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Influence of graphene as additive in soybean oil

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Abstract. Anti-wear additives and friction additives are used for medium stresses and the protective film relies heavily on adsorption processes and regeneration of the protective film. This study presents the influence of graphene concentration as additive in soybean oil and test regime (load and speed) on tribological characteristic (friction coefficient and wear rate of the balls used in a four-ball test). A general view of the results, easy to see by the plotted maps of the average value for friction coefficient depending on load and additive concentration and of wear rate of the scar diameter, reveals that the wear rate is almost non-sensitive to the test parameters and this zone is limited by F = 200 ...300 N, for all the sliding speeds. As for the friction coefficient, the additivation does not lower this tribological parameter in a spectacular way for the additivated lubricants. These results encourage to use the additive for tribosystems that function with variable load and speed, but in the ranges as the tests done by the authors.

1. Introduction

Anti-wear additives and friction additives are used for medium stresses and the protective film relies heavily on adsorption processes and on regeneration of the protective film, even if it partially deteriorates during the exploitation.

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 could chemically react with the surface to form a protective film. Vegetal oils and animal fats have such molecular structures and, therefore, they have good results in reducing friction.

In addition to organic friction modifiers, some solid lubricants are added to oils with the same purpose of reducing friction. This group of friction modifiers includes carbon materials (fulerene, nanotubes, graphite, graphene, etc.), but also molybdenum and wolfram sulphides, fluorinated polymers, such as polythetrafluorethylene and perfluoropolyalkylethers. These can also be added in greases and composites that will function in dry conditions [1].

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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), also producing a reduction in wear. They are added to lubricants that come into contact with surfaces with which EP additives cannot chemically react, such as polymers and ceramics and some of their composites [2].

Wu et al. [3] propose a model that takes into account the lubricating additive concentration. The mechanism for reducing friction and wear of nano particles in lubricants has been investigated and it is based on the following processes [4]:
- micro-roll process,
- process of forming a protective film,
- smoothing/leveling process,
- polishing process.

Berman et al. [5], [6] did outstanding research on friction of graphene on metallic surfaces, but the tests are still short as duration or sliding distance to be related to practical applications in tribosystems that are presumed to function a long time. As additive, the graphene was added in engine oils [7].

Xu et al. [8] used graphene as additive in a mix with MoS2 in esterified bio-oils, obtaining a synergistic effect on tribological behavior for lubricated steel/steel contact. When tested on a four ball tester, the mix of graphene with MoS2 gave smaller wear scar diameter and lower values for friction coefficient as compared to the same quantity of MoS2 without graphene. But the influence of ratio between the two mixed additives that will have a sum concentration of 0.5% wt is not obvious.

Zhang et al. [9] reported better tribological properties (friction coefficient and wear scar diameter of the four-ball tester) reduced with 17% and 15%, respectively, when using oleic acid with modified graphene as lubricant.

Thus, this study on the influence of graphene as additive in soybean oil could motivate the use of bio-lubricants, additized or not, especially because results on four-ball tester are easy to be compared.

2. Lubricants and testing methodology
The materials tested for this study are lubricants based on soybean oil supplied by Prutul Galati and nano additive in various concentrations (0.25% wt, 0.5% wt and 1.0% wt.).

The composition in fatty acids for the tested soybean oil is: 0.11% acid myristic acid (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% eicosadienoic acid (C20:2).

The graphene was supplied by PlasmaChem [10], as nano plates with a thickness of 1.4 nm and a particle size of up to 2 microns (see figure 1).

A relatively good dispersion till the lubricant was used for testing was solved by making a premix of additive + dispersion agent, here guaiacol, supplied by Fluka Chemica, with the chemical formula C6H5(OH)OCH3 (2-methoxyphenol).

The formulated lubricants were obtained in a small amount of 200 g, each, by sonication and the laboratory-scale manufacturing is given in [11].

The test balls are lime polished, made of chrome alloyed steel balls (EN31), having 12.7±0.0005 mm in diameter, with 805 N/mm² hardness VHN, as delivered by SKF. The sample oil volume required for a test was 8 ml ± 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 [12].

The test parameters for each tested lubricant were:
- loading force - 100 N, 200 N and 300 N (± 5%),
- sliding speed of 0.38 m/s, 0.53 m/s and 0.69 m/s, corresponding to the spindle speeds of the four-ball machine 1000 rpm, 1400 rpm and 1800 rpm (± 6 rpm), respectively,
- test time - 60 minutes (± 1%);
- the concentration of the graphene as additive in the formulated lubricants is 0.25%, 0.50% and 1% (wt), respectively.

![Figure 1. SEM image of the graphene.](image)

3. Results on tribological behavior

The evolution of friction coefficient (COF) in time is given in figure 2, better evolution being obtained for the highest concentration of the additive. COF variations have short cuts or growth levels, which can be explained by the dynamics of COF components (dry friction, third body rubbing in areas with graphene nanoparticles, partial fluid friction). At \( v = 0.38 \text{ m/s} \), the COF value, as an average of the values obtained for two tests, can be considered in two areas: around 0.1 (mixed and/or boundary lubrication) and below 0.1 (with EHD film, maybe partial). The smallest value was recorded for graphene in soybean oil, at the lightest load, but for \( F = 200 \ldots 300 \text{ N} \), the lowest values were obtained for non-additivated oil.

![Figure 2. The evolution of COF in time, depending on load and speed, for two tests with the same parameters (F, v) and graphene concentration of 1%wt.](image)

The addition of graphene does not improve COF, but keeps it very close to the values of neat soybean oil (see figure 3). 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 mainly due to the increase in speed [13] and not on the additive, but the graphene does not prevent the formation of the film.
Figure 3. Average values and spread ranges for two tests performed with the same parameters (F, v, C).

It is possible that the simple graph of the wear scar diameter dependence on additive concentration, load and speed is not relevant due to the difference in the sliding distances. Thus, on the basis of the literature [14], the wear was evaluated by a parameter called the wear rate of wear scar diameter:

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

where WSD is the wear scar diameter average for a test (the average value of six diameter measurements, two on each fixed balls [12]), F is the load applied on the four balls and L is the sliding distance.

The downward trend of $w(WSD)$ had a higher gradient for lubricants with 1% nano graphene, which would recommend further testing for more severe regimes, where additive is likely to better protect the surfaces of the contact.
Figure 4 presents photos of the wear scars for different loads and speeds, pointing out an increase of the WSD more with load and less with speed, but also a change in the texture of the worn surfaces.

Figure 4. Optical microscope photos of wear scar diameter, after testing with soybean oil + 0.5% nano graphene.

Figure 5. The wear rate of scar diameter, w(WSD), when using neat soybean oil and soybean oil additivated with nano graphene.

Analyzing the charts in figure 5, it may be noticed the following for the wear rate of WSD.
High values were measured for the mildest test regime (F = 100 N and v = 0.38 m/s). For the additivated lubricants with graphene and for this regime, the w(WSD) is slightly increasing with the additive concentration, meaning that this additive does not protect the surfaces quite well. One could argue that contact oscillations do not keep the additive in contact.

A possible source of oscillations in contact could be the load re-distribution due to the interaction of the wear scars (the circular one of the mobile ball with those on the fixed balls). During the test, the circular wear scar generated on the mobile ball is changing its shape and its relative position to the wear scars developed on the fixed balls (see Figure 4).

The lowest values are obtained for the most severe regime (F = 300 N, v = 0.69 m/s) and that could be explained by forming the EHD film and maintaining the nano additive in contact.

The graphs in figure 5 show a trend of very small increase of w(WSD) with additive concentration, more visible at F = 300 N.

The wear rate of WSD are similar for 0.25% and 1% meaning the additive concentration (0.25% ... 1%) does not influence too much the wear. It seems that the wear is made in stages and is smaller for longer sliding distances. But, on the same graphs, there is visible a tendency of reducing the influence of speed on the w(WSD), when testing with higher loads (F = 200 N and F = 300 N).

4. Conclusions
For having a general view of the experimental results, the authors plotted maps of the average value for friction coefficient (COF) depending on load and additive concentration (figure 6) and for w(WSD) depending on the same parameters, in figure 7.

![Figure 6](image1.png)  
**Figure 6.** Friction coefficient maps for lubricants tested at extreme speed conditions.

![Figure 7](image2.png)  
**Figure 7.** w(WSD) maps for lubricants tested at extreme speed conditions.
When testing at the sliding speed $v = 0.69$ m/s, COF oscillated in a very narrow interval. For $F = 100$ N, regardless the value of sliding speed, COF is higher and increases with the additive concentration. The explanation could be that the nanoparticles are not kept in contact and/or agglomerate because of a too low pressure on them. Also, the regime characterized by low speed and low load is not capable to generate a fluid film, even partially. This effect for a combination of low load and low speed was also noticed by Georgescu [15], for other vegetal oils (non-additivated) tested on the same tribotester, meaning that a great influence is done by the low viscosity of vegetal oils in functioning.

When comparing the results obtained by Abdullah [16], which tested according to ASTM, a diesel oil SAE15W-40 nano additioned with 0.5 vol% of 70 nm hBN, obtained by ultrasonography, it was observed that, for the test interval of 200 ... 500 N, the WSD was lower for the additivated oil, but this decrease is not clearly highlighted in the range of 200 to 400 N.

This nano additive, the graphene, increases $w(WSD)$ with low values but, as an advantage, almost uniform values for $w(WSD)$ were obtained for different regimes (the additive lessens the influence of the test regime on this wear parameter).

The downward trend of $w(WSD)$ had a higher gradient for lubricants with 1% nano additive, which would recommend further testing for more severe regimes, where the additive is likely to better protect the surfaces of the contact.

Adding nano graphene in the soybean oil does not modify significantly the average value of COF as compared to values obtained for the neat soybean oil, but studying the influence of the additive concentration, the authors noticed that for the most severe tested regimes ($F = 300$ N and $v = 0.69$ m/s), the values of COF are very close. Higher values are obtained for the mild regime, especially for $F = 100$ N, meaning that this additive is not recommended for this regime, but for more severe ones.

On the maps in figure 7, the analysed wear parameter, $w(WSD)$, has a zone for which the wear rate of wear scar diameter is almost non-sensitive to the test parameters and this zone is limited by $F = 200$ ...300 N, for all the sliding speeds. These results encourage using this nano additive for tribosystems that function with variable load and speed, but in the same ranges as the done tests.

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