Tribology in Industry

RESEARCH

Investigation of Mixture of Vegetable Oil and Synthetic Esters as Environmentally Friendly Base Stock for Low-temperature Lubrication Applications

R. Kreivaitis[a], M. Gumbytė[a]

[a]Aleksandras Stulginskis University, Studentu 11, Akademija, LT-53361 Kaunas dist., Lithuania.

Corresponding author:

Raimondas Kreivaitis
Aleksandras Stulginskis University,
Studentu 11, Akademija, LT-53361
Kaunas dist., Lithuania.
E-mail: raimondas.kreivaitis@asu.lt

A B S T R A C T

Environmental issues are of great importance in all the areas of industry and transport. Usage of environmentally friendly, easily biodegradable lubricants has a benefit, when the oil can get into environment by using total loss lubricants, leakages or some accidents. Due to inherent biodegradability, extremely high viscosity index, lubricity, and low cost various vegetable oils are used to produce environmentally friendly lubricants. However vegetable oils have some drawbacks, in particular narrow temperature range and poor oxidation stability. The aim of current study is to evaluate possibility to improve vegetable oil cold temperature properties by dilution it with synthetic esters. The dilution of rapeseed oil is done up to 30 % by lower viscosity poly alpha olefins. The pure point, low temperature flow behavior and tribological properties of diluents are investigated. The results show significant improvement in pure point temperature and low temperature flow ability. Dilution has negative effect on tribological properties. However the investigated mixtures are compatible with antiwear additives and their tribological properties can be improved.

1. INTRODUCTION

It is already a few decades there is a concern to reduce pollution, therefore easily biodegradable, environmentally friendly lubricants are welcome in all the industrial and transport applications [1,2]. Vegetable oils and animal fats are major source for environmentally friendly lubricants base stocks production [2]. Vegetable oils are used pure as well as raw material for ester synthesis. While synthesis is energy consuming process, esters are used only where pure vegetable oils cannot satisfy requirements for certain applications [3,4].

As base stock vegetable oil possess superior viscosity index, low volatility, high flash point, friction and wear reduction in low loading conditions [5]. The main drawbacks of vegetable oils include poor low temperature behavior and poor oxidation stability at high temperature. At low temperature vegetable oils have a tendency to form macro-crystalline structure and solidify. At high temperature vegetable oils tend to rapid

oxidation, which leads the change of physicochemical properties. These are the main drawbacks which limits their wider use [6].

The low temperature properties usually are defined by pure point. According to the ASTM D97 standard test method the pure point is the lowest temperature at which movement of the specimen is observed. It is an index of the lowest temperature of its usage. The pure point of vegetable oils can be improved by using pure point depressants (PPD) and/or dilution. These two methods act in different ways. Commercially available PPD are known to contain a polymethacrylate backbone with the certain branching, which prevents formation of large crystals [7]. Dilution by some substance having lower viscosity and lower pure point enters the matrix of the oil making it less viscose and separating molecules which are crystal formation centers.

Most of PPDs effectively improve pure point, however they are not effective when oils are subjected to long term storage in cold environment. It is well known that vegetable oils possess different viscosity and cold flow behavior after being stored in a cold environment. For instance pure point of vegetable oil will be much higher after being stored in the cold environment in comparison to initial one [7].

The mixtures of canola and soybean oils with a few esters including poly alpha olefin were used to improve pure point temperature. It was found that PPD were superior to dilution. However they show synergistic effect when combined [7]. Other studies show that increasing amount of saturated fatty acids in vegetable oil can reduce efficiency of PPD [8].

The use of diluents in the same time can improve more than one characteristic of vegetable oils. There was an attempt to use oil mixtures in order to enhance oxidation stability of vegetable oils. Safflower oil was mixed with polyol esters and promising results were obtained [9]. Some other reports show that one base oil is more compatible with antiwear additives than another [10]. Therefore dilution is more versatile method than application of PPD.

Dilution is also covered by eco-labels for lubricants. According to European Union Commission 2005/360/EC hydraulic and two-stroke oils can be diluted up to 50 %, greases – 55 %, chainsaw oils, concrete release agents and other total loss lubricants up to 30 % by some non-renewable substances [11].

The aim of current study is to evaluate possibility to improve vegetable oil cold temperature properties by dilution it with synthetic esters.

2. MATERIALS AND METHODS

2.1 Materials used

The refined, bleached and deodorized low erucic rapeseed oil was used as vegetable oil representative (VO). Two low viscosity synthetic poly alpha olefins PAO 4 and PAO 6 were used for dilution of vegetable oil. 1 % of conventional ash less antiwear additive was used.

2.2 Preparation of diluents

Dilutions were made in two different concentrations 10 and 30 % (by wt.) of poly alpha olefins in VO. Based on EU commission regulation, for total loss lubricants, 30 % is the maximum content of non-renewable substance in total loss lubricants, while 10 % is the minimum value having significant difference in the results. To obtain homogeneous solutions samples were mixt on magnetic stirrer using 400 rpm, and 60 °C for 30 min. The obtained mixtures were stabile suspensions, and shoved no separation after 30 days of storage in the lab.

2.3 Physico-chemical properties

Viscosity and viscosity index were evaluated according to standard test methods ASTM D 445 and ASTM D 2270 respectively. Corrosiveness of tested samples was evaluated according to ASTM D 130 standard test method. The temperature of 100 °C and test duration of 3 hour were used. Pure point temperature was measured according to ASTM D97 standard test method.

2.4 Low-temperature flow behaviour

Before low-temperature tests all the samples were heated up to 60 °C to avoid influence of

thermal memory. The fluidity was evaluated using special equipment, similar to that used in diesel fuel CFPP determination (Fig. 1).
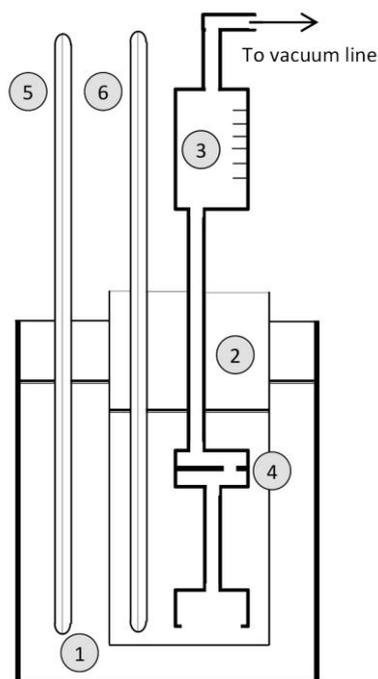

Fig. 1. Equipment for determination of low temperature fluidity. 1 – cooling bath; 2 – specimen bath; 3 – measuring vessel; 4 – calibrated hole; 5 – bath thermometer; 6 – sample thermometer.

The test procedure was done as follows. 50 ml of test oil sample was placed in the measuring vessel and its temperature is monitored. The cooling bath temperature is caped 10 °C lower that the expected sample temperature. Ones the particular temperature was reached the sample was pumped through the 4 mm hole with 1963 Pa vacuum. The time value is recorded when 30 ml of the sample was pumped. The test temperatures were: 20; 10; 5; 0; -5; -10; -15; -20; and -25 °C.

The long term cold storage fluidity was evaluated after 6 hours of exposure to the temperature of -10 °C.

2.5 Tribological teats

Four-ball type tribotester was employed for wear and friction evaluation using 12.7 mm diameter 100Cr6 bearing steel balls. The test sample of 22 ml was enough to fully submerge stationary balls. Under the applied load of 150 N, rotation speed of 1420 rpm, the machine was run for 1 hour. Friction coefficient between the balls was continuously recorded during the test. Prior to each experiment, all the appropriate parts of the machine, i.e. oil vessel and the test balls were washed in heptane, and then dried.

Friction surfaces were analysed using optical metallographic microscope NIKON Eclipse 1000 and SEM Quanta 650. For each run the scar measurements were reported as an average of the Wear Scar Diameter (WSD) of the three stationary balls.

All the tests were repeated at least 3 times to get variation coefficient ≤ 5 %.

3. RESULTS AND DISCUSSIONS

Physicochemical properties of pure base stocks and their mixtures are given in Table 1. It was observed that dilution leads to slightly decreased viscosity and viscosity index in comparison to pure VO. The pure point temperature is decreasing with increasing amount of synthetic oil. There is no significant difference between used synthetic oils. However the lowest pure point temperature is reached using 30 % of PAO 4.

As can be seen in Fig. 2 dilution with synthetic esters effectively improves low-temperature fluidity of vegetable oil and has negligible influence on fluidity above 0 °C. However, not like in the case of pure point, there is much more difference between efficiency of synthetic oils.

Table 1. Physicochemical properties of investigated base oils and their mixtures.

Base oil	Viscosity, mm2/s		Density 40 °C, g/cm3	Pure point, °C	Viscosity index
	40 °C	100 °C			
VO	34.0	8.0	0.899	-22	214
PAO 4	18.6	4.1	0.805	-68	128
PAO 6	29.6	5.9	0.811	-61	147
VO + 10 % PAO 4	33.2	7.6	0.893	-24	210
VO + 30 % PAO 4	28.8	6.6	0.827	-31	197
VO + 10 % PAO 6	33.9	7.8	0.894	-23	201
VO + 30 % PAO 6	32.1	7.2	0.873	-29	198

Dilution of vegetable oil with PAO 4 increased its fluidity in the temperature of -15 °C by 18.6 and 33.6 % for 10 and 30 % dilution respectively.
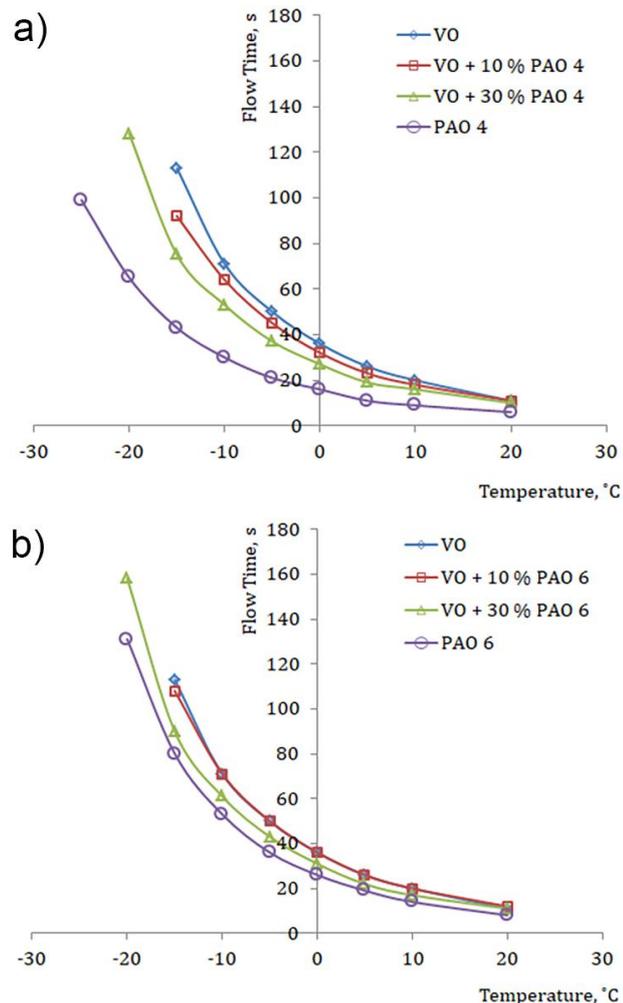

Vegetable oil and synthetic oils as well as their blends low-temperature fluidity fall in power law over the investigated temperature interval.

It is evident from Fig. 3 that vegetable oil possesses purer fluidity after being stored in -

10 °C. Flow time increased almost two times during 6 hours of storage. Dilution with synthetic esters improved VO fluidity, however esters have different influence. 10 % of PAO 4 increased VO fluidity by 43 %. Further increase in PAO 4 content has less influence. To improve VO fluidity using PAO 6, 30 % mixture is required. This data correlates with above discussed low-temperature fluidity. Despite of different efficiency in the mixtures both PAOs have stabile flow time before and after storage in cold environment.
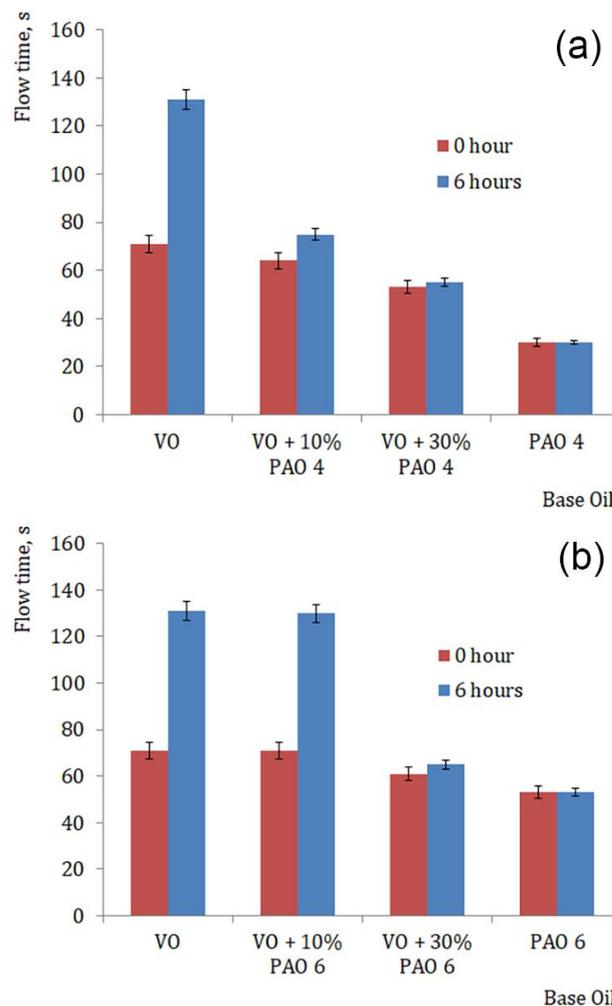

Fig. 2. Low-temperature flow behaviour of pure vegetable oil and synthetic esters as well as their mixtures. (a) – mixtures with PAO 4; (b) – mixtures with PAO 6.

In the same time dilution with PAO 6 was not so effective. 10 % of PAO 6 has almost no influence on VO fluidity down to -10 °C. In the temperature of -15 °C its improvement was 4.4 and 20.4 % for 10 and 30 % dilution respectively. The difference between PAO's can be described by lower viscosity of PAO 4 and slightly lower its pure point as referred in Table 1.

Fig. 3. Long term cold storage fluidity after 6 hours of exposing in -10 °C. (a) – mixtures with PAO 4; (b) – mixtures with PAO 6.

The short chain synthetic esters usually possess high corrosiveness to metal surfaces. The investigated synthetic oils PAO 4 and PAO 6 respectively have 3a and 3b copper corrosion values (Table 2). It is not allowed to use lubricants having such corrosiveness. In generall to reduce corrosiveness special additives are applied. In our study we tested and compared

corrosiveness of prepared samples. It was found that mixing with vegetable oil can reduce corrosiveness to appropriate values. Some substances of rapeseed oil act as corrosion inhibitors.

Table 2. Corrosiveness of investigated base oils and their mixtures.

Base oils		Corrosiveness
Pure	VO	1a
	PAO 4	3a
	PAO 6	3b
Mixtures	VO + 10 % PAO 4	1b
	VO + 30 % PAO 4	1b
	VO + 10 % PAO 6	1b
	VO + 30 % PAO 6	1b

The wear reduction results are shown in Fig. 4. It was expected and it is evident from the graph that both synthetic esters possess much lower wear reduction ability in comparison to VO. It is due to polar molecules presented in VO structure, which make adsorption layer on interacting surfaces. Adsorbed molecules prevent direct metal to metal contact and reduce friction. However physically adsorbed layers are relatively weak in comparison to chemisorbed

ones and are effective in low loads and moderate temperatures [12,13]. 10 % of synthetic oil in the mixture diminishes wear reduction ability of VO. However it is still better than that of pure synthetic oil. The further increase of synthetic oil part in the mixture up to 30 % makes the situation even worse, reaching ball wear greater than that observed using pure synthetic oil.

In all the mixtures AW additives demonstrated improved wear reduction. 1 % (by wt.) of AW additive significantly decreases ball wear, making it lower than that of VO. Moreover increasing amount of synthetic oil, in the mixture, slightly increases efficiency of AW additive. The reason can be better compatibility of AW with synthetic then vegetable base oil. Similar situation is observed in the cases of engine oil additives, where synthetic are superior to mineral base oils [10]. This result shows compatibility of AW additives with mixtures of VO and synthetic oil and should be further investigated for optimum concentration.

The friction reduction properties of synthetic oils and their mixtures with VO have poor correlation with wear reduction ability (Fig. 5).
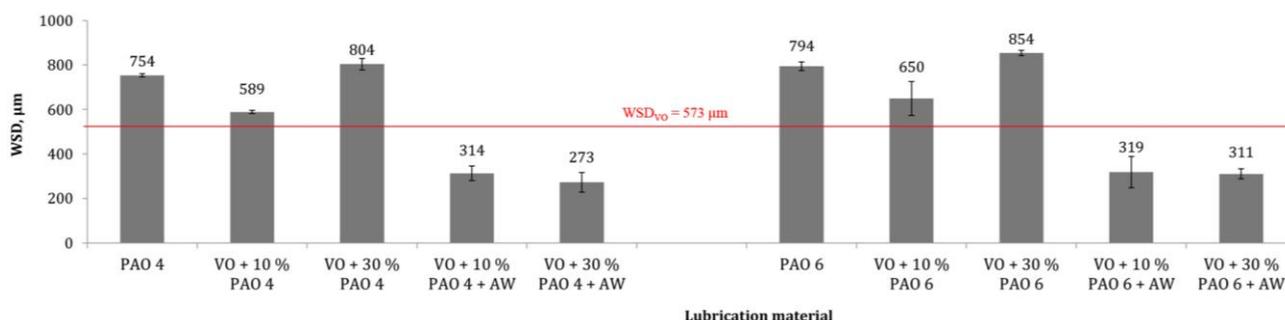

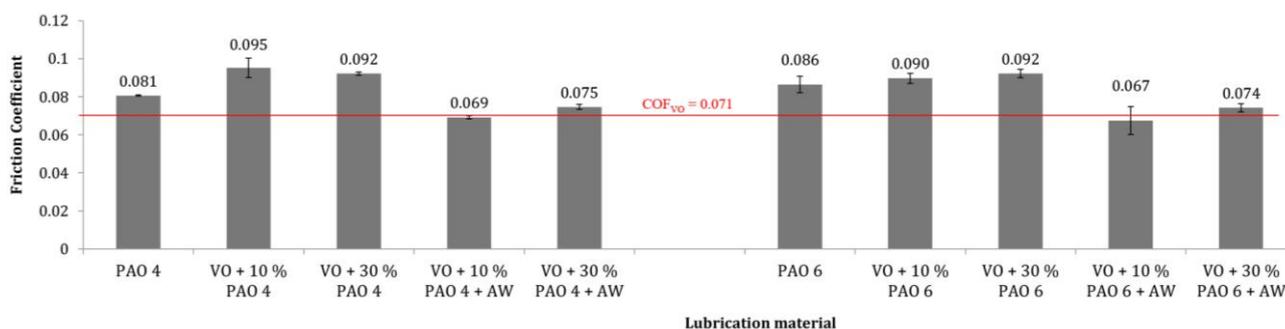**Fig. 4.** Wear reduction results observed after four-ball tribotest.

Fig. 5. Mean friction results observed during four-ball tribotest.
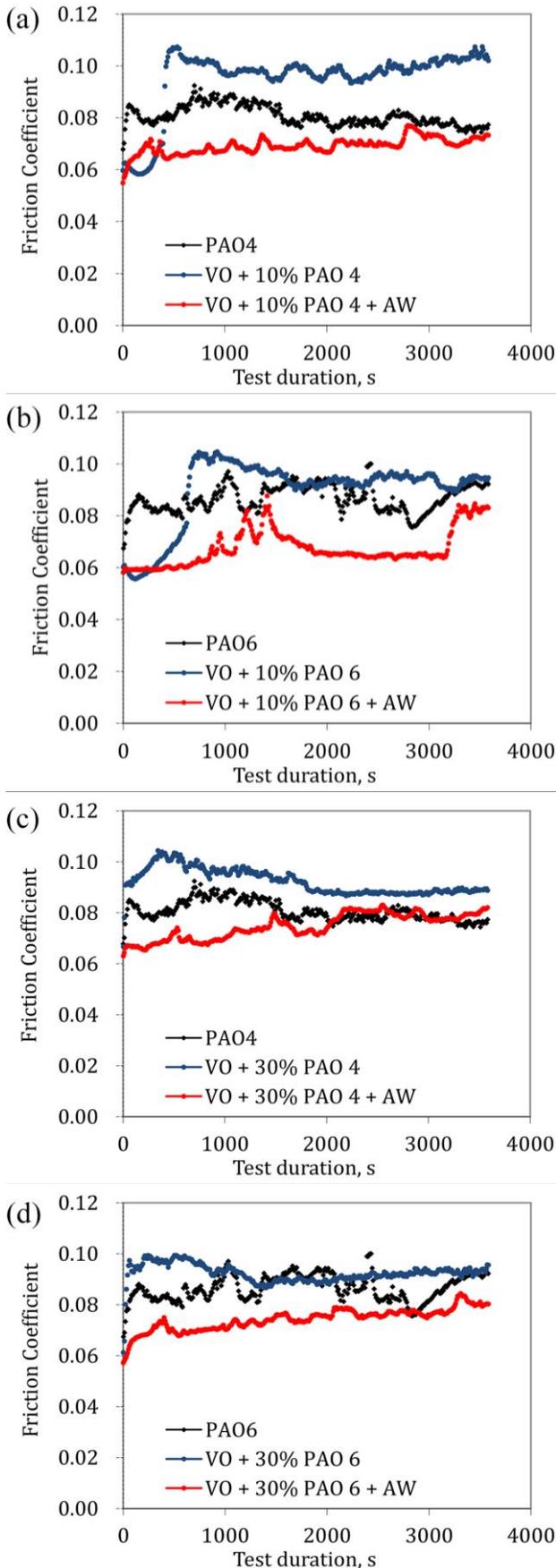
Fig. 6. Friction variation during the test when lubrication with the blends of VO and PAO 4 (a and c), and VO and PAO 6 (b and d).

According to average friction, the amount of synthetic oil in VO has no significant effect. However wear reduction results shoved 37 and 31 % wear increase going from 10 to 30 % of PAO 4 and PAO 6 in the mixture respectively. The mismatch can be explained analysing friction variation during the test (Fig. 6). When the mixture of VO + 10 % PAO is used the initial friction is low and close to that of pure VO (Fig. 6 a and b). However due to presents of PAO, lubrication is poor, leading to higher wear rate and contact temperature rise.

When contact temperature exceeds activation energy of adsorbed layer the layer disappears leading to friction increase [12]. In present case the friction starts to rise after 200 s of the test. Increasing amount of PAO reduces adsorption layer even more. In the cases of 30 % mixture there is high friction from the beginning of the test (Fig. 6 c and d).

The friction of AW additive loaded samples is similar than that of VO which is not in the line with wear results as well (Fig. 4 and 5). Most likely friction was increased due to chemisorption of AW additive. It is generally known that physical adsorption possess much lower friction than chemisorption. The friction increases slightly when VO content is reduced in the mixture (30 % of synthetic oil). Alternatively the wear was lower due to of stronger chemisorbed layer (Fig. 4).
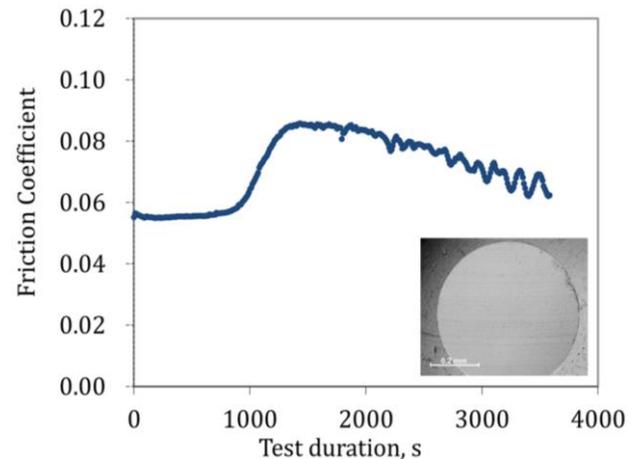

Fig. 7. Friction variation during the test and wear scar appearance when lubrication with pure rapeseed oil.

As can be seen in friction variation graphs the presents of AW additive in most cases slightly reduces friction variation during the test (Fig. 6).
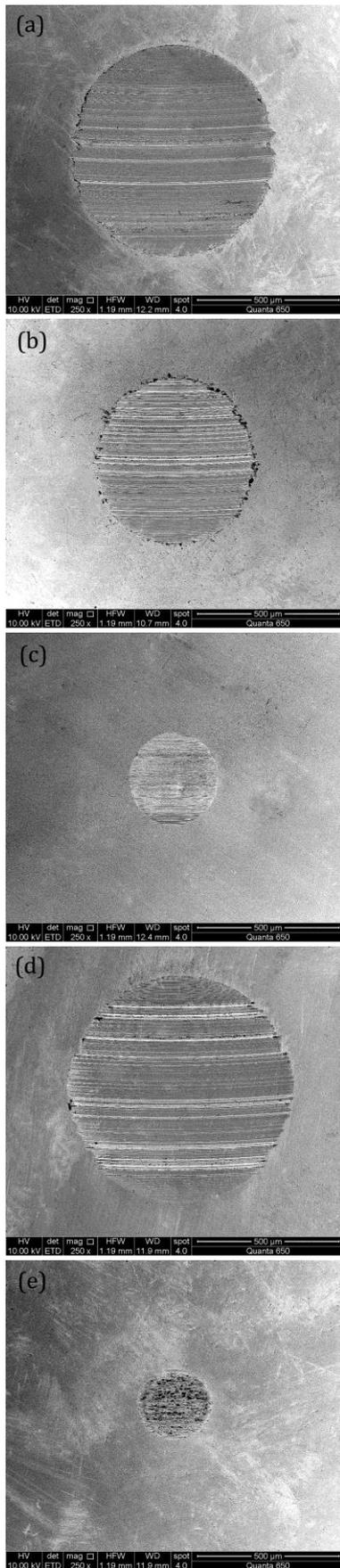
Fig. 8. WSD on the balls lubricated with PAO 4 (a); VO + 10% PAO 4 (b); VO + 10% PAO 4 + AW (c); VO + 30% PAO 4 (d); VO + 30% PAO 4 + AW (e).
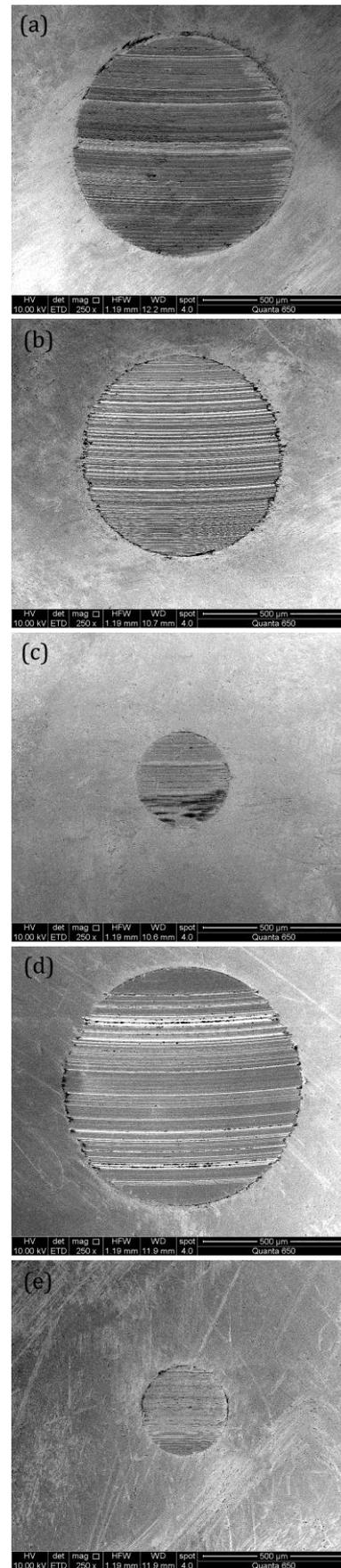

Fig. 9. WSD on the balls lubricated with PAO 6 (a); VO + 10% PAO 6 (b); VO + 10% PAO 6 + AW (c); VO + 30% PAO 6 (d); VO + 30% PAO 6 + AW (e).

However, the friction has tendency to increase. The increased friction variation, in the case of VO + 10 % PAO6 + AW, can be explained by competition of polar VO molecules and AW additive molecules. They both are seeking to reach the metal surface and make the situation worse.

For comparison the friction variation during the test lubricated with pure rapeseed oil is presented in Fig. 7. The friction process is smoother in comparison to that of synthetic oils and has three main steps.

In the beginning, while adsorbed layer separates the surfaces, there is a low and stabile friction region. When the contact temperature reaches adsorption activation energy the layer disappears or weakens leading to friction rise. The further decrease in friction is due to wear induced decrease in contact pressure.

Appearances of wear scars formed on the balls during friction are presented in Figs. 8 and 9. In all the cases without AW additives the abrasion is dominating wear mechanism. A lot of small groves are formed on the wear scars lubricated with pure synthetic oils as well as their mixtures with VO. It is an evidence of poor lubrication ability in boundary lubrication conditions. In contrast wear scar formed during the test lubricated with pure VO is very smooth (Fig. 7) The wear scars formed in the case of lubrication with pure PAO (Figs. 8a and 9a) has less abrasion than that observed in the case of both mixtures (Figs. 8b, 8d, 9b and 9d). This result is in the line with friction results (Fig. 5). In the case of AW additive loaded samples wear scars are smother and have some chemisorbed layer left on the surface (Figs. 7e and 8c).

4. CONCLUSIONS

Blending of rapeseed oil with poly alpha olefins improves its low temperature properties. More than 30 % improved low temperature fluidity can be reached using 30 % of PAO 4. In the same time pure point temperature is reduced from -22 °C to -31 °C for pure rapeseed oil and its blend respectively.

Blending is also effective in low temperature long term storage. 10 % of PAO 4 increased rapeseed oil's fluidity after 6 h of storage by

43 %. To reach similar results 30 % of PAO 6 mast be used.

Rapeseed oil in the mixture with synthetic oils reduces their corrosiveness;

Both synthetic oils diminishes rapeseed oil's lubricity, however their blends are compatible with antiwear additive which improves lubricity.

The investigated blends can be used as base stocks in production of environmentally friendly lubricants for instants hydraulic or total loss lubricants. Choosing particular application, all the other properties must be also improved.

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