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RESEARCH

Influence of Composition of Plant Oils on Their Tribological Properties

N.K. Myshkin [a], A.Ya. Grigoriev [a], I.N. Kavaliova [a]

[a] *V.A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus, Gomel, Belarus.*

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Corresponding author:

Nikolai K. Myshkin
MPRI NASB, 246050, Kirova street 32a, Gomel, Belarus.
E-mail: nkmyshkin@mail.ru

A B S T R A C T

Sunflower, corn, rapeseed, olive, and linseed oils were used for investigation. Their fatty-acid compositions have been evaluated by gas chromatography. The tribological properties were determined with a four-ball machine. Flash and set points, static and dynamic viscosity of the oils were estimated by standard methods. The results of tests show that refined plant oils possess better tribotechnical properties than the base mineral oil without additives. It was found that their antiwear and bearing resistance properties correlate with the structure of fatty acids molecules. It is demonstrated that the activation of unsaturated bonds as a result of the triglycerides oxidation has a positive influence on friction due to tribopolymerization and film formation on the contact surfaces.

1. INTRODUCTION

One of the goals of research in the fast growing area of “green” tribology is the selection of base plant oils. However, unfortunately, there are the conflicting data published in this area. Differences in tribological performance, e.g. wear, of similar oils reach 50 % [1–3].

An analysis of the known data shows that the variability of the fatty acid composition of the oils can be the cause of the observed differences. Independent studies show that the triglyceride composition can vary by more than an order of magnitude, depending on the plant source, agricultural methods, climatic and production factors [4,5]. For example, the content of triglycerides of erucic acid in rapeseed oil varies from 1 to 60 %. Furthermore, content of oleic acid in sunflower and corn oils can vary from 10 to 40 %. It is obvious that mainly variability of the fatty acid composition is the main cause of the observed differences in the tribotechnical properties of oils. However, there is a lack of research analyzing this problem.

The purpose of this work is to investigate the influence of fatty acid content and structure of edible plant oil alkyls on their main tribotechnical properties.

2. MATERIALS AND METHODS OF RESEARCH

Refined rapeseed, olive, corn and sunflower oils without additives are investigated. The choice of oil grade is determined by rigid sanitary and technical standards on their composition and impurity level.

Mineral oil without additives I-20 (GOST 20799-88), commonly used in low- and medium-loaded gears, ball bearings and slides of machine tools, is chosen for comparison.

The density of the lubricants is evaluated withDensito-30PX device (Mettler, Spain). Oil flash-point temperature is determined in an open cup by the Vspyshka-A (Elektronpribor, Russia) in accordance with GOST 4333 (ISO 2592) and GOST 6356 (ISO 2719). Thermal characteristics (freezing point) are estimated with scan differential calorimeter Diamond DSC (PerkinElmer, USA) at the heating rate 8 °C/min. Kinematic viscosity is determined in accordance with GOST 33.

Composition of plant oil fatty acids is defined on the gas chromatograph Crystall-500 (Chromatec, Russia) in accordance with GOST 30418–96. The content of mono-, di- and triglycerides, as well as higher alcohols and free fatty acids, are evaluated by the method of ascending onedimensional paper chromatography in the hexane – diethyl ether – acetic acid system (18, 3 and 0.2 ml, respectively). The content of the main frictionally active elements is evaluated by means of X-Ray fluorescent spectrometer XEPOS (Spectro, Germany).

Load-carrying capacity, antiwear and antiwelding properties of oils are estimated with the four-ball machine FBM-K1 (Ukraine), which has the test unit made as pyramid of four ball 12,7 mm in diameter down-dropped in a cup with lubricant. The balls are made of steel ShCh-15 (C – 1%, Cr – 1.5%; analog of USA 52100 steel USA). Three of them form the base of pyramid and rotate with cup about a top ball. Tests are carried out according GOST 9490-75 requirements. Friction surface morphology is studied with the scanning electron microscope Vega II-LSH (Tescan, Czech Republic).

3. RESULTS AND DISCUSSION

Data on basic physical, chemical mechanical and tribological properties of investigated lubricants are presented in Table 1.

In common, the obtained data showed that basic properties of vegetable oils are just as well or better than of standard mineral oil. For example, flash-point temperature of vegetable oils is higher by 30-50 % than that of I-20 oil on the average. The freezing temperature of rape oil is close to minus 20 °C, which is lower than I-20 oil by 5 %.

As can be seen, most of the mechanical properties of vegetable oils are fairly close in magnitude. The data of Table 2 show that the ratio of saturated and unsaturated fats for all oils is close to 1:8. The average lengths of the alkyl chains of these fatty acid groups are also similar. Differences in the content of potentially tribologically active substances are significant only for sulfur and phosphorus compounds. However, the concentration of these elements is too small to have a noticeable effect on friction.

Table 1. Functional properties of oils.

Properties	I-20A	Sun-flower	Corn	Rape-seed	Olive	Lin-seed
Physical and mechanical properties						
Density, kg/m^3	885.2	919.7	917.7	918	910.3	930
Kinematic viscosity at 40°C, mm^2/s	33.1	33.8	35.6	34.3	41.7	15.22
Kinematic viscosity at 100°C, mm^2/s	5.3	8.1	8.5	8.6	8.8	6.33
Ignition Temperature, °C	222	245	232	280	316	>280
Solidification point, °C	-15	-17	-14	-10	+2	-21
Tribotechnical characteristics						
Parameter of wear (40 kg)	1.65	0.67	0.73	0.67	0.68	0.73
Critical load, kg	40	80	80	80	80	80
Welding load, kg	119	126	126	133	126	168
Load wear index	15	35	36	33	35	56

Table 2. Composition of plant oils, wt%.

Composition	Plant oil				
	sun-flower	corn	rape-seed	olive	linseed
Concentration of fatty acids, wt%					
C16:0. palmitic	7.6	12.3	6.1	11.2	5.6
C18:0, stearic	3.5	2.0	1.6	3.5	3.4
C18:1. oleic	24.8	29.0	54.6	77.3	15.3
C18:2. linoic	61.5	54.2	20.0	4.8	14.0
C18:3, linolenic	—	1.0	10.0	—	60.5
Average length of alkyl group	17.8	17.8	17.9	17.8	17.8
Average number of unsaturated bonds	1.51	1.43	1.35	0.9	2.5
FAs with the concentration of less than 1 %	2.6	1.7	7.7	3.2	1.2
Concentration of active elements. I0^{-4} wt%					
Phosphorus	4.1 ±0.4	—	—	—	27 ± 0.6
Sulfur	2.9 ±0.2	8.4 ± 0.3	3.20 ±0.2	1.9 ±0.2	44.2 ±0.5
Calcium	10.0 ±0.1	10.0 ±0.1	10.0 ±0.1	10.0 ±0.1	10.0 ±0.1
Zinc	0.3 ±0.1	0.4 ±0.1	<0.1	<0.2	0.3 ±0.1

Thus, the composition of the investigated oils, in terms of the ratio of the saturated and unsaturated acids content, their alkyl chain lengths and concentrations of triboactive matters, looks similar.

Obviously, the proximity of the structural, physical and mechanical properties of plant oils largely determines the fact that with the exception of linseed oil, their tribological characteristics do not differ too. Thus, the results of testing the hypothesis of the equality of the average values of plant oil wear factors indicate that they are statistically similar with a significance level of 0.01. It is established in the work [6] that the wear of copper – steel pair is directly proportional to the length of alkyl radicals of cholesteric liquid crystals used as lubricants. We can assume that this is also true for the friction of samples in the media of plant oils. In this case, the constancy of the alkyl radical length of the triglycerides of the materials studied explains both their identical anti-wear properties and the range of action of the surfactants, estimated by the value of the critical load, which equals 80 kgf for all studied oils.

Analysis of the oil welding load and load wear index shows that linseed oil exceeds by these parameters the other materials by one or two stages of load according to GOST 9490–75. It is most likely that the observed advantage of linseed oil is associated with a high content of triglycerides of linolic acid, which is characterized by relatively large number of unsaturated bonds (Fig. 1).

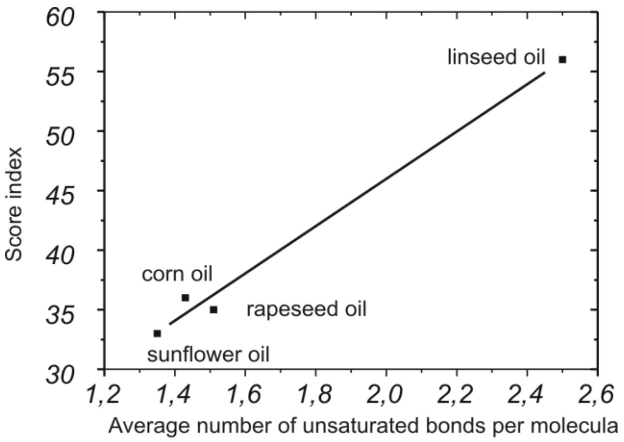

Fig. 1 Correlation of score index and relative number of the unsaturated bonds of plant oils.

Under the influence of tribomechanical factors, unsaturated compounds are easily oxidized and initiate the polymerization processes contributing to increase in the bearing capacity of the oil [7].

The formation of high-molecular resinous substances is confirmed by the presence of the typical deposit in the friction zone, the area of which is the larger, the greater the average number of unsaturated bonds of triglycerides (Fig. 2).

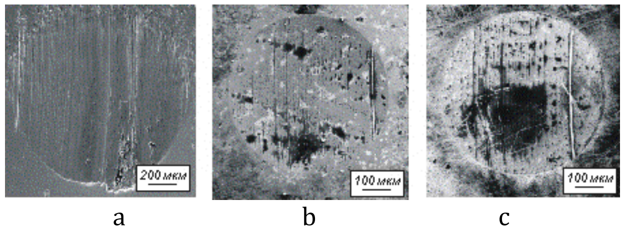

Fig. 2 Contact areas of samples after four-ball machine test in mineral (a), rapeseed (b) and linseed oil (b) correspondingly.

The influence of high temperature and pressure promotes the process of hydrolysis and oxidation of triglycerides.

The concentration of free fatty acids, mono- and diglycerides, mono- and oxy-acids must increase, and, most significantly, the synthesis of polymeric compounds (tribopolymers) should be present in the waste oils. IR spectra of oils before and after tribotechnical tests are analyzed to assess the degree of chemical degradation of plant oils. The obtained data indicate their small differences (Fig. 3).

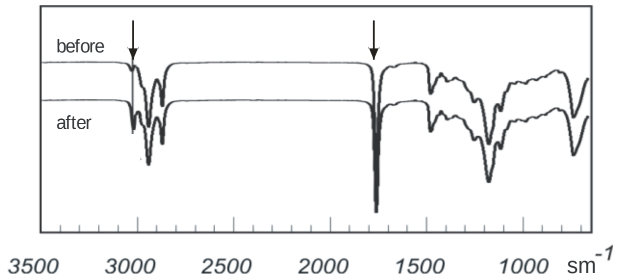

Fig. 3. IR absorbtion spectre of linseed oil before and after test on the four-ball machine.

Band intensity variation is observed at the frequency of 1746 cm^{-1}, typical of esters (C=O), and at the frequency of 3468 cm^{-1} specific to the functional group OH, while analyzing oil hydrolysis and polymerization processes. Thus, according to the data obtained by gas chromatography, the fatty acid composition of the initial and used oils differs insignificantly. In general, the results of the analysis of IR spectra and gas chromatography indicate that there is no significant destruction of triglycerides after the tests. To clarify this information, the observations of oils using thin layer paper chromatography were carried out.

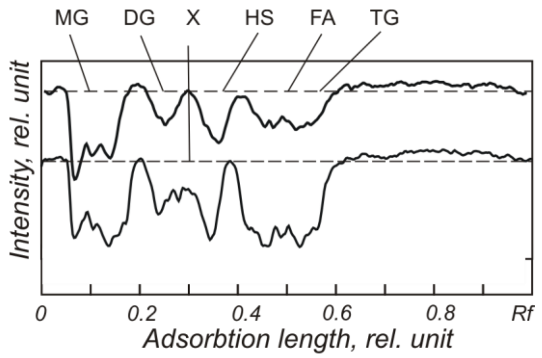

Fig 4. Chromatographic profile of linseed oil before (above) and after (below) test on the four-ball machine.

The chromatographic profiles of the initial waste linseed oil (the remaining oils have similar chromatograms) are shown in the Fig. 4. As can be seen, the relative spot intensities corresponding to mono- (MG) and dialcylglycerides (DG), fatty acids (FA), higher alcohols (HS), and triglycerides (TG) coincide rather well. The new X phase identified in the waste oil (Fig.4). Based on the position occupied on the chromategraphic profile between diacylglycerol (DG) and higher alcohols (HS), it can not be attributed to high molecular weight products. It is most likely that this phase is glycerol, formed as a result of hydrolysis of oil lipids. The absence of areas that could be attributed to high-molecular products is likely due to their low concentration. This means that the processes of oxidation and tribopolymerrization occur directly in the zone of frictional contact and do not enter in the bulk of lubricant.

4. CONCLUSION

The results of tests with four-ball machine show that refined plant oils have better complex of tribotechnical properties than the industrial base oil I-20A. All investigated oils are characterized by the same anti-wear properties and surfactants effective range that is associated with equality of values of their alkyl radicals average lengths.

It is shown that activation of unsaturated bonds as a result of oxidation and thermal-mechanical effects during friction positively affects friction. It is established that the processes of tribopolymerization occur directly in the zone of frictional contact, and High-molecular products do not come in significant quantities into lubricant. A comparative analysis of the chemical composition of the oils before and after tribotests does not reveal the products of destruction of triglycerides in significant amounts.

The obtained results suggest that decrease in the average length of alkyl radicals due to the introduction of lower unsaturated fatty acids into the triglyceride oils and the increase in the average number of unsaturated bonds by adding higher unsaturated fats can improve the tribotechnical characteristics of plant oils.

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