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BORON NITRIDE AS ADDITIVE IN RAPESEED OIL, TESTED ON FOUR BALL TESTER

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Abstract: This paper presents the influence of BN as additive in refined rapeseed oil in a mass concentration of 1%wt on the tribological parameters. Tests are done on a four-ball machine. The test parameters were load: 100 N...300 N and the the sliding speeds of 0.38 m/s, 0.53 m/s and 0.69 m/s, respectively. Particles of hexagonal BN have 500 ± 100 nm. The rapeseed oil was supplied by Expur SA Bucharest. For the tested ranges of the parameters, the additivation of rapeseed oil with BN does not improve the friction coefficient, but the wear rate of WSD seems to be less sensitive for the more severe regimes when the vegetal oil is additivated. The additivation of rapeseed oil with BN is still 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% BN in rapeseed oil.

Keywords: rapeseed oil, additive, BN, four ball test, friction coefficient, wear rate

1. INTRODUCTION

Rapeseed oil has a composition in fat acids that recommends it for lubricating systems that have to comply with more severe regulation concerning the environment protection, but designers have to make a compromise as its viscosity, life and acceptable regimes are lower than classical lubricants.

Anorganic additives are added in lubricants for improving their tribological parameters, for protecting initial texture of the bodies in contact. Most of them have lamellar or plaquette shapes and promote a fird-body friction instead on a direct contact between the triboelements.

In a recent review, Shahnazar et al. [1] dedicated a chapter for boron-based

nanoparticles that could act like friction modifier (cerium borate, boric acid, hexagonal boron nitride), anti-wear additive (hexagonal boron nitride, titanium borate, ferrous borate, magnesium borate), extreme pressure additive (potasium borate). One may notice that hexagonal boron nitride may reduce both friction and wear.

Wan et al. [2] found a an optimal BN nanoparticle concentration of 0.1 wt.% when comparing friction coefficient and aspect of wear surfaces of a commercial lubricating oil (SAE 15W-40, Sinopec Lubricants) and a new formulated lubricant based on this oil and hexagonal boron nitride nanoparticles with disk shape and an average diameter of ~120 nm and a single layer thickness of ~30 nm. Oleic acid was used as dispersant (25wt.% of

BN nanoparticle) for improving the stability of the suspension. Nano-BN oils containing 0.1wt.%, 0.5wt.% and 1.0wt.%, disk-on-disk tribo-tester, 500 N and The test time of 3 minutes is obviously too short to make the functioning stable or to compare to actual applications. The viscosities of all oils with/without BN nanoparticle additives decrease rapidly with the temperature increasing. Due to the polishing effect of the lubricating oil, all the worn surfaces become smooth after the friction test.

Hexagonal boron nitride (hBN) is attractive for replacing inorganic solid lubricants, such as graphite and molybdenum disulfide. Its lubricating performance is based on the easy shearing along the basal plane of its crystalline structure. Celik et al. [3] synthesized nano hexagonal boron nitride particles by reacting boron oxide with ammonia. Different amounts of nano hBN particles were added to an engine oil. The tribological properties of were investigated using a ball-on-disc tribometer. The addition of hBN particles did not change the viscosity of the lubricants, but changed the coefficient of friction. The presence of sufficient nano hBN additives in oil prevents direct contact and results in decreased friction and wear.

In a very recent review, Uflyand [4] mentioned the hexagonal boron nitride as additive in oils. Their mechanisms during lubrication are similar to those of metal and metal oxide nanoparticles.

The concentration of hBN in oil differs very much, also the basic oil could be mineral, synthetic and vegetal, the fast being in the research focus for formulating eco-friendly lubricants (Table 1).

Abdullah [5] reported results for seizure tests on four ball tribotester with ten increments of loading, from 196 N to 1,570 N, with 10 seconds for every test (at 1,760 rpm, 10 sec and initially 27°C). The test was repeated three times for each sample to ensure more precise and reliable results. The wear scar diameters lubricated with nano-

additivated oil were smaller than those lubricated with SAE 15W-40 engine oil only. Severe adhesive wear was observed on the worn surface of a ball bearing lubricated with SAE 15W-40 diesel engine oil.

Table 1. Examples of lubricants with hBN as additive

Base oil	BN / size / concentration	Reference
SAE 15W-40 diesel engine oil	hBN / 70 nm / 0.5 vol%	[5]
castor oil	1, 2, 5 and 8 wt% hBN, silane coupling agent A-151 (1:20)	[6]
jatropha oils	hBN, ranging between 0.05 and 0.5 wt%	[7]
water	1%, 0.05%, 0.01wt% with and without organic functionalization, 200 nm flakes	[8]

Wang et al. [6] tested two regimes on ball-on-disk: high speed-low load (0.52 m/s, 9.8 N, 10 min) and low speed-high load (0.13 m/s, 120 N, 30 min), the sliding distance being 313,8 m and 235 m, respectively. Thus, a direct comparison of wear reducing capacity of the lubricants by the help of the wear scar diameters for the two regimes is not proper. For low load-high speed that the COF of pure castor oil was the lowest as compared to the same oil, additivated with hBN, this parameter increasing with additive concentration, but the COF of the 2 wt% nanofluid is almost the same as that of pure castor oil. At higher concentration (5 and 8%), COF is only 20...25% greater. Under high load and low speed, COF of neat oil is the highest, but all values still presume a full film lubrication. The depth of the wear track is smaller for the additivated oils.

Cho [8] concluded that the repeated exfoliation and deposit of h-BN occurred on the sliding surfaces, forming tribo- films which can reduce friction and wear. The h-BN nano-sheets, inexpensively dispersed in water, may be a promising "green" lubricant.

Talib [7] investigated the turning performances of modified jatropha oils, with and without hBN particles, were investigated in comparison to a synthetic ester. 0.05 wt% of hBN particles in jatropha oil reduced the cutting force (by 9%), cutting temperature and surface roughness (by 8%) and extended the tool life, in terms of cutting length, by 78%. However, the excessive amount of hBN particles (>0.05 wt%) caused particle agglomeration, leading to poor machining performances, in terms of cutting force, cutting temperature and surface roughness.

The aim of this study is to assess the influence of BN in coarse rapeseed oil on the tribological characteristics. The authors analyzed the friction coefficient and the wear rate of wear scar diameter, but also recorded the temperature in the oil cup, during the tests.

2. THE LUBRICANT AND THE TESTING METHODOLOGY

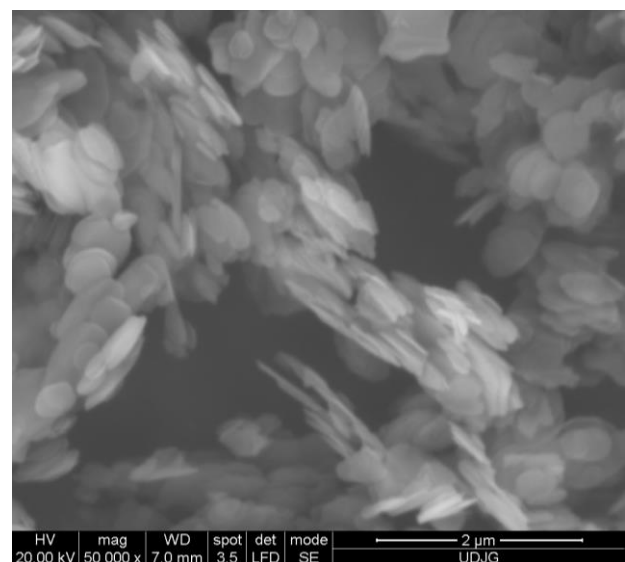
The hexagonal boron nitride was supplied by PlasmaChem [9] and has the following characteristics (Fig. 1): particle size full range: 100-1000 nm, Average particle size: 500 ± 100 nm, Specific surface: 23 ± 3 m²/g, purity: >98,5%; nitrogen content >55%, controlled admixtures, %: O<1; C<0,1; B₂O₃ < 0,1. Boron nitride withstands high temperatures and high loads, it is also non-reactive, thermally conductive, electrically insulating [10], [11].

The formulated lubricant was obtained in small amounts of 200 g, each. The steps followed in this laboratory technology were similar to those presented by Cristea [12]:

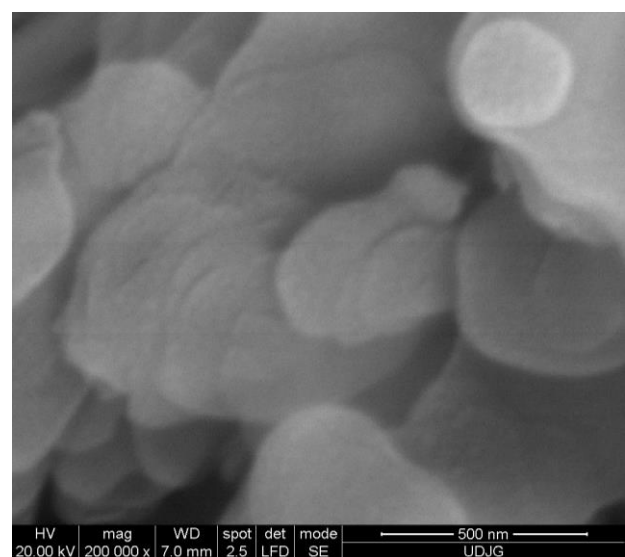
- mechanical mixing of additive and an equal mass of dispersing agent (guaiacol, supplied by Fluka Chemica, with the chemical formula C₆H₄ (OH) OCH₃, for 20 minutes;
- adding the rapeseed oil, mixing for 1 hour;
- ultrasonication + cooling of formulated lubricant in step of 10 minutes, for 6 times; The parameters of ultrasonic regime are power 100 W, frequency 20 kHz \pm 500 Hz, continuous mode.

Table 2. Composition in fatty acids of the tested 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



a)



b)

Figure 1. SEM images of the nanoparticles of BN

The 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 $8 \text{ ml} \pm 1 \text{ ml}$. The test method for investigating the lubricating capacity was that from SR EN ISO 20623:2018 [13].

The test parameters for each test were:

- loading force on the machine spindle - 100 N, 200 N and 300 N ($\pm 5\%$);
- 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.

3. RESULTS

3.1. Friction coefficient

Figure 2 presents the evolution in time of the friction coefficient (COF) and one may notice the differences of the lines. Even if the addition of nano hBN particles does not reduce COF, the evolution in time of this

tribological parameter is done in a narrow range and it seems to be less sensitive to load as compared to tests done with the same sliding speed, but with the neat vegetal oil as lubricant.

The more evident variation of COF was obtained for the tests done at $v=0.38$ m/s. Having as reference the average value of COF during 1h test, for $F=100$ N, for the rapeseed oil, COF increases with 88%. But for the additivated lubricant, there was a small reduction for COF, meaning 9%, when the load increased from 100 N to 300 N.

For the rapeseed oil, tested at $F=300$ N, COF decreases with the increase in sliding speed, meaning that a higher speed is favorable to generate a full fluid film. But for the additivated rapeseed oil, even if the average of COF for $F=300$ N and $v=0.69$ m/s (the most severe test) is lower as compared to that of the neat oil, there are oscillations produced by the behavior of nanoparticles, maybe agglomerated, in contact.

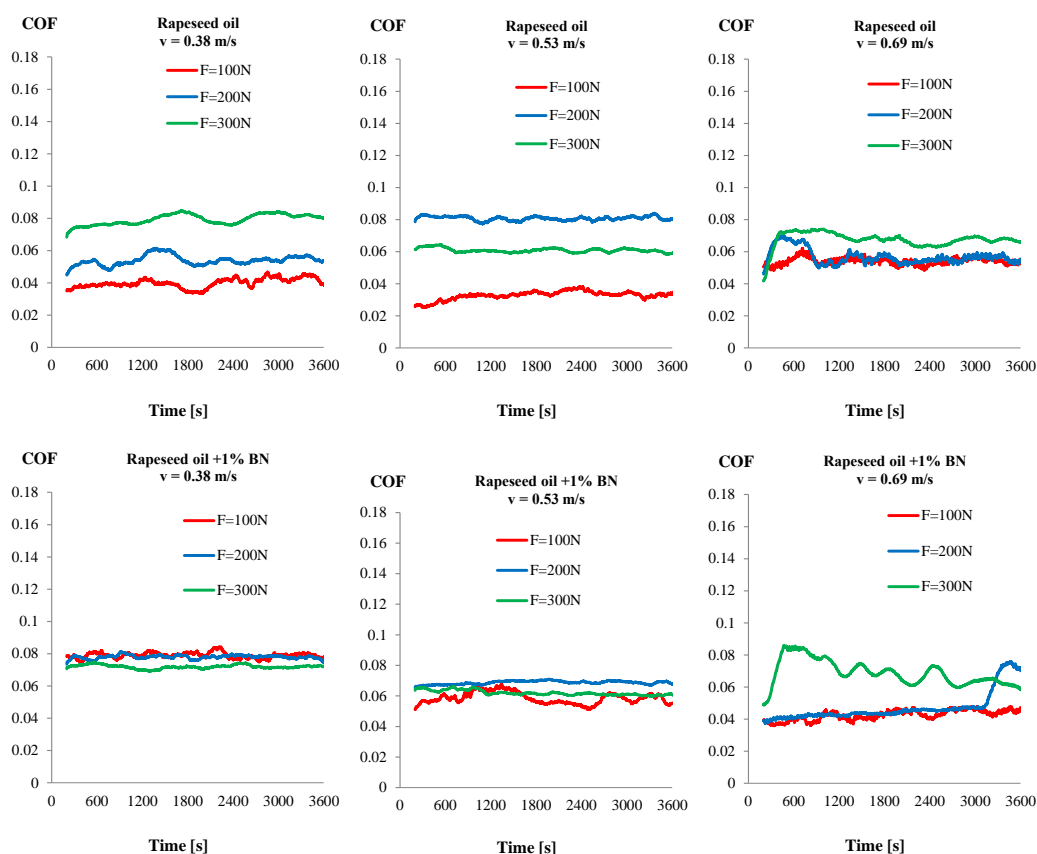


Figure 2. COF evolution in time

(2 sample per second and a moving average on 200 consecutive values)

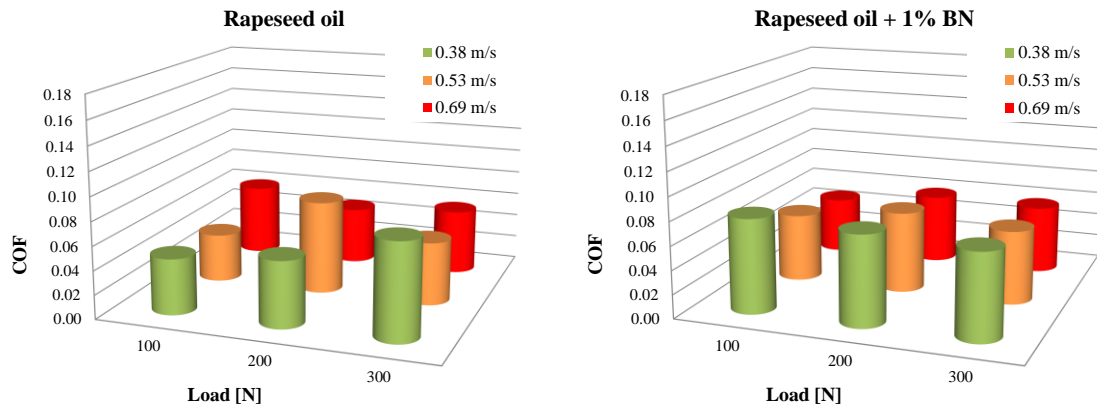


Figure 3. Average of COF for two values (two tests done under the same parameters)

Figure 3 presents the average value of COF as obtained from two tests, for both tested lubricants. It is obvious that the neat oil has lower values, especially for heavy regimes, but the additivated oil has this parameter less sensitive to sliding speed for $F=300$ N. This is recommended for machines that frequently change their working regime.

Lubrication may be theoretically done in three different regimes: boundary lubrication, mixed lubrication, and elastohydrodynamic lubrication. But the lines separating these regimes are very difficult to be drawn. Adding nanoparticles, generally increases the friction coefficient as average, but its evolution may have high or small oscillations.

3.2. Wear rate of the wear scar diameter

Measurement of wear trace diameters was performed with the optical microscope, in accordance with the procedure given in SR EN ISO 20623:2018 [13]. 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 performed tests.

The lubricants with nano-BN are beneficial for tribosystem due to mending mechanism and the higher high thermal conductivity of the formulated fluid.

The graphs of the wear scar diameters (WSD) as a function of speed could not reflect in a relevant way the influence of testing regimes, because all tests has 1 h (with different sliding distances for each speed), and, thus, the authors studied the influence of additive concentration with the help of wear rate of the scar diameter, noted by $w(\text{WSD})$. The $w(\text{WSD})$ is calculated with the help of the following relationship:

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

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 and L is the sliding distance. The product $F \times L$ is the mechanical work done by the tribotester. Thus, the wear rate of WSD reflects the modification of WSD for the unit of mechanical work.

Figure 4 shows images of the wear scars as obtained with the help of an optical microscope. One may notice that the contact surfaces as resulted after testing with the additivated oil is less damaged, this conclusion being more highlighted by comparing images for severe regime ($v=0.69$ m/s and $F=300$ N).

Figure 5 presents the wear rate of WSD, $w(\text{WSD})$. The values are lower for heavy regimes ($F=200 \dots 300$ N) for all sliding speeds, meaning the lubricant response is suitable for protecting the surfaces in contact. The additivated rapeseed oil have even lower values for the lower sliding speed ($v=0.38$ m/s).

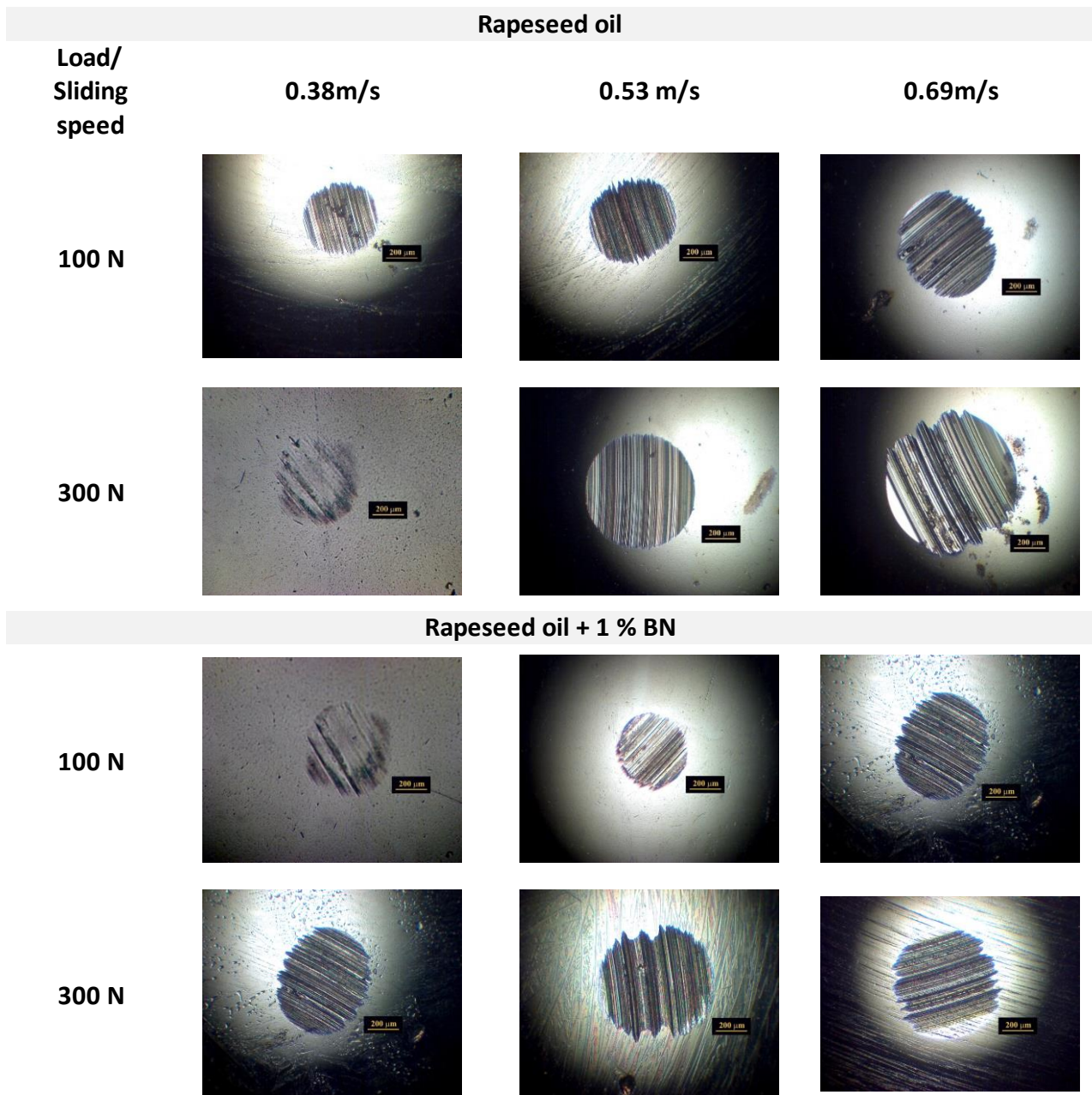


Figure 4. Typical wear scars for different regimes

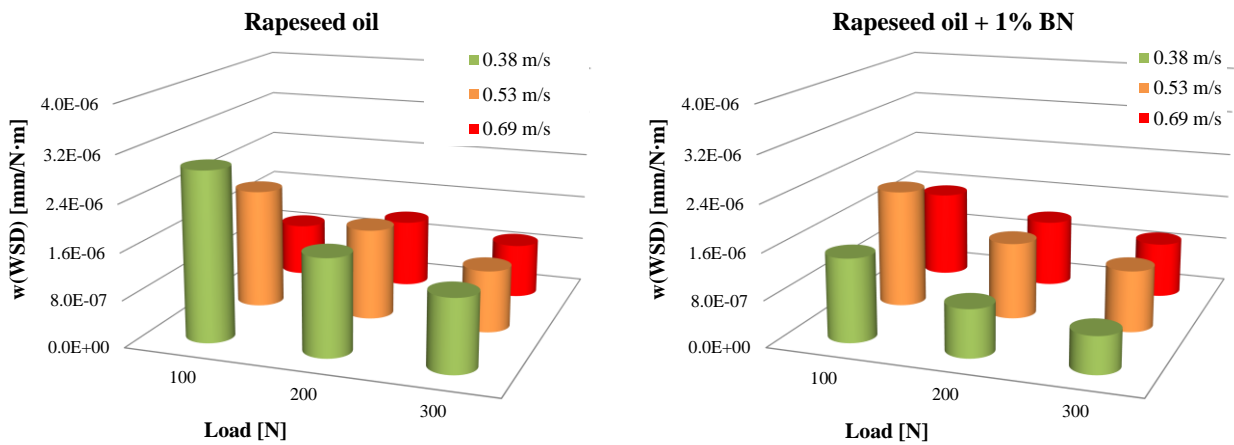


Figure 5. The wear rate of WSD for the base oil (rapeseed oil) and the new formulated lubricant with 1% BN in rapeseed oil

The reason of this better tribological behavior is that the nanoparticles act like rolling spacers between the solid macro bodies and prevent the wearing of them, even partially.

Table 3 presents the variation of $w(WSD)$, in percentage, relative to the lowest load (100 N), for each sliding speed. Analysing the values in this table, one may notice that the new formulated lubricant has lower wear rate of WSD when the load increases, for each tested sliding speed. For the highest speed, the rapeseed oil has this wear parameter greater than that for mild regime ($F=100$ N).

Table 3. The variation of $w(WSD)$, in %, relative to the lowest load (100 N)

Sliding speed	Variation of $w(WSD)$, %wt			
	Rapeseed oil		rapeseed oil + 1% BN	
	200 N	300 N	200	300
0.38 m/s	-42%	-56%	-43%	-56%
0.53 m/s	-24%	-48%	-35%	-48%
0.69 m/s	28%	2%	-22%	-36%

3.3. Temperature in the oil bath

The evolution of oil bath temperature during a test of 1 h is given in Figure 6. The difference among final registration of temperature (at the end of the test) is small for low regimes ($v=0.38...0.53$ m/s) and its value is kept in the range 43...55°C, but for the highest speed ($v=0.69$ m/s), the temperature values are spread on a larger interval. For the most severe regime, the final recorded temperature for the rapeseed oil is about 70°C. The rapeseed oil additivated with BN has these temperatures a little bit higher, in the range of 50...60°C for $v=0.38...0.53$ m/s and for the highest speed the interval is larger (60...77 °C). The supplementary heat generation BN could be explained by the friction of intermediate particles of NB, rolling or being dragged in contact. But there is no significant modification in the temperature range when comparing the temperature evolution for both tested lubricant.

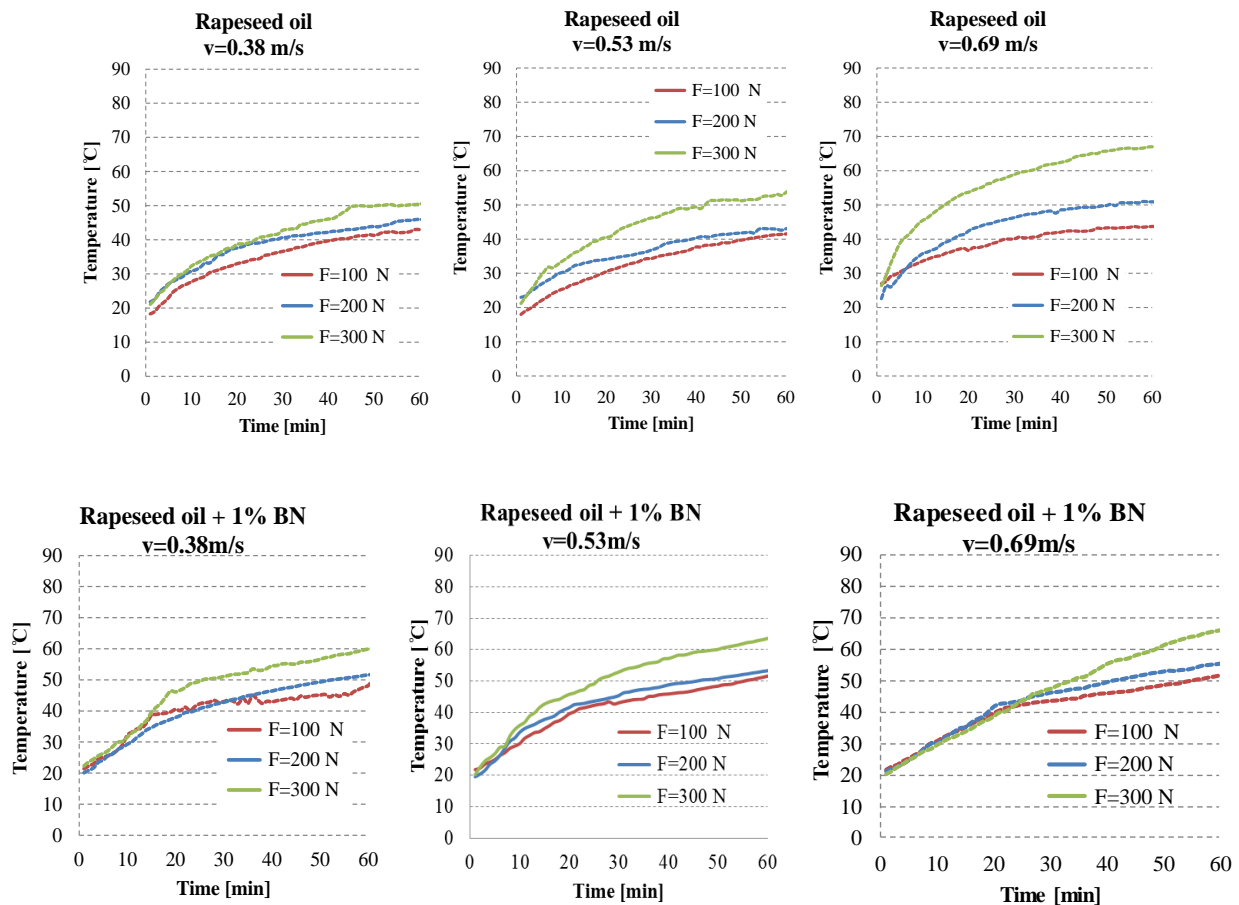


Figure 6. Temperature evolution in the oil bath

4. CONCLUSIONS

At least for the tested ranges of the parameters ($v=0.38\text{...}0.69$ m/s and $F=100\text{...}300$ N), the additivation of rapeseed oil with nanoparticles of BN improves the friction coefficient. But this additive was efficient for wear reduction, the authors pointed this out by comparing the values of the wear rate of wear scar diameter.

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