Synergisms and antagonisms between MoS₂ nanotubes and representative oil additives under various contact conditions

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ABSTRACT

MoS₂ nanotubes are known to enhance the tribological properties of lubricants thanks to support friction-reducing and anti-wear properties. However, in fully-formulated lubricants particularly for steel elements, other properties such as oxidation and corrosion protection are also necessary to provide a comprehensive lubricating performance and protection against oil degradation. As a consequence, the coexistence of MoS₂ nanotubes with other oil additives is unavoidable in immediate future lubrication technologies. This study investigates the influence of representative oil additives such as anti-wear (AW), extreme pressure (EP), detergents and dispersants on the rheological and tribological performance of lubricant mixtures containing MoS₂ nanotubes (NTs). The results obtained provide a wide overview on which of the current commonly used oil additives have a place in future nanolubricant formulations and which additives need to be reconsidered. In general, the synergy between the oil additives and the MoS₂ nanotubes strongly depends on the contact conditions. The reason lies in the interaction mechanisms between the MoS₂ nanotubes and the lubricated surfaces under the presence of the supplementary additive. MoS₂ have an excellent synergy with AW additives under mixed rolling/sliding conditions due to the exfoliation of MoS₂ platelets on top of the AW tribofilm. Under reciprocating sliding, the interaction between the MoS₂ nanotubes and dispersant leads to higher antagonisms. Under extreme pressure unidirectional sliding, their synergy is better with S containing EP additives.

1. Introduction

The two main constituents of tribology are friction and wear. The control and reduction of both parameters is critical to proper functionality of machine elements. High friction leads to energy losses, while excessive wear to catastrophic failure of mechanical systems. Therefore friction reduction and wear control are crucial, both for economic reasons and long-term reliability [1]. Liquid lubrication is one of the oldest method to reduce friction and wear in sliding contacts. Lubricant separates the surfaces through sustain a fluid film, thereby reducing metal to metal contact [2]. The performance of lubricants depends on several factors which include viscosity, pour point, flash point, thermal stability and resistance to oxidation [3]. Moreover, the operating conditions of a lubricant depend on the lubrication regimes which include boundary lubrication, mixed lubrication [4], elasto-hydrodynamic lubrication (EHL) [5] and hydrodynamic lubrication (HL) [6]. The performance of lubricants in machine elements operating

under mixed and/or boundary lubrication becomes even more critical since only a thin lubricant film can be maintained and the direct contact between the asperities plays a dominant role. A vast amount of research was originally focused towards the development of complex mixtures of appropriate hydrocarbon base oils and a number of possible additives [7–9].

Nanoparticles have attracted considerable attention as potential lubricant additives due to their excellent physical and chemical properties [10]. When Transition Metal Dichalcogenides (TMD) nanoparticles such as MoS₂ and WS₂ are dispersed into different base liquids, they will greatly enhance their thermal conductivity and tribological performance [11]. Nanoparticles have five different types of shape: spherical, onion, tube, granular, and sheet. The tube and onion morphology outperformed other morphologies as it is suggested in literature that these shapes are able to effectively roll in first step and later exfoliate in between the sliding surfaces [12]. The nanoparticles have high surface energy due to high surface area by volume ratio. In

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Table 1Overview of the MoS₂ nanotubes mixtures with selected oil additives together with their dynamic viscosities and sedimentation time.

Blend Designation	MoS ₂ NTs	Additive	Dynamic Viscosity [mPa·s]	Sedimentation time
PAO	–	–	33.26 ± 0.26	–
PAO + NTs	5%	–	45.60 ± 2.50	Start: 10 h Stop: 20 h
PAO + AW	–	2% ZDDP	37.23 ± 0.08	–
PAO + AW + NTs	5%	2% ZDDP	43.41 ± 0.36	Start: 25 h Stop: 40 h
PAO + EP	–	2% EP	29.76 ± 0.34	–
PAO + EP + NTs	5%	2% EP	39.10 ± 0.16	Start: 45 h End: 70 h
PAO + det	–	5% Detergent	37.52 ± 0.29	–
PAO + det + NTs	5%	5% Detergent	41.36 ± 0.13	Start: 40 h End: 70 h
PAO + disp	–	5% Dispersant	34.73 ± 0.26	–
PAO + disp + NTs	5%	5% Dispersant	38.16 ± 0.24	Start: n/a End: n/a

order to achieve the equilibrium state, the particles attract each other and agglomerate. In order to reduce the agglomeration, ultrasonication, homogenizing, magnetic force agitation, ball milling and high shear mixing is done [13].

The use of transition metal dichalcogenides nanoparticles in oils is an emerging concept in lubrication, to enhance tribological properties of lubricants, such as load-carrying capacity, anti-wear, and friction-reducing properties between moving mechanical components [14,15]. However, modern industrial elements require additionally other properties such as oxidation and corrosion protection or sludge control to provide a comprehensive protection against degradation. As a consequence, the use of conventional additives as extreme pressure (EP) and anti-wear (AW) additives are typically adopted to improve the tribological performance of a liquid lubricants in reducing surface damage under severe conditions [11,16,17]. Only few researchers were intending to use NPs in fully formulated lubricants, and it was found that the presence of other coexisting additives can influence their performance dramatically [18,19]. It is reported in Ref. [20] that IF-MoS₂ nanoparticles lost their lubricating abilities when added to fully formulated lubricants, due to the presence of dispersants, which prevented nanoparticles from forming tribofilms on the rubbing surfaces. On the other hand, the paradigmatic anti-wear additive zincdialkyl dithiophosphate (ZDDP) has also been investigated in combination with WS₂ [19]. The authors observed a synergistic effect between the two additives tested in PAO oil at 100 °C, it was concluded that WS₂ enhances the antiwear properties of ZDDP, while ZDDP protects WS₂ particles from oxidation and increases their friction reducing properties. In a similar work, it was found that MoS₂ nanoparticles having different morphologies and chemistries had a synergistic effect with ZDDP pre-formed tribofilms [11].

In view of the above, the present study aims to investigate the synergistic and antagonistic effects between conventional additives, such as AW, EP, detergents and dispersants with MoS₂ nanotubes (NTs) under various contact conditions. The tribological performance is investigated first under rolling/sliding conditions, followed discussion in conjunction with results using various experimental techniques with different contact geometry and loading condition. The results provide a wide database that shed some light on the fundamental interactions between MoS₂ nanotubes and commonly used additives. Further, employing an innovative approach dispersion analysis has shown that the additives affecting the nanotubes distribution in the lubricants. The dispersity of the NTs in the lubricant strongly influences the dynamic viscosity and flow curves. Chemical analyses has proved that interaction mechanisms of the nanotubes and surface changes depend on the temperature and on the presence of supplementary additive as well as its ability to form a durable tribofilm.

2. Experimental

2.1. Materials & lubricants

The material used for all tribological tests was AISI 52100 bearing steel. The specimens used for Mini-Traction Machine (MTM) tests had an initial disc and ball roughness of $R_a = 0.01 \mu\text{m}$, and their diameters were 46 mm and 19.05 mm, respectively (PCS instruments, London, UK).

The base oil used in this study was NEXBASE[®] 2008 poly-alphaolefine (PAO) with a viscosity of 24.6 mm²/s at 40 °C and 4 mm²/s at 100 °C. The zinc dialkyl dithiophosphate ZDDP used as AW additive had a primary alkyl structure, with 99% purity. Sulphurized olefin polysulphide (40% of sulphur content) was used as EP additive. Succinimide dispersant was based on long chained hydrocarbon amines with 2000 molecular weight and overbased Ca-sulfonate was used as detergent. The selected additives are commonly used in gear oils and their respective concentrations represent typical values found in fully formulated products. The nanotubes (NTs) investigated in this study were synthesized from MoS₂I₈ nanowires by the procedure reported in Ref. [21]. The diameter of the NTs is in the range of 100–150 nm, while their length is up to 3 μm . The walls of the NTs are approx. 10 nm thick and form dome terminations.

2.2. Nanofluids preparation and characterization

The base oil, additives and NTs used in this study were blended into following mixtures shown in Table 1, applying an ultrasonic processor VC 505 Sonics & Materials.

The dynamic viscosity measurements at 40 °C also listed in Table 1 were performed using an Anton Paar Physica Modular Rheometer Series (MCR) 101 parallel-plate system with a shear rate of 100 (1/s). The suspension stability of the nanofluids was evaluated based on optical camera photos of homogenized nanofluids captured every 1 h until complete precipitation of the nanopowder. The sedimentation time comprising sedimentation start (clear layer stratification) until sedimentation end (complete precipitation) is given in the last column in Table 1.

In order to characterize the distribution and dispersion of the NTs in the different lubricant mixtures immediately after homogenization, a nanofluid sample was prepared as a narrow liquid film placed between two thin glass slides of the thickness 0.15 mm and visualized using Nikon MM-40 microscope with the magnification of 200 $\times$ in order to make comparisons between the different blends.

2.3. Tribological test set up

In this study three types of tribological tests were selected in order to thoroughly investigate the interaction between the representative oil additives and the MoS₂ nanotubes in terms of tribological performance as function of the contact conditions. The focus of the present work is set for the first time on their synergisms and antagonisms under mixed rolling/sliding conditions, which is investigated using a Mini-Traction Machine (MTM). The results of these experiments aim to understand the behavior of the nanofluids in terms of tribofilm formation under this particular contact situation, since the synergistic and antagonistic effects between the MoS₂ nanotubes and the lubricant additives are known to depend on the contact conditions [16]. Once their behavior under mixed rolling/sliding is understood, in following sections 4.1 and 4.2 the results are discussed in conjunction with work previously published by some of the authors [16]. The goal is to provide a comprehensive overview of the fundamental interaction mechanisms between the MoS₂ nanotubes and individual oil additives as function of several contact conditions. To this end, the performed mixed rolling/sliding tests represent mild and/or moderate tests conditions in point contact so that the influence of rolling is addressed by comparing the data obtained with the reciprocating sliding ball-on-disc tests using a SRV[®] tribometer (Optimol Instruments Prüftechnik GmbH, Germany) (Table 2b in section 4.1). The role of more severe, extreme pressure testing conditions on the synergistic effects between the nanotubes and the additives is addressed using data obtained with Brugger tribotests (Table 2c in section 4.1). The Brugger tests is a standardized method for determining the lubrication ability of additivated oils under boundary lubricating conditions.

2.4. Mini-Traction Machine (MTM) tribotests

The MTM creates a mixed rolling/sliding contact between an independently driven ball and a disc. In our case, the disc was immersed in a lubricant bath, and the ball was loaded against the face of the disc (Table 2a) with a normal load of 35 N, which corresponds to a mean Hertzian contact pressure of 0.7 GPa. In order to evaluate the tribofilm formed under these conditions, the MTM experiments were performed using the following steps:

- Initial Stribeck curve taken at room temperature (25 °C), with the mean contact velocity decreasing from 3.2 to 0.002 m/s (transition from hydrodynamic to boundary lubrication regime) with SRR (Slide to Roll Ratio) 50% under load of 35 N.
- Running-in performed during 2 h at a constant mean velocity of 0.05 m/s, and at load of 35 N.
- Final Stribeck test under the same conditions as those employed initially.

This procedure using identical parameters was previously studied and validated by one of the co-authors. Further information on the procedure is given elsewhere [22]. The MTM was equipped with an optical interferometry module for imaging an additive derived film on the surface. Through the manuscript the initial Stribeck curves are presented (as those are the most representative) together with the acquired interferometric optical graphs of the tribofilm. The interferometry images show changes in color when agglomerated nanoparticles are trapped in the contact. However it has to be mentioned that sometimes the strong coloration can be also attributed to particles adhering to the glass window. Due to this fact, no clear correlation between the film thickness and color change in the optical images can be stated. The tests parameters and schematic of the test setup are summarized in Table 2 in section 4.1.

2.5. Surface analysis

The tribologically investigated samples after the tests were rinsed with Petroleum Ether followed by cleaning in ultrasonic bath using Isopropanol for 3 min (both solvents HPLC grade). Afterwards, the wear tracks were examined by using a series of surface characterization instruments including optical interferometer, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS).

Surface topography of the tested samples was evaluated using a Leica DCM 3D – combining interferometric and confocal microscopy (Leica, Japan). Surface roughness was measured before and after the tests according to ISO 4287. The Leica Map Premium 0.2.0190 software was used for the wear volume analysis. The measured wear volumes were normalized into wear coefficients (K) according to Archard's equation:

$$K = \frac{V}{F \cdot S} \quad (1)$$

where, V is the remove wear volume (m³), F the normal load (N), and S the sliding distance (m).

Scanning electron microscopy micrographs were obtained using Hitachi SU-70 Analytical Field Emission SEM. It is equipped with the Schottky electron source with ultra-high resolution, and EDS (Energy Dispersive X-ray Spectrometer of the Thermo Scientific), detecting elements from beryllium to uranium. The accelerating voltage range was 0.1–30 kV with an ultra-high resolution observation of secondary electrons of 1.0 nm for 15 kV, and 1.6 nm for 1 kV. The measurement magnification range was 30 × - 800000x with a high vacuum in the chamber 10⁻⁸ Pa. The spectra were acquired at an accelerating voltage of 15.0 kV and a take-off angle of 30.9 (distance sample-detector 15 mm).

X-ray photoelectron spectroscopy (XPS) analyses were performed using a Prevac UHV XPS System equipped with a non-monochromatic Al Kα X-ray source (hν = 1486.6 eV) and Ar + ion gun. During the measurements, the base pressure inside the XPS chamber was kept constant at values in the range of 3 × 10⁻⁹ mbar. The investigated samples after the tribological tests were rinsed with petroleum ether followed by cleaning in ultrasonic bath with isopropanol for 3 min (both HPLC grade) and subsequently sputtered in the XPS chamber using soft Ar⁺ for 30 min, at 1.5 kV and 7.5 mA sputter current in order to remove the remaining contaminants. The estimated cleaning rate is < 5 nm/30 min. The cleaning procedure and sputtering parameters follow the Prevac XPS specifications for tribologically tested samples. In contrast, XPS depth profiles were performed using much stronger sputtering parameters compared to cleaning. The Ar + ion gun were set for an energy of 5 keV with a emission current of 10 mA and a current density of 147 μA/cm². The estimated sputtering rate with this parameters is 15 nm/1 h. The high resolution spectra were taken at a pass energy of 200 eV and a step of 50 meV and the resulting binding energies were referenced to adventitious carbon at a binding energy of 284.8 eV.

3. Results and discussion

3.1. Stability of the nanofluid mixtures

The stability of the nanofluids (freshly homogenized) was evaluated based on optical camera images captured every hour until complete precipitation of the nanopowder as shown in Fig. 1. The sedimentation time is given in the last column in Table 1, defined as the time comprising between sedimentation start (clear layer stratification as visible in Fig. 1c and d) until completed sedimentation (complete precipitation as visible in Fig. 1a and b). Fig. 1 shows the images taken 50 h after homogenization. It is clear from it that first two blends: PAO + NTs and PAO + AW + NTs precipitate (clear layer of sedimented nanotubes on

Fig. 1. Images of dispersed nanotubes in lubricating blends 50 h after homogenization.

the bottom), while PAO + EP + NTs and PAO + det + NTs are still within the precipitation process. The last blend of PAO + disp + NTs remains stable.

A drop of the nanolubricants blends directly after homogenization was placed between two thin glass slides and was analyzed with optical microscopy in order to visualize the NTs dispersity as shown in Fig. 2. The micrographs present thin films of the nanofluids PAO + NTs (Fig. 2a), PAO + AW + NTs (Fig. 2b), PAO + EP + NTs (Fig. 2c), PAO + det + NTs (Fig. 2d), PAO + disp + NTs (Fig. 2e). It can be clearly noted that large agglomerates are formed in the blend PAO + NTs (Fig. 2a), so that the stability of this nanofluid is poor. It took ca. 10 h until start of precipitation of the NTs in PAO oil. The addition of selected additives to the NTs blends changes their dispersity and stability. Fig. 2b, c and 2 d show how AW, EP and detergent change the dispersity of the NTs in PAO oil. In the PAO + AW + NTs blend, the NTs still form agglomerates but smaller and more homogeneously distributed in the suspension, which leads to a stability time of 40 hours, more than double compared to the PAO + NTs blend (20 h). When EP or detergent are the accompanying additive for the NTs, even smaller

agglomerates are formed resulting in a stability time of approximately 70 h. When dispersant is used the NTs are completely homogenized and no clusters or agglomerates are visible as presented in Fig. 2e. Nevertheless, the blends of EP additive + NTs and detergent + NTs start to stratify in ca. 40–45 h after homogenization, while the dispersant + NTs blend remains stable. A detailed analysis of particle size distribution in the analyzed blends was the objective of a research separately published in Ref. [16].

3.2. Rheological properties

Dynamic viscosity and flow rate curves reveal information about the flowability of oils under different shear and simulated process conditions [23]. Fig. 3a presents the viscosity curves measured at 40 °C under a shear rate of 100 (1/s). It shows that pure base oil PAO has a dynamic viscosity value oscillating around 33.26 ± 0.26 mPa s. The addition of any conventional additives e.g. AW, EP, detergent or dispersant only changes the dynamic viscosity slightly to values ranging from 34–37 mPa s. On the other hand, the addition of 5% MoS₂ NTs to the PAO

Fig. 2. Microscopy images of a) PAO + NTs, b) PAO + AW + NTs c) PAO + EP + NTs d) PAO + det + NTs e) PAO + disp + NTs trapped between two thin glass plates.

Fig. 3. Influence of NTs on rheological properties of PAO base oil, AW additivated oil and base oil with dispersant on a) dynamic viscosity curves b) flow rate curves.

or PAO + AW strongly rises dynamic viscosity to the value of approx. 43–45 mPa s, while this is not the case for well dispersed NTs, where the dynamic viscosity only raises marginally to ~35 mPa s in PAO + disp blend and up to ~38 mPa s in PAO + disp + NTs. The detail measurements of dynamic viscosity for all investigated blends are given in Table 1. In Fig. 3a only results for selected blends are presented for clarity purposes. It can be noticed that the dynamic viscosity for the PAO + NTs blend is very unstable and oscillates. Other blends containing MoS₂ NTs showed a stable dynamic viscosity curve as for example PAO + AW + NTs and PAO + disp + NTs as shown in Fig. 3a. Further investigations reported in Fig. 3b presents dynamic viscosity (Pa·s) versus shear rate (1/s) at 40 °C. Similarly in this test, dynamic viscosity for the mixture of PAO + NTs is very unstable especially at low shear rates. These unsteady results of the dynamic viscosity for PAO + NTs blends can be attributed to the susceptibility of NTs to generate agglomerates as pictured in Fig. 2a. In case of the blend PAO + AW + NTs, its dispersity is much better, and as shown in Fig. 2b for PAO + disp + NTs no agglomerates were detected for the latter using optical microscopy.

3.3. Tribological performance under mixed rolling/sliding conditions

The initial Stribeck curves obtained using MTM are presented in Fig. 4. The Stribeck curves for each nanofluid combination were acquired thrice (the scatter was always below 10%), and representative measurements are presented in the diagrams. The initial (prior the running in) and the final (after the running in) Stribeck curves were practically the same for the testing blends, so that hereinafter only initial Stribeck curves are shown in the presented results. After running

in, an optical image was taken using the MTM instrument and are shown in the figure next to the Stribeck curve.

In the MTM tests, the largest effect of the nanotubes is achieved at the lowest sliding velocities, in the boundary lubrication regime. In the elastohydrodynamic lubrication (EHL) regime, the nanotubes do not function due to the absence of interaction between the NTs and the surfaces [24]. At 100 °C, a very low coefficient of friction (CoF) of 0.045 was reached for the base oil mixed only with NTs (Fig. 4b), while at room temperature of 25 °C the CoF for this blend was a bit higher reaching values of 0.065 (Fig. 4a), both in boundary lubrication regime. The temperature influences the shape of the Stribeck curve which is declining much slower at 100 °C with increasing speed. However at speeds below 100 mm/s, the CoF for non-additivated base oil PAO is almost the same at both temperatures. Clearly the NTs presented in the oil blend strongly affect the frictional characteristic at high temperatures compare to the response at room temperature. Optical images taken after running in are incorporated in Fig. 4a, which shows evidence of tribofilm presence after the test with the PAO + NTs blend. In contrast, a blank image was registered after the test with pure PAO. This confirmation explains the beneficial effect of the NTs. As mentioned earlier, the colours of the optical images shown within Fig. 4a can't be directly attributed to tribofilm thickness.

The presence of AW additive in PAO oil (purple color) marginally influence the oil performance in terms of friction at both testing temperatures of 25 °C and 100 °C, as it is shown in Fig. 5a and b. The addition of NTs to this blend (light purple color) caused a reduction in CoF of ~36% and 60% at 25 °C and 100 °C, respectively, in boundary lubrication regime. The optical image taken after running in and incorporated in Fig. 5a, clearly shows evidence of either a formed

Fig. 4. Initial Stribeck curves obtained using MTM for PAO and PAO + NTs at a) 20 °C and b) 100 °C.

Fig. 5. Initial Stribeck curves obtained using MTM for PAO + AW and PAO + AW + NTs at a) 20 °C and b) 100 °C.

Fig. 6. Initial Stribeck curves obtained using MTM for a) PAO + EP and PAO + EP + NTs, b) PAO + det and PAO + det + NTs, c) PAO + disp and PAO + disp + NTs at room temperature.

tribofilm or nanoparticles adhered to the glass window after test with PAO + AW + NTs blend. Alternatively, a blank image was observed after the test with PAO + AW.

In Fig. 6a, the MTM tests results are compared for lubricant blends containing EP additives: PAO + EP (light pink) and PAO + EP + NTs (dark pink). The presence of EP additive in PAO oil improves the base oil performance in terms of friction apparently due to the enough severe contact conditions achieved in order to be able to activate the EP additive. However no tribofilm could be noticed in the upper optical image incorporated in the figure. Fig. 6a also shows that the performance of PAO + EP can be even further improved by the presence of the NTs. The drop of CoF for the PAO + EP + NTs blend is 30%. An optical images taken after running in with PAO + EP + NTs and incorporated in the lower part of Fig. 6a, clearly shows changes in color, which can be an evidence for tribofilm formation or adhered nanoparticles after the test.

The presence of detergent in PAO oil did not affect the base oil performance in terms of friction as it is shown in Fig. 6b. The further addition of NTs to this blend reduces the CoF by ~35% in boundary lubrication regime. An optical images in Fig. 6b, clearly shows evidence of a tribofilm or adhered nanoparticles after the test with PAO + det + NTs blend, when compare to a blank image registered after test with PAO + det. When using dispersant in PAO oil, the frictional performance of the base oil improved, as shown in Fig. 6c. The addition of NTs to the blend further reduced friction by 24%. Optical images in Fig. 6c, indicate only a scent presence of NTs after test with PAO + disp + NTs blend.

3.4. Tribofilm formation under mixed rolling/sliding conditions

The disc surfaces after MTM tests at 20 °C and 100 °C with PAO, PAO + NTs, PAO + AW and PAO + AW + NTs blends were analyzed

using SEM/EDX in order to reveal the interaction mechanisms under mixed rolling/sliding conditions between NTs and additives. SEM/EDX and XPS analysis are shown in Fig. 7 a–h. Additionally, the roughness value R_a of the area 0.2×2 mm within the wear track measured at five different positions is also given in Fig. 7 a–f. The investigated MTM specimens after the tribological tests were rinsed with petroleum ether followed by cleaning in ultrasonic bath by isopropanol for 3 min (both HPLC grade). By observing the SEM morphologies of the wear tracks (Fig. 7 a–h) it is obvious that most of the NTs, which were richly covering the surfaces after the MTM tests (as shown at the embedded optical images in the Stribeck curves, Figs. 4–6) are gone after ultrasonic cleaning. Nevertheless, the EDX and XPS analysis confirmed the presence of Mo and S peaks, deriving from exfoliated MoS_2 nanotubes within a thin (not visible under SEM) tribofilm. On the specimens after tests with PAO + NTs, dark points were visible on the wear tracks as spotted in Fig. 7 c and d. EDX point analysis proved that those dark marks are rich in molybdenum and sulphur. On the surface outside the wear track the concentration of those elements was rather poor. It is also remarkable that the surface roughness within the wear scar after MTM tests at 25 °C with PAO is one order of magnitude higher compare to the test with PAO + NTs, while at 100 °C it is contrariwise. Surprisingly, surface roughness after the test with PAO + AW at both testing temperatures (Fig. 7e and f) and PAO + AW + NTs at room temperature (Fig. 7g) is very smooth and uniform with an R_a oscillating around 10 nm, although the SEM images show a rather groovy wear track. This can be explained as a consequence of ZDDP tribofilm formation. Despite the presence of grooves on the wear track, they are thoroughly covered by ZDDP tribofilm as shown by XPS analysis [25]. At 100 °C, the addition of NTs to the PAO + AW blend caused roughening of the surface within the wear track as visible in Fig. 7h. In summary, the presence of NTs at room temperature caused smoothing of the wear track surface, while roughening at high temperature.

The mechanism of NTs interaction with the surface when comparing PAO + NTs (Fig. 7c and d) and PAO + AW + NTs (Fig. 7g and h) is significantly different. In terms of morphology of the wear tracks, dark points are present after the tests with PAO + NTs at both testing temperatures (Fig. 7 c and d). EDX spot analysis proved that those dots are composed of molybdenum and sulphur. Those dark dots expand with temperature, so at 100 °C they become wider, resulting in a stronger EDX and XPS signal. After the test with PAO + AW + NTs

(Fig. 7g and h) apart from few dark points (same as in PAO + NTs), the analysis exposed pronounced smashed particles or their agglomerates present locally in the form of thick patches. EDX point analysis proved that those patches are composed of molybdenum and sulphur. In this case, the EDX and XPS signals after the tests at 100 °C is not much stronger compared to the test at room temperature.

For an insight into the surface chemistry XPS spectroscopy was performed on selected MTM discs within the wear track. Fig. 7 a–h next to the SEM/EDX results include pie charts with surface composition elements in at.%, with described chemical states, binding energies and uncovered chemical bonding. The MTM tests with pure PAO at 25 °C show a content of ~30% of iron, ~35% of carbon and ~35% of oxygen in the wear track (Fig. 7a). Through a fitting procedure, deconvolution of the O1s, C1s and Fe 2p_{3/2} was performed. Oxygen 1s peak is composed by 2 oxides states at binding energies 529.26 eV and 530.84 eV. Carbon 1s peak is composed by two states at energies 284.77 eV and 288.82 eV attributed to C-C/C-H and C=O chemical bonding. Iron 2p was deconvoluted into two doublets each composed by Fe 2p_{3/2} and Fe 2p_{1/2} peaks. The Fe 2p_{3/2} doublet is composed by peaks at 708.11 eV and 710.11 eV attributed to Fe_3O_4 and FeO [26,27]. On the wear track after the MTM tests with pure PAO at 100 °C it was detected 5% more oxides and 7% less iron compared to the tests at room temperature. The observation of a thicker oxidation layer at high temperature is in accordance to literature [19,25].

The elemental analysis performed on the wear tracks after the tests with PAO + NTs at 25 °C and 100 °C are given in Fig. 7c and d, respectively. At room temperature, it was found ~28% of iron, ~26% of carbon and ~42% of oxygen. Besides a notable presence of NTs products was found with Mo 3d at 1 at.% and S 2p almost at 3 at.%. The composition of the carbon 1s is relatively similar to the one detected with pure PAO. The main differences are for O 1s and Fe 2p peaks. O 1s at binding energy 530.66 eV was attributed to MoO_3 and Fe 2p_{3/2} at 711.33 eV to FeS/ FeSO_4 [26,27]. The molybdenum peak Mo 3d was deconvoluted into two doublets, each one composed of the Mo 3d_{5/2} and Mo 3d_{3/2} peaks as shown in Fig. 8a. The larger doublet Mo 3d_{5/2} is composed of two components: first at 229.6 eV attributed to Mo (4+) valence state originates from MoS_2 and second component at 232.55 eV attributed to Mo (6+) valence state originates from MoO_3 [24,27]. These findings are also supported by the deconvolution of the S 2p spectra shown in Fig. 8b. Similarly, as for Mo 3d, the S 2p was

Fig. 7. SEM images accompanied by EDX and XPS analysis, as well as roughness values acquired within the wear tracks on MTM discs tested with a) PAO at 25 °C b) PAO at 100 °C c) PAO + NTs at 25 °C d) PAO + NTs at 100 °C e) PAO + AW at 25 °C f) PAO + AW at 100 °C g) PAO + AW + NTs at 25 °C and h) PAO + AW + NTs at 100 °C.

Fig. 7. (continued)

deconvoluted into two doublets composed by the S 2p_{3/2} and the S 2p_{1/2}. The higher doublet S 2p_{3/2} consist of two components: at 162.6 eV attributed to S (2-) valence state originating from sulfides e.g., MoS₂ or/ and FeS and a second component at 168.6 eV attributed to S (6+) oxidation state originating from sulfates e.g., FeSO₄ [27–29]. The main difference in the elemental analysis performed on the wear track after the tests with PAO + NTs at 100 °C (Fig. 7d) is that the amount of oxygen from MoO₃ is 27% higher. On contrary, other oxides like Fe₃O₄ and FeO are 20% less when compare to samples tested at room temperature. Following the same trend, the amount of iron is almost a factor three smaller on the sample tested at high temperature meaning that tribofilm derived from exfoliated MoS₂ NTs is much thicker. This trend is confirmed by a much stronger signal from Mo and S on the sample tested at high temperature. This XPS results serve as explanation to the roughness changes observed. At room temperature, the tests with PAO + NTs caused smoothening of the wear track, while at high temperature roughening (Fig. 7c–d and 7 g–h). This effect is justified by the MoS₂ decomposition to MoO₃ and FeSO₄ and FeS resulting in a

more abrasive wear mechanism.

A similar chemical analysis was performed on the wear tracks of samples tested with PAO + AW and PAO + AW + NTs as shown in Fig. 7e–h. It was found ~21% of iron, ~37% of carbon, ~34% oxygen, ~4% zinc, ~1% phosphorus and surprisingly ~4% of sodium on the sample after tests with PAO + AW at 25 °C (Fig. 7e). On the sample tested with PAO + AW + NTs at 25 °C (Fig. 7g) the composition was ~30% of iron, ~29% of carbon, ~36% of oxygen, ~1% of zinc, ~1% of sulfur, ~1% of molybdenum and ~1% of potassium. The main differences between both samples are in the composition of the iron peak and the presence of molybdenum and sulfur in the sample after tests with PAO + AW + NTs. In Fig. 7g, the Fe 2p_{3/2} is formed by peaks at 709.18 eV and 712.23 eV attributed correspondingly to FeO and FeS/FeSO₄ [27]. The main difference with the sample tested with PAO + AW + NTs at 100 °C and shown in Fig. 7h is that the signal from additive derived tribolayer (Mo 3d, S 2p, Zn 2p, P 2p) is twice as large and signal from Fe 2p is by 10% weaker compare to the same test at 25 °C. These findings confirms that the tribofilm derived from AW

Fig. 8. a) Mo 3d and b) S2p spectra from the wear track after MTM test with PAO, PAO + NTs and PAO + AW + NTs at 25 °C.

Fig. 9. XPS depth profile of the wear track after MTM tests with a) PAO + NTs at 100 °C and b) PAO + AW + NTs at 100 °C blends.

additive and exfoliated MoS₂ NTs is much thicker on the sample tested at high temperature.

The XPS depth profiles on the selected MTM samples, inside the wear track region are presented in Fig. 9. Only representative depth profiles are shown for samples tested with PAO + NTs (Fig. 9a) and PAO + AW + NTs blends (Fig. 9b) at 100 °C. The wear track after the test with PAO + NTs first sputtering cycle exposed much more iron (88%) and less oxygen (5%) compare to the surface after test with PAO + AW + NTs where iron was at 60% and oxygen at 25% atomic concentration. This result is typical for a surface covered with Fe-oxide and tribochemically derived ZDDP layer, explaining the thickness of the layer which is thicker on the PAO + AW + NTs sample when compared to PAO + NTs. This result is not surprising, since it is known that AW layers are very thick and can reach over 100 nm.

In both cases on Fig. 9a and b, Mo and S are presented on the top most surface confirming the presence of tribochemically derived MoS₂

layer on top of iron oxide and on top of the AW tribofilm. In Fig. 9a, Mo and S peaks representing MoS₂ NTs derived products diminish after 4–5 sputtering cycles, meaning that nanosheets resulting from exfoliation of NTs are trapped within the bulk layer of the iron oxide tribofilm. SEM/EDX (Fig. 9b) and XPS results taken on the area of PAO + NTs tribofilm indicate that the bulk portion of the Fe-oxide tribofilm consist of oxides. Both facts explains that the mechanism of NTs acting on the surface are gradual exfoliation and a transfer of molecular sheets onto the asperities and it is in the agreement with the literature [11,30].

In Fig. 9b Mo and S peaks that represent the NTs layer diminish after 2 sputtering cycles, while the Zn peak representing AW derived layer (from ZDDP) is visible until the 5th sputtering cycle, meaning that AW layer is very deep reaching bare Fe, while MoS₂ derived layer from NTs is located of the top of the ZDDP tribofilm. The results from the XPS depth profile in Fig. 9b perfectly matches with those acquired by SEM/EDX in Fig. 7d where NTs are visible as smashed particles on the top of

AW derived layer. Furthermore, it can be deduced that MoS₂ nanosheets resulted from exfoliation are also partially embedded within the very top of AW derived layer, since the XPS has proven the presence of Fe-sulphides which are the dark spots visible in Fig. 7d. Nevertheless, it is evident that the MoS₂ derived products on the top layer did not degrade the structure of the ZDDP tribofilm.

4. Role of the contact conditions on the interaction between MoS₂ nanotubes and representative oil additives

4.1. Methodology for evaluating the role of contact conditions

In order to thoroughly understand the interaction between additives and MoS₂ nanotubes under diverse contact conditions, the results obtained within the present work are discussed in combination with previous results obtained by the authors [16]. In conjunction, the results provide a wide database of tribological methods and conditions that shed some light on the fundamental interactions between MoS₂ nanotubes and commonly used oil additives. The tests configurations comprised of mixed rolling/sliding and reciprocating sliding experiments, which represent mild and/or moderate contact conditions. The third experimental setup, the Brugger tribotest, represents the most severe, extreme pressure testing conditions.

The reciprocating sliding ball-on-disc tests were performed using a SRV[®] tribometer (Optimol Instruments Prüftechnik GmbH, Germany), where a 10 mm diameter bearing steel ball was loaded and reciprocated against a stationary steel disc under boundary lubricated, pure sliding conditions. The oscillation frequency was 10 Hz and the stroke 1.5 mm [16]. The Brugger tests is a standardized method for determining the lubrication ability of additivated oils under boundary lubricating conditions. The Brugger-test creates a wear scar under unidirectional sliding conditions in the contact zone between a friction ring ($\varnothing = 25$ mm) and a test cylinder ($\varnothing = 18$ mm) according to DIN 51347-1 and 2 [31]. The load-carrying capacity according to Brugger measured in N/mm² is the quotient of the normal force applied to the test specimen in N and the area of the wear scar on the test specimen in mm [31]. The mixed rolling/sliding MTM experiments are thoroughly presented in section 2. A summary of all tested conditions is given in Table 2.

4.2. Synergisms and antagonisms between MoS₂ nanotubes and oil additives as function of the contact conditions

Fig. 10 compares the performance of all the mixtures containing MoS₂ nanotubes for all contact conditions with the reference un-additivated and additivated base oil PAO. In what follows the mixed rolling/sliding (MTM) and pure reciprocating sliding (SRV) results are presented as frictional bars and the unidirectional sliding extreme pressure Brugger results in terms of load-carrying capacity (LCC) bars. It is important to note that the error bars presented represent the average of three repetitions, thus emphasizing the excellent reproducibility of the experiments.

As reported previously by many researches [16,18,24] the lowest coefficient of friction (CoF) of ~ 0.05 was reached for the base oil mixed only with NTs (grey color) under sliding and mixed rolling/sliding with reductions against the pure base oil (black color) of $\sim 32\%$ and $\sim 56\%$, respectively (Fig. 10a, Table 3). Under more severe extreme pressure contact conditions, the NTs also provide an excellent outcome in terms of load carrying capacity (LCC) with an increase 83% when compared to the pure PAO oil (Fig. 10a, Table 3). It was reported that under severe contact conditions, transition metal dichalcogenide nanoparticles, in particular IF-WS₂ and IF-WSe₂, build up under combined rolling/sliding a tribofilm formed by exfoliated WS₂ layers together with WO₃, iron oxides and iron sulfides that provides excellent friction and wear reduction properties [32].

The presence of AW additive in PAO oil marginally influenced the

base oil performance in terms of friction and load carrying capacity as it is shown in Fig. 10b and Table 3 (purple color). However, the subsequent addition of NTs to this blend (light purple color) leads to reductions of the CoF by $\sim 36\%$ in mixed rolling/sliding in the boundary lubrication regime and by $\sim 26\%$ in reciprocating sliding. Likewise the Brugger tests reveal a clear improvement of the load carrying capacity by 68% when NTs are added in PAO + AW blend. The reason for the excellent synergy between NTs and AW is due to the exfoliation of MoS₂ lamellas on top of ZDDP tribofilms, as shown in section 3.4 for combined rolling/sliding or as reported in literature under reciprocating sliding conditions [11,19].

The experimental results for lubricant blends containing EP additives, namely PAO + EP (pink) and PAO + EP + NTs (dark pink) are shown in Fig. 10c. SRV reciprocating sliding tests reveal very high and unstable CoF throughout the testing time, reaching 0.19 ± 0.03 towards the end of the test. The presence of EP additives results in a worse performance, when compared to pure PAO (Fig. 10a, Table 3). The presence of NTs reduces and stabilizes CoF to a fairly constant value of 0.12 ± 0.01 during the complete duration of the experiment, thus resulting in a friction reduction of 28%. Contrariwise, the EP additive in PAO oil improves the base oil performance in terms of friction and load carrying capacity in mixed rolling/sliding and unidirectional Brugger test, respectively, as it is shown in Fig. 10c and Table 3. The reason for the improved performance of PAO + EP under these conditions could be due to the enough severe conditions achieved in order to be able to activate the EP additive. Fig. 10c and Table 3 shows that the performance of PAO + EP can be even further improved by the presence of the NTs. The decrease of CoF in MTM test for the PAO + EP + NTs blend is 30%, and the increase in LCC is 38% in unidirectional sliding. From Fig. 10 it is clear that the highest load carrying capacity can be achieved with the PAO + EP + NTs blend. Under extreme pressure unidirectional sliding, MoS₂ nanotubes synergy is better with S containing EP additives. This is due to the fact that during these conditions, the EP additives are able to continuously re-sulfurize the oxidized tribofilm, leading to the in-situ formation of MoS₂. The proposed mechanism is in agreement with the recent research published by Rodríguez Ripoll et al. showing that EP additives are able to sulfurize MoO₃ nanotubes for producing MoS₂-containing tribofilms under severe contact conditions [17]. In contrast, MoS₂ nanotubes are known to partly oxidize during operation, leading to the formation of MoO₃. Therefore, the use of MoS₂ nanotubes in combination with EP additives leads to a steady re-sulfurization of the tribofilm that justifies the observed synergy.

The interaction between NTs and detergent additives PAO + det (light green) and PAO + det + NTs (dark green) is discussed in what follows. The presence of the detergent in the PAO oil did not strongly affect the base oil performance in terms of friction and load carrying capacity in any of the experiments, as it is shown in Fig. 10d compare to Fig. 10a and in Table 3. The further addition of NTs to this blend reduces the CoF by $\sim 35\%$ in mixed rolling/sliding in boundary lubrication regime and $\sim 40\%$ in reciprocating sliding conditions. It was observed that a very similar Ca-based tribofilm was formed in samples undergoing reciprocating sliding with or without the presence of MoS₂ nanotubes. The only difference was the presence of Mo on the tribofilm as detected per EDX, indicating that MoS₂ nanotubes are able to exfoliate on Ca-based tribofilms [17]. The Brugger test also shows an improvement of the load carrying capacity by 75% when NTs are added in PAO + det blend. In this case, the increase of LCC is attributed to the formation of a protective tribofilm formed by partly reaction of the NT with the steel substrate for forming iron sulfides and Mo oxides [17].

The performance of the NTs when accompanied by dispersants is presented in Fig. 10e and Table 3. Under reciprocating sliding conditions, a scant friction improvement of 11% could be achieved. On contrary, in mixed rolling/sliding, the addition of dispersant to PAO oil improves its frictional behaviour as shown in Fig. 10a and e and the addition of NTs to the blend further reduces friction by 35%. The

Table 2

Summary of the testing parameters including schematic of the experimental set-up of a) Mini Traction Machine (MTM) test device, b) SRV reciprocating sliding tribotests and c) Brugger tribotests.

Tribological test set-up	a) MTM test	b) SRV® test	c) Brugger-test

Contact conditions	Point contact at 50% rolling/sliding	Point contact at reciprocating sliding	Line contact at pure unidirectional sliding
Track length	46 mm	1.5 mm	78.5 mm
Speed	decreasing from 3.2 to 0.002 m/s	average 0.04 m/s (10 Hz)	1.25 m/s
Normal Load	35 N	25 N	400 N
Mean contact pressure	0.7 GPa	0.9 GPa	1.4 GPa
Temperature	25 °C and 100 °C	40°C	25 °C
Test duration	2 hours	2 hours	30 sec
Measured parameters	Coefficient of friction vs mean contact velocity (initial Stribeck curve) and Archard wear coefficient after entire tribotest	Coefficient of friction vs time and Archard wear coefficient	Load carrying capacity and Archard wear coefficient

antagonistic interaction between the dispersant and MoS₂ nanoparticles in reciprocating sliding contact condition was also reported by Ref. [20] what is in agreement with our SRV results and is a critical point for preparing viable stable dispersions for commercial applications. In the Brugger test, NTs are very effective under the presence of dispersants, although the results show a slightly higher standard deviation. Again the synergistic effect under severe contact conditions is attributed to the partially reaction of the NT with the steel substrate [16]. However, as indicated in this reference, the selection of dispersant is critical since other compounds such as TEPA could prevent an improvement in LCC despite the severe contact conditions.

4.3. Wear characteristics

The removed wear volumes after the experiments were measured using 3D microscopy. Based on these data, the Archard wear coefficient was calculated for each experiment performed. The Archard wear coefficients after the Brugger tests are about four orders of magnitude higher when compared to the reciprocating sliding and mixed rolling/sliding tests, as is shown in Fig. 11.

The wear coefficient in the reference tests performed with PAO is the highest. The addition of NTs in the base oil reduced wear by at least 80% in the SRV, 60% in MTM and over 90% in the Brugger tests. However further addition of the conventional additives, despite AW additives does not improve the results in such a large amount anymore. It is also remarkable that under the reciprocating sliding conditions, all lubricating mixtures provide a significant improvement in terms of

wear reduction, even though such a wear reduction is not always achieved in conjunction with a low friction (cf. Fig. 10). The wear results show that MoS₂ NTs are very active in tribological contact regardless the test condition, which indicate that MoS₂ NTs possess anti-wear properties by themselves. This fact is also confirmed by the detailed XPS analysis proving decomposition of MoS₂ and formation of MoO₃ and various sulphur compounds in form of sulphides and sulphates. It has been recently reported that under severe contact conditions, transition dichalcogenide nanoparticles, in particular IF-WS₂ and IF-WSe₂, build up under combined rolling/sliding a tribofilm formed by exfoliated WS₂ layers together with WO₃, iron oxides and iron sulfides that provides excellent friction and wear reduction properties [32].

5. Conclusions

General conclusion of this work state that MoS₂ have an excellent synergy with AW additives under mixed rolling/sliding conditions. Under reciprocating sliding, the interaction between the MoS₂ nanotubes and dispersant leads to higher antagonisms. Under extreme pressure unidirectional sliding, their synergy is the strongest with S containing EP additives. Detailed conclusions are as follow:

- MoS₂ nanotubes dispersed in the model PAO oil form agglomerates which strongly limits lubricant's stability and disturb the flow rate. Conventional additives such as AW, EP and detergents slightly improve the dispersity of the MoS₂ nanotubes in the nanofluids, while only the dispersant is able to constantly improve the stability and

Fig. 10. Tribological performance presented in form of frictional bars for MTM tests (rolling/sliding) and SRV tests (reciprocating sliding) and load-carrying capacity bars (unidirectional sliding) for Brugger tests using the following lubricating blends:

- PAO and PAO + NTs,
- PAO + AW and PAO + AW + NTs,
- PAO + EP and PAO + EP + NTs,
- PAO + det and PAO + det + NTs,
- PAO + disp and PAO + disp + NTs.

Table 3

Summary of the effectiveness of the MoS₂ nanotubes in combination with selected additives under various tribological contact conditions, when compared to PAO with the same additive in the absence of nanotubes.

Blends	Friction reduction in MTM tests (rolling/sliding)	Friction reduction in SRV tests (reciprocating sliding)	Load carrying capacity increase at Brugger tests (unidirectional sliding)
PAO + NTs	32%	56%	83%
PAO + AW + NTs	36%	26%	68%
PAO + EP + NTs	30%	28%	38%
PAO + det + NTs	35%	40%	75%
PAO + disp + NTs	24%	11%	78%

rheological properties. Hence, the presence of dispersants seems to be unavoidable for achieving stable dispersions.

- Stribeck curves obtained under mixed rolling/sliding showed that the addition of MoS₂ nanotubes to the lubricating blends led to a higher reduction of the coefficient of friction at high temperatures (up to 60%) compared to room temperature (up to 35%) particularly in the boundary lubrication regime.
- The friction performance of the MoS₂ nanotubes under mixed rolling/sliding is very similar for all lubricating blends containing MoS₂ nanotubes and show a high synergy independently of the accompanying additive. This is of particular application relevance since many engineering systems such as gears and bearings operate under mixed rolling/sliding.
- Under reciprocating sliding, the interaction between the MoS₂

Fig. 11. Archard's wear coefficient calculated for wear tracks on SRV discs, MTM disc and Brugger cylinders.

nanotubes and the selected oil additives leads to higher antagonisms. Only AW and detergent additives are able to have a high synergy. Particularly remarkable is the antagonism between the MoS₂ nanotubes and the dispersant, which provide a challenge for formulating lubricants containing MoS₂ nanotubes with high stability and excellent performance under these conditions.

- In severe contact conditions, all additives lead to an excellent synergy with MoS₂ nanotubes due to the formation of tribofilms formed by MoS₂, MoO₃ and iron sulfides and oxides in all cases. Particularly remarkable is the synergy with EP additives, attributed to the in situ re-sulfurization of MoO₃ in the tribocontact.
- MoS₂ nanotubes have a superb anti-wear performance regardless of the accompanying additive present and tribological contact conditions. The NTs alone owe anti-wear properties due to the tribochemical decomposition to MoO₃ and formation of various sulphur compounds.

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