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THE COMPARATIVE ANALYSIS OF ECOLOGICAL LUBRICANTS

ANALIZA PORÓWNAWCZA PROEKOLOGICZNYCH ŚRODKÓW SMAROWYCH

Key words: lubricant based on *Crambe Abyssinica* seed oil, thermal and mechanical stress, wear test, oxidation resistance, complex modulus.

Abstract: On the base of rheological tests, the resistance to deformation of lubricants elaborated on the base of *Crambe abyssinica* seed oil was evaluated. The developed lubricants were subjected to thermal and mechanical stresses, which allowed the evaluation of their resistance to the oxidation process and anti-wear properties. After tests, the rheological properties of tested lubricants were carried out by determining the complex modulus in oscillation tests. On the base of the rheological parameter, the resistance of lubricants to deformation and change of this indicator under the influence of thermal and mechanical stresses was evaluated. The carried out analysis of changes in the G* complex modulus showed that the tested lubricants show a different resistance to deformation depending on their type and depending on the impact of the extortion. It was found that the rheological index (complex modulus G*) determined in oscillation tests can be a successful criterion for the quality of pro-ecological lubricants.

Słowa kluczowe: środek smarowy na bazie oleju z nasion *Crambe Abyssinica*, wymuszenia cieplne i mechaniczne, test zużyciowy, odporność na utleniania, kompleksowy moduł zespolony.

Streszczenie: Na podstawie testów reologicznych oceniono odporności na deformację środków smarowych opracowanych na bazie oleju z nasion *Crambe abyssinica.* Opracowane środki smarowe poddano działaniu wymuszeń cieplnych i mechanicznych, co umożliwiło ocenę ich odporności na proces utleniania i właściwości przeciwzużyciowych. Po przeprowadzonych testach wyznaczono właściwości reologiczne badanych środków smarowych, wyznaczając moduł zespolony w testach oscylacyjnych. Na podstawie parametru reologicznego oceniono odporność smarów na odkształcenia i zmianę tego wskaźnika pod wpływem wymuszeń cieplnych i mechanicznych. Przeprowadzona analiza zmian modułu zespolonego G* wykazała, że badane środki smarowe wykazują zróżnicowaną odporność na odkształcenia w zależności od ich rodzaju oraz w zależności od oddziaływania wymuszeń. Stwierdzono, że wskaźnik reologiczny (moduł zespolony G*) wyznaczony w testach oscylacyjnych może z powodzeniem stanowić kryterium jakości proekologicznych środków smarowych.

INTRODUCTION

Technical progress occurring in industry and agriculture caused an increase in the exploitation of natural petroleum oil resources. The increase in consumption raises legitimate concerns about the exhaustion of valuable raw materials, which is a direct reason for the intensification of research in terms of the search and adaptation of alternative raw materials. On the other hand, the strain on the environment of processed petroleum products is a great ecological threat to soil, groundwater and

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organisms living in them **[L. 1, 2]**. In this situation, there is a real need to search for substitutes and develop new technologies for the production of lubricants according to the latest trends regarding products that are least harmful to the environment **[L. 3–4]**. Increasingly, inedible vegetable oils are used as oil bases, which successfully replace synthetic bases due to their favourable properties **[L. 5–9]**. Lubricants based on renewable raw materials should be characterised by functional properties comparable to products of petroleum origin because, as their substitutes, they must provide the required durability of the lubricated tribosystems of machines and devices **[L. 10–12]**.

At the same time, with the ever-increasing environmental awareness and sustainable development policies, the use of vegetable oils to produce products with higher added value, such as environmentally friendly lubricants, is becoming increasingly popular. The use of non-edible vegetable oils, including oil from seed *Crambe Abyssinica*, with resistance to oxidation comparable to mineral oils, opens up a new perspective for environmentally friendly lubricants **[L. 13–15]**.

Determining the characteristics concerning the stability of environmentally friendly lubricants has significant practical importance because these lubricants' tendency to irreversible physical or chemical changes causes the deterioration or loss of functional properties, which in turn leads to the elimination of the lubricant from further exploitation. The above recommendations also concern lubricants developed on the base of renewable raw materials, because as substitutes for petroleum products, they must fulfil planned functions and thus provide the required durability of lubrication systems of tribosystems **[L. 16]**.

The impact assessment of the oxidation process and thermal and mechanical extortions on the change of functional properties is an important aspect of research works on developing new, environmentally friendly lubricants, particularly based on vegetable oil **[L. 12, 18]**. The classification and specification systems define the ranges and acceptable limits of indicators of physicochemical properties or values of test parameters obtained under defined conditions. Changes occurring in lubricants during exploitation are mainly related to the influence of oxygen, increased temperature, the catalytic effect of metals and the influence of mechanical forces. These factors cause irreversible changes in the chemical composition of lubricants, leading to the deterioration of their quality and, consequently, loss of functional properties **[L. 15-18]**. One of the most important criteria for evaluating the suitability of vegetable oils for technical applications is their resistance to the oxidation process **[L. 15]**.

This paper presents the results of rheological tests of lubricants obtained on the base of inedible oil from seeds *Crambe Abyssinica* and on the base of mixtures of this oil with synthetic oil. The influence of components, in particular the content of vegetable oil, on the change of resistance to the oxidation process and the lubricating and rheological properties of the developed inorganic lubricants were presented. The influence of mechanical and thermal extortions carried out in tribological and thermo-oxidative tests on the change of resistance to deformation determined in rheological tests based on oscillation tests was evaluated.

MATERIALS AND METHODOLOGY OF RESEARCH

The test samples were grease (AB_100) developed on the base of vegetable oil from seeds *Crambe Abyssinica* and grease (AS_63) based on a mixture of vegetable oil and polyalphaolefin synthetic oil. The greases contained an inorganic thickener in the amount of 7% and 1.5% of the multifunctional additive Brad-Chem 351 from BRAD-CHEM Ltd, containing an EP/AW additive, an antioxidant and a corrosion inhibitor. The designation of the tested lubricants before and after the tests is summarised in **Table 1**. The prepared lubricant samples were carried out to the oxidation process at 80^{o}C and 120^{o}C (AB_100_80, AB_100_120, AS_63_80, AS_63_120) and the effect of mechanical extortions in hour-long wear test (AB_100_G_{oz}, AS_63_G_{oz}). After tests, the rheological properties were carried out, and on this base, the influence of the extortions on the change of resistance on the deformation of the tested vegetable lubricants was evaluated.

The PetroOxy™ apparatus by Petrotest Instruments was used to evaluate the thermo-oxidative stability of oil bases. The principle of the method was to pass oxygen through the 10 g lubricant sample, heated to 80 and 120^{o}C. The oxidative stability of the tested greases was carried out, and the time of pressure reduction by 10% was adopted as the evaluation criterion, **Table 1**.

Anti-wear properties were determined using the T-02 tribological tester in accordance with the PN-76/C-04147 standard, with the tribosystem load of 392 N, the spindle speed of 500±20 rpm and for 1 hour. The measure of wear resistance was the diameter of the flaws formed on the surfaces of the balls and the limiting load of wear, **Table 1**.

The rheological properties of the grease were determined using the classic rotational rheometer MCR-101 with air bearing by Anton Paar. The measurements were carried out using a cone-plate measuring system (CP25-1). The tests were carried out in an oscillatory mode at a temperature range of 20–120^{o}C, with a constant strain of 0.5% and a constant frequency of 1Hz. The control of the rheometer and the analysis of measurement data were carried out using the Rheoplus software. The dependence of the complex modulus (G*) on the temperature was determined, with the storage modulus (G') and the loss modulus (G') at the same time. The applied methodology allowed the comparison of deformation on resistance of lubricants before and after the tests: after an hour-long wear test and PetroOxy, **Table 2**.

Table 1. The type and designation of tested greases
Tabela 1. Rodzaj i oznaczenie badanych smarów

The type of grease	Designated of greases*			
	before tests	**after PetroOxy tests in temp. 80^{o}C**	**after PetroOxy tests in temp. 120^{o}C**	**after an hour-long wear test, G_{oz}**
Grease on oil base from seeds *Crambe Abyssinica* **Grease AB_100**	**AB_100**	**AB_100_80**	**AB_100_120**	**AB_100_G_{oz}**
Grease on mixed base oil from seeds *Crambe Abyssinica* and polyalphaolefin oil SpectaSyn 100 **Grease AS_63**	**AS_63**	**AS_63_80**	**AS_63_120**	**AS_63_G_{oz}**

* The meaning of symbols next to the name of grease:
– the symbol "100" means the content of vegetable oil in grease in %,
– the symbol "63" means the content of vegetable oil in grease in %,
– the symbol "80" means the temperature of tests in ^{o}C,
– the symbol "120" means the temperature of tests in ^{o}C,
– the symbol "G_{oz}" means the anti-wear test.

RESULTS

The obtained results of resistance grease on thermal oxidation carried out by the PetroOxy method at 80^{o}C and 120^{o}C in the oxidising atmosphere are presented in **Table 2**. The anti-wear properties of the tested greases were determined in an hour-long wear test by evaluating the wear scar and calculating the limiting load of wear G_{oz} with the formula: $G_{oz} = 0.52*(P/d^2)$, where: d – mean diameter of the friction scar, and P is a load of tribosystem. The obtained results are presented in **Table 2**.

The analysis of obtained results confirmed the significant effect of the dispersing phase on the anti-wear properties of vegetable lubricants, which directly affected the values of limiting load of wear G_{oz}. Comparable lubricating properties characterise grease based on vegetable oil AB_100

Table 2. The lubricating properties and oxidation stability for the greases AB_100, AS_63
Tabela 2. Właściwości smarne i stabilność oksydacyjna smarów AB_100, AS_63

The type of grease	Parameters			
	The oxidation induction time, h		**The anti-wear properties**	
	temp. 80^{o}C	**temp. 120^{o}C**	**d, mm**	**G_{oz}, N/mm^2**
Grease AB_100	81	6,6	0,43	1123
Grease AS_63	132	19	0,44	1058

to grease AS_63, which was developed based on vegetable-synthetic oil. However, the difference relies on thermo-oxidative stability. Vegetable grease is characterised by lower stability, expressed by oxidation induction time, than grease based on mixed vegetable and synthetic oil bases.

The resistance of the greases on deformation under the influence of thermal and mechanical extortions was determined on the basis of oscillation tests carried out in conditions of rheological measurements. The complex modulus G*'s dependences from the constant strain and frequency temperature were determined. The tested lubricants were subjected exposed to temperatures in the range of 20–120°C in order to evaluate the resistance of lubricants to deformation caused by these temperatures, **Fig. 1–3**. First, the influence of content the dispersion phase in lubricants on deformation was evaluated by comparing the total resistance based on the complex modulus (|G*|) in the temperature range of 20–120°C, **Fig. 1**.

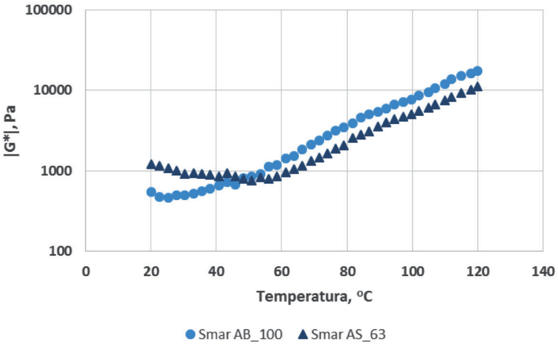

Fig. 1. The resistance of lubricants (AB_100, AS_63) on deformation G* determined in rheological tests, in constant frequency conditions of 1 Hz and at the deformation of 0.5%, in temperature range 20–120°C

Rys. 1. Odporność smarów (AB_100, AS_63) na odkształcenie G* wyznaczone w testach reologicznych w warunkach stałej częstotliwości 1 Hz i przy odkształceniu 0,5% w zakresie temperatury 20–120°C

The grease based on vegetable oil characterised a lower resistance to deformation caused by temperature than grease produced with a mixed vegetable/synthetic oil base AS-63. The grease AB-100 only up to 30°C shows the stability of the G* complex modulus, while in the case of the grease AS_63, a two-time increase of the stability range of this G* modulus up to the temperature of 60°C was observed. This shows that the structure of the grease AS_63 is more resistant to the deformation process than the vegetable grease AB_100 in the temperature range of 20–120°C.

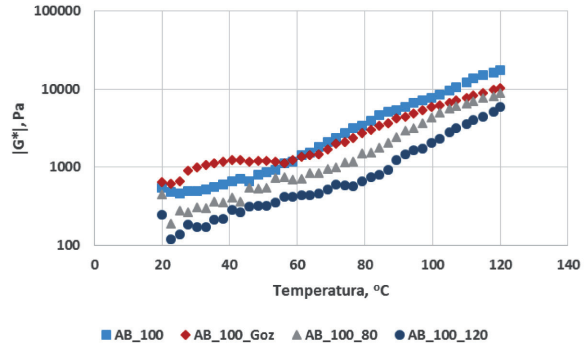

Fig. 2. The comparison of resistance on deformation G* of grease AB_100, after tribological test (AB_100_Goz) and oxidation stability tests, carried out at 80°C (AB_100_80) and 120°C (AB_100_120), determined in rheological tests, in constant frequency conditions of 1 Hz and at the deformation of 0.5%, in temperature range 20–120°C

Rys. 2. Porównanie odporności na odkształcenie G* smaru AB_100 po testach stabilności oksydacyjnej przeprowadzonej w temperaturze 80°C (AB_100_80) i 120°C (AB_100_120) oraz teście tribologicznym (AB_100_G_{oz}), wyznaczone w testach reologicznych w warunkach stałej częstotliwości 1 Hz i przy odkształceniu 0,5% w zakresie temperatury 20–120°C

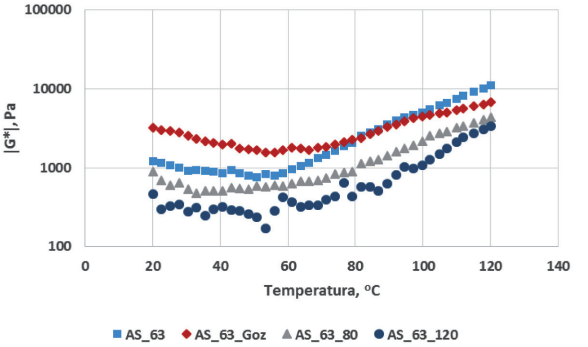

Fig. 3. The comparison of resistance on deformation G* of grease AS_63, after tribological test (AS_63_G_{oz}) and oxidation stability tests, carried out at 80°C (AS_63_80) and 120°C (AS_63_120), determined in rheological tests, in constant frequency conditions of 1 Hz and at the deformation of 0.5%, in temperature range 20–120°C

Rys. 3. Porównanie odporności na odkształcenie G* smaru AS_63, po teście tribologicznym (AS_63_G_{oz}) oraz po teście stabilności oksydacyjnej przeprowadzonym w temperaturze 80°C (AS_63_80) i 120°C (AS_63_120), wyznaczone w testach reologicznych w warunkach stałej częstotliwości 1 Hz i przy odkształceniu 0,5% w zakresie temperatury 20–120°C

After the oxidation stability test carried out at the temperature of 80°C and 120°C, the resistance of lubricants to deformation caused by these temperatures was determined in model rheological tests. It has been assumed that the working temperature of the tribosystem, where the

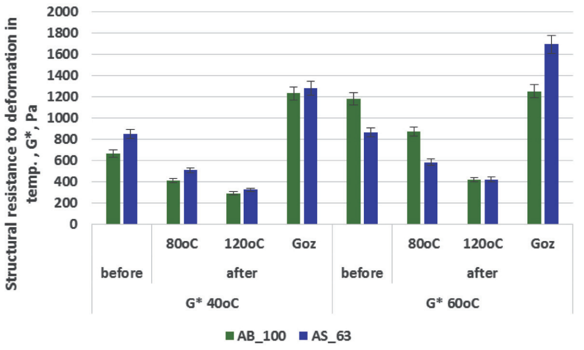

Fig. 4. Change of resistance on deformation of greases before and after thermal and mechanical tests
Rys. 4. Zmiana odporności na odkształcenia smarów przed i po wymuszeniach cieplnych i mechanicznych

lubricants will be applied, is a maximum of 60°C because below this temperature, the change of the resistance lubricants on deformation was evaluated, **Figs. 2, 3**.

Based on carried out experimental work, it was found that the vegetable grease (grease AB_100) and grease on a mixed oil base (AS_63) subjected to the thermo-oxidation process at 120°C showed a significant reduction of resistance to deformation (**Fig. 4**).

After PetroOxy tests (oxidative stability), a decrease in the resistance of greases on deformation caused by temperature was recorded, whereby grease containing a vegetable-synthetic oil base showed higher resistance to thermo-oxidative stresses than vegetable grease. At the exemplary working temperature of 60°C, the greases after the oxidation stability tests carried out at 80°C showed various resistance changes on deformation. In the case of grease AB_100, there was a decrease of approx. 42%, and in case of grease AS_63 by approx. 33%. The greatest changes were observed after thermo-oxidative tests carried out at 120°C, which were at the level of approx. 65% in the case of vegetable grease AB_100. However, after wear tests (G_{oz}) in the case of the evaluated greases, an increase in resistance to deformation was observed, which may indicate the reconstruction of the structure and its strengthening.

On the base of rheological tests, comparing the total resistance of greases on deformation (complex modulus G*) after the action of extortions, it is possible to evaluate the structural integrity of dispersion of the oil-thickener system during the exposure to increased temperature. Knowledge of the rheological properties of greases is important due to the working conditions of lubricated tribosystems. The analysis of rheological parameters allows the appropriate selection of lubricants with required rheological parameters for the tribosystems.

CONCLUSIONS

The developed pro-environmental lubricants are intended for use in the food zone of machines and devices of the agri-food industry, requiring food safety and hygiene behaviour during the production cycle. The innovative lubricants as products with ecological features are intended for use in tribosystems of machines exposed to thermal and mechanical extortions and require the use of certified lubricants.

The main purpose of the proposed rheological tests is to precisely fit the grease to the working conditions, without the risk of unfavourable thermal degradation processes during the formation of the lubricating layer, depending on the technological process conditions. Based on the determined rheological parameters, it is possible prevention of unfavourable degradation processes of the lubricant structure during the lubrication of tribosystems. The demonstrated relationship between the results of rheological tests and the structure's resistance to thermo-oxidative and mechanical extortions will allow for the selection of the proper grease for the working conditions.

The previous research with exploitation has confirmed a high service life of lubricants and their protective and corrosion function. The results of exploitation tests carried out in technological lines of the sugar and vegetable processing industry confirmed the high quality and durability of the developed lubricants in extreme conditions, which predestine these lubricants for use in machines and devices used in technological lines of food production in the food industry **[L. 17,18]**. Verifying the quality of the developed lubricants in extreme working conditions, i.e., in the conditions of dust, moisture, temperature and water environment, predestine these lubricants for use in other branches of the food industry, in conditions of thermal and mechanical extortions during exploitation.

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