

TRIBOLOGICAL EVALUATION OF SOYBEAN OIL ADDITIVATED WITH NANO GRAPHENE

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ABSTRACT

This paper presents the influence of adding nano graphene particles in soybean oil in different massic concentration (0.25%, 0.50% and 1%) on the tribological parameters: friction coefficient, wear scar diameter. Tests are done on a four-ball machine from the lubricant laboratory LubriTest, at “Dunarea de Jos” University of Galati. The test parameters were load: 100 N, 200 N and 300 N and the speed 1800 rpm. The additive was supplied by PlasmaChem and the dry graphene - nanoplatelets have a thickness: 1-4 nm; particles size: up to 2 μm , purity: 91 at.%. The soybean oil was supplied by Prutul Galati. The test balls are lime polished, made of chrome alloyed steel balls, having 12.7 ± 0.0005 mm in diameter, with 64-66 HRC hardness, as delivered by SKF. The sample oil volume required for each test was $8 \text{ ml} \pm 1 \text{ ml}$. The test method for investigating the lubricating capacity was EN ISO 20623:2003 Petroleum and related products - Determination of the extreme-pressure and anti-wear properties of fluids - four ball method.

Keywords: soybean oil, nano graphen, wear, friction coefficient.

1. INTRODUCTION

Soybean oil could become a source for the base oil in fields of activities that require non-polluting processes and materials [1, 2, 3, 4, 25]. As other vegetable oils, this one, too, has low viscosity [5] and research has been done for additivating this oil in order to increase its viscosity or/and to protect the rubbing surfaces by specialized additive (especially anti-wear and extreme pressure additives) [6, 17]. But vegetable oil-based lubricants have several disadvantages as compared to mineral and synthetic ones, including low viscosity that not encourage the generation of a continuous film when the tribosystem runs, consequently, implying a mixt or boundary lubrication. This is why the additivating of such vegetable oils is of great interests for researchers, producers and users [2, 6, 7].

Recent reviews of the mechanisms of friction reduction and anti-wear of nanoparticles in lubricants were published, pointing out lubrication

mechanisms as rolling effect, protective film, mending effect and polishing effect [7, 8]. Shahnazar et al. [9] presented a classification of nano additives in lubricants. Those based on carbon were included in four main allotropic classes: zero-dimensional (fullerene), one-dimensional (nanotubes, nanowires, nanorodes), two-dimensional (graphene), three-dimensional (graphite, nano-sized diamonds) [10, 11].

Hwang [12] concluded that lubricants with nano additives improve the tribological behavior as compared to microaddition in the same base oils. The nanoparticles play the role of nano ball bearings. He used several carbon-based additives tested on a disk-on-disk tribotester.

Hu et al. [13] investigated the efficacy of the carbon black as an engine soot substitute and concluded that WSD (wear scar diameter) increased with the content of black carbon in the range of 0...8% for a certain grade of engine oil, but for the other, the same parameter has lower values as those

for the neat oil. Tested time was only 0.5 h (too short for such tribosystems) but they concluded that friction coefficient depends on the base oil and carbon concentration.

Many research reports used a pin-on-disk tribometer for evaluating the anti-wear additives [14], but also, the four ball tribotester is favorable to compare experimental results [15, 26].

In 2014, Bergman [23] concluded that despite intense research efforts on graphene for existing and future applications, its tribological potential as a lubricant remains relatively unexplored. Recent tribological survey and research studies based on graphene from the nano-scale to macro-scale, were published by her team [23, 24], its use as a selflubricating solid or as an additive for lubricating oils was investigated but adequate applications are still far to be reported in literature.

This paper aims to report the influence of nano graphene as additive in soybean oil on the tribological behavior of the formulated lubricants by the parameters friction coefficient and the wear rate of wear scar diameter.

The aim of this paper is to present the influence of additive concentration on two important tribological characteristics, friction coefficient and wear scar diameter.

2. TESTING METHOD

This paper presents the influence of adding nano graphene particles in soybean oil in different mass concentration (0.25%, 0.50% and 1%) on the tribological parameters: friction coefficient, wear scar diameter. Tests are done on a four-ball machine from the lubricant laboratory LubriTest, at “Dunarea de Jos” University of Galati.

The rapeseed oil was processed and supplied by Prutul Galati.

Table 1. Typical fat acid composition for the tested soybean oil

Acid	Symbol	Concentration, %wt
Myristic acid	C14:0	0.11
Palmitic acid	C16:0	12.7
Palmitoleic acid	C16:1	0.13
Heptadecanoic acid	C17:0	0.05
Stearic acid	C18:0	5.40
Oleic acid	C18:1	21.60
Linoleic acid	C18:2	52.40
Linolenic acid	C18:3	5.70
Arachidic acid	C20:0	0.25
Gondoic acid	C20:1	0.20
Eicosadienoic acid	C20:2	0.50

The additive was supplied by PlasmaChem [16] and the dry graphene - nanoplatelets have a thickness: 1-4 nm; Particles size: up to 2 μm Specific surface area: 700-800 m^2/g , purity: 91 at.%, other elements: O<7 at.%, N < 2 at.%.

The degumming and refining process of soybean oil is done at Prutul SA Galati and prevents oil to form gum deposit and to ferment [17].

The test balls are lime polished, made of chrome alloyed steel balls (Table 2), having 12.7 ± 0.0005 mm in diameter, with 64-66 HRC hardness, as delivered by SKF. The sample oil volume required for each test was 8 ml \pm 1 ml.

The test method for investigating the lubricating capacity was EN ISO 20623:2003 Petroleum and related products - Determination of the extreme-pressure and anti-wear properties of fluids - four ball method [18].

Table 2. Chemical composition of the steel the balls are made of (wt%)

Element	C	Cr	Mn	Si	S	P
Steel grade EN31	1.0	1.3	0.5	0.35	0.05	0.05

The test parameters were: speed (1000 rpm, 1400 rpm and 1800 rpm corresponding to the following sliding speeds 0.383 m/s, 0.537 m/s and 0.691 m/s, respectively), normal load (100 N, 200 N and 300 N), testing time 1 hour.

The formulated lubricants were obtained in a small quantity of 200 ml each. The steps followed in this laboratory method were:

- weighting the additive and the dispersing agent with an accuracy of 0.1 mg,

- mechanical mixing of additive and equal mass of guaiacol (supplied by Fluka Chemical), chemical formula being $\text{C}_6\text{H}_4(\text{OH})\text{OCH}_3$ (2-methoxyphenol), for 20 minutes; this dispersing agent is compatible with both additive and vegetable oils,

- adding soybean oil for getting 200 g of lubricant with the desired concentrations of additive,
- stirring with a magnetic homogenizing device for 1 hour,

- sonication + cooling of 200 g lubricant for 5 minutes with the help of sonicator Bandelin HD 3200 (Electronic GmbH & KG Berlin); the cooling time was 1 hour; this step sonication + cooling is repeated 5 times for obtaining a total sonication time of 60 minutes. The parameters of sonicating regime are: power 100 W, frequency 20 kHz \pm 500 Hz, continuous regime.

3. Results

The evolution of friction coefficient (COF) in time was evaluated by a moving average function (for 200 recording samples) as the test is running for 1 hour with 2 recording samples per second).

Taking into account the stages of friction coefficient, as proposed by Czikos [19], one may notice that using these lubricants (soybean oil + nano-graphene), the first stages are almost insignificant as time duration.

For the soybean oil (without additive), the best results were obtained for the highest tested speed (1800 rpm), these results being supported by EHD theory that point out that speed is the most important parameter in increasing the minimum height of the lubricant film [20, 21, 22]. Under the lowest det of test parameters (100 N, 1000 rpm), COF has a slight tendency of increasing its value, very probably starting with a fluid film lubrication and finishing with a very probably mixt regime. All other regimes (speed 1400 rpm and 1800 rpm and load 100...300 N), the values for COF are below 0.7, meaning a complete fluid film lubrication. Under the most severe regime (F=300 N, v=1800 rpm) COF is not obviously dependent on load (Fig. 1c).

The lowest concentration of nanoadditive (Fig. 2) makes the friction coefficient more stable under the lowest speed (v=1000 rpm).

There is a slight increase of COF for the lowest speed (1000 rpm) when running tests with boybean oil, a tendency that is missing for the additivated oils, but not depending on additive concentration.

For 0.25% nano-graphene, the regime characterized by v=1400 rpm keeps COF very close, seeming not dependent on load (in the tested range F=100N ... 300N). Similar evolution of the friction coefficient in a narrow interval was noticed for concentration of 0.50% and 1.0%, but at higher speed (1800 rpm) (Figures 3 and 4).

In Figure 5, the average values of COF calculated for all test time (1h) are plotted. Comparing data for F=100 N, one may notice that adding nano-graphene this average is lower, but a tendency of dependence on speed is not obvious. For 0.25% additive, the COF average is higher than the neat base oil for F=200 N and F=300 N, but for the other two concentration, the values are lower than those obtained for the neat soybean oil.

Except for the regime F=100 N and v=1000 rpm, the lubricant formulation with nano-additive do not have the tendency to increase the value of COF in time. This means that the additive is acting during all test duration.

At v=1800 rpm, the friction coefficient is oscillating more than in other tested regime. This could be explained by a non-uniform migration of the additive in contact.

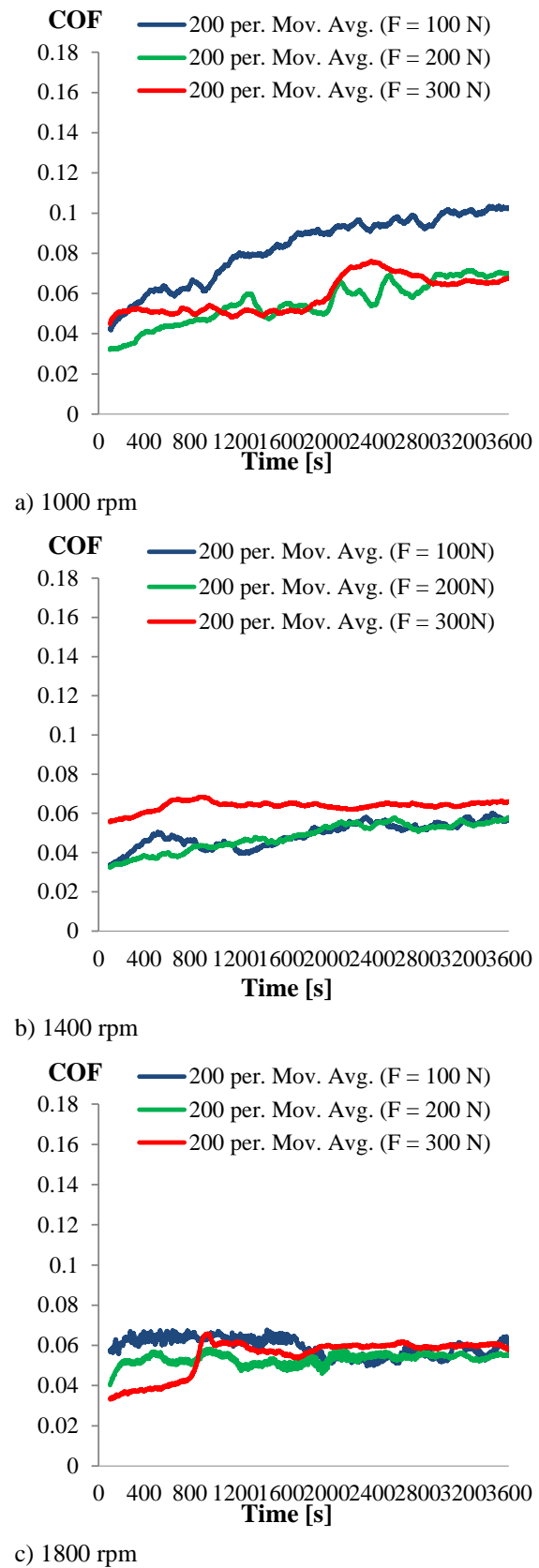
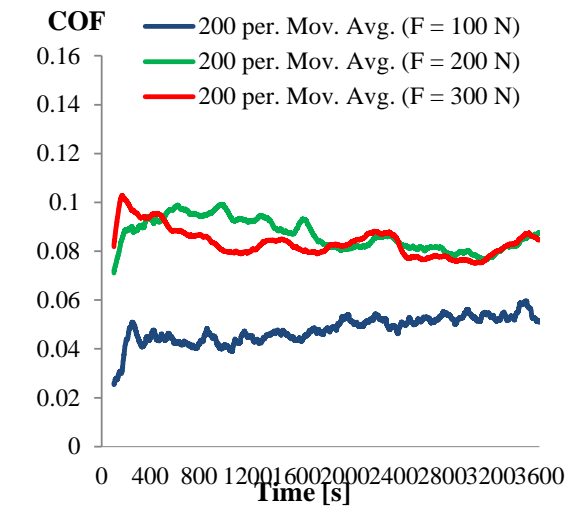
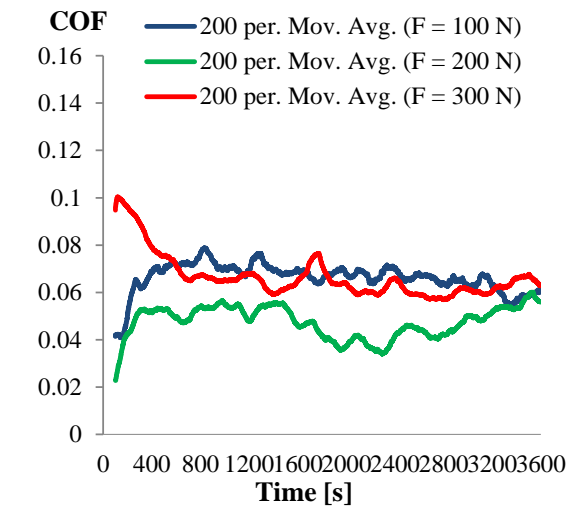


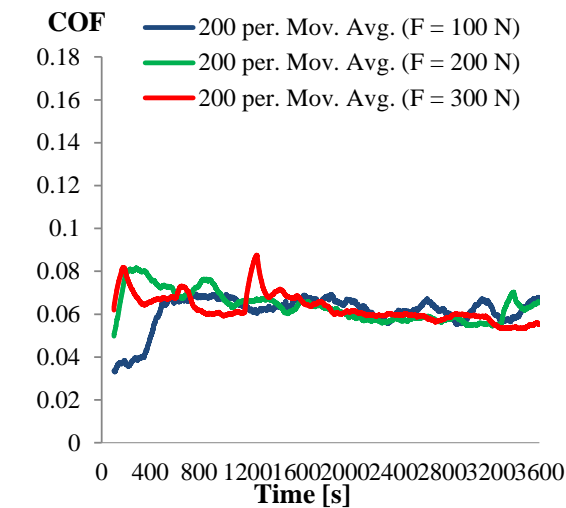
Fig. 1. Evolution of friction coefficient in time for the non-additivated soybean oil



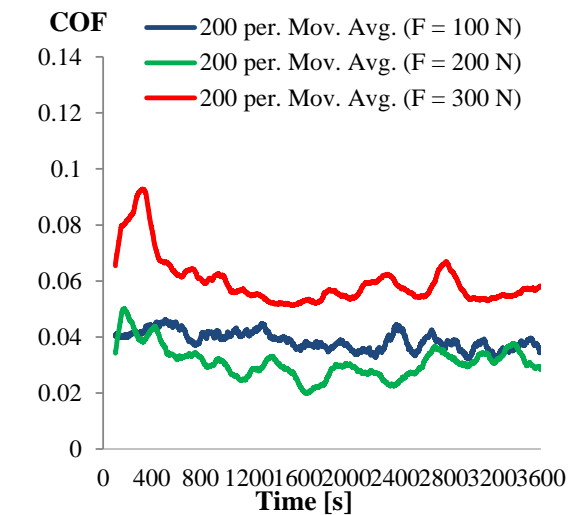
a) 1000 rpm



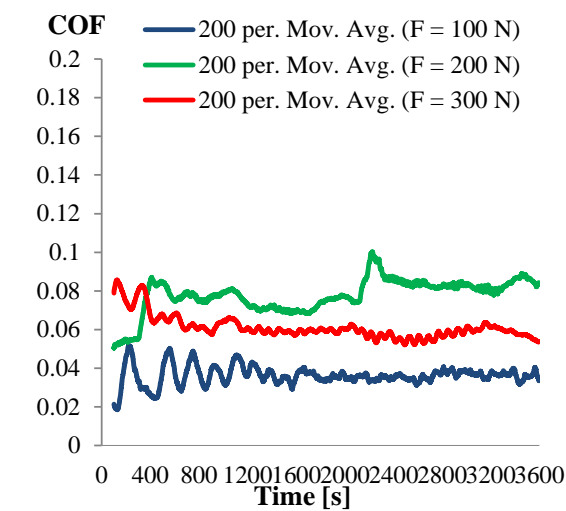
a) 1000 rpm



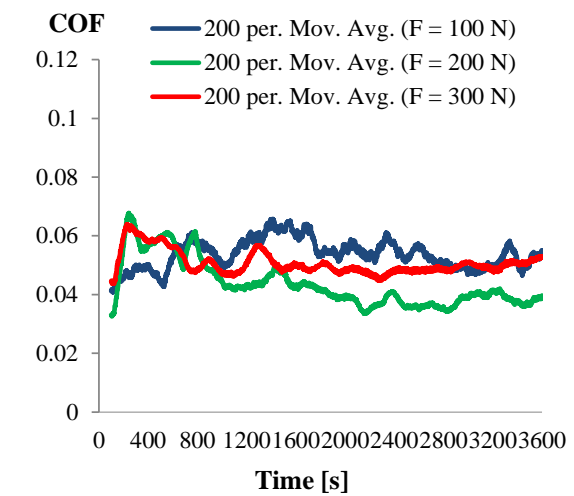
b) 1400 rpm



b) graphene, 1400 rpm



c) 1800 rpm



c) 1800 rpm

Fig. 2. Friction coefficient in time for soybean oil additivated with 0.25% nano graphene

Fig. 3. Friction coefficient in time for soybean oil additivated with 0.5% nano graphene

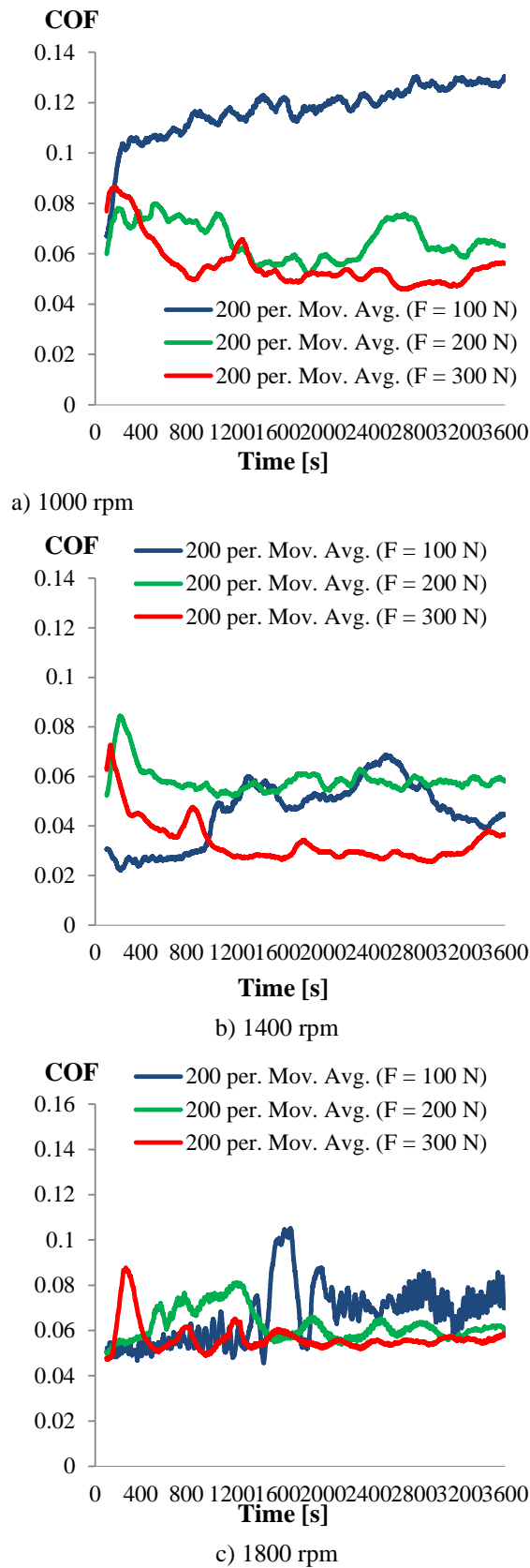


Fig. 4. Friction coefficient in time for soybean oil additivated with 1.0% nano graphene

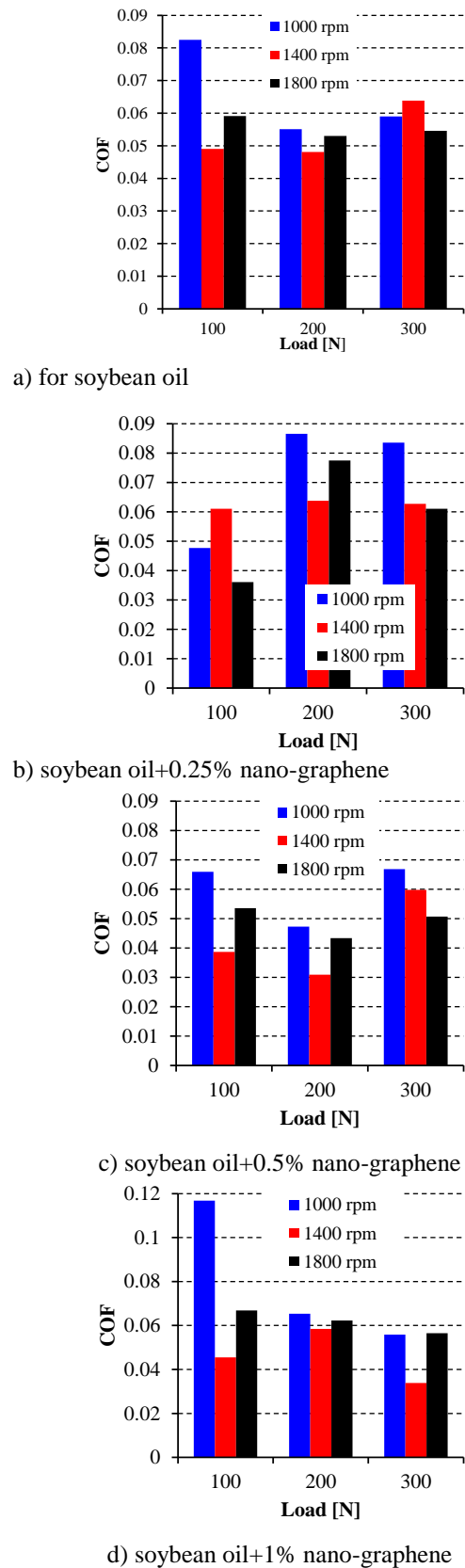


Fig. 5. The average values of COF (calculated for the entire test of 1 h)

As the test duration was 1 hour, the sliding distance for a test depends on the sliding speed. Thus, the sliding distances were calculated for this time, taking into account the sliding speed between balls: $L_{1000}(v=0.383 \text{ m/s})=1378.8 \text{ m}$, $L_{1400}(v=0.537 \text{ m/s})=1933.2 \text{ m}$, $L_{1800}(v=0.691 \text{ m/s})=2487 \text{ m}$.

Due to this aspect, the authors selected as parameter for wear evaluating the wear rate of WSD, calculated with the following relationship.

$$w(WSD) = \frac{WSD}{F \times L} [mm/N.m] \quad (1)$$

where WSD is the average value of those measured for the three balls involved in one test. The product $F \times L$ is the work done by the tribosystem and, thus, $w(WSD)$ is this wear rate is reported to the work unity.

Figure 6 presents the wear scar for a set of three balls, tested with soybean oil +0.5% nanographene, under the test conditions of 100 N, 1000 rpm, 1h. Wear is more intense in the middle of scars, but the diameters are close for all balls, meaning a stable regime on each ball.

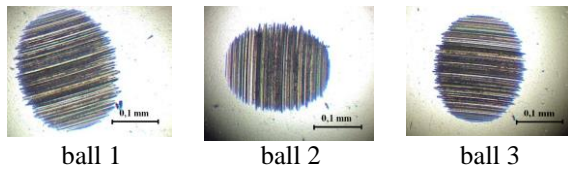


Fig. 6. Example of wear scars after testing the soybean oil + 0.5% nano-graphene, 100 N, 1000 rpm

Under the load of 100 N, a clear dependence of the WSD rate was not possible to be obtained, but for 200 N and 300 N, the results make possible to formulate several conclusions:

- under the heavier load of 300 N, the WSD rates are lower than those for 200 N, for all tested concentrations and speeds, meaning that a greater load makes the additive to remain in contact and protect the surfaces,
- also, for this load, additive concentration of 0.5% and 1% generates only slight differences for the rate of WSD.

3. Conclusions

For the tested regimes ($F=100 \text{ N} \dots 300 \text{ N}$ and $v=1000 \dots 1800 \text{ rpm}$), the results are not in the favour of the additivated lubricant formulations.

The addition of nanographene increases the WSD rate. As comparing only the additivated oil, it seems that under low speed, when the load increases the WSD rate increases, too. Under the loads of 200 N and 300 N, WSD rate is less depending on speed

and load for the concentrations of 0.5% wt and 1.0% wt nanographene.

It seems that this anti-wear additive (nanographene) does not have a very clear influence on improving the tribological behavior of soybean oil.

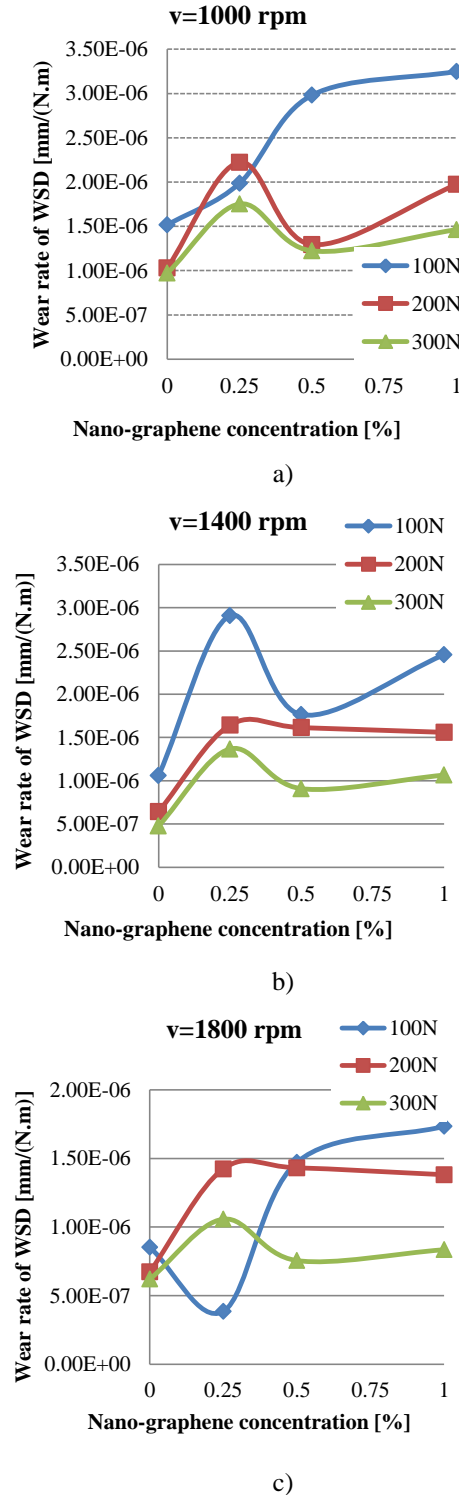


Fig. 7. Influence of nano-graphene concentration on the wear rate of WSD

Even if the mechanism of reducing friction exists in the presence of the additive, that is interposing particles of nanographene between the rubbing surfaces and having a third body friction, the migration of these particles (because they are not bonded to the surfaces by chemical reaction as other additives) and the uneven distribution in contact make the tribosystem to behave more unstable than in the presence of the neat soybean oil. In a statistical approach, at a moment, there could be enough nano particles in contact to reduce friction and wear but, during running, there could be moments when this number is low enough to have mixt regime and the oscillations between these two situations could explain the variations of the friction coefficient and the higher values for WSD rate.

This type of anti-wear additive, because the particle distribution is not even in contact during the running could not help improving the tribological behavior, as it does not reduced the friction coefficient and wear scar diameter as compared to the neat soybean oil, at least for the teste range of load and speed. The authors think that the additive should be bonded (physically or chemically) for having better results.

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