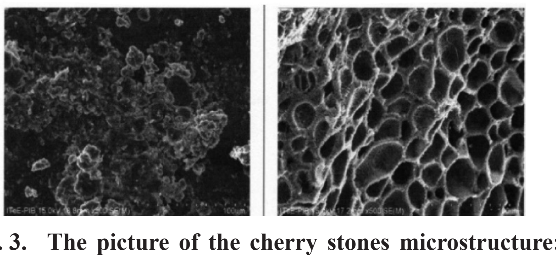

Fig. 3. The picture of the cherry stones microstructure: a) before pyrolysis, b) after pyrolysis

Rys. 3. Obraz mikrostruktury pestek wiśni: a) przed pirolizą, b) po pirolizie

a) b)

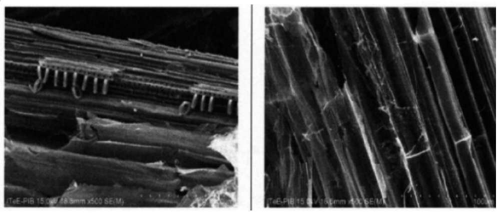

Fig. 4. Image of wheat straw microstructure: a) before pyrolysis, b) after pyrolysis
Rys. 4. Obraz mikrostruktury słomy pszenicznej: a) przed pirolizą, b) po pirolizie

Based on the analysis of the obtained microscopic images, it can be concluded that the used plant waste wheat straw, flax straw, and maize corn retained their fibrous structure after the pyrolysis process, while in the case of cherry stones after the pyrolysis process, a porous structure with open spaces is observed.

The characterized biocarbons were used to prepare grease samples of the second consistency class. The subject of research were compositions of greases with the participation of biocarbon in which biocarbon derived from the pyrolysis of plant waste was added to the initial grease (90% highly refined mineral oil+10% lithium thickener-stearate produced in the Ł-ITEE laboratory). The homogenization of the grease mixture with biocarbon was carried out in a laboratory Z-mixer at room temperature for 30 minutes. The compositions and determinations of the samples are shown in **Table 1**.

Table 1. The plastic greases tested
Tabela 1. Smary plastyczne poddane badaniom

Sample symbol	The composition of the grease
Initial sample	Highly refined mineral oil 90% + thickener (lithium stearate) 10%
Cherry stones	Initial sample + 5% m/m biocarbon from cherry stones
Corn maize	Initial sample + 5% m/m biocarbon from corn maize
Flax straw	Initial sample + 5% m/m biocarbon from flax straw
Wheat straw	Initial sample + 5% m/m biocarbon from wheat straw

METHODOLOGY OF TRIBOLOGICAL RESEARCH

The T-02 four-ball apparatus was used to determine the tribological properties of the tested lubricating 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 was made 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 PN-76 / C-04147. However, the measurement of lubricating properties under scuffing conditions (i.e. under constantly increasing load during the test run) was carried out in accordance with the methodology developed by Ł-ITEE **[L. 11]**. 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. When there is a sudden increase in the frictional moment, the node load level is referred to as P_t scuffing load. The measurement was carried out until the limit friction moment of 10 Nm was reached or the maximum load of the 7200N apparatus. This point is defined as the limiting load of seizure P_{oz}. The limiting pressure of seizure (p_{oz}) is a measure of anti-seizing greases under seizing conditions. This parameter was determined by calculating its value in accordance with the formula: $p_{os} = 0.52 * P_{os}/d_{oz}^2$, where P_{oz}– limiting load of seizure, and d_{oz}– 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.

METHODOLOGY OF PHYSICOCHEMICAL TESTS

The dropping point of grease was measured according to PN-ISO 2176: 2011. The principle of the determination was to determine the temperature at which the first drop of lubricant flows out of the test vessel during its even heating. The arithmetic mean of three measurements and indications of two thermometers was taken as the result of the determination, i.e. from a test tube with a tested grease and an oil bath.

The grease penetration test was carried out according to PN-ISO 2137:2011. The method of determination consists in measuring the depth of gravitational immersion, a normalized cone in the tested grease, at a temperature of 25°C, falling within 5 seconds. Penetration is expressed in “penetration units” (unnamed number corresponding to 0.1 mm of the taper cavity in the grease tested). The result was the arithmetic average of three measurements.

The study of thermo-oxidative stability was carried out using a PetroOxy apparatus. A sample of 5 g of grease was introduced into the test chamber of the device and subjected to oxygen oxidation at a constant temperature of 120°C. The filling pressure was 700 kPa and the oxygen pressure was 8 bar (800 kPa). The final result was the time necessary to achieve a 10% drop in maximum pressure in the measuring chamber.

RESULTS

Figure 5 shows the impact of biocarbon additives used on anti-wear properties (G_{oz} limiting load of wear) of test greases.

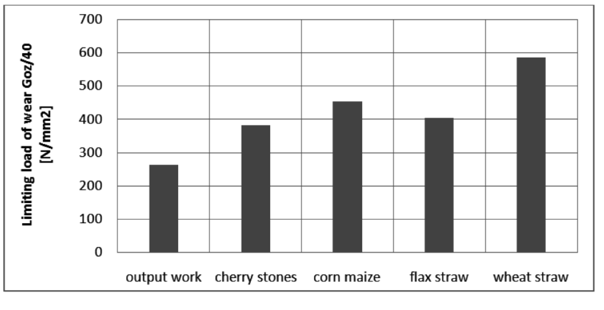

Fig. 5. The effect of biocarbon on anti-wear properties (G_{oz} limiting load of wear) of plastic greases
Rys. 5. Wpływ biowęgli na właściwości przeciwzużyciowe (graniczne obciążenie zużycia Goz) smarów plastycznych

Based on the results obtained (**Fig. 5**), it can be observed that all biocarbon used significantly increase the limiting load of wear (G_{oz}). The best results were obtained for biocarbon, which have a fibrous structure (corn maize, flax straw, wheat straw). For flax straw and corn maize, we note an increase in the limiting load of wear (G_{oz}) from about 50 to 70%, while, in the case of biocarbon derived from pyrolysis of wheat straw, we observe about a double (over 100%) increase in the limiting load of wear compared to the initial sample. It can be concluded that the used biocarbon with a fibrous structure, especially those derived from wheat straw pyrolysis, favour the formation on the surface of cooperating steel balls of a protective layer with high adhesion preventing excessive wear. This effect can be caused by the ordered structure biocarbon or good sorption properties of this additive. However, this requires confirmation by further research.

Anti-seizing properties of greases using biocarbon, the measure of which is, among others, the limiting pressure of seizure (p_{oz}) is shown in **Fig. 6, Figures 7–11** contain examples of moments of friction change as a function of linearly increasing load.

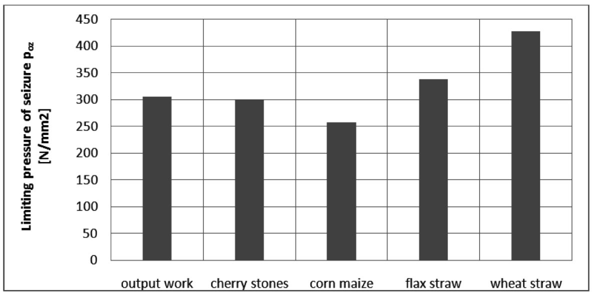

Fig. 6. The effect of biocarbon on anti-seizing properties (limiting pressure of seizure p_{oz}) of plastic greases
Rys. 6. Wpływ biowęgli na właściwości przeciwzatarciowe (graniczny nacisk zatarcia p_{oz}) smarów plastycznych

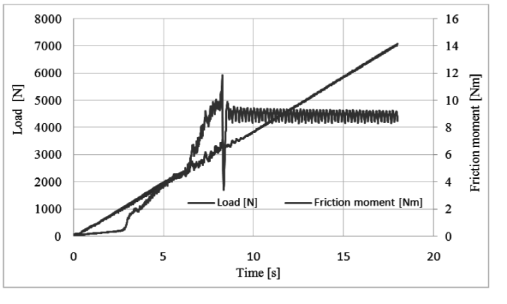

Fig. 7. The course of changes in the moment of friction of a steel – steel combination lubricated with plastic grease without additives (initial sample)
Rys. 7. Przebieg zmian momentu tarcia skojarzenia stal – stal smarowanego smarem plastycznym bez dodatków (próbka wyjściowa)

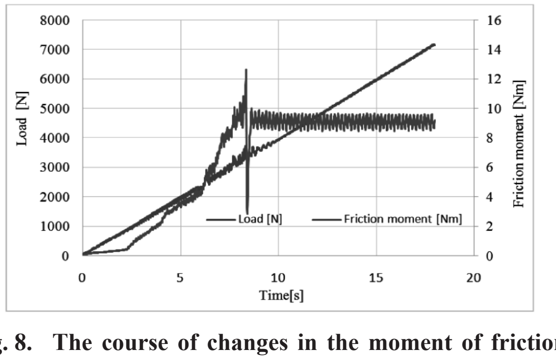

Fig. 8. The course of changes in the moment of friction a steel – steel combination lubricated with plastic grease with the participation of biocarbon from cherry stones pyrolysis
Rys. 8. Przebieg zmian momentu tarcia skojarzenia stal – stal smarowanego smarem plastycznym z udziałem biowęgla z pirolizy pestek wiśni

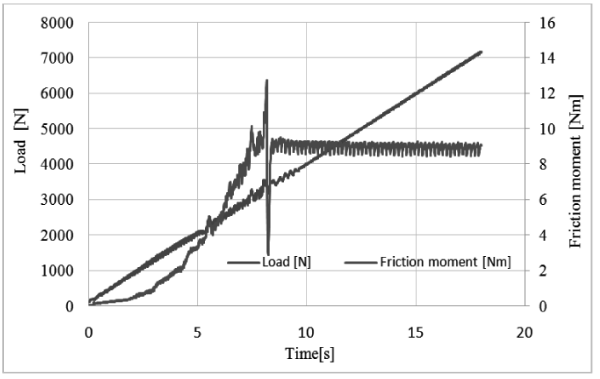

Fig. 9. The course of changes in the moment of friction a steel – steel combination lubricated with a plastic grease with the addition of biocarbon from corn maize pyrolysis

Rys. 9. Przebieg zmian momentu tarcia skojarzenia stal – stal smarowanego smarem plastycznym z dodatkiem biowęgla z pirolizy kukurydzy

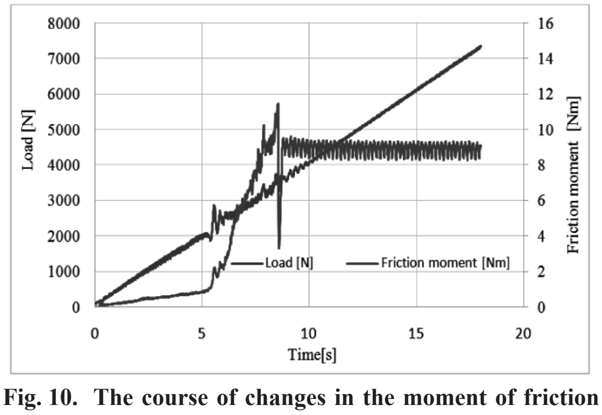

Fig. 10. The course of changes in the moment of friction a steel – steel combination lubricated with plastic grease with the participation of biocarbon from flax straw pyrolysis

Rys. 10. Przebieg zmian momentu tarcia skojarzenia stal–stal smarowanego smarem plastycznym z udziałem biowęgla z pirolizy paździerzy lnianych

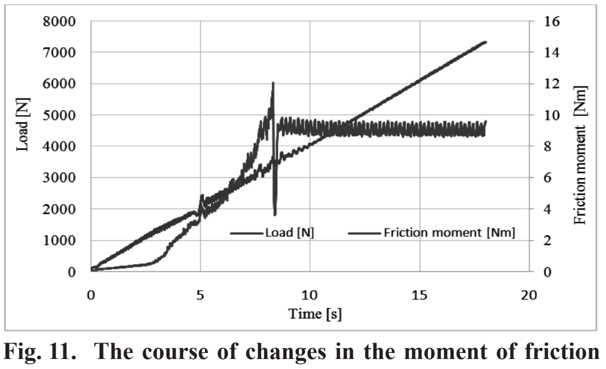

Fig. 11. The course of changes in the moment of friction a steel – steel combination lubricated with plastic grease with the participation of biocarbon from wheat straw pyrolysis

Rys. 11. Przebieg zmian momentu tarcia skojarzenia stal–stal smarowanego smarem plastycznym z udziałem biowęgla z pirolizy słomy pszenicznej

The impact of biocarbon on the anti-seizing properties of greases is more diverse than on their anti-wear properties. Some biocarbon, such as those derived from cherry stones pyrolysis, do not affect the change in the value limiting pressure of seizure (p_{oz}), and biocarbon from corn maize adversely affects the change (p_{oz}). The value of the limiting pressure of seizure (p_{oz}) is, in this case, about 15% lower than for the initial grease. Similarly as in the case of anti-wear properties, the best results were obtained for the plastic grease with the addition of biocarbon from wheat straw pyrolysis. The limiting pressure of seizure (p_{oz}) for this grease is about 40% higher than for the initial grease without additives.

Another parameter determining the anti-seizing properties of greases, including plastic greases, is the indicator scuffing load (P_t) determined in conditions of linearly increasing load. On its basis, we conclude the initiation of the blurring process. **Figure 12** shows the impact of biocarbon on changes in this parameter.

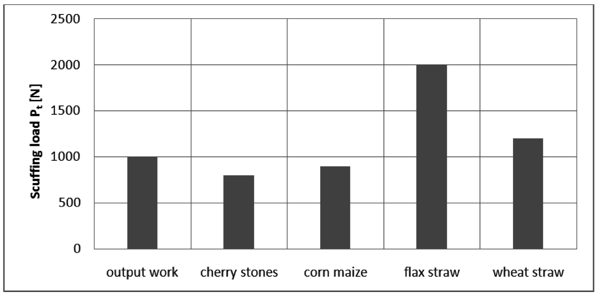

Fig. 12. The impact of biocarbon on changes in the scuffing load indicator (P_t) of developed grease compositions

Rys. 12. Wpływ biowęgli na zmiany wskaźnika obciążenia zacierającego (Pt) opracowanych kompozycji smarów plastycznych

From the data presented in **Fig. 12**, it follows that the scuffing load indicator (P_t) for plastic greases with biocarbon from cherry stones and corn maize pyrolysis, similar to the limiting pressure of seizure (p_{oz}), is slightly lower than for the initial sample. For plastic greases containing biocarbon from the pyrolysis of flax straw and wheat straw, we observe a clear increase in the scuffing load indicator (P_t), and the largest load is about twice as high in the case of flax straw. This suggests that, for this biocarbon, the durability of the lubricating film formed on the surface of cooperating steel balls is the greatest. In conclusion, the obtained results of research on the impact of biocarbon on the tribological properties of plastic greases indicate that they depend on the type, including biocarbon microstructure and potentially also on their surface and adsorption properties. The greases containing biocarbon with a fibrous structure produced from flax straw and wheat straw have the best tribological properties.

PHYSICOCHEMICAL PROPERTIES OF PLASTIC GREASES CONTAINING BIOCARBON

Beyond the friction and wear characteristics of plastic greases, their physicochemical properties affecting operation are also important. These properties include, but are not limited to the dropping point of the grease, penetration, and oxidative stability. **Figures 13–15** show the impact of biocarbon additives on changes in the parameters listed.

Fig. 13. The dropping point of biocarbon greases
Rys. 13. Temperatura kroplenia smarów plastycznych zawierających biowęgle

One of the basic parameters for plastic greases is the dropping point of grease, which is a measure of the beginning of destruction (degradation) of the sponge structure of the thickener and the separated liquid phase from the grease composition. The dropping point of grease depends essentially on the type of thickener, the method of obtaining grease, as well as the presence of other additives. The data presented in **Fig. 13** shows that the biocarbons of plant origin used as tribological additives do not significantly change the dropping point of grease, and the observed differences are within the error of measurement.

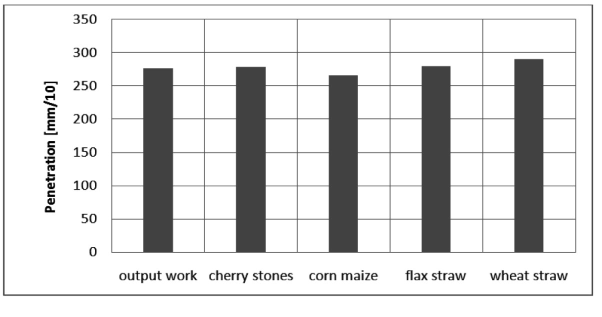

Fig. 14. The impact of biocarbon on the penetration of greases
Rys. 14. Wpływ biowęgli na penetrację smarów plastycznych

The introduction to the grease 5% by weight biocarbons also does not cause changes in the consistency class, which results from the penetration measurement data given in **Fig. 14**. All tested greases have a second (2) consistency class according to NLGI classification.

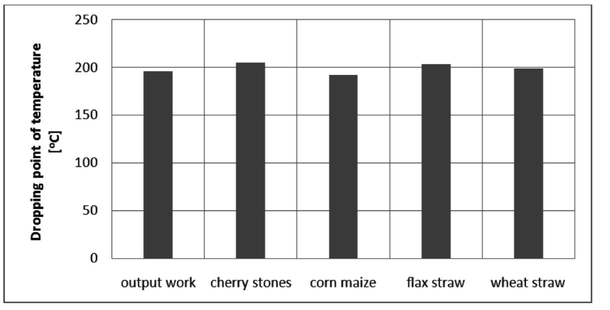

Fig. 15. The oxidative stability of biocarbon plastic greases
Rys. 15. Stabilność oksydacyjna biowęglowych smarów plastycznych

Based on the data presented in **Fig. 15**, it can be concluded that biocarbon greases have a lower oxidation stability than the original sample. Biocarbon greases obtained as a result of corn maize and flax straw pyrolysis were characterized by a significantly lower oxidation time than the initial sample; whereas, the grease with the addition of biocarbon from wheat straw was characterized by only about 4% decrease in the oxidation time compared to the initial sample.

CONCLUSIONS

Tests on tribological properties (anti-wear and anti-seizing) have shown that biocarbon from plant waste have a positive effect on friction and wear characteristics of plastic greases. The tribological properties of plastic greases with biocarbons depend on their qualitative composition as well as the physical structure and surface properties of the biocarbon used in the experiment. Based on the tribological characteristics of mineral-based plastic greases, it can be observed that the use of biocarbon with fibrous structure obtained from the waste of corn maize, flax straw, and wheat straw as better functional results gives. In the case of these biocarbon, a significant increase in the anti-wear and anti-seizing parameters of the developed plastic greases was noted compared to the original sample. Identification of the mechanism of biocarbon interactions in the friction node and their impact on the tribological properties of plastic greases, however, requires additional tests to determine the structure and properties of biocarbon, as well as surface analyses of friction steel cooperating. Biocarbon additives in an amount of 5% wt do not change the consistency and dropping point of greases; however, in some cases, they cause a decrease in oxidative stability. Biocarbon plastic greases containing pyrolysis products of plant waste can be used to lubricate such tribological systems as truck tractor saddles, joints, spring leaves, and thus can be an alternative to classic graphite greases. Taking into account the tested operational parameters of the test compositions, biocarbon additives obtained from wheat straw can be recommended as an effective substitute for graphite in plastic greases.

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