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Surface Modification of Silica Nanoparticles with Ethyl Oleate for the Purpose of Stabilizing Nanolubricants Used for Tribological Tests

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Abstract: Long-term sustainability and decreasing amount of fossil oil reserves require a partial or complete transformation of traditional lubricating oils. The use of silica nanoparticles as a lubricant additive has a huge tribological potential, which has already been discussed in numerous articles. Nanosized silica shows excellent results in reducing friction and preventing wear, but they quickly aggregate and settle after homogenization in oils. For long-term stable dispersion of lubricating oils containing nanoceramics, the surface of the particles was modified with ethyl oleate. The surface modification, the ethyl oleate applied to the surface of the nanosilica, was confirmed by Fourier-transform infrared spectroscopy. Group III based lubricating oil was prepared using the surface-modified nanosilica. The particle size of the nanoparticles in the lubricating oil dispersion was examined by dynamic light scattering. Oscillating tribometer measurements were performed with different concentrations (0.1; 0.2; 0.3 wt%) of nanolubricants. Based on the tribological results, the friction coefficient of the surface-modified nanosilica is more stable, its wear is 15% lower compared to the reference. There is no significant change in the magnitude of the friction coefficient. It can be concluded that the ethyl oleate surface modification method may be suitable for tribological investigations of the acting mechanisms of nanoparticles.

Keywords: tribology; additive; lubricant; silicon dioxide; silica; surface modification; friction; wear; nanoparticle; ethyl oleate

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1. Introduction

To meet the challenges of the global energy crisis and increasingly strict environmental protection regulations, lubricating oil manufacturers are faced with a complex task. Increasing the tribological performance of lubricants has become crucial for the sustainable operation of any system. Modern lubricating oil development is looking for new directions and opportunities. Traditional lubricants have difficulty meeting the expectations of the new, increased requirements. Therefore, the research and development directions of lubricating oils turned towards the search for new bases and new additives. One such development option, which promises significant potential in the future, is doping with nanoadditives.

Lubricating oils doped with nanoparticles are part of colloid chemistry, in which the main components are distinguished as a dispersion medium and a dispersion/dispersed part. Based on this, it can be stated that the dispersion medium is the connected, molecularly continuous part of the system, while the dispersed part is made up of the so-called colloidal particles dispersed in the continuous medium, the size of which is 1–500 nm.

Attractive and repulsive effects prevail between the surfaces of the particles mixed in the dispersion medium, which can be explained by several models, and which are all based on the formation of the electric double layer. One such important theory is DLVO (from Derjaguin, Landau, Verway, and Overbeck), according to which the effects are governed by electric double-layer repulsion and dispersion attraction [1]. The effects occurring between nanoparticles are directly and indirectly influenced by many factors, for example, the permittivity of the medium itself. The permittivity of organic compounds, oils, and fats is lower ($\varepsilon < 5$) than that of water-based media ($\varepsilon = \sim 80$), that is, in the case of oils, the lack of adequate repulsion can cause the formation of agglomerates. That is why the polarity of lubricants makes it difficult to maintain a stable dispersed system [2]. For particles smaller than 100 nm, quantum physical mechanisms also occur. Moreover, due to the large specific surface area of the particles, they easily stick to each other, i.e., they can aggregate, form agglomerations, and settle [3]. In the case of lubricating oils doped with nanoparticles, it causes a big problem in that after a while they do not distribute homogeneously, but rather clump together and settle after mixing. As a result of the Brownian movement, the suspended particles collide with each other and, considering that the specific surface area of the small particles is large, secondary bonding forces, including Van der Waals forces, cause them to stick together, i.e., aggregate.

The size of the nanoparticles is a critical factor because if the particles are too large, or if they aggregate into larger clumps, they will not be able to penetrate the gaps of the surface roughness or between the tribological contact surfaces. In this case, they will not be able to exert their beneficial effects. From a tribological point of view, particles below 100 nm are suitable [4].

Nanoparticles can be separated in an oily environment by several mechanical mixing methods. However, after a while, these particles aggregate and settle down. The aggregation and sedimentation can be inhibited and slowed down with different surface modification solutions. Surface modification is essential to disperse nanoparticles into lubricating oils. Bagwe et al. investigated different surface modification options for reducing the aggregation of silica nanoparticles in a water-in-oil emulsion. They used a wide variety of microscopy analyses supplemented by dynamic light scattering and zeta potential measurements [5]. The test methods can be supplemented with infrared spectroscopy, hydrophobicity measurement, interfacial tension test, emulsion stability analysis [6], X-ray diffraction, X-ray photoelectron spectroscopy, and thermogravimetric analysis [7]. Chen et al. summarized the various influences of material, particle size, and surface modification on dispersion. They concluded that steric stabilization plays the most important role in the preparation of nanolubricants with non-polar solvents such as oils. The steric stabilization of the nanolubricant oil can be enhanced by the organic layer (long alkyl chains are recommended) formed on the surface of the nanoparticles—although this reduces the tribological effects of the particles. For oxide particles larger than 10 nm in diameter, silanization is recommended as a surface modification method [8]. Silica nanoparticles can be surface modified without a solvent by using mild ball milling [9]. Wang et al. present a successful synthesis of oleic acid on Superparamagnetic Fe_3O_4 Nanoparticles in an aqueous medium. The synthesized iron oxide nanoparticles were characterized: it was shown that the surface modification of the nanoparticles can be investigated with Fourier-transform infrared spectroscopy (FTIR) [10]. Relying on these results, but further developing them, Alves et al. modified the CuO nanoparticles synthesized by themselves by oleic acid esterification. The polyalphaolefin-based (PAO) nanolubricant was prepared using toluene solvent in three different concentrations. The adequate dispersion of the method is shown by the fact that, according to their report, no sedimentation is observed on the oil samples kept still for 30 days. The results of tribological tests with oil samples were positive, both friction and wear were improved by using the PAO + surface modified (SM) CuO nanolubricant [11] and the paraffin + SM SiO_2 nanolubricant [12,13]. In a later paper, Peng et al. reported a high-magnification electron microscope image of spherical nanoparticles modified with oleic acid [14]. The surfaces of WS_2 and MoS_2 nanoparticles were modified with oleic acid

to reduce aggregation. The particle size distribution in these PAO-based nanolubricants was investigated by dynamic light scattering. Tribological tests showed a wear reduction of around 45% [15].

Due to its favorable and interesting properties, silicon dioxide is a substance that occurs regularly in a wide range of industry and research areas. The purpose of this article is to present the possibility, process and beneficial tribological effects of this ethyl oleate surface modification using silica nanoparticles.

The favorable friction and wear properties of silica nanoparticles have been demonstrated in the broad areas of tribology. Tribology tests have already been carried out in which silica is added as a drilling fluid additive. A significant reduction in drilling costs can be achieved with the 30–45% friction reduction effect of nanosilica [16]. Certain research has shown that when added to an aqueous medium, nanosilica is deposited on the Si_3N_4 surface and supports superlubricity. Different SiO_2 nanoparticle concentrations result in different run-in times, which helps to achieve superlubricity even faster [17]. In a study, the tribological properties of neem oil are improved with silica nanoadditives, thus presenting the possibility of an alternative, environmentally friendly lubricating oil [18]. The synergistic tribological effects of graphene and silica have already been proven experimentally. Castor oil was used as the base of the lubricating oil, which was tested on steel-steel test specimens. Based on the tribology results, it was established that using nanosilica-graphene blend used as an additive reduced friction by 22.4% and wear by 46.1%. When examining the synergy of graphene and nanosilica, it was established that when the two are used together, a protective layer forms on the surface. Due to the easy-shear nature of graphene and the rolling properties of silica, they reduce friction together [19]. Some studies show that the tribological properties of base oil can be improved with silica nanoparticles [20–23]. The polydopamine + SiO_2 nanoparticle underlayer increased the critical loads for crack initiation and delamination of diamond-like carbon coatings in the oscillating tests [24]. In the research of Heymans et al., composite gold coatings were reinforced with silica nanoparticles. Silica is integrated into the gold matrix, thereby increasing its hardness, and the result is a more wear-resistant surface [25]. An ultralow coefficient of friction of graphene covered and fullerene-encapsulated silica nanoparticles was predicted in simulation models [26]. Tribology tests show that surface-modified silica nanoparticles open up possibilities for making flexible or soft armor [27].

Several articles demonstrated that silica nanoparticles modified by silanization are well dispersible in organic media. The dispersible nanosilica particles were characterized by different methods (transmission electron microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis). Excellent dispersing ability has been demonstrated in the application of lubricating oils. The friction and wear-reducing effect of surface-modified silica nanoparticles was proven by tribological tests [28–32]. Depending on the type of surface modification, friction can be reduced by 40% and wear by 60% [7]. López et al. modified the surface of silica nanoparticles with lauric acid and decanoyl chloride. A complex characterization analysis was performed on the surface-modified particles. The particles were mixed into ISO standardized base oil, which was stable even after 8 days. Four-ball tribological measurements were performed with the nanolubricants to determine that the surface modified silica slightly increases wear but significantly reduces friction [33].

If silica is used as a grease additive, there is no need to modify its surface—this was tested by many scientists. The results showed a reduction in friction and wear after the tribological tests of different greases doped with silica nanoparticles [34,35].

2. Materials and Methods

The Group III type refined mineral base oil with a viscosity of 4 cSt used for the measurements was provided by MOL-LUB Ltd., Almásfüzitő, Hungary. The base oil consists of a mixture of C20-C50 hydrocarbons (CAS 64742-54-7; CAS 72623-87-1) and

does not contain any additives to exclude the possibility of any additives reacting with the SiO_2 nanoparticles.

The silica (CAS 7631-86-9) nanoparticles used for the tests were provided by Reanal Laborvegyszer Kereskedelmi Kft., Budapest, Hungary. The purity of the spherical nanoparticles used was 99.5%, and their size range was 5–20 nm. The silica nanoparticles (see Figure 1) were used for the measurements in two forms, first in their unchanged form, and then after surface modification with ethyl oleate.

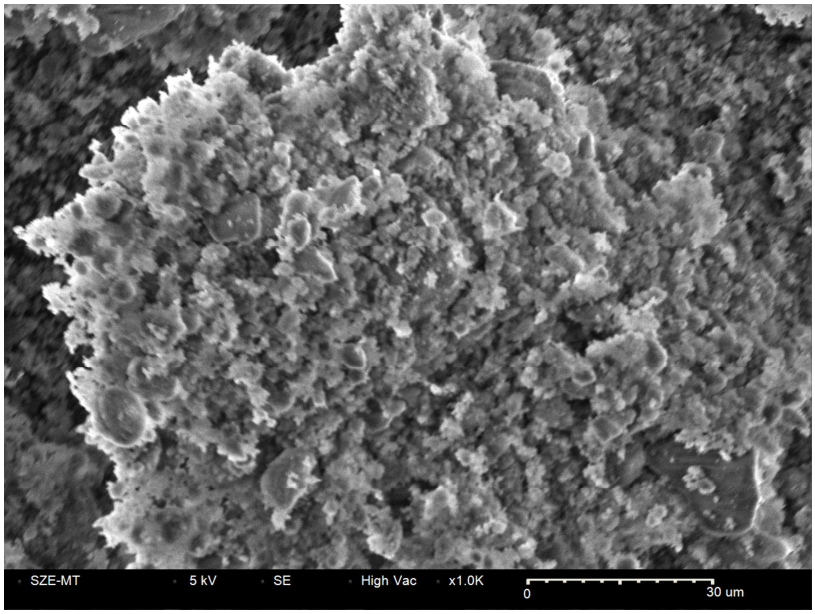

Figure 1. SEM image of the investigated, unchanged silica nanoparticles with 1000× magnitude.

2.1. Nanoparticle Surface Modification

Lubricating oil preparation consists of two parts: the surface modification of the silica nanoparticle, then the assembly of the lubricating oil, and its homogenization. The surface of the silica nanoparticles was modified by oleic acid esterification to minimize agglomeration. Ethyl oleate formed from the reaction of oleic acid and ethyl alcohol precipitates on the nanoparticles. Thus, an ethyl oleate layer is created on the surface of the nanoparticles, which can be used to improve the stability of the dispersed oil sample over time. After all, the ethyl oleate layer helps to avoid an increase in size that negatively affects tribological properties. During the surface modification, 0.1 g of 90% pure oleic acid (CAS 112-80-1) and 65 g of 99.8% pure ethyl alcohol (CAS 64-17-5) are added to 0.8 g of silica nanopowder. Both fluids were purchased from Reanal Laborvegyszer Kereskedelmi kft. The sample was kept at 75 ± 5 °C while stirring at 400 rpm on a heated magnetic stirrer for 2 h. In this temperature range, ethyl alcohol reacts with oleic acid and ethyl oleate is formed (esterification). The oleic acid was converted into ethyl oleate, and the remaining ethyl alcohol must be evaporated [36]. The sample was placed in a dryer at 80 °C for 16 h. During the evaporation of the ethyl alcohol, this ethyl oleate precipitated on the surface of the particles (and on the wall of the beaker). The result was a solid, dry cracked material (see Figure 2), which after grinding was stored in an airtight seal until use.

Figure 2. Tools and materials used for surface modification are on the (**left**). On the (**right**), the nanopowder was obtained at the end of the surface modification.

2.2. Nanolubricant Preparation

During the preparation of the lubricating oil sample used for tribological measurements, the already surface-modified nanopowder was added to the oil with the help of toluene (CAS 108-88-3) dispersant. Toluene is a widely used laboratory solvent, which is recommended by several studies as a dispersant for surface-modified nanoparticles [11,30,32,33]. Each gram of surface-modified nanopowder was dissolved in 57.8 g of toluene by using a magnetic stirrer. After mixing, the appropriate amount of Group III base oil was added to the sample, depending on the desired concentration. Toluene is a highly volatile, moderately toxic compound, so the dispersion prepared in this way was placed in a fume hood for 16 h and the toluene was allowed to evaporate completely with magnetic stirring (400 rpm). In 16 h, the toluene evaporated completely. After that, the oil sample was placed in an ultrasonic mixer for 15 min at a temperature of 50 °C. The oil sample prepared in this way showed adequate homogeneity and was ready for tribology measurement.

2.3. Methods of Oil Sample Inspection

The tests were carried out by the Department of Pharmaceutics and the Department of Pharmaceutical Administration of University Pharmacy, Semmelweis University, Budapest. The lubricant sample was checked by examining the size of the silica nanoparticles mixed in the base oil. The particle size of nanoparticles was determined via the dynamic light scattering technique using Malvern Zetasizer Nano ZS (Malvern Panalytical Ltd., Malvern, UK). Measurements were carried out in disposable polystyrene cuvettes (DTS0012) at 20 °C, on samples in original concentration and after dilution. Dilution was performed by mild homogenizing of 10 µL original sample with an automatic pipette in 2 mL base oil. The refractive index of the dispersant (Group III base oil) was 1.4619 (at 20 °C) measured by Abbemat 3000 (Anton Paar Hungary Ltd., Budapest, Hungary).

2.4. Methods of Nanoparticle Inspection

The results of the surface modification were inspected directly on the nanopowders with attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR) examinations carried out on Jasco FT/IR-4200 spectrophotometer. The tests were carried on between 4000 and 500 cm^{-1}—with a resolution of 4 cm^{-1}—equipped with ATR PRO470-H single reflection accessory (JASCO Corporation, Tokyo, Japan). Solid nanopowder samples stored at room temperature (22 ± 2 °C and 65 ± 5% RH) in well-closed amber glass vials—were examined. A concave ATR (attenuated total reflectance) head was used with high pressure to obtain a stable and homogenous layer on the surface of the ATR crystal (diamond) maintaining the reproducible quality of spectra. The measurements were performed in absorbance mode. From each sample, three parallel spectral measurements (100 scans/samples) were carried out, then measurements were evaluated with the FTIR software Spectra Manager-II, Jasco. At the ATR-FTIR spectroscopy, the incident infrared

(IR) beam was totally reflected at the ATR crystal and sample interface, only an evanescent wave protrudes into the sample with a depth of only a few microns, thus there was good contact between the crystal and sample. A homogeneous sample layer was created on the surface of the crystal. Where the sample absorbs energy in the IR spectrum the evanescent wave will be attenuated or altered. Then, this energy from each evanescent wave was passed back to the IR beam, which then exited the opposite end of the crystal on the way to the detector. Finally, the system then generated an infrared spectrum.

2.5. Methods of Tribological Inspection

The tribology tests were performed at the Department of Propulsion Technology, Széchenyi István University, Győr. The prepared nanolubricants were tested with the ball-on-disc tribosystem of an Optimol SRV®5 tribometer (Optimol Instruments GmbH., Munich, Germany). This frictional machine is widely used for the tribological analysis of materials, coatings, or lubricants according to their tribological performance [37]. Standardized [38] Ø10 mm ball and Ø24 mm × 7.9 mm disc specimens were used for the tribological experiments, which were purchased directly from the manufacturer of the tribometer. During the tribotests, the ball specimen was pushed onto the flat surface of the disc specimen with the defined normal force and was moved with a sinusoidal oscillation movement pattern with 50 Hz frequency and 1 mm stroke length. According to previous results of the authors [39], an external peristaltic pump was added to the measurement system to provide a continuous oil flow onto the contacting surface of the oscillating ball specimen to provide better lubrication and avoid overheating of the surfaces. Each tribological experiences consist of two steps: a 30-s low-load step to provide minor tribological load (50 N) for the system establishing the necessary oil film between the rubbing surfaces, and a 2-h long test step with higher normal force (100 N) to analyze the tribological parameters and investigate the long-running property of the lubricant samples. The exact parameters of the used ball and disc specimens can be observed in Table 1, while Table 2 shows the setup parameters of the tribological measurements. Figure 3 shows the used tribometer, its peripheries, and the realized ball-on-disc tribosystem.

Table 1. Parameters of the ball and disc specimens used for tribological experiments.

Specimen	Dimensions	Material	Heat Treatment	Hardness	Machining	Surface Roughness
Ball	Ø10 mm	100Cr6	-	61 ± 1 HRC	polishing	Ra 0.025 ± 0.005 µm
Disc	Ø24 mm × 7.9 mm	100Cr6, vacuum arc melted	spherodized and annealed	62 ± 1 HRC	lapping	0.035 < Ra < 0.05 µm 0.5 < Rz < 0.65 µm

Table 2. List of setup parameters of the tribological experiments.

Parameter	Stroke	Frequency	Specimen T	Oil T	Oil Flow Rate	Load	Time
Step 1	1 mm	50 Hz	100 °C	100 °C	225 mL/h	50 N	30 s
Step 2	1 mm	50 Hz	100 °C	100 °C	225 mL/h	100 N	2 h

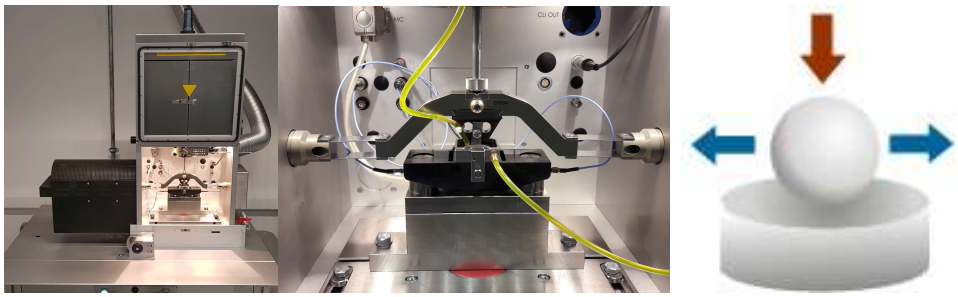

Figure 3. The used Optimol SRV®5 tribometer, and the realized ball-on-disc tribosystem.

To evaluate of the frictional losses of the oil samples including nanoparticles with and without surface activation, the integral average of the friction coefficient values was continuously measured with a 1 Hz sampling frequency by the tribometer. This friction average integral (FAI) is calculated according to the following formula:

$$\mathrm{FAI} = \frac{1}{s_{max}} \cdot \int_{s_0}^{s_{max}} |\mu(s)| \mathrm{ds} \quad (1)$$

where 's' is the applied stroke and 'μ' is the measured friction coefficient.

To evaluate of the wear images on the contact surfaces of the used specimens, a Keyence VHX-1000 (Keyence International, Mechlin, Belgium) digital microscope was used, which is capable of capturing maximum 1000× magnitude images and measuring the dimensions on these pictures. The mean wear scar diameter (MWSD) was measured according to ISO 19291:2016 norm [38]: two wear scar diameter (WSD) values were measured in the directions parallel and perpendicular to the sliding directing and their average value is the MWSD. Figure 4 presents the used digital microscope and an example of measuring the WSD values on the circular wear image of the ball specimen.

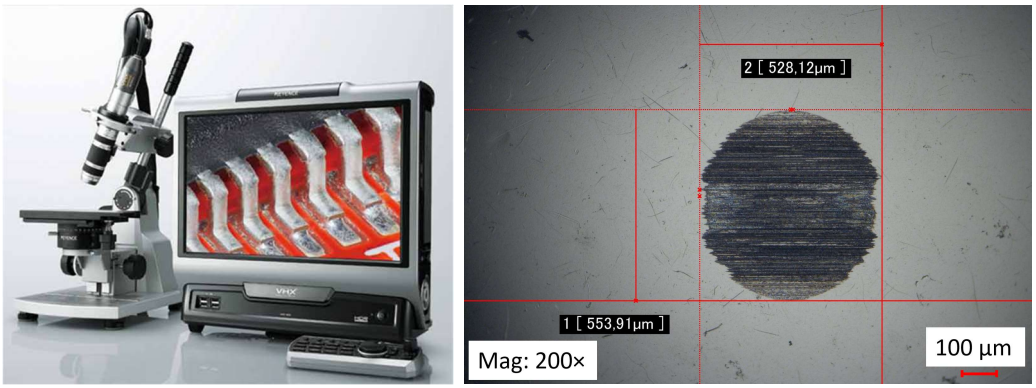

Figure 4. The used Keyence VHX-1000 digital microscope (**left**) and an example of defining the WSD values on a ball specimen (**right**).

3. Results

The homogenization of the nanoparticles into the used liquid is crucial to produce nanolubricants with positive tribological properties. Nanoparticles can exert their tribological effect if they can get between the contact surfaces. For this, the bulk powder has to be separated into individual particles. In the homogenized oil mixture with separated particles, the particles reassemble after a while, form larger agglomerates, and then settle. This phenomenon is prevented by the ethyl oleate layer on the surface of the SiO_2 particles. To investigate this, the size of the particles in the homogenized mixture was first examined, and then the surface modification of the particles with ethyl oleate was proven. Finally, the tribology effect of the surface-modified particles was investigated.

3.1. Silica Particle Size Measurement

SiO_2 nanoparticles were chosen to determine the average size because these samples were transparent. It revealed that the base oil itself contains nano and micro-scale impurities, which can be explained by the fact that engine lubricant production does not require high purity. Two populations of these impurities were reproducibly measurable, resulting in average values of 8.824 nm and 4382 nm (Figure 5).

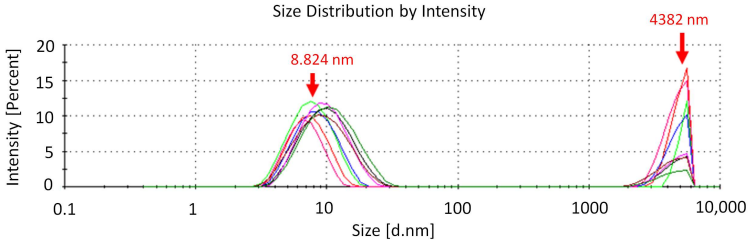

Figure 5. Average sizes of impurities in the base oil as dispersant medium measured in the range between 0.1 nm and 10 µm. Shown the averages of Peak Mean Values (PMV): 8.824 nm and 4382 nm.

The presence of these contaminating particles shifts the Z-average value calculated by the software, which does not describe the size of the particles we are investigating. For this reason, the peak mean intensity values were used for evaluation. Initial/original samples containing surface modification (SM SiO_2) and non-surface modified pure SiO_2 particles (SiO_2), showed an average diameter of 957 nm and 991 nm, respectively (Figure 6).

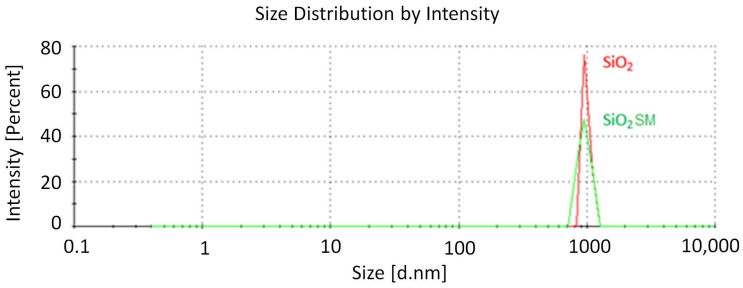

Figure 6. Size distribution of surface modified (SM SiO_2) and not modified SiO_2 nanoparticles in original concentration in the base oil.

These size values are much higher than the size of the original solid nanoparticles produced by the manufacturer (5–20 nm), which suggests a non-primary particle size. It was investigated if the average size changes after dilution in the base oil. After dilution and a mild homogenization, a population of particles below 10 nm was observed for both SM and unchanged SiO_2 particles, as one example is shown in Figure 7.

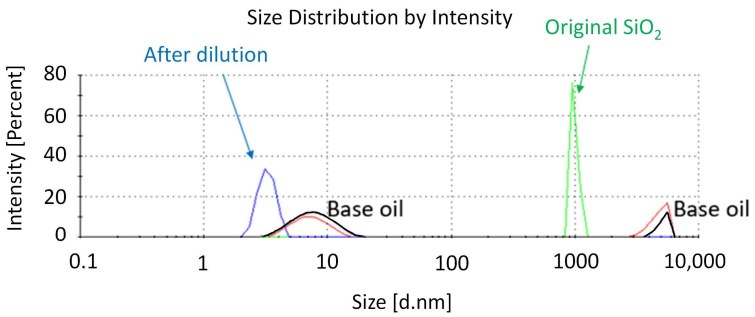

Figure 7. Examples of peaks of the size distribution of the original SiO_2 sample, the same after dilution and the base oil.

This shows that there is only a loose bonding between nanoparticles, samples can be easily redispersed, again reaching the size of less than 100 nm, which is necessary to be effective in tribosystems. It was found that homogenization had to be carried out with special care and that the measurement results of freshly agitated samples are difficult to reproduce. This can be because of the high viscosity of the oil, bubbles can get into the system, etc. In further measurements, the samples were prepared at a lower concentration to avoid the need for further dilution to determine and compare the primary particle size of SM and pure SiO_2 nanoparticles more accurately. Preparation was carried out as it was written above. From size distribution curves the average of mean peak values and their standard deviation were calculated by the Malvern Zetasizer software. Results corresponding to both types of nanoparticles and the base oil are shown in Table 3.

Table 3. Average Peak Mean Values (PMV) and their standard deviation (SD) of surface modified (SM) and pure SiO_2 nanoparticles.

Sample	Average PMV (nm)	SD ($n > 3$)
SM SiO_2	5.0	0.87
SiO_2	5.5	0.6
Group III base oil	8.8	1.6

Data show that SM and pure SiO_2 nanoparticles do not aggregate or can be easily redispersed by the application of low shear force. Evaluating the average of PMVs, the size values of ceramic nanoparticles can be separated from the impurities of the base oil. The size of nanoparticles with and without surface modification were 5.0 and 5.5 nm, respectively. This shows that there is no difference in primary size between the two types of nanoparticles, so surface modification did not result in a change in size.

3.2. ATR-FTIR Spectroscopic Examinations

The presence of ethyl oleate, which modified the surface of nano-sized silica particles, was investigated by FTIR. The FTIR spectra of SiO_2 nanoparticles after surface modification (SM SiO_2) and without modification (SiO_2), are presented in Figure 8.

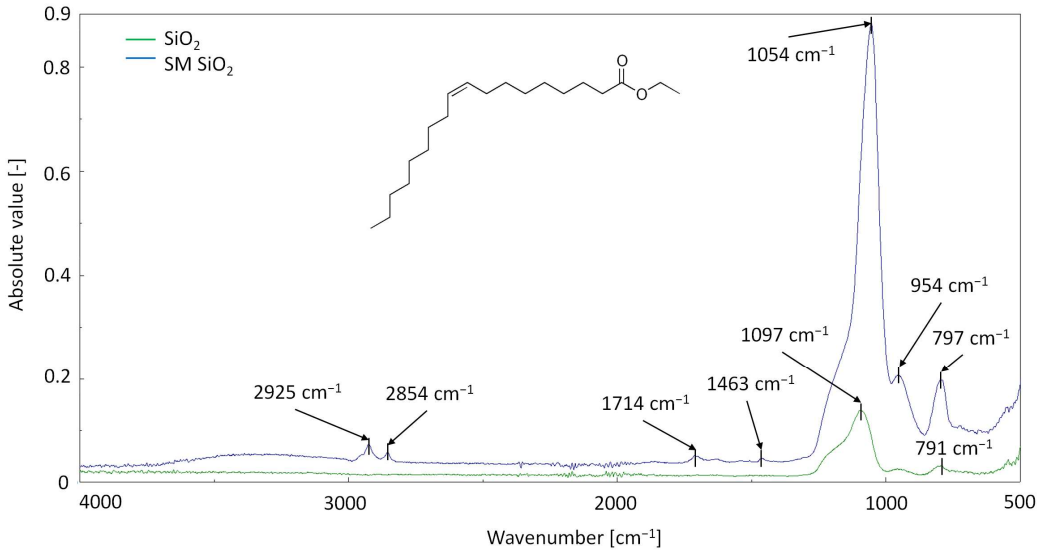

Figure 8. FTIR wavenumber diagram of unmodified (green) and surface-modified (blue) silica nanoparticles. In the wavenumber diagram of the surface-modified nanoparticles, the signs of ethyl oleate surrounding the nanoparticles appear as a visible difference. The line structure of the ethyl oleate is shown in the middle of the diagram.

The characteristic peaks of the stretching vibration of Si-O-Si are around 1000–1100 cm^{-1}. While the asymmetric stretching vibrations of Si-O can be found between 790–800 cm^{-1}. Peak intensity between 700–1100 cm^{-1} increased significantly. In the case of SM nanomaterial, these peaks are identical, not shifting significantly, but new two peaks appeared. The peaks at 2925 cm^{-1} (-CH_2-CH_2-) and 2854 cm^{-1} (-CH_2-CH_3) both show that long alkyl chains are presented on the surface of the nanoparticles. The peak at 1714 cm^{-1} belongs to the characteristic stretching vibration of C=O in the ethyl oleate molecule. The peak at 1463 cm^{-1} means the appearance of the CH_2 bending vibration. The peak at 954 cm^{-1} is associated with the stretching vibration of –Si–OH groups. The novum peaks indicated that the coater material (ethyl oleate) appeared and was incorporated, which also proved that FTIR is a suitable method to detect it in a solid form.

3.3. Tribological Experiments

Figure 9 represents the friction coefficient comparison of SiO_2 containing nanolubricants with (orange bars) and without (blue bars) surface modification. Similar tendencies can be observed in the case of nanoparticles with and without surface modification because both increase the friction coefficient value compared with the 0 wt% results up to 0.2 wt% NP concentration and above 0.2 wt% the frictional loss starts to decrease. The main difference between these nanoparticles is the relative increase (without SM + 69% at 0.2 wt%, while with SM + 9% at 0.1 wt%) and the reproducibility of the measurements (the maximum width of the error bar is without SM 0.052 at 0.3 wt%, while with SM it is 0.012 at 0.3 wt%). According to these results, it can be suspected that the surface modification preparation process has increased the stability of the silica-containing nanolubricant samples, because the measured values can be placed in a significantly smaller range, compared with the similar nanolubricants without surface-modified silica particles.

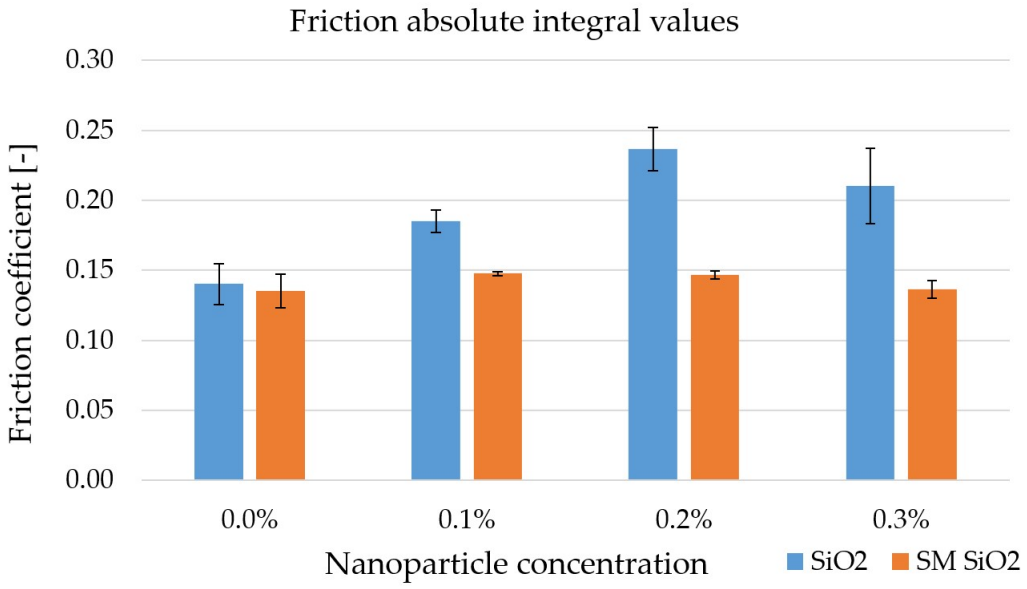

Figure 9. Comparison of the measured friction coefficient values of nanolubricants with different SiO_2 concentrations without (blue) and with (orange) surface modification.

Figure 10 illustrates the measured mean wear scar diameter (MWSD) values from the contact surface of the ball specimen. The tendency difference between the two types of nanoparticles is visible: without surface modification, the MWSD increases continuously with increasing concentrations, while it decreases in the case of surface-modified silica nanoparticles. The stability-increasing property of the surface modification is visible from these results as well: the width of the error bars was reduced from 270 µm (0.1 wt% result without SM) to 20 µm (0.3 wt% result with SM) in the presence of surface-modified silica nanoparticles. This error bar reduction leads to the result that the surface modification

process improves the repeatability and reproducibility of the tribological measurements by stabilizing the nanolubricant and providing homogeneous silica distribution in the investigated oil samples. It can be defined that the surface-modified silica nanoparticles provide wear-reduction properties for the oil samples, with the highest wear-decreasing potential of 15% in the case of 0.2 wt% silica concentration.

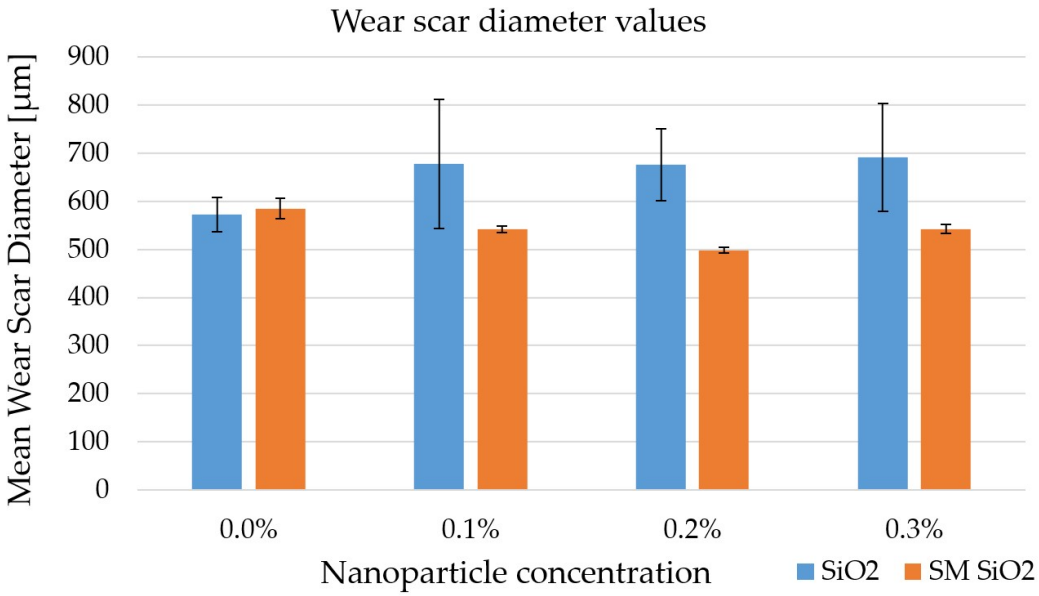

Figure 10. Comparison of the measured mean wear scar diameter (MWSD) values of nanolubricants with different SiO_2 concentrations without (blue) and with (orange) surface modification.

Figures 11 and 12 present the acquired digital microscope images about the wear images of the ball and disc specimens in the case of 0.3 wt% silica containing nanolubricants. The pictures prove the previously defined results: the chemical modification of the surfaces of the silica nanoparticles provided anti-wear properties for the used lubricant, compared to the nanolubricant measurements without surface modification. Analyzing the acquired images, the modification process not just decreased the wear dimensions, but also modified the wear mechanisms: the wear without surface modification shows signs of pitting (fatigue) and deep abrasion (without a high amount of burned oil on the surface), while only a slighter abrasion with burned oil molecules can be observed in the case of the variation with surface modified silica nanolubricants. The wear depth is significantly lower, which can be observed in the images acquired from the disc specimens: minor surface grooves from the original starting surface can be observed on the right image in Figure 12, while this cannot be seen in the case of measurements without surface modification.

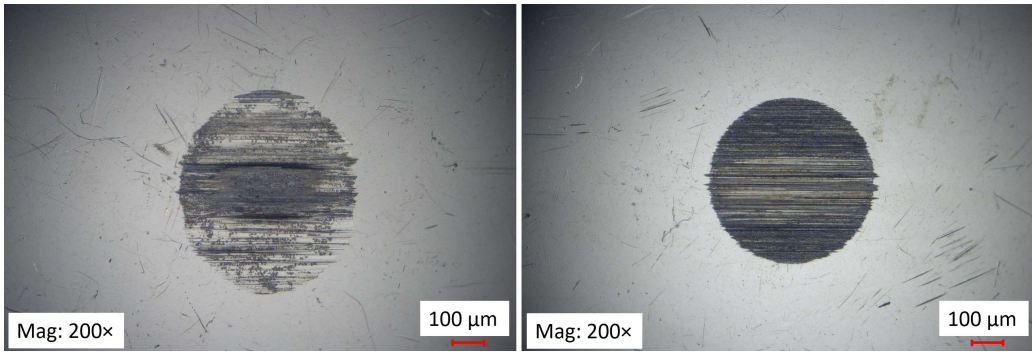

Figure 11. Comparison of the wear scar images on the surface of the ball specimens with 0.3 wt% silica nanoparticles without (**left**) and with (**right**) surface modification.

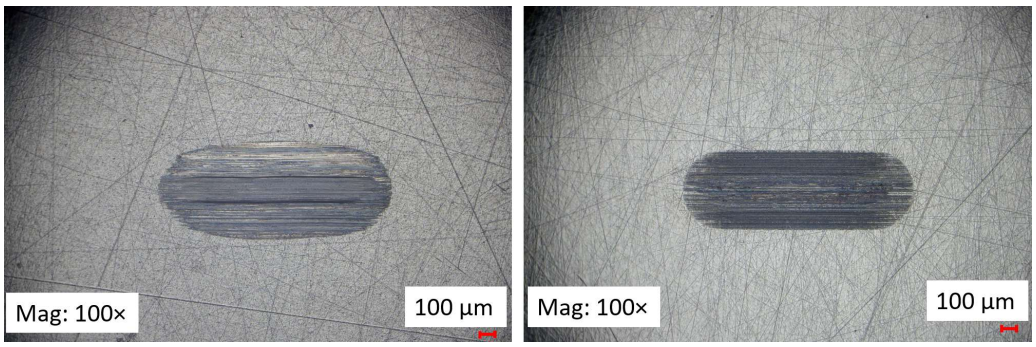

Figure 12. Comparison of the wear scar images on the surface of the disc specimens with 0.3 wt% silica nanoparticles without (**left**) and with (**right**) surface modification.

4. Discussion and Conclusions

This article demonstrated that the surface of silicon dioxide nanoparticles can be modified by esterification. During the surface modification, ethyl oleate is produced from the reaction of ethyl alcohol and oleic acid. Ethyl oleate is deposited on the surface of the SiO_2 nanoparticles during the drying of the sample, thereby coating them. The FTIR test confirmed that ethyl oleate is present on the surface of the nanoparticles. The long carbon chain alkyls from the ethyl oleate molecules occur on the surface of the silica nanoparticles, which helps to create a stable dispersion in Group III based lubricants. By using the surface modified silica nanoparticles, three Group III based lubricating oil were prepared (0.1 wt%; 0.2 wt%; and 0.3 wt% in concentration), which were suitable for tribology tests.

The particle size analysis of the lubricating oil sample was carried out by the Department of Pharmaceutical Administration of University Pharmacy, Semmelweis University, Budapest. It was established that the lubricating oil needs to be diluted to measure the particle size distribution of the lubricating oil sample. From the results of the dynamic light scattering measurements, it can be established that the sizes of the nanoparticles are adequate (5.0–5.5 nm). The applied homogenization method properly separates the nanoparticles in the lubricant.

The tribological tests of the lubricating oil samples were carried out by the Department of Propulsion Technology, Széchenyi István University, Győr. Lubricating oils were tested on an oscillating tribometer. The worn surfaces were evaluated using a standard evaluation. Based on the results, the tribological results are adequate, and the application of the surface modification slightly changes the friction. The surface modification increases the repeatability and reproducibility of the measurements, as the standard deviation of the measured values is significantly lower. The surface modification of the silica nanoparticles could reduce the amount of wear (MWSD) by 15%. The explanation for this is that after the surface modification, the nanoparticles agglomerate and settle more slowly. With the ethyl oleate layer on their surface, they can function properly in the oil.

It can be stated that certain properties of the lubricating oil doped with surface modified SiO_2 are not yet known and require further investigations. The present surface modification method may be suitable for tribology tests of future engine lubricant developments, as well as for investigations of the acting mechanisms of nanoparticles.

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