lubricants

Article

Experimental Investigation of Tribological Properties of Two Fully Formulated Engine Oils with Additional Nanoscale Spherical Zirconia Particles

Rajmund Kuti [1], Ádám István Szabó [2] and Álmos Dávid Tóth [2,*]

[1] Faculty of Mechanical Engineering, Informatics and Electrical Engineering, Széchenyi István University, H-9026 Győr, Hungary
[2] Department of Propulsion Technology, Széchenyi István University, H-9026 Győr, Hungary
* Correspondence: toth.almos@sze.hu

Abstract: Decreasing harmful emissions of vehicle engines is becoming more and more challenging due to stricter standards. A possible solution is to improve the tribological attributes of lubricants, which can be achieved through the application of appropriate additives. According to preliminary studies conducted by the authors, ZrO_2 (zirconium-dioxide) nano-sized ceramic particles as lubricant additives have overwhelmingly positive tribological attributes in the presence of non-metallic superficial materials. Additive concentration, as well as cross-effects with other additives were investigated in order to determine a formulation resulting in optimal tribological attributes. In this paper, the experimental investigation of ZrO_2 nano-ceramic powder as a lubricant additive is presented. The tribological performance of individually samples were experimentally investigated on a ball-on-disc translational tribometer. The experiments revealed an optimal additive content of 0.3 wt%. Increasing the quantity of additives further ruined friction and wear properties of the examined tribological system.

Keywords: ZrO_2 nano-ceramic; lubricant; tribology; engine oil

check for updates

Citation: Kuti, R.; Szabó, Á.I.; Tóth, Á.D. Experimental Investigation of Tribological Properties of Two Fully Formulated Engine Oils with Additional Nanoscale Spherical Zirconia Particles. *Lubricants* **2022**, *10*, 246. https://doi.org/10.3390/lubricants10100246

Received: 31 August 2022
Accepted: 26 September 2022
Published: 30 September 2022

1. Introduction

Global laws and standards regarding harmful emissions are becoming ever stricter, which leads to the demand for developing the operational condition of internal combustion engines. One of the most important areas of development is to increase the efficiency of internal combustion engines, which is achieved through decreasing working losses (e.g., friction). Several research papers have dealt with the increase of internal combustion engine efficiency, which can be accomplished through e.g., improved lubricating ability. In order to achieve that, low viscosity lubricants, special oil-additives, or low friction coatings can be applied to decrease the mechanical loss of rotating or sliding parts. Targeted investigations and experiments are needed to optimize oil additives, and to improve tribological attributes of lubricants. Our research results so far provide a good starting point for the investigations.

Lubricants and their additives are crucial to the operation of internal combustion engines. Their task is complex, including the separation of solid surfaces, prevention of wear and corrosion of components, as well as the reduction of frictional losses.

These tasks are only achievable through an optimal concentration of appropriate additives. Different lubricant additives were investigated in several research papers, verifying that a suitable additive can exert a positive effect due to its polarity difference and it can develop a nano-sized protection layer on frictional surfaces. Recently, the investigation of the compatibility of lubricant additives and exhaust gas aftertreatment systems is gaining importance, since certain additives—e.g., phosphorus and zinc—can cause solid reaction products during combustion (ash), that can obstruct the channels of particulate filters, or damage the catalytic converter system of vehicles. We would like to point out, that inadequate lubricant additives can lead to energy losses, and to the malfunction of mechanical systems as a consequence of exaggerated friction and wear. These losses can strongly influence fuel-consumption, harmful emissions, and the lifespan of components in engines and vehicles.

Because of this reason, we consider the investigation of different engine oil additives to be of great importance, hence we elected to investigate nanoparticles. These particles can be made from several different materials, which possess diverse physical and mechanical properties. The impact of nanoparticles on friction and wear has numerous influencing factors, e.g., material type, particle size, agglomeration, concentration, or presence of surface-active solvents. Clarifying cross-effects with these influencing factors requires comprehensive research activities.

The main goal of this article to investigate the tribological attributes of nano-sized spherical zirconia (ZrO_2) nanoparticles, particularly their effect on friction and wear in a fully formulated engine oil. The presented research is part of a comprehensive research project focusing on nanoscale spherical particles as tribological lubricant additives. In previous papers of the authors, the positive effects of zirconia particles in neat Group III base oil with a kinematic viscosity of 4 cSt measured at 100 °C temperature were published; however, the tribological impact of these nanoparticles in fully formulated engine oils are not yet known. Furthermore, no information was found regarding the potential advantages or downsides of nanoscale ceramic particles and conventional engine oil lubricants.

The development of modern engine lubricants takes place on several fronts. One of the defining trends today is the reduction of viscosity, thus minimizing in-engine friction losses, and increasing overall efficiency of the system. Zinc dialkyldithiophosphates (often referred to as ZDDP) developed in the late 1930s were a huge milestone in motor oil development. ZDDP works as an excellent anti-wear additive, and in addition has a significant antioxidant and anti-corrosion effect, making it a popular engine oil additive. ZDDP as an additive exerts its effect by coating the contact surfaces during the operation of a tribological system [1]. Dias et al. examined in detail the operation of ZDDP in fully formulated lubricants and the tribofilm formation mechanism on a real cylinder liner. The worn surfaces were examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) [2]. Peeters et al. showed the adsorption and decomposition of ZDDP on lightweight metallic substrates by simulation. The results were validated by atomic force microscopy (AFM) [3]. Experiments conducted by Zhou et al. showed that increasing ZDDP concentration caused increased friction but showed no clear trend in terms of wear resistance. The binding energy of phosphorus was examined on maps generated by X-ray photoelectron spectroscopy (XPS) to determine in what form and mechanism ZDDP binds to the surface [4]. Hunynh et al. started forward-looking studies, the long-term goal of which is to reduce or eliminate the ZDDP content. During their studies, they showed that modern motor oil additives such as cyclopropanecarboxylic acid (CPCa) and nickel nanoparticles have a competitive effect on ZDDP. The result of the competitive effect was presented by Raman spectroscopy and SEM+EDX examination. Based on their tests, it can be stated that CPCa as a carbon-based tribofilm precursor is competitive against ZDDP-based tribofilms, so neither of them can exert an adequate effect during their joint application. The nano-sized nickel particles reacted with ZDDP to form a Ni-S tribofilm. In their conclusion, they stated that to reduce ZDDP in the future, they should focus on the development of carbon-based tribofilms [5].

Zhao et al. investigated the tribological effect of graphene and ZDDP in PAO lubricant. It was found that the addition of 1% monosuccinimide to the mixture greatly increased its stability. The nanolubricant was tested at different loads using a ball-on-disc tribometer. It was found that at low loads, the deposition of graphene on the worn surface is greater, while at high loads ZDDP covers the contact surface. It can be concluded that the graphene/ZDDP composite can work well under all loads; therefore, it can reduce wear by up to 77% [6]. Mittal et al. studied chemically functionalized nanosized hexagonal boron nitride (h-BN) with 1% tert-butoxy (TBO) in ZDDP containing base oil. The functionalization of h-BN improves dispersion stability. The combined tribological effect of TBO functionalized h-BN and ZDDP on an Al-Si alloy surface was studied with atomic force microscopy (AFM). The results showed improved tribological properties due to the synergistic interaction of the additives. It can be concluded that a protective layer rich in ZDDP has formed on the surface [7]. Vyavhare et al. synthesized core-shell structured ZnO nanoparticles through plasma polymerization. ZnO nanoparticles were coated with fluorine-rich polymer films to enhance the formation of surface protective tribofilms. The shell of this structure is a methacrylate-based coating to reduce the size of agglomerations and simultaneously induce a stable dispersion in the lubricant. The synergy of ZnO nanoparticles and ZDDP was investigated in a Group III mineral base oil. The results of the surface analysis showed that a thick protective layer formed on the surface containing fluorinated ZnO, enriched with phosphates and sulfates, sulfites and fluorides, improves wear resistance even with a lower ZDDP content [8]. Sharma et al. created TiO_2 particles with a similar core-shell structure by plasma functionalization with a boron coating and an acrylate shell. The chemistry and structure of tribofilms from TiO_2 and ZDDP were investigated by AFM, SEM, ECR, XPS and XANES. Both synergistic and antagonistic interactions between additives were observed [9].

Nowadays, the soot emission of spark-ignition engines increases parallel to the spread of high-pressure direct injection gasoline engines. As a result of increasingly strict emission regulations, even vehicles powered by new gasoline engines must be equipped with an Otto/gasoline particle filter (OPF/GPF). One of the main problems with these particle filters occurs when they become clogged with particles that the engine cannot regenerate by burning [10]. Wang et al. investigated the clogging process of particulate filters. According to the tests, zinc, phosphorus, calcium and magnesium-containing ash are most often responsible for the irreversible clogging of particle filters. A significant part of the ash can originate from the ZDDP content of the engine oil, as it is produced during both partial and complete combustion [11]. Nagy et al. artificially aged Shell SAE 0W30 commercially available fully synthetic engine oil. Aged oil samples were analyzed by FTIR spectroscopy, viscometry and titration. Based on the results, it can be concluded that ZDDP content gradually decreases during ageing, and after a certain point, no anti-wear additive can be found in the sample [12]. Many engine oils contain ZDDP additives; however, several research activities are being conducted to improve engine lubricant components due to the aforementioned reasons. Numerous studies report nanoparticles in fully formulated engine lubricants. Wu et al. added CuO, TiO_2 and diamond nanoparticles to API-SF oil, examined the prepared mixture on an oscillating tribometer, and found that the particles change the viscosity of the lubricant. CuO nano additive reduces friction by 18.4% and wear depth by 16.7% [13]. Luo et al. modified the surface of Al_2O_3 nanoparticles with hydrolyzed KH-560 additive. During the process, the surface of the nanoparticles changed from hydrophilic to hydrophobic. The purpose of the surface modification was to homogenize and stabilize the mixture more conveniently. The surface-activated Al_2O_3 nanoparticles were mixed into pure lubricating oil and reduced friction by 17.61% on a 4-ball tribometer, as well as wear by 41.25% compared to the reference. The surface analysis of the worn balls showed that a kind of self-laminating protective film has formed on the worn surface, as a result of which the sliding friction turned into rolling friction [14]. Mohan et al. also added Al_2O_3 nanoparticles to a fully formulated SAE 20W40 lubricating oil. The friction and wear of the components were examined in two different lubrication conditions (flooded, starved) on a pin-on-disc tribometer. In both lubrication conditions, the 0.5 wt% mixture proved to be better. Compared to the reference, the friction was reduced by 49.1% and 21.6% while the wear was reduced by 20.1% and 31.1% under flooded and starved conditions, respectively [15]. Studies were conducted by Akl et al., who added 0.1 wt% CuO nanoparticles to Mobil 1 SAE15W-40SF lubricating oil at a temperature of 75 °C for 6 h. Two experimental engines (A154F) were run for 1000 h, one with nano-doped oil and the other with reference lubricating oil. During the 1000-h measurement, samples were taken 12 times from the lubricating oil, the composition of which was examined by spectrometry. They were able to determine the wear of individual parts and groups of parts from the spectrometric results. A relevant decrease in engine temperature (~10 °C), was found as well [16]. The study by Ali et al. presents the tribological properties of a 5W30 lubricating oil doped with nano Al_2O_3 and TiO_2. Oleic acid was also added to the mixture for proper suspension of the nanoparticles. The mixture was prepared after 4 h of mixing and tested on a self-developed tribometer. A Stribeck curve was measured, according to which the friction coefficient decreases by 9–50%, depending on the type of lubrication condition. Wear is reduced by 29% due to the rolling nature of the nanoparticles [17,18].

In another study by Akl et al., commercial Total Fluide AT42 automatic transmission oil was used. A mixture of 0.4–0.75 wt% Al_2O_3, CuO nanoparticles and carbon nanotubes (CNT) were added to the transmission oil and consecutively mixed in with ultrasound for 1 h. The prepared mixture was tested on a pin-disc tribometer, and results have shown that wear and friction can be reduced by 60.83 and 33.1%, respectively, compared to the reference [19]. Maheswaran et al. added CuO nanoparticles to Maxol 85W140 (API GL-5) gear oil. CuO was synthesized using the sol-gel method. The concentration dependence of thermal stability, heat transfer, and heat absorption were described [20].

Binu et al. prepared a very similar mixture from SAE 5W30 lubricating oil, to which TiO_2 nanoparticles were added, and the stability of the mixture was increased with oleic acid (against the formation of agglomerations). A modified Krieger–Dougherty viscosity model was used to model the viscosity of the mixture. It was found that the load-bearing capacity of plain bearings increases with the use of TiO_2-doped lubricant [21]. Esfe et al. investigated the rheological properties of 10W40 engine lubricant doped with nanosized ZnO. The rheological tests were performed in a temperature range of 5 °C to 55 °C and the nanolubricant showed non-Newtonian shear thinning behavior. A correlation was established for viscosity, taking into account temperature and nanoparticle concentration. Using the DoE method, the mathematical basis of a multi-layer artificial neural network was created, which can be used to predict the desired viscosity parameter [22]. A similar mathematical method was used when determining the rheological properties of SAE50 lubricant doped with a mixture of multi-walled carbon nanotubes (MWCNT) and Al_2O_3 nanoparticles. The results calculated this way were validated by measurement [23].

2. Materials and Methods

The main goal of this research is to investigate the tribological properties of nanoscale spherical zirconia nanoparticles as friction reduction and antiwear lubricant additives in fully formulated engine oil. For the investigations, the used zirconia particles (CAS-number: 1314-23-4) were provided by Reanal Laborvegyszer Kereskedelmi Ltd. (Budapest, Hungary). The physical properties of the zirconia nanoparticles can be observed in Table 1.

Table 1. Physical properties of the used ZrO_2 nanoparticles.

Purity	Density	Particle Size	Morphology	Crystal Structure
99%	5.89 g/cm^3	15–25 nm	Spherical	Monoclinic

In a former paper of the authors [24], the previously defined nanoparticles were homogenized in a neat Group III base oil. Results of friction and wear experiments have shown excellent antiwear properties with a concentration of 0.4 wt% zirconia, as the saturation of surface grooves with nanoparticles during the experiment resulted in a smoother contacting surface. To analyze the properties of the same nanoparticle in a fully formulated engine oil, two conventional engine lubricants were chosen: Shell 0W-30 PC 1654 with the kinematic viscosity of 12.5 mm^2/s measured at 100 °C, and MOL Dynamic Gold DX 0W-20 with the kinematic viscosity of 8.3 mm^2/s measured at 100 °C (provided by MOL-Lub Ltd., Almásfüzitő, Hungary).

As homogenization is one of the key preparation processes for the measurements, a thorough mixing process was used prior to the investigations. After defining and preparing the necessary nanoparticle and oil volumes, a magnetic stirrer was used for 15 min at laboratory temperature to mix the two ingredients together into a homogeneous state. After the magnetic stirring, the sample was placed into an ultrasonic homogenizer to decrease the secondary Van der Waals forces between the nanoparticles, in order to avoid the formation of larger agglomerates inside the oil samples. The ultrasonic homogenization process was carried out at an increased 70 °C temperature for 30 min. The last step of the mixing procedure was to place the sample back into the magnetic stirrer and agitate until the sample was filled into the lubrication dosing system of the measurement equipment.

For the tribological measurements, the ball-on-disc module of an Optimol SRV® 5 tribometer (Optimol Instruments GmbH, Munich, Germany) was used. This type of tribometer is known for its reliability and reproducibility; furthermore, a number of published international standards recommend using this equipment (e.g., ISO 19291:2016 [25]). A custom testing program was used with the ball-on-disc oscillation module realizing an alternating movement with 1 mm stroke and 50 Hz frequency. The temperature of the used ball and disc specimens was set to 100°C to simulate a temperature similar to the conditions in an internal combustion engine. An external oil circuit was also used during the experiments with a preheating device (the oil sample was heated to 100 °C as well) with an oil flow rate of 225 mL/h. The tribological properties of the lubricant samples were tested under two different loading circumstances separately (200 and 300 N), and during the tribological measurements the friction force was measured by piezoelectric force transducers with high sampling frequency. Standardized [25] ball and disc specimens used in the experiments were purchased from the manufacturer of the tribometer (Optimol Instruments GmbH, Munich, Germany). The applied ball specimens were 10 mm diameter bearing balls made from 100Cr6 steel (1.3505), were hardened to 61 HRC, and surface finished to Ra 0.025 µm. Disc specimen (24 mm diameter and 7.9 mm height) were also manufactured from 100Cr6 steel (1.3505), with a nominal surface hardness of 62 HRC, and a grinded and lapped top surface finished to Ra 0.035 µm.

Each tribological measurement was followed by a thorough analysis of the worn surfaces to define the type and extent of wear. Mean wear scar diameter (MWSD) was measured for all individual ball specimens according to ISO 19291:2016 [25]. The mean wear scar diameter should be calculated as the average value of the measured wear scar diameters on the worn surface of the ball specimen in the directions parallel and perpendicular to the sliding direction. A Keyence VHX-1000 digital microscope was used to define the wear scar diameter values and to document the wear images on both specimens. Paulovics et al. have investigated the correlation between wear width and wear volume in case of tribological research results with timing chain components. Wear in a cylindric pin on chain bush configuration was investigated and an excellent correlation between the quick wear diameter values (MWSD) and the slower but more accurate wear volume results [26] was found. According to these results and the similarity of the geometries of ball and cylindric pin specimens, only the mean wear scar diameter values of the ball specimens (MWSD) were measured and evaluated for this paper. The digital microscope analysis was also supported with investigations on a Hirox SH 4000M scanning electron microscope (Hirox Europe, Limonest, France) equipped with an EDX sensor to measure the element distribution on the worn surface, define the main wear mechanism, and find indication related to the working mechanism of the investigated nanoparticles.

3. Results of the Experiments

The starting point of the investigation is the previous result of the authors in which the tribological properties of the zirconia nanoparticles were investigated in neat Group III type base oil with a kinematic viscosity of 4 cSt measured at 100 °C [24]. In the previous paper, zirconia nanoparticles with the same physical properties were investigated and these physical properties are presented in the current paper, in Table 1. In this paper, excellent antiwear properties of the nanoparticles were reported with the working mechanism of filling up the grooves of the surfaces resulting in a smoother contact surface. Furthermore, larger agglomerates were also found on the worn surface. Figure 1 presents the tribological results of the zirconia nanoparticles in neat base oil and Figure 2 illustrates the acquired SEM images during the preliminary research.

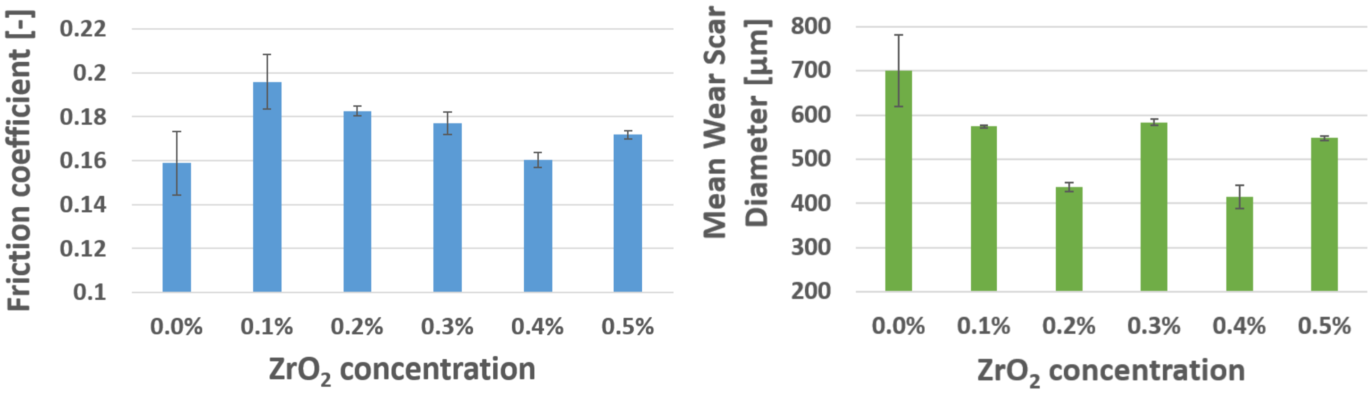

Figure 1. Tribological results of zirconia nanoparticles in neat Group III type base oil under 100 N load [24], friction coefficient (**left**), mean wear scar diameter on the ball specimens (**right**).

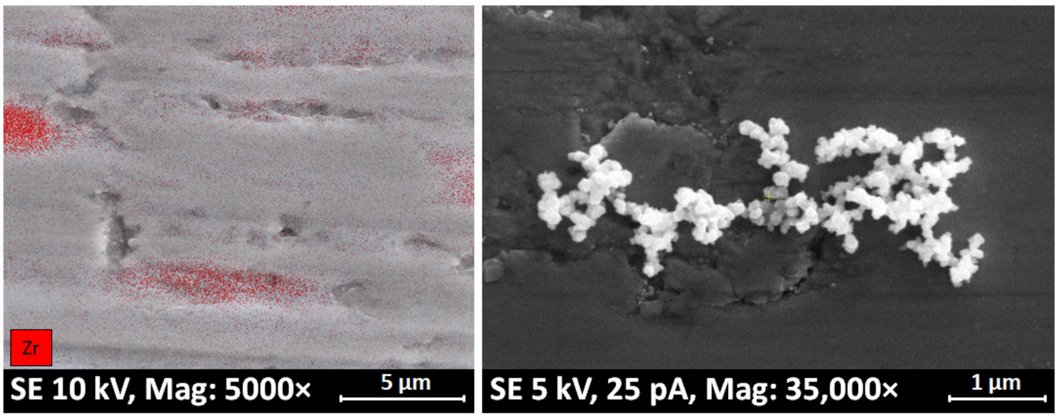

Figure 2. SEM images depicting the worn surface of the disc specimens after testing with 0.4 wt% zirconia containing base oil [24]. Zr-distribution highlighted in red on the surface (**left**), and zirconia-agglomerates found on the worn surface (**right**).

According to the results with the zirconia in base oil it can be concluded that zirconia can provide positive tribological properties to the rubbing surfaces and the investigation of its further potential in a fully formulated lubricant sample is reasonable.

A decision had to be made, which type of fully formulated engine oil should be used for the thorough investigation. For that, two different engine oils were selected, and 0.5 wt% of zirconia nanoparticles were homogenized into these lubricants with the previously mentioned method. Tribological tests were carried out with these samples in two different load cases (200 N and 300 N). With each variation (normal force, type of engine oil and concentrations), at least 3 independent tribological measurements were carried out to define the tribological parameters of the lubricant samples. As a reference for the measurements, the fully formulated engine oils without nanoadditives were used, producing the following tribological results:

- Shell 0W-30 on 200 N: 0.1314 friction coefficient and 574.535 µm MWSD
- Shell 0W-30 on 300 N: 0.10058 friction coefficient and 565.87 µm MWSD
- MOL 0W-20 on 200 N: 0.13614 friction coefficient and 676.034 µm MWSD
- MOL 0W-20 on 300 N: 0.12618 friction coefficient and 800.222 µm MWSD

The results of measurements with 0.5 wt% zirconia added engine oils can be observed in Figure 3.

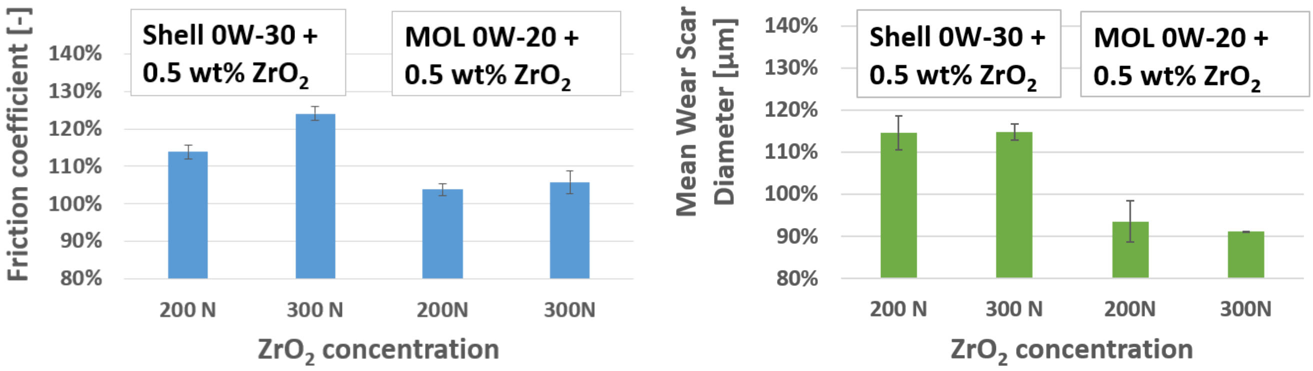

Figure 3. Comparison of the tribological results of the zirconia nanoparticles in two different fully formulated engine oils, friction coefficient (**left**) and mean wear scar diameter on the ball specimens (**right**).

The tribological results clearly show a significant difference between the two engine oils. The additional zirconia nanoparticles have increased both the measured friction coefficient and mean wear scar diameter value in case of the Shell 0W-30 oil, while they provided positive antiwear properties with just a slight friction increase for the MOL 0W-20 oil with the same nanoparticle concentration. To understand this significant difference between the two types of engine oils, a thorough microscopical analysis was carried out on the worn surfaces. The left 4 pictures on Figure 4 presents the digital microscope images showing specimens after measurements with 200 N, while the right ones illustrate wear on the surfaces measured with 300 N normal force.

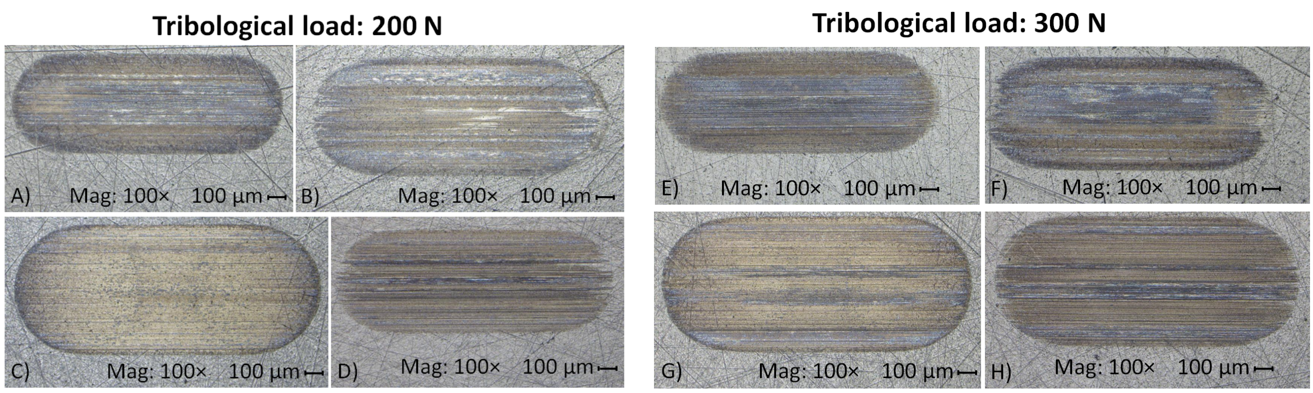

Figure 4. Digital microscope images about the disc specimens, (**A**,**E**) Shell 0W-30, (**B**,**F**) Shell 0W-30 + 0.5 wt% ZrO_2, (**C**,**G**) MOL 0W-20, (**D**,**H**) MOL 0W-20 + 0.5 wt% ZrO_2 (white lines: adhesion wear, grey lines: abrasion wear, yellow line: polished surface area).

The digital microscope images highlight the main difference between the two engine oils without additional zirconia: MOL 0W-20 provides lower antiwear properties to the rubbing surfaces than Shell 0W-30, based on the significant difference in the corresponding MWSD values: 565–575 µm in the case of Shell 0W-30 under both load values, compared to 675 and 800 µm MWSD in the case of MOL 0W-20 under 200 N and 300 N, respectively (no additional zirconia nanoparticles). This difference stems from the different compositions and additive content of the lubricants. However, it is also obvious that the additional zirconia nanoparticles provide different properties to the lubricants: these nanoparticles increase the quantity of wear in case of the Shell engine oil, but they provide increased wear resistance for the investigated MOL lubricant.

Scanning electron microscope analysis was carried out to define the modus operandi and distribution of ZrO_2 particles on the worn surfaces during the tribological tests. For this investigation, the steel specimens measured with 0.5 wt% zirconia containing engine oils were used. Before the SEM analysis, the disc specimens were clean in an ultrasonic bath in brake cleaner multiple times to make sure no contaminants were on the surfaces. The results of the element distribution measurements with the EDX sensor of the scanning electron microscope can be observed in Table 2.

Table 2. Element distribution on the worn surfaces of the disc specimens measured with 0.5 wt% zirconia added engine oils, results are in mass %.

Oil Sample	Fe	Cr	Si	O	C	Zr	Zn	P	Ca	S	Mg
Shell 0W-30	85.55	1.29	0.12	18.01	3.71	0.00	0.95	1.01	0.11	0.47	0.00
MOL 0W-20	79.36	1.17	0.58	9.75	4.56	0.39	1.23	0.99	0.69	0.54	0.73

The main difference in observed element distribution is the zirconium content on the worn surfaces: there was no zirconium found on the surface measured with Shell 0W-30, whereas almost 0.4 wt% zirconium was found in the case of MOL 0W-20. The lack of zirconium indicates that no zirconia nanoparticles attached to the contacting surfaces, therefore the zirconia nanoparticles in the lubricant could possibly form larger agglomerates, which increased the friction and the mean wear scar diameter with the oil by increasing the 3-body abrasion between the surfaces, larger linear wear grooves can be observed in Figure 4 B, F. Furthermore, higher oxygen content can be observed in the case of Shell 0W-30 compared to the MOL oil, which also indicates a worse anticorrosion property of the Shell engine oil, which can lead to increased oxidation wear. The Zn, P, Ca, and Mg content represents the number of oil additives on the worn surfaces, which shows a slight difference between the additive content of the engine oil samples.

There may be several possibilities why zirconia nanoparticles could not attach to the surfaces and accumulate in the surface grooves, but the most plausible one is that a protective additive layer was formed on the surface and the molecules forming this layer have higher attraction to the metal surfaces than the zirconia nanoparticles. From the conventional oil additives, the surface-active additives work accordingly, attaching to the metal surfaces due to polarity difference, and ZDDP (zinc dialkyldithiophosphate) has a very high attraction to the surfaces. It is highly possible that because of this property of the ZDDP molecules the zirconia nanoparticles could not form weak bonds with the metal surface, and they could not provide their positive tribological properties through filling up the surface grooves and forming a tribological protective boundary layer. It can be seen from the EDX results that both Shell 0W-30 and MOL 0W-20 engine oil contains ZDDP (indicated by the presence of Zn on the worn surfaces); however, there is no clear proportional correlation between Zn content on the worn surface and ZDDP content of the engine oil.

The following measurements were only carried out with the MOL 0W-20 engine oil, established on the previously mentioned positive tribological effects, compared with the Shell 0W-30.

Further investigation was carried out to define the optimal zirconia concentration in the used MOL 0W-20 fully formulated engine oil. The zirconia concentration was varied between 0.1 and 0.5 wt% in 0.1%. increases. Both the preparation of the oil samples and the parameters of the tribological experiments were identical to methods outlined in Section 2. As a reference, lean MOL 0W-20 engine oil without nanoparticles was used. The friction coefficient and mean wear scar diameter results can be observed in Figure 5.

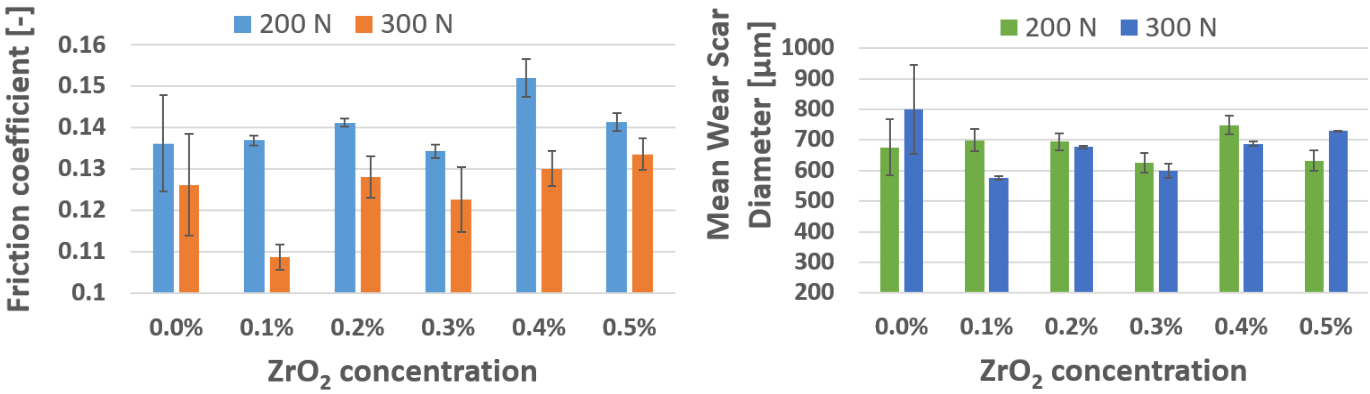

Figure 5. Comparison of the tribological results of different zirconia nanoparticle concentrations under two different normal force values, friction coefficient (**left**) and mean wear scar diameter on the ball specimens (**right**).

It is visible from the bar charts in Figure 5, that the positive tribological effects of zirconia nanoparticles could be measured, especially under the higher (300 N) normal force value. Zirconia nanoparticles can primarily provide improved antiwear properties to engine oil—0.3 wt% provides the best values considering both loading forces, but 0.1 wt% is also excellent under 300 N–, whereas 0.1 wt% concentration also shows promising friction reduction potential under 300 N load. As these engine oils are originally formulated for modern engines with high surface pressures, high temperatures, and low frictional losses, low load circumstances do not provide relevant information regarding the performance of the engine oil. Hence, results with both 200 N and 300 N convey important data about the tribological parameters of this lubricant.

Several possible reasons can be formulated to explain the tendencies between the tribological values (COF and MWSD) and the zirconia concentration:

- larger nanoparticle agglomerates can form in case of higher zirconia concentrations, which lead to an increasing amount of 3-body abrasion and increased friction, or
- a functional collision emerges between higher concentrations of nanoparticles and the conventional engine oil additives.

It is also possible, that because of the higher amount of spherical zirconia nanoparticles inside the engine oil, the surface grooves get saturated with more particles, resulting in a smoother contact surface and establishing a nano ball-bearing effect. It is also possible, that in reality a combination of the aforementioned effects exists. To answer these questions, further research activities need to be carried out, which can prove the previously described hypotheses.

Figures 6 and 7 present digital microscope images of worn surfaces of the disc specimens with different zirconia concentration values under the applied two different load values. These images confirm the results of the mean wear scar diameter measurements, and provide the information, that zirconia nanoparticles can reduce wear losses of this tribosystem. Furthermore, an optimum concentration can be defined at 0.3 wt% considering both 200 N and 300 N load cases.

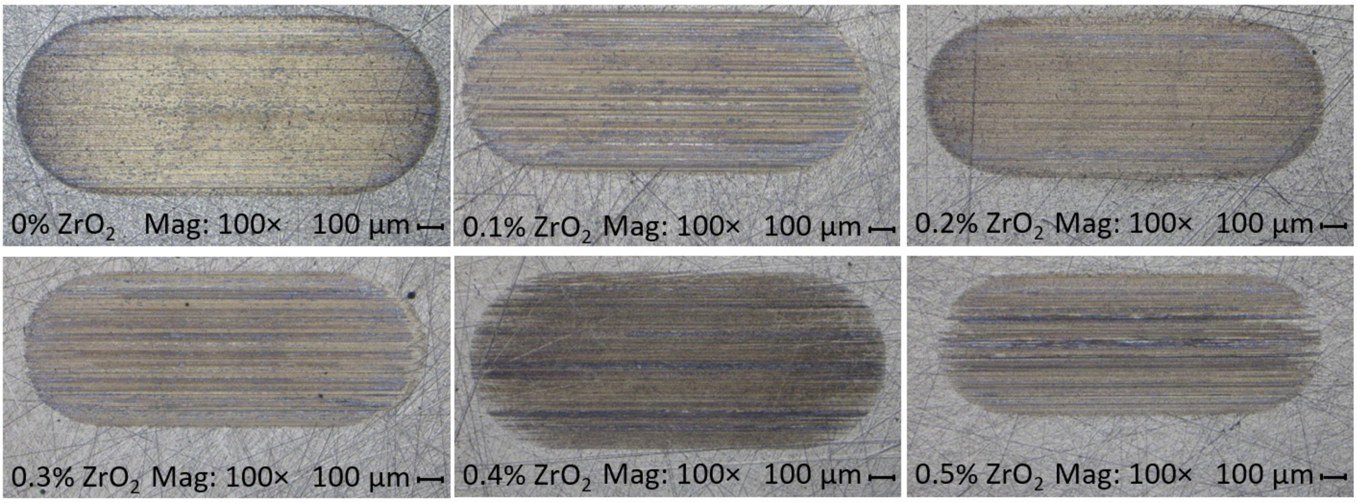

Figure 6. Digital microscope images of disc specimens tested with different zirconia nanoparticle concentrations under 200 N normal force.

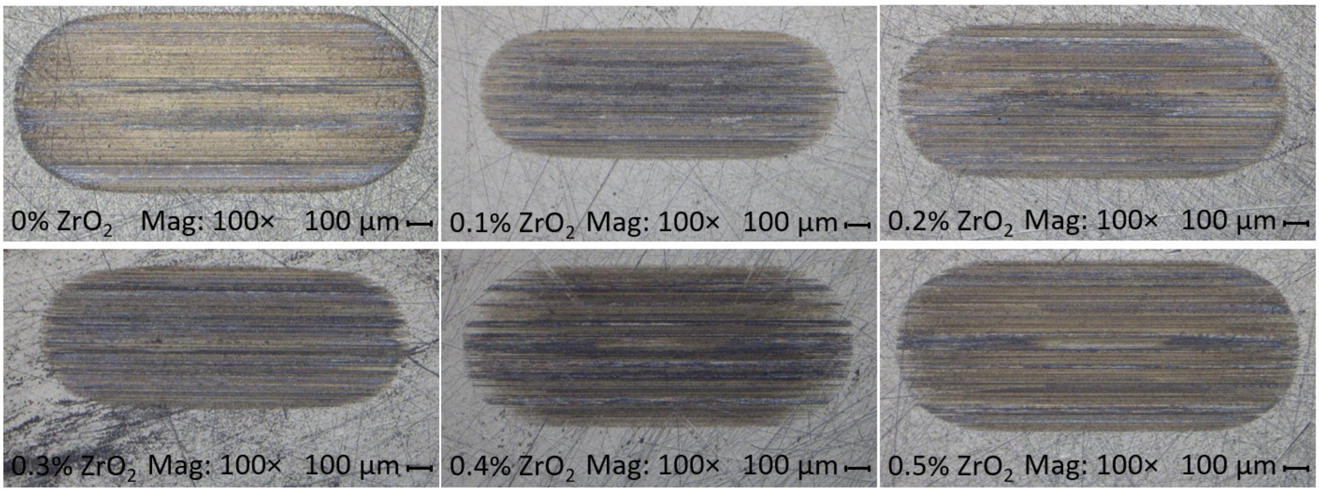

Figure 7. Digital microscope images of disc specimens tested with different zirconia nanoparticle concentrations under 300 N normal force.

4. Discussion

The conducted investigation revealed an interesting property of the nanoparticles: due to their working mechanism (attaching to the surfaces and filling up the grooves of the surface) they cannot act properly when another lubricant additive with higher affinity to the surface (e.g., ZDDP) is also present in the lubricant. In this case, ZDDP molecules have adhered to the metal surfaces forming a protective tribological boundary layer on the metal surfaces. The zirconia nanoparticles appear to have lower affinity to a ZDDP boundary layer than to the metal surfaces, hence they were just collected inside the lubricant. Due to their nano size and spherical form, they have accumulated into larger agglomerates inside the lubricant and these agglomerates have had negative influence on both the friction and wear behaviour of the tribosystem through increasing 3-body abrasion.

The ZDDP additive also has a negative property when used in an internal combustion engine oil: due to the zinc content of the molecule, it cannot be burnt completely if it reaches the combustion chamber (e.g., by attaching to the cylinder liner surfaces), and zinc ash will form during the combustion of ZDDP molecules as a result. This zinc ash will leave the combustion chamber through the exhaust system into the exhaust gas aftertreatment system and particle filters, where it will be filtered out, and stored inside the particle filters. Consequently, this ash cannot be burned out, and thus the particle filter cannot be fully regenerated, and the complete particle filter will be blocked after a given operation time of the vehicle [10,11]. Because of this property, the replacement of zinc-containing lubricant additives has increasing importance for the sake of the environment and human habitats.

According to the current knowledge about nanoparticles, they can be one of the possible solutions used as friction and wear reducing lubricant additives; however, their influence on the aftertreatment systems is yet unknown. Further investigations are necessary to understand how these additives could be used in a fully formulated engine oil, and for that the interaction properties of these nanoadditives and the conventional engine oil additives should also be thoroughly investigated. The full potential of nanoparticle additives is yet to be determined.

5. Conclusions

This paper presented the results of a number of experiments with nanoscale spherical zirconia particles homogenized in two types of fully formulated engine oils. The main goal of this research was to present the cross-effect between conventional engine oil additives and zirconia nanoparticles.

The results of this investigation can be summarized as follows:

- The addition of 0.5 wt% zirconia provided negative tribological properties to the Shell 0W-30 engine oil, both friction coefficient and mean wear scar diameter were increased by 15–25% under two different load values.
- Meanwhile, the same amount of zirconia nanoparticles in the MOL 0W-20 engine oil decreased the mean wear scar diameter measured on the disc specimens, with a mild increase in friction.
- The significant antiwear property difference between the two types of engine oils was explained based on the results of SEM-EDX analysis. No zirconium was found on the worn surface measured with Shell 0W-30, but almost 0.4 wt% of zirconium was measured on the surface after testing with MOL 0W-20.
- The SEM analysis revealed that the zirconia nanoparticles could not attach to the metal surfaces in case of Shell 0W-30 because of a previously formed antiwear layer of ZDDP. As a result, the zirconia nanoparticles formed larger agglomerates in the oil, and affected the tribological properties of the lubricant negatively by increasing the 3-body abrasion in the system. However, this phenomenon was not experienced by the measurements with MOL 0W-20, because the ZDDP antiwear layer formation was hindered, hence the zirconia nanoparticles could adhere to the surface.

This research paper revealed how important it is to understand the cross-effect between nanoscale ceramic particles and conventional engine oil additives. To formulate an engine oil in the future using the full potential of nanoparticle additives, this cross-effect has to be investigated. In addition, in the case of a mass product, the financial background of both research and manufacturing have to be considered as well. If the cost introduced by nanoparticles is too high, the resulting engine oil will not be financially feasible. For mass production, the lowest possible nanoparticle concentration is probably the best solution, where the positive effects of the nanoparticles are already measurable and significant.

Author Contributions: Conceptualization, R.K. and Á.D.T.; methodology, Á.I.S. and Á.D.T.; formal analysis, Á.I.S. and Á.D.T.; investigation, Á.I.S. and Á.D.T.; resources, R.K. and Á.D.T.; data curation, Á.I.S. and Á.D.T.; writing—original draft preparation, R.K., Á.I.S. and Á.D.T.; writing—review and editing, R.K., Á.I.S. and Á.D.T.; visualization, Á.I.S. and Á.D.T.; supervision, R.K.; project administration, Á.D.T.; funding acquisition, Á.D.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Dóra Olimpia Csepreghy, Boglárka Nagy, and Jan Rohde-Brandenburger for their general support, for András Lajos Nagy for his linguistic advice and for the financial support of AUDI HUNGARIA Zrt.

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

References

1. Spikes, H. The History and Mechanisms of ZDDP. *Tribol. Lett.* **2004**, *17*, 469–489. [CrossRef]
2. Dias, L.C.; Pintaude, G.; Vittorino, A.A.O.F.; Costa, H.L. ZDDP Tribofilm Formation from a Formulated Oil on Textured Cylinder Liners. *Lubricants* **2022**, *10*, 118. [CrossRef]
3. Peeters, S.; Barlini, A.; Jain, J.; Gosvami, N.N.; Righi, M.C. Adsorption and decomposition of ZDDP on lightweight metallic substrates: Ab initio and experimental insights. *Appl. Surf. Sci.* **2022**, *600*, 153947.
4. Zhou, Y.; Weber, J.; Viola, M.B.; Qu, J. Is more always better? Tribofilm evolution and tribological behavior impacted by the concentration of ZDDP, ionic liquid, and ZDDP-Ionic liquid combination. *Wear* **2019**, *432–433*, 202951.
5. Hunynh, K.K.; Tieu, K.A.; Pham, S.T. Synergistic and Competitive Effects between Zinc Dialkyldithiophosphates and Modern Generation of Additives in Engine Oil. *Lubricants* **2021**, *9*, 35.
6. Zhao, Y.; Geng, Z.; Li, D.; Wang, L.; Lu, Z.; Zhang, G. An investigation on the tribological properties of graphene and ZDDP as additives in PAO4 oil. *Diam. Relat. Mater.* **2021**, *120*, 108635. [CrossRef]
7. Mittal, P.; Rai, H.; Kumari, S.; Khatri, O.P.; Gosvami, N.N. Efficient friction and wear reduction of Al-Si alloy via tribofilms generated from synergistic interaction of ZDDP and chemically functionalized h-BN additives. *Appl. Surf. Sci.* **2022**, *595*, 153520. [CrossRef]
8. Vyavhare, K.; Timmons, R.B.; Erdemir, A.; Edwards, B.L.; Aswath, P.B. Tribochemistry of fluorinated ZnO nanoparticles and ZDDP lubricated interface and implications for enhanced anti-wear performance at boundary lubricated contacts. *Wear* **2021**, *474–475*, 203717. [CrossRef]
9. Sharma, V.; Timmons, R.B.; Erdemir, A.; Aswath, P.B. Interaction of plasma functionalized TiO_2 nanoparticles and ZDDP on friction and wear under boundary lubrication. *Appl. Surf. Sci.* **2019**, *589*, 372–383. [CrossRef]
10. Nagy, P.; Zsoldos, I. A Review on the Differences between Particle Emission, Filtration and Regeneration of Particulate Filters of Diesel and Gasoline Engines. *Veh. Automot. Eng.* **2020**, *3*, 158–173.
11. Wang, Y.; Kamp, C.J.; Wang, Y.; Toops, T.J.; Su, C.; Wang, R.; Gong, J.; Wong, V.W. The origin, transport, and evolution of ash in engine particulate filters. *Appl. Energy* **2020**, *263*, 114631. [CrossRef]
12. Nagy, A.L.; Rohde-Brandenburger, J.; Zsoldos, I. Artificial Aging Experiments of Neat and Contaminated Engine Oil Samples. *Lubricants* **2021**, *9*, 63. [CrossRef]
13. 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]
14. Luo, T.; Wei, X.; Huang, X.; Huang, L.; Yang, F. Tribological properties of Al_2O_3 nanoparticles as lubricating oil additives. *Ceram. Int.* **2014**, *40*, 7143–7149. [CrossRef]
15. Mohan, N.; Sharma, M.; Singh, R.; Kumar, N. *Tribological Properties of Automotive Lubricant SAE 20W-40 Containing Nano-Al_2O_3 Particles*; SAE Technical Paper 2014-01-2781; SAE: Warrendale, PA, USA, 2014.
16. Akl, S.; Abdel-Rehim, A.; Khafagy, E. *Tribological Properties of Engine Lubricant With Nano-Copper Oxide as an Additive*; SAE Technical Paper 2016-01-0487; SAE: Warrendale, PA, USA, 2016.
17. Ali, M.K.A.; Xianjun, H.; Mai, L.; Qingping, C.; Turkson, R.F.; Bicheng, C. Improving the tribological characteristics of piston ring assembly in automotive engines using Al_2O_3 and TiO_2 nanomaterials as nano-lubricant additives. *Tribol. Int.* **2016**, *103*, 540–554. [CrossRef]
18. Ali, M.K.A.; Xianjun, H.; Mai, L.; Bicheng, C.; Turkson, R.F.; Qingping, C. Reducing frictional power losses and improving the scuffing resistance in automotive engines using hybrid nanomaterials as nano-lubricant additives. *Wear* **2016**, *364–365*, 270–281.
19. Akl, S.Y.; Abdel-Rehim, A.A.; Elsoudy, S. *An Experimental Investigation of Tribological Performance of a Lubricant Using Different Nano Additives*; SAE Technical Paper 2018-01-0833; SAE: Warrendale, PA, USA, 2018.
20. Maheswaran, R.; Sunil, J.; Vettumperumal, R.; Velu Subhash, S. Stability analysis of CuO suspended API GL-5 gear lubricant sol. *J. Mol. Liq.* **2018**, *249*, 617–622.
21. Binu, K.G.; Shenoy, B.S.; Rao, D.S.; Pai, R. A Variable Viscosity Approach for the Evaluation of Load Carrying Capacity of Oil Lubricated Journal Bearing with TiO_2 Nanoparticles as Lubricant Additives. *Procedia Mater. Sci.* **2014**, *6*, 1051–1067. [CrossRef]
22. Esfe, M.H.; Saedodin, S.; Rejvani, M.; Shahram, J. Experimental investigation, model development and sensitivity analysis of rheological behavior of ZnO/10W40 nano-lubricants for automotive applications. *Phys. E Low-Dimansional Syst. Nanostruct.* **2017**, *90*, 194–203.
23. Esfe, M.H.; Alidoust, S.; Esfandeh, S.; Toghraie, D.; Ardeshiri, E.M. Laboratory and statistical evaluations of rheological behaviour of MWCNT-Al_2O_3 (20:80)/Oil SAE50 as possible modified nano-lubricants. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *641*, 128503. [CrossRef]
24. Tóth, Á.D.; Szabó, Á.I.; Kuti, R. Tribological Properties of Nano-Sized ZrO_2 Ceramic Particles in Automotive Lubricants. *FME Trans.* **2021**, *49*, 36–43. [CrossRef]

25. *ISO 19291:2016(E)*; Lubricants—Determination of Tribological Quantities for Oils and Greases—Tribological Test in the Translator Oscillation Apparatus. International Organization for Standardization: Geneva, Switzerland, 2016; Volume 1, pp. 1–13.
26. Paulovics, L.; Tavakov, Z.M.; Tóth-Nagy, C.; Rohde-Brandenburger, J.; Kuti, R. Comparison of timing chain wear produced on engine dynamometer and tribometer using 3D-scanning of wear scar. In Proceedings of the 12th IEEE International Conference on Cognitive Infocommunications (CogInfoCom 2021), Online, 23–25 September 2021; pp. 485–490.