lubricants

MDPI

Article

The Performance of SiO_2 and TiO_2 Nanoparticles as Lubricant Additives in Sunflower Oil

Vicente Cortes, Karen Sanchez, Ramiro Gonzalez, Mataz Alcoutlabi and Javier A. Ortega *

Department of Mechanical Engineering, The University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, TX 78539, USA; vicente.cortes01@utrgv.edu (V.C.); karen.sanchez01@utrgv.edu (K.S.); ramiro.gonzalez02@utrgv.edu (R.G.); mataz.alcoutlabi@utrgv.edu (M.A.)

* Correspondence: javier.ortega@utrgv.edu

Received: 22 December 2019; Accepted: 11 January 2020; Published: 15 January 2020

check for updates

Abstract: In recent years, there has been growing concern regarding the use of petroleum-based lubricants. This concern has generated interest in readily biodegradable fluids such as vegetable oils. The present work evaluated the rheological and tribological characteristics of sunflower oil modified with silicon dioxide (SiO_2) and titanium dioxide (TiO_2) nanoparticles as lubricant additives at different concentrations. A parallel plate rheometer was used to evaluate the effects of concentration and shear rate on the shear viscosity, and the experimental data was compared with conventional models. The wear protection and friction characteristics of the oil-formulations were evaluated by conducting block-on-ring sliding tests. Surface analysis-based instruments, including scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and profilometry, were used to characterize the morphology and structure of the worn surfaces. The experimental results showed that the coefficient of friction decreased with the addition of SiO_2 and TiO_2 nanoparticles by 77.7% and 93.7%, respectively when compared to base sunflower oil. Furthermore, the volume loss was lowered by 74.1% and 70.1%, with the addition of SiO_2 and TiO_2 nanoparticles, respectively. Based on the experimental results, the authors conclude that modified sunflower oil enhanced with nanoparticles has the potential for use as a good biodegradable lubricant.

Keywords: sunflower oil; nano-lubricant; nanoparticles additives; rheological behavior; wear; friction coefficient

1. Introduction

There has been growing concern over the environmental impact of the use of petroleum-based lubricants. Every year, about 38 million metric tons of lubricants are used worldwide, and the most common lubricant is petroleum-based [1]. Furthermore, the depletion of fossil fuels and the fluctuation of petroleum prices has raised interest in biodegradable lubricants. Lubricants play an important role in decreasing friction and wear of mechanical contacts [2].

Before mineral oil was discovered, vegetable oils were extensively used in machinery. Given its relatively low cost and good performance, mineral oil has been used extensively. In recent years, due to price fluctuations, legal issues, and growing concerns around environmental health, biodegradable oil has gained an increased scope in lubrication [3]. Recently, significant focus has shifted towards vegetable oils, such as canola oil, sunflower oil, coconut oil, rapeseed oil, jojoba oil, soybean oil, and pongamia oil, among others. Vegetable oils possess high lubricity, a high viscosity index, and low volatility, which are excellent lubricating properties [4,5]. Since the main drawback of vegetable oils is poor oxidation, there have been efforts in improving thermo-oxidation [6]. Oxidation occurs in vegetable oils through the free radical mechanism and it can be reduced by decreasing free fatty acids.

Recently, some focus has been on sunflower oil which is readily available, eco-friendly, and renewable [7]. Vegetable oils contain natural esters that promote a natural attraction to metals. This is due to the fact that vegetable oils in nature are amphiphilic, meaning they have polar groups and long fatty acid chains. The natural esters of vegetable oils provide the advantage of a high flash point and biodegradability, but one disadvantage of a natural ester is oxidation. Sunflower oil consists of 59% polyunsaturated fat, linoleic acid, and 30% monounsaturated fat, oleic acid. Given its oleic acid concentration, sunflower oil has good oxidation properties [8].

Additives have been used to improve lubricant oil properties. These include antiwear additives, extreme pressure additives, viscosity control additives, film-forming additives, and deposit control additives [9]. Recently, much attention has been given towards nanoparticles since they possess unique properties when compared to their bulk counterparts. Studies in the use of nanoparticles as additives have shown to reduce friction and wear. Peng and co-workers found that by adding SiO_2 and diamond nanoparticles in liquid paraffin, friction decreased when compared to plain liquid paraffin oil [10]. Hernandez studied the effect of adding ZnO, CuO, and ZrO_2 nanoparticles in polyalphaolefin, and found that friction and wear decreased due to the nanoparticles acting as load-bearings [11]. Different lubrication mechanisms, namely the mending effect [12], the rolling effect [13–15], polishing effect [16–19], and protective film [20–22] have been proposed to describe the role of nanoparticles in lubricant oil. Although nanoparticles have proven to enhance lubricant properties, the current issue is compatibility, as stated by Gulzar and co-workers [23]. After a while, nanoparticles tend to sediment making the lubricant no longer uniform. Therefore, a key challenge in nano-lubrication is formulating stable suspension since sediments and agglomerates will form due to less stable suspension over a long period of lubricant in static conditions [3].

The main aim of this study was to evaluate the lubrication performance of sunflower oil modified by the addition of SiO_2 and TiO_2 nanoparticles at different concentrations. The study is divided into two stages. In the first stage, we evaluated the effect of concentration and shear rate on the viscosity, and the experimental data were compared to the power-law and the Cross-equation theoretical models. In the second stage, the coefficient of friction (COF) and wear volume loss were evaluated under sliding conditions using block-on-ring testing. After the tribological tests, the worn surfaces were analyzed via scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and profilometry.

2. Materials and Methods

2.1. Formulation of the Nano-Lubricants

Different concentrations of SiO_2 and TiO_2 nanoparticles from US Research Nano Co. (Houston, TX, USA) were dispersed in commercially available sunflower oil to formulate the nano-lubricants. Figure 1 shows the morphology of the nanoparticles. SiO_2 nanoparticles with particle sizes between 20 and 30 nm can be observed in Figure 1a. Figure 1b shows a SEM micrograph of TiO_2 nanoparticles, with particle sizes between 25 and 35 nm.

The main characteristics of the lubricant and the nanoparticles are presented in Table 1. A Mettler Toledo XS205DU electronic balance (Mettler-Toledo LLC, Columbus, OH, USA) to an accuracy of 0.01 mg was used to measure the density of the sunflower oil on a weight to volume basis using a 25 mL flask. A field emission scanning electron microscope (FE-SEM) ZEISS SIGMA VP (Carl Zeiss SBE, Thornwood, NY, USA) was used to analyze the morphology of the nanoparticles. To prepare the nano-lubricants, we added different nanoparticle concentrations (0.25, 0.50, 0.75, 1.00, and 1.25 wt. %) separately 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 done at a frequency of 20 kHz to guarantee uniform dispersion and good stability of the suspension.

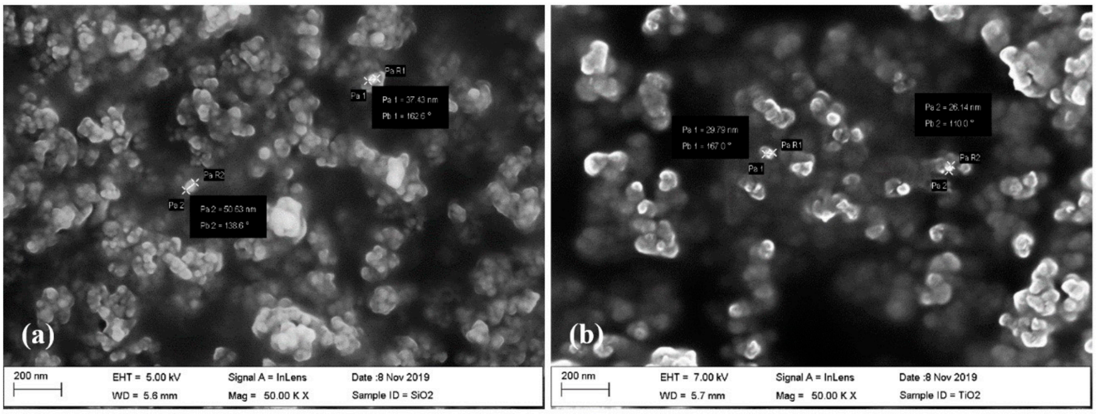

Figure 1. Scanning electron microscopy (SEM) micrographs of (**a**) SiO_2 nanoparticles, and (**b**) TiO_2 nanoparticles.

Table 1. Material properties.

Material	Properties
Lubricant	
Sunflower oil	Density (40 °C): 0.90 g/cm^3 Viscosity (40 °C): 35 mPas
Nanoparticles	
Silicon dioxide	Chemical Formula: SiO_2, Purity: 99.5% Particle size: 20–30 nm
Titanium oxide	Chemical Formula: TiO_2 (anatase), Purity: 99.9% Particle size: 18 nm
Specimens	
Blocks	AISI 304 steel, dimensions: 14 × 6.35 × 6.35 mm, hardness: 128 HRB
Rings	AISI 52100 steel, d = 40 mm, hardness: 60 HRC

2.2. Rheological Measurements

The rheological characterization of the SiO_2 and TiO_2 nanoparticles dispersed in sunflower oil was carried out using a commercial rheometer HAAKE RS-150 RheoStress (Haake Instruments, Inc., Paramus, NJ, USA) with a double parallel plates spindle. The distance between the upper and lower plates was 0.5 mm. A volume of 0.9 mL of the testing sample was used for the analysis. The sunflower oil-nanoparticle system is considered as a colloidal suspension or non-Newtonian fluid with either shear thinning or thickening characteristics depending on the nanoparticle size [24,25]. The rheological characterization was performed at 22 °C, which was controlled during the measurements. The viscosity and shear stress of all samples was set from a shear rate in a range from 10 to 120 s^{-1}.

2.3. Tribological Characterization

A custom-made block-on-ring tribostester was used to perform sliding wear tests to determine the COF and volumetric wear under extreme pressures following the ASTM G-077-05 [26] procedure. Figure 2 shows a schematic diagram of the block-on-ring tribotester, with its main components. An oil bath chamber fixture was used for the tribological experiments. The characteristics of the tested materials are presented in Table 1. During the sliding wear tests, nano-lubricants were placed in the oil bath chamber to allow constant lubrication, while the test ring rotated, covering it in lubricant by the action of centrifugal forces. Tribological tests were run using a load of 400 N (corresponding to a contact pressure of 335 MPa), at an environment temperature of 25 °C, at 172 rpm, over 1200 s. A Mettler Toledo XS205DU electronic balance (Mettler-Toledo LLC, Columbus, OH, USA) to an accuracy of 0.01 mg was used to determine the wear mass loss gravimetrically. Before the gravimetric measurement of wear, specimens were washed in soapy water, thoroughly rinsed in water, cleaned ultrasonically in ethanol for 20 min, and then left in an atmosphere-controlled room for 24 h to dry and thermally stabilize. We used a specific density of 8 g/cm^3 for AISI 304 steel blocks to convert wear mass loss into wear volume loss. The friction force was recorded continuously during each test. To assure reliability and reproducibility, we repeated the sliding tests three times.

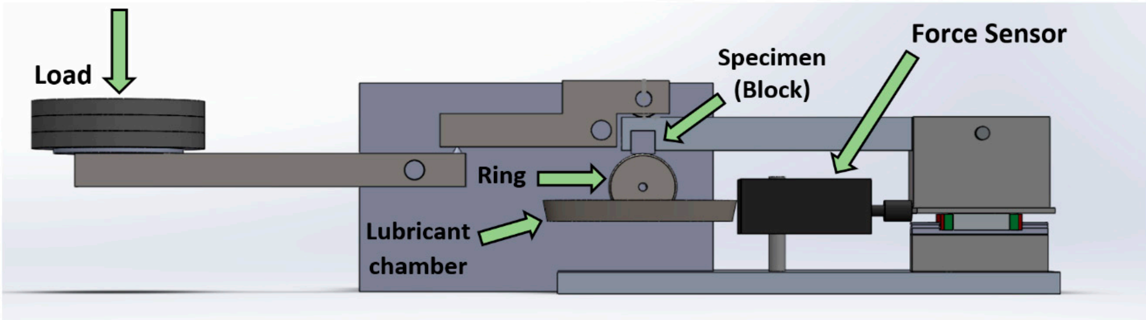

Figure 2. Schematic diagram of the block-on-ring tribotester.

2.4. Surface Analysis

Surface morphology characteristics of the wear scars on the worn specimens and their surface roughness were analyzed using 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). A MahrSurf M300 C surface profilometer (Mahr Inc., Providence, RI, USA) was used to analyze the surface roughness on the wear scars.

3. Results and Discussion

3.1. Rheological Characterization

To better understand the behavior of the lubricant oils with nanoparticles, we studied the rheological properties. Figure 3 displays the viscosity of sunflower oil without any nanoparticles. The viscosity seemed to remain constant at 73 cP from 20 s^{-1} to 120 s^{-1}. The addition of nanoparticles can alter the viscosity as seen in Figures 4–7. Figures 4 and 5 show the effect of adding SiO_2 nanoparticles to a base sunflower lubricant. As the concentration of SiO_2 increased, the measured viscosity increased. The highest viscosity observed was 128 cP at a concentration of 1.25% SiO_2. Another notable characteristic observed was shear thinning behavior in the new nanoparticle-based lubricant. This behavior agrees with findings obtained by Sanukrishna and coworkers, who studied the rheological behavior of SiO_2 nanoparticles dispersed into synthetic polyalkylene glycol (PAG) refrigerant compressor oil [27].

The rheological behavior for sunflower oil with TiO_2 nanoparticles is shown in Figures 6 and 7. Contrary to SiO_2 nanoparticles, TiO_2 nanoparticles in sunflower oil lowered the viscosity. The viscosity showed similar behavior in 0.25% and 0.50% TiO_2 concentrations. The lowest viscosity behavior was observed at a 1.00% TiO_2 concentration. Similar behavior was also observed at 0.75% and 1.25% TiO_2 nanoparticle concentrations. Although the viscosity decreased with the addition of TiO_2, shear thickening behavior was observed when TiO_2 was added given that the power-law index was greater than 1. Similar results were obtained by Ghasemi et al. when they studied the rheological behavior of (TiO_2) nanoparticles dispersed in an engine lubricant oil [28]. It is well known that the nanoparticle size and concertation can affect the rheological properties of colloidal suspensions such as oil/nanoparticle systems [25].

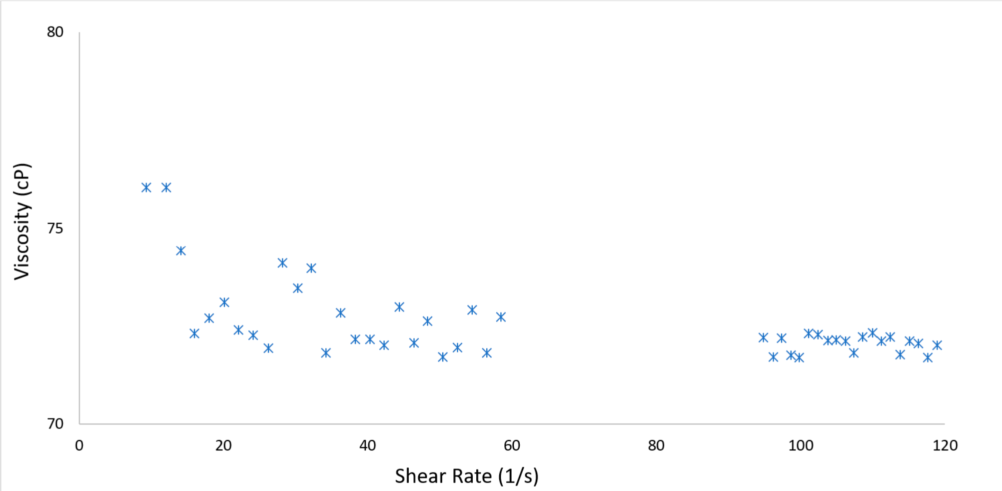

Figure 3. Shear viscosity versus shear rate for sunflower oil without additives.

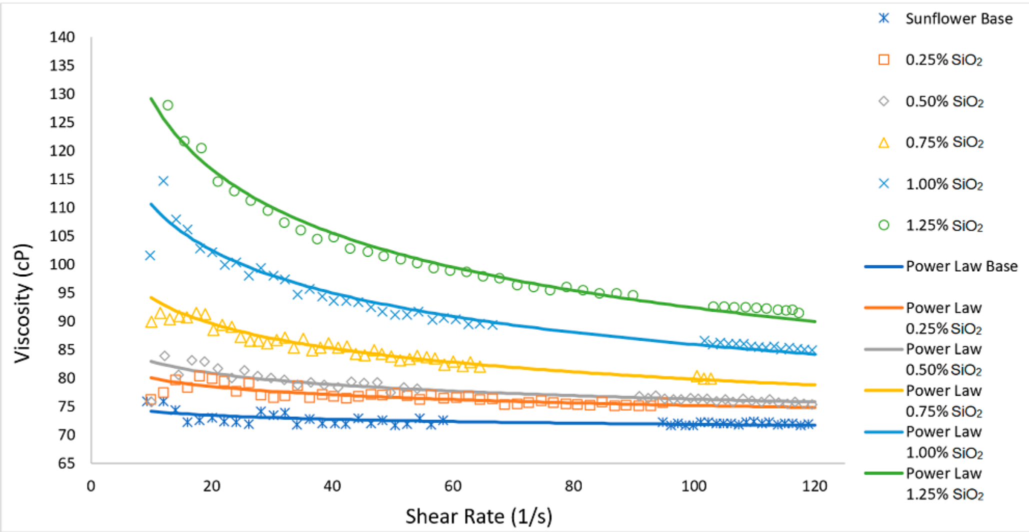

Figure 4. Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in sunflower base oil with the power-law applied.

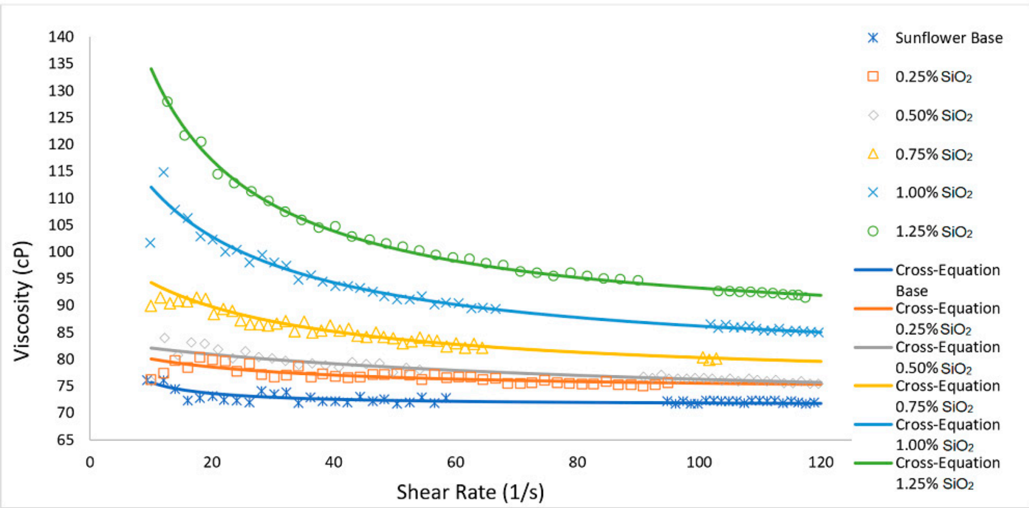

Figure 5. Effect of shear viscosity versus shear rate for SiO_2 dispersion in various weight fractions in sunflower base oil with the Cross model applied.

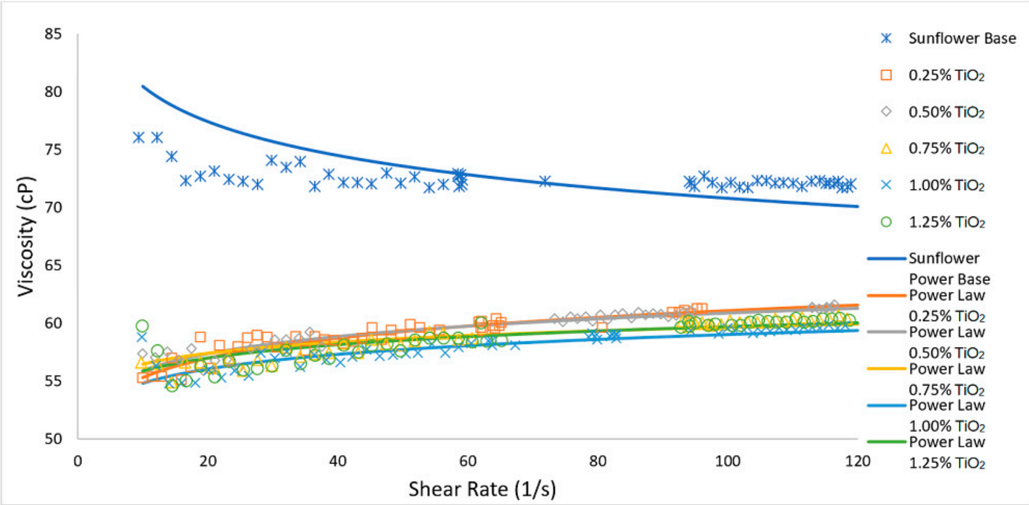

Figure 6. Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in sunflower base oil with the power-law applied.

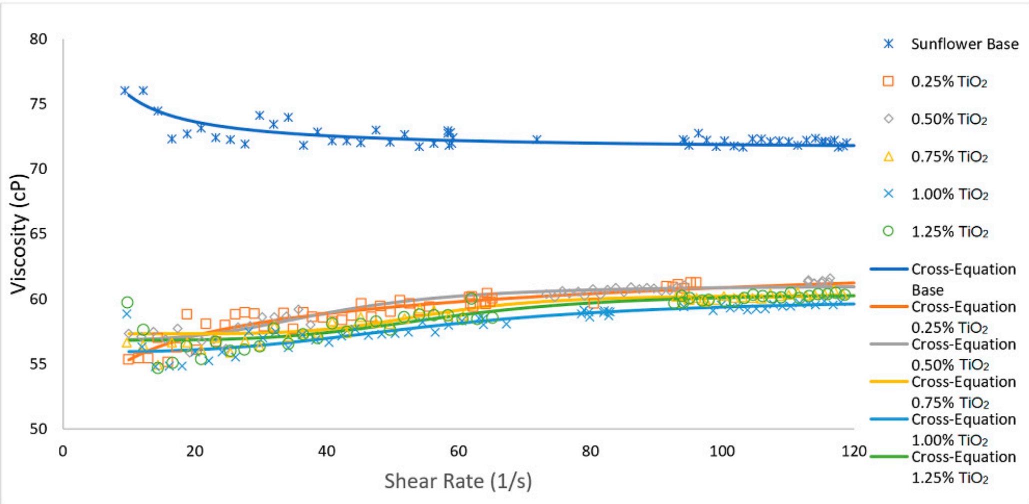

Figure 7. Effect of shear viscosity versus shear rate for TiO_2 dispersion in various weight fractions in sunflower base oil with the Cross model applied.

3.2. Power Law and Cross-Equation Rheological Models

The power-law is the simplest model to describe shear viscosity as a function of the rate of deformation. The power law consists of two parameters which, as shown in Equation (1), help to express viscosity.

$$\eta = K\left(\dot{\gamma}\right)^{n-1} \tag{1}$$

In Equation (1), K represents the consistency coefficient and n the power-law index. If $n < 1$, the behavior of the fluid is shear thinning; when $n = 1$ it represents a Newtonian fluid, and when $n > 1$ the fluid is shear thickening. The power law-fitted equations are shown in Figures 4 and 6. On the other hand, the Cross method can be used to improve the empirical model further. The Cross-model is shown below in Equation (2).

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + \left(K\dot{\gamma}\right)^n} + \eta_\infty \tag{2}$$

Here, K is a consistency index, η_0 represents viscosity at a very low shear rate, η_∞ represents infinite viscosity, and n is the flow behavior index [28]. Figures 5 and 7 show the Cross-equation data for sunflower base oil with SiO_2 and TiO_2, respectively. Table 2 displays the empirical model's parameters, accompanied with the error sum of squares (SSE).

Table 2. Regression parameters for 1.25% SiO_2 and 1.00% TiO_2 concentrations in sunflower base oil.

Model	Configuration	K	n	R^2	η_0	η_∞	SSE
Power Law	Sunflower Oil w/1.25% SiO_2	180.4	0.8547	0.8516	N/A	N/A	110.3
Cross Equation	Sunflower Oil w/1.25% SiO_2	0.1134	0.9874	0.8877	190	84.49	8.347
Power Law	Sunflower Oil w/1.00% TiO_2	50.92	1.0320	0.7395	N/A	N/A	27.16
Cross Equation	Sunflower Oil w/1.00% TiO_2	0.0175	3.3032	0.8245	55.91	59.99	18.3

The better empirical model to fit to the experimental data was the Cross-equation model based on the coefficient of determination (R^2). At higher shear rate values, the nanoparticle-based lubricants presented a nonlinear behavior; therefore, the parameters of η_0 and η_∞ were needed to express this behavior.

3.3. Tribological Results

The tribological performance of the sunflower oil was assessed with and without nanoparticle additives. Figure 8 shows the effect of nanoparticle concentration on the friction force with respect to time. These values were determined from the block-on-ring configuration tribological tests. Equation (3) was used to calculate the coefficient of friction, and it is shown below,

$$\mu = F/N \tag{3}$$

where μ is the coefficient of friction, F is the friction force measured by a force sensor built-in the tribotester, and N is the applied normal force. From Figure 8a, it is noted that the addition of SiO_2 nanoparticles decreases the frictional force. The coefficient of friction was also lowered with the addition of nanoparticles, which was similar to Peng and co-workers' findings [10]. For sunflower oil with SiO_2, the coefficient of friction was lowered from 0.0511, which corresponded to sunflower without nanoparticles at 0.0141, corresponding to a 0.25% SiO_2 concentration, as shown in Figure 9a. From there, the COF increased up to a value of 0.0190 at 0.75% SiO_2, and afterward, it decreased to its minimum value of 0.0144 corresponding to a concentration of 1.25% SiO_2. The effect of TiO_2 nanoparticles on the COF is shown in Figure 9b. The addition of TiO_2 nanoparticles resulted in decreased values of coefficient of friction, which agreed with Saravanakumar and co-workers' findings [29]. As the concentration of nanoparticles increased, the COF decreased until the TiO_2 concentration reached 1.00%, as shown in Figure 9b. By adding SiO_2 and TiO_2 nanoparticles to the sunflower based oil, the COF was decreased by 77.7% and 93.7%, respectively.

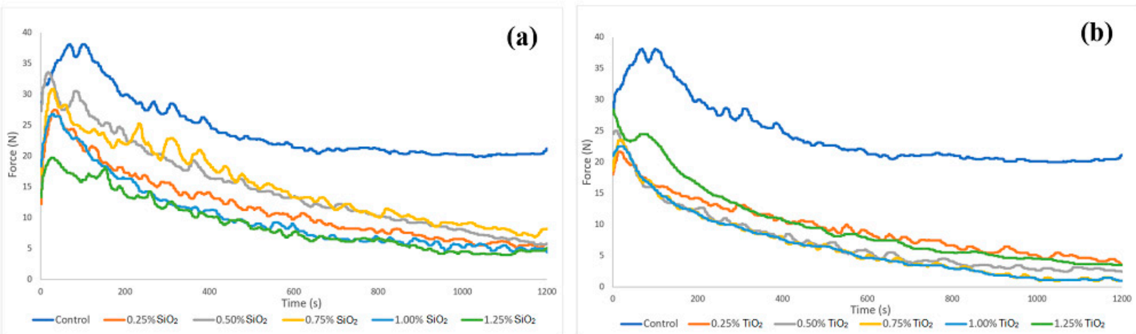

Figure 8. Frictional force versus time for sunflower oil with (**a**) SiO_2, and (**b**) TiO_2 nanoparticles.

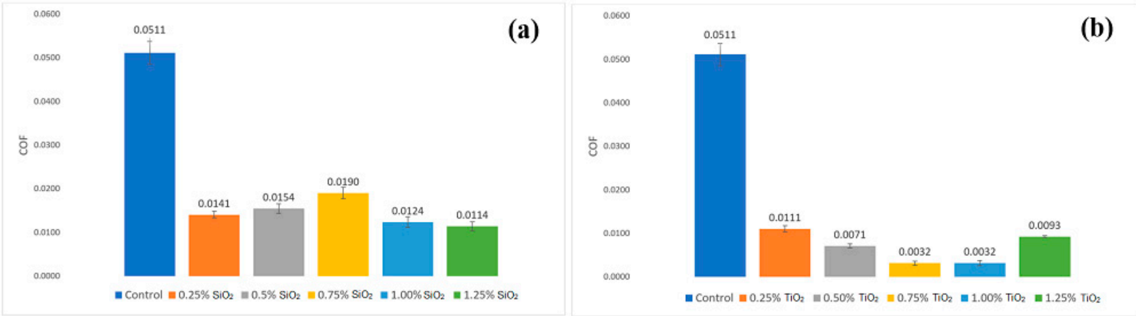

Figure 9. Coefficient of friction (COF) results for sunflower oil modified with (**a**) SiO_2, and (**b**) TiO_2 nanoparticles.

The volumetric wear loss of the AISI 304 stainless steel specimens after the block-on-ring runs is shown in Figure 10. From Figure 10a, it could be observed that as the addition of SiO_2 increased, the volumetric wear decreased initially and then increased, but eventually reaching a minimum value at the highest SiO_2 concentration of 0.25%. Compared to the sunflower base oil without nanoparticle additives, the addition of 1.25% SiO_2 lowered the volumetric wear by 74.1%. Similar to the SiO_2 nanoparticles, the addition of TiO_2 nanoparticles lowered the volumetric wear. At the concentration of 1.00% TiO_2, it could be observed that the volumetric wear decreased by 70.1% compared to the sunflower base oil, as shown in Figure 10b.

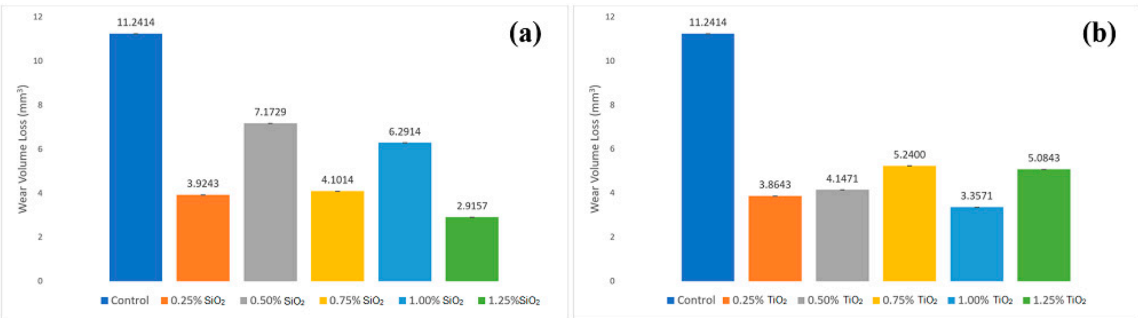

Figure 10. Mean volumetric wear of AISI 304 specimens lubricated with sunflower oil modified with: (**a**) SiO_2, and (**b**) TiO_2 nanoparticles.

3.4. SEM and EDS Analysis

SEM and EDS analyzed the worn surfaces of the tested blocks. SEM images showing the surface morphology of the wear scars produced during the wear trials are presented in Figure 11. The SEM image of the wear scar produced during the wear test lubricated with sunflower oil without additives is shown in Figure 11a. The wear scar presents a harsh surface with numerous grooves and deep furrows that are evenly spread on the contact zone. Figure 11b shows a SEM micrograph of the wear scar produced with sunflower oil enhanced with SiO_2 nanoparticles, at a concentration of 1.25 wt. %. Grooves and furrows could be observed in the wear track, along with localized micro-pitting. A Figure 11c shows a SEM micrograph of the wear scar produced with coconut oil enhanced with 1.0 wt. % TiO_2 nanoparticles. It could be observed that at an optimum concentration of TiO_2 nanoparticles, the wear track revealed shallow and smooth micro-grooves, as well as shallow furrows. Furthermore, small quasi-spherical debris was observed as adhered to the worn surface.

According to the SEM images shown in Figure 11, the change in the morphology of the wear scar produced by the nano-lubricants can be attributed to the polishing effect, which reduces friction and increases antiwear capacity [16–19]. The mechanism of the nanoparticles polishing has been reported for sliding tests by Chang, et al. [17], using nano-TiO_2 as an additive. Work by Peng et al. confirmed this polishing effect when nano-SiO_2 and Al nanoparticles were used as lubricant additives [18,19].

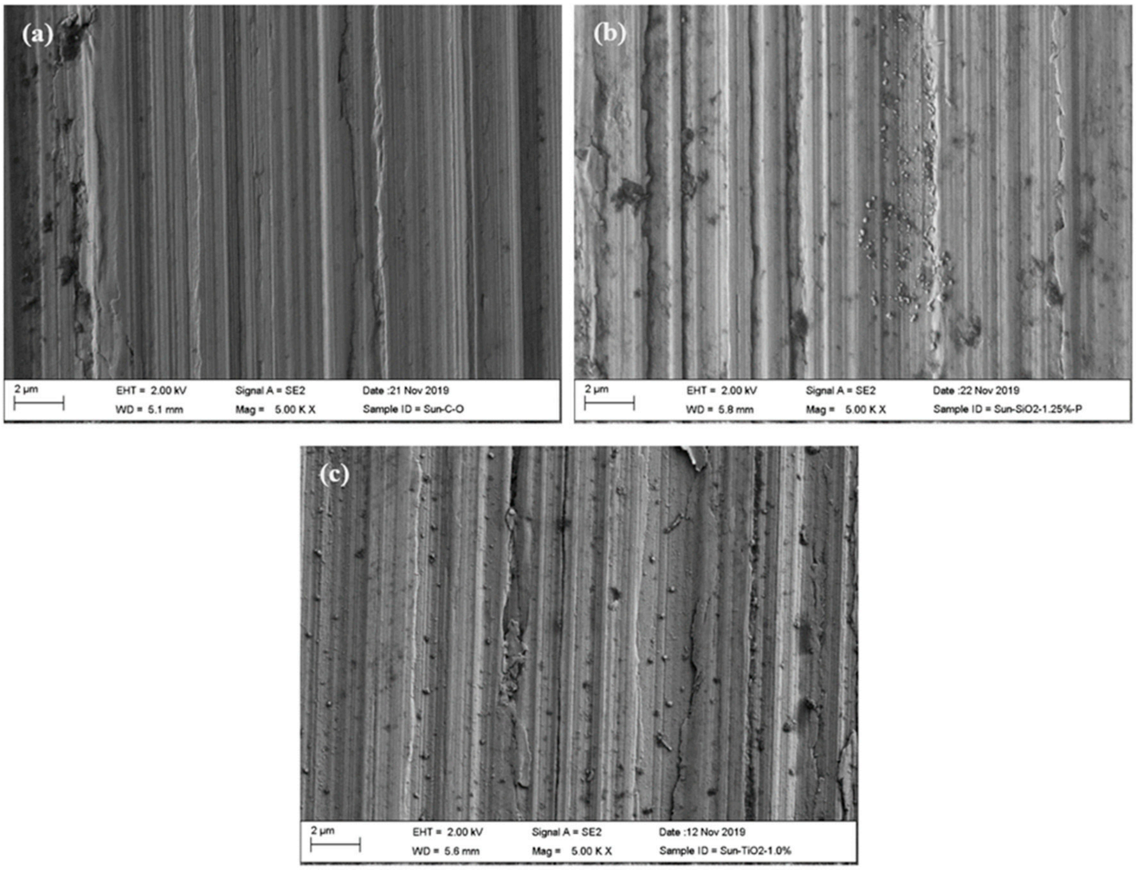

Figure 11. Morphology of wear scars produced during wear tests lubricated with (**a**) sunflower oil, (**b**) sunflower oil with SiO_2 nanoparticles at 1.25 wt. %, and (**c**) sunflower oil with TiO_2 nanoparticles at 1.0 wt. %.

Figure 12a,b, respectively, show the 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 SiO_2 nanoparticles at 1.25 wt. %. For these two specimens, the EDS spectra as shown in Figure 12a,b are almost identical, presenting peaks for the elements contained in the AISI 52100 alloy, including silicon (Si). Figure 11c shows a SEM micrograph of the wear scar and the related EDS elemental analysis of specimens tested with the nano-lubricant containing TiO_2 nanoparticles at a 1.0 wt. %. For this specimen, the EDS spectra presented peaks for the elements contained within the AISI 52100 alloy, similar to the two previous conditions. Titanium (Ti), which is not part of the AISI 52100 alloy, was also detected. The elemental weight percentages of the wear scars on the specimens tested with different nano-lubricants are presented in Table 3. A high Ti content (i.e., 9.31%) was observed on the worn surface of the specimen tested with sunflower oil with TiO_2 nanoparticles at a 1.0 wt. %. This concentration could be attributed to the protective film effect [20–22]. Gulzar et al. obtained similar results during tribological studies of chemically modified palm oil (CMPO) by the addition of copper oxide (CuO) and molybdenum disulfide (MoS_2) nanoparticles [30].

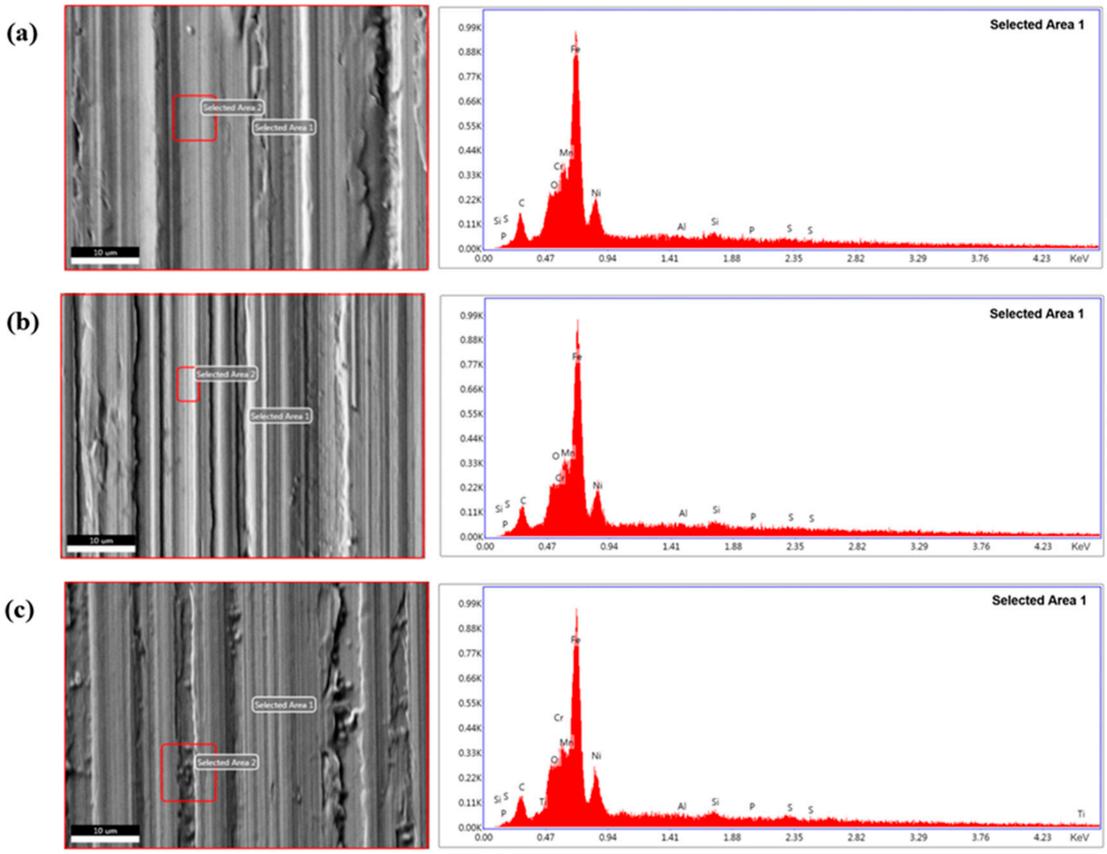

Figure 12. SEM micrograph and Energy-dispersive spectroscopy (EDS) spectra of worn surfaces produced during wear tests lubricated with (**a**) sunflower oil, (**b**) sunflower oil with SiO_2 nanoparticles at 1.25 wt. %, and (**c**) sunflower oil with TiO_2 nanoparticles at 1.0 wt. %.

Table 3. Elemental analysis of the wear scars produced with different nano-lubricants.

Element	Sunflower Oil (SO) Conc. (wt. %)	SO with SiO_2 1.25% Conc. (wt. %)	SO with TiO_2 1.0% Conc. (wt. %)
C K	9.66	9.70	7.46
O K	3.04	3.44	5.54
Cr L	12.08	11.19	8.65
Mn L	2.92	2.81	4.54
Fe L	56.22	57.20	51.58
Ni L	11.44	11.44	10.77
Al K	0.49	0.56	0.10
Si K	1.53	1.61	0.69
P K	0.98	0.79	0.20
S K	1.66	1.25	1.14
Ti L	0	0	9.31

3.5. Surface Roughness Analysis

The average values of the arithmetical mean height (*Ra*) of the assessed profile of the wear scars produced during wear testing with different lubricants are shown in Figure 13. The *Ra* value of the specimen before testing was included for comparison. The surface roughness of the wear scar produced during the wear test lubricated with sunflower oil without additives increased from 0.195 to 0.432 μm, as compared to that of the specimen before testing. However, the surface roughness on the wear scars decreased considerably from the inclusion of SiO_2 and TiO_2 nanoparticles as lubricant additives. In the case of the sunflower oil nano-lubricant with 1.25 wt. % SiO_2 nanoparticles, there was a decrease of 69.9% in the surface roughness compared to that on the wear scar produced by sunflower oil without additives. The addition of TiO_2 nanoparticles with a concentration of 1.0 wt. % to the sunflower oil resulted in a surface roughness reduction of 78.0%, as compared to the roughness on the wear scar produced by sunflower oil without additives. The presence of the polishing effect could be confirmed by the reduction in the surface roughness of the wear scars produced by the nano-lubricants. The polishing effect is known as a lubrication mechanism present when the roughness of the lubricating surface is reduced by abrasion assisted by nanoparticles [16–19]. Previous studies [31,32] reported similar results where the tendency of surface roughness reduction was attributed to the polishing effect produced by nanoparticles for all nano-lubricants.

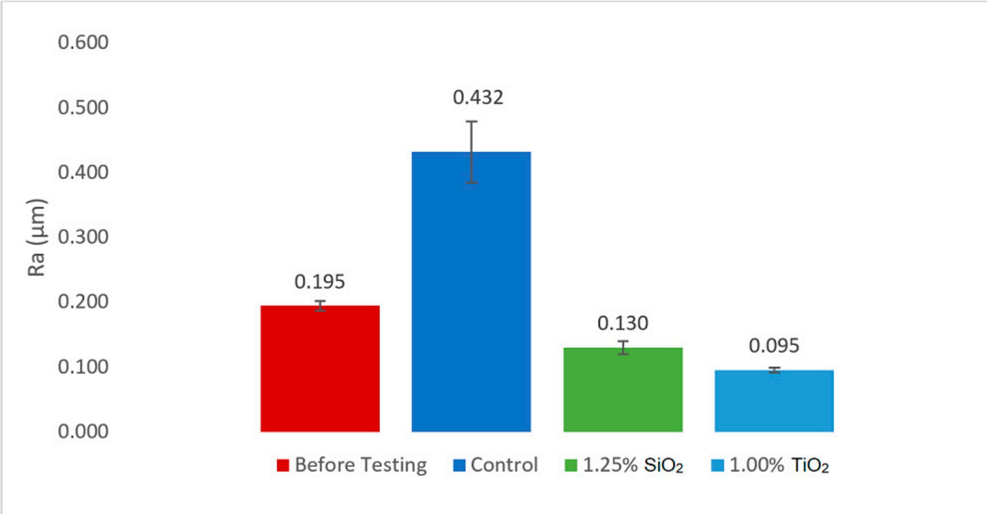

Figure 13. Average surface roughness values (*Ra*) measured on the wear scars produced during wear testing.

4. Conclusions

In the present study, the effects of SiO_2 and TiO_2 on the rheological behavior and lubrication performance of sunflower oil were investigated. The conclusions drawn from the results are summarized as follows:

- The rheological behavior of the sunflower nano-lubricant is dependent on the concentration and type of nanoparticles. For sunflower oil enhanced with SiO_2 nanoparticles, the viscosity increased at higher concentrations, whereas for sunflower oil enhanced with TiO_2 nanoparticles, the viscosity decreased as the concentration of TiO_2 nanoparticles increased.
- Different rheological behaviors were observed by adding SiO_2 and TiO_2 into the sunflower oil. The sunflower oil enhanced with SiO_2 nanoparticles presented a shear-thinning behavior, whereas the sunflower oil enhanced with TiO_2 nanoparticles showed a shear thickening behavior.
- SiO_2 and TiO_2 nanoparticles were effective additives for incorporation into the sunflower oil; where they reduced the COF and wear volume loss by 77.7 and 74.1%, and 93.7 and 70.1%, respectively.
- The surface enhancement of the worn surfaces via the polishing effect produced by the nanoparticle additives was confirmed using SEM and profilometry analyses. The protective film lubrication mechanism was discovered using EDS elemental analysis on the worn surfaces.

Author Contributions: Conceptualization, J.A.O.; data curation, R.G.; formal analysis, V.C. and K.S.; investigation, V.C. and J.A.O.; methodology, V.C., K.S. and J.A.O.; software, V.C. and K.S.; supervision, M.A. and J.A.O.; validation, V.C.; Writing—Original draft, V.C. and J.A.O.; Writing—Review & editing, M.A. and J.A.O. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: M. Alcoutlabi would like to acknowledge the support from USDA, the National Institute of Food and Agriculture, and the Integrating Food Science/Engineering and Education Network (IFSEEN) with award number: 2015-38422-24059.

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

References

1. Siniawski, M.T. Influence of fatty acid composition on the tribological performance of two vegetable-based lubricants. *J. Synth. Lubr.* **2007**, *24*, 101–110. Available online: https://onlinelibrary.wiley.com/doi/abs/10.1002/jsl.32 (accessed on 20 November 2019). [CrossRef]
2. Quinchia, L.A.; Delgado, M.A.; Reddyhoff, T.; Gallegos, C.; Spikes, H.A. Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers. *Tribol. Int.* **2014**, *69*, 110–117. [CrossRef]
3. Darminesh, S.P.; Sidik, N.A.C.; Najafi, G.; Mamat, R.; Ken, T.L.; Asako, Y. Recent development on biodegradable nanolubricant: A review. *Int. Commun. Heat Mass Transf.* **2017**, *86*, 159–165. [CrossRef]
4. Jayadas, N.H.; Nair, K.P. Coconut oil as base oil for industrial lubricants—Evaluation and modification of thermal, oxidative and low temperature properties. *Tribol. Int.* **2006**, *39*, 873–878. [CrossRef]
5. Zareh-Desari, B.; Davoodi, B. Assessing the lubrication performance of vegetable oil-based nano-lubricants for environmentally conscious metal forming processes. *J. Clean. Prod.* **2016**, *135*, 1198–1209. [CrossRef]
6. Fox, N.J.; Stachowiak, G.W. Vegetable oil-based lubricants—A review of oxidation. *Tribol. Int.* **2007**, *40*, 1035–1046. [CrossRef]
7. Jabal, M.H.; Abdulmunem, A.R.; Abd, H.S. Experimental investigation of tribological characteristics and emissions with nonedible sunflower oil as a biolubricant. *J. Air Waste Manag. Assoc.* **2019**, *69*, 109–118. [CrossRef] [PubMed]
8. Gnanasekaran, D.; Chavidi, V.P. Vegetable oil based bio-lubricants and transformer fluids. In *Materials Forming, Machining and Tribology*; Springer: Singapore, 2018. [CrossRef]
9. Rudnick, L.R. (Ed.) *Lubricant Additives: Chemistry and Applications*, 3rd ed.; Chemical Industries; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2017.
10. Peng, D.X.; Kang, Y.; Hwang, R.M.; Shyr, S.S.; Chang, Y.P. Tribological properties of diamond and SiO_2 nanoparticles added in paraffin. *Tribol. Int.* **2009**, *42*, 911–917. [CrossRef]
11. Hernández Battez, A.; González, R.; Viesca, J.L.; Fernández, J.E.; Díaz Fernández, J.M.; Machado, A.; Chou, R.; Riba, J. CuO, ZrO_2 and ZnO nanoparticles as antiwear additive in oil lubricants. *Wear* **2008**, *265*, 422–428. [CrossRef]
12. Liu, G.; Li, X.; Qin, B.; Xing, D.; Guo, Y.; Fan, R. Investigation of the mending effect and mechanism of copper nano-particles on a tribologically stressed surface. *Tribol. Lett.* **2004**, *17*, 961–966. [CrossRef]
13. Rapoport, L.; Leshchinsky, V.; Lvovsky, M.; Nepomnyashchy, O.; Volovik, Y.; Tenne, R. Mechanism of friction of fullerenes. *Ind. Lubr. Tribol.* **2002**, *54*, 171–176. [CrossRef]
14. Wu, Y.Y.; Tsui, W.C.; Liu, T.C. Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. *Wear* **2007**, *262*, 819–825. [CrossRef]
15. Chiñas-Castillo, F.; Spikes, H.A. Mechanism of action of colloidal solid dispersions. *J. Tribol.* **2003**, *125*, 552–557. [CrossRef]
16. Tao, X.; Jiazheng, Z.; Kang, X. The ball-bearing effect of diamond nanoparticles as an oil additive. *J. Phys. D Appl. Phys.* **1996**, *29*, 2932–2937. [CrossRef]
17. Chang, L.; Zhang, Z.; Breidt, C.; Friedrich, K. Tribological properties of epoxy nanocomposites: I. Enhancement of the wear resistance by nano-TiO_2 particles. *Wear* **2005**, *258*, 141–148. [CrossRef]
18. Peng, D.-X.; Chen, C.-H.; Kang, Y.; Chang, Y.-P.; Chang, S.-Y. Size effects of SiO2 nanoparticles as oil additives on tribology of lubricant. *Ind. Lubr. Tribol.* **2010**, *62*, 111–120. [CrossRef]
19. Peng, D.-X.; Kang, Y.; Chen, S.-K.; Shu, F.-C.; Chang, Y.-P. Dispersion and tribological properties of liquid paraffin with added aluminum nanoparticles. *Ind. Lubr. Tribol.* **2010**, *62*, 341–348. [CrossRef]
20. Hu, Z.S.; Lai, R.; Lou, F.; Wang, L.G.; Chen, Z.L.; Chen, G.X.; Dong, J.X. Preparation and tribological properties of nanometer magnesium borate as lubricating oil additive. *Wear* **2002**, *252*, 370–374. [CrossRef]
21. Xiaodong, Z.; Xun, F.; Huaqiang, S.; Zhengshui, H. Lubricating properties of Cyanex 302-modified MoS_2 microspheres in base oil 500SN. *Lubr. Sci.* **2007**, *19*, 71–79. [CrossRef]
22. Rastogi, R.B.; Yadav, M.; Bhattacharya, A. Application of molybdenum complexes of 1-Aryl-2,5-dithiohydrazodicarbonamides as extreme pressure lubricant additives. *Wear* **2002**, *252*, 686–692. [CrossRef]
23. Gulzar, M.; Masjuki, H.H.; Kalam, M.A.; Varman, M.; Zulkifli, N.W.M.; Mufti, R.A.; Zahid, R.; Yunus, R. Dispersion stability and tribological characteristics of TiO_2/SiO_2 nanocomposite-enriched biobased lubricant. *Tribol. Trans.* **2017**, *60*, 670–680. [CrossRef]

24. Lee, M.; Alcoutlabi, M.; Magda, J.J.; Dibble, C.; Solomon, M.J.; Shi, X.; McKenna, G.B. The effect of the shear-thickening transition of model colloidal spheres on the sign of N1 and on the radial pressure profile in torsional shear flows. *J. Rheol.* **2006**, *50*, 293–311. [CrossRef]
25. Alcoutlabi, M.; Baek, S.G.; Magda, J.J.; Shi, X.; Hutcheson, S.A.; McKenna, G.B. A comparison of three different methods for measuring both normal stress differences of viscoelastic liquids in torsional rheometers. *Rheol. Acta* **2009**, *48*, 191–200. [CrossRef]
26. G02 Committee. *Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test*; ASTM International: West Conshohocken, PA, USA, 2017.
27. Sanukrishna, S.S.; Vishnu, S.; Jose Prakash, M. Experimental investigation on thermal and rheological behaviour of PAG lubricant modified with SiO_2 nanoparticles. *J. Mol. Liq.* **2018**, *261*, 411–422. [CrossRef]
28. Ghasemi, R.; Fazlali, A.; Mohammadi, A.H. Effects of TiO_2 nanoparticles and oleic acid surfactant on the rheological behavior of engine lubricant oil. *J. Mol. Liq.* **2018**, *268*, 925–930. [CrossRef]
29. Saravanakumar, N.; Jothi Saravanan, M.L.; Barathkumar, K.E.; Gokula Kannan, K.; Karthikeyan, R. Development and testing of nano particulate lubricant for worm gear application. *J. Mech. Sci. Technol.* **2019**, *33*, 1785–1791. [CrossRef]
30. Gulzar, M.; Masjuki, H.; Varman, M.; Kalam, M.; Mufti, R.A.; Zulkifli, N.; Yunus, R.; Zahid, R. Improving the AW/EP ability of chemically modified palm oil by adding CuO and MoS_2 nanoparticles. *Tribol. Int.* **2015**, *88*, 271–279. [CrossRef]
31. Lee, C.-G.; Hwang, Y.-J.; Choi, Y.-M.; Lee, J.-K.; Choi, C.; Oh, J.-M. A study on the tribological characteristics of graphite nano lubricants. *Int. J. Precis. Eng. Manuf.* **2009**, *10*, 85–90. [CrossRef]
32. Arumugam, S.; Sriram, G. Synthesis and characterization of rapeseed oil bio-lubricant dispersed with nano copper oxide: Its effect on wear and frictional behavior of piston ring–cylinder liner combination. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* **2014**, *228*, 1308–1318. [CrossRef]

© 2020 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 (http://creativecommons.org/licenses/by/4.0/).