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Tribological behavior of rapeseed oil mixtures with mono- and diglycerides

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1. Introduction

Typical lubricants for high performance devices consist mainly of base oil and functional additive packages to maintain specific properties such as wear and friction reduction, to improve temperature – viscosity behavior, to stabilize oxidation, etc. [1 - 3]. High performance lubricants can have up to 10% of various additives. These additives must be compatible with the base oil and fulfill all tribological requirements. On the other hand, the majority of antiwear (AW) and extreme pressure (EP) additives contain Zn, P and S which are not compatible with the environment [4, 5].

Recently, a growing concern of reducing pollution influences the composition and properties of additives. For this reason, many researches are done in the field of optimization of additive's packages. While the most important additives are AW, EP, and antifrictional they are in the focus of optimization. It should be noted that some additives as ZDDP (zinc dialkyldithiophosphate) can be used for a few purposes: for wear reduction and as an antioxidant that reduces the total amount of additives [1, 2, 6-8].

The choice of AW, EP and friction modifier additives depends on the operating conditions of a particular mechanism. Under hydrodynamic lubrication the friction is very low and it is limited just by viscosity of the lubricant. Wear rate of this type of lubrication is close to zero and no special additives are needed. When friction comes up to either mixed or boundary lubrication, AW and EP additives come to play their role. Under these conditions the ability to protect surfaces against wear is very important. There are two main types of wear reduction mechanisms – adsorption and chemosorption. Both of them are based on the ability to separate surfaces by forming relatively weak adsorbed or strong chemisorbed layers [4, 6, 9].

Layers formed by physically adsorbed polar substances like fatty oils, fatty acids and the others exhibit only poor or moderately high pressure properties. They can not withstand high temperatures. Because of the polar structure molecules of the fatty acid align themselves normally to the surface, acting as an effective barrier to metal to metal contact. These kinds of additives are called friction modifiers [1, 2, 6, 9].

In the case of a chemisorbed anti-wear mechanism when the mixed or boundary lubrication takes place, the temperature will increase and both AW and EP additives can react with the metal surface forming tribochemical reaction layers (iron phosphites, sulfides, sulfates, oxides and carbides – depending on the additive's chemistry) that will prevent a direct contact between the sliding metal surfaces. This type of protection against wear can serve at high or very high temperatures and loads [9].

In the case of chemisorbed layers chemical reaction of additives plays an important role in wear protection properties. Interaction between an additive and metal surface consists of two competing effects. By reacting with a metal surface, AW additives reduce adhesive wear at the same time producing chemical wear [2].

The additives are not alone in having polar molecules to form adsorption layers. The molecules of base oil can also possess some polarity and it makes influence on lubricity of a final product. It is determined that polarity of the base oil has a great effect on effectiveness of ZDDP additive. Polarity of ZDDP itself let it easily reach the wearing surface when it is combined with nonpolar base oil. Nonpolar base oil + ZDDP form a thicker lubricating layer and formation of this layer is much faster than that with polar base oil [6].

The aim of the study is to estimate the influence of mono- and diglycerides on tribological properties of rapeseed oil.

2. Tested materials

Refined rapeseed oil satisfying the requirements of standard LST 1959 was used in testing. It was mixed in appropriate proportions with an oleic acid glycerolysis product obtained by esterification of oleic acid (analytical grade, "Ecros", Russia) with glycerol (analytical grade, Penta, Czech Republic). Ferment preparation Novozym 435 (lipase from Candida Antarctica, immobilized on polypropylene, activity – PLU/mg from Novo Nordisk, Denmark) was used as a catalyst for esterification reaction. The molar ratio of oleic acid and glycerol in the reaction medium was 1:1, reaction temperature – 50°C, duration 24 h. During the esterification reaction mono- (MG) and diglycerides (DG) were formed. Their concentration in reaction product was the following: MG – 24.5%, DG – 44.9%. The reaction product contained triglycerides – 5.4%, unreacted glycerol - 5.2%.

Pure and various concentrations of rapeseed oil (RO) and mono- and diglyceride (MDG) mixtures were tribologically tested. The MDG quantity in rapeseed oil amounted from 5 to 70% (according to the volume). The main physical and chemical properties of materials used in experiments are given in Table. Mixtures were blended with magnetic mixer TK22.

A commercial lubricant based on rapeseed oil was used as the "Reference" in these experiments.

Table

Physical and chemical characteristics of selected lubricating oils

Characteristic	Test Method	Value				
		Reference	RO	MDG	MDG (10%) + RO (90%)	MDG (30%) + RO (70%)
Density at 15°C, g/cm^3		0.922	0.921	0.939	0.923	0.927
Viscosity, mm^2/s						
at 40°C	ISO 3104	63.48	34.82	60.87	35.85	39.44
at 100°C		14.36	8.07	8.79	7.94	8.02
Viscosity index	ISO 2909	238	217	119	203	181

3. Experimental procedures

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 10^4 MPa; v = 0.3; 63 - 66 HRC). The testing procedure was adapted from the standard DIN 51 350, Part 3 [10].

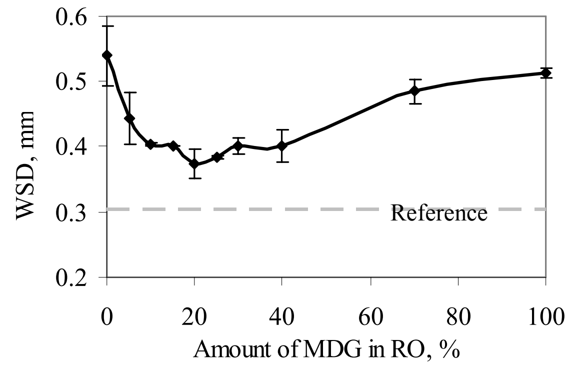
The test oil sample of 22 cm^3 was poured into the sample compartment, fully submerging the stationary balls. Under the applied load of 150 N or 300 N, rotation speed of 1420 rpm, the machine was run for 1 hour (DIN 51350/3). Prior to each experiment, all the appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and the test balls were washed in an ultrasonic bath with hydrocarbon solvents, and then dried.

Friction surfaces were analyzed with optical microscope. The diameters of the circular wear tracks (wear scars) on three stationary balls were measured with an optical microscope (accuracy 0.007 mm). For each run the scar measurements were reported as an average of the Wear Scar Diameter (WSD) of the three balls in millimeters. The friction moment between the balls, represented by torque, and temperature change of the liquid sample was also recorded during the test.

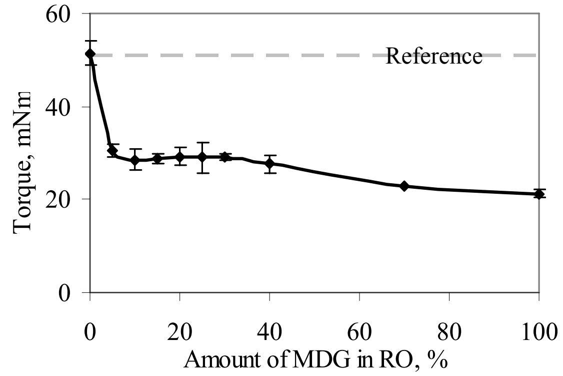
4. Results and discussion

Tribological experiments of pure RO, MDG and RO and MDG mixtures have shown that the ratio of these components affects wear reduction and friction extent. In Fig. 1, a the influence of MDG concentration on the wear reduction properties of the mixture is distinctly seen. When lubricating the interacting surfaces with pure RO or MDG, the wear is significantly more intensive than in a case of using standard commercial oils (reference). But, RO and MDG mixture when MDG amounts to 10 - 30% of its volume has better wear reduction characteristics than its pure components. The mixture of the above mentioned concentration, compared to pure RO, has reduced the diameter of a wear scar on lubricated balls by 1.44 times. The material possessing these wear reduction properties is close to commercial oils and can be used for lubricating lightly loaded surfaces.

With an increase in MDG concentration friction between the balls decreases (Fig. 1, b). When lubricating with pure MDG the torque is 2.4 times lower than that when lubricating with pure RO. With a decrease in the MDG quantity (from 100 to 5%) in the mixture, the friction increases. In a case of greatest protection against the wear concentration (10 - 30% MDG) the friction is 1.8 times lower than that when lubricating with reference oil.



a



b

Fig. 1 Influence of MDG concentration in rapeseed oil on balls WSD (a) and the friction (b) (150 N load)

Taking into account the properties and composition of contained components, wear reduction may be caused by several factors. The greatest influence might be exerted by polarity of mono- and diglycerides molecules. Differently from triglycerides which are not polar compounds, MG and DG molecules, due to free hydroxyl groups, enjoy polar properties which are stronger in the case of monoglycerides, while in the case of DG they depend on the condition of the attachment of two free fatty acids on to a glycerol molecule. Polar MG and DG molecules with nonpolar TG which form vegetable oil and which enter into the MDG composition are thought to form a micelle on whose surface there is a layer of polar MG and DG molecules. The possibility of micelle formation is demonstrated by a real and negligible quantity of MDG (up to 30%) which inserted into rapeseed oil produces a positive effect as to the friction reduction. Some MG and DG molecules break off from the micelle surface and approach the lubricated metal surface forming an adsorption layer which separates interacting surfaces and prevents their direct contacting. When, due to friction and temperature, adsorbed MG and DG molecules disintegrate, the other micelles broken off from oil MDG move towards the surface. After some time the ratio of polar and non-polar molecules in the lubricating material varies and micelle disintegrates, the lubricant loses its lubricating properties. Since the adsorption layers are not sufficiently strong (compared to chemical adsorption) the advantage of the reference oil (modified with special additives) is quite clear.

Oleic acid contained in MDG composition may be the other factor which causes wear reduction in RO and MDG mixture. This fatty acid is attributed to polar molecules forming an adsorption layer. Oleic acid is well known as an additive for improving lubricating properties of rapeseed oil [4]. It is oleic acid which increases mixture acidity thus allowing the formation of a tribochemical layer. In this case wear would decrease due to formation and renewal of a steady oxide film. The oxide film formed during the tribochemical process is significantly harder than the basic metal and more resistant to wear. A certain proportion of components in the mixture ensuring good protection against wear may be explained by equilibrium between oxidation and wear processes taking place in the tribochemical layer. In the mixture with an increase in the MDG quantity acidity increases, thus the oxidation rate, i.e. chemical wear, increases intensifying the wear. In the mixture with a decrease in the MDG quantity acidity also decreases, and when MDG amounts to less than 10% acidity slackens, the destroyed oxide film is slowly restored and mechanical wear intensifies. The model of a tribochemical layer, however, does not explain the decreasing of friction which during the test should be much higher than that of balls lubricated with RO. When lubricating with MDG a complex process might take place resulting in wear and friction values.

A very low friction represents an effect of an adsorption layer. It should be noted that during the test lubrication with both pure MDG and its mixture with RO the friction is smoothly decreasing and at the end it is minimal (Fig. 2). The given curves of the torque variation when lubricating with pure MDG, RO and their mixture indicate that the most intensive decrease occurs under lubrication with MDG. Lubricating with pure RO the torque increases irregularly for 40 min, after that it smoothly decreases. Lubricating with rapeseed oil and MDG mixture with 20% of MDG, a decrease in the torque is not as intensive as it is when lubricating with pure MDG, but its tendency remains. A conclusion can be drawn that the growing surfaces contact area (diminishing pressure) during the wear process improves adsorption properties of the lubricating layer, and even small quantities (up to 5%, Fig. 1, b) of MDG have a great influence on RO friction reduction characteristics.

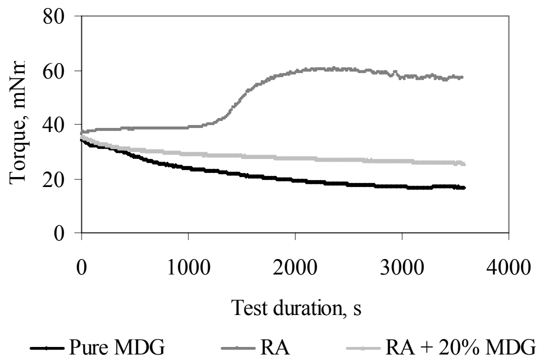


Fig. 2 Variation of friction (torque) when lubricating with pure MDG, RO and MDG (20%) + RA (80%) mixture (150 N load)

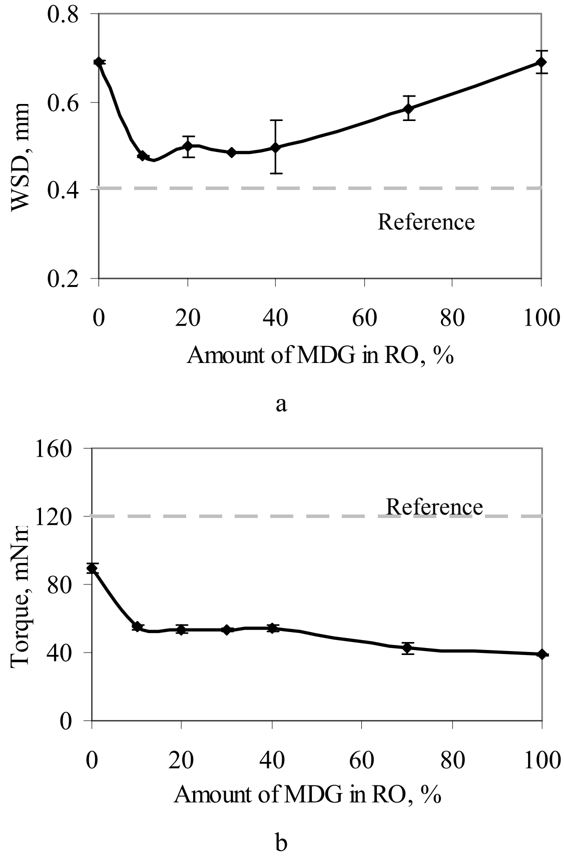


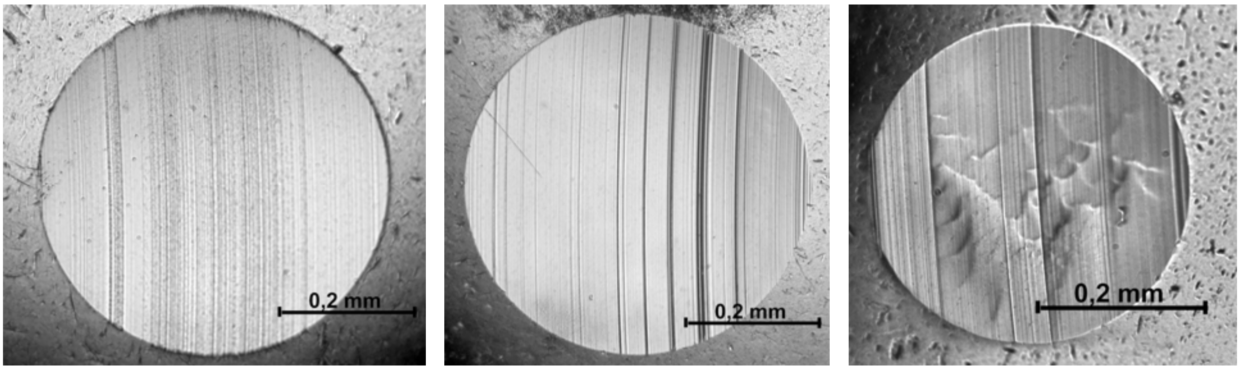
Fig. 3 Influence of MDG concentration in rapeseed oil on balls WSD (a) and friction (torque) (b), (300 N load)

With an increase in load and temperature the effectiveness of adsorption layers decreases [1]. However, neither the load nor the temperature boundaries of the adsorption process are indicated. To find out the influence of

RO and MDG mixtures on lubricating properties, the tests have been carried on under a higher 300 N load. The obtained results have shown the analogical tendencies as under the lower load conditions (Fig. 3).

The mixture of rapeseed oil and MDG with 10 - 30% of MDG is the most efficient in wear reduction (Fig. 3, a). Lubricating with this mixture the surfaces wear (WSD), compared to pure RO, has diminished up to 1.45 times. The obtained wear reduction efficiency is close to the result of lubrication with reference oil (difference about 15%). The MDG quantity over 40% aggravates wear reduction properties, but it effectively decreases friction (Fig. 3, b). Under operating conditions of both high and low loads, pure MDG is the best to reduce the friction of contacting surfaces. In the region of the efficient wear reduction (10 - 30% of MDG) friction is 1.66 times lower than lubricating with pure RO, and 2.24 times lower than lubricating with reference oil. The results obtained under operating conditions of high loads indicate the proper lubricating properties of the mixture.

Fig. 4 presents the optical images of wear scars of the balls tested in rapeseed oil, monodiglycerides and in the mixture of these materials.



a b c

Fig. 4 Optical images of wear scars of the balls lubricated with RO (a), MDG (b) and the mixture of MDG 20% + RO 80% (c) (150 N load)

Estimating the worn surfaces it is evident that the wear character is mechanical with the scars left by abrasion (RO – slight, several deep scars on ball surfaces when working with MDG, in the case of RO and MDG mixture several deep scars are visible). The worn surfaces of tested balls in RO and MDG are spheres, and after working in that mixture the surfaces of balls are in relief. The latter mixture ensures the best protection against wear.

Wear mechanism of the balls tested in the RO and MDG environment may be either mechanical or oxide-mechanical. However, when testing the balls in the RO and MDG mixture their wear traces surface in the sliding direction has significant (several hundredth parts of a millimeter) differences in height. Therefore, it cannot be explained by an oxide wear whose film layers, as a rule, are never thicker than 50 nm. On the other hand, the existing significant differences in height should influence the load distribution (concentrations) on the surface and under 300 N load seizing of the surfaces would occur, but neither the seizure signs nor the values of friction show this process.

Due to the interaction between the absorption layer and ball surface, the Rebinder's effect (reduction in absorption surface layer strength) might appear. Under the action of active-to-surfaces materials the surface is deformed, due to adsorption of the material molecules the strength of the face layer of juvenile surfaces is reduced and then the surface microhardness and the face layer yield point also decreases. For this reason the friction losses as well as surface wear also decrease. This effect helps in explaining the relief wear scars surface obtained when lubricating with RO and MDG mixture (Fig. 4, c).

5. Conclusions

Minimal surface wear is obtained when lubricating with rapeseed oil containing 10 - 30 % of MDG. This result is steady under the operating conditions of 1050 - 1325 MPa loads and is close to the reference oil.

Friction reduction is induced by increasing MDG concentration, however, in the optimal wear reduction concentration range (10…30 % of MDG) the value of friction does not depend on the concentration.

The observed behavior of friction and wear reduction can be explained by several processes – adsorption, effect of Rebinder and tribochemical processes. For the detail explanation the further research must be done.

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RAPSŲ ALIEJAUS MIŠINIŲ SU MONO- IR DIGLICERIDAIS TRIBOLOGINĖS SAVYBĖS

R e z i u m ė

Straipsnyje pateikti rapsų aliejaus (RA) ir jo mišinių su mono- ir digliceridais (MDG) tribologinių tyrimų rezultatai. Bandymai atlikti keturių rutulių trinties mašina pagal standartą DIN 51350/3. Nustatyta, kad grynų RA ir MDG dilimo slopinimo savybės, palyginti su etalonine alyva, nėra labai geros, tačiau tepant grynais MDG gerokai sumažėja trintis. Tepant RA ir MDG mišiniais gaunamas gerokai didesnis efektas, nei šiuos komponentus naudojant atskirai. Nustatyta RA ir MDG mišinio sudėtis, leidžianti sumažinti dilimą, palyginti su grynu RA, pagal rutuliuko nudilimo pėdsako skersmenį iki 1.45 karto ir trinties momentą iki 1.8 karto. Straipsnyje aptariamos galimos tirto mišinio dilimo slopinimo ir trinties mažinimo priežastys. Tikėtina, kad RA ir MDG mišinyje esančios paviršinio aktyvumo medžiagos sudaro adsorbcinį sluoksnį, efektyviai mažinantį trinties nuostolius ir paviršiaus dilimą. Susidarius tokio tipo sluoksniui gali pasireikšti Rebinderio efektas. Neatmetama taip pat ir tribocheminio sluoksnio susidarymo galimybė. Dilimo pėdsakų analizė rodo, kad, tepant RA ir MDG mišiniu, veikia kitoks dilimo slopinimo mechanizmas, nei tepant grynomis medžiagomis.

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TRIBOLOGICAL BEHAVIOUR OF RAPESEED OIL MIXTURES WITH MONO- AND DIGLYCERIDES

S u m m a r y

The paper presents the results of tribological research on the rapeseed oil (RO) and its mixtures with mono- and diglycerides (MDG). The tests are carried out with four ball tribometer according to the standard DIN 51350/3. It is determined that the lubrication with pure RO and MDG, comparing it with reference oil, does not ensure good wear protection. However the lubrication with pure MDG can considerably reduce the friction losses. The lubrication with mixture of RO and MDG is significantly more efficient comparing to its separate using. Optimal concentration of RO and MDG mixture which can enable to reduce the wear spot of the test ball up to 1.45 times and friction torque - up to 1.8 times comparing it to pure RO is determined. The paper presents discussion on the possible reasons of wear and friction reduction by the investigated mixture. It is seems likely that in RO and MDG mixture forms the surface active materials and the absorbed layer which efficiently decreases the friction losses and surface wear. Under the influence of such layer the Rebinder phenomenon could take place and also the formation of tribochemical layer is possible. The analysis of wear scars shows that different wear reduction mechanism is taking place when lubricating with RO and MDG mixture and with pure materials.

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ТРИБОЛОГИЧЕСКИЕ СВОЙСТВА СМЕСЕЙ РАПСОВОГО МАСЛА С МОНО- И ДИГЛИЦЕРИДАМИ

Р е з ю м е

В статье приведены результаты трибологических исследований рапсового масла (РМ) и его смесей с моно- и диглицеридами (МДГ). Исследования выполнены на четырехшариковой машине трения согласно стандарту DIN 51350/3. Установлено, что чистое РМ и МДГ по сравнению с эталонным маслом, не обладают хорошими противоизносными свойствами, однако смазывание чистыми МДГ значительно снижает трение. Смазывание смесью РМ и МДГ является значительно более эффективным. Установлен состав смеси РМ и МДГ, который позволяет снизить износ до 1.45 раза и момент трения до 1.8 раза. В статье обсуждаются возможные причины снижения износа и потерь на трение. Предполагается, что активные материалы находящиеся в смеси РМ и МДГ поверхностно образуют адсорбционный слой, который эффективно снижает потери на трение и износ поверхности. При образовании такого слоя может проявиться эффект Ребиндера. Не отвергается также возможность образования на поверхности трибохимического слоя. Анализ следов износа свидетельствует о том, что при смазывании смесью РМ и МДГ, а также чистыми РМ и МДГ, действуют разные механизмы снижения износа.

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