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Tribological Behavior of Soybean Oil

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Abstract

This chapter presents experimental data in the favor of using soybean oil, additivated or not, as lubricants, the market share of the soybean oil on the lubricants' market, a SWOT analysis for better configuring the tribological characteristics of the soybean oil and tribological parameters as friction coefficient, wear scar diameter, wear rate of wear scar diameter, etc. and their dependence on testing regime (load and speed). Also, the influence of temperature, shear rate, and oxidation parameters on the soybean oil viscosity is discussed.

Keywords: soybean oil, viscosity, tribology, friction, wear, scar wear diameter

1. About soybean oil, in the favor of using it as lubricant

1.1 SWOT and market analysis

The world vegetal oil production was around 182 million tons in 2016/2017 [1]. In 2017, the bio-lubricants market was evaluated at 2.47 billion USD, and it would value 3.36 billion USD by 2022, at a growth rate of 6.4%.

Environmental regulations, increasing production of vegetal oils, and their applications are market drivers. But their still high price and the decline in petrol resources are factors hindering the growth of this particular market [2]. North America is intended to be the largest market by 2022, but Europe led bio-lubricants market in 2016 and some of its member states (Germany, France, and Finland, but also Norway as an economic partner) ask for environment protection and biodegradability standards and regulations in the favor of these lubricants. For instance, the focus on "green chemistry", the regulation on environment protection and advances in research, should lead the bio lubricants to develop and gain the market on longer term, as an increase of using them is estimated if a more strong incentive policy is applied in European Union (**Table 1**).

The major restraints are deficiency in interconnecting regulations and higher prices than petroleum-based lubricants. The North American market for soy-based lubricants was estimated at USD 191.5 million in 2016 [4].

The Ag-Based Industrial Lubricants Research Center (USA, Northern Iowa) patented 30 genetically modified soybean lubricants (oils and greases) for tractor, chains, compressor, manufacturing processes and transmissions, metalworking and cooling fluids, fluids for the food industry, oils, transformer oils, greases for cars, railways, etc. [5].

Industrial applications	2008	Production forecast 2020		
	Lubricants [t]	Biolubricants [t]	Biolubricants, if a moderate incentive policy will act [t]	Biolubricants, if a strong incentive policy is applied [t]
Hydraulic fluids	650,000	68,000	155,000	230,000
Oils for chainsaws	50,000	29,000	37,000	40,000
Mold release oils	100,000	9000	15,000	30,000
Other uses*	3,600,000	31,000	70,000	120,000
Total	4,400,000	137,000	277,000	420,000

*Lubricants for gears, engine, metal working, electric transformers, and base-stock for greases.

Table 1.
Estimation of consumption of biolubricants [3].

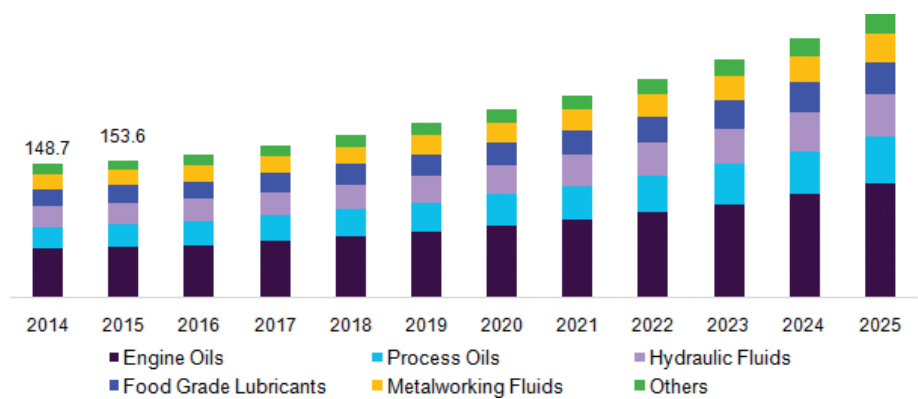


Figure 1.
Soybean lubricant market in the USA, depending on the application, for the time interval 2014–2025 (in million USD) [4].

A study of the American market reveals that the value of lubricants based on soybean oil will constantly increase, almost similar for major applications of these lubricants (engines, food processing, manufacturing process, and hydraulics) (**Figure 1**).

Research on soybean oil as gear lubricant was published by Ibrahim [6]. Soybean oil is used as biodiesel in a small share as compared to other vegetal oils, especially rapeseed oil, but the tribological characteristics are important even in this application [7].

Energy resources from renewable crops have gained prominence in order to replace petroleum products. Bio-lubricants become acceptable alternatives to conventional lubricants. Despite their benefits, these are still far from being practical. Since bio-lubricants are produced from raw vegetal oils, they have poor flow properties at low temperature and poor thermo-oxidative and hydrolytic stability. However, these shortcomings can be addressed by modifying the vegetal oils chemically [8] or incorporating additives into the oils [9, 10]. From **Figure 2**, one may notice that the production of soybean oil has been increasing constantly, and a considerable amount is used for producing lubricants.

Figure 3 presents the diversity in composition in fatty acids of several vegetal oils [12]. This would be the explanation of the very particular behavior of vegetal oils under boundary or fluid lubrication. Hence, it is necessary to control the fatty acid composition of vegetal oils [13]. The composition in fatty acids could also vary

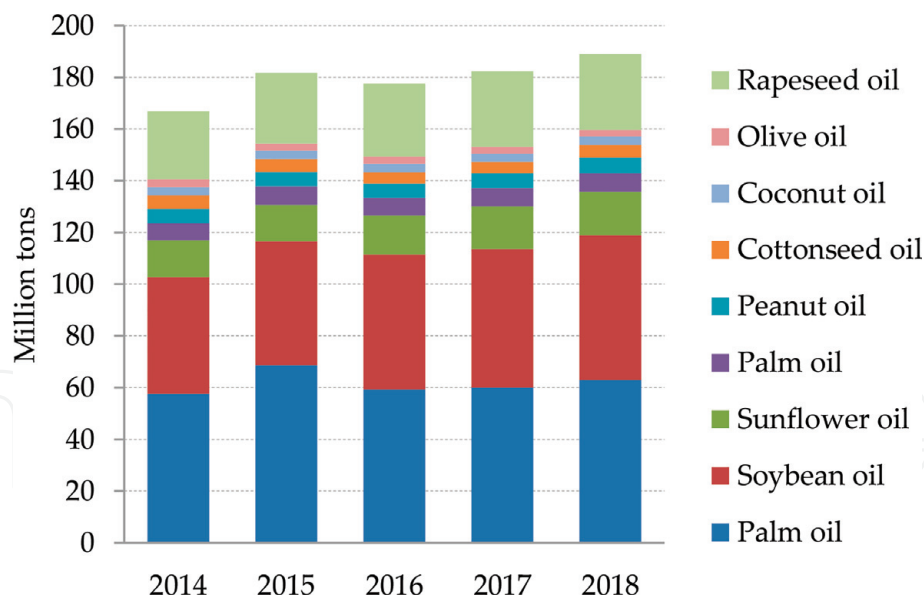


Figure 2.
Consumption of vegetal oils (adapted from [11]).

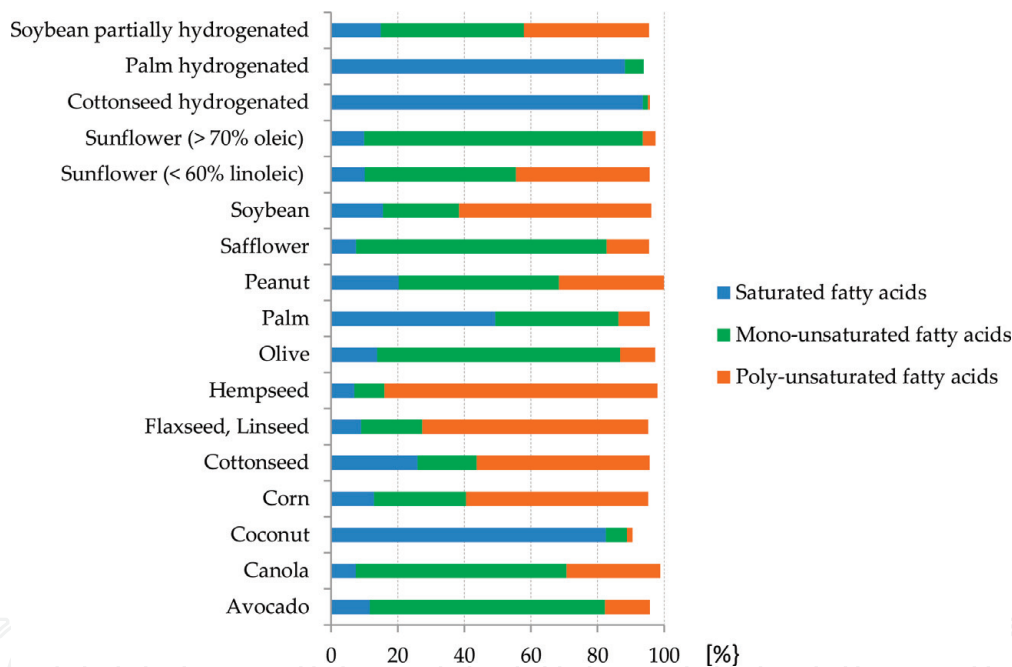


Figure 3.
Vegetal oils and their composition in fat acids [12].

with soil nature, climate, and human intervention on seeds, and even for the same place and the same type of seed, the annual conditions may influence the quality of vegetal oil.

Strengths, weaknesses, opportunities, and threats, well known as a SWOT analysis [14], for introducing vegetal oils in environmentally sensitive industries, agriculture, and transport, including soybean oil, as lubricants, underlines that a set of properties should be considered when the designer decides this lubrication solution [15–17].

Strengths in the favor of using soybean oil as oil for lubrication, either as neat, chemically modified or additivated, are discussed:

- biodegradability [18],
- a better lubricity, low volatility and a high viscosity index [17],

- better flammability characteristics (auto ignition points and higher ignition temperature on hot surfaces) than many mineral oils and similar to those of the rapeseed oil [19, 20],
- a good solubility for contaminants, additives, and polar deposits as compared to mineral oils [16, 17],
- environmental (nonpolluting or environmentally friendly) [21–23],
- extraction from renewable resources (even with a reference to 100 years) or the possibility of recycling or re-use of the lubricant [24].

Weak points for this vegetal oil include:

- lower viscosity as compared to mineral and synthetic oils [25–28],
- oxidation stability [9, 16, 19, 29–31],
- temperature range lower than that of mineral and synthetic oils [32],
- poorer properties at low temperature as compared to other lubricants [27, 29, 33].

The user should expect this vegetal oil to change its viscosity, oxidation stability, and polymerization during exploitation in a more intense way than mineral and synthetic lubricants. Chemical modification of soybean oil and/or the use of anti-oxidants [23, 34–36] could positively influence, but these will increase the cost of lubricant.

Opportunities are related to complying with more stringent environmental protection requirements that will minimize health and pollution risks. The new market shares for organic and biodegradable lubricants (obtained from renewable resources, especially plants) have increased for areas such as hydraulic fluids, chain lubricants, mold lubricants, two-stroke engines, turbine fluids, etc. [21].

Threats are the following:

- the need to redesign systems using bioliquids, a possibly costlier solution,
- accepting lowering some system operating parameters (especially load and maintenance, but not limited to) [22],
- the price still high (but not forgetting that, for example, synthetic oils in the 1990s were almost 10 times more expensive than mineral ones, today the ratio being only 3 to 1), market and users' inertia, the diversity of environmental and safety specifications, and a global policy that has not yet been clearly addressed on environmental issues.

1.2 Viscosity of soybean oil and soybean oil-based lubricants

For a lubricant to exhibit a better tribological behavior, it has to have an appropriate viscosity that will not decrease excessively when the working temperature increases. For many vegetal oils, their viscosity is low even at room temperature and it decreases dramatically when the oil is heated [19, 23, 26, 37].

Solea [19] did a comparative study for evaluating the viscosity of four vegetal oils, including soybean oil, experimental data proving the dependence of viscosity on temperature and shear rate (**Figure 4**), and tests done with the help of a rotational viscometer Rheotest2. The mineral oil OMV VG 46 was tested for comparison reason. In the temperature range 30–60°C, a more accentuated decrease of dynamic viscosity is noticed as compared to that characterizing the range 60–90°C. On the entire range of tested shear rates, the lowest decrease of viscosity was obtained for the corn oil (75.81%) and for the soybean oil (76.25%). For all tested vegetal oils, the dynamic viscosity decrease was 75–80%. This “agglomeration” of data may be the results of similar composition in fatty acids (see **Table 2**).

The dynamic viscosity of oils also decreases when temperature increases, for different shear rates (**Figure 5**), and for the lubricants tested in [19], the values have the tendency to agglomerate in the narrow range at higher temperatures (60–90°C) and for higher shear rates (**Figure 5**). This behavior has been also noticed in [38, 39].

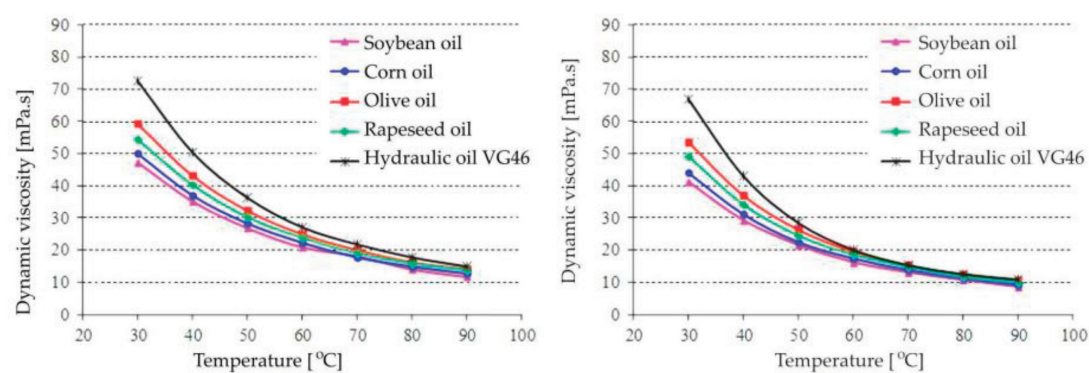


Figure 4. Viscosity as a function of temperature for four vegetal oils and a hydraulic mineral oil for comparison reason (OMV ISO VG46), at two shear rate [19]. (a) Shear rate 10 s⁻¹. (b) Shear rate 80 s⁻¹.

Fatty acid	Symbol	Olive oil	Soybean oil	Corn oil	Rapeseed oil
Myristic acid	C14:0	—	0.11	0.05	0.05
Palmitic acid	C16:0	12.6	12.7	12.4	4.84
Palmitoleic acid	C16:1	1.20	0.13	—	0.06
Heptadecanoic acid	C17:0	0.10	0.05	0.12	0.14
Heptadecenoic acid	C17:1	0.10	0.06	0.05	—
Stearic acid	C18:0	—	5.40	2.10	0.14
Oleic acid	C18:1	79.30	21.60	28.45	62.73
Linoleic acid	C18:2	4.70	52.40	54.10	22.4
Linolenic acid	C18:3	0.80	5.70	1.10	7.50
Arachidic acid	C20:0	0.40	0.25	0.40	0.50
Eicosenoic acid	C20:1	0.25	0.20	0.35	1.25
Behenic acid	C22:0	—	0.50	0.10	0.30
Erucic acid	C22:1	—	0.16	—	—
Lignoceric acid	C24:0	0.16	0.20	0.10	—

Table 2. Fatty acid composition of the tested oils [19].

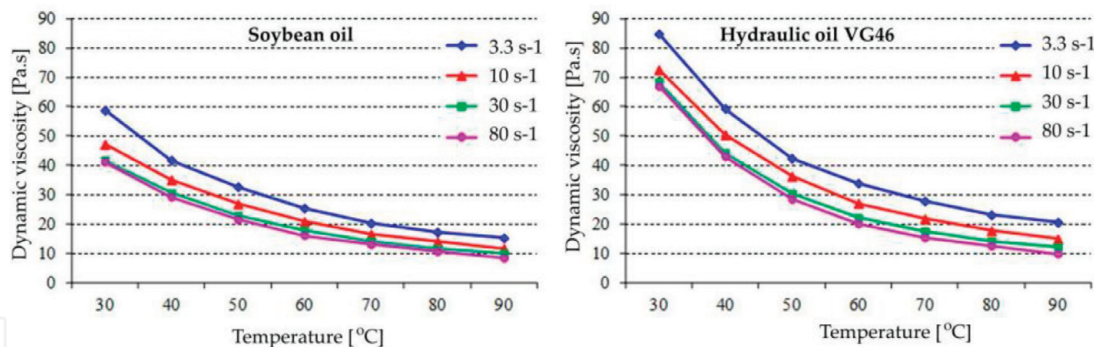


Figure 5. Dynamic viscosity of soybean oil and a hydraulic mineral oil OMV ISO VG46, for different shear rates [19].

The temperature increase intensifies the intermolecular movement and reduces the attraction among oil molecules.

Solea [19] also measured the viscosity of soybean oil after oxidation, and data reveal a weak point of this vegetal oil: the oxidized soybean oil has an increasing viscosity with the time it bears oxidation (**Figures 6 and 7**). The forced oxidation is realized by circulating air in the oil with a stable temperature.

Only a difference of 10°C of oil in the oxidation test (from 110 to 120°C) for tests during 10 hour modifies the dynamic viscosity of soybean oil, measured at 30°C

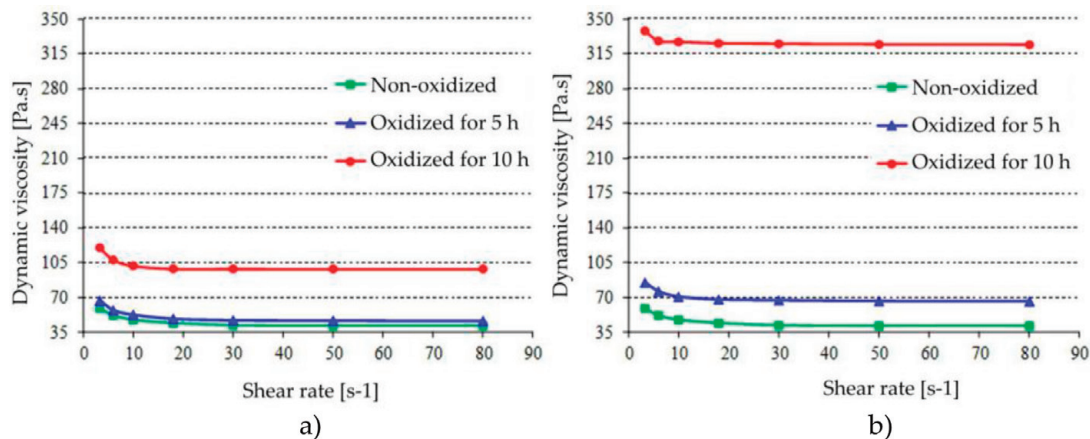


Figure 6. Dynamic viscosity of soybean oil at 30°C, as a function of shear rate and oxidation time, after oxidation [14]. (a) After oxidation at temperature of 110°C. (b) After oxidation at temperature of 120°C.

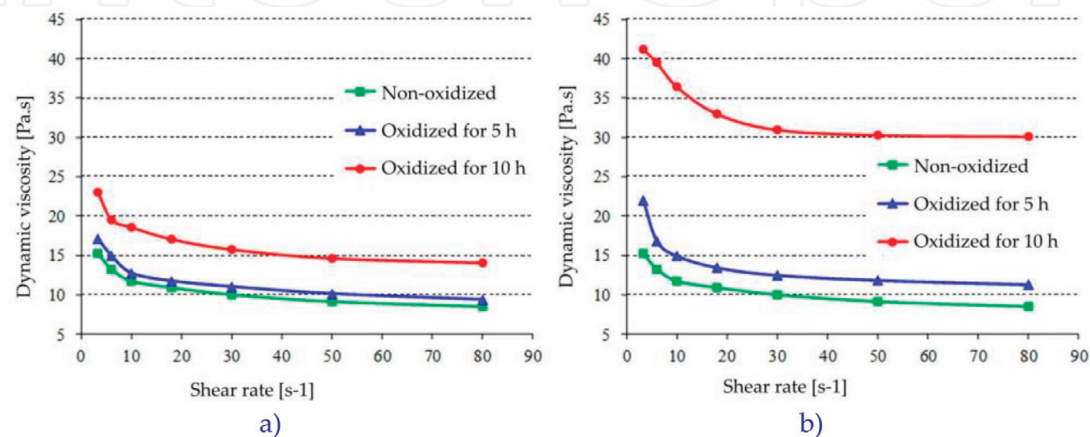


Figure 7. Dynamic viscosity of soybean oil at 90°C as a function of shear rate and oxidation time (air flow 20 l/h in 25 ml of oil) [19]. (a) After oxidation at temperature of 110°C. (b) After oxidation at temperature of 120°C.

(Figure 6), but also at 90°C (Figure 7), with more than 300%, making the oxidized oil not to be recommended in applications where this oil has a working temperature more than 110°C and the oxidation could be generated (splash lubrication).

Figure 8 presents the influence of temperature on the dynamic viscosity of soybean oil when it is measured after oxidation during 5 and 10 hours, respectively, at constant temperatures of 110 and 120°C.

A similar tendency of evolution for soybean viscosity with shear rate and temperature obtained Esteban [40] and Cristea [41] but the latter for higher shear rates, using a Brookfield CAP 2000+ viscometer with cone 8 (Figure 9).

In terms of temperature viscosity dependence, the nanoadditives based on carbon (black carbon, graphite, and graphene) are separated in two groups:

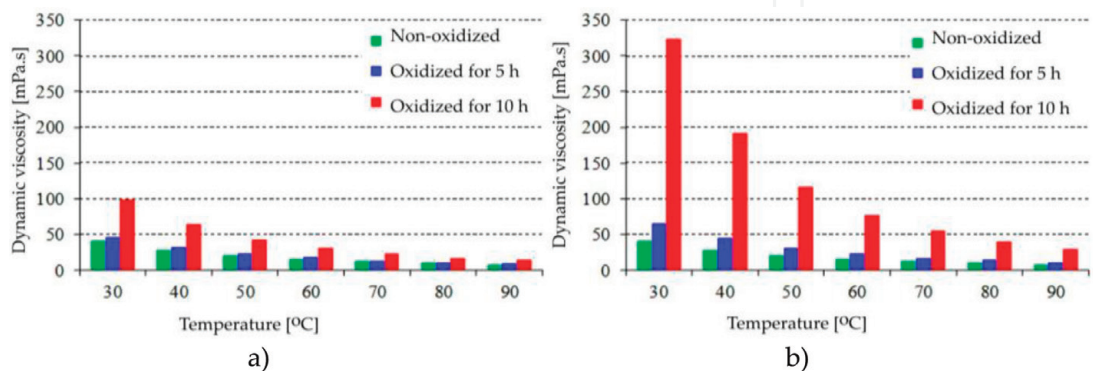


Figure 8.
Variation of dynamic viscosity of soybean oil, at shear rate of 80 s^{-1} , non-oxidized and oxidized at different temperatures: (a) Oxidation at constant temperature 110°C. (b) Oxidation at constant temperature 120°C [19].

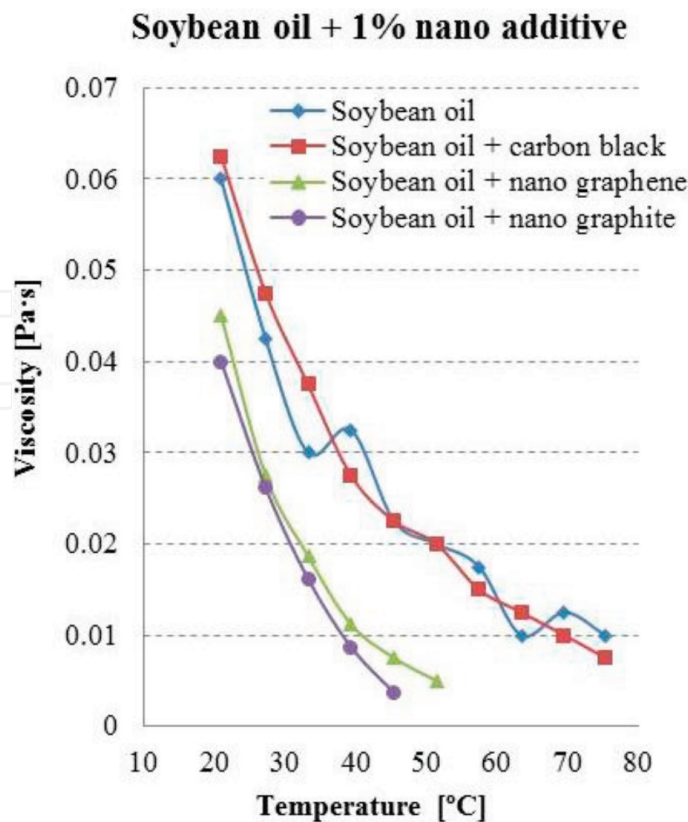


Figure 9.
Dynamic viscosity of soybean oil, nonadditivated, and additivated with 1% wt nanoadditive (tests done at shear rate 1000 s^{-1}) [41].

- black carbon does not significantly affect this dependence,
- nanographite and nanographene move down the curves of the dynamic viscosity dependence on temperature.

For any tested temperature and shear rate, the dynamic viscosity of soybean oil may be ordered [19]:

$$\eta_{\text{soybean oil}} < \eta_{\text{5 hour oxidation soybean oil}} < \eta_{\text{10 hour oxidation soybean oil}}$$

The increase in dynamic viscosity could be a criterion when evaluating the oxidation of vegetal oil. The soybean oil in modern applications especially needs a high degree of chemical stability of the lubricant.

2. Additivation of soybean oil

2.1 Classification of additives

Based on several relevant works in the literature [12, 42–45], the authors propose the classification given in **Table 3**.

Friction modifiers are adsorbed or fixed to the surface and form a film or a powdery intermediate layer that reduces friction. They can be classified into two distinct groups depending on the friction reduction mechanism:

- through the adsorbed film,
- by friction with the third body.

The first is generally due to polar molecules having a polar functional radical (alcohols, aldehydes, ketones, esters, and carboxylic acids) and a nonpolar terminal group. The polar group of the molecule adheres to the surface with long chains exposed to moving surfaces, reducing friction. They may also have polar elements that can chemically react with the surface to form a protective film. Vegetal oils and

Additives for lubricants			
Modifiers of chemical properties	Modifiers of physical properties	Improvers of tribological behavior	
		Antiwear and friction modifiers	Extreme pressure additives
Deposit control additives	Viscosity control additives	Inorganic	Phosphorus additives, like dialkyldithiophosphate (ZDDP), sulfur additives, sulfur–phosphorus additives, phosphorus–nitrogen additives, nitrogen additives, halogen additives, mixt additive package
Antioxidation additives	Poor point depressants	Organic	
Detergents	Antifoaming additives		
Toxicity	Dispersants		
Biodegradability			

Table 3.
A classification of additive for lubricants.

animal fats have such molecular structures, and therefore, they have good results in reducing friction.

Solid lubricants are added to vegetal oils with the same purpose of reducing friction and wear. This group includes not only carbon materials (fullerene, nanotubes, graphite, graphene, etc.) but also molybdenum and wolfram sulfides and fluorinated polymers, such as polytetrafluorethylene (PTFE) and perfluoropolyalkylethers (PFPAE). These can also be added in greases and composites that will function in dry conditions [46]. Solid lubricants (micro or nano) also help in situations where sliding surfaces have a rougher texture, “leveling” the profile of both surfaces. They are also recommended for reciprocal movements (in the case of the piston ring), which also produces a reduction in wear. They are added to lubricants that come into contact with surfaces with which EP (extreme pressure) additives cannot chemically react, such as polymers and ceramics and some of their composites [42].

Friction modifying and wear reducing additives can be grouped into solid lubricants and organic modifiers. The first group consists of carbon materials (graphite, graphene, black carbon, and fullerene), lamellar sulfides (tungsten and molybdenum), metal salts (boron nitride), and metal oxides (CuO, ZnO, and TiO₂ [47], which is not mentioned in [23]) but also linear polymers (polytetrafluoroethylene) [48]. Among the organic additives that act as friction modifiers are carboxylic acids or derivatives (stearic acid and esters), amides, imides, amines and their derivatives (oleyl amide, etc.), phosphoric and phosphonic acid derivatives, and organic polymers (methacrylates) [42, 43]. Regeneration of the friction reducing layer depends on additive concentration and conditions in which the tribosystem operates (speed, load, temperature, and contamination) [42].

Literature reported relatively low results on nanofluids as lubricants, mostly on transformer oil, silicon oil, gear oil, and heat transfer oil [49]. Limited investigations on the influence of nanoadditives on vegetal oils are presented [12]. Even if modern equipment working under high load, speed, and thermal conditions requires cooling and efficient lubrication, and for this concept, mineral and synthetic oils are still preferred and investigations on vegetal oils are needed for particular applications with environmental impact and in the perspective of oil resources extinction [50].

2.2 Specific processes for lubrication with nanoadditives

Wu et al. [43] propose a model that considers the lubricating additive concentration (see **Figure 10**). Although the model was created after experiments with TiO₂ as additive, it can be used to explain the behavior of lubricants with other nanoscale particles (metal 40 oxides, carbon materials, etc.). The fluid lubrication mechanism with nanoadditives has been also described in the works [52–54].

The mechanism for reducing friction and antiwear mechanism of nanoparticles in lubricants has been investigated, and it is based on the following processes [43]:

- micro-roll process [51, 55],
- process of forming a protective film [56–59],
- smoothing/leveling process [60],
- polishing process [51, 61], (**Figure 10**).

The first two mechanisms have a direct effect on lubrication [61]. In the case of rolling, no chemical reactions occur, and spherical or oval nanoparticles are willing

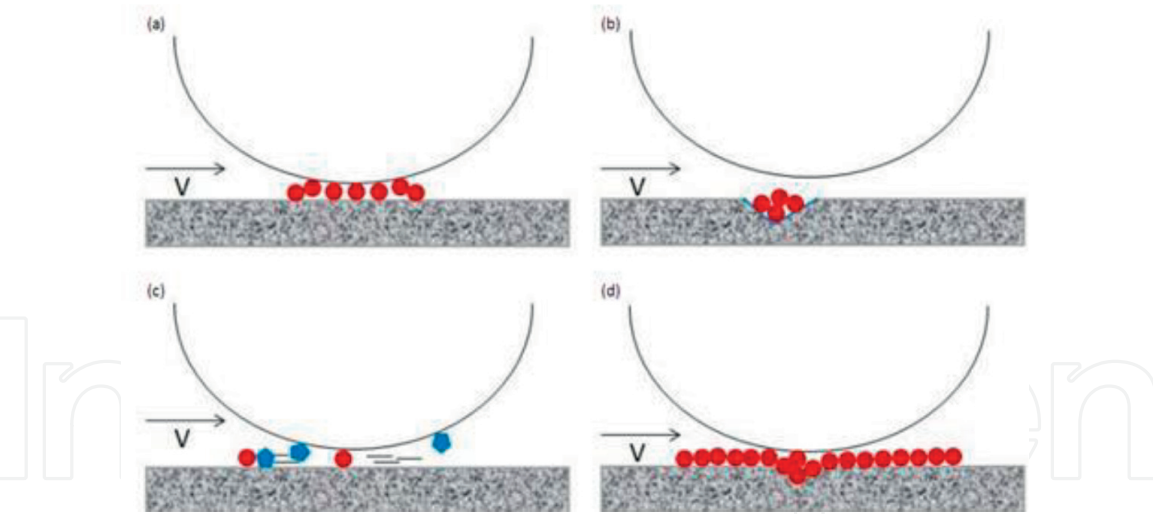


Figure 10. The lubricating mechanism of water-based lubricants and TiO_2 as an additive. (a) rolling effect, (b) mending effect, (c) polishing effect, and (d) effect of protective film [51].

to roll. The lubrication mechanism of nanoparticles as friction modifiers includes three types of friction [62]:

- rolling friction—spherical nanoparticles act as micro or nano ball roller bearings between triboelement surfaces under light load conditions,
- sliding—nanoparticles serve as spacers and eliminate direct metal/metal contact between the asperities of the two triboelements, under higher load conditions,
- rubbing with the third body—exfoliating nanoparticles and their outer layers gradually transfer to surface texture, providing easier friction under high load conditions, when the third body can be considered a mixture of oil, nanoparticles, and wear particles.

The use of nanoparticles as lubricant additives is a top issue of research in the last decades [43, 63].

A spherical nanoadditive in contact [63] could act like a damper between two asperities in contact. It could change its shape becoming flatter when the load increases, thus, protecting a larger surface against rubbing (**Figures 11 and 12**).

Jayadas et al. [64] calculated the advantage of using additives in oils, based on the results of the shear rate and the temperature influence on the viscosity of the additivated lubricant. Wu et al. [51] reported increased load capacity of the additivated lubricants. Many studies were based on a single concentration of the additive. The effect of varying viscosity due to nanoparticle concentration is difficult to model, and therefore, tests become relevant.

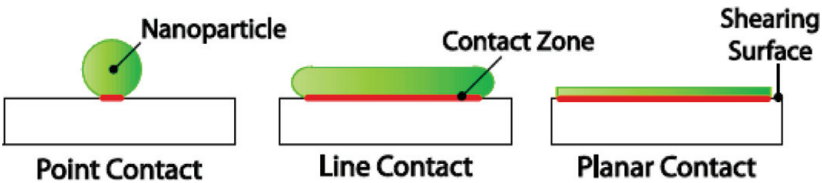


Figure 11. Shape of a nanoparticle with the surface, under different operating regime [63]: punctual contact (low or no load), linear contact (mild load), and severe load (the move of surfaces one against another produces the shearing between additive and surface and not one among asperities).

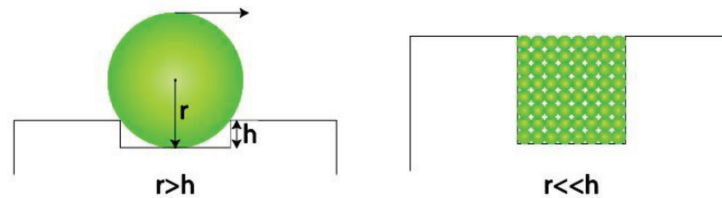


Figure 12.
 The effect of relative size of surface texture and additive particles: particle with similar dimensions as the profile and particles smaller than the valleys of the texture [63].

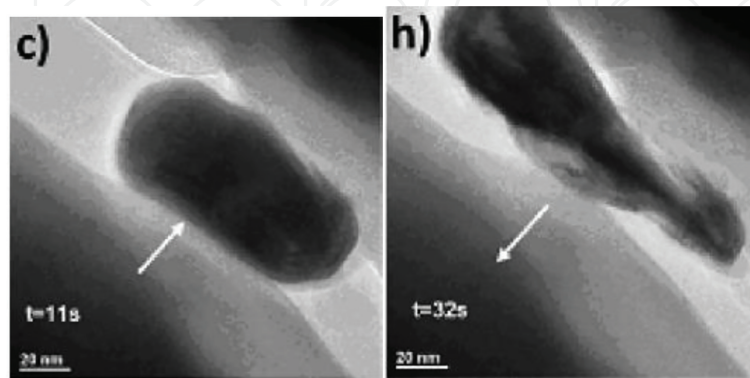


Figure 13.
 Photos taken from the work of Lahouij et al. [65], the steps (here only two) through which a particle of WS₂ (wolfram disulfide) passes into a loaded contact.

A study by Lahouij et al. in 2012 [65] shows how the WS₂ (wolfram disulfide) particle protects the direct contact between metal asperities (**Figure 13**). The ovoid structure functions as a shock absorber and either the structure collapsed, or the particle was fragmented, it continued to remain between the two solid bodies. The hollow core of the particle was visible, and the deformation was large at the beginning of the stress, but as the load increased, the particle behaved like a variable-elasticity spring, the elastic characteristic actually increasing. Then, the particle begins to tear or scissor, and, finally, the WS₂ particle exfoliated in fragments.

From the studied literature, there is a tendency for deep research on additives in vegetal oils, especially those intended for lubrication. Attention should be focused on the dispersion of nanoadditive and the selection of dispersant.

3. Tribological characterization of lubricants based on soybean oil

3.1 Tribological parameters and testing equipment related to lubricants

In order to assess the quality of lubricants, it is important to establish the test methodology (equipment, parameters, and investigations during and after testing). Their selection depends primarily on the practical use for which the lubricant is tested, and the selected tribotester should approach as much as possible to the technical system in which the lubricant will be introduced.

Tribological tests can be grouped in severe tests and tests under normal working conditions. The here-presented results could be appreciated as moderate regimes.

Depending on the future application and the researchers' abilities and knowledge, tribological characterization will be done by a set of parameters, one being insufficient for this purpose. The evaluation of the results is often done by accepting a compromise, as durability and reliability of a system are influenced by synergic effects of actual dynamic parameters. There are presented several parameters that

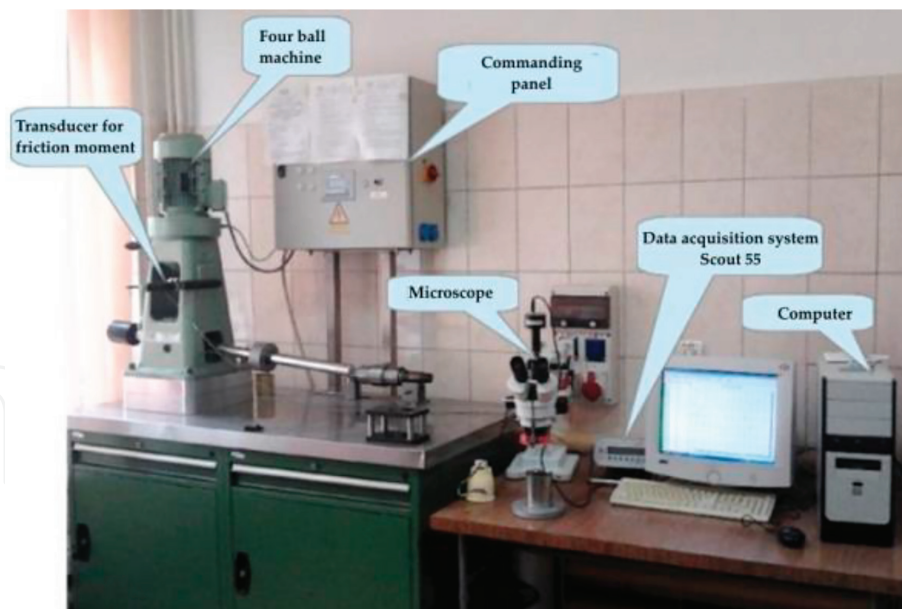


Figure 14.
Four ball machine ("Lubritest" Laboratory, "Dunarea de Jos" University of Galati).

could be taken into account for evaluating tribological behavior, with particular reference to four-ball tester (**Figure 14**), even if there are other tribotesters used for establishing the lubricating capabilities of vegetal oils: pin-on-disc, ball-on-disc, reciprocating rigs [66], etc.

The coefficient of friction (COF) may be analyzed by the following parameters:

- instantaneous value (i.e. at t time), paying attention to minimum and maximum values,
- mean value over the duration of the test (1 hour in this study, the number of samples per second being important in getting some peak values),
- average value over the last minutes of the test (argumentation: there are research reports presenting the average for 10 minutes, 5 minutes, as these time intervals are considered to be a stabilized domain),
- variation interval of the friction coefficient for 1 hour and for the last 10 minutes.

Several wear parameters for the tests done on four ball machine are given below:

Wear scar diameter (WSD) is the arithmetic average of the six diameter 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. This value represents the diameter of the wear scar reported for each of the performed tests. The same method of obtaining the wear diameter is also given in specialized literature [66–68].

Wear as volume loss, considering the surface of wear scar as plane [69], is calculated as a sphere calotte having the diameter equal to the average wear scar diameter (see **Figure 15**):

$$V = \pi \cdot R^3 \left(1 - \sqrt{1 - \frac{1}{4} \left(\frac{D}{R} \right)^2} \right)^2 \left[1 - \frac{1}{3} \left(1 - \sqrt{1 - \frac{1}{4} \left(\frac{D}{R} \right)^2} \right) \right] [\text{mm}^3] \quad (1)$$

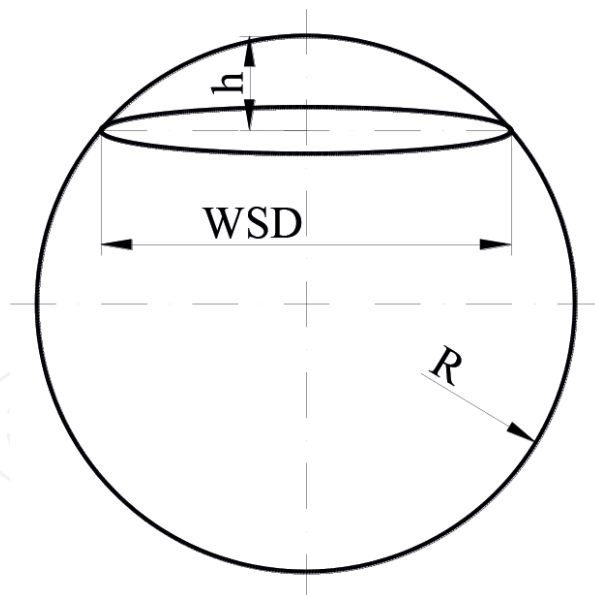


Figure 15.
The sphere calotte for calculating the worn volume on a ball.

where R is the ball radius; WSD is the wear scar diameter (calculated as average of six values of wear scars on fixed balls along sliding and perpendicular to it).

Wear rate of wear scar diameter is still rarely used, but it is more convenient for comparing results on four ball tribotester. Since the duration of the test is 1 h, the sliding distances are different for different speeds. For instance, for ball of 12.7 mm in diameter, tested 1 hour (this time being often selected by researchers), the sliding distance depends on the sliding speed in contact (that could be calculated knowing the rotational speed of the main shaft of the four ball machine): $L(v = 0.38 \text{ m/s}) = 1378.8 \text{ m}$; $L(v = 0.53 \text{ m/s}) = 1933.2 \text{ m}$; $L(v = 0.69 \text{ m/s}) = 2487 \text{ m}$. It is possible that the simple graph of the WSD dependence on additive concentration, load, and speed is not relevant due to the difference in the sliding distances, and then, on the basis of the literature [70], the wear can be also evaluated by another parameter called the wear rate, w :

$$w = \frac{\Delta V}{F \times L} \text{ [mm}^3\text{/(N} \cdot \text{m)]} \quad (2)$$

where ΔV is the variation in sample volume (volume of removed material), F is the loading force; L is the sliding distance. The product $F \times L$ is the mechanical work done by the tribosystem; in other words, the wear rate shows the loss of material volume for the mechanical work unit performed by the system. The authors used a parameter named the wear rate of wear scar diameter, $w(\text{WSD})$, calculated as:

$$w(\text{WSD}) = \frac{\text{WSD}}{F \times L} \text{ [mm/(N} \cdot \text{m)]} \quad (3)$$

where WSD is the wear scar diameter (calculated as average of six values of wear scars on fixed balls, along sliding and perpendicular to it), F is the load applied on the four balls, L is the sliding distance.

Since Blok had developed the concept of “flash-temperature” [71] in 1963, even critical comments on the constraints and limitations characterizing the model have accepted that this parameter is strongly depending on the local peak of the heat flow generated by friction [72]. Flash temperature parameter (FTP) is related to the

critical flash temperature, above which a given lubricant does not operate in a convenient manner (it becomes ineffective) under the imposed conditions. Literature offers several relationships for calculating FTP, the authors selecting the one given by Marcher [72]:

$$FTP = \frac{F}{WSD^{1.4}} \text{ [N/mm}^{1.4}\text{]} \quad (4)$$

where F is the applied load on the four ball tribotester, in N; WSD is the average of the six measured wear scar diameters on the fixed balls in one test. Under constant load, there is an indirect proportionality between FTP and wear scar diameter.

FTP allows for evaluating the lubrication capacity of a fluid, especially under high loads, as these generate high temperature on rubbing surfaces, as it is the case of rolling mill and cutting processes. For a lubricant, FTP reflects the lowest temperature at which the liquid evaporates, risking auto-ignition in air. High values of this parameter are associated with a positive characteristic of a lubricant as it does not evaporate if the temperature in contact is low and the fluid film is thick enough to reduce friction and to avoid direct contact of asperities. Thus, the heat flow generated by friction will not be so high. These low temperatures and a reduced friction may also characterize boundary lubrication. Low values of FTP indicate the damage of the fluid film.

Oil film strength (OFS) is calculated using the load on a contact between the mobile and fix balls, Q, in N:

$$OFS = \frac{Q}{A_s} = \frac{0.408 \cdot F}{A_s} = \frac{1.632 \cdot F}{\pi \cdot WSD^2} \quad (5)$$

$$Q = \frac{F}{3 \cos \theta} \cong 0.408 \cdot F \quad (6)$$

F is the applied load on the four ball tribotester, [N]; θ is the angle between the load direction on the main shaft of the four ball machine and the direction of normal load in the contact between the rotating ball and one fixed ball ($\theta \approx 35.264^\circ$); A_s is wear area, calculated with the average WSD for the three fixed balls [mm^2].

Maps in tribological analysis are useful in assessing trends and determining test regimens for which two or more variables influence the tribological parameters; thus, the tribological behavior of the system is better revealed.

Investigations of the worn surfaces and used lubricants could be done with the help of FTIR (Fourier Transform Infrared) spectrometry, 3D profilometry [73, 74].

3.2 Tribological characteristics of soybean oil

Lubricant properties influence the tribological behavior of a system, one of the most important being the dynamic viscosity.

Georgescu presented a report [75] on different grade of rapeseed and soybean oils. The antiwear characteristics were tested for the following parameters: load on four ball tester—100 N, 200 N, and 300 N; sliding speed—0.46 m/s (1200 rpm), 0.57 m/s (1500 rpm), and 0.69 m/s (1800 rpm); test duration—60 minutes (rpm—rotations per minute of the main shaft of the four ball machine). Balls, as delivered by SKF (Swedish Ball Bearing Factory), are mirror-finished, with the arithmetic mean of absolute values of the ordinates $z(x)$, measured from the mean line $Ra = 0.02\text{--}0.03 \mu\text{m}$ and made of EN31 steel grade (also named 100Cr6) steel grade, having a hardness of 60–66 HRC and a diameter of $12.7 \pm 0.0005 \text{ mm}$. Average

values of friction coefficient (COF) for the 1 hour testing on four ball machine are acceptable for the tested soybean oils (below 0.1), but generally higher than those for mineral oil, a proof for a thinner film generated in contact at least for the tested parameters (**Figure 16**).

Comparing the wear rates of WSD for the tested oils, one may notice that the two soybean oils produced lower values than those obtained with the transmission mineral oil T90, for the load range 100–200 N (see **Figure 17**). At $F = 100$ N, both vegetal oils are acceptable for actual applications, but at $F = 200$ N, FTP is almost double for vegetal oils as compared to T90 and at high speed, the degummed soybean oil becomes competitive. At highest speed and load, values of FTP are closer, above $800 \text{ N/mm}^{1.4}$. T90 has a more pronounced increase of FTP with load and less with speed. This difference suggests the necessity of testing a lubricant and not to estimate by general considerations.

Based on four ball test data, Georgescu concluded that the vegetal oils could be acceptable and comparable with nonadditivated mineral oils like T90 [75]. The degumming process makes this soybean oil to generate a more intense wear, meaning that the eliminated substances would have contributed to a better tribological behavior. The problem is that the coarse oil is less stable in time and exposed to oxidation.

Values of COF are higher for the soybean oils suggesting a mixt or boundary regime, especially for load of 100 N. FTP was better, its values being greater than $1200 \text{ N/mm}^{1.4}$ for soybean oils, under the load of 200 N. For $F = 100\text{--}200$ N, FTP for T90 was in the range $550\text{--}680 \text{ N/mm}^{1.4}$. For $F = 300$ N, this parameter is kept at $1000\text{--}1200 \text{ N/mm}^{1.4}$ for all tested oils, only for speeds of 0.46 m/s and 0.57 m/s. The conclusion of the study presented by Georgescu [75] is that these two soybean oils could be used as lubricants for low loads and moderate speeds, and the degumming process does not influence significantly the tribological behavior, at least for the tested regimes, as evidenced by FTP values in **Figure 18** and by those for OFS in **Figure 19**. Each parameter has values in a narrow range for both coarse and degummed soybean oils. The higher difference in FTP for these soybean oils

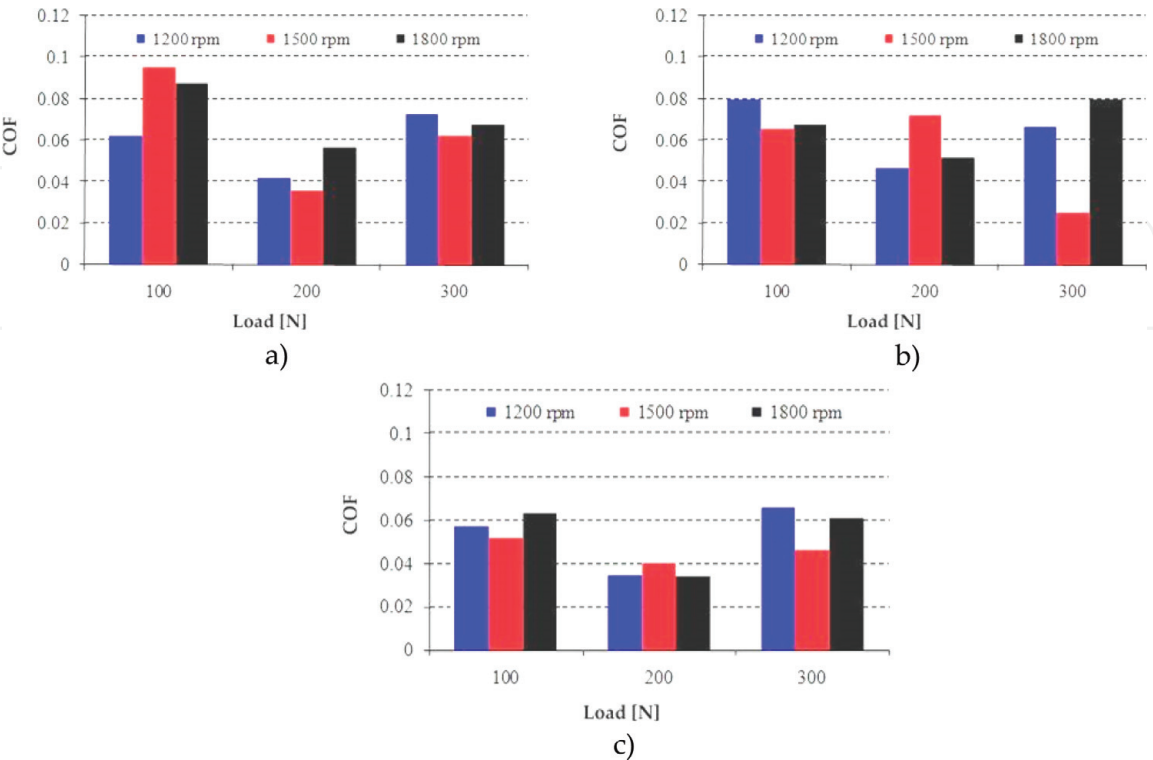


Figure 16. Influence of load and sliding speed on the average value of COF [75]. (a) Coarse soybean oil (cold pressed). (b) Degummed soybean oil. (c) Transmission oil T90.

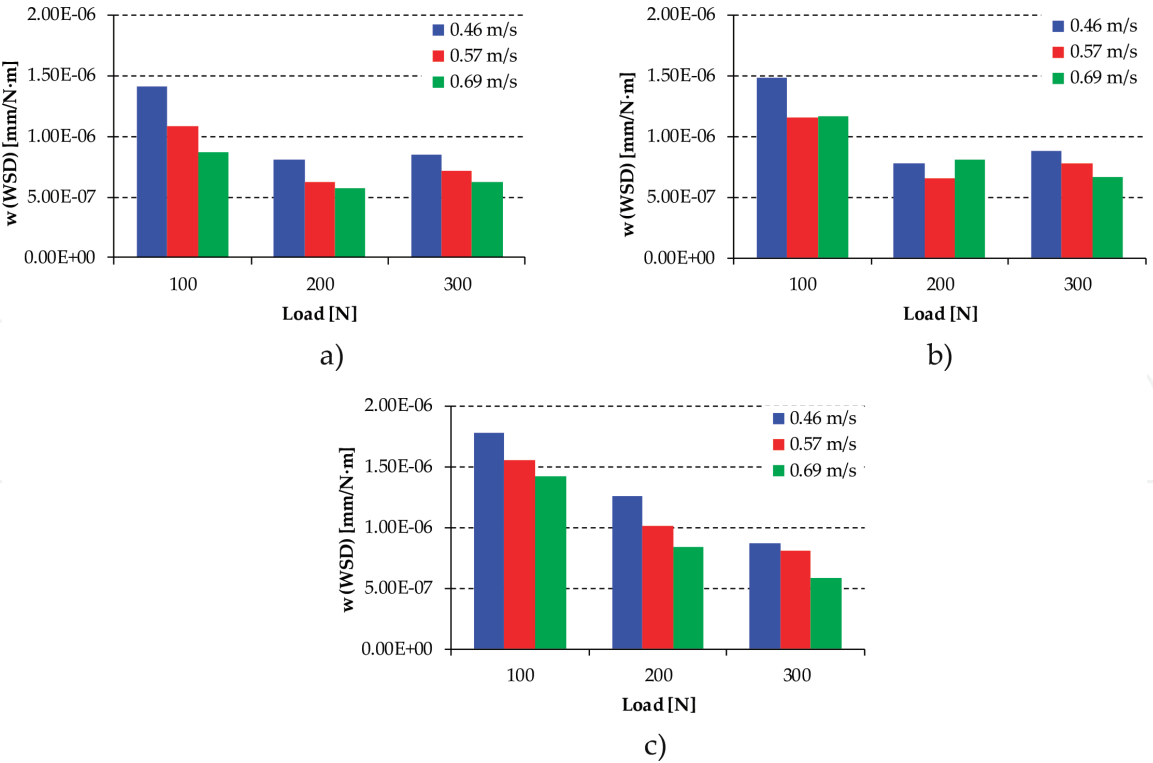


Figure 17. Influence of load and sliding speed on the wear rate of WSD (wear scar diameter) [75]. (a) Coarse soybean oil (cold pressed). (b) Degummed soybean oil. (c) Transmission oil T90.

was noticed only for moderate load and that could be explained by the presence of gummy products in coarse soybean oil.

Cristea [41] reported the tribological behavior of soybean oil and soybean oil additivated with carbon-base nanoparticles, in different concentration (0.25, 0.5,

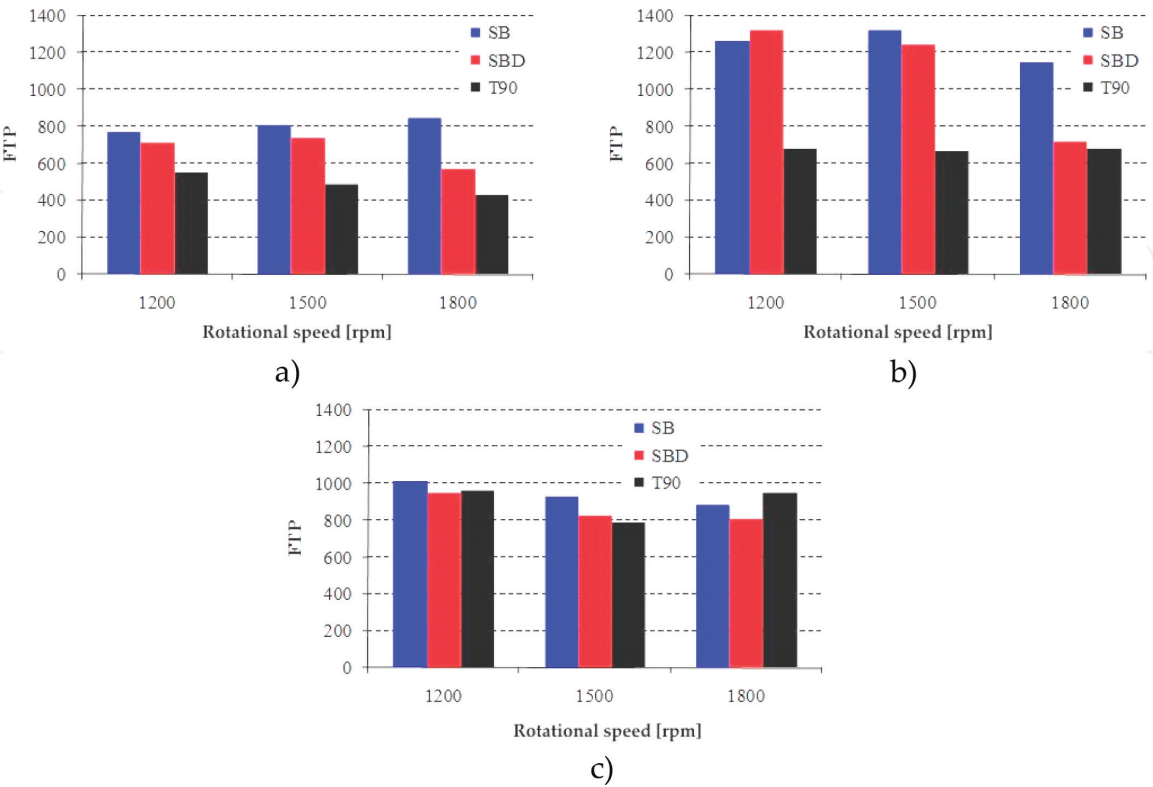


Figure 18. FTP as function of load and sliding speed [75]. SB—coarse soybean oil, SBD—degummed soybean oil, T90—transmission oil. (a) 100 N. (b) 200 N. (c) 300 N.

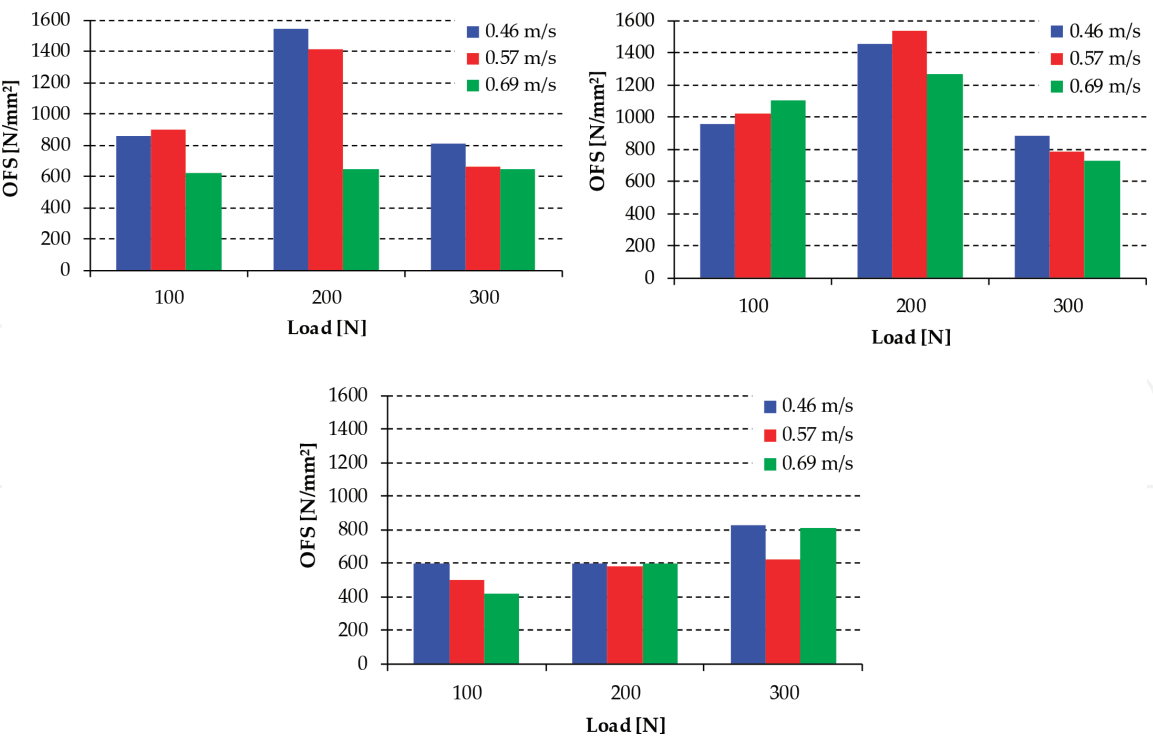


Figure 19.
Influence of load and sliding speed on the oil film strength (OFS) [75].

and 1%wt). **Figure 20** presents scanning electron microscopy (SEM images) for the nanoadditives that were supplied by PlasmaChem [76]:

- nanoamorphous carbon—average particle size ~ 13 nm, specific surface area ~ 550 m²/g,
- nanographite—average particle radius 400–450 nm,
- graphene—nanoplates with a thickness of 1.4 nm and a particle size of up to 2 μ m.

Figure 21 presents the evolution of COF over time, depending on load and speed, for two tests with the same parameters (F, v) when the four ball tribotester is lubricated with soybean oil. One may notice that, at the tested highest speed (v = 0.69 m/s), COF is less influenced by the applied load and performs in a narrow range meaning that speed is more important in generating a continuous fluid film, as argued by Dowson and Higginson for elasto-hydrodynamic lubrication [37].

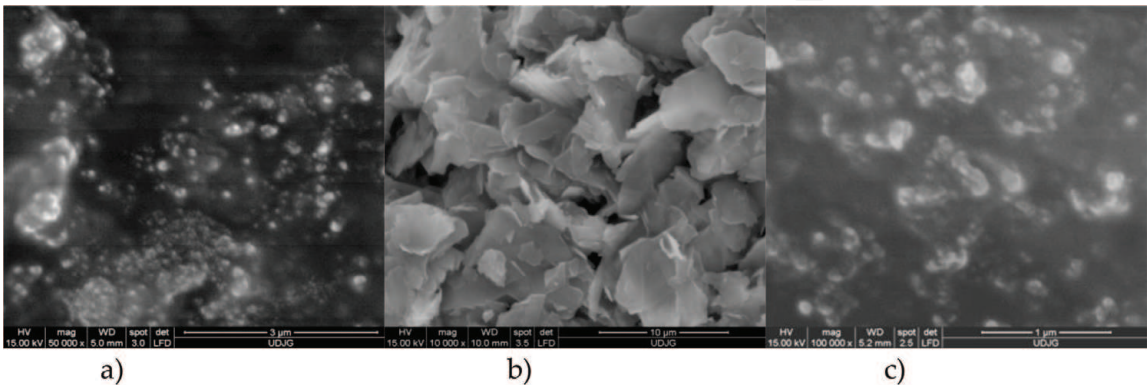


Figure 20.
Scanning electron microscopy for nanoparticles added in soybean oil [41]. (a) Black carbon. (b) Graphite. (c) Graphene.

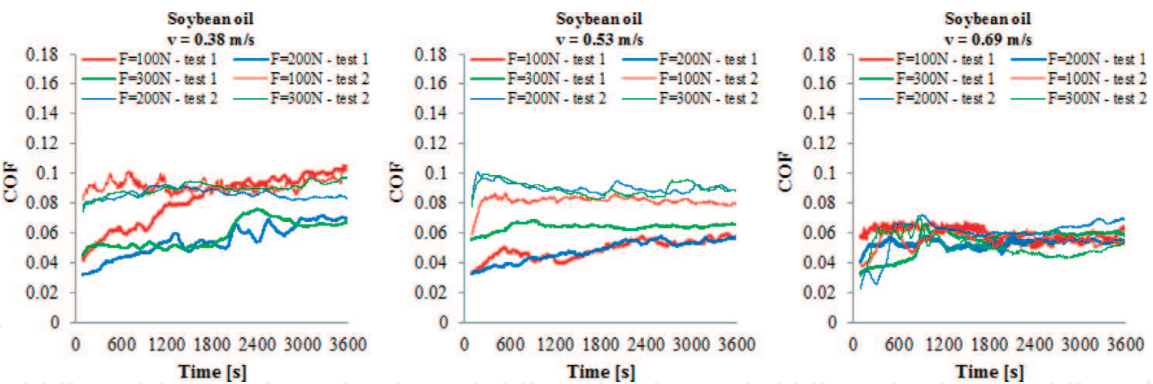


Figure 21.
The evolution of COF over time, depending on load and speed, for two tests with the same parameters (F, v) [41].

A representation of the wear rate of WSD (**Figure 22**) helps the researcher to observe the evolution trends of the parameter of interest according to two variables, here the tribotester load and the sliding speed of the rotating ball on the three fixed balls. For the range of analyzed loads and speeds, nonadditivated soybean oil had a downward trend with increasing load and speed. This trend is also consistent with Dowson and Higginson’s argument on generating the elasto-hydrodynamic film [37] as wear will be reduced if the fluid film interposes between solid triboelements. They have shown that the speed factor $U = \eta_0(U_1 + U_2)/(2E' \cdot R_e)$ has the greatest influence on the minimum thickness of the fluid. For low-viscosity oils, the material factor $G (\alpha \cdot E')$ cannot participate in film formation to the same extent as the viscous oils at the working temperature of the contact [77]. (U_1, U_2 are the relative speeds of triboelements in contact, η_0 is the lubricat viscosity at areference temperature, E' is the equivalent Young modulus of the solid elements and, R_e is the equivalent radius of the contacting surfaces, α is the pressure-viscosity coefficient of the lubricant). In addition, vegetal oils are characterized by a high viscosity index, that is, the variation of this characteristic with the temperature is low, especially at temperatures above 50–60°C (see **Figure 4**). Images of wear scars in **Figure 23** point out a change of texture quality, especially when load increases to $F = 300$ N, even if the wear rate of WSD is the lowest for this load and all the tested speeds.

Cheenkachorn [78] studied three types of soybean oils (two given in **Table 4**, the third being an epoxidized soybean oil is simply the conventional soybean oil, in which all double bonds are epoxidized to form epoxide rings. Each of these oils was additivated with 1% ZDDP (Zinc dialkyldithiophosphates).

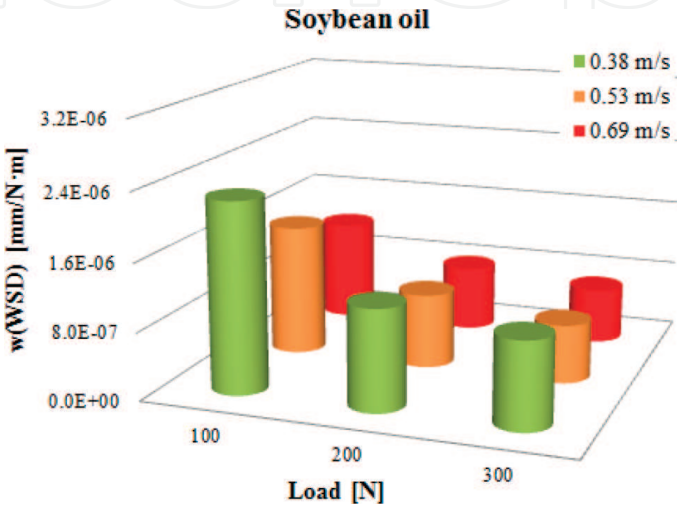


Figure 22.
Wear rate of WSD for the nonadditivated soybean oil [41].

The values of friction coefficient for all six oils (**Figure 24a**) show no clear trend. At 25°C and all speed conditions, epoxidized soybean oil without an antiwear additive has the highest friction coefficient. This is due to the fact that viscosity of

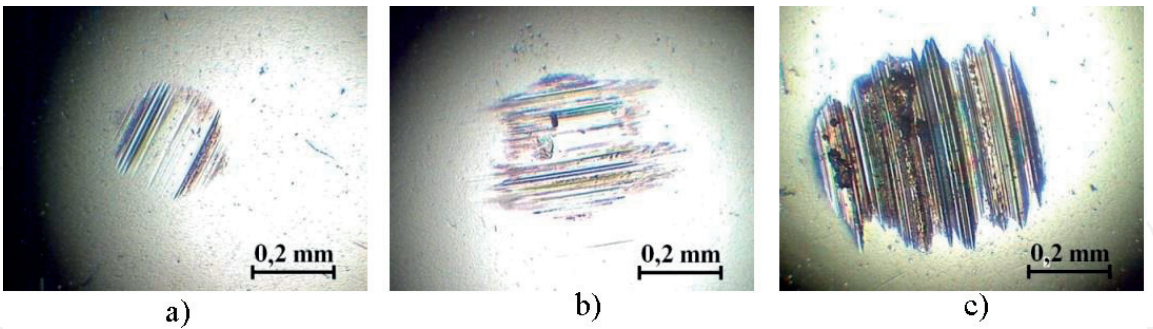


Figure 23.
The wear scars obtained with the soybean oil without additives $v = 0.69\text{ m/s}$ [41].

Fatty acid	Symbol	Concentration, %wt			
		Refined soybean oil [41]	Soybean oil [78]	High oleic soybean oil [78]	Soybean oil [79]
Miritic acid	C14:0	0.11			0.1
Palmitic acid	C16:0	12.7	10.5	7	15
Palmitoleic acid	C16:1	0.13			0.15
Heptadecanoic acid	C17:0	0.05			0.15
Stearic acid	C18:0	5.40	4.1	4	6.78
Oleic acid	C18:1	21.60	23.4	83	26.6
Linoleic acid	C18:2	52.40	52.6	3	46.3
Linolenic acid	C18:3	5.70	7.2	2	2.69
Arachidic acid	C20:0	0.25			0.61
Gondoic acid	C20:1	0.20			
Eicosadenic acid	C20:2	0.50			

Table 4.
The characteristic fatty acid composition for the soybean oil, modified or not.

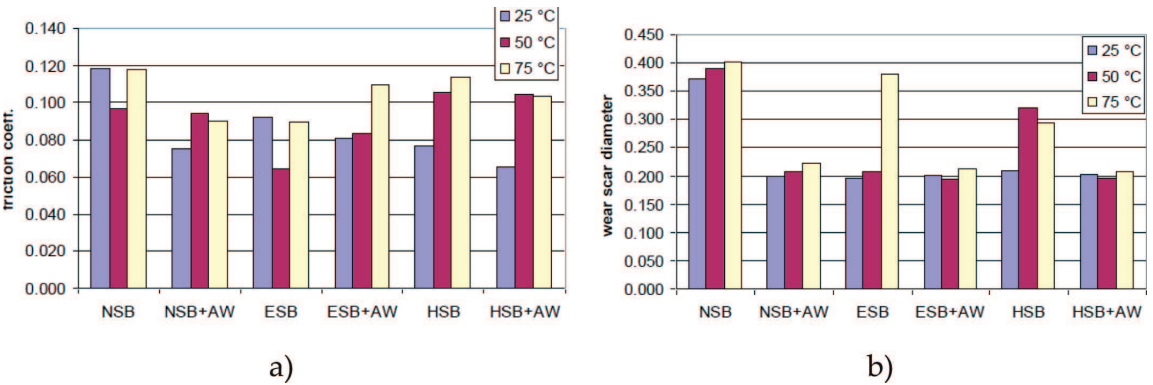


Figure 24.
Influence of different grades of soybean oil on friction coefficient (a) and wear scar diameter (b). Test conditions: 0.5 h, $F = 110\text{ N}$, $v = 900\text{ rpm}$, NSB—normal soybean oil, ESB—epoxidized soybean oil, HSB—high-oleic soybean oil, +AW—additivated with 1% ZDDP [78].

epoxidized soybean oil is higher than those of conventional soybean oil and high-oleic soybean oil. When the temperature increases, the viscosity of epoxidized soybean oil decreases. This results in a better oil circulation and forming of a multiple-layer film, which reduces the friction coefficient.

When comparing the results obtained by Cristea for refined soybean oil (see the first column in **Table 4**) with balls with very close characteristics [41], but for 1 hour test, 100 N at 1000 rpm, the higher value of WSD (0.413 mm) was just a little bit higher than that obtained by Cheenkachorn [78] for half testing time, meaning that during a longer time test, the wearing process is more intense especially in the beginning of the test, and the wearing process is slowing down due to lubricity of the lubricant (boundary lubrication) but also to the accommodation of surface textures in contact. ZDDP showed no clear influence on the trend of friction coefficient. For epoxidized soybean oil and high-oleic soybean oil, the temperature predominantly affected the wear scar diameters. This additive introduced in tested vegetal oils makes the temperature to have less influence on WSD (**Figure 24b**), and this being explained by the protection offered by the additive to the rubbing textures of the balls.

Zhao et al. [79] tested two types of oils with high viscosity, synthesized by nitrogen plasma polymerization of soybean oil. The nitrogen atoms were incorporated into the molecule of polymerized oil, and these three nitrogen heterocyclic compounds played a key role in improving tribological characteristics of polymerized oils. The lubricating properties of polymerized oils were tested on the four ball tester. The load-carrying capacities of polymerized oils reached 940.8 and 1049 N, respectively, higher than that of the unmodified soybean oil (646.8 N). They showed better antiwear properties under all tested loads and possessed preferable friction-reducing performances when the applied load surpassed 250 N. It was found that the nitrogen heterocyclic structure containing six atoms of nitrogen possessed higher coordination capacity than the ester groups of soybean oil and could form a durable organic nitrogen complex film on the metal surface. Simultaneously, the blended oils with different viscosity grades, which were prepared by diluting the polymerized oil with dioctyl sebacate, show excellent receptivity on the antiwear/extreme pressure additives of zinc dialkyl dithiophosphates and sulfurized isobutylene. Nitrogen plasma was used to open the C=C of soybean oil for polymerization. The values of kinematic viscosity (at 40°C) of the two polymerized soybean oils (PSO1 and PSO2) increased to 285 cSt (100 cSt = 1 cm²/s) and 576 cSt from 33.8 cSt, respectively, and the viscosity indexes of PSO1 and PSO2 reached 220 and 283, respectively. The tribological characteristics (wear scar diameter and friction coefficient) are given in **Figure 25**, showing that the polymerization of soybean

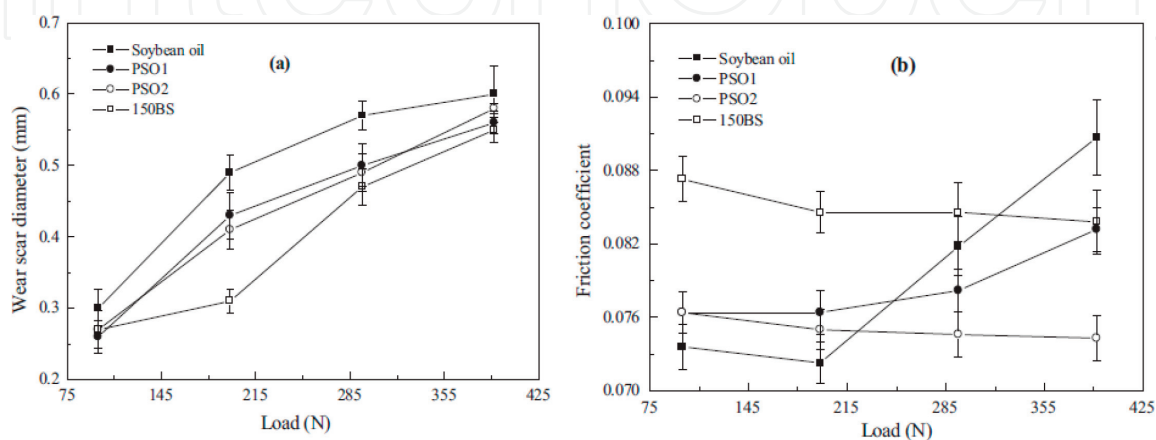


Figure 25.

Tribological characteristics of soybean oil, polymerized soybean oils (PSO1 and PSO2) and 150BS (industrial mineral oil with kinematic viscosity 601 cSt at 40°C and 31.4 cSt at 100°C, viscosity index 77) at different loads [79]: wear scar diameter (a), friction coefficient (b).

oil produces a decrease of WSD as compared to that produced by soybean oil. The friction coefficient seems to depend on the polymerization process, its values being less influenced by the load for the soybean oil PSO2. These better results for PSO2 may be explained by the nitrogen content, higher for PSO2, as result of a different time of polymerization.

3.3 Soybean additivation with carbonic materials

3.3.1 Laboratory formulations of additivated lubricants

The problem to be solved with such antiwear additives is their dispersion in oil. Cristea [41] proposed a method of obtaining a good dispersion taking into account that the tested base oil is a mixture of fatty acid triglycerides (see Table 4, first column). The steps followed in this laboratory technology were:

- mechanical mixing of the additive and an equal amount of guaiacol (supplied by Fluka Chemical) with the chemical formula $C_6H_4(OH)OCH_3$ (2-methoxyphenol) for 20 minutes; this dispersing agent is compatible with both the additive and the soybean oil (the mass ratio of the additive in the dispersing agent is 1:1, with an accuracy of 0.1 mg);
- gradually adding the soybean oil, measured to obtain 200 g of lubricant with the desired additive concentration (0.25%wt, 0.5%wt or 1%wt), by mixing with a magnetic homogenizer during 1 h;
- ultrasonication + cooling: 200 g of lubricant for 5 minutes using the Bandelin HD 3200 sonicator (Electronic GmbH & KG Berlin) sonicator; the lubricants are heated to about 70°C; the cooling time was 1 hour; this ultrasonic + cooling step is repeated five times to obtain a total of 60 minutes of sonication. The parameters of the ultrasonic regime are: 100 W power, frequency 20 kHz \pm 500 Hz, continuous mode.

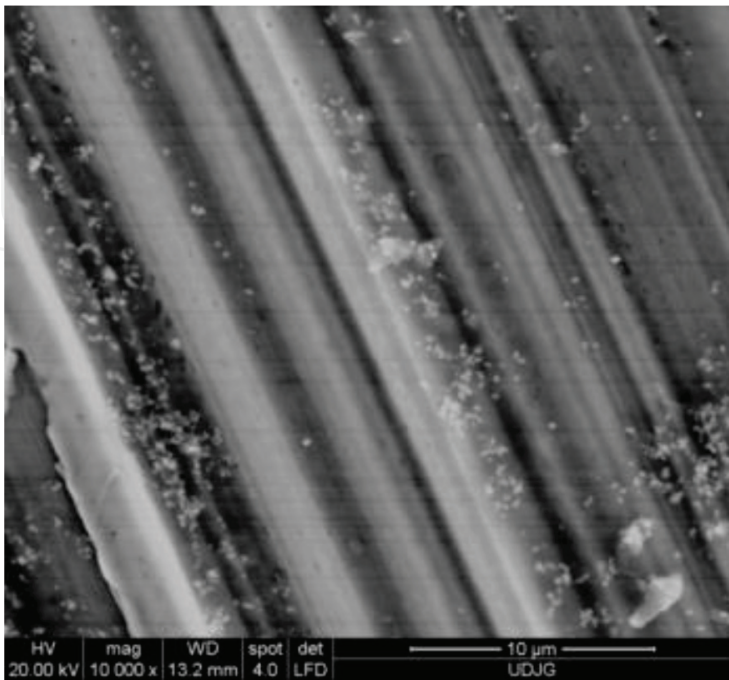


Figure 26.
Particles of nanoblack carbon on wear scar. Test conditions: $v = 0.38\text{ m/s}$, $F = 200\text{ N}$, time 1 h, lubricant: soybean oil +1% nanoblack carbon [47].

The method of sonication was also used for getting an acceptable dispersion of nanoparticles in lubricants by [80, 81].

3.3.2 Soybean oil additivated with nano carbon

Investigations by the help of scanning electron microscopy show that nanocarbon particles are on the friction surfaces as nanoagglomerations (**Figure 26**), on the surface texture of the wear scar. These particles or agglomerations appear to be rolled up and are likely to act as nanorolling elements, which explain low friction coefficients during the test (see **Figures 27** and **28**). The problem is that these particles are not uniformly distributed over the contact surfaces, producing a preferential wear on the particle-free areas. As the particles migrate in motion, these areas are prone to direct contact. This may be the explanation for the variation of the friction coefficient over time and with large amplitudes (**Figure 27**) and the variation of the average value of friction coefficient in larger ranges (**Figure 28**).

The friction coefficient plots of **Figure 27** are done using a moving average of 200 values, the recorded samples being of 2 values per second. The discussion of the

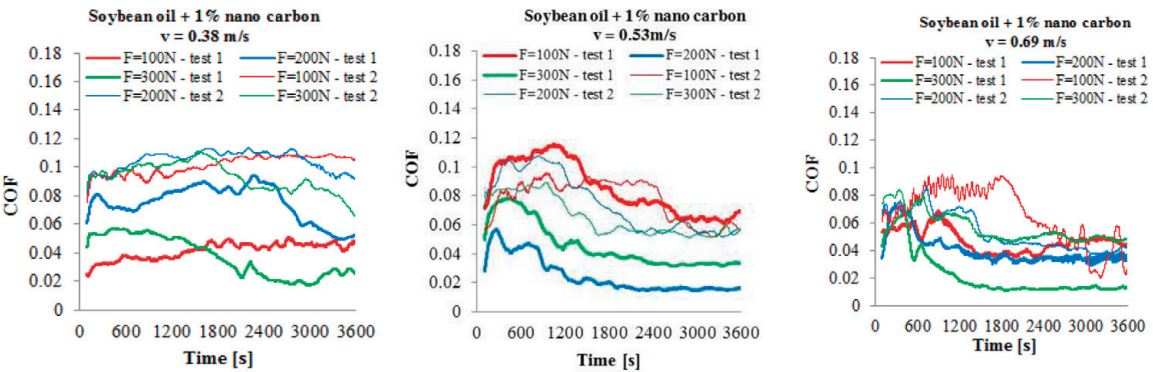


Figure 27.
The evolution of COF over time, depending on load and sliding speed for two tests with the same parameters (F, v) Cristea [82].

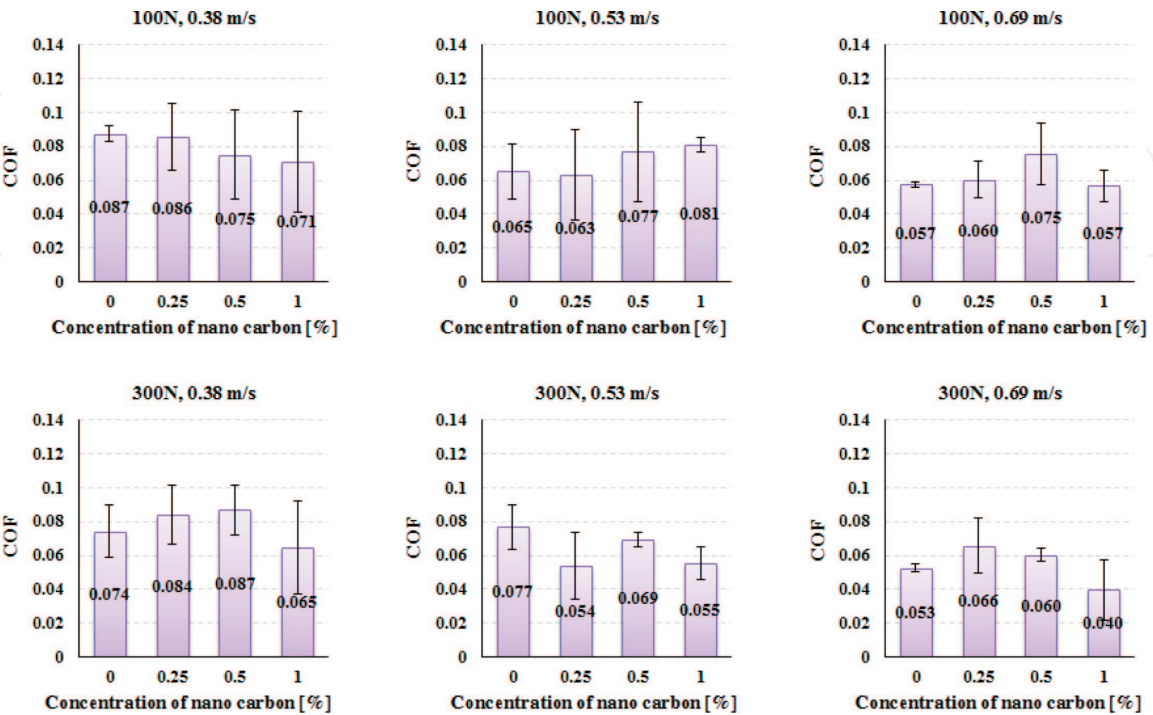


Figure 28.
Average values of friction coefficient (COF) during a test of 1 hour (two tests with the same parameters) [82].

evolution of the friction coefficient over time is based on the comments done by Czikos [66]. Thus, the coefficient for the soybean oil with nanocarbon is spread on a large interval for the lowest speed, but at $v = 0.69 \text{ m/s}$, after a period with high values, COF performs in a narrow interval, under 0.06, meaning a full lubrication (Figure 27). For additivated lubricants, the tendency is to reduce the friction coefficient after a period of operation of 10–15 minutes.

Analyzing Figure 28, it is noted that at a concentration of 1.0% of nanocarbon, the friction coefficient becomes lower for higher load ($F = 300 \text{ N}$) and high speed ($v = 0.69 \text{ m/s}$). Under the minimum test load ($F = 100 \text{ N}$), the COF oscillation range is the largest. Also, this regime gives less influence on wear rate of WSD (see Figure 30).

For nanocarbon additivated lubricants, average values of COF below 0.1 were obtained for all tests, except for the regime $F = 100 \text{ N}$, $v = 0.38 \text{ m/s}$, and $v = 0.53 \text{ m/s}$ and for $F = 300 \text{ N}$, $v = 0.38 \text{ m/s}$ but just a little over 0.1. Addition of nanocarbon in soybean oil resulted in a COF decreasing trend for extreme test regimes ($[F = 100 \text{ N}$, $v = 0.38 \text{ m/s}]$ and $[F = 300 \text{ N}$, $v = 0.69 \text{ m/s}]$). In the remaining combinations of test parameters, the influence of additivation on COF is not obvious.

This antiwear additive does not have a very clear influence on improving the tribological behavior of the soybean oil. Although the friction reduction mechanism exists in the presence of the additive, which is the interposition of carbon nanoparticles between the friction surfaces, as a third body friction, due to the migration of these particles (because they are not bonded to the surfaces) and to their uneven distribution in the contact, the tribosystem behaves more unstable than that using neat soybean oil. In a statistical approach, at some time moment and area of the contact, it could come in contact with particles sufficiently to reduce friction and wear, but during operation, there could be times when this number is low enough to have a mixt contact, and the oscillations between these two situations could explain the variations in friction coefficient and higher values for WSD.

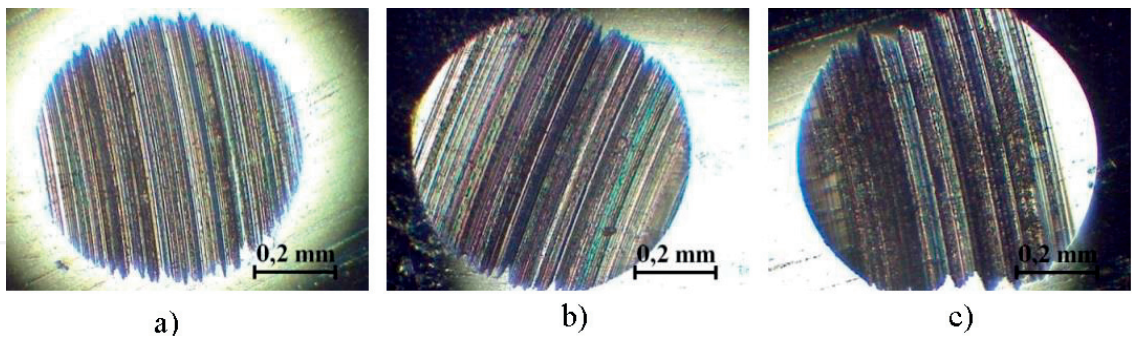


Figure 29.
Wear scar obtained with soybean oil + 0.25% nanocarbon, $F = 300 \text{ N}$ (optical microscopy) [82]: $v = 0.38 \text{ m/s}$ (a), $v = 0.53 \text{ m/s}$ (b), $v = 0.69 \text{ m/s}$ (c)

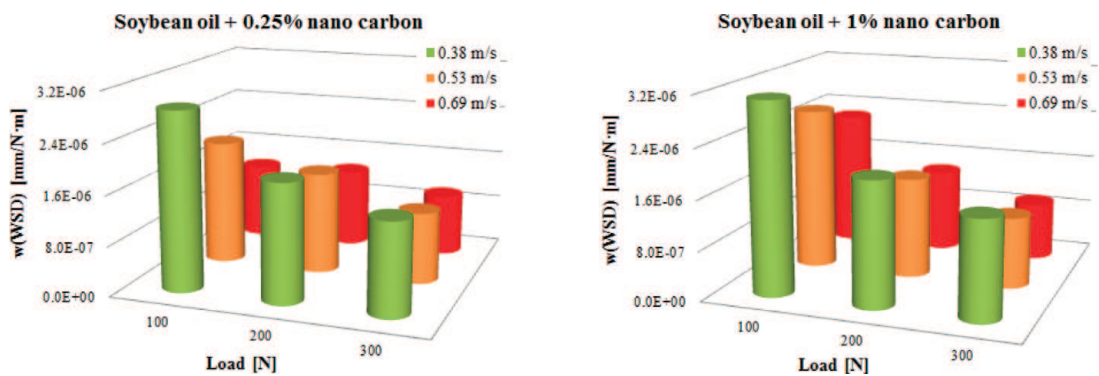


Figure 30.
Wear rate of wear scar diameter (WSD) for amorphous nanocarbon-additivated lubricants [41].

Since particle distribution is not even in contact during operation, this type of antiwear additive cannot help to improve tribological behavior because it does not reduce the friction coefficient and does not reduce the WSD as compared to those produce with neat soybean oil. The authors believe that the additive should be bonded (physically or chemically) for better results.

From **Figure 29**, it is noticed that the wear pattern did not increase too much with the speed, but the quality of the surface has considerably worsened, which justifies the profilometry study in [41, 73].

The wear rate of wear scar diameter, $w(WSD)$, helps to determine the influence of the concentration of this nanoadditive. In graphs in **Figure 30**, the neat oil is not given. The additive, either with 0.25% or 1%, makes the wear parameter to visibly decrease with speed only for low load ($F = 100\text{N}$). Comparison with nonadditivated soybean oil is highlighted on the maps in **Figure 39**, where 0% additive concentration is for the neat oil. It can be noted a decrease of $w(WSD)$ with load for all concentrations and speeds, for the additivated lubricants; the slope of the speed dependence for the same load is lower. At $v = 0.38\text{ m/s}$, the influence of the additive concentration is insignificant and the additivation would be justified in the field of high force for all speeds.

For nanocarbon additivated lubricants, $w(WSD)$ is less sensitive to additive concentration, especially for $F = 300\text{ N}$. The nonadditivated soybean oil can be recommended for light regimes (equivalent to $F = 100\text{--}200\text{ N}$ and speed $v = 0.38\text{--}0.69\text{ m/s}$). The almost linear dependence of WSD on the concentration of this additive is only observed for combinations with $F = 100\text{ N}$. For the tested regimes ($F = 100\text{--}300\text{ N}$ and $v = 0.38\text{--}0.69\text{ m/s}$), the results are not in the favor of nanocarbon additivation of the soybean oil.

3.3.3 Soybean oil additivated with nanographite

Figure 31 shows the evolution over time of COF for all tests performed with soybean oil additivated with nanographite. There is a narrowing of its evolution range for $v = 0.69\text{ m/s}$ for all loads and a scattering of higher COF values for low speeds and loads.

Analyzing **Figure 32**, it can be noticed that, at $F = 100\text{ N}$ (first horizontal line), the nanoadditive does not dramatically alter COF average. At high load ($F = 300\text{ N}$), COF increased for all additivated soybean oils as compared to the neat oil. The explanation would be that the graphite does not cover the entire surface of the contact but is only present in contact in the form of nanorolls, the reduced friction being zonal. There are also direct friction areas and friction areas with the third body (where nanoparticles or microparticles generated by agglomerating the first

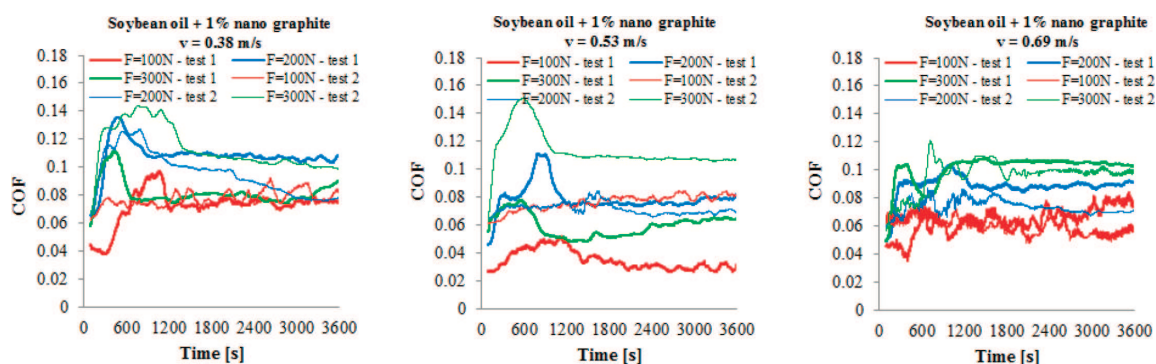


Figure 31.

The evolution of COF over time, for different loads and speeds, for two tests with the same parameters (F, v) [82].

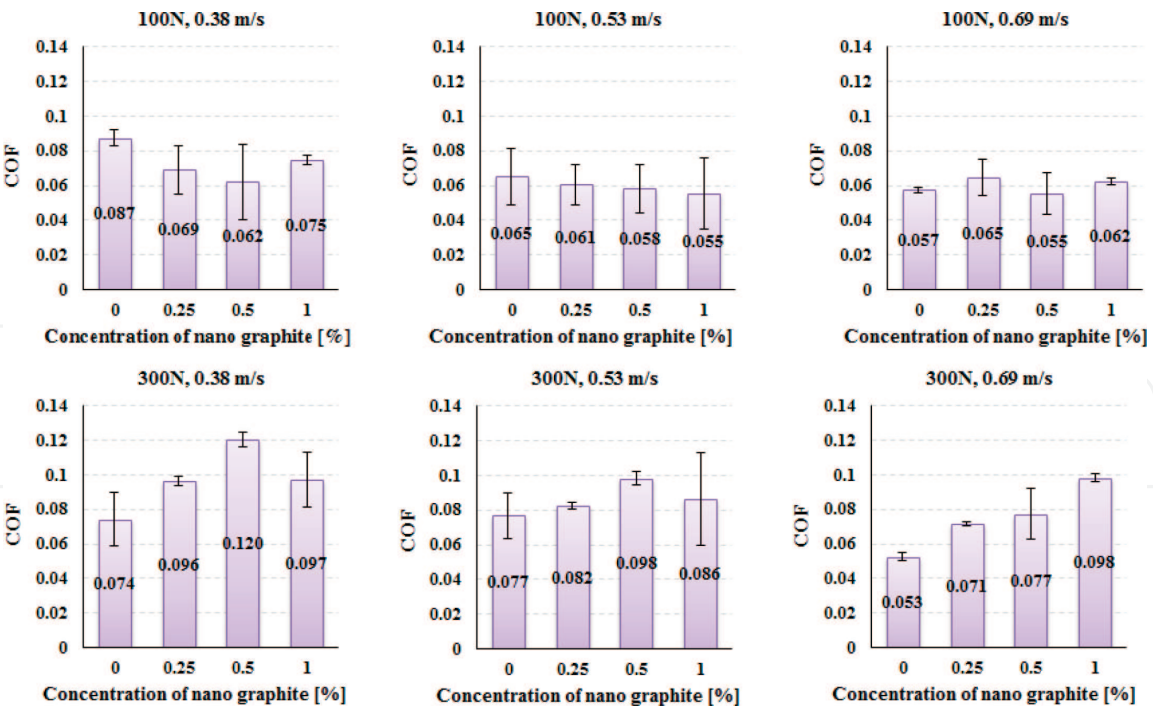


Figure 32. Average values and scattering intervals for two tests performed with the same parameters (F , v , c) [82, 83].

ones due to load and surface texture). It appears that the presence of graphite prevents the generation of EHL (elasto-hydrodynamic lubrication) film as COF has higher values, toward 0.1, especially for $F = 300$ N. No lower average COF values than those for the soybean oil have been obtained, except for tests: ($F = 100$ N, $v = 0.38$ m/s) and ($F = 100$ N, $v = 0.53$ m/s), with a graphite concentration of 0.25%wt. But the differences are too small to highlight an influence of the additive or the test regime. High values for wear rate of WSD at low load and speed imply more intense abrasion, which occurs if the lubricant film does not form and/or if the additive does not protect the contact. Maybe local particle agglomerations make the friction coefficient to oscillate and, when they migrate in contact, they allow one triboelement to fall over the other, in direct contact under higher load than if it had not encountered the graphite agglomerations.

Analyzing the photos in Figure 33, it can be noticed that the nature of the wear pattern does not change significantly, resulting from the abrasive wear process and with rare adhesive wear spots at higher loads.

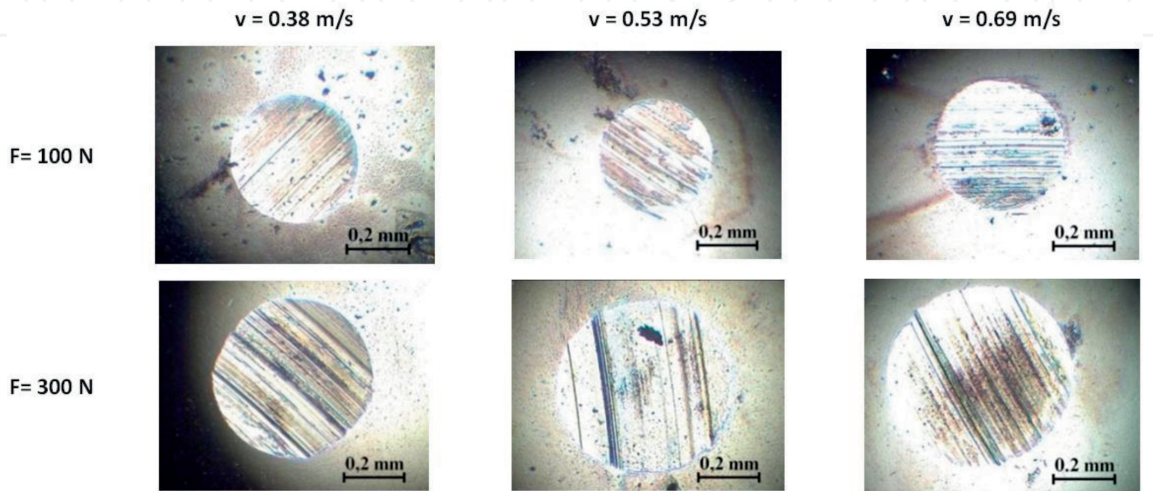


Figure 33. Photos of the wear scars of the soybean oil + 1% nanographite [82].

Comparing the graphs in **Figure 34**, they are similar in appearance, regardless of the concentration of the nanoadditive. The wear rate decreases with increasing load; for load $F = 300\text{ N}$, the wear rate of WSD is less influenced by speed.

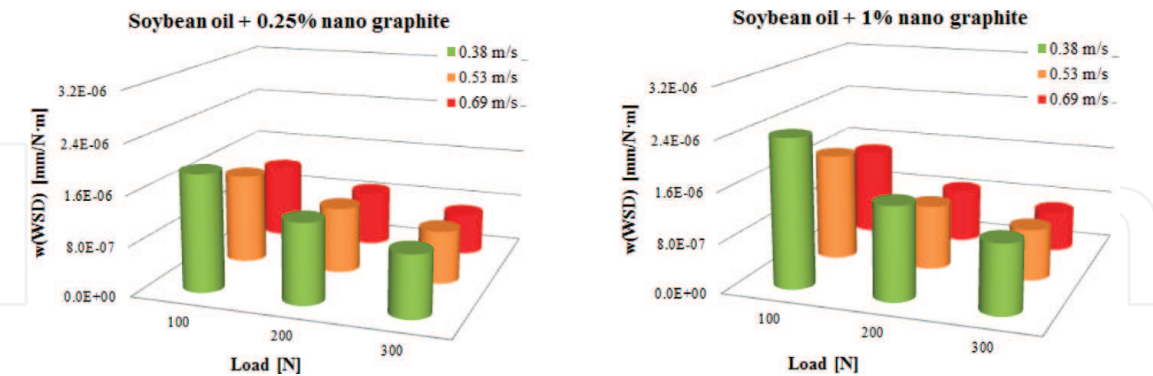


Figure 34.
Wear rate of WSD for nanographite additivated lubricants [82].

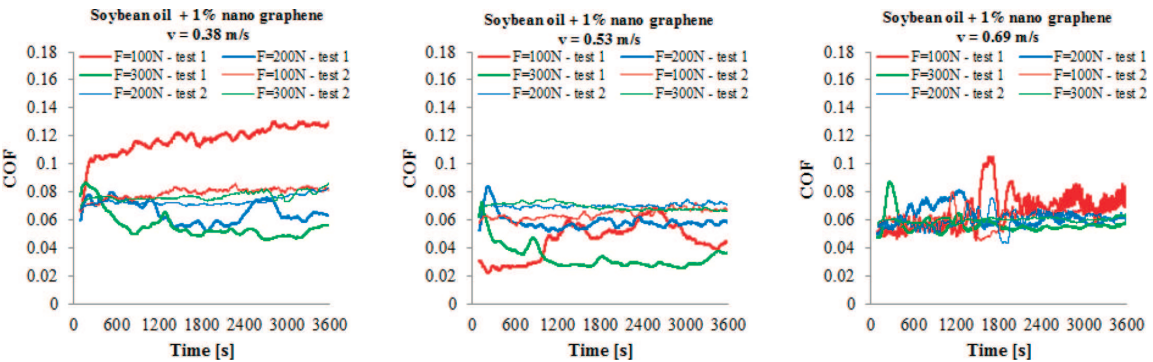


Figure 35.
The evolution of COF in time, depending on load and speed, for two tests with the same parameters (F, v) [41].

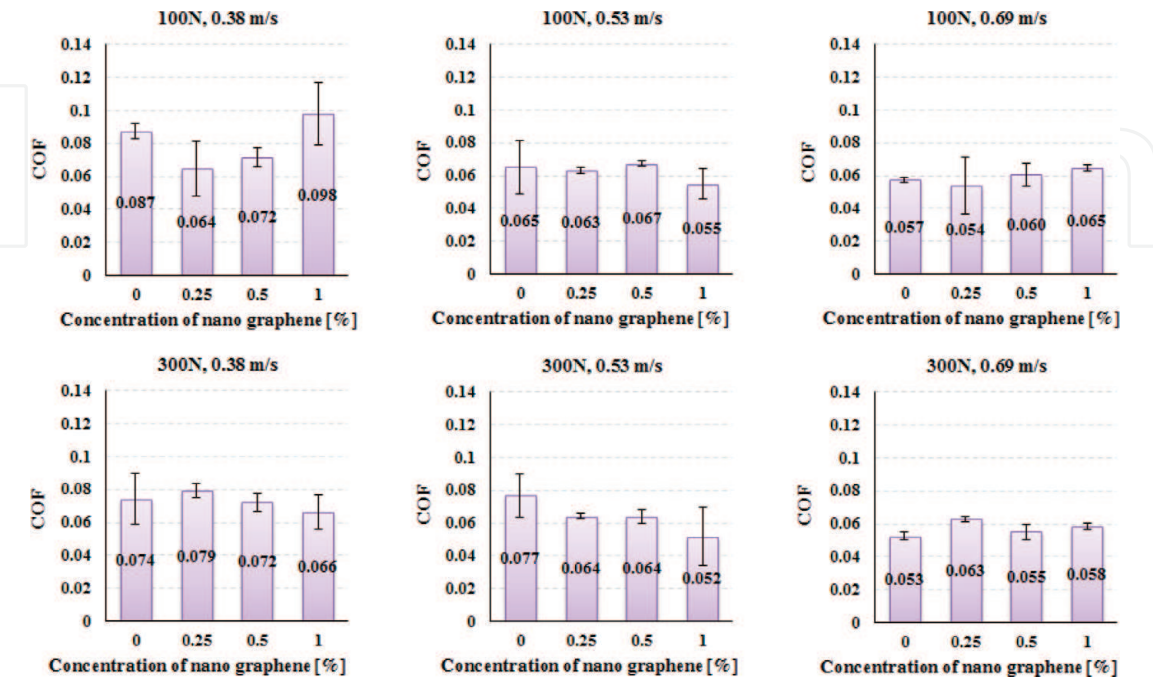


Figure 36.
Average values and spread range of friction coefficient (COF) for two tests performed with the same parameters (F, v, C) [41].

3.3.4 Soybean oil additivated with graphene

The evolution of COF over time is given in **Figure 35**, better ones being obtained for the highest concentration. COF variations have shortcuts or growth levels, which can be explained by the dynamics of COF components (dry friction, third body rubbing in areas with graphene nanoparticles, and partial fluid friction).

The addition of graphene does not improve COF but keeps it very close to the values of neat soybean oil. At $v = 0.38 \text{ m/s}$, the highest values were obtained irrespective of the concentration of the additive, suggesting that the improvement in friction (in the sense of reducing it) is due to the increase in speed (**Figure 36**) [41] and not on the additive, but the graphene does not prevent the formation of the fluid film.

WSD does not significantly increase but the texture of the surface visibly changes (**Figure 37**), and the wear rate of WSD indicates a better tribological behavior of additivated soybean oil with graphene, but for more severe regimes ($F = 200\text{--}300 \text{ N}$ and $v = 0.53\text{--}0.69 \text{ m/s}$), from this set of observations, the importance of correlation in the interpretation of several tribological parameters is pointed out.

High values were obtained for the mildest test regime ($F = 100 \text{ N}$, $v = 0.38 \text{ m/s}$). One could argue that a low loaded contact does not keep the additive in contact (pressed and hung on the texture). The lowest value for the most severe regime ($F = 300 \text{ N}$, $v = 0.69 \text{ m/s}$) was explained by forming the EHD film and maintaining the nanoadditive in contact.

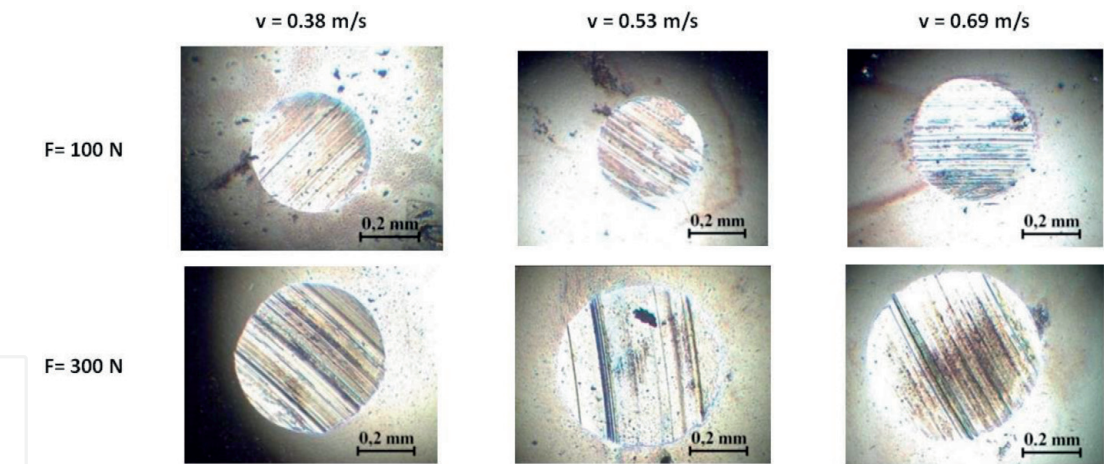


Figure 37.
Optical microscope photos of wear scar diameter, after testing with soybean oil + 0.5% nanographene [41].

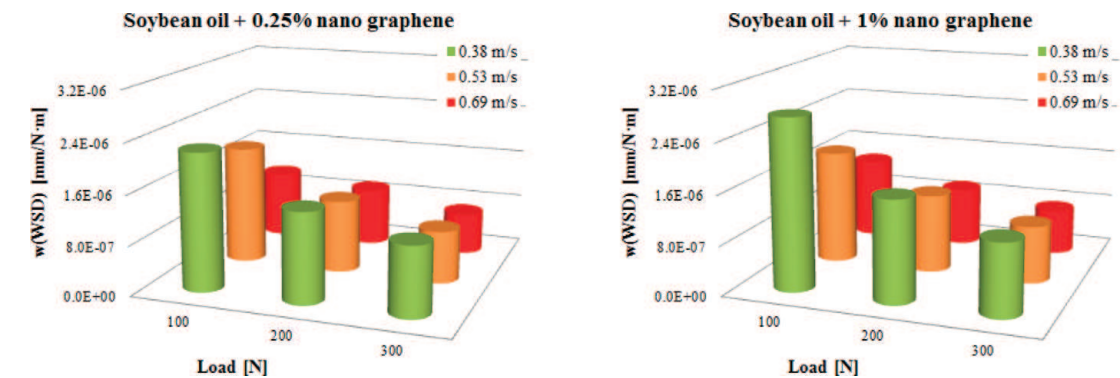


Figure 38.
 $w(WSD)$ of soybean oil additivated with nanographene [41].

The wear rate of WSD (**Figure 38**) is 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 smaller for longer sliding distances and higher sliding speeds.

3.4 Maps for tribological parameters

The influence of the quality of the additive is manifested not only by the minimum value but also by the map area for which the minimum values of $w(WSD)$ are spread (**Figure 39**). The lower surface of the map was noticed for graphene at 1% wt, between $F = 200\text{ N}$ and $F = 300\text{ N}$ and $v = 0.69\text{ m/s}$, less influenced by the amount of additive. For carbon, the low wear rate area is narrower. At $v = 0.38\text{ m/s}$ and the lowest tested load, the lowest value of $w(WSD)$ is obtained for graphite. The concentration of 1% nanoadditive enlarges the domain of reduced wear rate, meaning the load and speed have less influence on the test regime, especially for higher values for both parameters.

Maps were represented using a spline interpolation, and the surfaces are “compelled” to include the experimental data. A point on a wear rate map area is the wear rate of WSD for a test characterized by the set of input parameters ($F\text{ [N]}$, $v\text{ [m/s]}$,

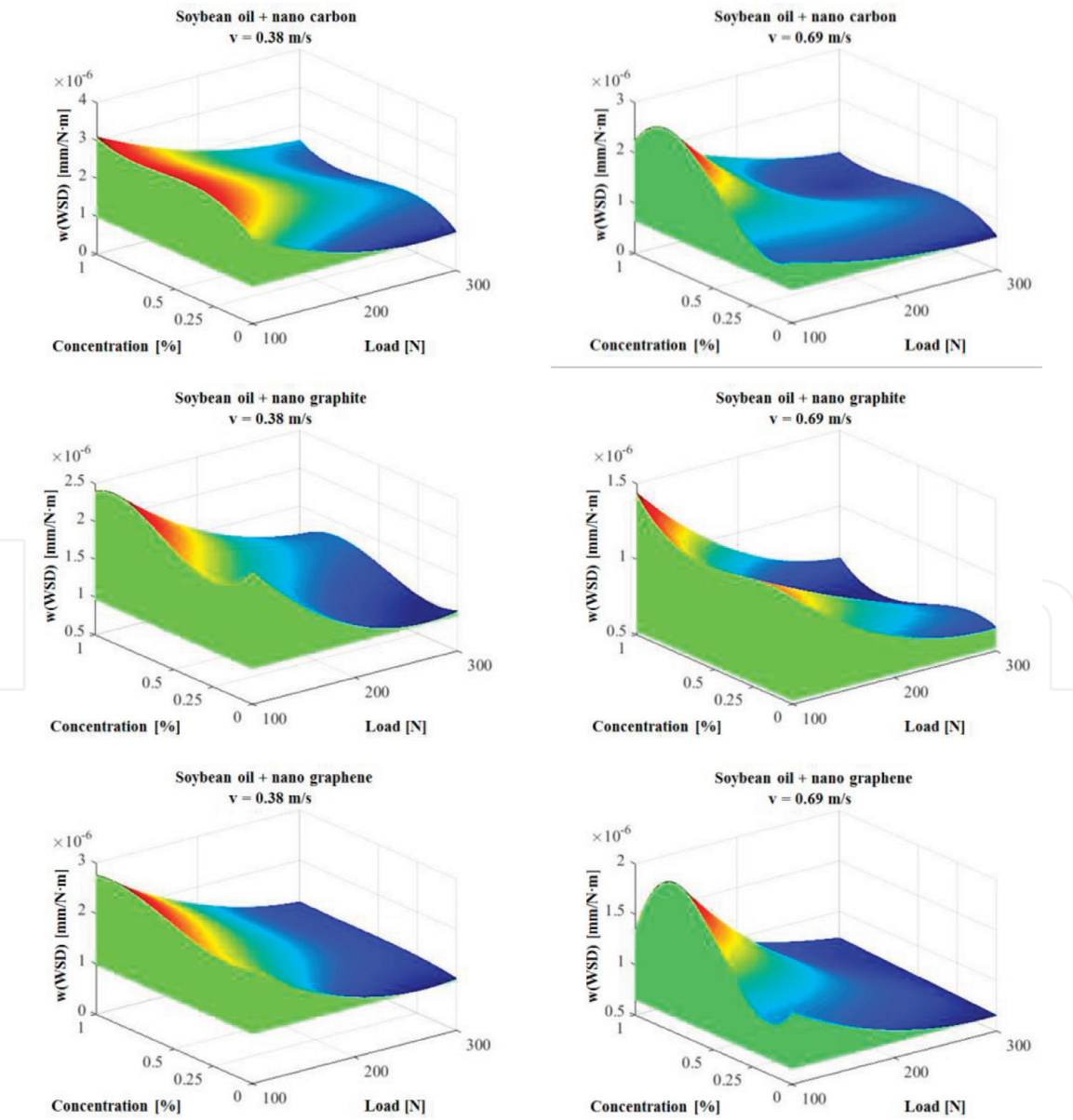


Figure 39. Maps of $w(WSD)$ for lubricants tested at two sliding speeds [41].

and c [%]), where F is the normal load on the four ball tribotester, v is the sliding speed, and c is the mass concentration of nanoadditive.

4. Conclusions and new trends in using soybean oil as lubricant

Friction coefficient and wear rate of wear scar diameter are important tribological characteristics, and they are compared in **Figures 40** and **41** for neat soybean oil and the same oil additivated with nanocarbonic additives. COF has higher average values for soybean oil with graphite. This fact could be explained by local agglomerations of the nanosheets of graphite that migrate in contact, causing a mixt regime especially when the COF values overpass 0.1. Agglomeration of nanoparticles could also explain the balls. The high values in light regimes could be explained by the fact that the particles are not pressed enough to fill and remain on the surface texture).

The downward trend of wear rate of wear scar diameter, $w(WSD)$, had a higher gradient for lubricants with 1% nanoadditive (**Figure 41**), which would recommend further testing for more severe regimes, where additives are likely to better protect the surface of the contact.

Analyzing these tribological parameters, the authors consider that a combination (a low and constant evolution in time of friction coefficient, a small WSD, and a high value of FTP) makes the lubricant to have a good reliability in functioning. These laboratory test results have to be carefully applied when designing an actual applications with such a lubricants as in practice, the range of parameter variations is larger because of perturbations like vibrations, mechanical shocks, operator's errors, humidity, higher temperature gradients, etc.

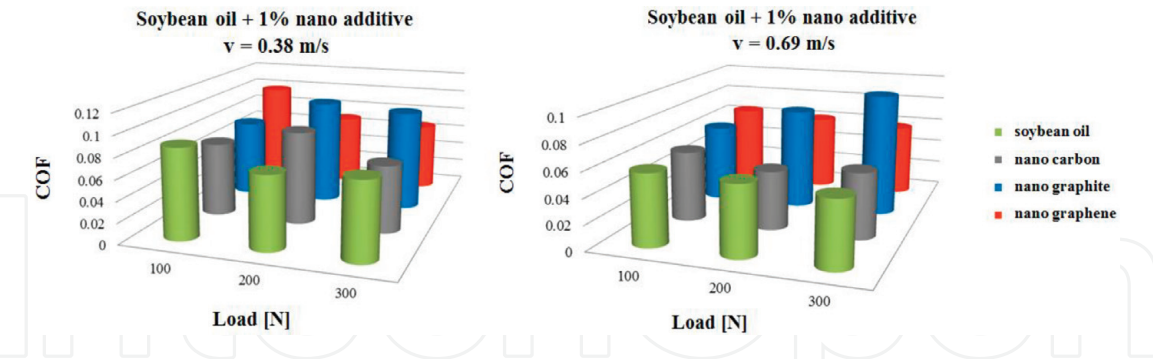


Figure 40.
Influence of additive in concentration of 1% on the friction coefficient [41].

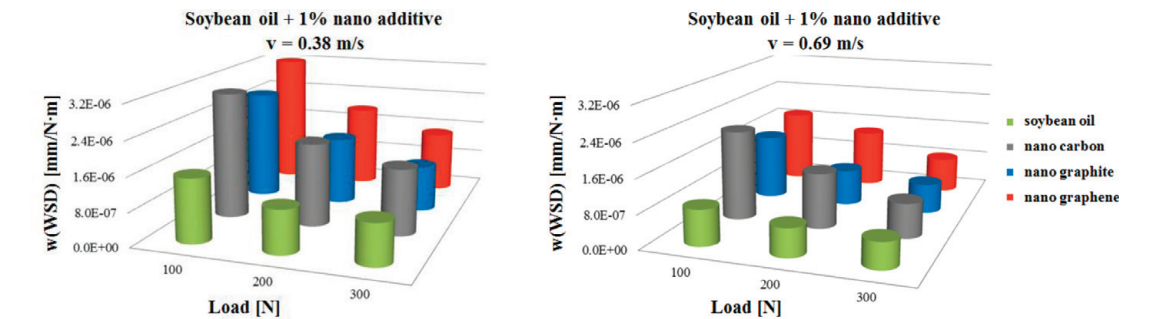


Figure 41.
Maps of the wear rate of WSD for lubricants additivated with 1% nanoadditive [41].

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