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Examination of the Tribological Mechanism of Various Ceramic Nanoparticles in an Oil-Based C_{60} Fullerene Solution

Ádám I. Szabó*[,a], Fevzi Kafexhiu[b], Igor Velkavrh[b]

[a]Department of Propulsion Technology, Széchenyi István University, Győr, Hungary
[b]Department Tribo Design, V-Research GmbH, Dornbirn, Austria
szabo.adam@sze.hu

This study aims to evaluate the tribological mechanisms of CuO, SiO_2, and Y_2O_3 ceramic nanoparticles in an oil-based C_{60} fullerene solution using experimental tribotests. The goal is to investigate the impact of these nanoparticles on friction and wear, offering insights into their potential for enhancing lubrication efficiency in automotive applications. Nanoparticles were homogenized using ethyl oleate surface modification. Testing involved a simplified ball-on-disc specimen in a linear oscillating configuration. Results show that the nanoparticles reduce dynamic friction by up to 10 % and static friction by 6 %. They reduce wear on test specimens by 45–81 %. CuO and SiO_2 components are typically used for harder specimens, and Y_2O_3 nanoparticles for softer ones. Scanning electron microscopy identifies characteristic wear mechanisms, and energy-dispersive X-ray spectroscopy determines nanoparticle distribution on worn surfaces. The potential of nanoparticle additives in enhancing automotive lubrication and reducing friction and wear is highlighted, contributing to the industry's pursuit of efficiency and environmental sustainability.

1. Introduction

This study investigates the tribological mechanisms of different oxide ceramic nanoparticles when dispersed in an automotive-lubricant-based C_{60} fullerene solution. Oxide ceramic nanoparticles are advantageous as sustainable lubricant additives due to their availability, grindability, natural occurrence, and versatile applications, making them ideal for optimizing mechanical efficiency and durability as multi-purpose lubricant additives in many environments (Zhao et al., 2021). Silica (SiO_2) nanoadditives in lubricating oils are known to reduce friction and wear in mechanical systems (Ismail and Wan Hamzah, 2022), anti-wear properties acting as a ball bearing (Bao et al., 2017), dispersion stability and versatility (Duan et al., 2023). Tribological tests have demonstrated that CuO nanoparticles can effectively reduce friction because of the layer-forming effect in almost any lubricant environment, whether it be semi-synthetic base oil (Tóth et al., 2021), synthetic oil (Azam and Park, 2023), off-the-shelf formulated engine lubricant (Asrul et al., 2013) and vegetable oil-water emulsions (Seyedzavvar et al., 2020). Yttria (Y_2O_3) nanoparticles are primarily used as components in solid lubricants and coatings due to their anti-wear properties, often in combination with other additives. E.g., 2 vol.% Y_2O_3 improved the wear resistance and reduced friction when combined with hexagonal boron nitride in SiC ceramic matrix composites (Kumar et al., 2023). Y_2O_3 is also effective in polymeric composites and CrNi coatings, significantly enhancing dry lubrication by minimizing adhesive wear (Li and Kong, 2022). The use of Y_2O_3 nanoparticles in liquid lubricants has been scarcely researched. The studies by Tóth et al. (2022) showed that applying 0.5 wt% yttria as a nanoparticle additive does not significantly alter the friction coefficient. However, it can reduce the wear volume of components by up to 90 %. A mending and tribo-sintering mechanism explains this wear-reducing effect, demonstrated through the combined results of SEM and EDX analyses (Tóth et al., 2022).

C_{60} fullerenes can function as nano-additives in the automotive industry, offering a sustainable alternative to traditional additives. Due to its unique chemical structure, the C_{60} fullerene additive has excellent properties as an extreme pressure additive and hydraulic stability when tested in hydraulic oil. The solid and stable spherical arrangement of carbon atoms within the fullerene molecule contributes to its ability to withstand high pressures and protect surfaces under extreme conditions. This structure allows C_{60} to form a protective layer on metal surfaces, reducing wear and friction, particularly in high-stress environments. Its extreme stability in hydraulic

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fluids helps maintain the efficiency and longevity of the lubricating oil (Jing-Shan et al., 2021). In turbojet engine tests, C_{60} fullerene proved effective under extreme temperatures (up to 540 °C) and high pressure, forming a tribofilm that reduces wear by 10-15 % and enhances lubrication efficiency. This makes it valuable for high-performance engines where temperature and stress are critical factors (Oleksandrenko et al., 2023). Recent research investigated the mechanisms of fullerenes in tribological systems using machine learning algorithms (Feng et al., 2024). The algorithms predicted the friction-reducing potential of fullerenes, similar to 2D computational fluid dynamics simulations conducted for piston ring-cylinder wall pairings, demonstrating a 42 % lower friction (Tsakiridis and Nikolakopoulos, 2023). Practical experiments have shown a 4–8 % improvement in friction with fullerenes (Tóth-Nagy and Szabó, 2023). Bon-Cheol et al. (2010) determined the viscosity and lubrication characteristics of fullerene solutions using the Stribeck curve experiment.

The novelty of this research lies in addressing the lack of studies on the synergistic effects between nanoparticles and fullerenes. Given the varied mechanisms of different nanoparticles in tribological systems, detailed exploration is essential, particularly of SiO_2 and CuO in oil-based fullerene solutions, which remain underexplored. Additionally, Y_2O_3's role in liquid lubricants is a crucial knowledge gap. This research is relevant for improving automotive lubrication by reducing friction and wear with nanoparticle additives like CuO, SiO_2, and Y_2O_3 combined with C_{60} fullerenes, potentially enhancing fuel efficiency, component lifespan, and environmental sustainability.

2. Materials and methods

The basis for the C_{60} solution used in the tribological tests was a Group III 4 cSt type base oil (MOL-LUB Ltd.), widely used in modern engine oils. This base oil is a mixture of hydrocarbons and contains no additional additives. 0.0055 wt% of solid C_{60} fullerene (99.5 % purity; TCI, Ltd.) was added to the oil. The dissolution and proper dispersion of the fullerene are crucial for exerting positive tribological effects. However, C_{60} dissolves poorly in nonpolar solvents such as oil. The dissolution of the fullerene was carried out using a magnetic stirrer, with continuous stirring at 25 °C for 96 h, in a closed container under CO_2 gas to decrease oxidative aging of the base oil. The resulting solution is homogeneous and stable over time. The prepared fullerene solution was stored in a cabinet protected from light. SiO_2, CuO, and Y_2O_3 nanoparticles were added to the lubricating oils as well. These were available in bulk powder form with an average particle size shown in Table 1.

Table 1: Applied nanoparticles and their characteristics

Nanoceramic	Particle size	Purity
SiO_2	5-20 nm	99.5 %
CuO	30-50 nm	>99 %
Y_2O_3	<50 nm	99.999 %

For the nanoparticles in the lubricant to function well and exert their beneficial effects, they need to be present in a homogeneous dispersion (Figure 1). The temporal stability of the lubricant is essential for both the measurements and real-life operational demands. Therefore, the surfaces of the nanoparticles, which otherwise behave passively in the oil and settle quickly, need to be modified according to the process flow diagram shown in Figure 1. The nanoparticles were treated with an ethyl oleate surface modification, the effectiveness of which had been previously examined by the author (Tóth et al., 2023). The ethyl oleate surface-modified nanoparticles (0.3 wt%) were introduced into the C_{60} fullerene solution using toluene dispersion with a magnetic stirrer over 16 h. The oil sample was homogenized with ultrasonic mixing at 50 °C for 30 min immediately before the tribometer friction test, after which it was ready for testing.

The tribometric tests were conducted using an RVM1000 (Werner Stehr Tribologie GmbH) tribometer in a linear oscillating ball-on-disk configuration. The ball (60 HRC) and the disk (62 HRC) test specimens were made of DIN 100Cr6 bearing steel. After cleaning the test specimens, they were installed in the tribometer. Lubrication was provided by an oil bath system filled with 2 ml of oil. Each measurement result was derived from three tests' average and standard deviation. The tribometric test parameters are summarized in Table 2.

In the first 60 s, the test runs at a lower frequency with a preload of 50 N for the purpose of running. Afterward, the test runs for 2 h at a frequency of 25 Hz and a normal load of 100 N, generating wear on both test specimens. High-resolution friction data collection (1 kHz) is performed in the third step. The tests consider two friction values: (1) the static coefficient of friction (CoF) occurring during the ball's initial movement from the endpoints and (2) the absolute integral value of friction (FAI) calculated throughout the stroke length. The CoF value represents poor lubrication friction conditions (short-term 0 velocity), while the FAI characterizes the friction over the entire stroke length. The authors have elaborated on the static CoF evaluation procedure (Velkavrh et al., 2023). Each sample's tribological measurement was conducted 4 times, and the characteristic friction parameters (CoF and FAI) were obtained from the measurements' average values of the last 5 min.

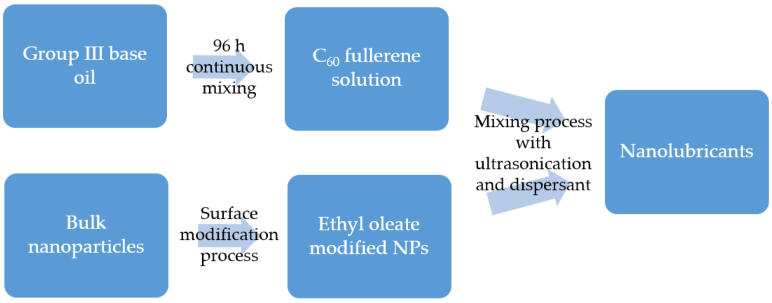

Figure 1: Process flow diagram for preparing the nanolubricants used in the experiments

Table 2: Steps, parameters and goals of tribometric tests.

	Duration	Load	Frequency	Stroke	Temperature	Aim
Step 1	0-60 s	50 N	16.7 Hz	2 mm	100 °C	Running-in
Step 2	60-7260 s	100 N	25 Hz	2 mm	100 °C	Wear
Step 3	7,260-7,320 s	100 N	25 Hz	2 mm	100 °C	High res. friction rec.

During the tribometric tests, wear develops on the ball and the disk. The wear volume (WV) measurements were performed using a DCM 3D confocal microscope (Leica Camera AG), which digitizes the worn surfaces (Figure 2) and calculates the missing volume using the least squares method based on the provided geometry. To determine the WV, the total system wear is considered by summing the ball's and the disk's wear volumes.

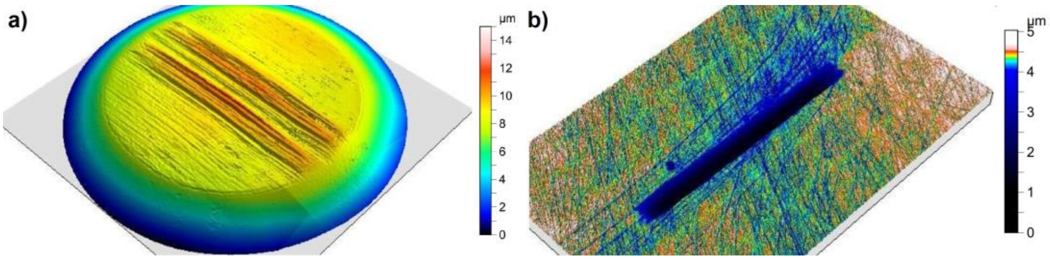

Figure 2: Wear pattern maps digitized by the Leica DCM 3D confocal microscope: ball (left) and disk (right)

The wear analysis is complemented by images taken with a JEOL JSM-7100F scanning electron microscope (SEM), providing insight into the wear processes occurring on the surface. The SEM images were acquired at 1000x magnification from the center of the disk's wear track (area with the highest relative speed) and from the center of the stroke's endpoint (point with 0 relative speed). The SEM images were taken in SE mode at an accelerating voltage of 15 kV with a working distance set between 10–10.5 mm. The localization and quantitative analysis of the nano-additives were performed using the microscope's EDX module with ZAF correction. All test results were compared with the reference results of the oil-based C_{60} fullerene solution.

3. Experimental results

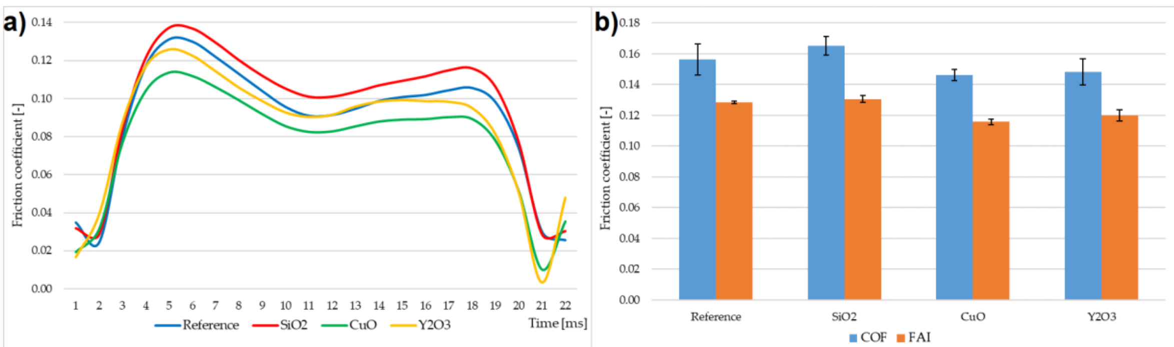

Figure 3: Comparison of the frictional wear curves by each tested lubricating oil sample (left). Static friction (blue) and friction absolute integral (orange) results of the tested nanolubricants (right)

High-resolution data acquisition allows a real-time depiction of friction evolution within a single stroke (Figure 3a). The static coefficient of friction (CoF) peak is initially observed in the left graph. As the ball accelerates, friction decreases, reaching its minimum at the highest velocity in the midpoint of the stroke (Stribeck curve), which then starts to increase as the velocity decreases to zero. The friction evolution for the 4 tested lubricating oils is nearly identical, with notable differences in the oil with Y_2O_3. During the deceleration phase of the ball, this additive performs better than others, resulting in a flatter friction curve over the second half of the stroke. This phenomenon is observed to a lesser extent with the CuO nanoadditive. The results (Figure 3b) indicate no difference in the trends of CoF and FAI. Compared to the value of the non-additivated C_{60} fullerene solution, the SiO_2 additive increased CoF by 6 % and FAI by 2 %. Both CuO and Y_2O_3 nanoadditives reduced friction values. CuO nanoadditive, through triboreduction, form a low-friction Cu coating on the surface (Tóth et al., 2021), decreasing CoF by 6 % and FAI by 10 %. The Y_2O_3 nano-additive resulted in -5 % CoF and -7 % FAI.

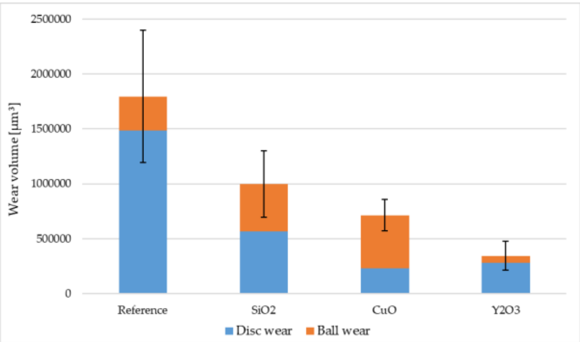

Figure 4: Comparison of total wear volume values produced by different nano-lubricating oils

From the examination of the total wear volume in the tribosystem, it can be observed that all nanoparticle additives improved the wear resistance (see Figure 4). The reductions in wear volume compared to the reference are SiO2: -45 %, CuO: -60 %, and Y_2O_3: -81 %. By analyzing the distribution of wear across the disk and ball, it was noted that both the reference C_{60} solution (4.8:1) and the oil with Y_2O_3 additive (4.2:1) exhibited similar wear ratios between the test specimens. In contrast, the SiO_2 disk-ball wear ratio was 1.3:1, indicating that it could not protect the softer ball material from the harder disk material. In contrast, the wear volume ratio measured with CuO nano-additive was very high, with a disk-ball wear ratio of 1:2. This indicates minimal material loss of the hard disk and significant wear of the softer ball, making it the most worn ball specimen.

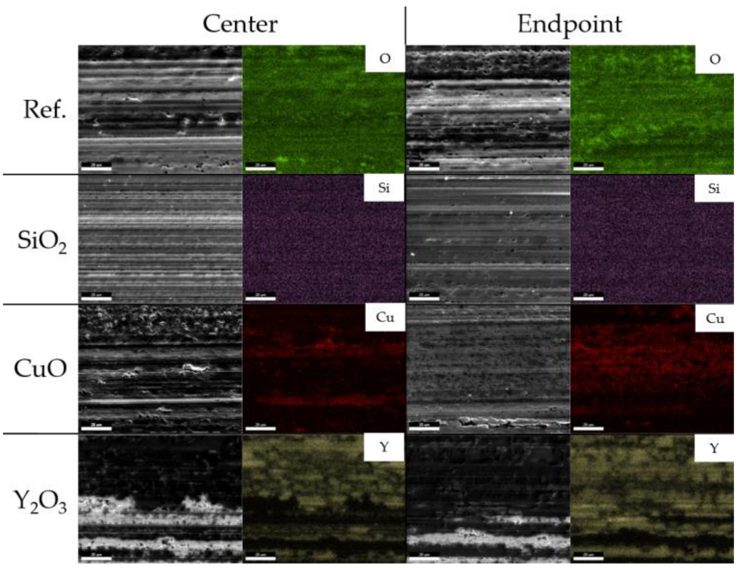

Figure 5: SEM images were taken at the center and endpoints of the disk, along with corresponding elemental maps highlighting the distribution of the analyzed elements in those areas

Figure 5 presents the SEM and EDX results: the left columns show the center of the wear tested with each oil sample, while the right columns show the dead center of the wear. The colored elemental maps on the right were made using EDX to display the presence of the investigated elements in relation to the locations shown on the left. The more colorful an area, the higher the intensity of the signal received by the detector from the examined element. Based on SEM images of the wear scars, it can be observed that the application of the C_{60} fullerene solution results in primarily abrasive and mild fatigue wear in the center and endpoints of the wear. Fatigue wear occurring at the dead centers is more significant and advanced, as indicated by the higher intensity of oxygen on the wear surface than the center area. Using SiO_2 nanoparticles causes intense abrasive wear on the disk, with minimal fatigue wear and significant debris accumulation. The central region of the wear scar and the dead center region experienced overall similar wear, but the dead center shows slightly more signs of fatigue wear and plastic deformation. The CuO undergoes triboreduction to elemental copper, depositing onto the surface, particularly at the endpoints, as previously observed by (Tóth et al., 2021). Significant fatigue wear is also observed on the surface alongside major abrasive grooves. Particularly in the central area of the dead center region, within the area covered by elemental copper, a characteristic feature is the presence of clusters of oxidation spots, visible as small dark patches in the SEM image. Y_2O_3 covers the worn surface, forming a robust tribofilm with excellent wear resistance, showing only mild abrasion and minimal fatigue. The micro-plastic deformation-promoting behavior characteristic of using Y_2O_3 nanoadditives can also be observed in the current wear scars (Tóth et al., 2022).

Table 3 summarizes the quantitative results of the elemental composition of the worn surfaces in normalized atomic percent form. The presence of oxidation processes resulting from the fatigue wear at the dead center of the wear scar tested with the reference C_{60} fullerene solution is supported by the fact that the carbon content of the surface is lower. In comparison, the oxygen content is higher than measured in the wear scar's center. It can be observed that all three nanoparticles are present on the worn surfaces, with approximately 0.3 norm.at% silicon alongside 3.5–8 % copper and 4.7–6 % yttrium remaining on the surface (marked blue in Table 3). The triboreduction of the CuO nanoadditive is evidenced by the particularly low oxygen content on the surface (22.6-22.8 norm. at%). Y_2O_3 nanoparticle additive inhibits the detection of iron, and the elevated oxygen content is attributed to the increase in the nanoparticle's inherent oxygen content.

Table 3: Normalized atomic percentage values from quantitative elemental composition analysis conducted on the center and endpoints of wear scars on the disk test specimens.

	Fe	O	C	Cr	Si	Cu	Y
Ref Center	58.0	24.6	16.3	0.8	0.3	0.0	0.0
SiO_2 Center	60.0	25.0	13.4	1.0	0.6	0.1	0.0
CuO Center	58.9	22.8	13.9	0.8	0.1	3.5	0.0
Y_2O_3 Center	44.7	32.9	16.6	0.6	0.4	0.1	4.7
Ref Endpoint	58.3	26.3	13.9	1.1	0.3	0.1	0.1
SiO_2 Endpoint	59.0	28.4	11.0	0.9	0.6	0.1	0.1
CuO Endpoint	58.0	22.6	10.4	0.9	0.0	8.0	0.0
Y_2O_3 Endpoint	40.5	36.1	16.1	0.7	0.5	0.0	6.0

4. Conclusions

The present study is unique in examining the tribological effects of SiO_2, CuO, and Y_2O_3 ceramic nanoparticles when applied in an oil-based C_{60} fullerene solution. The experimental results align with prior literature on the tribological performance of SiO_2, CuO, and Y_2O_3 nanoparticles in lubricants, confirming their friction-modifying and wear-reducing properties. SiO_2, while providing wear protection, slightly increased friction, a trend observed in earlier studies (Duan et al., 2023). CuO demonstrated excellent friction reduction by forming a copper tribofilm, consistent with findings by Tóth et al. (2021). Y_2O_3 proved the most effective, reducing wear by 81% and maintaining low friction through tribofilm formation, reinforcing its underexplored potential in liquid lubricants.

The SiO_2 nanoadditive shows a wear-reducing effect (-45 %), primarily protecting the harder disk specimen from the softer ball but slightly increasing friction (+2–6 %). Its wear scar exhibits pronounced abrasion and contains approximately 0.3 norm.at% Si. The CuO nanoadditive creates a surface coated with Cu (up to 8 norm.at%), demonstrating excellent friction (-6–10 %) and wear reduction (-60 %). The applied tribological system exhibited significant wear resistance of the harder material. The Y_2O_3 nano-additive adheres to the worn surface. The tribofilm that forms (up to 6 norm.at% Y content) keeps the friction low (-5–7 %) during the deceleration phase of the oscillating motion, protects both components from wear (81 % wear reduction), and prevents surface fatigue. In addition, while all three nanoparticles showed improved wear resistance, Y_2O_3 demonstrated the most balanced performance, reducing friction and wear with a minimal impact on both components. The study's

findings contribute to understanding how nanoparticles interact in liquid lubricants, addressing a gap in current research on synergistic effects between nanoparticles and fullerenes.
The main limitation of this study is that lubricants were tested only in linear oscillating tribometers with simplified specimens; more complex environments should be examined. Future research should focus on thin-film analysis of tribofilms to understand the tribochemical interactions between nanoparticle additives and fullerenes, offering insights into their mechanisms and advancing lubrication technologies.

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