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Oxidation Effect on Tribological Properties of Rapeseed Oil and Lard Mixtures Containing Monoglycerides and Fatty Acids

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Vegetable oils and animal fats are increasingly popular base material for producing environmentally friendly lubricants. This material is renewable and easily biodegradable in the natural environment. Main disadvantage of vegetable oils and animal fats as raw material and its lubricants is poor oxidation stability. There is already a wide range of environmentally friendly lubricants in the market, whereas the variety of grease offer is not so high. This research aims to explore the properties of prepared compositions of lubricating grease produced from rapeseed oil and lard, modifying it with monoglycerides, stearic and oleic acids. Plastic properties (penetration) and oxidation influence on tribological and corrosive properties of these compositions have been studied. It is found that modifying rapeseed oil and lard with monoglycerides, oleic and stearic acids a few lubricating compositions of NLGI grades can be obtained, namely, soft or very soft rapeseed oil based grease and medium or nearly hard consistency lard based compositions. The studies of oxidation have shown that it decreases tribological properties of both base and monoglycerides modified lubricants. Oxidation has a greater negative impact on lard and lard based compositions. Oleic and stearic acids reduce or completely eliminate negative influence of oxidation. Corrosion studies have shown that both fresh and oxidized lubricant compositions have no significant effect on copper strip corrosion.

Key words: *grease, oxidation, lubrication, monoglycerides, fatty acid.*

1. Introduction

Vegetable oils and animal fats were one of the first materials used for lubrication. Since the 19th century however, they have been gradually replaced by lubricants produced from petroleum hydrocarbons. The latter have not always met technical requirements. It has stimulated us to analyze synthetic lubricants and introduce them to industry as they have become the equivalent to mineral lubricants.

Nowadays great attention is being paid to natural triglycerides, to fatty acids produced from them and to their applications. This raw material is renewable and does no harm to the environment.

The use of environmentally friendly products is valued due to their low soil pollution, minimal threat to the human health and safety and also to their biodegradability. Lubricants make an impact on the environment in all stages of their production, use and utilization. Accidental lubricant spills or their leakage when used in the environmentally sensitive places, such as agriculture, forestry, mining districts, construction sites, water ways and reservoirs, may cause ecological disasters. Taking it into account most European countries have set the requirements stimulating the use of environmentally friendly lubricants. This situation has created a unique possibility to develop environmentally friendly lubricants from natural esters whose quality and price may compete with synthetic lubricants produced from petroleum (Gryglewicz et al. 2003; Kodali 2002).

The base material for biological grease is either of vegetable (rapeseed, sunflower, soy, flax or other oil) or animal (lard, beef tallow, fish and other oils) origin. It is environmentally friendly and 80 % biodegradable, while only 15-20 % of mineral oils degrade during the same period (Bartz 2006).

Grease is made of base stock lubricant (oil or fat), thickeners and multi-purpose additives improving their exploitation properties (Fig. 1).

Grease contains about 60-95 % of base oil, 5-25 % of thickener and 0-10 % of additives (Adhvaryu et al. 2005; Sukirno et al. 2009).

Thickener is one of the main grease components rendering it the form. The primary requirement for thickener is to have especially small uniformly distributed particles and to be able to form a fairly stable gel material structure with liquid lubricant.

Oxidation is a basic disadvantage restricting the use of vegetable oil for lubrication. Oxidation causes polymerization and degradation. During the latter the decomposition products appear which may be volatile, start corrosion and diminish oil lubricating properties. Resistance to oxidation depends on the composition of vegetable oil fatty acids. The oxidation rate is determined by the temperature, the contact of metals with oil, the amount of water and oxygen in oil. The effect of the temperature is very important – with its increment by 10 °C the oxidation rate may rise three times (Kodali 2002).

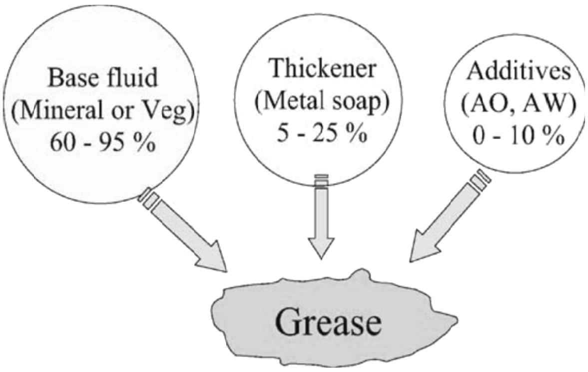


Fig. 1. Typical composition of grease (AO - antioxidant, AW - antiwear) (Adhvaryu et al. 2005)

The main oxidation result is an increase in thickness and acidity. Increased acidity may start the concentrated corrosion of some mechanical parts such as washers and bearings.

Vegetable oils are composed of triglycerides which determine their physical and chemical properties. Triglycerides are composed of glycerol and fatty acids. Fatty acids making triglyceride may be saturated and unsaturated. As it is mentioned, triglycerides are composed of fatty acids: saturated stearic, monounsaturated oleic and polyunsaturated linoleic ones. These sorts of fats determine lubricating, oxidative and temperature properties of oil (Erhan and Perez 2002; Lämsä and Kosonen 2008; Murrenhoff 2004; Kab 2001).

Saturated fatty acids have no double bonds in hydrocarbon chains, therefore they are particularly resistant to oxidation. They are desirable in lubricating materials for improving their oxidative stability. However, with elongation of hydrocarbon chains the saturated fatty acids increase the pour point of mixture. For comparison, the pour point of C 12:0 (Lauric) fatty acid is about 44°C and the pour point of C 20:0 (Arachidic) reaches even 76°C. It is stated that high freezing points are influenced by long straight hydrocarbon chains capable of occupying a very close inter-position (Erhan and Perez 2002; Kab 2001).

In addition to stability the saturated fatty acids possess one more positive feature ensuring the boundary lubrication of friction surfaces. It has been tested that stearic fatty acid contained in palm oil methyl ester forms on the friction surface an adsorption layer of polar molecules which reliably separates the interactive surfaces (Maleque et al. 2000). In estimating the temperature stability, higher unsaturation always reduces the pour point. The reason of the pour point reduction lies in the geometric structure of unsaturated fat acids. The ‘cis’ double bond induces fatty acid molecules to kink. The larger number of double ‘cis’ bonds, the higher the deformation of a fatty acid molecule. Deformation slows down the possibility of close arrangement of atoms i.e. their crystallization. Thus, molecules occupying a larger volume remain in the liquid form to the comparatively low temperatures. For comparison, the pour point of oleic acid C 18:1 is about 4°C while that of linoleic C 18:3 is – 11°C, and that of arachidonic C 20:4 is only – 50°C (Erhan and Perez 2002).

The aim of the study was to analyze the possibility of using rapeseed oil and lard as the base stock for both the production of biological grease and modification of its properties by monoglycerides and fatty acids. The tasks of the study were:

- To study an impact of monoglycerides, oleic and stearic acids on plastic properties of lubricating compositions of rapeseed oil and lard.
- To determine an oxidation effect on corrosion properties of lubricating mixtures according to the corrosive effect on a copper plate.
- To study an oxidation effect of monoglycerides, oleic and stearic acids and lubricating compositions on tribology properties.

2. Methods

Refined rapeseed oil (RO), lard fat (LF) and the mixtures obtained by modifying them with mono glycerides (MG), stearic (SA) and oleic acids (OA) were studied. The rapeseed oil and lard were modified with 20 % of monoglycerides and 2 % of stearic and oleic acids (by wt.).

Monoglycerides contain only one fatty acid in their structure. They are frequently used as emulsifiers, stabilizers and thickeners for increasing the consistence (Gumbytė and Makarevičienė 2007; Kreivaitis et al. 2009).

Monoglycerides were used as thickeners for changing the consistence of rapeseed oil and lard. In preliminary tests it was determined that 20% of them were sufficient to achieve the desired consistence class according to NLGI (RO - 0 class, LF - 2 class). Stearic and oleic acids were used as additives for friction and wear reduction.

Four-ball type tribotester was used to perform tribological tests. The balls of 12.7 mm diameter were made of 100Cr6 bearing steel (E = 21.98 104 MPa; ν = 0... 3; 63…66 HRC). The testing procedure was adapted from the standard DIN 51 350, Part 3.

The test oil sample of 22 ml was poured into the sample compartment, fully submerging the stationary balls. Under the applied load of 150 N, at the rotation speed of 1420 rpm, the machine was run for 1 hour. Prior to each experiment, all the appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and test balls were washed in an ultrasonic bath with hydrocarbon solvents and then dried.

The wear scar diameter on three stationary balls was measured with an optical microscope. The results were recorded and reported as the medium of the wear scar diameter (WSD) of the three balls in millimeters. During the test the torque between the balls and the temperature change of sample oil were recorded.

The penetration was determined according to the ASTM D 217-97. The test temperature was 25°C. The 102.5 g weight penetration cone was used.

Accelerated oxidation of lubricating mixtures was tested according to the standard AOCS CG-5-97 when storing them in an oven. The samples, 10 ml each, were stored in closed 250 ml volume glass vessels. During testing the constant temperature of 70ºC was maintained. The samples were kept in the oven for 50 days. The test of the copper corrosion was performed according to the standard LST EN ISO 2160: 1998. The copper plates were kept in the tested lubricating mixture at the temperature of 70ºC The test duration was 24 hours. The corrosion effect was evaluated by a comparative method using standard copper plates.

3. Results and Discussion

Results of penetration measurements are given in Table 1. They indicate that in all cases lubricating mixtures were of sufficient thickness, the thickest was that of lard (80 %) and monoglycerides (20 %). The mixtures composed on the basis of RO were less thick. It is of interest that application of SA or OA to lubricating mixtures based on LF and RO had a different effect on their thickness (penetration). In the mixtures based on RO the acids increased their thickness, while in the mixtures based on LF they reduced it.

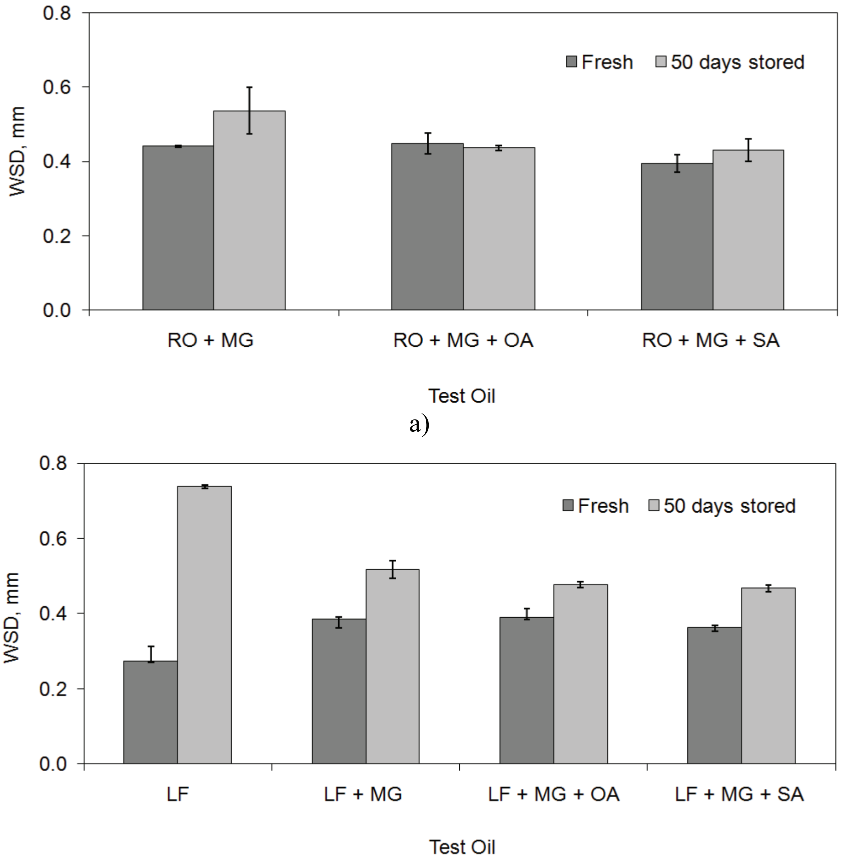
Table 1. Penetration of lubricating mixtures

Tested samples	RO+MG	RO+MG+ OA	RO+MG+ SA	LF+MG	LF+MG+ OA	LF+MG+ SA
NLGI class	000	0	0	4	2	2
Penetration	471	353	352	194	272	280

Tribological results of modification of rapeseed oil and lard by stearic and oleic acids and by monoglycerides are given in Figs 2-4. The diagrams show that using fresh rapeseed oil with monoglycerides the wear of balls is the same as that when using rapeseed oil with monoglycerides and oleic acid, while when using rapeseed oil with monoglycerides and stearic acid it is 1.1 times lower. After 50 days of storage oxidation the lowest wear was noticed when lubricating with rapeseed oil containing monoglycerides and stearic acid. Comparing the lubricating properties of fresh and 50 days aged, pure and modified with monoglycerides rapeseed oil, it is determined that when lubricating with the fresh mixture the wear was 1.2 times lower. Only one version was an exception, when lubricating with monoglycerides and oleic acid modified, fresh and 50 days aged rapeseed oil, the ball wear was practically the same. Whereas lubricating with fresh rapeseed oil containing monoglycerides and stearic acid the ball wear was 1.07 times lower than lubricated with a 50 days aged sample. The analysis of the diagrams shows that when lubricating with pure and modified lard it is evident that pure lard loses its lubricating properties due to oxidation. Lubricating with oxidized lard the ball wear is 2.6 times greater than that lubricated with fresh lard.

An oxidation effect on wear reduction decreases considerably when adding monoglycerides into lard: when lubricating with the oxidized sample the wear scar is 1.3 times larger than that observed when lubricating with a fresh one. Addition of oleic or stearic acids into the lard had no essential effect on the oxidation properties: lubricating with the oxidized sample the wear scar was from 1.2 to 1.3 times larger than that observed when lubricating with a fresh one.

In summarizing the oxidation effect of rapeseed oil and lard modified with monoglycerides, oleic and stearic acids on wear reduction properties, main results are as follows: a) the use of monoglycerides, oleic and stearic acids reduces the wear reduction properties of fresh lard (1,2 times), nevertheless they reduce the oxidation effect on wear reduction; b) the mixtures of fresh lard, monoglycerides, oleic or stearic acids provide better protection against wear than the same mixtures of rapeseed oil; on the other hand, the rapeseed oil mixtures are less affected by oxidation, i.e. their wear reduction properties are more stable. The reason is likely to be the natural antioxidants in rapeseed oil which stabilize the oxidation process. In animal fats the appearance of natural antioxidants is very limited. The greatest wear reduction efficiency has been reached by modifying rapeseed oil and lard with monoglycerides and stearic acid. Both monoglycerides and stearic acid have no double bond in hydrocarbon chains, thus they increase oxidation stability.



a)

b)

Fig. 2. The ball wear observed when testing the samples modified with additives: a) – rapeseed oil b) - lard

Corrosion tests have been also carried out. A corrosive effect of the mixtures was evaluated after having stored them in the oven at 70°C for 1 and 4 days. The modified rapeseed oil and modified lard are estimated to correspond to the 1a corrosiveness category which indicates that the oxidation products of the tested samples have no significant impact on corrosiveness of the tested lubricating mixtures.

Diagrams of the torque variation of the tested lubricating mixtures during testing are given in Figs 3 and 4. On the basis of the torque analysis the mean torque when lubricating with fresh rapeseed oil containing monoglicerides is found to be 1.15 times lower than that observed when lubricating with the 50 days stored in oven rapeseed oil. In the case of rapeseed oil modification with monoglicerides and oleic or stearic acids this difference diminishes up to 5 %.

The medium torque of pure lard after oxidation compared to the fresh lard has increased 1.3 times; however situation changes to the opposite when lard was modified by monoglycerides - the mean torque of the oxidized mixture is 1.3 times lower than that of the fresh one. With addition of oleic or stearic acids in the lard containing monoglycerides the torque decreases. When comparing the torque variation observed during the testing period it is clear that oxidation has a lower effect on rapeseed oil mixtures (Fig. 3) than on lard ones (Fig. 4).

Typically, after oxidation the rapeseed oil mixtures containing oleic or stearic acids distinguish themselves for a higher torque, while the analogous lard mixtures after oxidation have a lower torque than the fresh ones. It should be noted that during testing in all cases when lubricating with rapeseed oil and lard mixtures containing oleic or stearic acids a gradual decline in the torque has been determined.

In the analysis of worn surfaces different traces have been noticed (Figs 5 and 6). In the picture of a wear scar observed when lubricating with fresh rapeseed oil containing monoglycerides a lot of small scars are seen, while after storage oxidation the wear scar changes - a number of small groves decreases considerably and on the scar surface a blurred relief is seen (Fig. 5 b). With addition of oleic acid the number of groves decreases greatly and the scar relief becomes more distinct, especially after oxidation (Fig. 5 d). The analogous picture is obtained when lubricating with rapeseed oil modified with stearic acid (Fig. 5 e and f). The possible reason may be that when deformed surface is subjected to fatty acids the strength and microhardness of the surface layer decrease, especially lubricating with oxidized samples. Due to these reasons the Rebinder's effect (reduction in hardness of an adsorption surface layer) may take place. In all cases, after 50 days of storage oxidation the wear scars are larger.

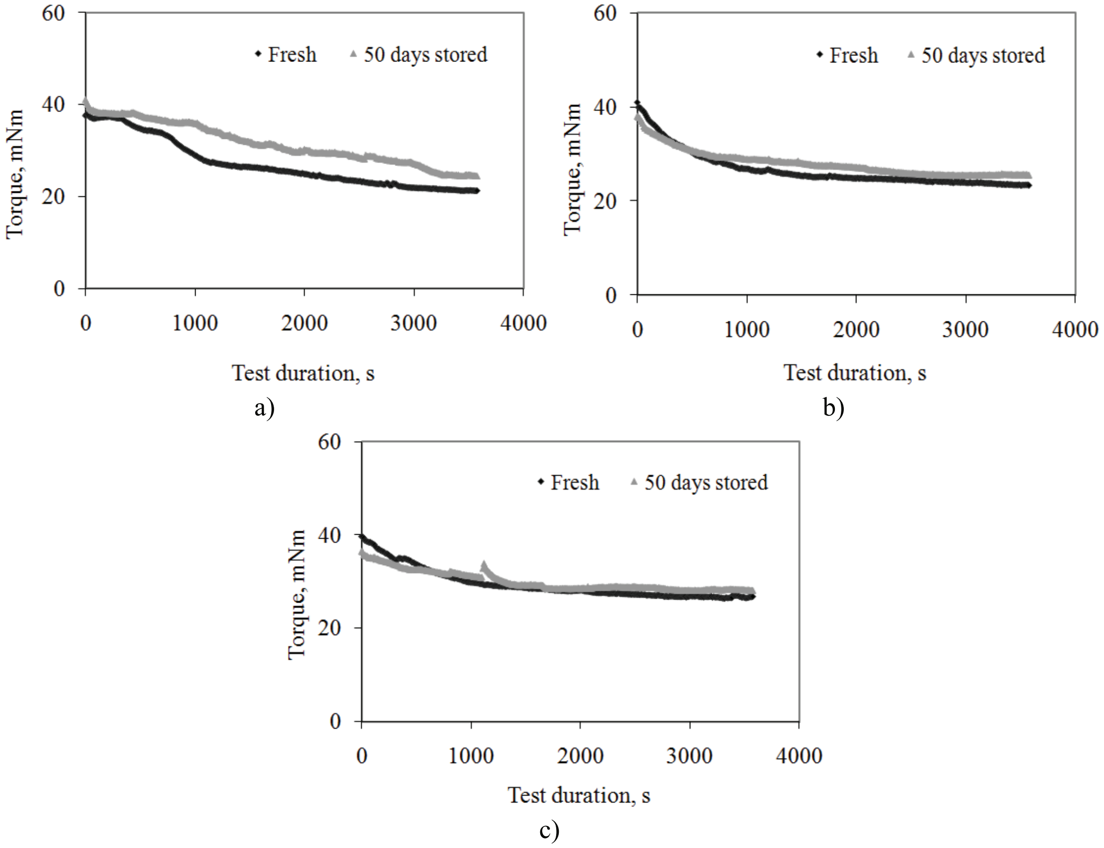


Fig. 3. *The torque variation during the four ball test lubricated with a) RO+MG; b) RO + MG + OR; c) RO + MG + SA*

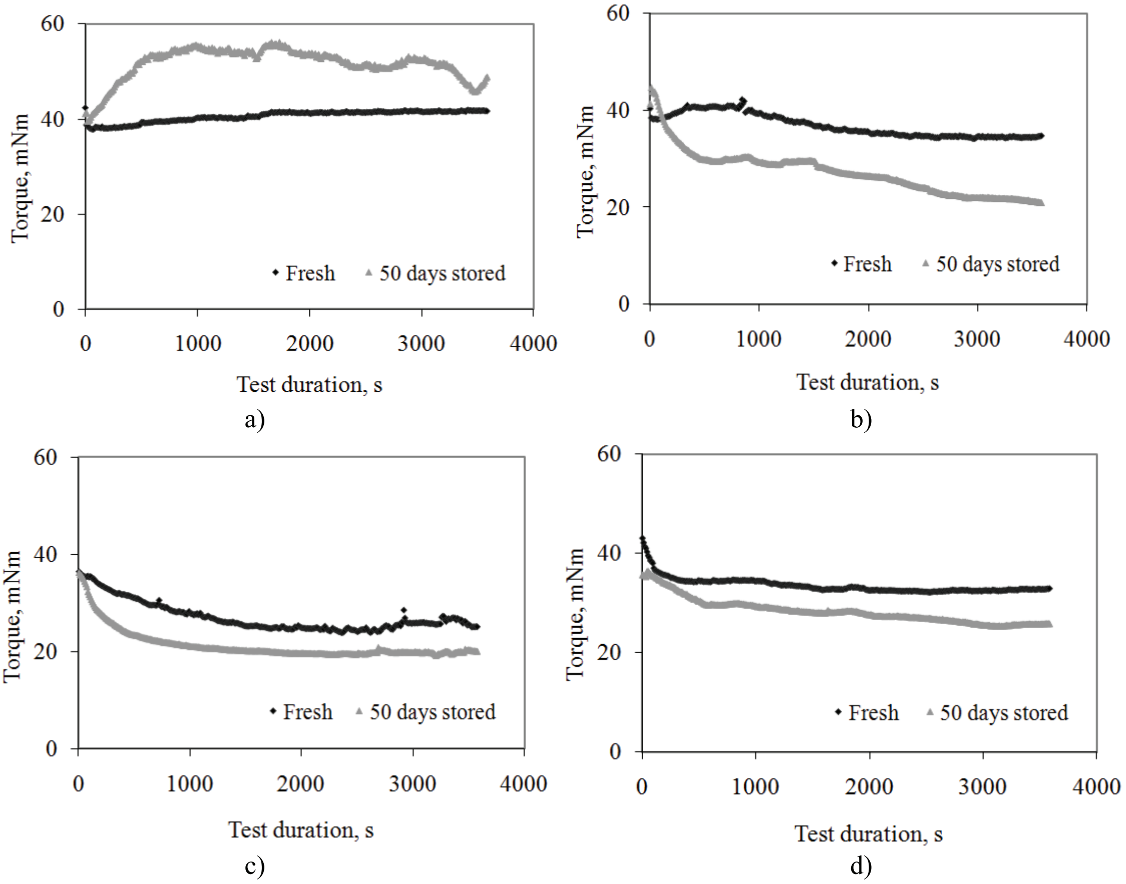
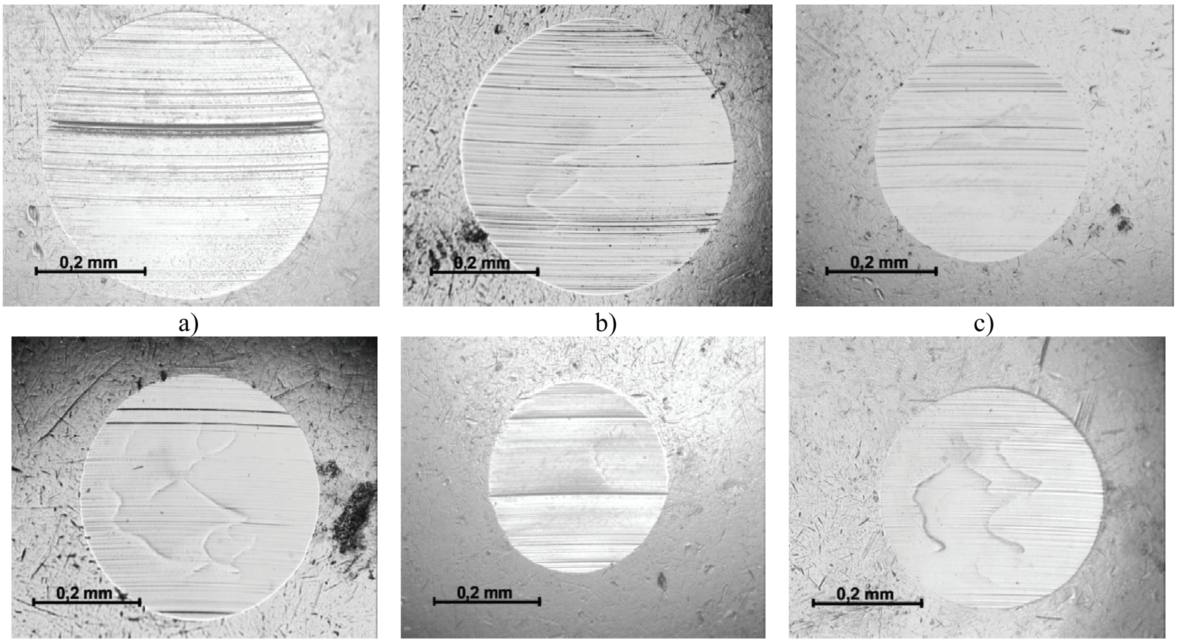


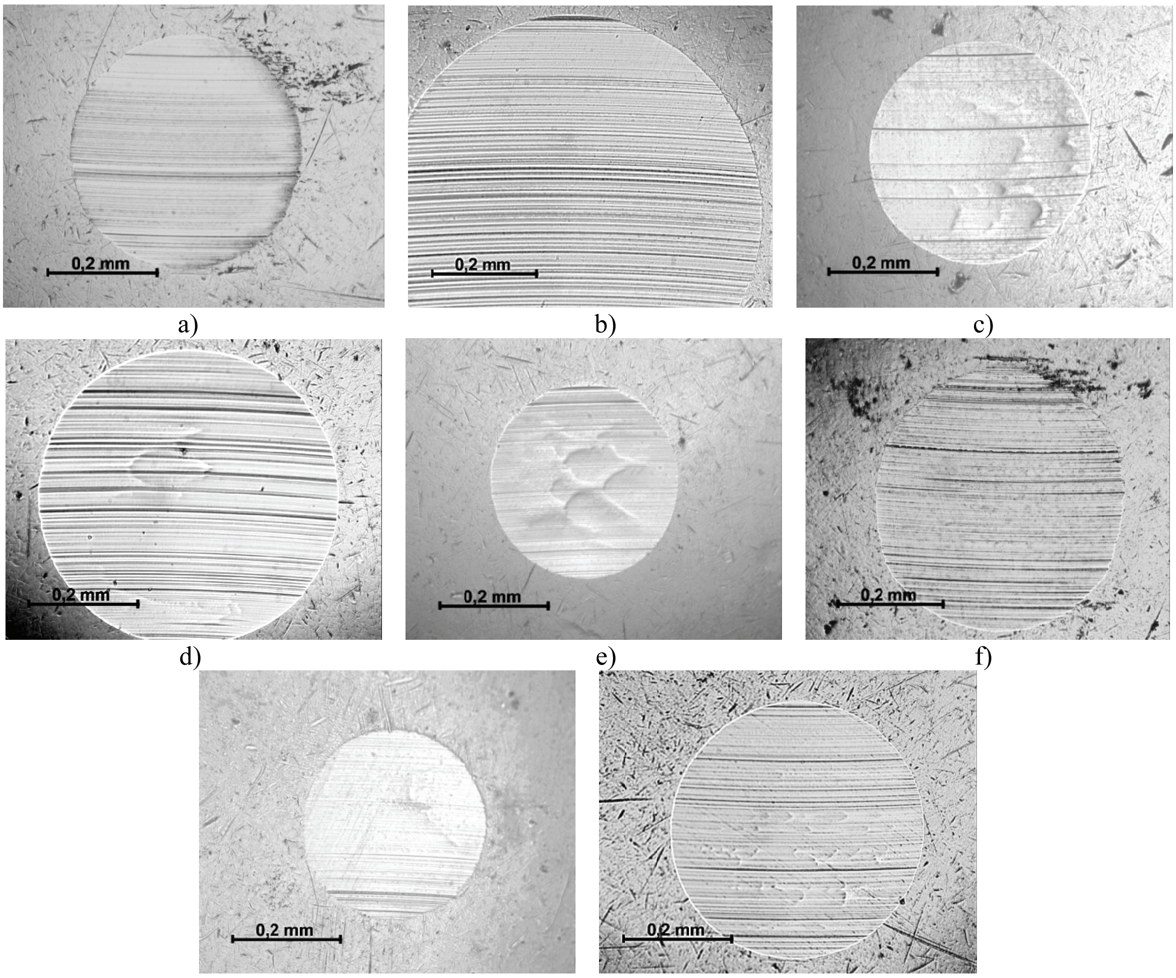
Fig. 4. *The torque variation during the four ball test lubricated with: a) LF; b) LF+MG; c) LF + MG + OA; d) LF + MG + SA*



a) b) c)

d) e) f)

Fig. 5. Optical pictures of wear scars of the balls lubricating with: a) RO + MG - fresh; b) RO + MG - stored; c) RO + MG + OA - fresh; d) RO + MG + OA - stored; e) RO + MG + SA - fresh; f) RO + MG + SA - stored



a) b) c)

d) e) f)

g) h)

Fig. 6. Optical pictures of wear scars of the balls lubricating with: a) LF - Fresh; b) LF - Stored; c) LF+ MG - Fresh; d) LF + MG - Stored; e) LF + MG + OA - Fresh; f) LF + MG + OA - Stored; g) LF + MG + SA - Fresh; h) LF + MG + SA - Stored

The wear scar pictures obtained in testing the lard are of interest. The wear scar obtained when lubricating with oxidized lard is twice larger than lubricating with fresh lard (Fig. 6 a and b), the distinct clearly seen scratches evidence decreasing lubricating properties. It was also clear when the torque variation was analyzed (Fig.4 a). Using the lard modified with monoglicerides the oxidation impact on wear reduction decreases and waviness of the wear surface arises (Fig. 6 c and d). Analogous wear trace pictures are obtained by additionally modifying lard with oleic and stearic acids (Fig. 6 e - h). Clear waviness is characteristic of wear scars observed when lubricating with fresh lubricating mixtures (Fig. 6 c, e and g). The cause of this phenomenon is thought to be the same as in the case of rapeseed oil mixtures, i.e. a strength decrease effect of the surface layer due to fatty acids adsorption influence. Formation of scratches is typical of wear scars of oxidized lubricating mixtures. It seems that impaired protection of lubricating the mixture wear due to oxidation accounts for it. Lubricating the samples containing oleic and stearic acids usually leave fewer scratches in wear scars.

4. Conclusions

1. Biological grease can be made of soft or very soft, the same as medium or nearly hard, consistency respectively from rapeseed oil and lard modifying them with monoglycerides (20 %) and oleic (2 %) and stearic (2 %) acids.
2. Oxidation of lubricating compositions on the base of rapeseed oil and lard, according to the effect on the copper strip, has no impact on their corrosion properties: all tested compositions meet category 1a (without any significant corrosion effect).
3. Monoglycerides and oleic and stearic acids reduce wear reduction properties of fresh lard for about 20%, but they significantly reduce the oxidation effect on wear reduction. Fresh lard mixtures protect more significantly against wear than rapeseed oil mixtures do, however oxidation has a lower effect on rapeseed oil mixtures i.e. their wear reduction properties are more stable.
4. According to the friction losses during testing, oxidation has a lower effect on rapeseed oil mixtures than on lard ones. Due to oxidation a slight increase in the torque at the end of testing is characteristic of rapeseed oil mixtures, whereas its decrease is typical of lard ones.

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Rapsų aliejaus ir kiaulinių taukų, modifikuotų monogliceridais ir riebalų rūgštimis, oksidacijos įtaka tribologinėms savybėms

Artūras Kupčinskas, Raimondas Kreivaitis, Juozas Padgurskas, Violeta Makarevičienė, Milda Gumbytė
Aleksandro Stulginskio universitetas

(gauta 2012 m. gegužės mėn., priimta spaudai 2012 m. rugsėjo mėn.)

Augalinis aliejus ir gyvūniniai riebalai yra sparčiai populiarėjanti bazinė medžiaga aplinkai draugiškiems tepalams gaminti. Tai atsinaujinanti ir gamtinėje aplinkoje lengvai suirstanti žaliava. Pagrindinis augalinės ir gyvulinės kilmės žaliavų ir iš jų gaminamų tepalų trūkumas – mažas atsparumas oksidacijai. Šiuo metu jau yra siūlomas platus įvairių aplinkai draugiškų alyvų asortimentas, o plastinių tepalų nėra daug. Šiame darbe siekiama ištirti iš rapsų aliejaus ir kiaulinių taukų, modifikuojant juos monogliceridais ir oleino ar stearino rūgštimis, pagamintų plastinių tepamųjų kompozicijų savybes. Buvo tirta šių kompozicijų plastinės savybės (penetracija) ir oksidacijos įtaka jų tribologinėms bei korozinėmis savybėms. Nustatyta, kad monogliceridais, oleino ir stearino rūgštimis modifikuojant rapsų aliejų ir kiaulių taukus galima sudaryti keleto NLGI klasių tepamąsias kompozicijas: minkštas ar labai minkštas rapsų aliejaus pagrindu ir vidutinės ar beveik kietos konsistencijos kiaulių taukų pagrindu. Atliekant oksidacijos tyrimus, nustatyta, kad ji blogina bazinių ir monogliceridais modifikuotų tepalų tribologines savybes. Didesnę neigiamą įtaką oksidacija turi kiaulinių taukų pagrindu pagamintoms kompozicijoms. Oleino ir stearino rūgštys sumažina arba visiškai panaikina neigiamą oksidacijos įtaką. Korozinio poveikio tyrimai parodė, kad tiek šviežios, tiek oksiduotos tepamosios kompozicijos reikšmingo korozinio poveikio vario plokštelei neturi.