Influence of TiO$_2$ as nano additive in rapeseed oil

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Abstract. This paper presents the influence of TiO$_2$ as additive in refined rapeseed oil in different massic concentration (0.25%wt, 0.50%wt and 1%wt) on the tribological parameters. Tests are done on a four-ball machine from the laboratory LubriTest, at “Dunarea de Jos” University of Galati. The test parameters were load: 100 N, 200 N and 300 N and the rotational speed 1000 rpm, 1400 rpm and 1800 rpm. Particles of TiO$_2$ have an average size of 21±5 nm. The rapeseed oil was supplied by Prutul Galati. For the tested ranges of the parameters, the additivation of rapeseed oil with TiO$_2$ do not improve the friction coefficient and the wear rate of WSD. The additivation of rapeseed oil with TiO$_2$ is still less efficient for the tested ranges of load and speed as compared to the neat rapeseed oil, but there is visible that friction coefficient and analysed wear parameter are less influenced by the regime for the concentration of 1% TiO$_2$ in rapeseed oil.

1. Introduction

Vegetal oils, even if they have some undesirable properties, including the low oxidative stability, low values of the dynamic viscosity at higher temperatures [1], [2], [3], a narrow temperature range of using etc. [4], [5], are asked for “green” industrial activities for which rules and regulations are more severe (forestry industry, ship industry, water supply industry, food processing, agriculture etc.) [6], [7]. Scientists have been trying to improve vegetal oil properties by additivation [8] and they tested lubricants based on vegetal oils and different additives, from those used with mineral, but also synthetic ones, to additives that are particularly fitted for renewable resources.

The rapeseed oil is an available resource for producing the so-called environmentally-adapted lubricants and its additivation for improving its tribological behavior is of interest for researchers. Some research reports the influence of TiO$_2$ added in lubricants, especially as micro-sized powder, but there are several works dealing with nano scale of this additive.

The additivation of rapeseed oil could improve some tribological characteristics, but the influence of the additive on long time is far from being understood or explained [9]. Lyu [10] reported experimental results using a modified rapeseed oil by a silan coupling agent and montmorillonite powder for leather processing and concluded that the formulated lubricant is friendly with the environment.

The mechanism of reducing friction and wear using nano additives in oils is based on the following processes [11], [12]: micro- or nano-rolling (especially when nano particles are ovoidal or almost...
spherical), generating a protective powdery film on the solid triboelements [13], [14], levelling or smoothing process of the surface texture [15], polishing [16].

The introduction of friction and wear modifiers conducts to the appearance of several friction mechanisms [17]:
- rolling friction - the nano particles, especially with spherical shape, act as nano or micro rolls between the triboelements’ surfaces, especially when load is not great enough to flatten/break the particles,
- sliding friction - the nanoparticles being as spacers or separators between solid surfaces in contact and when the load increases, they are positioned between asperities,
- third body friction - the particles’ exfoliation and their mechanically fixing on the contact surfaces protect the bodies; the third body is now a mixture of lubricant, nano additives, but also nano and micro wear debris.

The arguments in the favour of using nanoparticles of TiO$_2$ as additive include the fact that the oxide is chemically stable (they will not react with the base oil and solid triboelements), it is commercially available not only at laboratory scale and it is not a hazard for human operators.

Yathish et al. [18] used an engine oil (SAE 30) with the viscosity of 0.1078 Pa·s at 40°C and nano particles of TiO$_2$ as a mix of rutile and anatases phases, with the size less than 100 nm. The oleic acid was used for surfactant and satisfactory dispersion.

The titanium dioxide (TiO$_2$), as an oxide of a transitional metal included in the family of dicalcogenide, is a friction modifier as molybdenum disulphide (MoS$_2$) and tungsten disulphide (WS$_2$), these ones reducing friction and wear both in solid friction and the fluid one.

The recent research pointed out that nanoparticles added into lubricants do not have the same or similar influences, some being promising, others still having prohibited costs, others do not evidence a clear tendency of improving the lubricant performances [11].

The four-ball tribotester allows for easier comparing the lubricants and there are papers reporting results for vegetal oils, additivated or not [19], [20], [21], but data are far for being reliable and useful for actual applications. Thus, knowing the behavior of these vegetal lubricants on the four-ball machine helps to accelerate their introduction in actual systems as it is easy to compare their results with those obtained for “classical” solutions (using mineral or synthetic base oils).

Luo [22] tested a mix of Al$_2$O$_3$/TiO$_2$ as additive in oil, with five different amounts: 0%, 0.05%, 0.1%, 0.5% and 1% (wt.) and friction coefficient and wear scar diameter were reduced. Ali et al. [23] minimized the boundary friction coefficient in automotive engines using Al$_2$O$_3$ and TiO$_2$ nanoparticles. Binu et al. [24] evaluated the load carrying capacity of an oil lubricated journal bearing with TiO$_2$ nanoparticles as lubricant. Hemmat and Rostamian [25] proposed a non-Newtonian power-law for the behavior of TiO$_2$/SAE 50 nano-lubricant. Ingole et al. [26] reported the influence of TiO$_2$ as nano additive in oils (rutile and anatase phases), the base oil being mineral. All concentrations of additive increased the coefficient of friction, but they reduced the variability and stabilized the lubricant behavior. Salimi-Yasar et al. [27] did experimental investigation on cutting fluids using soluble oil-based TiO$_2$ nanofluid.

Taking into account [28], [12], [29], the authors selected TiO$_2$ as a nano additive for this vegetal oil. This paper presents the influence of this additive in refined rapeseed oil, in different mass concentrations, on the tribological parameters.

2. Formulated lubricants and testing methodology

The materials tested for this study are lubricants based on refined rapeseed oil supplied by Prutul Galati and TiO$_2$ as nano additive in various concentrations (0.25 wt%, 0.5 wt% and 1.0 wt%). The composition in fat acids of the rapeseed oil is shown in Table 1.

Additive was supplied by PlasmaChem [30]. Thus, the nanopowder of TiO$_2$ (code PL-TiO-P25-HPB) is a mixed rutile/anatase phases and has the following characteristics: obtained by photocatalytic process, the average size of particles was 21±5 nm, specific surface 50±10 m$^2$/g, purity after ignition
>99.5%, ignition loss < 2%; humidity <1.5%, other elements: Al₂O₃<0.3 wt%; SiO₂ < 0.2 wt%, density: approx. 130 g/L, delivered in 50 g pack.

Table 1. Typical composition in fatty acids of the rapeseed oil.

| Fat acid                  | Symbol | Composition, % wt |
|---------------------------|--------|-------------------|
| Myristic acid             | C14:0  | 0.05              |
| Palmitic acid             | C16:0  | 4.84              |
| Palmitoleic acid          | C16:1  | 0.06              |
| Heptadecanoic acid        | C17:0  | 0.14              |
| Stearic acid              | C18:0  | 0.14              |
| Oleic acid                | C18:1  | 62.73             |
| Linoleic acid             | C18:2  | 22.4              |
| Linolenic acid            | C18:3  | 7.50              |
| Arachidic acid            | C20:0  | 0.50              |
| Eicosenoic acid           | C20:1  | 1.25              |
| Behenic acid              | C22:0  | 0.30              |

The problem to be solved with such an additive is its dispersion in oil. Thus, since the tested base oil is a mixture of fatty acid triglycerides (Table 1), the authors proposed a method of obtaining a good dispersion. The formulated lubricants were obtained in a small amount of 200 g, each. The mass ratio of the additive in the dispersing agent is 1:1, with an accuracy of 0.1 mg. The steps followed in this laboratory technology were similar to those presented by Cristea [31]:

- mechanical mixing of additive and an equal amount of dispersing agent (guaiacol, supplied by Fluka Chemica, with the chemical formula C₆H₄(OH)OCH₃(2-methoxyphenol)), for 20 minutes; this dispersing agent is compatible with both the additive and the rapeseed oil;
- gradually adding the rapeseed oil, measured to obtain 200 g of lubricant with the desired additive concentration, by mixing with a magnetic homogenizer during 1 hour;
- ultrasonication + cooling of lubricant for 5 minutes using the Bandelin HD 3200 (Electronic GmbH & KG Berlin) sonicator; the lubricant is heated to about 70°C; the cooling time was 1 hour; this ultrasonic + cooling step is repeated 5 times to obtain a total time of 60 minutes of ultrasonication. The parameters of ultrasonic regime are power 100 W, frequency 20 kHz ± 500 Hz, continuous mode.

The test balls are lime polished, made of chrome alloyed steel balls, having 12.7±0.0005 mm in diameter, with 64-66 HRC hardness, as delivered by SKF. The sample oil volume required for each test was 8 ml ±1 ml. The test method for investigating the lubricating capacity was that from EN ISO 20623:2003 Petroleum and related products - Determination of the extreme-pressure and anti-wear properties of fluids - four ball method [32].

The test parameters for each tested lubricant were:
- loading force on the machine spindle - 100 N, 200 N and 300 N (± 5%);
- sliding speeds 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 each additive in the formulated lubricants is 0.25%, 0.50% and 1% (wt), respectively.

Lubricants have been inserted into the fixed balls cup to cover these balls. After each test, the ball fastening system and the balls were cleaned and degreased with isopropyl alcohol and ethyl ether, then dried in air stream.
Measurement of wear trace diameters was performed with the Neophot 2 optical microscope, in accordance with the procedure given in EN ISO 20623:2003 [32]. Three wear marks were obtained for each test, these being located on the three fixed balls. Two diameters, the first diameter measured along the sliding direction, the second diameter measured perpendicular to the first, were measured for each wear trace. With three traces of wear, six diameters were obtained and their mean value was calculated. This value represents the diameter of the wear scar, reported for each of the tests performed. The same method of obtaining the wear diameter is also given in specialized reports [31], [33].

3. Results on tribological behavior of formulated lubricants

There is reported the influence of additive concentration on tribological parameters, friction coefficient - COF and wear rate of the wear scar diameter - w(WSD).

The graphs in figure 1 were plotted using a floating (mobile) average for 200 successive values. A test has a time duration of 1 hour and it gives 7200 records of the resistant moment, the sampling being 2 values per second.

Figure 1 presents a slightly decrease of the friction coefficient when the sliding speed increased from 0.38 m/s to 0.69 m/s, for the neat rapeseed oil as lubricant, this being in agreement with the EHD theory. The stable evolution of COF is approximative 500 s, at \( v = 0.38 \) m/s, approximative 1500 s at \( v = 0.53 \) m/s and at \( v = 0.69 \) m/s, this duration is reduced to approximative 700 s. As the friction coefficient is evolving around 0.1, the regime could be considered mixt or boundary.

![Graphs showing COF vs. Time for different loads and speeds.](image)

**Figure 1.** Evolution in time of the friction coefficient (COF) for the non-additivated rapeseed oil.

For the rapeseed oil additivated with 0.25% TiO\(_2\) (see figure 2), the following comments may be done:

- the evolution of friction coefficient for \( v = 0.38 \) m/s proves a mixt regime, the percentage of direct contact diminishes when the sliding speed increases. At lower load (\( F = 100 \) N), the value for the friction coefficient is higher, meaning that, under low load, the additive is not pressed on the asperities and does not mechanically fix on the surface texture; another explanation is that a low load does not favour the generation of micro and nano rolls that could modify the friction mechanism, from sliding to rolling;

- the stable regime is obtained after a shorter period of time for the lower speed;

- for higher sliding speeds (0.53 m/s and 0.69 m/s), the lower values of friction coefficient are obtained for \( F = 100 \) N and \( F = 300 \) N, arguing a regime change as compared to that with \( v = 0.38 \) m/s.
Figure 2. Evolution in time of the friction coefficient (COF) for the rapeseed oil additivated with TiO₂.

Analysing figure 2, one may notice the following:
- the increase of friction coefficient with load, at v = 0.38 m/s, indicates that an EHL regime is generated under lower load, but for F = 300 N the regime becomes a mixt one;
- at v = 0.53 m/s, it is supposed that the mixt or boundary regime is generated also for F = 200 N;
- at v = 0.69 m/s and F = 100 N, friction coefficient becomes unstable, probably because the uneven migration of the additive or its agglomerations between the surfaces in contact;
- the decrease of friction coefficient was obtained for F = 300 N, but only during half the test time, supposing the generation of an EHL regime.
For the lubricant additivated with 1% wt TiO\textsubscript{2} (the plots in figure 2), the following comments could be done:

- at higher speeds and low loads, the influence of additive is not beneficial as the values for friction coefficient suggest a mixt or boundary regime, higher than those obtained for the neat vegetal oil;
- for high loads and speeds, an EHL regime is generated, but not during all the test period (about 60%);
- for the sliding speed of \(v = 0.69\) m/s, the stable period could not be defined.

A conclusion could be drawn plotting the influence of additivation on the average values of friction coefficient for all the test (1 hour) and for the last 10 minutes of running (figure 3).

**Figure 3.** Average values of friction coefficient.
Analyzing the friction coefficient for $F = \text{constant}$, one may notice a decrease of its average value for 1 hour, when the sliding speed increases. The tendency is more pronounced for high loads ($F = 200 \text{ N}$ and $F = 300 \text{ N}$) and high sliding speeds ($v = 0.53 \text{ m/s}$ and $v = 0.69 \text{ m/s}$).

For the sliding speeds of 0.53 m/s and 0.69 m/s, all the average values of friction coefficient are under 0.1, meaning a very probable EHL regime, the lubricant film being almost continuous. Analyzing the average values of friction coefficient for the last 10 minutes of a test, time interval considered as suggesting a stable evolution, one may notice that the rapeseed oil gave closer values to that obtained for the entire tests, meaning that the friction coefficient variation is small during all the test period.

For the rapeseed oil additivated with 0.25% TiO$_2$ there is a similarity among the plots of friction coefficient, during all the test time and those obtained for the last 10 minutes of running. Thus, the additivation with this additive helps reducing the running-in period. The recorded values of COF for both tests ($F=100 \text{ N}$, $v=0.38 \text{ m/s}$, $c=0.25\%\text{wt nano additive}$) are unexpectedly higher suggesting a mixt severe regime of lubrication. This could be explained by the local agglomeration of the nano additive and high oscillations of bodies in contact. Even for higher loads ($F = 200 \text{ N}$ and $F = 300 \text{ N}$), COF is above 0.15, meaning that the regime is still mixt. For the other regimes, the values of friction coefficient are maintained under 0.1, without a clear dependence on load.

For the regime with sliding speed of $v = 0.38 \text{ m/s}$, there is a tendency of increasing friction coefficient with the load. At $v = 0.53 \text{ m/s}$, the friction coefficient increases from $F = 100 \text{ N}$ to $F = 200 \text{ N}$, but at $F = 300 \text{ N}$, its value decreases. For $v = 0.69 \text{ m/s}$, friction coefficient is less influenced by the load value, all its values being towards 0.1.

For a concentration of 1%wt TiO$_2$, at the sliding speed of $v = 0.38 \text{ m/s}$, the friction coefficient has the tendency to increase with load, with higher values in the last 10 minutes, supposing that the additive agglomerations become non-uniform in time and on the contact space (figure 4). Figure 4 presents particles of TiO$_2$ on the fixed balls. After being tested, the balls were dried in hot air in order to make the oil film solid (by slow evaporation of volatile components) and to facilitate the SEM imagining.

The simple graphs of the wear scar diameter (WSD) as a function of speed and load could not reflect in a relevant manner the influence of testing regimes. Thus, the authors studied the influence of additive concentration with the help of wear rate of the scar diameter, noted by $w(WSD)$. As each test duration was 1 hour, the sliding distance of the rotating ball on the fixed balls depends on the sliding speed in contact: $L(v = 0.38 \text{ m/s}) = 1378.8 \text{ m}$, $L(v = 0.57 \text{ m/s}) = 1933.2 \text{ m}$ and $L(v = 0.69 \text{ m/s}) = 2487 \text{ m}$. The $w(WSD)$ is calculated with the help of the following relationship:

$$w(WSD) = \frac{WSD}{F \times L} \text{[mm/N·m]}$$  \hspace{1cm} (1)
where WSD is the average value of six measurements of the wear scar diameter, two on each fixed ball (one along the sliding direction and the other perpendicular to it), F is the load applied on the main shaft of the tribotester (carrying the rotating ball) and L is the sliding distance. The product F×L is the mechanical work done by the tribotester. Thus, the wear rate of WSD reflects the dimensional modification of WSD for the unit of mechanical work.

For the most severe regime (v = 0.69 m/s, F = 300 N and F = 200 N), w(WSD) takes values between 1×10⁻⁶ and 1.7×10⁻⁶ mm/N·m (figure 5), meaning that the additivation with TiO₂ makes this parameter lower under higher load. For F= 300 N and v = 0.69 m/s, the influence of additivation is difficult to be noticed.

![Figure 5. Wear rate of the wear scar diameter.](image)

The wear rate of WSD has values in a narrow range, with low values for the highest sliding speed (v = 0.69 m/s), meaning the EHL lubrication is more stable for this speed and also the generation of a continuous film makes the wear to be less affected by the additive concentration. Adding TiO₂, the wear rate of wear scar diameter is slightly increasing, but at v = 0.69 m/s the influence of additivation is not noticed for F = 300 N.

4. Conclusions
At least for the tested ranges of the parameters (v = 0.38...0.69 m/s and F = 100...300 N), the additivation of rapeseed oil with nanoparticles of TiO₂ does not improve the friction coefficient and the wear rate of WSD. The lowest increase of w(WSD) was obtained for F = 300 N and further tests should be done for higher load and speed because in figure 5 there is a tendency of keeping wear rate close to those obtained with the neat vegetal oil.

The additivation of rapeseed oil with TiO₂ is still less efficient for the tested ranges of load and speed, but there is visible that friction coefficient and wear are less influenced by the regime (load and speed) for the concentration of 1% TiO₂ in rapeseed oil. And this aspect could be useful for trybosystems that ask for variations in the regime parameters due to the manufacturing or functioning processes they have to bear.
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