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Lubrication Performance of Sunflower Oil Reinforced with Halloysite Clay Nanotubes (HNT) as Lubricant Additives

Md Abu Sayeed Biswas [1], Md Mashfiqur Rahman [1], Javier A. Ortega [1,*], Laura Peña-Parás [2], Demófilo Maldonado-Cortés [2], José A. González [2], Ricardo Cantú [2], Adrián Campos [2] and Eugenio Flores [2]

[1] Department of Mechanical Engineering, The University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, TX 78539, USA; mdabusayeed.biswas01@utrgv.edu (M.A.S.B.); mdmashfiqur.rahman01@utrgv.edu (M.M.R.)

[2] Departamento de Ingeniería Mecánica y Electrónica, Universidad de Monterrey, San Pedro Garza García 66238, NL, Mexico; laura.pena@udem.edu (L.P.-P.); demofilo.maldonado@udem.edu (D.M.-C.); joseandres.gonzalez@udem.edu (J.A.G.); ricardo.cantu@udem.edu (R.C.); adrian.campos@udem.edu (A.C.); eugenio.floresg@udem.edu (E.F.)

* Correspondence: javier.ortega@utrgv.edu

Abstract: This study evaluates the tribological performance of nanolubricants of a vegetable oil (sunflower oil) reinforced with different concentrations of environmentally-friendly nanoparticles of halloysite clay nanotubes (HNTs). Tribological characterization was performed under different conditions to determine its effect on the nanolubricants' performance and optimal HNT concentration. The tribological performances under low and high contact pressures were analyzed with a block-on-ring tribometer following the ASTM G-077-05 standard procedure. The extreme pressure (EP) properties of the nanolubricants were determined with a T-02 four-ball tribotester according to the ITeE-PIB Polish method for testing lubricants under scuffing conditions. In addition, the lubrication performance of the newly-developed vegetable oil-based nanolubricants was evaluated in an industrial-type application through a tapping torque test. The results indicated that at a low contact pressure 1.5 wt.% HNTs/sunflower oil provided the best tribological behavior by decreasing the coefficient of friction (COF) and wear volume loss by 29 and 70%, respectively. For high contact pressures, 0.05 wt.% HNTs lowered COF and wear by 55% and 56%, respectively. The load-carrying capacity increased by 141% with 0.10 wt.% HNTs compared to the sunflower oil. A high tapping torque efficiency was obtained with HNTs that can prolong tool life in the machining process. Therefore, this study suggests that HNTs/sunflower oil could be used as green lubricants for industrial applications.

Keywords: halloysite nanotubes; sunflower oil; anti-wear; extreme pressures; tribological performance

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1. Introduction

Nowadays, 29% of the energy consumed worldwide is used for general industry applications and 28% for the mobility of combustion cars, which already total over 700 million in the world. These two industries require the intensive use of lubricants to be able to facilitate machinery operation and maintenance [1]. As both sectors use internal combustion equipment, they emit a considerable amount of CO_2 into the atmosphere. Given the above, there are efforts in the scientific community to develop alternatives that reduce emissions such as the use of new materials, new coatings, new lubricants, and through nano-additives [1]. Even with these efforts, the use and disposal of mineral or synthetic lubricants and conventional additives which have been used for decades have shown to be harmful to the environment [2]. Recently, studies have been conducted to find new additives and lubricants that are friendly to the environment [2–7]. The use of vegetable oils was common until the nineteenth century as they are easily obtainable from natural sources. After the nineteenth century, the requirement for lubricants became very high because of rapid industrialization and there was a shift to petroleum-based lubricants.

However, petroleum-based lubricants are less degradable and represent a great threat to the environment when released. Therefore, interest in bio-lubricants has risen in recent years. The use of vegetable oils as lubricants offers a wide range of advantages such as a high biodegradability [8,9], low environmental pollution, compatibility with additives, low production cost [10], low toxicity, high flash point, low volatility, and high viscosity indices. Moreover, many food-based biodegradable lubricants have been shown to have good tribological properties [2,6,7]. Vegetable oils are also a source of fatty acids for polyol esters [11,12] and are also base oils for environmentally-friendly lubricants. The primary drawbacks for the use of vegetable lubricants [13,14], however, are their relatively high freezing points and low thermo-oxidative stability [15]. Nanoparticles (NPs) have been studied as additives in order to improve the properties of vegetable lubricants. For example, Yu et al. [16] achieved reductions in the coefficient of friction (COF) and wear of up to 53% and 11%, respectively, using vegetable-based oils with graphite nanoparticles. Cortes et al. [17] decreased the COF and wear by up to 94% and 74.1%, respectively, using sunflower lubricants with SiO_2 and TiO_2 NPs. Omrani et al. [18] improved the sliding contact using vegetable oil with added nano-graphene and obtained COF improvements of up to 84%. Important COF reductions in vegetable oil lubricants with NPs were also obtained by Baskar et al. [19] and Behrooz et al. [20]. Finally, Avinash et al. [21] found potential applications for lubricants in automobiles with bio-based lubricants from vegetable oils and NPs as additives.

Sunflower oil is a non-volatile vegetable oil extracted by pressing sunflower seeds. It is biodegradable, readily available, eco-friendly, and can be renewable. Sunflower oil is primarily composed of approximately 15% saturated and 85% unsaturated fatty acids. Sunflower oil is one of the most important vegetable oils in terms of oil composition and among the most important oils in human nutrition [22]. Sunflower seeds and oils have undergone considerable improvement, specifically in fatty acid profiles. Plant breeders and geneticists have successfully brought mid- and high-oleic varieties to commercialization within the past 20 years to overcome the stability issue. Modified sunflower oils have been shown to have an excellent oxidative stability in both high-temperature applications and where foods require a long shelf life due to the high percentage of oleic acid compared to other vegetable oils [17,23,24]. Moreover, sunflower has good tribological characteristics and a predominantly polyunsaturated fatty acid composition [17]. The different fatty acid profiles in sunflower oils positively influence its tribological properties by decreasing friction and wear. However, as sunflower oil is mainly composed of less stable monounsaturated and polyunsaturated fatty acids, it can be easily susceptible to degradation by heat and air, which can easily accelerate its oxidation. Additionally, the lubrication properties of sunflower oil can be improved using lubricant additives [17].

Halloysite clay nanotubes (HNTs), with reported dimensions of 50–80 nm in external diameter and lengths of up to 1000 nm [25], are naturally occurring NPs that can be found in large deposits in several countries [26]. They are low-cost [27] and non-toxic, and studies have shown that they are biocompatible so they could even be used for biomedical applications [28,29]. Therefore, HNTs have been explored as "green" additives [30,31]. Clay-based nano-additives have proven beneficial when added to water-based, oil-based, and polymeric lubricants to improve tribological properties, mainly friction and wear [32,33]. However, few studies with vegetable oils reinforced with HNTs can be found in the literature. For instance, Ahmed et al. [34] studied HNTs as additives for date seed and castor oil blends and was able to reduce the wear scar diameter (WSD) by up to 21.32% at a concentration of 1 wt.%. Similarly, Suresha et al. [35] obtained reductions in friction and wear of 14.3% and 10.64%, respectively, with 1.5 wt.% HNTs added to pongamia oil. The combined use of sunflower oil and environmentally-friendly nanoclays such as HNTs has not been deeply explored. Therefore, the main objective of the present study was to investigate the lubrication performance of sunflower oil reinforced by the addition of HNTs as lubricant additives under different testing conditions: low (218 MPa) and high (490 MPa) contact pressures, and extreme pressure (EP) conditions. It should be noted that the EP test was performed with a linearly increasing load in order to determine the pressure at which the lubricant film disappears. The effect of HNT concentration on the tribological performance of the sunflower oil was evaluated experimentally through four-ball, block-on-ring experiments and tapping torque tests. The worn areas in the specimens were analyzed via scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and profilometry.

2. Materials and Methods

2.1. Materials

The morphology of the HNT NPs used for this study (SIGMA-ALDRICH Co., St. Louis, MO, USA) obtained by a field-emission scanning electron microscope (FE-SEM) ZEISS SIGMA VP (Carl Zeiss SBE, Thornwood, NY, USA) is shown in Figure 1. It can be observed that the shape of the HNTs is hollow tubular. The NPs safety data sheet can be found in [36]. The length and diameter of the nanotubes were measured by using more than fifty data points. The maximum and minimum lengths of the nanotubes were 677 and 125 nm, respectively. The average length of the HNT nanotubes was 303 nm with a standard deviation of 149 nm, obtained from the SEM images. The average diameter was 65 nm with a standard deviation of 19 nm, where the maximum diameter was 130 nm, and the minimum was 31 nm. A mid-oleic commercially-available sunflower oil was used as a base oil. The aspect ratio of the HNTs was 4.6. Table 1. shows the characteristics and properties of the sunflower oil, NPs, and specimens for the tribological tests.

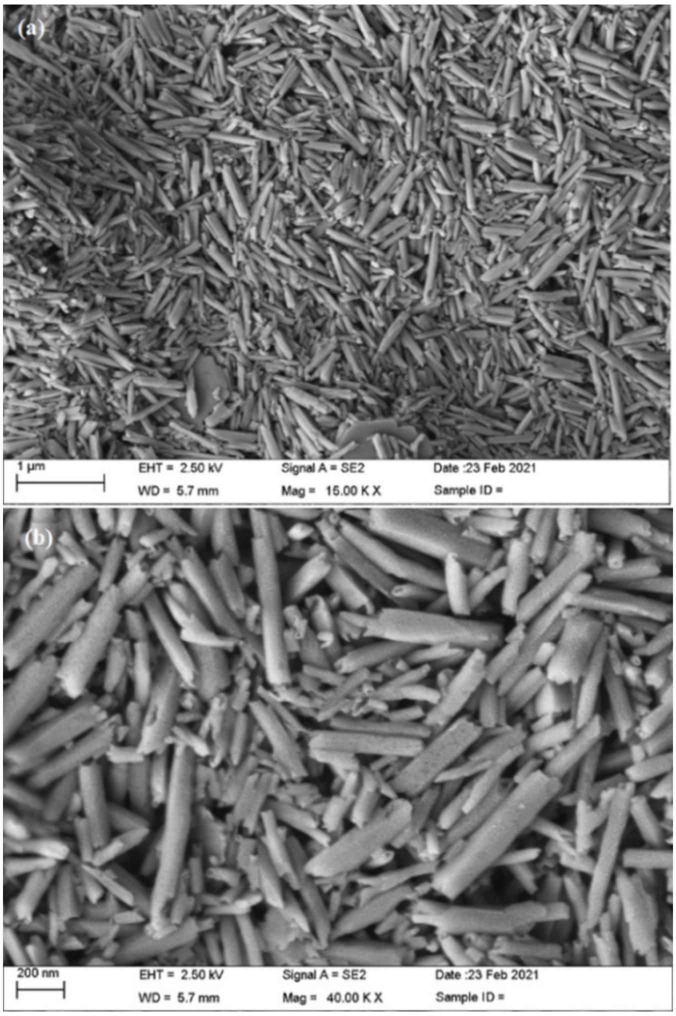

Figure 1. Morphology of halloysite nanotubes at (**a**) 15.00 KX, and (**b**) 40.00 KX magnifications.

Table 1. Material properties.

Material	Properties
Lubricant	
Sunflower oil	* Density (40 °C): 0.90 g/cm^3 Iodine value: 120–145 gI/100 g Acid number: 0.2–0.5 KOH/1 g Fatty acid content: 4% palmitic acid, 65% oleic acid, 26% linoleic acid, 5% stearic acid
Nanoparticles	
Halloysite clay nanotubes (NHT)	Chemical formula: $H_4Al_2O_9Si_2 . 2H_2O$ Molecular weight: 294.19 g/mol Specific gravity: 2.57 g/cm^3
Specimens	
Low loads	
Blocks	AISI 304 steel, dimensions: 14 × 6.35 × 6.35 mm, hardness: 128 HRB
Rings	AISI 52,100 steel, d = 40 mm, hardness: 60 HRC
High loads	
Blocks	AISI 1018 steel, dimensions: 15.75 × 10 × 6.35 mm, hardness: 78 HRB
Rings	AISI D2 steel, d = 35 mm, hardness: 62 HRC
Extreme pressures	
Balls	AISI 52,100 steel, d: 12.7 mm, hardness: 60 HRC

*** A Mettler Toledo XS205DU electronic balance was used to measure the density on a weight to volume basis using a 25 mL flask.**

2.2. Preparation of Nanolubricants

Nanolubricants were prepared using commercially-available sunflower oil and halloysite clay nanotubes (HNTs) at different concentrations. The HNTs were dispersed in vegetable oil to formulate nanolubricants. Different HNT concentrations (0.01, 0.05, 0.10, 0.50, 1.00, 1.50, 2.00, 2.50, and 3.0 wt.%) were used to prepare the nanolubricants in separate vials. The HNTs were added into the sunflower oil, followed by ultrasonication for 5 min using a 120 Watt Fisherbrand™ Model 120 sonic dismembrator (Thermo Fisher Scientific Inc., Waltham, MA, USA). The process was conducted at a frequency of 20 kHz to guarantee uniform dispersion and a good stability of the suspension. Figure 2 shows images of the prepared nanolubricants at 0 h (Figure 2a) and 7 days (Figure 2b) after the dispersion process by ultrasonication. Samples were tested within 30 min of the mixing process. Some sediments can be found 7 days after sonication (Figure 2b).

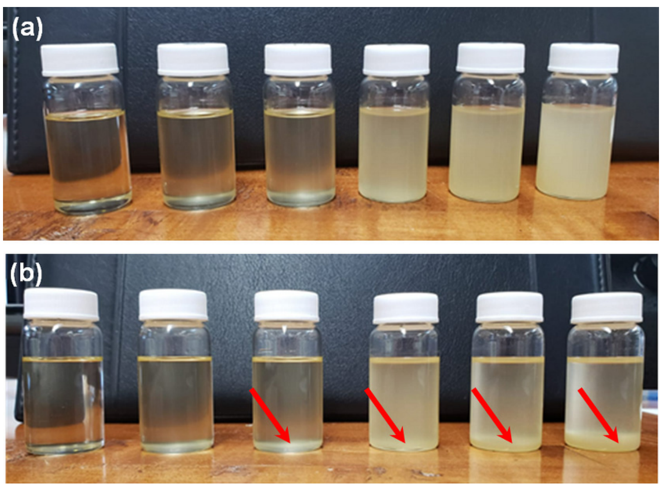

Figure 2. Images of prepared sunflower nanolubricants at 0, 0.05, 0.10, 0.5, 1.0, 1.5 wt.%: (**a**) 0 h after the sonication process, and (**b**) 7 days after sonication.

2.3. Tribological Characterization of Nanolubricants

Tribological tests were performed on sunflower oil filled with HNTs under different conditions: low contact pressure, high contact pressure, and extreme pressures, as observed in Figure 3. These tests were conducted to determine the optimal HNT concentration according to the testing conditions, since various manufacturing processes are performed under a wide range of contact pressures and the purpose of this study was to propose sunflower nanolubricants for possible industrial applications.

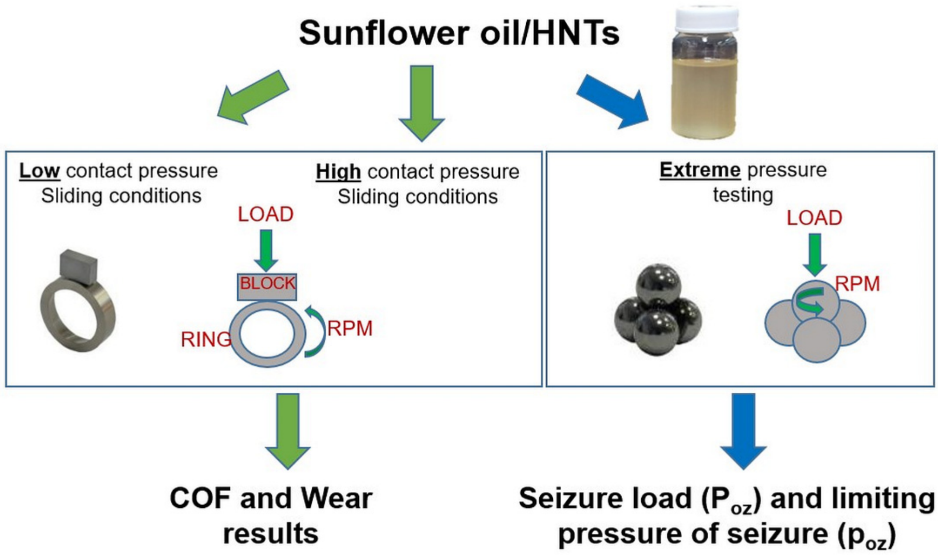

Figure 3. Tribological testing performed in this study on sunflower oil nanolubricants.

2.3.1. Low Contact Pressure Testing

A block-on-ring tribotester was used to evaluate the lubrication performance of sunflower oil with and without HNTs additives under sliding conditions. The tribological experiments were carried out following the ASTM G-077-05 [37] standard procedure. During the experiments, an AISI 304 stainless-steel block was pressed against a rotating ring of AISI 52,100 steel. To allow constant lubrication during the tribological experiments, the lubricants were placed in an oil bath container while the test ring rotated, covering it in lubricant by the action of centrifugal forces. The tribological experiments were performed at a room temperature of 25 °C, at 172 rpm, during 1200 s, using a load of 266 N and a contact pressure of 218 MPa. A Mettler Toledo XS205DU electronic balance (Mettler-Toledo LLC, Columbus, OH, USA) was utilized to determine the wear mass loss gravimetrically. A specific density of 8.0 g/cm^3 was used for the AISI 304 stainless steel blocks to convert the wear mass loss into wear volume loss. During each test, the friction force was monitored continuously and recorded. To ensure reliability and reproducibility, the tribological experiments were performed three times.

2.3.2. High Contact Pressure Characterization

Tribological testing under high loads was performed with a T-05 Block-on-ring tribotester. Sliding wear experiments were carried out according to the ASTM G-077-05 [37] standard procedure. Here, AISI 1018 steel blocks were pressed against a rotating ring of AISI D2 steel (Table 1) with an oil batch chamber fixture for the HNT/sunflower lubricants. Tests were run at a temperature of 25 °C, at 200 rpm, time of 78 s, using a load of 1177 N and a contact pressure of 490 MPa. The friction force was recorded for each test and divided by the applied load to obtain the COF. Wear loss was obtained from the total displacement of the tribosystem obtained from both the block and ring materials.

2.3.3. Extreme Pressure Testing

The extreme pressure tribological properties of nanolubricants were determined with T-02 four-ball equipment, according to the ITeE-PIB Polish test method for testing lubricants under scuffing conditions [38,39]. Here, three AISI 52,100 lower steel balls (Table 1) were covered in 8–10 mL of lubricant, and an upper ball rotated at 500 rpm, where a linearly increasing load (0–7200 N) was applied for a total test duration of 18 s. Testing was performed in triplicate at room temperature (25°). The frictional torque was recorded until a value of 10 N·m was reached and seizure occurred due to the oil film disappearing. The load where this occurs is called the seizure load (P_{oz}). Afterwards, the wear scar diameter (WSD) of the three lower steels for each test was obtained by an optical microscope. The load-carrying capacity p_{oz} was the calculated through the following relationship:

$$p_{oz} = 0.52 \frac{P_{oz}}{WSD^2} \quad (1)$$

2.4. Tapping Torque Test

Tapping torque tests for the newly-developed nanolubricants were carried out on a Grizzly milling machine model G0796 (Grizzly Industrial Inc., Springfield, MO, USA), installed with a tapping torque set up [40]. Tapping torque tests were carried out according to the ASTM D5619 (2011) standard procedure [41]. The tests were conducted using aluminum 6061 cylindrical specimens with dimensions of 25.4 mm of diameter and 38.1 mm of length. Tapping was performed using M6 × 1.00 mm high-speed steel tapping tools. The testing conditions were: a machining speed of 90 rpm, a hole depth of 33.02 mm, and a hole diameter of 5 mm. Approximately 0.5 mL of the lubricant sample was poured into the specimens to lubricate the tools during the tapping process. The tapping process was repeated five times, prior to averaging the thrust force and torque values.

2.5. Surface Analysis

A field-emission scanning electron microscope (FE-SEM) ZEISS SIGMA VP (Carl Zeiss SBE, Thornwood, NY, USA) equipped with an energy-dispersive X-ray spectrometer (EDS) analyzer (EDAX Inc., Mahwah, NJ, USA) was used to characterize the surface morphology of the wear scar produced in the blocks during the tribological tests. In addition, a MahrSurf M300 C surface profilometer (Mahr Inc., Providence, RI, USA) and an Alicona EdgeMaster optical measurement system (Bruker Alicona, Graz, Austria) were used to measure the surface roughness of the blocks before and after the wear tests.

3. Results and Discussion

3.1. Low Contact Pressures

The tribological performance of sunflower oil was analyzed with and without the addition of halloysite clay nanotubes at different concentrations. In this case, the concentrations ranged from 0.5 to 3.0 wt.%, since at low pressures the lubricant film thickness is thicker and lower concentrations provide a negligible effect. The experimental data was collected from the block-on-ring experiments under the same test conditions for each sample. It was found that the addition of different concentrations of halloysite nanotubes had a great impact on decreasing the friction force during the tribological tests. Figure 4 shows the friction force recorded during the tribological tests lubricated with sunflower oil-based nanolubricants. The frictional force of sunflower base oil was initially 35 N whereas, with the addition of HNT nanoclay, the initial friction force decreased to less than 20 N. This could be attributed to the shape of the nanotubes. With the inclusion of NPs, the friction force was reduced, resulting in thin-film lubrication and a change in friction type from sliding to rolling. This result agreed with that of Peña-Parás et al. [42], who reported that the presence of HNT particles reduced the contact area.

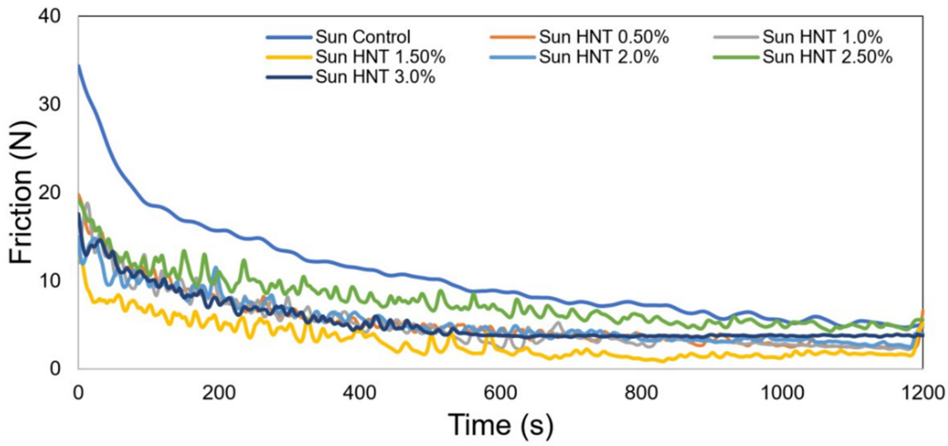

Figure 4. Friction force vs. time graph for sunflower oil-based nanolubricants at a contact pressure of 218 MPa.

Figure 5 shows the COF results for the sunflower oil nanolubricants tested at a contact pressure of 218 MPa. It can be observed that the COF for the sunflower base oil was 0.0398 and, with the addition of HNT at different concentrations, the coefficient of friction was reduced significantly. The lowest COF was obtained with the 1.5 wt.% concentration, 70% lower than the COF obtained with the base sunflower oil. The maximum COF was obtained with the 2.5 wt.% HNT concentration among all the other sunflower nanolubricants. A previous study of sunflower nanolubricants with TiO_2 and SiO_2 NPs showed decreases in the COF of 94% and 78%, in comparison [17].

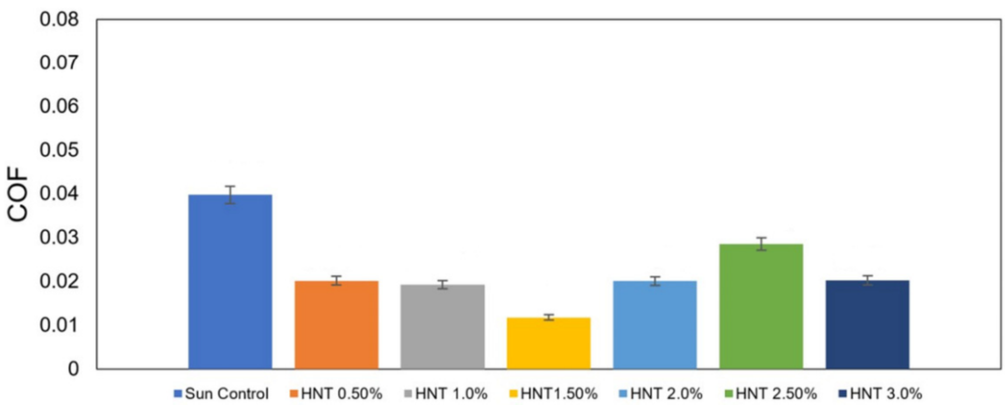

Figure 5. Coefficient of friction results for sunflower oil reinforced with HNT nanotubes at different concentrations at 218 MPa.

The mean volumetric wear for the blocks lubricated with sunflower oil-based nanolubricants is shown in Figure 6. In the case of sunflower oil without NPs, the volumetric wear loss was 9.013 mm^3; with the addition of HNT at 1.5 wt.%, the volumetric wear was reduced to 6.425 mm^3. We assume that the volumetric wear was reduced due to the rolling effect or load-bearing mechanism of HNTs [32]. From Figure 4, it can be observed that the volumetric wear increased with the increase in concentration from 2.0 to 3.0 wt.%. This could be attributed to agglomeration of the HNT NPs. The overall percentage of wear reduction for the best concentration was approximately 29% compared to the base sunflower oil. Cortes et al. [17] performed similar tribological testing with sunflower oil nanolubricants with 1.25 wt.% SiO_2 (20–30 nm) and 1.0 wt.% TiO_2 (18 nm) and obtained reductions in volumetric wear of 74% and 70%. The better results obtained by these spherical NPs compared to HNTs can be attributed to their very small size, which can provide a mending effect and form a protective film. Future work with sunflower nanolubricants should focus on combining HNTs and TiO_2/SiO_2 to take advantage of the tribological mechanism of each NP and study a possible synergistic effect. For our nanolubricants, after adding a HNT percentage of more than 1.5 wt.%, the volumetric wear loss started to increase and exceeded the base sunflower volumetric wear loss. Here, volumetric wear is reduced by adding NPs up to a specific concentration, as demonstrated by Cortes and Ortega [43], who found that adding 1.00 wt.% of CuO NPs to coconut oil reduced the volumetric wear by 33% compared to the base oil.

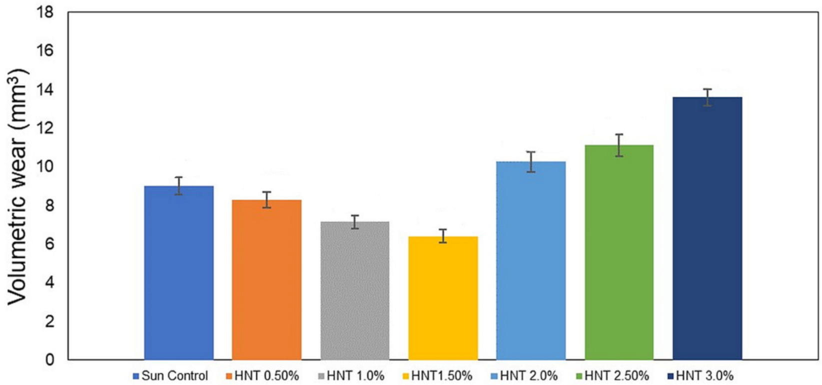

Figure 6. Mean volumetric wear of AISI 304 specimens lubricated with sunflower oil reinforced with HNTs.

During the experiments, a temperature sensor was used to monitor the lubricant temperature. From the experimental data, it was observed that for the sunflower oil-based nanolubricants, the lubrication temperature decreased with the addition of halloysite nanotubes. The results of the lubrication temperature analysis are shown in Figure 7.

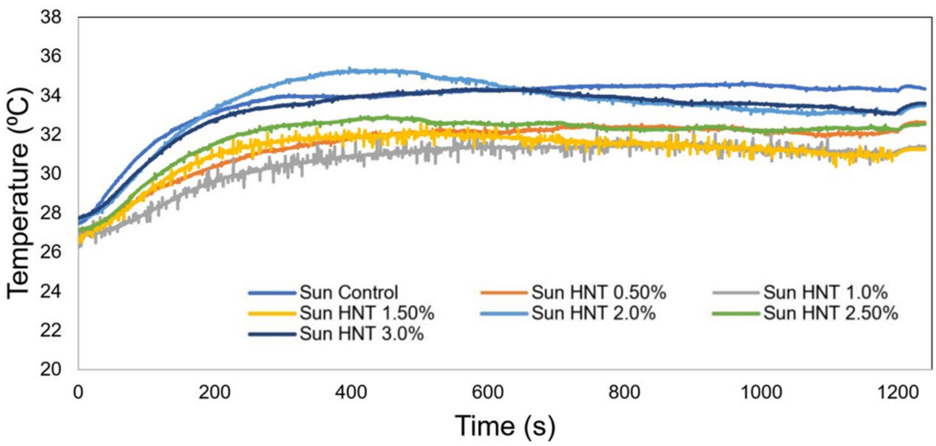

Figure 7. Temperature of sunflower oil-based nanolubricant during tribological test.

As shown in Figure 7, the sunflower oil lubrication temperature was higher compared to the HNT-reinforced sunflower nanolubricants. With the addition of HNT at different concentrations, the lubrication temperature was reduced. The 1.0 wt.% HNT concentration nanolubricant showed the lowest lubrication temperature, which was approximately 20% lower than the final base sunflower lubrication temperature. This could be due to the HNTs reducing the real area of contact between metallic surfaces. From the lubrication temperature profile, it is also clear that the lubrication temperature rises initially, and afterwards adopts a steady-state condition.

3.2. High Contact Pressures

Figure 8 shows the COF results for the sunflower oil nanolubricants tested at a contact pressure of 490 MPa. Due to the higher loads and applied pressure of the experiments, lower HNT concentrations were used as additives (0.01, 0.05, 0.10 wt.%), compared to the low-pressure tests (0.5–3 wt.%). This was performed since, as the lubricant film thickness is reduced, lower concentrations of HNTs with fewer agglomerates can better infiltrate the contact regions and withstand higher loads [44]. Furthermore, as previously proposed [32,42], HNTs may provide a load-bearing mechanism—particularly at higher pressures— as well as separating the surfaces, reducing the real area of contact, and thus lowering the COF and wear. As depicted in Figure 8, a reduction of up to 55% was obtained with 0.05 wt.% compared to the base sunflower oil. Higher HNT concentrations presented a smaller improvement of 26%, likely due to the presence of larger agglomerates due to the higher concentration. In a previous study by our group with similar testing conditions [42], a synthetic fluid was reinforced with HNTs and reduced from 0.088 for the synthetic fluid to 0.06 with 0.1 wt.% HNTs. Thus, the results obtained by sunflower oil nanolubricants are superior, due to the lower COF values obtained.

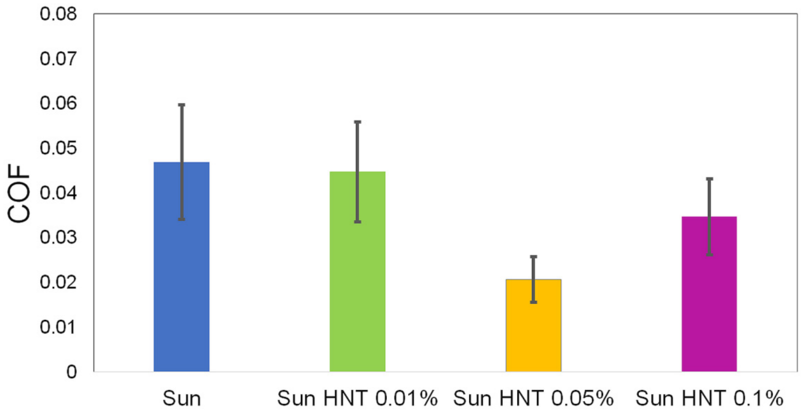

Figure 8. Coefficient of friction results for sunflower oil reinforced with HNT nanotubes at different concentrations at 490 MPa.

Figure 9 depicts the wear loss at high loads for sunflower nanolubricants with varying HNT concentrations. Similar to the values obtained for the COF (Figure 8), there is a trend of decreasing wear with increasing HNT content up to 0.05 wt.%. At this concentration, wear was lowered by 56%, whereas for 0.10 wt.% the improvement was 37%. The average wear obtained by the base sunflower oil and by the 0.05 wt.% HNTs were 60 µm and 26 µm, respectively; in comparison, a commercial graphite and triazine forging lubricant obtained a displacement of 25 µm [45].

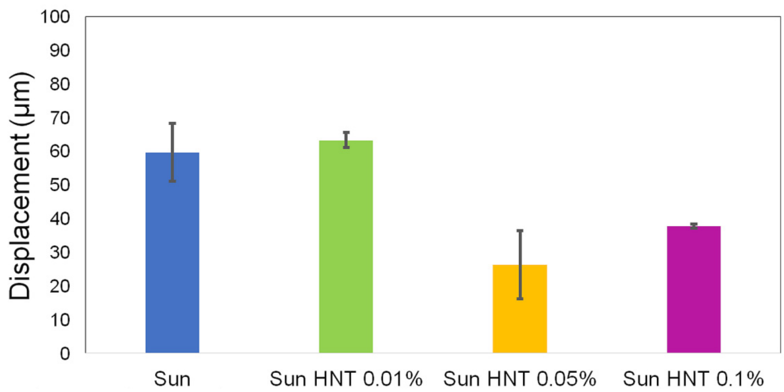

Figure 9. Wear loss of HNT–sunflower nanolubricants obtained from the displacement in microns of the tribosystem.

3.3. Extreme Pressure Properties

Figure 10 depicts the frictional torque at linearly increasing loads of 0–7200 N of sunflower nanolubricants obtained by the extreme pressure four-ball test. The seizure load (P_{oz}) occurred between around 11–12 s for all lubricants, with average values of

4407–4466 N (Figure 11). For sunflower oil, P_{oz} was ~4450 N; therefore, HNTs had a negligible effect on increasing this value. However, the effect of HNTs was observed in the WSD of the three lower steel balls; at 0.1 wt.% the WSD was 2.13 mm, compared to 2.50 mm for the base oil. As a reference, the previously-obtained value of P_{oz} for distilled water is 810 N [46]; for commercially-formulated lubricants of oil-based synthetic, water-based semi-synthetic, and grease, these values are 2933 N, 3300 N, and 7200 N, respectively [33]. Therefore, the results obtained by the sunflower nanolubricants are comparable and in some cases superior to those obtained by commercial oil-based and water-based lubricants.

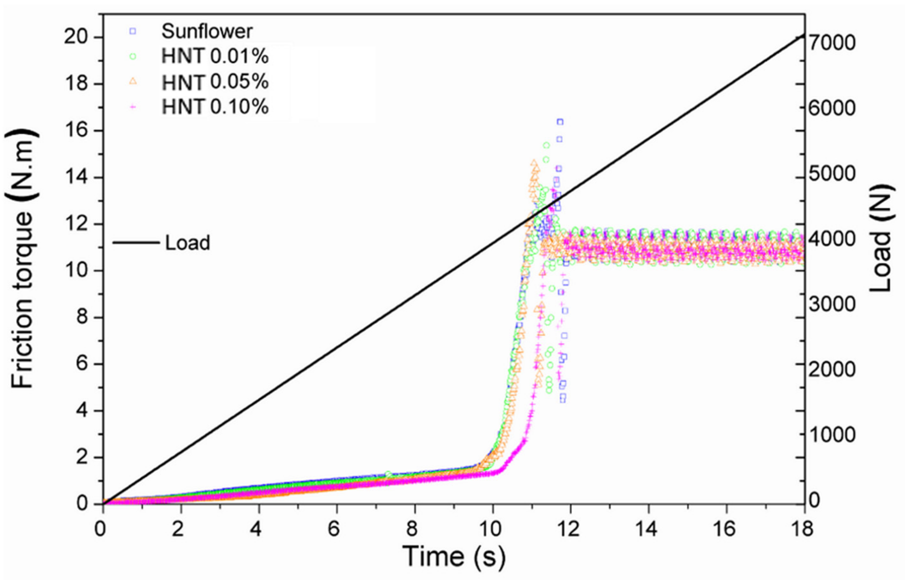

Figure 10. Friction torque curves vs. time at continuously increasing loads for sunflower nanolubricants with varying concentrations.

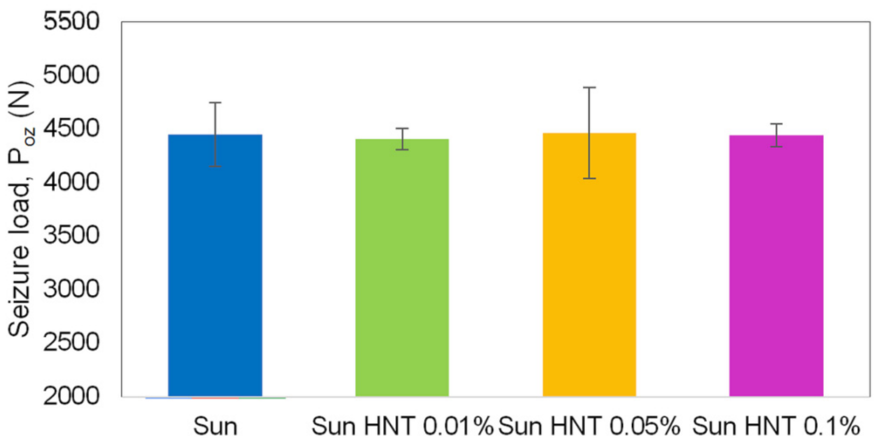

Figure 11. Seizure load (N) of sunflower nanolubricants under extreme pressures.

As shown in Equation (1), load-carrying capacity is calculated by taking into account the seizure load and the WSD of the three lower steel balls of the four-ball extreme pressure test. Figure 12 shows the increase in the load-carrying capacity of HNT–sunflower nanolubricants (N/mm^2 = MPa). The addition of HNTs was able to provide a load-bearing effect, reducing the contact area, which in turn lowered the WSDs of the ball bearings and increased p_{oz}. For sunflower oil, p_{oz} was 259 MPa. For comparison, the reported p_{oz} values of distilled water, RzR rapeseed refined oil, and synthetic oil PAO8 are 260 MPa [46], 230 MPa, and 225 MPa [47], respectively. Additionally, the p_{oz} values of commercially-formulated lubricants of an oil-based synthetic, water-based semi-synthetic, and grease were 140 MPa, 210 MPa, and 407 MPa, respectively [33].

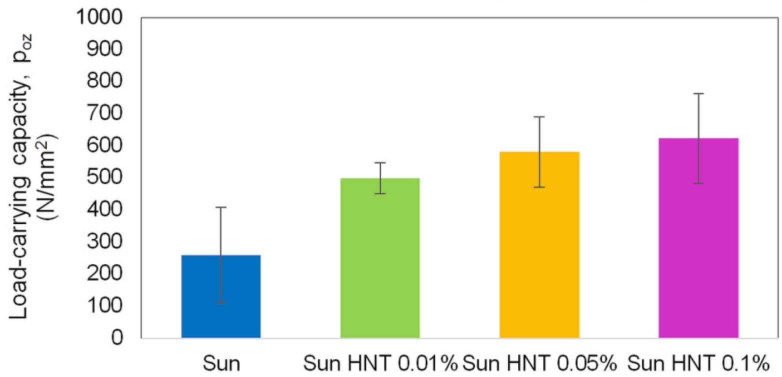

Figure 12. Load-carrying capacity of sunflower nanolubricants under extreme pressure conditions.

With 0.01 wt.%, 0.05 wt.%, and 0.10 wt.%, the p_{oz} of sunflower oil increased to 500 MPa, 581 MPa, and 623 MPa, respectively. This represents an increase of up to 141% of the maximum pressure the sunflower lubricant film withstands before it breaks down and metal–metal contact is obtained. Furthermore, these values are higher than those obtained for distilled water, synthetic lubricants, semi-synthetic lubricants, and greases [33,47].

3.4. Tapping Torque Behavior

Figure 13 shows the results obtained from tapping torque tests conducted in the Grizzly mill following the ASTM D5619 standard procedure. The base sunflower oil showed a maximum tapping torque of 1.64 N·m whereas the best concentration of sunflower nanolubricant results in a torque of 1.11 N·m which is 32.31% lower than the maximum torque produced by the sunflower base oil. This is because the corn base oil produced a lower roughness, requiring the milling machine to spend less energy to do the treads. The presence of HNT NPs in sunflower oil created a thin lubricating film that allowed the particles to transition from sliding to rolling friction, lowering the force and torque required for tapping. Similar results were obtained by Talib et al. [48] when evaluating the lubrication performance of jatropha reinforced with hBN NPs.

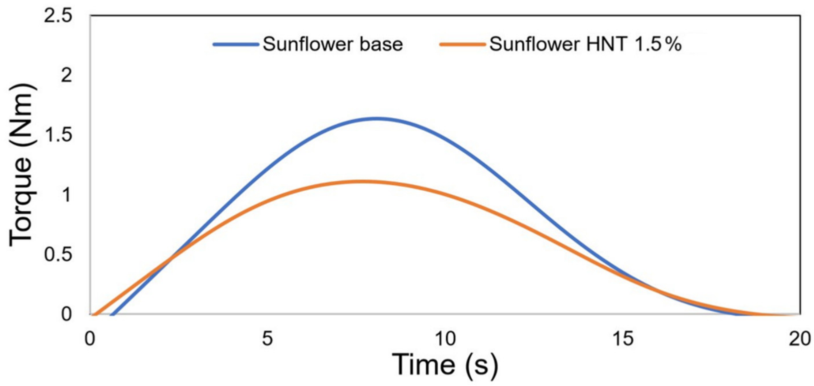

Figure 13. Tapping torque results for base sunflower oil and best concentration sunflower nano-lubricant.

3.5. Surface Analyses

3.5.1. Wear Scar Analysis

Figure 14 shows the SEM images of wear scars on the blocks after the wear tribological tests. In the case of sunflower oil, Figure 14a, it is observable from the wear scars that there are a large number of burrs and furrows. These burrs and furrows increase the friction between the sliding surfaces, thus resulting in a higher mass loss. Large pits and grooves were also found in the wear surface, which increased friction and wear between the sliding surfaces. Figure 14b shows the wear scar produced with the 1.5 wt.% HNT-reinforced sunflower oil. It presents a limited number of burrs and furrows, reducing the frictional force, and resulting in a low volumetric wear. Moreover, the exfoliation that occurs on the surface of the block with the 1.5 wt.% HNT-reinforced sunflower oil also helps to reduce the overall friction during lubrication. It was also noticed that there were fewer grooves on the surface of the used blocks when compared the to base oil used blocks. As it acts as a rolling contact bearing, the inclusion of HNT nanotubes has an impact on the sliding surface, reducing contact. This result indicates that halloysite clay nanotubes play an active role in the contact zone [20].

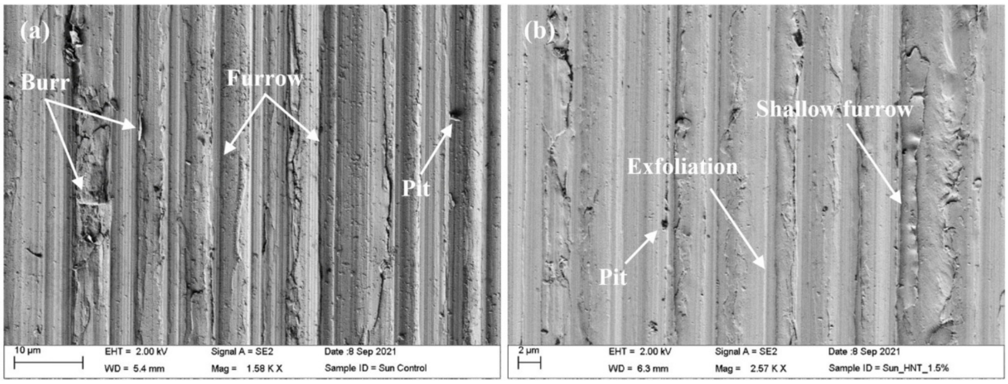

Figure 14. SEM micrographs of worn block surfaces lubricated with (**a**) sunflower oil, and (**b**) sunflower oil reinforced with HNTs at 1.5 wt.%.

3.5.2. Surface Roughness Analysis

The surface roughness of the blocks was measured before and after the tests lubricated with sunflower oil and the nanolubricants reinforced with HNTs at different concentrations. For the low contact pressure tests, the average surface roughness Ra values, acquired by the Mahrsurf M300C surface profilometer, are shown in Figure 15. The average roughness of the block used for the sunflower base oil was higher when compared to the untested specimen. The lowest average roughness was found in the wear scar of the block lubricated with 1.5 wt.% HNT–sunflower oil nanolubricant. It can be observed that the average roughness was decreased by 41.32% compared with the block lubricated with the base sunflower oil. This is due to the higher concentrations of palmitic and oleic acids, which help with friction and roughness due to the double bonds in their chemical compositions. For the high contact pressure tests, the Ra values of sunflower oil, 0.01, 0.05, and 0.10 wt.% HNTs were 0.48 µm, 0.46 µm, 0.37 µm, and 0.45 µm, respectively. Therefore, there was a maximum reduction of 22%. For the extreme pressure test (Figure 16a–d), HNTs were also able to reduce the surface roughness due to the reduced real area of contact. Figure 16a shows the higher amount of debris for the base oil which adhered to the surface providing an Ra of 2.3 µm. With 0.01, 0.05, and 0.10 wt.%, the Ra values were lowered to 0.81 µm, 0.77 µm, and 0.46 µm. Peña-Parás et al. [32] found similar results, in which lower roughness values delayed the loss of the lubricant layer film thickness, explaining anti-wear and friction reduction.

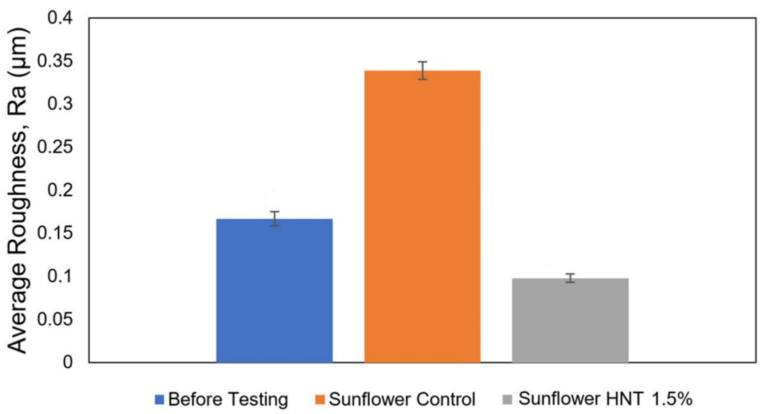

Figure 15. Average surface roughness of AISI 304 blocks before and after wear tests.

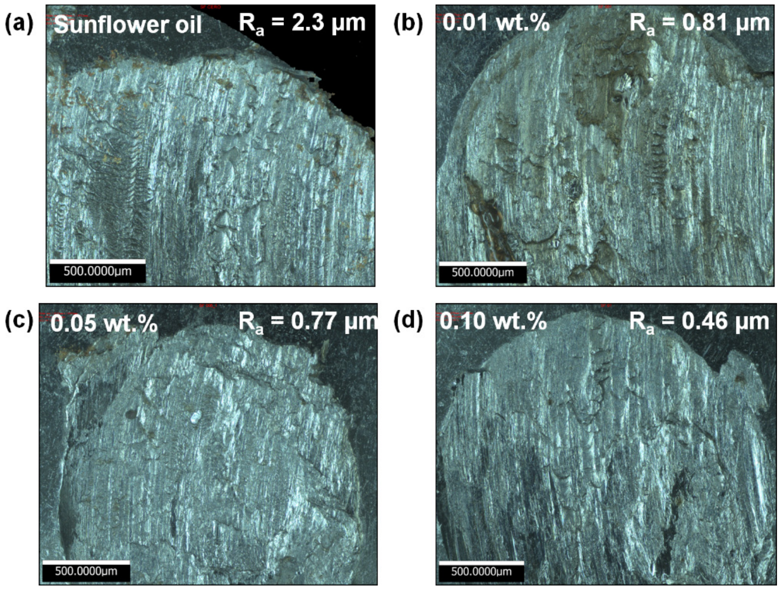

Figure 16. Average surface roughness of ball bearings after the extreme pressure test lubricated with (**a**) sunflower oil and sunflower oil reinforced with HNTs at (**b**) 0.01, (**c**) 0.05, and (**d**) 0.10 wt.%.

3.5.3. Tribological Mechanism of HNTs

SEM images of the wear scars and the related EDS elemental analysis of selected areas for specimens tested with sunflower oil without nanoparticle additives and with HNT nanoparticles at 1.5 wt.% are shown in Figure 17a,b, respectively. EDS analysis was performed to compare the Al and Si levels on the wear track to indicate the presence of HNT nanoparticles. However, for these two specimens, the EDS spectra as shown in Figure 17a,b are almost identical, presenting peaks for the elements contained in the AISI 304 stainless steel. There was no trace of HNT nanoparticles on the wear scar, as shown in Table 2, indicating that HNTs did not form a protective film due to their dimensions—which are larger than the surface roughness of the samples. In this case, a rolling effect or load-bearing mechanism is proposed. A similar behavior was observed in a previous study with mineral oil and synthetic fluid lubricants reinforced with HNTs tested at a contact pressure of 500 MPa [42].

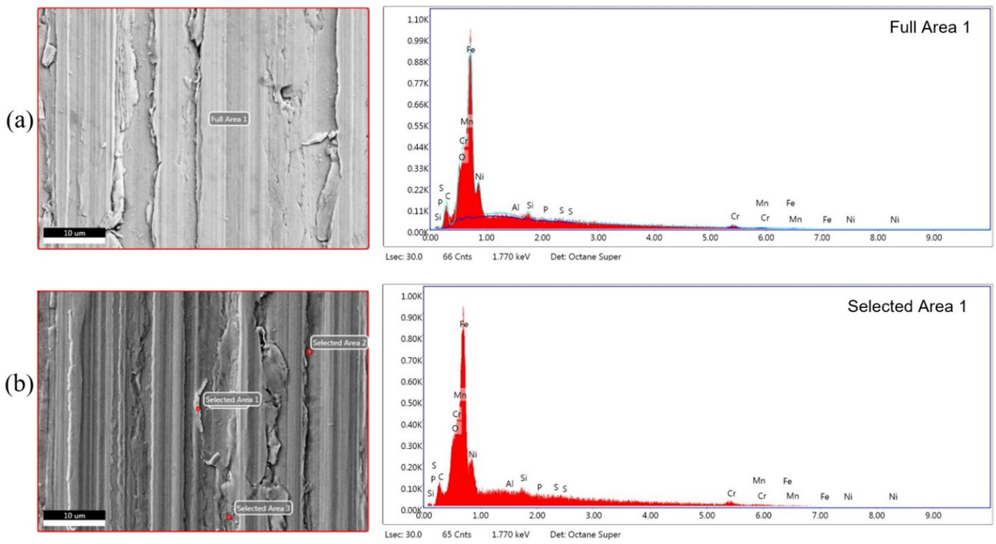

Figure 17. SEM images of the wear scars and the related EDS elemental analysis of selected areas for specimens tested with (**a**) sunflower oil without nanoparticle additives, and (**b**) with HNT nanoparticles at 1.5 wt.%.

Table 2. Elemental analysis of the wear scars produced with sunflower oil with and without HNT nanoparticles.

Element	Sunflower Oil	Sunflower Oil/1.5 wt.% HNT
C K	8.38	8.40
O K	3.60	5.06
Cr L	13.74	12.56
Fe L	58.77	59.42
Ni L	11.54	10.73
Al K	0.18	0.23
Si K	1.78	1.80
P K	0.86	0.85
S K	1.66	0.94

Figure 18 depicts the schematic representation of the proposed tribological mechanism of HNTs under different testing conditions. At low contact pressures, a thicker lubricant film is formed and a higher concentration of HNTs is able to infiltrate the contact area between the surfaces to provide a rolling effect or load-bearing mechanism, requiring in this case an optimal concentration of 1.5 wt.%. However, at high contact pressures or extreme pressure conditions, the lubricant film thickness is reduced and a smaller quantity of HNTs (optimal concentration of 0.05–0.10 wt.%) can enter the contact area between the materials to effectively reduce the real area of contact and lower the friction and wear. Therefore, for industrial applications, the effect of the manufacturing process parameters should be taken into account to determine the optimal HNT concentration in sunflower oil.

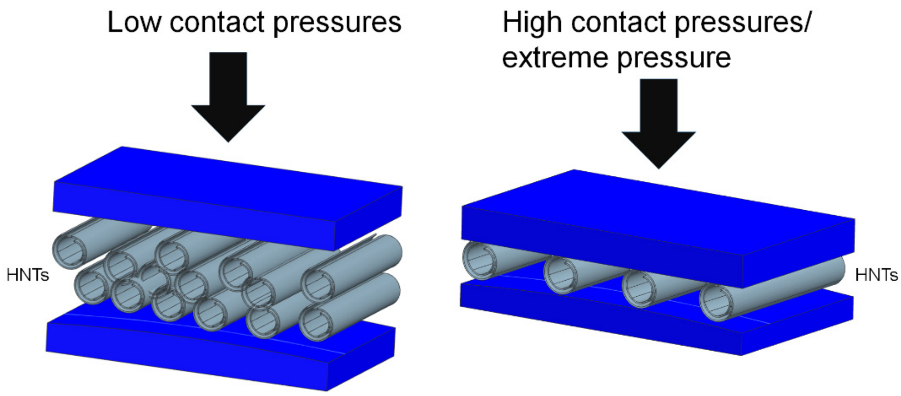

Figure 18. Graphic representation of the proposed tribological mechanism of HNTs at low contact pressures and high contact pressures/extreme pressure.

4. Conclusions

In this work, the lubrication performance of sunflower oil reinforced with HNTs was discussed broadly and the following conclusions were reached:

- The tribological performance of sunflower nanolubricants varied according to the testing conditions (contact pressure), particularly the optimal HNT concentration.
- For the block-on-ring tests, contact load played an important role in the tribological performance and the HNT concentration required for improving tribo-characteristics. HNTs provided a load-bearing tribological mechanism that reduced the real area of contact, thus lowering the COF and wear.
- Under low pressures, sunflower oil mixed with 1.5 wt.% HNTs provided the best tribological behavior. The wear volume loss and COF were lowered by 29% and 70% with the addition of 1.5 wt.% of HNT compared to the base oil.
- Due to the reduction of lubricant film thickness at higher contact pressures, lower concentrations of HNTs with fewer agglomerates can better infiltrate the contact regions and withstand higher loads. Here, the highest reduction in wear was obtained

with 0.05 wt.%. Higher concentrations reduced the enhancement due to the larger particle size caused by agglomeration.

- Extreme pressure testing of the nanolubricants indicated an increase of up to 141% in the load-carrying capacity of sunflower oil with 0.10 wt.% HNTs, from 259 MPa to 623 MPa.
- The frictional force of each nanolubricant was lowered notably from the base oil, which is another indication of improved tribological behavior. The tapping torque test results also provided a high tapping torque efficiency that can prolong tool life in machining processes. The overall tapping torque was reduced by 32.31% for sunflower oil with 1.5 wt.% HNT-reinforced nanolubricant compared to the base oil.
- It can be concluded from these results that sunflower oil reinforced with halloysite clay nanotubes represents a great alternative to mineral and synthetic lubricants. Moreover, its adverse effect on the environment is negligible compared to alternative sources.

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