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TRIBOLOGICAL PROPERTIES OF BLACKBERRY WASTE SEED EXTRACT OBTAINED UNDER SUPERCRITICAL CO_2 CONDITIONS WITH SORBITAN ESTERS COMPOSITONS

WŁAŚCIWOŚCI TRIBOLOGICZNE KOMPOZYCJI EKSTRAKTU Z ODPADOWYCH NASION JEŻYNY OTRZYMYWANEGO W WARUNKACH NADKRYTYCZNEGO DWUTLENKU WĘGLA Z ESTRAMI SORBITANU

Key words: blackberry extract, extraction under supercritical carbon dioxide conditions, sorbitan esters.

Abstract

This paper presents results of tribological research of a composition containing as a base, extract of waste blackberry seeds obtained by extraction under supercritical carbon dioxide conditions with sorbitan esters as additives (sorbitan trioleate (STO) sorbitan monolaurate (MLS) and etoxylated sorbitan monolaurate (EO20MLS)). The influence of the concentration of surfactants on the motion resistance, wear and anti-seize properties of the obtained lubricants was analysed. Two types of tests were performed: seizure, with linear load increase and constant load (four-ball device T02). The obtained test results compared to the results for the base (pure extract) to paraffin oil and rapeseed oil were related. It was found that the addition of sorbitan esters to the extract has a greater effect on the improvement of anti-seizure properties than on the reduction of resistance to movement and wear to the base.

Słowa kluczowe: ekstrakt z jeżyny, ekstrakcja w warunkach nadkrytycznego CO_2, estry sorbitanu.

Streszczenie

W artykule przedstawiono wyniki badań tribologicznych kompozycji smarowych zawierających jako bazę ekstrakt z odpadowych nasion jeżyny pozyskany metodą ekstrakcji w warunkach nadkrytycznego dwutlenku węgla i jako dodatki estry sorbitanu: trioleinian sorbitanu (STO), monolaurynian sorbitanu (MLS) i oksyetylenowany 20 molami tlenku etylenu monolaurynian sorbitanu (EO20MLS). Analizowano wpływ stężenia i rodzaju surfaktanta na opory ruchu, zużycie oraz właściwości przeciwzatarciowe otrzymanych środków smarowych. Wykonano dwa rodzaje testów: zatarciowe, z liniowym narostem obciążenia oraz przy stałym obciążeniu (aparat czterokulowy-T02). Otrzymane wyniki badań odniesiono do rezultatów otrzymanych dla bazy (czysty ekstrakt) oraz do oleju rzepakowego i parafinowego. Stwierdzono, że dodatek estrów sorbitanu do ekstraktu w większym stopniu wpływa na polepszenie właściwości przeciwzatarciowych niż na obniżenie oporów ruchu i zużycia względem bazy.

INTRODUCTION

Activities aimed at environmental protection, such as limiting the use of oils and working fluids based on crude oil, has resulted in the search for new, biodegradable lubricating bases with good tribological properties and non-toxic lubricating additives. Currently, the subject of lubricants is also strongly influenced by trends related to "clean technologies" through the use of waste materials and elimination of additives modifying the lubricating properties, i.e. molybdenum disulphide, graphite, and boron nitride [**L. 1–8**].

Data from literature [**L. 9–11**] indicate high interest in the use of berry extracts, including blackberry extract, obtained under supercritical CO_2 conditions for manufacture of cosmetics, pharmaceuticals, and products for household and chemistry industries. The raw materials are easily extracted from the waste following the process of juice and fruit production.

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Poland is a significant producer of berry seeds, mainly for feed purposes. About 300–350 thousand tons of marc (pomace) are produced annually, of which 30–50% are seeds. The raw materials are often processed using new technologies, depending on the purpose of the final product. Of special interest are products obtained by supercritical extraction with the use of carbon dioxide. These include hydrophobic extracts, oleoresins, unsaturated oils, polyphenols, and many other substances. This is a modern and competitive technology, in which the process of obtaining the extract is carried out at a low temperature and the main extracting agent is carbon dioxide compressed to approximately 300 bar. After the process, the CO_2 escapes from the extract and is returned to production. Due to the lack of air, the extract is characterized by very high purity (no residual solvent) and efficiency [**L. 9**].

The paper describes research on a lubricating substance in which the base oil was blackberry seed extract (Rubus fruticosus) obtained by supercritical extraction by use of carbon dioxide, the active additives were sorbitan esters. The choice of this group of surfactants was dictated by the fact that they are fat and sugar derivatives obtained in the esterification reaction of sorbitol with fatty acids. In addition, they are non-toxic and biodegradable. MLS and its oxyethylene derivatives have already been used as additives to improve the lubrication of paraffin oil [**L. 12**]. The research showed that the applied additives positively modified the tribological properties as a base.

MATERIALS AND METHODS

The research material consisted of lubricating compositions based on blackberry seed extract (blackberry oil), obtained under conditions of supercritical extraction with the use of carbon dioxide as an extracting agent. The extract was obtained at the Institute of New Chemical Syntheses in Puławy. Active additives used were the following: sorbitan trioleate (Sorbitan Trioleate, STO), sorbitan monolaurate (Sorbitan Monolaurate, MLS) and etoxylated with 20 moles of ethylene oxide sorbitan monolaurate (EO20MLS) from Fina Chemicals.

Tribological properties of blackberry seed oil without additives and compositions containing 0.01, 0.1, 1.0, and 10% by weight were studied. To compare the results, tests for Croda paraffin oil and Oleofarm rapeseed oil were also performed.

Tribological tests were carried out with the use of a four ball device (Tester – T02U) according to the following standards: ASTM D 2783, ASTM D 2596, ASTM D 4172, ASTM D 2266, IP 239, DIN 51350 and the method developed by the ITeE – PIB in Radom, as presented in the literature [**L. 13–14**]. The test pieces were balls with a nominal diameter of ½", made of CRG 100 (EN ISO 68317) bearing steel and a roughness of 0.030 μm. Two types of studies were carried out:

- Tests were carried out under constant load, allowing the determination of changes in the resistance to movement in time, by individual lubricating compositions. A constant, pre-set load of 2 kN was applied. The tests were carried out at a constant speed of 200 rpm. The duration of the tests was 900 s. On the basis of the measurements, the diameter of the wear scar on test balls and the average coefficient of friction were determined. For the 900-second tests, the points on the figures were averaged over 30-second intervals and three independent measurement series.
- Tests were carried out with increases in linear load to determine the anti-seizure properties of the obtained lubricating compositions. On the basis of the measurements, scuffing load (Pt), seizure load (Poz) and limiting pressure of seizure (poz) were determined. Tests were performed at a speed of 409 N/s, a spindle speed of 500 rpm at the beginning load of the friction node 0 N at the temperature of 20°C. At least three test runs were made on each lubricant.

The Student's test was used to calculate the confidence limits of friction coefficient (μ), wear scar diameter (d), scuffing load (Pt), seizure load (Poz), and limiting pressure of seizure (poz). For a confidence level of 0.90, the intervals which were the measurement errors were determined

A typical dependence of the moment of the friction force as a function of the load is shown in **Fig. 1**. The scuffing load and seizure load is shown.

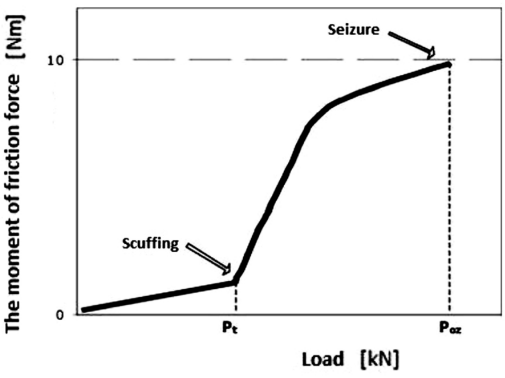

Fig. 1. Dependence of the moment of friction force on the load

Rys. 1. Zależność momentu siły tarcia od obciążenia

RESULT AND DISSCUSION

The influence of the type and concentration of sorbitan esters on movement resistance and wear was evaluated by means of the average friction coefficient (μ) and wear scar diameter (d) in the tests under constant load (2kN). The 900-second tests for pure blackberry extract and

mixtures of esters (MLS, EO20 MLS and STO) with the extract in the concentration range 0.01–10% were performed. The obtained results were referred to mineral oil as the most commonly used base oil and rapeseed oil as a plant base. The results are shown in **Figure 2** and **Figure 3**.

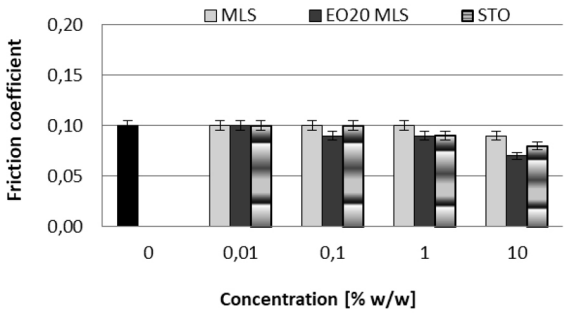

Fig. 2. Friction coefficient (μ) as function of concentration of sorbitan esters in the extract of blackberry seeds obtained by extraction under supercritical carbon dioxide conditions for the load 2 kN

Rys. 2. Zależność współczynnika tarcia od stężenia estrów sorbitanu w ekstrakcie z nasion jeżyny otrzymanym w warunkach nadkrytycznego dwutlenku węgla dla obciążenia 2 kN

For rapeseed oil as a reference, the average friction coefficient was 0.09, and for paraffin oil, the values were about 0.23%. It was concluded that the addition of sorbitan esters to the extract does not significantly affect the friction coefficient in comparison to the pure extract. The μ values for most of the analysed lubricating compositions oscillate at a level of approx. 0.10. Only the lubricating compositions containing 10% ethoxylated with 20 moles of sorbitan monolaurate (EO20 MLS) showed a decrease in the friction coefficient by about 20% compared to the base oil. Similar results were obtained by Wasilewski and Sułek for the discussed additive and paraffin oil as a base, carried out under the same conditions [**L. 12**]. It should be noted that the decrease of friction coefficient for the mixture containing 1% of additive was about twice as high as for base oil (μ = 0.1). A similar course of change is observed for the diameter of the wear scar after friction (**Fig. 3**).

It was found that, with the addition of three types of sorbitan esters to the concentration of 0.1% in the extract, the values of the measured wear scar diameter were almost identical to those of the base oil (about 0.7 mm). A slight decrease in d for compositions containing 1 and 10% EO20 MLS and STO in the extract to the value of approx. 0.6 mm is observed. However, it should be noted that the obtained values of the wear scar diameter are about 40% lower than for rapeseed oil (d = 1 mm) and about 2.5 times lower than for paraffin oil (d = 1.6 mm). It can be concluded that the compositions containing EO20 MLS and STO compounds and blackberry extract

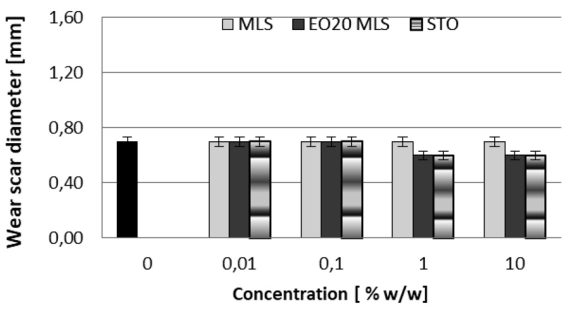

Fig. 3. Dependence of diameter of wear scar (d) on the concentration of sorbitan esters in the extract of blackberry seeds obtained by extraction under supercritical carbon dioxide conditions for the load 2 kN

Rys. 3. Zależność średnicy śladu zużycia od stężenia estrów sorbitanu w ekstrakcie z nasion jeżyny otrzymanym w warunkach nadkrytycznego dwutlenku węgla dla obciążenia 2 kN

have good lubricating properties, reducing wear of the friction couple elements.

Compared to the tests under constant load, the anti-seizure tests for lubricants are carried out under more extreme conditions. The speed of the load increase is decisive (409 N· s^{-1}). The load at which the moment of friction force increases significantly, which is the scuffing load (P_t), is one of the most important values characterizing the reliability of machines and devices. Under this load, the lubricant film is damaged and the seizure process begins. Therefore, P_t values can be a measure of the stability of the lubricating film [**L. 14**]. The values of the scuffing load (P_t) were also analysed. Under this load, the moment of friction force is higher than 10 N·m, and the elements of the friction node are

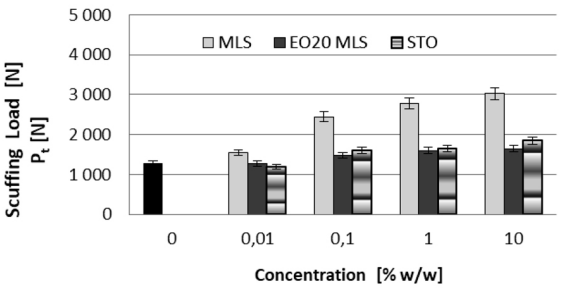

Fig. 4. Dependence of scuffing load (P_t) on the concentration of sorbitan esters in the extract of blackberry seeds obtained by extraction under supercritical carbon dioxide conditions. Tests were performed with increasing load at a speed of 409 N/s and a spindle speed of 500 rpm

Rys. 4. Zależność obciążenia zacierającego (P_t) od stężenia estrów sorbitanu w ekstrakcie z nasion jeżyny otrzymanym w warunkach nadkrytycznego dwutlenku węgla. Test przy narastającym obciążeniu 409 N/s, prędkość wrzeciona 500 obr./min

in seizure. The limit values for the limiting pressure of seizure (poz) were also determined. The influence of the type and concentration of sorbitan esters in blackberry extract on the anti-seizure properties was evaluated (**Figs. 4, 5**, and **6**).

Analysis of the obtained results shows that the addition of MLS to blackberry extract causes a significant increase in the scuffing load from 1000 N (base) to about 3000 N (10% MLS). This indicates an increase in the service life of the lubricating film relative to the base. The obtained P_t values of 0.1% in the extract are also higher than for rapeseed oil (1200 N) and paraffin oil (820 N). For the other two additives (EO20MLS and STO), in the range of concentrations presented, the Pt values are slightly higher than those for base oil and range from 1300 N to 1800 N. In the case of the load analysis at which the seizure took place (P_{oz}), a similar tendency of changes only for mixtures of sorbitan monolaurate in blackberry extract is observed (**Fig. 5**). At a concentration of 0.01%, the value of P_t is comparable to that of the base. From a concentration of 1% to 10%, the value of this parameter increases slightly from 3700 N to approx. 3850 N.

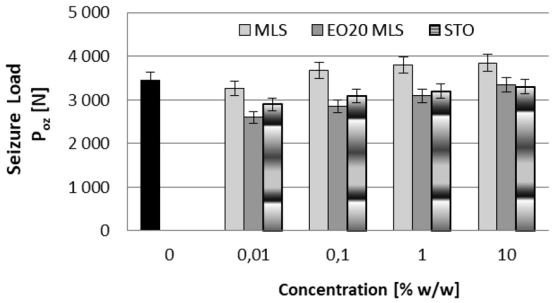

Fig. 5. Dependence of seizure load (P_{oz}) on the concentration of sorbitan esters in the extract of blackberry seeds obtained by extraction under supercritical carbon dioxide conditions. Tests were performed with increasing load at a speed of 409 N/s and a spindle speed of 500 rpm

Rys. 5. Zależność obciążenia zatarcia (P_{oz}) od stężenia estrów sorbitanu w ekstrakcie z nasion jeżyny otrzymanym w warunkach nadkrytycznego dwutlenku węgla. Test przy narastającym obciążeniu 409 N/s, prędkość wrzeciona 500 obr./min

For the other surfactant mixtures (EO20MLS and STO), the seizure occurs at a lower load than for the base oil. This indicates a reduction of the ability to transfer higher loads for these lubricating compositions compared to the reference sample. However, comparing the obtained P_{oz} values for paraffin oil (2600 N) and rapeseed oil (2700 N), both the base and the analysed lubricating compositions are comparable. The values of the limiting pressure of seizure are shown in **Fig. 6**.

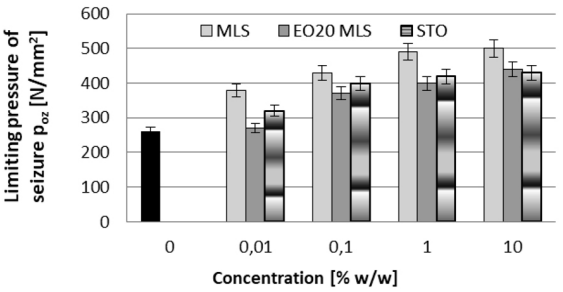

Fig. 6. Dependence of limiting pressure of seizure (p_{oz}) on the concentration of sorbitan esters in the extract of blackberry seeds obtained by extraction under supercritical carbon dioxide conditions. Tests were performed with increasing load at a speed of 409 N/s and a spindle speed of 500 rpm

Rys. 6. Zależność granicznego nacisku zatarcia (p_{oz}) od stężenia estrów sorbitanu w ekstrakcie z nasion jeżyny otrzymanym w warunkach nadkrytycznego dwutlenku węgla. Test przy narastającym obciążeniu 409 N/s, prędkość wrzeciona 500 rpm

The value of the limiting pressure of seizure for paraffin oil is low at 130 N/mm^2. In turn, for rapeseed oil, the value of p_{oz} fluctuates at a level of approx. 230 N/mm^2. In general, all mixtures with blackberry extract obtained, as well as the extract as a base, show values of this parameter higher than for the presented reference points. It has also been observed that the increase in concentration causes a visible increased poz value, especially in the case of MLS compounds, where the values of p_{oz} can even be increased 200% in relation to the base oil.

CONCLUSIONS

The presented results show that the use of sorbitan esters as additives to blackberry seed extract under supercritical carbon dioxide conditions obtained is justified. It should be noted that in tribological tests at constant load (2 kN) no significant influence of concentration and type of analyzed surfactants in the extract on movement resistance and wear of elements of friction couple was observed. The values of the wear scar diameter and friction coefficient were comparable to those of the base and rapeseed oil, but more than twice lower than those of paraffin oil. However, in the anti-seizure tests, the type of ester had a significant effect on the anti-seizure properties.

In the tests with linear load increment, a significant increase in all P_t, P_{oz}, p_{oz} values was observed, with an increase of the concentration for sorbitan monolaurate in the extract. The presented values are higher than for rapeseed oil and paraffin oil as reference points. In practice, this means greater durability of the lubricating film and ability of the obtained lubricating compositions to prevent wear and friction of the elements of the friction

node. The use of oxyethylene sorbitan monolaurate and sorbitan trioleate as additives slightly deteriorates the anti-wear properties of blackberry extract in relation to the base. However, it should be underlined that the anti-seizure properties are comparable to those of rapeseed oil. In conclusion, the compositions proposed, especially those with the addition of MLS, may be an alternative to vegetable oil-based lubricating substances.

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