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# Tribological behavior of rapeseed oil additivated with boron nitride

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**Abstract.** This paper presents results of testing the coarse rapeseed oil additivated with 1%wt hexagonal boron nitride (hBN). Tests are done on a four-ball machine from the laboratory LubriTest, at "Dunarea de Jos" University of Galati. Tests were done in mild regime (recommended for applications) and in severe regime. The mild test parameters were: load on the main shaft of the machine (100 N, 200 N and 300 N) and the sliding speed of 0.38 m/s, 0.53 m/s and 0.69 m/s, test duration 1 h. Severe test were run in step of 50 N till 900 N, each test being run for 1 minute at 0.53 m/s. The concentration of 1%wt hBN does not improve the friction coefficient, but it makes it stable for a larger domain of test parameters. The wear rate of wear scar diameter was lower than that obtained with the base oil, especially for high loads. Also, the paper presents the influence of the additive on the temperature of oil bath and the wear load curve of the neat oil and the additivated one. The additivation of rapeseed oil with hNB is still efficient for the tested ranges of load as compared to the rapeseed oil. The load-wear curve for the severe regime points out a sudden increase of wear scar diameter (WSD) for the rapeseed oil +1% hNB at 700 N, but the neat vegetal oil starts the increase of WSD at 550 N, followed by a greater slope, meaning the additive protect the rubbing surfaces under these high loads.

## 1. Introduction

Vegetal oils consist of triglycerides that influence their performance limits, as poor thermal, hydrolytic and oxidation stability, but also low viscosity. Most natural vegetal oils cannot withstand reservoir temperatures greater than 80ºC [1].

Boron nitride is a compound with heat and chemical resistance, good thermal conductivity, making it an excellent choice for lubricant applications that require rapid heat evacuation and it exists in several crystalline structures. The hexagonal structure of this boron nitride (hBN) similar to graphite is the most stable and soft and is recommended as solid lubricant or as additive in liquid lubricants [2].

Bondarev et al. [3] utilized hBN nanoparticles (NPs) with different morphologies (hollow NPs with smooth surface (H-BNNPs), solid NPs with "pompon"-like or petalled structure (P-BNNPs), and globular NPs formed by numerous thin hBN nanosheets (N-BNNPs)) as additives to PAO6 oil. Triboelements were made of steel 100Cr6, the same steel grade as in this study, were tested in lubricants with PAO6 + BNNP, with a concentration 0.1% and 0.01% of BNNPs, respectively. The positive effect of BNNP additives increased along the row P-BNNPs → H-BNNPs → N-BNNPs. Utilization of N-BNNPs allowed for decreasing the friction coefficient from 0.1 to 0.06 and for reducing significantly the wear rate.

Mariano [4] considered it an additive for niche applications when design requirements make graphite or molybdenum disulphide unacceptable. Only the hexagonal structure has lubricating ability.

Cubic boron nitride is a very hard substance used as an abrasive and cutting tool component and has no lubrication value. The bond with high strength between boron and nitrogen within hexagonal rings supplies a good load-carrying capability that is necessary to maintain the separation of rubbing surfaces. Particle size influences the adhesion to substrate and particle orientation within an already formed tribolayer. Impurities, such as boric oxide, will influence the ability of the powder to reduce the coefficient of friction.

Boron nitride was added in liquids with low viscosity for improving wear resistance of bodies in contact as full film generation to separate them is difficult to maintain in actual regimes. Cho et al. [5] added hexagonal boron nitride (h-BN, 300 nm wide and >30nm thick flakes) nano-sheets in water, in concentrations of 1%, 0.05% or 0.01wt%, without any surfactant or organic functionalization, using sonication for a good dispersion. The friction and wear were evaluated using a SiC ball sliding on a disk arrangement. Even small amounts of hBN nano-sheets improve wear resistance and reduce friction coefficient. Tribofilms (but not continuous) were observed to have formed on worn surfaces due to repeated exfoliation and deposition of hBN nano-sheets during sliding. This process is responsible for tribological improvements. hBN could be a promising "green" additive for water.

This study aims to emphasis the influence of 1% BN in rapeseed oil, both in typical regimes and severe ones, using a four-ball tester

## 2. Lubricant formulation and test method

The laboratory methodology of obtaining the lubricant with 1% BN is given in detail in Cristea [6] and the authors used the same regime of sonication and cooling and also the same dispersant, guaiacol, supplied by Fluka Chemica, with the chemical formula $C_6H_4(OH)OCH_3$ (2-methoxyphenol), in the ratio 1:1 to the additive.

The additive nano particles (figure 1), supplied by PlasmaChem [7], have the following characteristics: size full range 100-1000 nm, average particle size 500 ± 100 nm, specific surface 23 ± 3 $m^2/g$, purity > 98.5%, Nitrogen content > 55%.

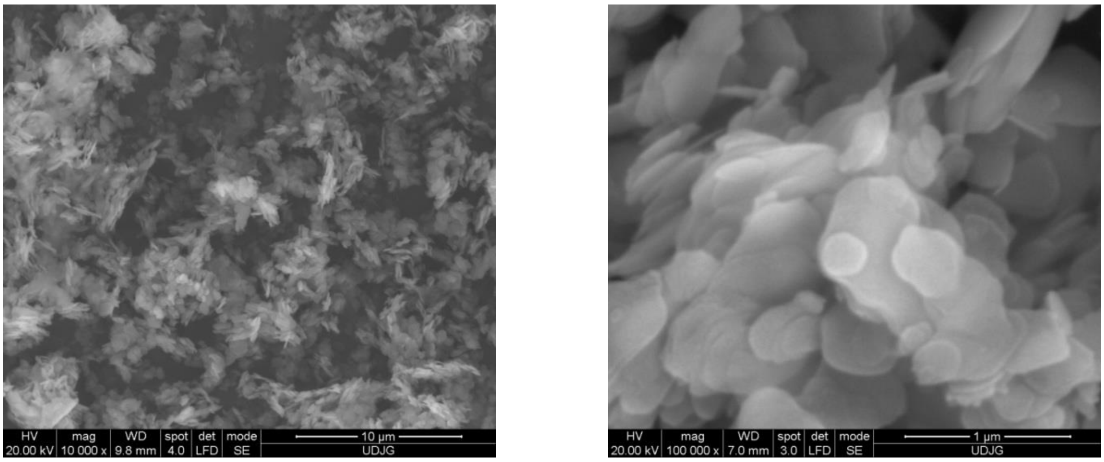


**Figure 1.** Boron nitride, before being added in rapeseed oil.

Bondarev et al. [3] also prepared lubricating suspensions, each type of BNNPs in the amount of 0.01% and 0.1% was added into 30 ml of PAO6 oil (Neste) and then twice sonicated for 10 min with an interval of 5 min, but it is difficult to compare those tests in reciprocating mode using a 3 mm-sized 100Cr6 ball on plate with the results of these tests. The normal load and sliding speed were 1 N and 0.05 m/s. Under these conditions each sample passed 10,000 cycles.

Table 1 presents the composition in fatty acids of the rapeseed oil used in this research study.

The parameters for mild regime 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 rotational speeds of the four-ball machine of 1000 rpm, 1400 rpm and 1800 rpm (± 6 rpm), respectively, test time - 60 minutes (± 1%).

For the severe regime, tests were done in step of 50 N, from 500 N till 900 N, for 1 minute, at 0.53 m/s and there were measured the wear scar diameter (WSD) and the final temperature in the bath oil.

The test balls are lime polished, made of chrome alloyed steel, with 12.7±0.0005 mm in diameter, with 64-66 HRC hardness, as supplied by SKF. The oil volume required for each test was 8 ml ±1 ml.

The testing method for investigating tribological characteristics is following the recommendations from SR EN ISO 20623:2018 [8].

**Table 1.** Typical composition in fatty acids of the rapeseed oil (from Expur Bucharest).

| Fat acid | Symbol | Composition (%wt) |
|---|---|---|
| Myristic acid | C14:0 | 0.06 |
| Palmitic acid | C16:0 | 4.60 |
| Palmitoleic acid | C16:1 | 0.21 |
| Heptadecanoic acid | C17:0 | 0.07 |
| Heptadecenoic acid | C17:1 | 0.18 |
| Stearic acid | C18:0 | 1.49 |
| Oleic acid | C18:1 | 60.85 |
| Linoleic acid | C18:2 | 19.90 |
| Linolenic acid | C18:3 | 7.64 |
| Arachidic acid | C20:0 | 0.49 |
| Eicosenoic acid | C20:1 | 1.14 |
| others | | 3.37 |

## 3. Results

### *3.1. Mild test regime*

Figure 2 presents the average value of friction coefficient (COF), for both tested lubricants. It is obvious that the neat oil has, generally, lower values, especially for low regimes, but the additivated oil has this parameter less sensitive to sliding speed for all loads. This is recommended for machines that frequently change their working regime.

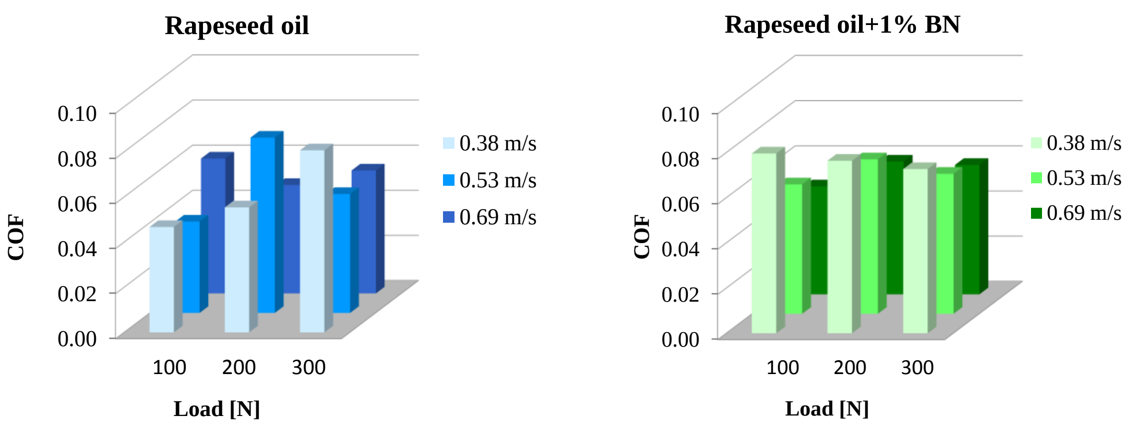


**Figure 2.** The friction coefficient (average value for each test of 1 h).

Diameters of wear scars were measured with an optical microscope, in accordance with the procedure given in SR EN ISO 20623:2018 [8] (for each scar, a diameter along the sliding direction and the other perpendicular to it). Each test supplies three wear scars, these being located on the three fixed balls. Wear scar diameter (WSD) is the average of the six diameter measurements and this value is given in graphs in figure 3. This value represents the diameter of the wear scar, reported for each of the tests performed.

Comparing values of WSD for the same sliding speed, for v = 0.38 m/s, WSD is almost twice lower for the additivated lubricant, but for higher loads and speed, the influence of additive is low.

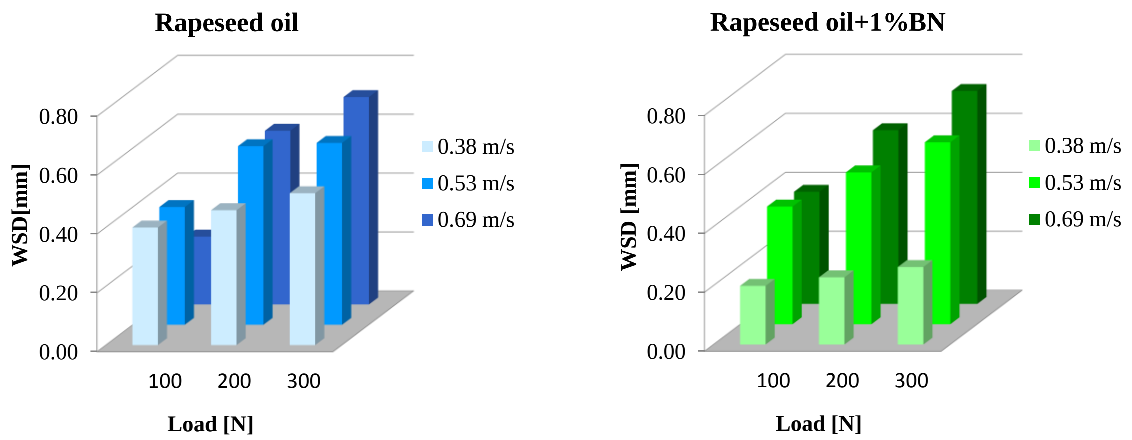


**Figure 3.** WSD for the rapeseed oil (left) and the rapeseed oil + 1% hBN (right).

The graphs of the wear scar diameters (WSD), as a function of speed, are difficult to be compared as they were done for all tests during 1h, meaning different sliding distances for each speed. The authors studied the influence of additive, using a tribological parameter that takes into account the sliding distance, a parameter also recommended by Holmberg [9], the wear rate of the wear scar diameter, noted by w(WSD) and calculated with the help of the following relationship:

$$w(WSD) = \frac{WSD}{F \cdot L}\left[mm/(N \cdot mm)\right] \tag{1}$$

where WSD is the average value of six measurements of the wear scar diameter, two on each fixed ball, F is the load applied on the main shaft of the tribotester and L is the sliding distance. The product F×L is the mechanical work done by the system. Thus w(WSD) is the modification of WSD for the unit of mechanical work.

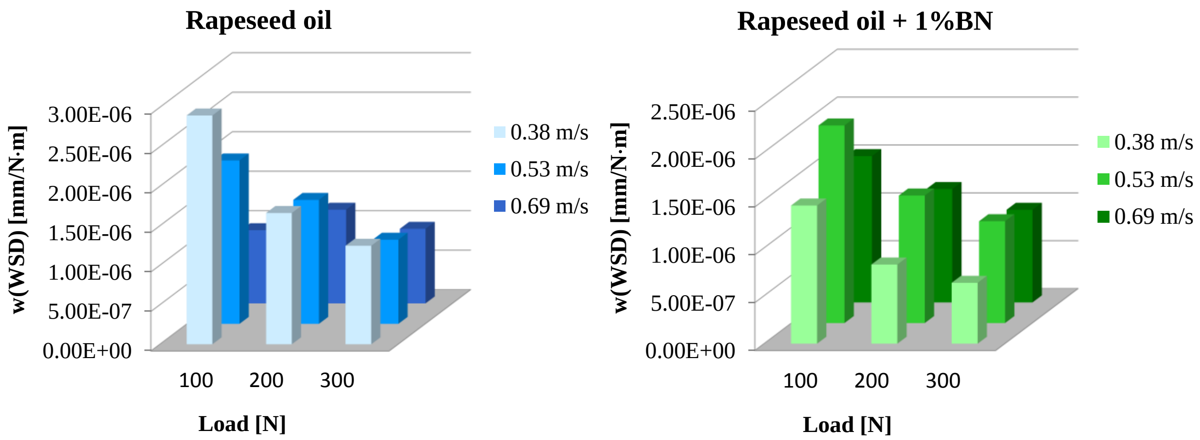


**Figure 4.** The wear rate of WSD for the rapeseed oil (left) and the rapeseed oil +1% hBN (right).

When calculating this parameter for these tests (figure 4), the additivated lubricant produces lower values for v = 0.38 m/s, meaning that surfaces of solid bodies are protected by hBN powder, reducing their wear by particular mechanisms of nano-rolling, smoothing/levelingor mending process by filling the valleys of the profiles, coating the higher asperities with nano sheets that reduce friction and local load, with a minor component of smoothing/leveling by abrasion. This comment is based on discussions done by Wu et al. [10], Chinas-Castillo and Spikes [11], Liu et al. [12]. The leveling by abrasion is supposed to increased under higher loads, as both graphs of WSD increase with load (figure 3), but photos in figure 8 show, for F = 500 N, qualitatively, less abrasion, for the additivated lubricant.

Figure 5 presents the evolution of temperature in the lubricant bath. At the same speed, the temperature lines are ordered from low to higher load. This similarity in load and speed dependence points out that the lubricating regime is not changing (very probably a EHL regime, with locally temporary contact among rare high asperities

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or due to additive agglomerations dragged through contact. It is worthy to mention that the temperature for the additivated oil is only few dregrees higher for the combinations (low load - low speed) but for (high speed - high load), this difference diminishes, probably due to the influence of additive in evacuating the heat generated by friction.

When plotting a graph with the final measured temperature in the lubricant bath (figure 6), the differences are small, several degrees Celsius higher for the additivated lubricant. For the additivated lubricant, this could be explained by two balacing processes: the friction increased by the movement of the nano sheets or their agglomerations through contact, that will increase the temperature and the other process of heat evacuation due to the good thermal properties of the additive.

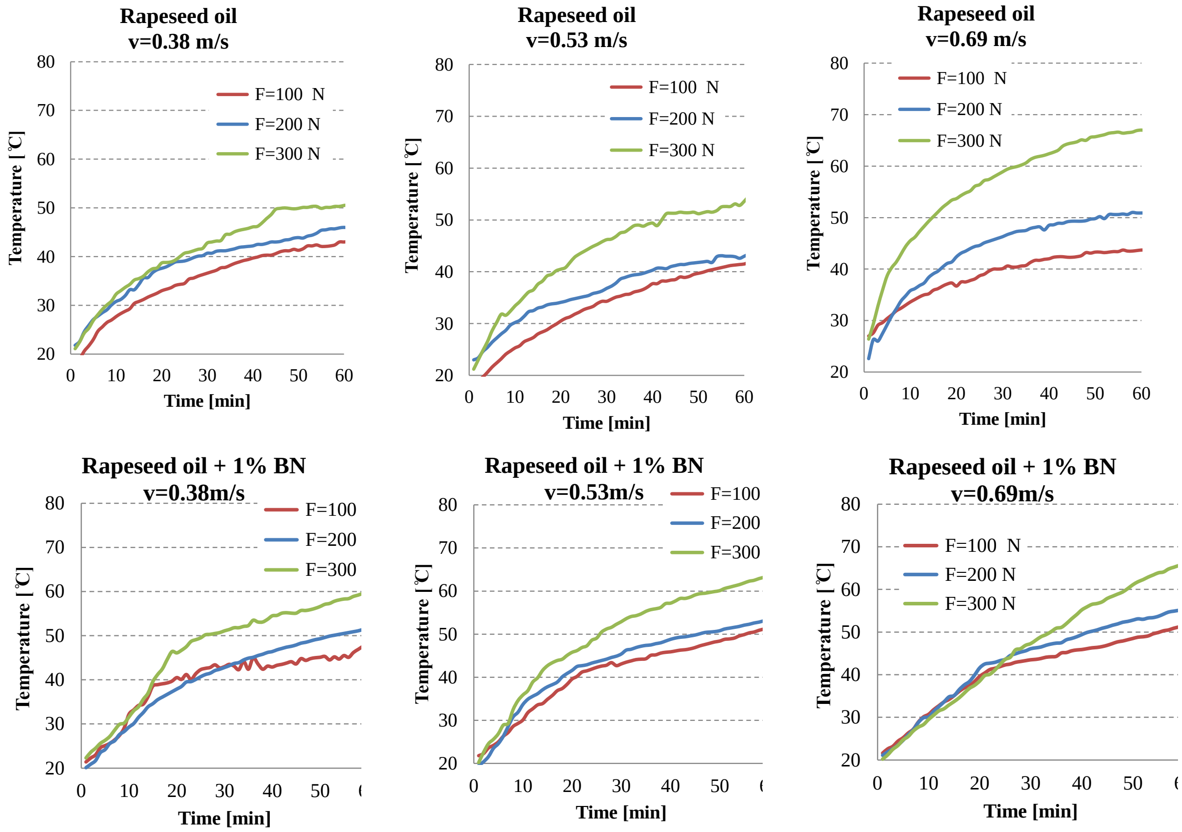



**Figure 5.** Temperature evolution for 1 h test (sampling at 1 minute).

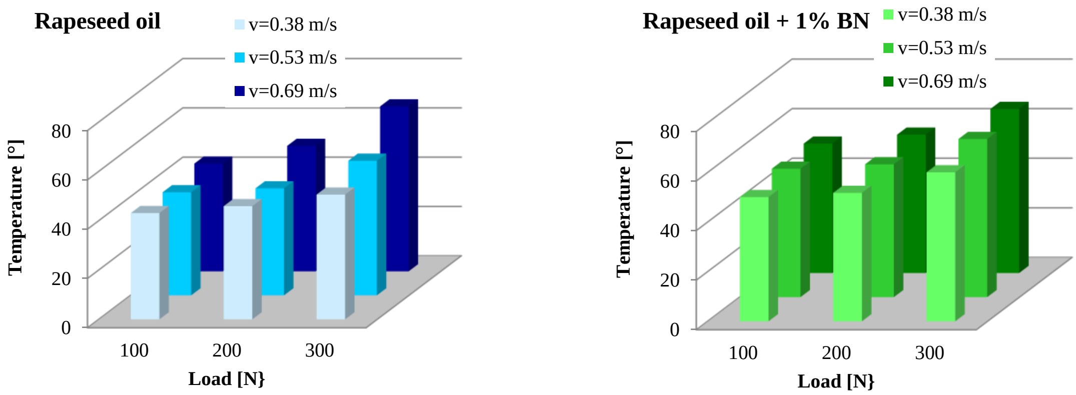



**Figure 6.** Temperature at the end of a test of 1 h.

### 3.2. Severe regime (seizure)

Bondarev et al. [3] studied the structure of wear debris and the worn surfaces of triboelements and concluded that the N-BNNPs split into thinner nanosheets due to weak Van der Waals forces, which, under applied load, could easily be reoriented parallel to the friction direction, thus minimizing the resistance to shear. BN nanosheets formed aggregates (typically 200–800 nm in size, also retaining oil), uniformly distributed over the area of tribological contact, contributing to separate the surfaces in contact (even partially).

In 2014, Abdullah et al. [13] obtained results in the favor of adding hBN in engine oil (SAE 15W-40) The trend of the obtained curves underlined that diesel engine oil started the incipient seizure on contact surfaces at 618 N, but the nano-lubricant (0.5% vol. of 70 nm hBN in oil) had this point at 785 N, indicating that with this additive, the lubricant sustain a higher load before seizure takes place.

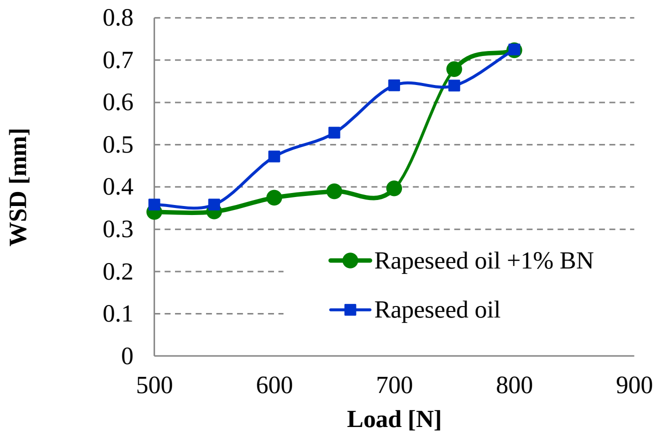



**Figure 7.** Wear load curve for the tested lubricants.

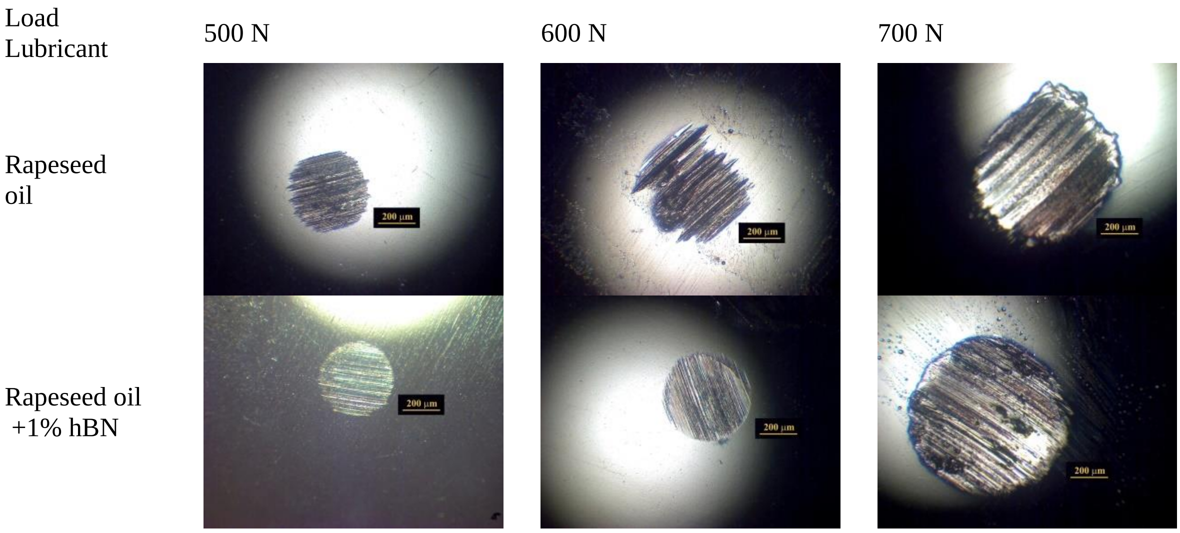



**Figure 8.** Images of wear scar in the severe regime.

Analysing the wear load curve in figure 7, the additivated lubricant keeps WSD stil lower at 550 N. This is a strong point in a SWOT analysis for selecting a lubricant, especially when the designer is aware of the exploitation regime. For instance, when this regime could have load fluctuations and even small shocks (from actual reasons as applied technology), this lubricant behaves better than the oil without additive. This is obvious from images of the wear scars, as presented in figure 8. One may notice that at 500 N the abrasive tracks on the wear scar resulted after testing the rapeseed oil seems rougher and the wear scar has bigger area as compared to that obtained with rapeseed oil + 1% hBN.

As compared to results in Abdullah et al. [13], the additivated rapeseed oil start seizure after 700 N, this being remarcable in comparison to the mineral oil tested by Abdullah et al.

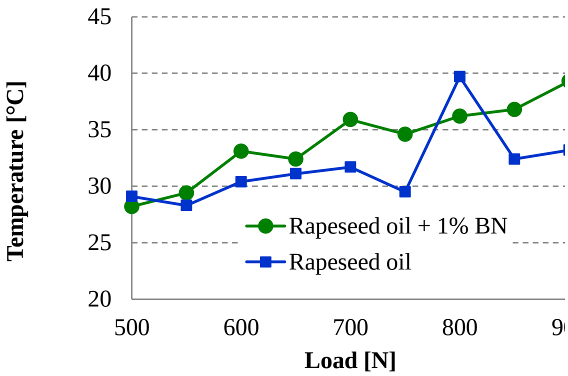



**Figure 9.** Bath oil temperature at the end of the test.

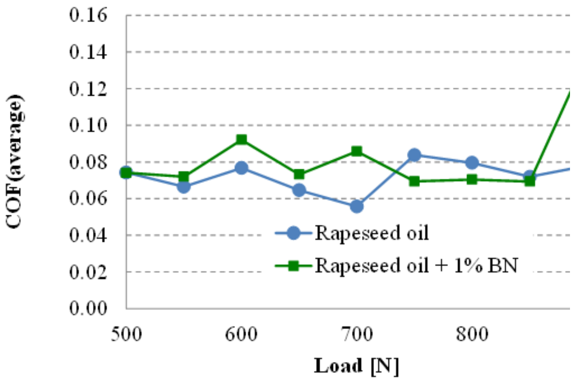
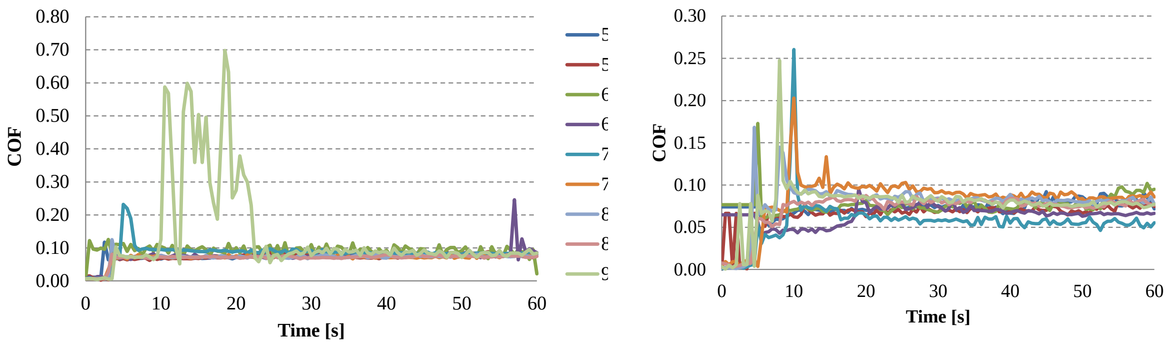



**Figure 10.** The average value of COF for 1 minute of severe test

Because of the short test time, the temperature in the bath oil is less important when evaluating the lubricating capability of a lubricant, figure 9 presents the evolution of the recorded temperature just at the end of a test. The additivated oil has higher values but in a trend with smaller slope. The rapeseed oil has values that evoluate in a larger band, due to a more aggressive abrasive wear, caused by the direct contact of the steel balls. The nano hBN protected the surfaces in contact and the image for F = 700 N has a different aspect as compared to the that obtained with neat oil, meaning the aditive could remain on the rubbing surfaces (see figure 8). Further studies on SEM and with EDX are necessary for proving that.




a) rapeseed oil

b) rapeseed oil + 1% BN

**Figure 11.** Friction coefficient.

Figure 11 presents the evolution in time of friction coeffficient (COF) for loads greater than 500 N (1 minute test). High oscillating values were recorded in the first 20 s, meaning that aggressive wear could be generated at test start. The average value of COF (figure 10) is similar for both lubricants (additivated and not additivated) only under load lower than 850 N. Further, at F = 900 N, this value has a sharp increase for the neat vegetal oil.

## 4. Conclusions

This research presented the tribological behavior of rapeseed oil additivated with 1% hBN in comparison to the neat vegetal oil. Tested were done for normal (useful) regimes (F = 100...300 N and v = 0.38...0.69 m/s), but also for severe regime in order to determine the influence of additivation on these regimes.

For normal regimes, the value of 1% wt does not improve the friction coefficient, but it makes it stable for a larger range of test parameters. The wear rate of WSD was lower than that obtained with the base oil.

This study presents the seizure curve of the neat oil and the additivated one. The additivation of rapeseed oil with hNB is still efficient for the tested ranges of load as compared to the rapeseed oil as WSD start seizure at higher load and with a lower slope.

For severe regimes, it was obvious that the lower load wear curve recommends the additivated lubricants in systems with possible higher loads around the nominal ones as triboelements are the surfaces protected by additive deposition in the surface textures.

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