lubricants

Article

Tribological Properties of h-BN, Ag and MgO Nanostructures as Lubricant Additives in Vegetable Oils

Victoria Granja [1], Kollol Jogesh [2], Jaime Taha-Tijerina [3] and C. Fred Higgs III [1,*]

[1] Particle Flow and Tribology Laboratory, Department of Mechanical Engineering, Rice University, 6100 Main Street, Houston, TX 77005, USA; victoria.granja@rice.edu
[2] Department of Mechanical Engineering, The University of Texas Rio Grande Valley, 1201 W. University Drive, Edinburg, TX 78539, USA; kollolsarker.jogesh01@utrgv.edu
[3] Department of Informatics and Engineering Systems, The University of Texas Rio Grande Valley, Brownsville, TX 78520, USA; jose.taha@utrgv.edu
* Correspondence: higgs@rice.edu

Abstract: There exists an ever-growing need for sustainable engineering solutions to improve emission control and the energy efficiency of tribosystems. This study examines the tribological properties of two environmentally friendly vegetable fluids, soybean and sunflower oil, with the addition of three non-toxic nanostructures (h-BN, silver and MgO) at different concentrations. It was found that nanostructures added to vegetable oils at specific concentrations can exhibit good friction reduction and wear preventive properties. The addition of h-BN nanosheets in sunflower oil decreased the coefficient of friction and the wear damage, as measured by the wear scar diameter. Silver and magnesium oxide nanoparticles further reduced the friction and wear, respectively. In addition to the tribological testing of the samples, investigations were performed using an optical microscope, SEM and EDX to elucidate the mechanisms that may have led to the observed friction reduction and wear-preventive properties of different nanostructure additives. The thermophysical properties of the samples were also measured. It was found that the thermal conductivity of both base oils could be enhanced by 24% when using h-BN at 0.25 wt% concentration.

Keywords: green lubricants; biolubricants; nanoparticles; nanosheets; nanostructures; tribological performance

check for updates

Citation: Granja, V.; Jogesh, K.; Taha-Tijerina, J.; Higgs, C.F., III. Tribological Properties of h-BN, Ag and MgO Nanostructures as Lubricant Additives in Vegetable Oils. *Lubricants* **2024**, *12*, 66. https://doi.org/10.3390/lubricants12030066

Received: 13 January 2024
Revised: 13 February 2024
Accepted: 16 February 2024
Published: 21 February 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The use of vegetable lubricants as alternatives to mineral oils has garnered growing interest, aiming to reduce the carbon footprint of industrialization [1]. The rising adoption of biolubricants stems from global policies that prioritize green chemistry and a circular economy and has attracted significant interest in scientific and industrial realms [2,3]. Vegetable lubricants not only showcase good lubricating properties, but more significantly, they are inherently biodegradable, which results in minimal environmental harm [4,5]. Their biodegradability ranges from 90% to 100%, as compared to mineral oils that showcase a biodegradability of just 10–45%, and they are characterized by their non-hazardous nature and renewable composition, making them a sustainable choice in various technical applications [6]. Studies have demonstrated that the use of biofuels and vegetable lubricants can effectively decrease the emission of contaminants and pollutants, such as CO_2 and other hydrocarbons [7–10]. These types of environmentally friendly and biodegradable lubricants manufactured from vegetable or other natural resources are often referred to as "green lubricants".

When compared to petroleum-based fluids, green lubricants possess a variety of benefits and advantages, including higher lubricity, lower volatility and higher shear stability, detergency, dispersancy and viscosity index [11]. Due to their superior biodegradability and reduced toxicity when compared to traditional petroleum-based products, green lubricants hold significant promise for industrial applications. For this reason, vegetable oils are having a slow but steady comeback in different industry sectors where petroleum-based oils have traditionally been used [7].

However, one of the main challenges in using vegetable oils as lubricants is their poor thermo-oxidability [7,12], which compromises their effectiveness at elevated temperatures. The incorporation of nanostructures to base lubricants have traditionally been explored as a way to reduce the coefficient of friction and enhance its wear-preventive properties. However, nanostructures can also act as thermal dissipators of the heat generated in the tribosystem [13–16], ultimately resulting in an overall improved performance.

Numerous investigations have explored the utilization of nanoparticles in lubrication [17]. The effectiveness in decreasing friction and wear is closely linked to the specific attributes of nanoparticles, including their size, shape and concentration, as highlighted by Hu et al. [18]. The diminutive size of nanoparticles can be deemed as the most important feature that facilitates their penetration into the contact area, yielding a favorable lubrication effect [19,20].

The majority of papers reporting the effect of nanoparticles on lubricants have focused on mineral or synthetic base oils. However, research is now leaning towards the development of effective combinations of biolubricants and nanostructures and the study of their tribological performance. In a recent study, Kumar et al. [21] reported that adding CuO nano-oxides into sunflower and soybean oil resulted in a 35% and 29% reduction in coefficient of friction (COF) at a concentration of 0.25 wt%. Conversely, the addition of ZrO_2 reduced the COF by 27% in sunflower oil but showed no improvement in soybean oil. A different study by Alves et al. [22] found that zinc oxide and copper oxide nanoparticles were ineffective as anti-wear additives for soybean and sunflower oils, leading to increased abrasive wear on the worn surfaces. It is important to note that due to the various types, sizes and morphology of nanoparticles, and the different intrinsic properties of the base oils, each combination of nanoparticles and lubricants will exhibit completely different tribological performances.

In this work we explore the tribological performance and thermophysical properties of a set of novel green multi-functional lubricants that combine environmentally friendly oils with nontoxic nanoparticles and nanosheets. These results will inform the viability to use these mixtures in different applications where traditional petroleum-based lubricants are used.

2. Experimental

2.1. Materials

Soybean and sunflower vegetable oils are used as base lubricants (Table 1). The oils are obtained from Aceites, Grasas y Derivados, S.A. de C.V. (Zapopan, Jalisco, Mexico). Three different nanostructures (h-BN, Ag and MgO) are added at various filler fractions (0.01, 0.05, 0.10 and 0.25 wt%) to the base oils to formulate vegetable nanolubricants.

Nanostructures can be classified based on their shape and dimensionality into nanoparticles, nanofibers, nanosheets, nanorods, etc. In this study, 2D nanosheets of h-BN are synthesized according to Taha et al. [23] by the liquid exfoliation method. Ag and MgO 0D-nanoparticles are obtained from Sigma Aldrich (See Table 2). The nanolubricants are prepared by homogeneously dispersing the nanostructures within the vegetable lubricants. First, the mixtures are manually agitated for 10 min. Then, the samples are further homogenized using a Bransonic CPX5800 water bath ultrasonicator for 6 cycles of 1 h each. Fresh water is used in every cycle to avoid changes of temperature due to vibration.

Table 1. Properties of base oils [24].

Raw Lubricant	Viscosity @ 50 °C [mPa·s]	Density @ 20 °C [kg/m^3]	Thermal Conductivity @ 50 °C [W/m K]
Sunflower	28.50	917.8	0.163
Soybean	23.59	910.6	0.155

Table 2. Properties of h-BN, Ag and MgO nanostructures.

Nanostructures	CAS	Size [nm]	Hardness [MPa]	Density [kg/m^3]	Thermal Conductivity [W/m K]
h-BN	10043-11-5	300 by 400	660–3000	2100	220–420
Ag	7440-22-4	<100	250–1100	10,490	430
MgO	1309-48-4	<50	5000–7000	3600	30–60

2.2. Tribological Testing—Four-Ball Configuration

The tribological performance of the samples is studied by means of a four-ball tribometer (Figure 1). The testing parameters are set in accordance to the ASTM standard D4172-A, i.e., speed 1200 rpm, load 147 N, duration of the test 3600 s. The temperature is adjusted to 50 °C instead of 75 °C to guarantee the thermal stability of the samples.

In a four-ball test, three chromium steel, AISI 52100, grade 25 balls that are 12.7 mm in diameter are clamped together in a triangular formation, and an upper fourth ball is rotated against the lower three balls, generating a point contact with each of them. The whole assembly is then immersed in the fluid of interest and loaded from the bottom.

The coefficient of friction (COF) is recorded as a function of time for all the tests. The average of the time-series coefficient of friction is reported for each test. After running evaluations for one hour, the wear scar diameter (WSD) of the lower three balls is measured by means of an optical microscope. The average value of these measurements for a given test is the reported value of WSD. Three tests are conducted for each mixture to report the standard error.

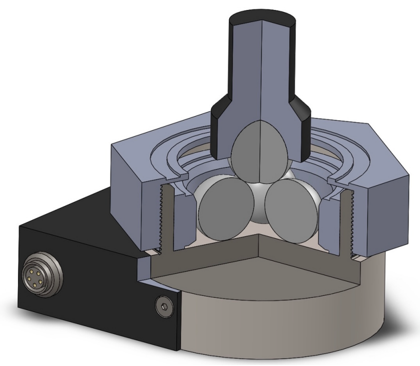

Figure 1. Schematic of the Four-ball testing assembly.

2.3. Thermophysical and Fluid Property Evaluation

2.3.1. Thermal Conductivity

The transient hot-wire technique was employed to determine the thermal conductivity of the mixtures. In this method, a line heat source probe is inserted into a glass vial containing the nanolubricant which is initially at constant and uniform temperature. The line heater is supplied with power and the temperature adjacent to the heat source is monitored and recorded over time. The system waits for 30 s for thermal equilibrium of the evaluated material before the heating stage starts for over 30 s. The temperature is then recorded both during the heating and cooling phases. A KD2 Pro thermal analyzer equipped with a KS-1 sensor is used for this purpose. Meaurements are conducted at room temperature (300 K).

2.3.2. Viscosity

The viscosity was measured using a Haake Mars 40 Rheometer (Thermo Fisher Scientific, Waltham, MA, USA) with a parallel-plate configuration. Each sample was evaluated at a shear rate ranging from 0.1 to 1000 1/s. All the reported values were measured at 50 °C (323 K), which is the temperature at which the tribological tests are run.

2.4. *Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)*

Energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM) images of the wear scars after tribological evaluations were obtained using a high-resolution field emission scanning electron microscope (FEI Quanta 400 ESEM FEG, Waltham, MA, USA). The SEM images are captured at 200× and 600× magnification with a dwell time per pixel of 60 µs and an 11.3 mm working distance in high vacuum. The electron landing energy is set to 15 kV using the through lens detector in the back scatter electron detection mode. The EDS spectra is captured with a resolution of 131.3 eV and amp time of 7.68 µs.

3. Results and Discussion

3.1. *Tribological Tests*

Figures 2 and 3 show the average COF and average WSD of the different mixtures as a function of concentration. In the secondary vertical axes, the thermal conductivity and the viscosity of the mixtures are displayed. For all parameters, the error bars represent one standard error (n = 3).

In these Figures, green boxes are placed on top of the best-performing mixtures to indicate the % of reduction in COF or WSD obtained by the incorporation of the nanostructure into the base oil. For instance, Figure 2 shows that the addition of 0.05 wt% h-BN in sunflower oil lead to the largest reduction in COF, i.e., 21% . A clear U shape is observed when analyzing the bar plot of COF as a function of h-BN concentration. As h-BN has a similar lamellar structure to graphene [25], the tribological performance of the mixtures can be explained by the mechanism proposed in Zhang et al. [26] for lubricants using graphene as additives. Zhang et al. claims that at lower concentrations the lamellar structures can form a protective layer atop the interacting surfaces reducing wear, and at slightly higher concentrations these lamellar structures can slide upon each other reducing the COF. However, as the additive exceeds a critical concentration, it can pile up and the oil film becomes much more discontinuous, thus degrading the lubricating properties.

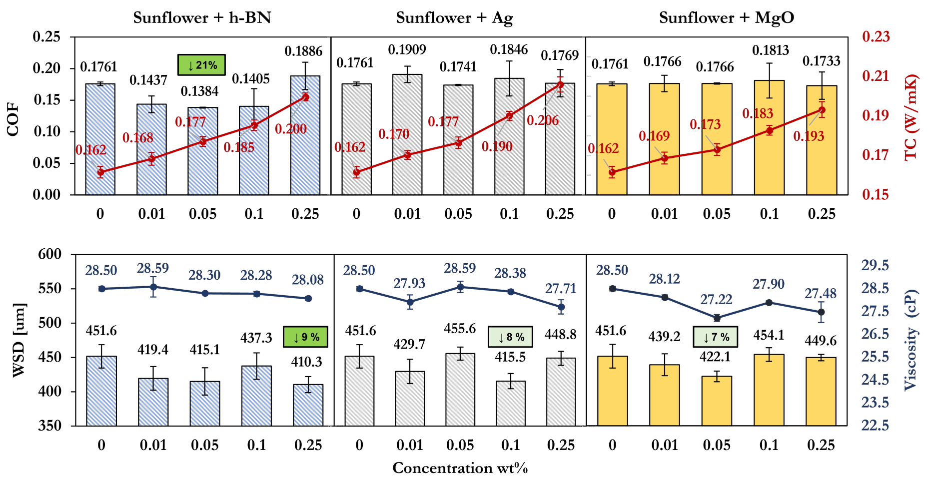

Figure 2. Tribological properties of sunflower oil cs. wt% concentration of h-BN, Ag and MgO nanostructures. The error bars represent one standard error (N = 3). The first data point is representative of the base oil.

From Figure 2, it can also be noted that the addition of Ag and MgO nanoparticles did not have a significant effect on the COF of the mixtures. However, the addition of the three types of additives did show a meaningful change in the wear-preventive properties at specific concentrations. In the case of h-BN, the highest reduction of WSD was obtained with the addition of 0.25 wt%, leading to a reduction of 9% in WSD. While the addition of 0.1 wt% of Ag and 0.05 wt% of MgO lead to a reduction in WSD of 8% and 7%, respectively.

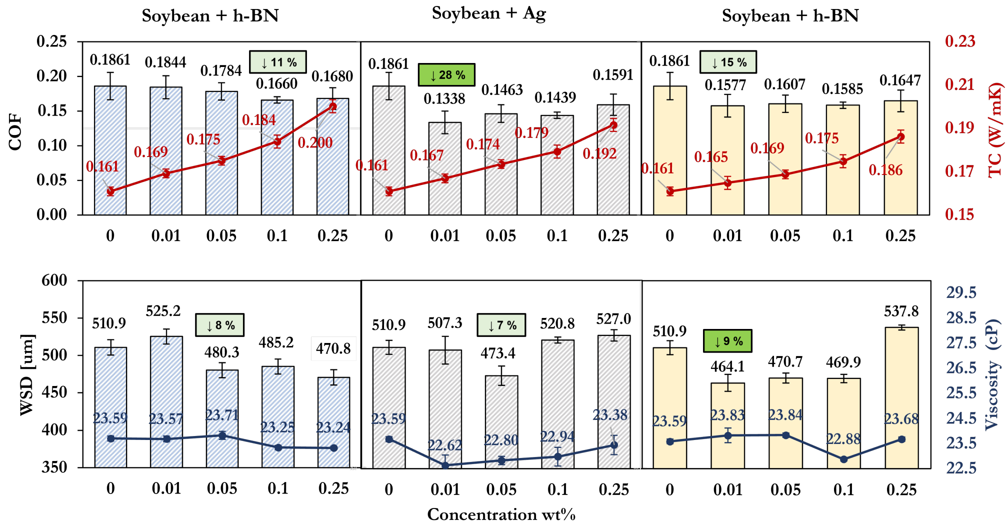

Figure 3. Tribological properties of soybean oil cs. wt% concentration of h-BN, Ag and MgO nanostructures. The error bars represent one standard error (N = 3). The first data point is representative of the base oil.

In the case of soybean oil (Figure 3), it is observed that the average COFs of all mixtures are lower than that of pure base oil, indicating that the three additives can enhance the friction reduction ability. The best performing samples in terms of COF are soybean oil with the addition of 0.01 wt% Ag, which lead to a reduction in COF of 28%, soybean oil with 0.1 wt% h-BN and soybean oil with 0.01 wt% MgO with a reduction of 11% and 15% in COF respectively. In all cases there is a decreasing trend in COF for lower concentrations of nanostructures; however, when exceeding a threshold in concentration, an increase in COF is observed.

The trend is the same in terms of WSD as a function of concentration when using Ag and MgO nanoparticles. This illustrates that h-BN, Ag and MgO nanostructures adhere to the surface of the rubbing metallic balls, forming a protective film that prevents direct contact of the friction pairs, thus reducing friction. This remains true until a certain value of concentration is exceeded generating the discontinuity of the lubricating film, thus leading to the degradation of the tribological properties. This discontinuity is caused by the aggregation and entanglement of nanostructures at higher concentrations. The agglomeration effect restricts the additives and base oil to enter the surface of the rubbing friction pairs, leading to a reduction in the friction-reduction and wear-prevention performance.

In summary, no meaningful change in COF is evidenced with the incorporation of the reinforcing nanostructures in the case of sunflower oil, except for the addition of h-BN. In the case of soybean oil, a decrease in COF was observed with the addition of any of the three nanostructures. On the other hand, a reduction in wear scar diameter of around 10% could be obtained for both vegetable oils using any of the nanostructures at specific concentrations.

3.2. Nanostructures Size

An extensive research has been conducted to determine the effect of additive size on system performance [27–30]. Previous studies have shown in numerous instances that sub-micron-sized powder lubricants demonstrate superior tribological abilities in comparison to micron-sized powder lubricants due to their size being similar to the surface asperities [31–33].

In this study, no clear effect of nanostructures' size over the tribological performance of the samples is evidenced in the results. One would expect smaller nanostructures to have a more meaningful effect in the lubricating performance of the sample, as the nanostructures would more easily and readily be introduced in between the asperities of the contacting surfaces [25,27]. However, an improvement of the tribological properties of the samples when using smaller nanostructures is not clearly evidenced in this study, as all the additives used in this study are nano-sized structures. Previous studies have concluded that an optimal size of nanostructures is required below which no improvement in frictional properties occur [11], implying that the size of the nanostructures used in this study was below the optimum size.

3.3. Thermophysical Properties

Thermal conductivity is a critical property of lubricants because thermal dissipation can enhance the tribological performance of the system. In general, previous studies have shown that an enhanced thermal conductivity will not just translate to higher cooling rates, but also to reduced friction and improved wear resistance [34–39].

It is observed that for all the mixtures, an increase in reinforcing filler fraction translates to an improvement in thermal conductivity. This was expected since prior research has proven that thermal conductivity enhancement of nanofluids directly depends on the thermal conductivity and concentration of the reinforcing solid particles [40–42].

Results show that the addition of 0.25 wt% h-BN increase the thermal conductivity of both conventional vegetable oils by approximately 24%. In the case of MgO nanolubricants, thermal conductivity increased by 22% at 0.25 wt%. Meanwhile, with Ag nanofiller as a reinforcement, the thermal conductivity of sunflower oil increased by almost 28%, and of soybean oil by 19%.

3.4. Lubrication Mechanism

Viscosity seems to have a more meaningful effect on the wear rate of the samples than thermal conductivity. No meaningful change in viscosity is evidenced with the addition of nanostructures at different filler fractions; however, it can be observed that in general, sunflower oil exhibits a higher viscosity than soybean oil, as expected from its lower unsaturation levels. It is observed that higher viscosities translate into less wear. Sunflower oil mixtures display notably smaller WSD values compared to soybean oil mixtures.The samples with combined highest viscosity and highest thermal conductivity are the ones that exhibit the lowest WSD amongst all samples.

On the other hand, viscosity does not seem to have such a noticeable effect on the COF. This could be explained by the fact that, as predicted by Hamrock and Dowson (Equations (1)–(3)), the system operated in the boundary lubrication regime. In this regime, the COF is affected by the nature of the surface and lubricant type but is largely independent of viscosity [43,44].

$$H_c = 2.69U^{0.67}G^{0.53}W^{-0.067}(1 - 0.61e^{-0.73k}) \quad (1)$$

$$H_{min} = 3.63U^{0.68}G^{0.49}W^{-0.073}(1 - e^{-0.68k}) \quad (2)$$

$$H_c = h/R^{'} \quad (3)$$

The tribosystem and test conditions are represented by the parameters listed in Table 3. The Hamrock and Dowson equations predict central film thicknesses within the range of 28.6–29.6 nm and minimum film thicknesses of 16.7–17.2 nm for sunflower oil, and central film thicknesses within the range of 25.3–26.2 nm and minimum film thicknesses of

14.7–15.2 nm for soybean oil. The roughness of the chrome steel balls was measured using a white light interferometer and it was found to be 126 nm. Therefore, the ratio of the film thickness to the surface roughness, λ, is found to be less than unity, clearly indicating that the system operated in boundary lubrication conditions.

Table 3. Tribosystem constants and parameters used to calculate lubricant film thickness.

Parameter	Equation	Sunflower Oil	Soybean Oil
Reduced radius, R′ [m]	$1/R_x = (2/R_1 + 2/R_2)$	0.00159	0.00159
Reduced Youngs' modulus, E′ [Pa]	$E' = E/(1-\nu^2)$	2.31×10^{11}	2.31×10^{11}
Contact load (per ball), F [N]	$F = (1.224745P)/3$	60.012505	60.012505
Viscosity, η [mPa·s]	measured exp	27.22–28.59	22.62–23.84
Elliptical parameter, k	$k = 1.03(R_y/R_x)^{0.64}$	1.03	1.03
Asymptotic isoviscous pressure, P_{ivas} [Pa]	$P_{ivas} = 1/\alpha$	1.09×10^8	1.14×10^8
Pressure viscosity coefficient, α [GPa^{-1}]	α	9.2	8.8
Dimensionless speed parameter, U	$U = \eta_0 V/E'R'$	3.06×10^{-11}	2.54×10^{-11}
Dimensionless material parameter, G	$G = E'/P_{ivas}$	2123.08	2123.08
Dimensionless load parameter, W	$W = F/E'R_x^2$	1.03×10^{-4}	1.03×10^{-4}

As nanostructures are most efficient in boundary and mixed lubrication [45], two basic mechanisms of nanoscale reinforcement efficiency are considered. The first mechanism is the "mending effect", which includes the filling of the micro-asperities of the friction surface with the nanostructures from the lubricating fluid. This can cause the increase of contact area of friction surfaces, the decrease of the contact pressure and the replacement of the sliding friction with the rolling effect [46,47]. The second mechanism is related to the formation of a physical and/or chemical tribofilm. The presence of a tribofilm usually translates to an enhancement of the tribo-system's performance due to its low shear resistance in boundary lubrication conditions [48]. Such tribofilm operates as a soft coating of the substrates reducing the friction force and protecting the surfaces from wearing by preventing their direct contact [49]. Research indicates that the formation of a tribofilm occurs in two distinct stages, which are categorized based on the intensity of tribochemistry reactions [50,51]. Initially, nanoadditives can adhere to the surface through van-der-Waals force and/or electrostatic attraction, forming a protective film without chemical reactions. As friction continues, the film decomposes due to high pressure and frictional heat, leading to tribochemical reactions and the formation of a new tribofilm that gradually replaces the physical film, and leads to significant improvements in the tribological performance of the system [52–54].

SEM-EDX analysis is conducted to investigate the lubrication mechanism of the top-performing samples. After the tribological tests, the balls are cleaned using acetone and heptane. Electron microscopy images of the worn and unworn surfaces of the balls are then collected, and EDS analysis are performed to provide a combined morphological and chemical overview of the samples. The aim of these analyses is to determine the formation or not of a tribofilm during the tribological tests.

As observed in Figures 4 and 5, small traces of elements not detected on the wear scars of the samples lubricated by just base oils, are found on the worn area of the samples lubricated by the mixtures. However, the intensity of the peaks (weight %) of these additional elements in the EDS analysis are not pronounced enough to imply the formation of a chemical tribofilm after the tribo tests. Therefore, it is believed that there existed a formation of a solely physical tribofilm, which was likely removed during the cleaning process since physical films are typically susceptible to removal through mechanical or chemical cleaning methods without undergoing chemical reactions.

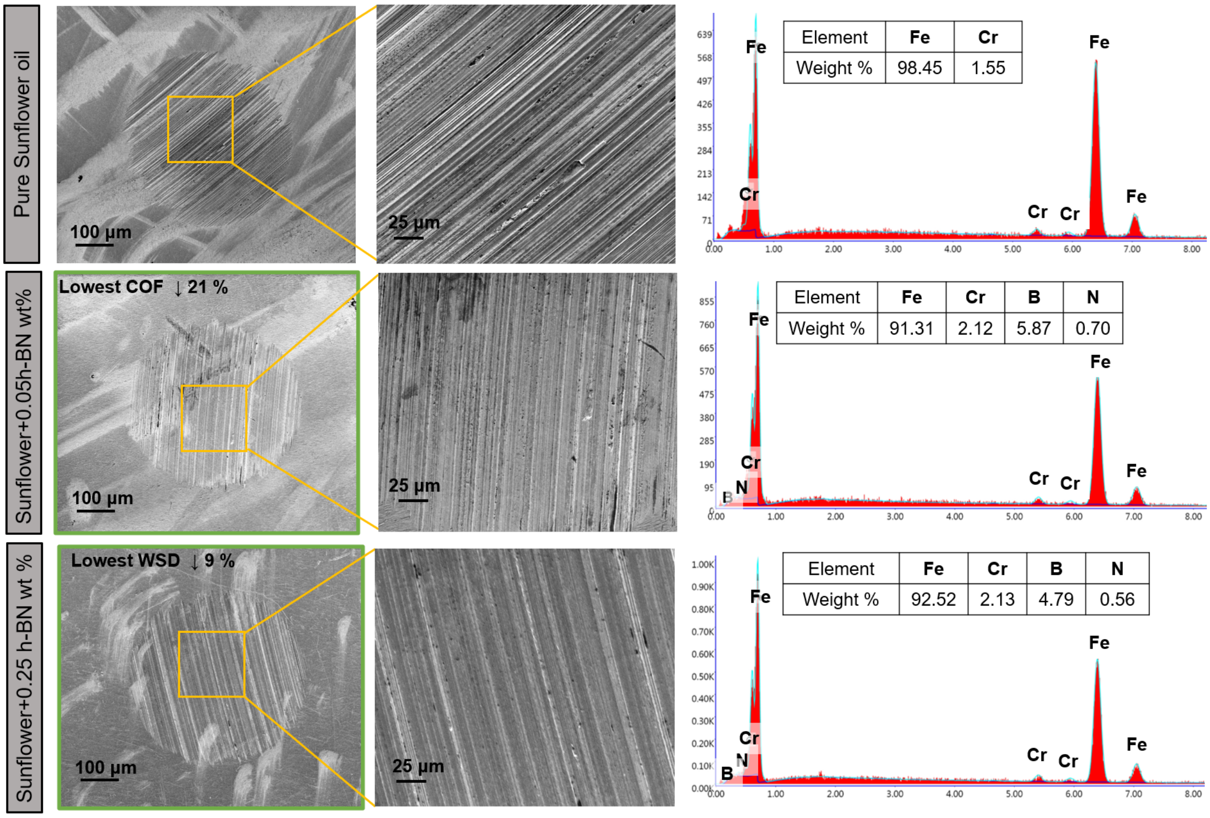

Figure 4. SEM and EDS analysis of the wear scar of the best performing samples of sunflower oil.

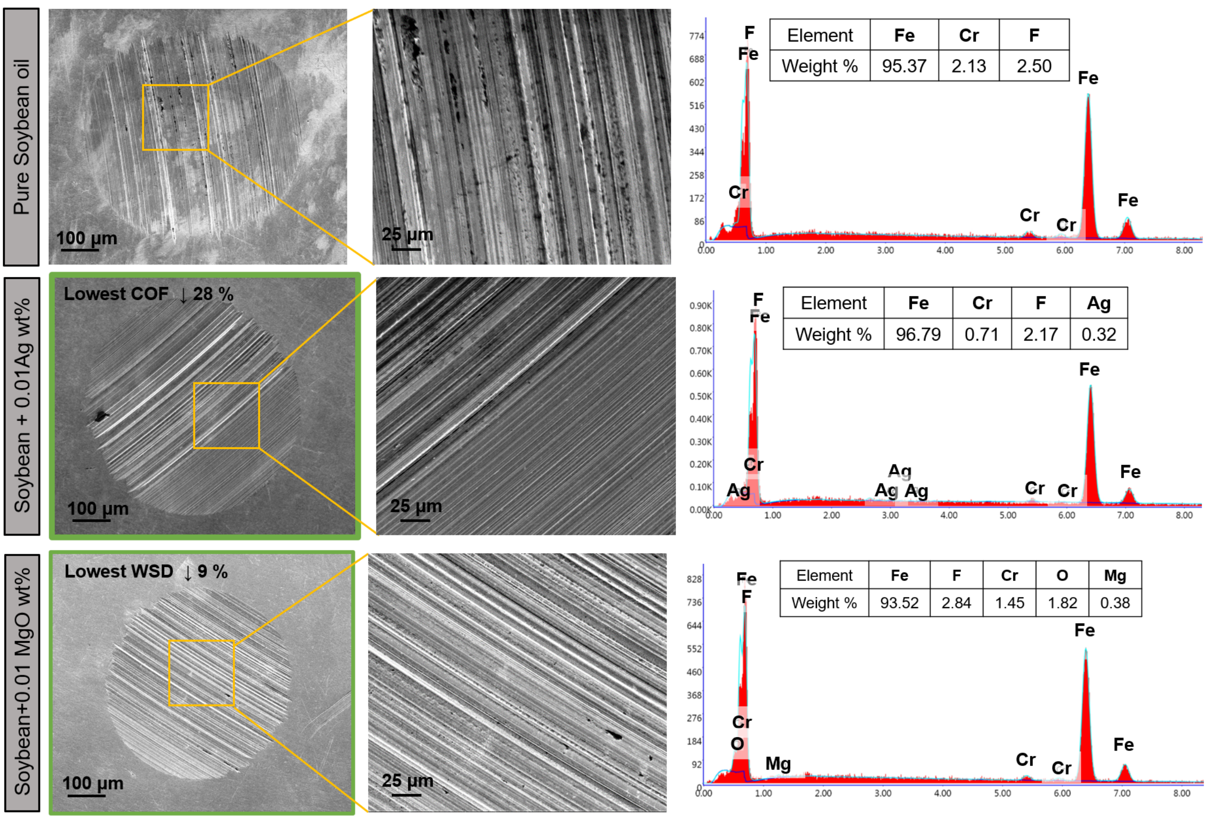

Figure 5. SEM and EDS analysis of the wear scar of the best performing samples of soybean oil.

It is also observed that the wear scars of the samples lubricated by pure base oils are evidently rough with many thick and deep furrows, while the wear scars lubricated by base oil with nanostructures are comparably rather smoother and the furrows are shallower. Moreover, the samples lubricated with pure base oils show signs of pitting on the worn tracks, which occurs when surface-defect fatigue leads to the creation of small, shallow craters.

The long parallel grooves are a clear indication of abrasive wear. This type of wear could be a product of two-body or three-body abrasion. For conventional oils, the third body could be the debris generation from the direct contact of the surfaces and the polishing of asperities removed by the sliding movement of the top ball against the lower three balls. When adding nanostructures, depending on their hardness, they can act as abrading third bodies. It can be noted from Figure 4 that not significant signs of abrasion (deep furrows) could be identified in the wear scars when using h-BN as an additive . This means that h-BN nanosheets were deposited on the surface and acted as soft third body particles, which decreased the shear stress. These deposited nanostructures were more stable than the debris of the sliding materials.

When analyzing the microscopy wear-scar images captured before cleaning the samples (Figure 6), it is observed that debris was not welded to or formed a transfer film on the sliding surfaces after the evaluations. However, a black sediment is observed on most of the samples after the tribological tests. This black sediment formation could be a consequence of the oxidation or carbonization of the oil. Vegetable oils are susceptible to oxidation when exposed to high temperatures or oxygen in the air. This process can lead to the formation of dark-colored sediments due to the breakdown of oil molecules. Additionally, it is common that under high-pressure and high-temperature conditions, some components of vegetable oils can undergo carbonization, forming black sediments resembling carbon or soot.

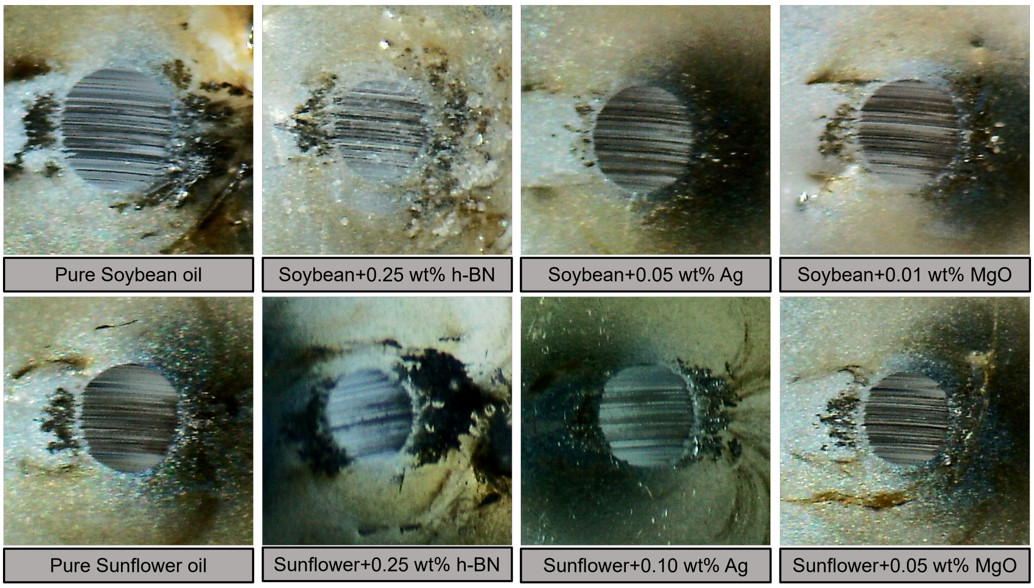

Figure 6. Microscopy images of the wear scar captured before cleaning the samples.

4. Conclusions

By means of four-ball tribotesting, it was found that the COF of vegetable oils can be enhanced with the incorporation of solid nanostructures. Results show that the addition of 0.25 wt% of h-BN nanosheets led to reductions in COF of up to 28% in the case of soybean oil and 21% in the case of sunflower oil. Ag and MgO nanoparticles did not show significant reduction for the sunflower nanolubricants. On the other hand, both of these Ag and MgO nanostructures performed slightly better at lower filler fraction, showing improvements of 28% and 15% for soybean oil at 0.10 wt% and 0.01 wt%, respectively. From these evaluations, reductions in wear rate of up to 10% for both vegetable oils were observed.

The thermal conductivity of both vegetable oils could be improved by 24%, 22% and 28% when using h-BN, MgO and Ag at 0.25 wt% filler fraction. Thus, the lubricant is multi-functional with enhanced tribological and thermal performances.

These results show that vegetable oils with the addition of h-BN, Ag and MgO nanostructures are promising as a safe, environmentally friendly and sustainable lubricant that may enhance the tribological performance and extend the lifetime of mechanical systems. However, more work is necessary to develop additives that prevent the oxidation and carbonization of vegetable oils when working at high pressures and temperatures.

Author Contributions: Conceptualization, V.G., K.J. and J.T.-T.; Methodology, V.G.; Formal analysis, V.G.; Investigation, V.G. and K.J.; Resources, J.T.-T. and C.F.H.III; Data curation, V.G.; Writing—original draft, V.G.; Writing—review & editing, J.T.-T. and C.F.H.III; Visualization, V.G.; Supervision, J.T.-T. and C.F.H.III; Funding acquisition, C.F.H.III. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Willing, A. Lubricants based on renewable resources—An environmentally compatible alternative to mineral oil products. *Chemosphere* **2001**, *43*, 89–98. [CrossRef]
2. Nogales-Delgado, S.; Encinar, J.M.; González, J.F. A Review on Biolubricants Based on Vegetable Oils through Transesterification and the Role of Catalysts: Current Status and Future Trends. *Catalysts* **2023**, *13*, 1299. [CrossRef]
3. Hamnas, A.; Unnikrishnan, G. Bio-lubricants from vegetable oils: Characterization, modifications, applications and challenges—Review. *Renew. Sustain. Energy Rev.* **2023**, *182*, 113413. [CrossRef]
4. Shafi, W.K.; Raina, A.; Ul Haq, M.I. Friction and wear characteristics of vegetable oils using nanoparticles for sustainable lubrication. *Tribol.-Mater. Surf. Interfaces* **2018**, *12*, 27–43. [CrossRef]
5. Murru, C.; Badía-Laíño, R.; Díaz-García, M.E. Oxidative stability of vegetal oil-based lubricants. *ACS Sustain. Chem. Eng.* **2021**, *9*, 1459–1476. [CrossRef]
6. Boyde, S. Green lubricants. Environmental benefits and impacts of lubrication. *Green Chem.* **2002**, *4*, 293–307. [CrossRef]
7. Panchal, T.M.; Patel, A.; Chauhan, D.; Thomas, M.; Patel, J.V. A methodological review on bio-lubricants from vegetable oil based resources. *Renew. Sustain. Energy Rev.* **2017**, *70*, 65–70. [CrossRef]
8. Choi, U.; Ahn, B.; Kwon, O.; Chun, Y. Tribological behavior of some antiwear additives in vegetable oils. *Tribol. Int.* **1997**, *30*, 677–683. [CrossRef]
9. Karmakar, G.; Ghosh, P.; Sharma, B.K. Chemically modifying vegetable oils to prepare green lubricants. *Lubricants* **2017**, *5*, 44. [CrossRef]
10. Erhan, S.Z.; Asadauskas, S. Lubricant basestocks from vegetable oils. *Ind. Crop. Prod.* **2000**, *11*, 277–282. [CrossRef]
11. Menezes, P.L.; Lovell, M.R.; Kabir, M.; Higgs, C.F.; Rohatgi, P.K. Green lubricants: Role of additive size. In *Green Tribology: Biomimetics, Energy Conservation and Sustainability*; Springer: Berlin/Heidelberg, Germany, 2012; pp. 265–286.
12. Fox, N.; Stachowiak, G. Vegetable oil-based lubricants—A review of oxidation. *Tribol. Int.* **2007**, *40*, 1035–1046. [CrossRef]
13. Sharma, A.K.; Tiwari, A.K.; Dixit, A.R. Progress of nanofluid application in machining: A review. *Mater. Manuf. Process.* **2015**, *30*, 813–828. [CrossRef]
14. Ben Said, L.; Kolsi, L.; Ghachem, K.; Almeshaal, M.; Maatki, C. Application of nanofluids as cutting fluids in machining operations: A brief review. *Appl. Nanosci.* **2023**, *13*, 4247–4278. [CrossRef]
15. Kishawy, H.A.; Hegab, H.; Deiab, I.; Eltaggaz, A. Sustainability assessment during machining Ti-6Al-4V with nano-additives-based minimum quantity lubrication. *J. Manuf. Mater. Process.* **2019**, *3*, 61. [CrossRef]
16. Kadirgama, K. A comprehensive review on the application of nanofluids in the machining process. *Int. J. Adv. Manuf. Technol.* **2021**, *115*, 2669–2681. [CrossRef]
17. Gulzar, M.; Masjuki, H.; Kalam, M.; Varman, M.; Zulkifli, N.; Mufti, R.; Zahid, R. Tribological performance of nanoparticles as lubricating oil additives. *J. Nanopart. Res.* **2016**, *18*, 1–25. [CrossRef]
18. Hu, Z.; Dong, J.; Chen, G.; He, J. Preparation and tribological properties of nanoparticle lanthanum borate. *Wear* **2000**, *243*, 43–47. [CrossRef]
19. Demas, N.G.; Timofeeva, E.V.; Routbort, J.L.; Fenske, G.R. Tribological effects of BN and MoS 2 nanoparticles added to polyalphaolefin oil in piston skirt/cylinder liner tests. *Tribol. Lett.* **2012**, *47*, 91–102. [CrossRef]
20. Ghaednia, H. An Analytical and Experimental Investigation of Nanoparticle Lubricants. Ph.D. Thesis, Auburn University, Auburn, AL, USA, 2014.

21. Kumar, R.; Gautam, R. Tribological investigation of sunflower and soybean oil with metal oxide nanoadditives. *Biomass Convers. Biorefinery* **2024**, *14*, 2389–2401. [CrossRef]
22. Alves, S.M.; Barros, B.S.; Trajano, M.F.; Ribeiro, K.S.B.; Moura, E. Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions. *Tribol. Int.* **2013**, *65*, 28–36. [CrossRef]
23. Taha-Tijerina, J.; Narayanan, T.N.; Gao, G.; Rohde, M.; Tsentalovich, D.A.; Pasquali, M.; Ajayan, P.M. Electrically insulating thermal nano-oils using 2D fillers. *ACS Nano* **2012**, *6*, 1214–1220. [CrossRef]
24. Rojas, E.E.G.; Coimbra, J.S.; Telis-Romero, J. Thermophysical properties of cotton, canola, sunflower and soybean oils as a function of temperature. *Int. J. Food Prop.* **2013**, *16*, 1620–1629. [CrossRef]
25. Advincula, P.A.; Granja, V.; Wyss, K.M.; Algozeeb, W.A.; Chen, W.; Beckham, J.L.; Luong, D.X.; Higgs, C.F., III; Tour, J.M. Waste plastic-and coke-derived flash graphene as lubricant additives. *Carbon* **2023**, *203*, 876–885. [CrossRef]
26. Zhang, W.; Zhou, M.; Zhu, H.; Tian, Y.; Wang, K.; Wei, J.; Ji, F.; Li, X.; Li, Z.; Zhang, P.; et al. Tribological properties of oleic acid-modified graphene as lubricant oil additives. *J. Phys. D Appl. Phys.* **2011**, *44*, 205303. [CrossRef]
27. Lovell, M.R.; Kabir, M.; Menezes, P.L.; Higgs, C.F., III. Influence of boric acid additive size on green lubricant performance. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2010**, *368*, 4851–4868. [CrossRef]
28. Ilie, F.; Tita, C. Tribological properties of solid lubricant nanocomposite coatings on base of tungsten disulphide nanoparticles. *Tribol.-Finn. J. Tribol.* **2008**, *27*, 5–11.
29. Hu, X.; Hu, S.; Zhao, Y. Synthesis of nanometric molybdenum disulphide particles and evaluation of friction and wear properties. *Lubr. Sci.* **2005**, *17*, 295–308. [CrossRef]
30. Hu, X. On the size effect of molybdenum disulfide particles on tribological performance. *Ind. Lubr. Tribol.* **2005**, *57*, 255–259. [CrossRef]
31. Cizaire, L.; Vacher, B.; Le Mogne, T.; Martin, J.; Rapoport, L.; Margolin, A.; Tenne, R. Mechanisms of ultra-low friction by hollow inorganic fullerene-like MoS2 nanoparticles. *Surf. Coat. Technol.* **2002**, *160*, 282–287. [CrossRef]
32. Leshchinsky, V.; Popovitz-Biro, R.; Gartsman, K.; Rosentsveig, R.; Rosenberg, Y.; Tenne, R.; Rapoport, L. Behavior of solid lubricant nanoparticles under compression. *J. Mater. Sci.* **2004**, *39*, 4119–4129. [CrossRef]
33. Rapoport, L.; Leshchinsky, V.; Lvovsky, M.; Lapsker, I.; Volovik, Y.; Feldman, Y.; Popovitz-Biro, R.; Tenne, R. Superior tribological properties of powder materials with solid lubricant nanoparticles. *Wear* **2003**, *255*, 794–800. [CrossRef]
34. Xu, Z.Y.; Hu, K.H.; Han, C.L.; Hu, X.G.; Xu, Y.F. Morphological influence of molybdenum disulfide on the tribological properties of rapeseed oil. *Tribol. Lett.* **2013**, *49*, 513–524. [CrossRef]
35. Saidur, R.; Leong, K.; Mohammed, H.A. A review on applications and challenges of nanofluids. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1646–1668. [CrossRef]
36. Liu, M.S.; Lin, M.C.C.; Huang, I.T.; Wang, C.C. Enhancement of thermal conductivity with carbon nanotube for nanofluids. *Int. Commun. Heat Mass Transf.* **2005**, *32*, 1202–1210. [CrossRef]
37. Ismail, M.F.; Azmi, W.H.; Mamat, R.; Ali, H.M. Thermal and tribological properties enhancement of PVE lubricant modified with SiO2 and TiO2 nanoparticles additive. *Nanomaterials* **2022**, *13*, 42. [CrossRef]
38. Ahmed Abdalglil Mustafa, W.; Dassenoy, F.; Sarno, M.; Senatore, A. A review on potentials and challenges of nanolubricants as promising lubricants for electric vehicles. *Lubr. Sci.* **2022**, *34*, 1–29. [CrossRef]
39. Zhao, J.; Yang, G.; Zhang, C.; Zhang, Y.; Zhang, S.; Zhang, P. Synthesis of water-soluble Cu nanoparticles and evaluation of their tribological properties and thermal conductivity as a water-based additive. *Friction* **2019**, *7*, 246–259. [CrossRef]
40. Taha-Tijerina, J.; Aviña, K.; Martínez, J.M.; Arquieta-Guillén, P.Y.; González-Escobedo, M. Carbon Nanotori Structures for Thermal Transport Applications on Lubricants. *Nanomaterials* **2021**, *11*, 1158. [CrossRef]
41. Hwang, Y.; Park, H.; Lee, J.; Jung, W. Thermal conductivity and lubrication characteristics of nanofluids. *Curr. Appl. Phys.* **2006**, *6*, e67–e71. [CrossRef]
42. Ji, J.; Lu, W.; Si, C.; Zhang, S.; Yao, X.; Wang, W.; Chu, D. Overview on the preparation and heat transfer enhancement of nanofluids. In *Journal of Physics: Conference Series*; IOP Publishing: Bristol, UK, 2020.
43. Porgar, S.; Vafajoo, L.; Nikkam, N.; Vakili-Nezhaad, G. A comprehensive investigation in determination of nanofluids thermo-physical properties. *J. Indian Chem. Soc.* **2021**, *98*, 100037. [CrossRef]
44. Porgar, S.; Vafajoo, L. Experimental investigation on viscosity and density of MWCNT-Transformer oil nanofluid: Developed a new correlation. *J. Chem. Lett.* **2021**, *2*, 133–143.
45. McGrory, S. Lubrication. In *Plant Engineer's Handbook*; Elsevier: Amsterdam, The Netherlands, 2001; pp. 915–960.
46. Abdollah, M.F.B.; Amiruddin, H.; Azmi, M.A.; Tahir, N.A.M. Lubrication mechanisms of hexagonal boron nitride nano-additives water-based lubricant for steel–steel contact. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* **2021**, *235*, 1038–1046. [CrossRef]
47. Basiron, J.; Abdollah, M.F.B.; Abdullah, M.I.C.; Amiruddin, H. Lubricant mechanisms of eco-friendly lubricant blended with mineral oil for steel-steel contact. *Tribol. Int.* **2023**, *186*, 108653. [CrossRef]
48. Williams, J.A. *Engineering Tribology*; Cambridge University Press: Cambridge, UK, 2005.
49. Zhao, J.; Yang, G.; Zhang, Y.; Zhang, S.; Zhang, C.; Gao, C.; Zhang, P. Controllable synthesis of different morphologies of CuO nanostructures for tribological evaluation as water-based lubricant additives. *Friction* **2021**, *9*, 963–977. [CrossRef]
50. Choi, Y.; Lee, C.; Hwang, Y.; Park, M.; Lee, J.; Choi, C.; Jung, M. Tribological behavior of copper nanoparticles as additives in oil. *Curr. Appl. Phys.* **2009**, *9*, e124–e127. [CrossRef]

51. Xie, H.; Jiang, B.; He, J.; Xia, X.; Pan, F. Lubrication performance of MoS2 and SiO2 nanoparticles as lubricant additives in magnesium alloy-steel contacts. *Tribol. Int.* **2016**, *93*, 63–70. [CrossRef]
52. Nehme, G.; Mourhatch, R.; Aswath, P.B. Effect of contact load and lubricant volume on the properties of tribofilms formed under boundary lubrication in a fully formulated oil under extreme load conditions. *Wear* **2010**, *268*, 1129–1147. [CrossRef]
53. Chen, Y.; Yang, K.; Lin, H.; Zhang, F.; Xiong, B.; Zhang, H.; Zhang, C. Important contributions of multidimensional nanoadditives on the tribofilms: From formation mechanism to tribological behaviors. *Compos. Part B Eng.* **2022**, *234*, 109732. [CrossRef]
54. Wang, H.; Liu, Y.; Liu, W.; Wang, R.; Wen, J.; Sheng, H.; Peng, J.; Erdemir, A.; Luo, J. Tribological Behavior of NiAl-Layered Double Hydroxide Nanoplatelets as Oil-Based Lubricant Additives. *ACS Appl. Mater. Interfaces* **2017**, *9*, 30891–30899. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.