U.P.B. Sci. Bull., Series B, Vol. 83, Iss. 4, 2021 ISSN 1454-2331

WEAR-LOAD CURVES IN SEVERE REGIME FOR RAPESEED OIL ADDITIVATED WITH ZnO

Traian-Florian IONESCU[1], George-Cătălin CRISTEA[2], Dionis GUGLEA[3], Dumitru DIMA[4], Constantin GEORGESCU[5], Lorena DELEANU[6]

This paper presents characteristics of severe regime, tested on four ball machines for rapeseed oil and new formulated lubricant based on rapeseed oil and additivated with nano ZnO (average particle size 14 nm), in different concentrations (0.25% wt, 0.50 %wt and 1.0 %wt, respectively). Tests were done taking into account the procedure in SR EN ISO 20623:2018 Petroleum and related products — Determination of the extreme-pressure and anti-wear properties of lubricants — Four-ball method (European conditions): starting from 500 N and increasing load in step of 50 N, at 1400 rpm, for 1 minute. There were recorded the wear scar diameter (WSD), the friction coefficient and the temperature of the oil bath, at the end of each test. Except for the concentration of 0.25% nano additive, the other two additivated lubricants have the wear-load curve lower meaning that, under higher loads, the nano additive prevents the severe wear of the ball surface.

Keywords: rapeseed oil, nano additive concentration, ZnO, wear scar diameter, 3D texture parameters

1. Introduction

Renewable resources are welcome in the industrial and transport domains as they could replace fossil resources, more pollutant and endangered to be exhausted. Rapeseed oil has been introduced as lubricant especially in Europe. Rapeseed oil is of interest for researchers because it is obtained from an available crop, especially in economically advanced countries and various types have been

[1] PhD Student, eng., Department of Mechanical Engineering, "Dunărea de Jos" University of Galati, Romania, e-mail: traian.ionescu@ugal.ro
[2] PhD eng., Structures and Materials Department, "National Institute of Aerospace Research "Elie Carafoli" (INCAS), Bucharest, Romania, e-mail: cristea.george@incas.ro
[3] PhD student, eng., Department of Mechanical Engineering, "Dunărea de Jos" University of Galați, Romania, e-mail: guglea.dionis@gmail.com
[4] Lecturer, PhD eng., Department of Chemistry, Physics and Environment, "Dunărea de Jos" University of Galati, Romania, e-mail: dimadumitru@yahoo.com
[5] Ass. Prof., PhD eng., Department of Mechanical Engineering, "Dunărea de Jos" University of Galați, Romania, e-mail: constantin.georgescu@ugal.ro
[6] Prof., Department of Mechanical Engineering, "Dunărea de Jos" University of Galați, Romania, e-mail: lorena.deleanu@ugal.ro

tested, including raw (cold pressed), non-additivated, but also additivated variants, to improve tribological and rheological properties.

As lubricants based on bio-resources have several disadvantages, the researches try to improve their behavior, especially the easy to compare tribological parameters [1] by additivation [2], [3], [4].

Oxides are used as additives in lubricants due to their influence in reducing wear and friction. This is why these additives, at micro and nano size are also added in lubricants based on vegetal oils. Alves et al. [4] used ZnO and CuO as additives in epoxidized soybean and sunflower oil, but also in a mineral oil for comparison reason. The average crystallite size of ZnO and CuO powder are about 11.71 nm and 4.35 nm, respectively. The anti-wear behavior of these oxides depends on the lubricant base oil, for the same concentration of additive (0.5 wt%). They do not exhibit good anti-wear behavior in epoxizided sunflower and soybean oil because of polar groups that adhere to metallic surface and the nanoparticles acted as a third body, increasing the friction. ZnO shows better results in friction and wear reduction when combined with mineral oil. Battez et al. [5] investigated the tribological behavior of a synthetic oil (PAO6) with ZnO as additive and dispersing agents (OL100 and OL300), on a four-ball machine. For 1 and 1.5% of ZnO in PAO6 + 3% OL300, the non-coated ZnO nano particles had an abrasive behaviour, despite their lower hardness; ZnO nano particles do not act in a efficient way under low loads but for loads seizure load, they decrease wear.

In 2011, Jianhua et al. [6] tested different concentrations (1% to 4%) of modified ZnO nanoparticles (average size of 125 nm) in a base oil on four-ball tester and the measured WSD was significantly reduced, especially for 400...500 N, for the standard speed of 1450 rpm.

The relevance of testing lubricants on four-ball machines is also pointed out by Seyfert [7]. The aim of this study is to characterize the tribological behavior of rapeseed oil additivated with nano particles of ZnO, by the help of four ball machine and for severe regime.

2. Lubricant formulation and testing methodology

The rapeseed oil was supplied by Expur SA Bucharest Romania, together with the analysis of the vegetal composition in fatty acids, done by gas chromatography. The tested base oil is a mixture of fatty acid triglycerides. The fatty acid composition (%wt) for the tested rapeseed oil is: myristic acid (C14:0) 0.06%, palmitic acid (C16:0) 4.6%, palmitoleic acid (C16:1) 0.21%, heptadecanoic acid (C17:0) 0.18%, stearic acid (C18:0) 1.49%, oleic acid (C18:1) 60.85%, linoleic acid (C18:2) 19.9%, linolenic acid (C18:3) 7.64%, arachidic acid (C20:0) 0.49%, eicosadenic acid (C20:2) 1.14%.

The nanoparticles of ZnO (Fig. 1) [8] have the average size of 14 nm, specific surface area of 30±5 m^2/g, purity > 99%.

The massic ratio of the nano additive in the dispersing agent (supplied by Fluka Chemica, with the chemical formula C6H4(OH)OCH3 (2-methoxyphenol) is 1:1, with an accuracy of 0.1 mg. This dispersing agent is compatible with both the rapeseed oil and each of the two additives (separately).

The stages for obtaining 200 ml of additivated rapeseed oil are:

- mechanical mixing of the additive and an equal amount of guaiacol for 20 minutes,
- gradually adding the rapeseed oil, measured to obtain 200 g of lubricant with the desired additive concentrations, by mixing with a magnetic homogenizer during 1 h,
- ultrasonication for 10 minutes with the help of Bandelin HD 3200 (Electronic GmbH & KG Berlin) sonicator; during this sonication, the lubricant is heated to about 70 °C; this is why the process of dispersing by sonication is followed by 1 hour cooling; this step involving (sonication + cooling) was repeated 5 times to obtain a total of 50 minutes of sonication. The parameters of sonicating regime are: 100 W power, frequency 20 kHz ± 500 Hz, continuous mode.

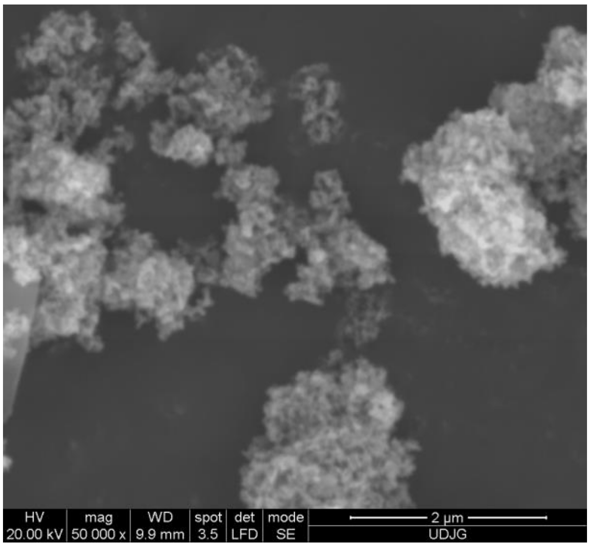


Fig. 1. Aspect of the nanoparticles of ZnO

The balls are made of chrome alloyed steel (100Cr6), with 12.7 mm ± 0.0005 mm in diameter, with 64-66 HRC hardness, as delivered by SKF. For each test, 8 ml ± 1 ml lubricant is introduced in the ball cup. The test method for investigating the lubricating capacity was that from SR EN ISO 20623:2018. Wear-load curve, welding load, and initial seizure load [1]. Tests were done for 60 s ± 0.5 s, with normally applied force in 50 N steps, from 500 N up to 900 N, at

1400 rpm, Lubricants, lubricant cup and balls were used at room temperature (20...23 ºC). Such anti-wear additives, at nano size, are difficult to be evenly dispersed in oil. There was applied a laboratory formulating method, also used by [9], [10]. The formulated lubricants were obtained in a small amount of 200 ml each.

3. Results

Fig. 2 presents the evolution of friction coefficient (COF) and one may notice that for these severe regimes, higher values are presented in the first half of the test, both for the rapeseed oil and the additivated lubricants. This means that major changes are taken place at the beginning of the test (plastic deformation and abrasive wear that generate large wear scars). Higher values are noticed for the lowest concentration of ZnO, meaning that the additive is locally agglomerated and in other zones of the contact it could be absent and the friction increases for steel-to-steel contact.

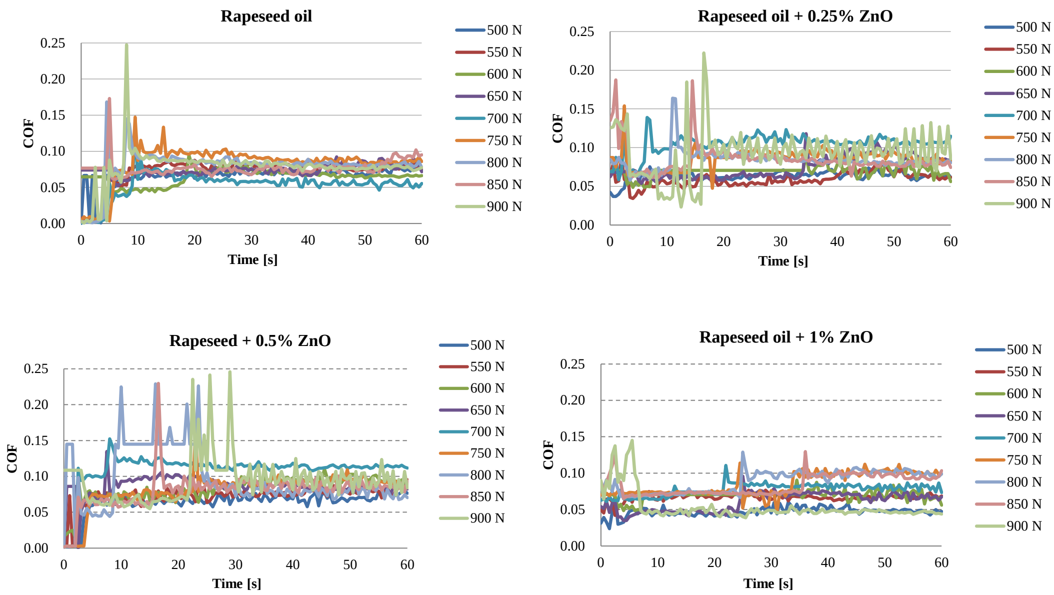


Fig. 2. The evolution of friction coefficient (COF) in time, for all tested lubricants

The wear-load curve is the important information on severe regime as the shape of the curve and the values of WSD reveal if the behavior of the lubricant is adequate for the future application. The first sharp increase of WSD points out the initial seizure load. Tests under 500 N and 550 N have the values for WSD almost identical, meaning that all lubricants behavior is similar and have the same small slope as for normal regime. But from 550 N till 800 N (including), all tested lubricants followed a similar curve, with slightly more tilting lines, the band including the results being 10 %...40 % of the lowest values measured for higher concentrations of ZnO (0.5 %wt and 1.0 %wt). Starting with 850 N, the curves become different, the greater slope being obtained for the non-additivated rapeseed oil. The lubricant with the higher concentration of additive (1% ZnO) continues the previous line (obtained for lower loads), this being a good tribological characteristic to have this line as long as possible, meaning that the lubricant bears greater loads than the others. The last value of WSD is measured for 900 N and between 850 and 900 N the slope of each lubricants is different. The better tribological behavior is revealed for the lubricant with 1% ZnO, by the lowest value of WSD and also by the smaller slope for these loads.

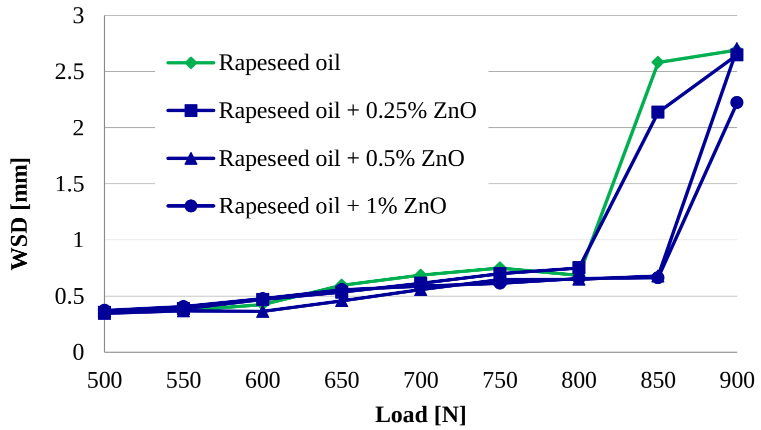


Fig. 3. Evolution of WSD (wear scar diameter) as a function of load and nano additive concentration

In a qualitative way, this conclusion could be drawn from the photos in Fig. 4, but one may pay attention to the scale in each photo. At 850 N, the wear scar is much bigger after testing the neat rapeseed oil as compared to the same base oil additivated with 1% ZnO.

The recorded temperature at the end of the test is given in Fig. 5 and it is obvious that adding nanoparticles of ZnO in rapeseed oil increases this parameter, less for the lowest concentration and similarly higher for the lubricants with 0.5% and 1% ZnO. Thus, when using this vegetal oil additivated with ZnO, the user has to take into account that, in case of severe loads, even accidentally, the temperature will rise and the cooling system has to maintain this parameter under the oxidation temperature of the vegetal oil [11]. The author reported that, for rapeseed oil, after oxidation with air circulation, at 120 ºC and 130 ºC, for 5 hours and 10 hours, respectively, the oil viscosity decreases but transmittance of the oxidized samples has no significative modifications.

Studying several 3D parameters of the wear scar texture could point out the load under which the surface quality becomes worse due to severe adhesive and/or abrasive wear.

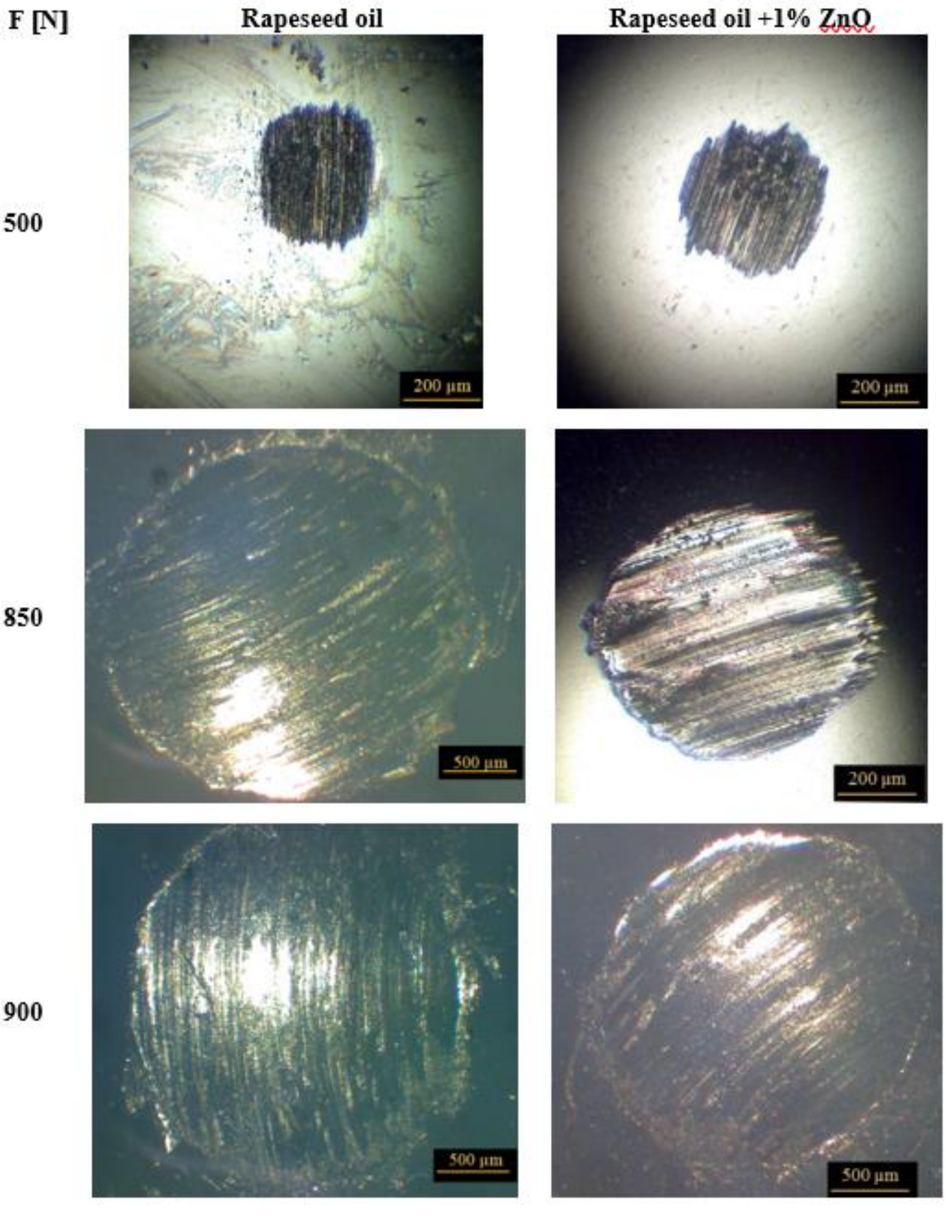


Fig. 4. Images of wear scars on balls lubricated with rapeseed oil and rapeseed oil+1% ZnO, obtained from an optical microscope. Pay attention to scales for F=850 N and F=900 N.

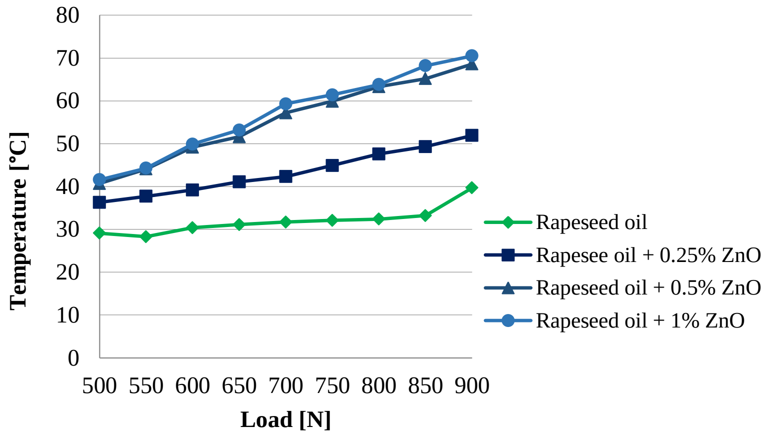


Fig. 5. Evolution of temperature in the lubricant bath at the end of the test as a function of load and nano additive concentration

This study was done using the laser profilometer Nanofocus µScan, from „Ştefan cel Mare" University, Suceava (Romania) and the results were calculated with the help of the dedicated software Mountains 8.1 [12]. From the initially measured surfaces of 1500 µm x 1500 µm containing the wear scar, there was isolated an ellipse with the same values of the axes as those measured with the optical microscope.

The measuring methodology is an issue of measuring and evaluating the surface parameters. Changing the cut-off length or/and the filter, the results could be different. This is why it is important to describe the measuring technology, especially for non-flat and/or worn surfaces. After consulting [13]-[18], the methodology for evaluating the texture parameters has several steps:

1. Loading the files (type. OMS) for each square area that was investigated with the laser profilometer in Mountains 8.1.

2. Leveling the extreme points of the spherical surface in an horizontal plane.

3. The rotation of the entire recorded surface in order to have the sliding direction in a vertical plane. This will allow to easier compare the virtually re-built images of the wear scars (as in Fig. 7).

4. Removing of the ideal spherical shape of the recorded surfaces, considering the radius of this sphere 6.350 mm and reducing the surfaces to a plane.

5. Another cutting of the ellipse zone of the wear scar. As the ellipse is regular, the axes have the measured values of the true wear scar, the actual wear scar could differ from a regular ideal ellipse, but the difference are of several microns, accepted in this study.

6. The calculation of 3D parameters for the selected ellipse as wear scar, the values depending of the applied filtering parameters (here the robust Gaussian regression filter, cut-off λ_s=10 µm and wavelength cutoff λ_c= 0.25 mm). The ends of profiles were not cut as they could include extreme values, important for a solid evaluation of the worn surfaces. The specialists recommend that for random surfaces as those that have been grinded or worn.

7. Extraction of the 2D profile perpendicular to the sliding direction (as those in Fig. 8). This profile allows for measuring one of the axes of the wear scar (as ellipse) and the authors noticed that the differences are very small (between 7% and 0.6% of the values as measured under the optical microscope.

8. Calculating 2D parameters for the selected profiles and getting the Abbott-Firestone curves. Fig. 6 presents only two parameters, Sa and St, these being important to be evaluated for the worn surfaces. The first value in each graph is for the non-worn surface of the ball, measured using the same methodology. The average value is obtained from measuring the three wear scars on the set of the non-rotating balls.

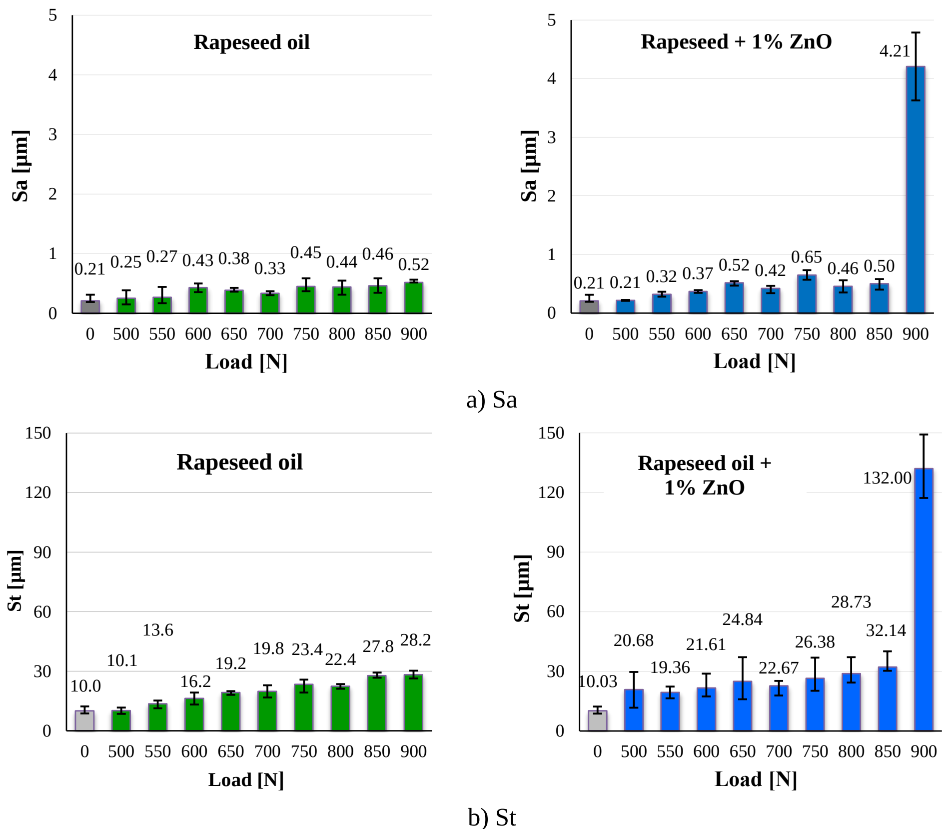
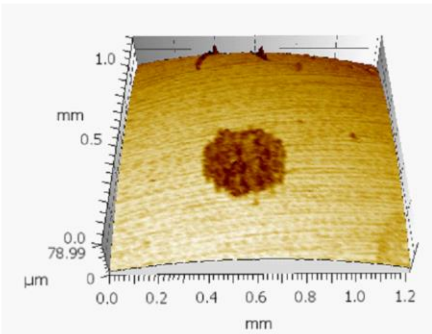


Fig. 6. Texture parameters analyzed for the worn surfaces of the scars

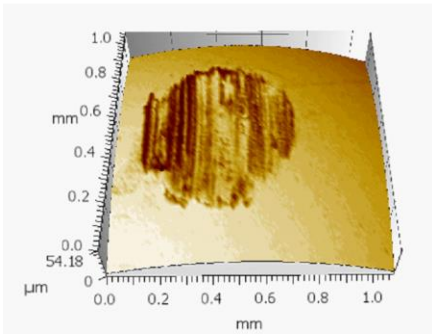
"Sa" is the average arithmetic deviation of the surface and "St" is the maximum surface height, the distance between the highest peak and the deepest valley in the investigated area [18]. This parameter is also denoted by Sz (according to ISO SR EN ISO 4287:2000 [19]), St (according to ASME B46.1:2009 [20]) or Sy.

When using the vegetal oil as lubricant, the lowest values for Sa and St were obtained, meaning that the nature of the oil (fatty acid composition) help keeping the surface quality even if there are large wear scars and the wear is producing with small debris, the surface having the parameters (Sa and St) similar to those after a coarse turning. When adding 1% ZnO in rapeseed oil, the values are only a little bit greater till 850 N, but 900 N this parameter increases 9 times and had a much larger spread range.

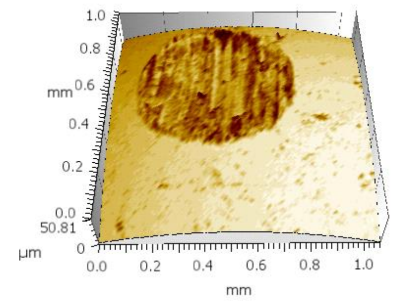
When adding a nano additive in a vegetal oil (and also in other types of base-oil, mineral or synthetic, it is very probable not to improve all the set of tribological characteristics. Sa parameter is increased for the additivated oil but the WSD-load curve is kept low for 0.25% wt ZnO and 1%wt ZnO till 850 N, this being an improved behavior when the system works in severe conditions.



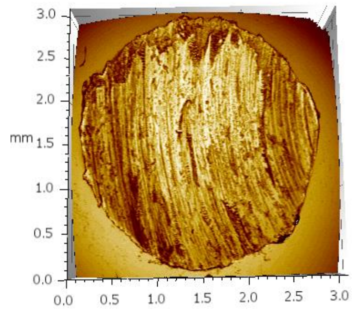
a) 500 N



b) 800 N



c) 850 N



d) 900 N

Fig. 7. Virtual aspect of worn scars for different loads, for the non-rotating balls lubricated with rapeseed oil +1% Zn

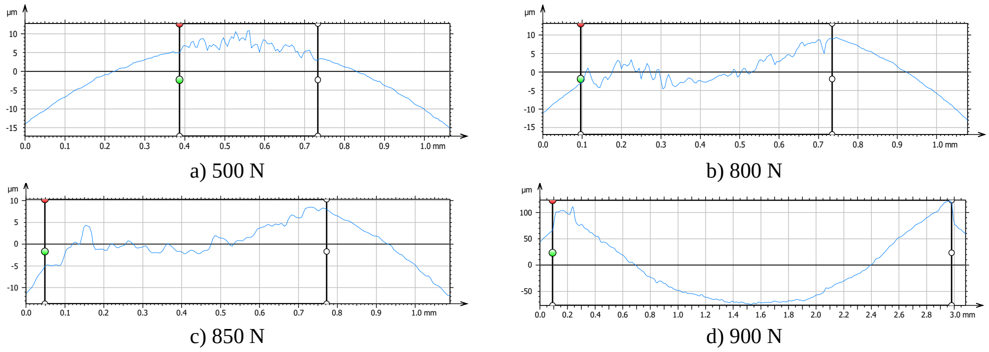


Fig. 8. Profiles of the wear scars, perpendicular to the sliding direction, for lubricant rapeseed oil +1% ZnO

Fig. 7 shows the virtual reconstruction of wear scars for the additivated lubricants and their aspects is in good agreement with the photos in Fig. 4, these being obtained with the help of an optical microscope.

The same trend is obvious for St, but the difference between values recorded for vegetal oil and those for the additivated lubricant, at 900 N, are four times greater for St. This could be explained by the fact that extreme peaks and valleys could be generated on the worn surfaces lubricated by new formulated lubricants by bonding or embedding agglomerations of nanoparticles. And even if the worn surfaces are rougher, their areas are smaller as compared to those lubricated with the neat rapeseed oil.

Fig. 8 presents the measurement of one axis of the wear scar on the 2D profiles perpendicular to the sliding direction, extracted from the worn surfaces. It is obvious that, under severe regime, the surface layer of the ball is damaged by a complex process of plastic deformation (see the increasing shoulders, from b) to d), the first profile having no visible sign of plastic deformation). The smoother shape of the wear scar in Fig. 8d points out more plastic deformation due to the larger load. It is very possible that an intense abrasive wear to take place at the beginning of the test, argued by higher values of the friction coefficient, but increasing the contact area, the high stress values are diminished.

4. Conclusions

Analyzing the test data in severe regime (500 N till 900 N, in steps of 50 N), the additivation of rapeseed oil with ZnO improves the wear scar diameter (WSD), at least for the highest applied loads. The additivation of rapeseed oil with this nano-additive is still efficient for the tested ranges of load as compared to the neat rapeseed oil. For the nano additive concentration of 1%wt ZnO, the curve load - WSD has a very low slope and, only for a load of 900 N, the WSD has a sharp increase but its value is the smallest as compared to those obtained for the neat rapeseed oil and the lubricants additivated with 0.25% and 0.50% ZnO.

The profilometry study pointed out that surface quality for the wear scars is worse for the additivated lubricant as compared to worn surfaces obtained with rapeseed oil, but the wear-load curve emphasis lower values of the average wear scar diameter, meaning that the additive slow down the wear process especially under higher loads.

Acknowledgement

This work has been supported by the European Social Fund through the Sectorial Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title „Burse pentru educaţia antreprenorială în rândul doctoranzilor şi cercetătorilor postdoctorat (Be Antreprenor!)" "Scholarships for entrepreneurial education among doctoral students and postdoctoral researchers (Be Entrepreneur!)", Contract no. 51680/09.07.2019 - SMIS code: 124539

R E F E R E N C E S

[1]. *** EN ISO 20623, Petroleum and related products. Determination of the extreme-pressure and anti-wear properties of fluids. Four ball method (European conditions), 2018

[2]. *Y. Y. Wu, W. C. Tsui and T. C. Liu,* Experimental analysis of tribological properties of lubricating oils with nanoparticle additives, in Wear, **vol**. **262**, pp. 819-825, 2007

[3]. *M. Akbulut*, Nanoparticle-based lubrication systems, *Journal of Powder Metallurgy and Mining,* 1, pp. 101, 2012.

[4]. *S. M. Alves, B. S. Barros, M. F. Trajano, K. S. B. Ribeiro and E. Moura,* Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions, in Tribology International, **vol**. **65**, pp. 28–36, 2013

[5]. *H. A. Battez, J. E. Fernandez Rico, A. Navas Arias, J. L. Viesca Rodriguez, R. Chou Rodrigue and J. M. Diaz Fernandez,* The tribological behaviour of ZnO nanoparticles as an additive to PAO6, in Wear, **vol. 261**, pp. 256–263, 2006

[6]. *Q. Jianhua, Z. Yu, W. Lingling and X. Jinjuan,* Study on Lubrication Properties of Modified Nano ZnO in Base Oil, in China Petroleum Processing and Petrochemical Technology, **vol**. **13**, no. 3, pp. 69-73, 2011.

[7]. *C. Seyfert,* Tribometers, Rotational, for Sliding Wear and Friction. In: Mang T. (eds) Encyclopedia of Lubricants and Lubrication. Springer, Berlin, Heidelberg, https://doi.org/10.1007/978-3-642-22647-2_144, 2014

[8]. *** Nanomaterials and related products, PlasmaChem GmbH, Germany, http://www.plasmachem.com/download/PlasmaChem-General_Catalogue_Nanomaterials.pdf, 2016

[9]. *G. C. Cristea, C. Dima, D. Dima, C. Georgescu and L. Deleanu*, Nano graphite as additive in soybean oil, MATE C Web Conf., vol. 112, 21st Innovative Manufacturing Engineering & Energy International Conference – IManE&E, https://doi.org/10.1051/matecconf/201711204023, 2017

[10]. *G. C. Cristea, C. Dima, C. Georgescu, D. Dima, L. Solea, L. Deleanu,* Evaluating lubrication capability of soybean oil with nano carbon additive, 15th International Conference on Tribology, Kragujevac, Serbia, 17 – 19 May 2017.

[11]. *L. C. Şolea*, Contributions on studying the rheological and tribological behavior of lubricants based on vegetal oils (in Romanian), PhD thesis, "Dunărea de Jos" University of Galati, Romania, 2013.

[12] *** Mountains Lab Premium, Version 8.1, http://www.imagemet.com/WebHelp/spip.htm, 2020.

[13]. *J. Schmit, S. Han and E. Novak*, Ball bearing measurement with white light interferometry, The International Society for Optical Engineering, 2009

[14]. *K. J. Stout, P. J. Sullivan, W. P. Dong, E. Mainsah, N. Luo,T. Mathia and H. Zahouani*, The development of methods for the characterisation of roughness in three dimensions, Publication no. EUR 15178 EN of the Commission of the European Communities: Brussels-Luxembourg, 1994

[15]. *C. Georgescu, L. Deleanu and C. Pirvu,* Evaluating Lubricant Performance by 3D Profilometry of the wear scars, The 6th International Conference on Advanced Concepts on Mechanical Engineering, Iasi, 2016

[16]. *C. Pirvu, C. Georgescu and L. Deleanu*, Influence of grinding feed speedon 3D texture parameters, in Mechanical Testing and Diagnosis, **vol**. **2**, pp. 19-28, 2013

[17]. *F. Blateyron*, États de surface: la norme, Mesures,**vol**. **787**, pp. 44-47, 2006

[18]. *L. Blunt and X. Jiang,* Advanced techniques for assessment surface topography, London, Butterworth-Heinemann, 2003

[19]. *** SR EN ISO 4287:2000 Geometrical product specifications (GPS) — surface texture: profile method — terms, definitions and surface texture parameters

[20]. *** ASME B46.1:2019 Surface Texture (Surface Roughness, Waviness, and Lay)