Influence of Additive concentration in Soybean Oil on Rheological and tribological Behavior

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Abstract*: The rheology of vegetal oils, additivated or not and the factors that influence their viscosity have been studied by specialists, in order to introduce these oils as lubricants in green industries as agriculture, food processing, transportation and for complying with environmental and health regulations; the vegetal oils are also envisaged as an eco-friendly alternative to similar mineral and synthetic products. This study presents the influence of nature and concentration of additive in soybean oil on its rheological and tribological behavior, reflected by shear stress - shear rate, viscosity - temperature curves and by the wear scar diameter (WSD) after testing the formulated lubricants on a four- ball machine.*

Key Words: *soybean oil, black carbon, graphite, graphene, viscosity, shear rate*

1. INTRODUCTION

The rheology of vegetal oils, additivated or not, and the factors that influence their viscosity have been studied by specialists, in order to introduce these oils as lubricants in green industries as agriculture, food processing, transportation and for complying with environmental and health regulations; the vegetal oils are also envisaged as an eco-friendly alternative to similar mineral and synthetic products [1], [2]; Quinchia et al. [3] reported a viscosity increase for low-viscosity vegetable oils (sunflower oil, high-oleic sunflower oil and soybean oil), at moderate temperatures when adding 3...4 %wt. ethylene–vinyl acetate copolymer. Additives based on allotropic phase of carbon are added in lubricants but their influence on the rheological behavior of vegetal oil are still under research [4]. The purpose of this study is to evaluate rheological and tribological properties of non-additivated soybean oil and lubricants formulated with carbon nanoparticles (amorphous carbon, graphite and graphene), in different concentrations.

2. METHODOLOGY, EQUIPMENT AND MATERIALS

2.1 Materials

The refined soybean oil, as supplied by Prutul Galati has the following composition in fatty acids (in wt%): 0.11% acid myristic (C14:0), 12.7% palmitic acid (C16:0), 0.13% palmitoleic acid (C16:1), 0.05% heptadecanoic acid (C17:0), 5.40% stearic acid (C18:0), 21.60% oleic acid (C18:1), 52.40% linoleic acid (C18:2), 5.70% linolenic acid (C18:3), 0.25% arachidic acid (C20:0), 0.20% gondoic acid (C20:1), 0.50% eicosanoic acid (C20:2).

Additives were supplied by PlasmaChem [5]: nano amorphous carbon (average particle size ~ 13 nm), nano graphite (average particle radius: 400 - 450 nm), nano grafene (nano plates with a thickness of 1.4 nm and a particle size of up to 2 microns), each added in different concentrations (0.25%, 0.50%wt, 1.0%wt).

The experimental test equipment for evaluating the rheology of lubricants is a Brookfield CAP 2000+ rotational viscometer, controlled by a dedicated software, CAPCALC 32. In order to determine the rheological model for the analyzed lubricants, an "imposed gradient" type test was used, at a constant temperature, using as working geometry the cone 8 (Table 1). The viscometer has the possibility to perform thermal determinations, namely, for this study, the variation of the rheological parameters with the temperature, in the range of 5°C to 75°C.

One of tribotsters recommended for evaluating the tribological behavior of lubricants is the four-ball system.

Table 1. Geometry and cone viscosity measuring beach 8

Cone number	Cone radius [mm]	Angle at the top of the cone [°]	Measured viscosity [Pa·s]	Shear rate [s^{-1}]
8	15.11	3	0.312 ... 3.12	200 … 2000

The formulated lubricants were obtained in a small amount of 200g each, by sonication and the laboratory-scale manufacturing is given in [6]. A good dispersion till the lubricant was used for testing was solved by making a premix of additive + dispersion agent (1:1), here guaiacol (from Fluka Chemica), having the formula C_6H_4 (OH) OCH_3 (2-methoxyphenol).

For these lubricants, the following rheological and tribological properties were determined: the law of variation of shear stress depending on the speed gradient (shear rate), the dependence of viscosity on the temperature, for a certain value of the shear rate and the wear rate of wear scar diameter – w(WSD).

2.2 Rheological Tests

Tests were performed twice for the same fluid, characterized by the concentration and nature of the additive. Figure 1, presents comparative reports for neat and additivated soybean oil with different concentrations of nano additive. The following graphs gives only one test for each set of parameters (shear rate – shear stress, temperature - viscosity).

In viscous fluids, the shear leads to increased internal friction forces, which dissipate some of their kinetic energy as heat. At low shear rates, in low-viscosity fluids, the phenomenon is minor, the fluid temperature increase due to energy dissipation being negligible. High viscosity fluids can generate significant amounts of heat, which results in changes in fluid properties, including in viscosity.

The main cause of fluid deviation from the Newtonian behavior is the modification of its structure under the action of the shear stress [7].

For the soybean-oil based lubricants, additivated with nanoparticles, the following analyzes were performed:

- comparative graphs of neat soybean oil and formulated lubricants for shear stress depending on shear rate and modelling of their behavior with a power law;
- temperature viscosity dependence for the gradient of 2000 s^{-1} speed and modelling the temperature dependence of viscosity and the additive concentration.

2.3 Four-ball testing and the wear rate of wear scar diameter

Wear scar diameter (WSD) is characteristic of the four-ball machine and many authors also give the results of wear using this parameter [8].

WSD is the arithmetic mean of the six measurements, two on each of the three fixed balls of a test.

For each ball, the wear diameter was measured in the direction of sliding and perpendicular to it.

Since the authors estalished the duration of the test at 1h, the sliding distances are different at different speeds: $L_{(v = 0.38\ m/s)}$ = 1378.8 m (1000 rpm for the rotating ball); $L_{(v = 0.53\ m/s)}$ = 1933.2 m (1400 rpm for the rotating ball); $L_{(v = 0.69\ m/s)}$ = 2487 m (1800 rpm for the rotating ball). Thus, the graph of the WSD as a function of additive concentration, load and speed is not relevant due to the difference in the sliding distances, and then, based on [8], the wear can be also evaluated by another parameter, called the wear rate, where:

$$w = \Delta V / (F \cdot L) \tag{1}$$

where ΔV represents the variation in sample volume (volume of removed material), F is the loading force and L is the sliding distance.

The product is the mechanical work of the tribosystem, in other words, the wear rate shows the loss of volume material for the mechanical work unit performed by the system; the wear rate of WSD (wear scar diameter) is:

$$w(WSD) = \frac{WSD}{L \cdot F} \quad [mm/(N \cdot m)] \tag{2}$$

3. RHEOLOGICAL EVALUATION

3.1 Shear stress dependence on shear rate for the formulated lubricants

From a rheological point of view, the soybean oil has an increased thixotropy in both neat and additivated state.

It is interesting to note that, at low shear rates below 600...700 s^{-1}, this thixotropy disappears for all formulated lubricants (see Fig. 1).

For the soybean oil, the additivation with nano additives has a very limited influence on changing the thixotropic behavior, specific to non-additivated oil. So, lubricants formulated with these nano additives also have a similar hysteresis to that exhibits by the neat soybean oil. From a rheological point of view, the soybean oil has an increased thixotropy in both neat and additivated state.

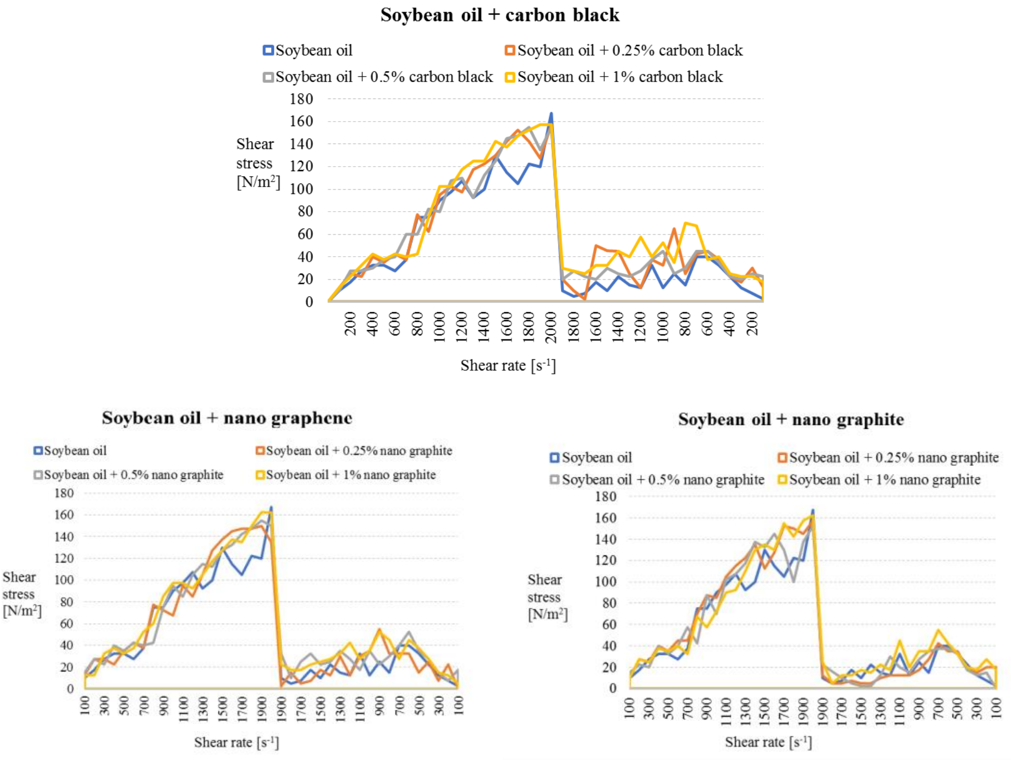

Figure 1 - Comparative reports for neat and additivated soybean oil with different concentrations of nano additive and shear rates

Based on experimental data, the authors modeled the rheological behavior of these lubricants with the help on a power law:

$$\tau = m \cdot \dot{\gamma}^n \tag{3}$$

where m and n are material constants; m is called the consistency index [$m^{-1} \cdot s^{n-2}$] and n – the flow index (non-dimensional), $\dot{\gamma}$ is the shear rate [s^{-1}].

Table 2. Variation of the consistency index and flow index depending on the concentration of lubricant additive

		Power law	
Lubricant	Additive concentration [%wt]	Consistency index [Pa×s^n]	Flow index
Soybean oil	0%	2.02	0.454
Soybean oil + carbon black	0.25%	1.78	0.473
	0.5%	1.63	0.494
	1%	1.07	0.578
Soybean oil + nano graphite	0.25%	5.58	0.26
	0.5%	1.9	0.435
	1%	2.49	0.41
Soybean oil + nano graphene	0.25%	2.71	0.384
	0.5%	1.06	0.548
	1%	0.426	0.686

The variation of rheological parameters (consistency index and flow index) depending on the concentration and nature of the additive is shown in Table 2. Because of the pronounced hysteresis, the correlation coefficient is small. This is also visible in Figure 1.

Analyzing the values in Table 2 with respect to those for the neat soybean oil, the consistency index decreases with the increase of nano carbon concentration and the same evolution is for the lubricants with graphene. The lowest value was obtained for the soybean oil + 1% nano graphene. Except the high value at a concentration of 0.25% nano graphite, the consistency index is almost equal for concentration of 0.5% nano graphite to that of soybean oil and for concentration of 1% nano graphite it increases only to 2.49.

The flow index increases with low gradient for fluids with carbon and with a higher one for the fluids with nano graphene. The influence of nano graphite concentration on the same parameter has a less clear tendency of increasing. The authors divided the field of shear stress evolution depending on shear rate in two areas (Fig. 1):

- an area with pronounced thixotropy (between 600 ... 700 s^{-1} and 2000 s^{-1}, for the tested lubricants), less sensitive to additive concentration and nature;

- an area in which the fluids do have a dependence on the shear rate variation (100 s^{-1}...600-700 s^{-1}) with low gradient, the influence of additive being difficult to be established. The delimitation seems to depend more on the concentration of the additive and less on its nature. The thixotropy is manifested at a lower shear rate (600 s^{-1}) for lubricants with 1% nano additive.

Increasing the shear rate has increased the shear stress, but the obtained curves evolve in a narrow range, being almost insensitive to the addition of the nano particle and concentration, this fact being more visible when drawing the plot only for the increasing or decreasing shear rate, as in Fig. 1. For the soybean oil, the additivation with these nano additives (black carbon, nano graphite and nano graphene) has a very limited influence on changing the thixotropic behavior.

3.2 Temperature dependence of viscosity for the formulated lubricants

The dynamic viscosity decreases with the temperature rise. The values of the dynamic viscosity of the vegetal oils tend to become very close as the temperature increases [9], [10]. The increase in temperature tends to increase intermolecular motion and reduces the attraction forces among the oil molecules.

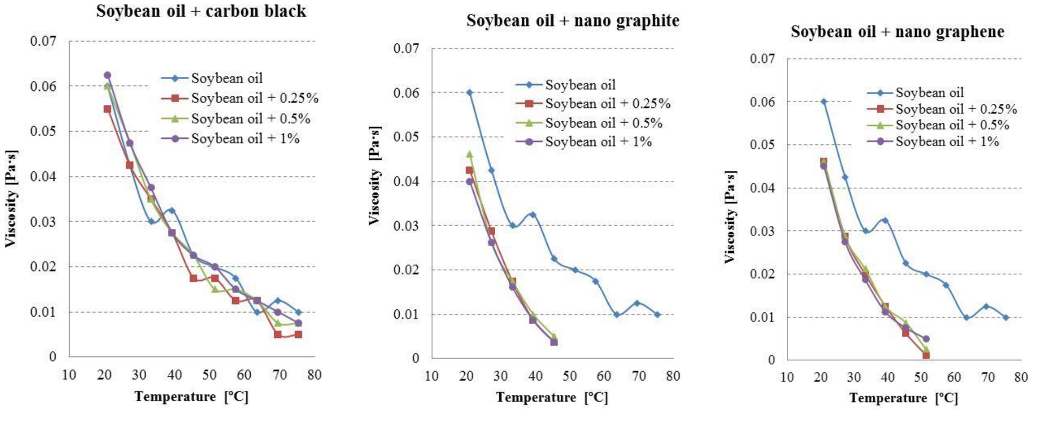

Figure 2 - The dependence of dynamic viscosity on the concentration of the additive and temperature

A similar study was conducted by Solea [9], but for lower shear rates (3.3...80 s^{-1}). The soybean oil had the lowest viscosity temperature curves of the tested oils (corn oil, rapeseed oil, corn oil). Analyzing the graphs in Figure 2, the following conclusions can be drawn concerning the influence of the nature of nano additive on the dynamic viscosity dependence of temperature.

The addition of nano black carbon does not significantly alter the viscosity dependence on temperature, at least for the temperature range at which rheological tests have been performed and as compared to the neat soybean oil.

For all formulated nano lubricants, the viscosity does not depend significantly on the additive concentration.

The formulated lubricants can be grouped into two categories:

- soybean oil and soybean oil additivated with nano carbon, characterized by higher values of dynamic viscosity;
- lubricants additivated with nano graphite and nano graphene, with lower values of dynamic viscosity.

For the soybean oil additivated with graphene and graphite, the curves superpose, having a greater slope than that of the neat soybean oil, with a slight scattering at 50°C.

Wang et al. [11] reported rheological measurements of graphite/oil nanofluids and they noticed an obvious shear thinning, significant viscosity increase, for a nanofluid containing 1.36 vol.% graphite with dispersant, offering the evidence for generating percolating aggregate structures.

But the authors' results pointed out a systematically decrease of the dynamic viscosity when adding graphite and graphene as additive in the soybean oil. Only black carbon had not a sensitive influence on the viscosity, the values being very close to those for the neat soybean oil (Figure 2).

The lowering of curves characterizing the lubricants with graphene and graphite may be explained by the reduction in internal friction when oil molecules slide against those carbonic materials. Logically, the friction of black carbon against oil molecules would have similar values as the friction between the molecules themselves. This tendency is not obviously dependent on the additive concentration.

In a recent review, Murshed and Estellé [7] underlined that rheology of nanofluids demonstrate that they could have both Newtonian and non-Newtonian behavior, depending on many factors, including temperature, base fluid viscosity, shear rate as well as concentration, type and size of nanoparticles, but they did not mentioned a decrease of viscosity when adding a friction and wear modifier.

For the tested nano additives, no clear dependences of the parameters can be established depending on additive concentration and its nature, when added in the soybean oil.

4. ANALYSIS OF THE WEAR RATE OF THE WEAR SCAR DIAMETER

Figures 3, 4 and 5 presents plots of the wear rate of the wear scar diameter only for two additive concentrations: 0.25%wt and 1%wt. Values for 0.5%wt concentration is given in [6]. The fallowing conclusions may be formulated:

- high values were obtained for the mildest test regime (F = 100 N and v = 0.38 m/s); one could argue that contact oscillations do not keep the additive in contact,
- the lowest value was for the most severe regime (F = 300 N, v = 0.69 m/s), explained by forming a total or partial EHD film and maintaining the nano additive in contact due to higher pressure,
- the wear rate of WSD are similar for 0.25% and 1% meaning the additive concentration (0.25%...1%) does not influence to much the wear.

It seems that the wear is made in stages and is smaller for longer sliding distances (obtained for the higher speed).

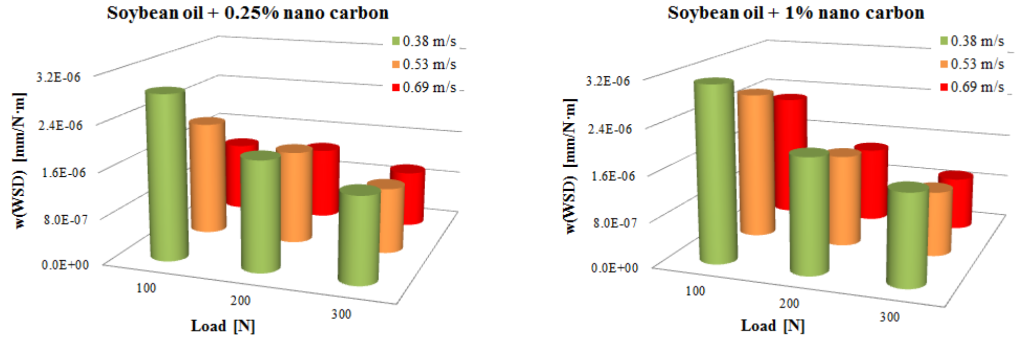

Figure 3 - WSD wear rate for amorphous nano carbon - additivated lubricants

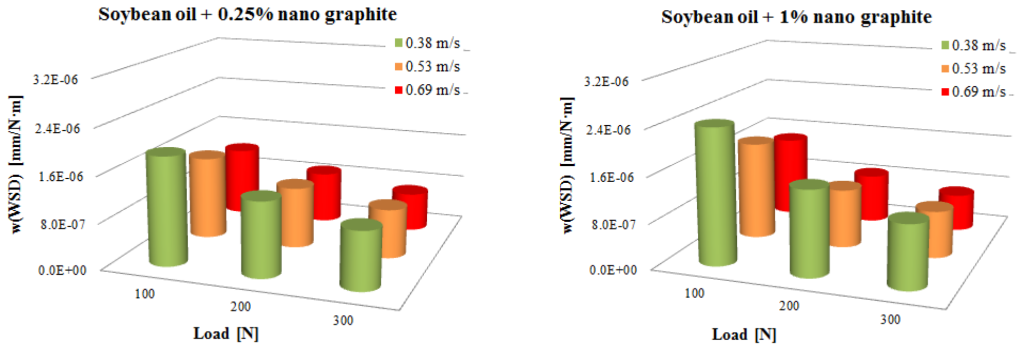

Figure 4 - WSD wear rate for nano graphite additivated lubricants

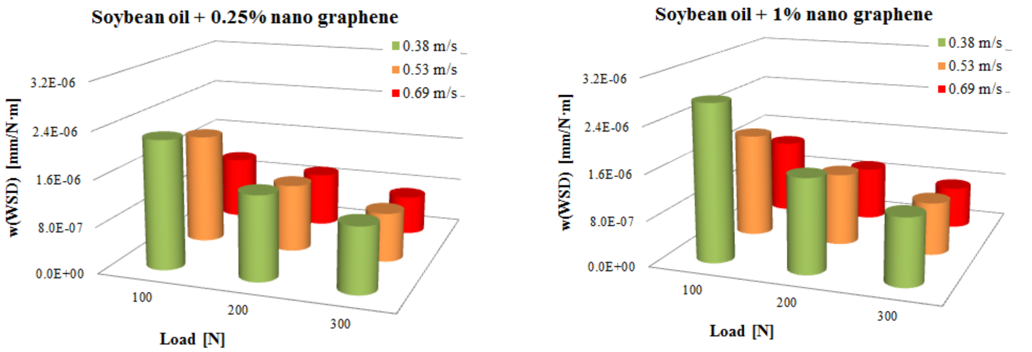

Figure 5 - WSD wear rate of lubricant additivated with nano graphene

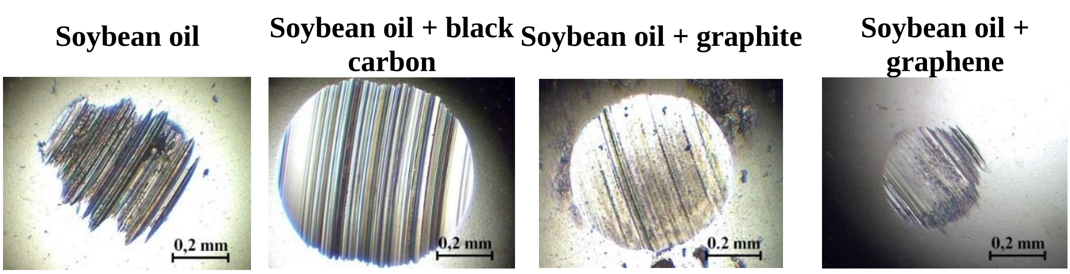

Figure 6 - WSD for the formulated lubricants + 1% nano additive, tested at v = 0.69 m/s and F = 300 N

Even if the average value of w(WSD) for the regime (v = 0.69 m/s, F = 300 N) had the lowest value for the neat soybean oil, the nano additivated lubricants giving values just a little bit greater, the surface quality was better [6].

This can be noticed from Figure 6 when comparing the wear scar obtained with soybean oil with that after lubrication with 1% graphene, under the same test condition.

5. CONCLUSIONS

For nano graphene and nano graphite added lubricants, the curves temperature - viscosity have lower values and a greater slope than the neat soybean oil, with a slight scattering at 50° C. The rheological model that characterizes the behavior of the studied lubricants is the model of power law, but with a low correlation coefficient. This is due to the phenomenon of pronounced thixotropy for the neat soybean oil, but also for the additivated lubricants. If only the loading curve for shear stress – shear rate dependence is considered, this tends to be close to the linear one. All tested lubricants, including the neat soybean oil, have an increased thixotropy after a certain shear rate value, which does not depend on the nature of the nano additive, but on the additive concentration. The lubricant formulated with soybean oil and nano carbon does not significantly affect the dependence temperature – viscosity as compared to that of the neat oil. But nano graphite and nano graphene as additive move down the curves of the dynamic viscosity dependence on temperature, for all the tested concentrations of the additive, in the temperature range of 20....80°C.

Analyzing a tribological characteristic, the wear rate w(WSD) determined by testing on the tribotester with four-balls points out the best tribological behavior for the nano graphite and black carbon lubricants in the concentration of 1.0 % wt.

The tendency of decreasing the wear rate of WSD had a sharper gradient for the lubricants additivated with 1% wt additive, this fact recommending the testing program for more severe regimes as it is highly probably that the additive would protect better the surfaces in contact. From a tribological point of view, degummed soybean oil can be used as a basic material for biodegradable lubricants.

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