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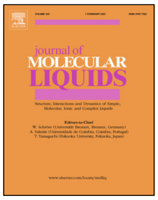

Electrochemically exfoliated graphene and molybdenum disulfide nanoplatelets as lubricant additives

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ABSTRACT

In this work, two different 2D materials, molybdenum disulfide nanoplatelets (MSNP) and graphene nanoplatelets (GNP), prepared by electrochemical exfoliation, were used as additives to prepare nanolubricants. The tribological behaviour of the nanolubricants was evaluated under two configurations (pure sliding and rolling/sliding) using two different tribometers: an Universal Macro Materials Tester (UMT-3) and a Mini Traction Machine (MTM2). Wear volume was determined, after the sliding tests, in a confocal microscope (Leica DCM 3D) and the worn surface was analyzed by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Raman microscopy. Lubrication mechanisms of GNP and MSNP dispersed in an engine oil for improving its antifriction and antiwear capabilities are proposed. The traction coefficient determination was performed at a 50% of slide-to-roll ratio and at different temperatures. The results showed that the nanolubricants formulated with both types of additives, in their lowest concentration, improved friction and wear in sliding tests, compared to neat engine oil. In addition, only the nanolubricants with the MSNP nano additive at loadings of 0.05 and 0.2 wt% showed friction reductions compared to the commercial engine oil under the rolling/sliding tests.

1. Introduction

Recent studies suggested that 33% of the fuel energy in passenger cars is dissipated to overcome friction losses [1]. Similar energy losses are also observed in other moving parts, such as electric motors and wind turbines. Therefore, there is a growing demand for more efficient lubricants to fulfil the low carbon emission and fuel economy requirements in car engines and wind turbines applications [2,3]. Lubrication are usually classified into four different regimes: boundary lubrication (BL), elastohydrodynamic lubrication (EHL), hydrodynamic lubrication (HL), and mixed lubrication (ML). The engine and transmission systems in cars work under all the lubrication regimes. However, the valve train is mostly under ML and accounts for 15% of the total engine friction losses, while the engine bearings and seals work under HL and produce 30% of the whole engine friction losses [1]. These high friction losses are reflected in higher engine wear and fuel energy loss [4]. For this reason, there is a need to develop new lubricants that can efficiently and simultaneously reduce friction and wear of the moving parts.

The application of nanomaterials as additives has shown great potential for enhancing both wear and friction properties of commercial lubricants [5–13]. Although most published studies on this topic were conducted under boundary lubrication conditions, some researchers have reported improvements by adding nano additives under the other lubrication regimes. For instance, Shafi et al. [14] studied the tribological behaviour of avocado oil additised with copper nanoparticles in mixed and boundary lubrication regimes. They attributed the improvement in the frictional characteristics to a tribofilm formation between the sliding surfaces. Hernández Battez et al. [15] evaluated the antiwear behaviour under a mixed lubrication regime of nanolubricants formed by adding metal oxide nanoparticles (CuO, ZrO_2 and ZnO) to a polyalphaolefin (PAO6). They observed a friction and wear reduction for all nanolubricants mainly due to the tribo-sintering of the nanoparticles on the worn

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surfaces. Liñeira del Río et al. [16] have obtained the full Stribeck curves (from boundary to elastohydrodynamic lubrication) of magnetic nanoparticles (Fe_3O_4 of 6.3 nm and 10 nm-size and Nd alloy compound) coated with oleic acid in an ester-based oil (TMPTO). A decrease in the coefficient of friction under all lubrication regimes at high temperatures was found when Fe_3O_4 (6.3 nm) nanoparticles were used as additives. For the rest of the nanoparticles, the frictional behaviour was similar to that of the base oil.

With the emergence of graphene, the focus of the research was shifted to 2D materials as nanolubricants additives. 2D materials offer a unique set of properties that make them ideal candidates for nanolubricants formulation [17]. They possess a unique molecular structure, with high in-plane strength and low interlayer shear strength. Besides, 2D materials have a higher specific surface area, allowing them to cover wider areas with very thin layers [18]. Like many other nano additives, most of the studies focused on the tribological performance under the boundary lubrication regime, with very few reports on their performance under other lubrication conditions. In addition, most of the 2D materials were used in the form of graphene oxide (GO) or liquid mechanically exfoliated chalcogenides in liquid phases [19–21]. Using GO might have some restrictions on the development of the next lubricants generation, where the anti-thermal, anti-corrosion and load-carrying properties are also required. The 2D materials produced by mechanical forces in liquid phases, such as by the sonication and high-shear mixers methods, usually have a high edge/flake ratio, subjecting the substrate surfaces to wear by the sharp edges of the 2D materials [22]. In the recent past, in addition to graphene, nanostructural MoS_2 has been utilised as a lubricant additive for reduction of friction and wear [23–25]. For instance, Wan et al. [26] investigated the rheological and tribological performance of commercial lubricating oil (SE 15 W-40) containing platelet MoS_2 nanoparticles using a dispersant to ensure a good suspension stability. These authors concluded that the use of MoS_2 nanoparticles could enhance significantly the tribological performance of the lubricating oil in BL conditions. It is important to note that most of the work that can be found in the literature focuses on the study of graphene and molybdenum disulphide as lubricant additives for base oils in BL regime. However, work in the literature on the use of fully-formulated lubricants is scarce, specially in ML and EHL regimes, as the additive package contained in these lubricants already gives them good tribological properties and improving this aspect is a challenge. In addition, the incorporation of nanoparticles usually competes with existing additives and results in very poor stability, so the use of a surfactant/dispersant is often necessary.

In this work, the lubricant properties (traction and antiwear behaviours) of two 2D nanomaterials used as additives in a fully-formulated commercial engine oil have been evaluated. Both materials, graphene and MoS_2, are produced by the electrochemical exfoliation method, which allows the production of large flakes and controlled numbers of layers. This study aims to complete the tribological characterisation carried out in a previous work [27] and to check the tribological behaviour of these surfactant-free nanolubricants in mixed and elastohydrodynamic lubrication regimes.

2. Experimental details

2.1. Preparation of the nanolubricants

Electrochemical exfoliation was used for producing both the GNP and MSNP. A description of the process and further analysis of these materials were previously published [28]. Both nano additives were added to the commercial engine oil 5W-30 at concentrations of 0.05, 0.1 and 0.2 wt%. This engine oil was previously characterised [27] showing a viscosity index (VI) of 163, density of 848.6 $kg{\cdot}m^{-3}$ at 298.15 K and kinematic viscosity of 112.74 and 11.83 $mm^2{\cdot}s^{-1}$ at 303.15 K and 373.15 K, respectively. The formulation and stability of the nanolubricants studied were reported in a previous work [27].

The engine oil and the electrochemically exfoliated 2D materials were characterised as-received with Raman microscopy. The Raman spectrum of the engine oil (Fig. 1 a) revealed peaks in two regions: the fingerprint region in the range 800–1800 cm^{-1} and the high wavenumber region covering 2800–3500 cm^{-1} due to the hydrocarbon content of the sample. The peaks found at 1441 and 1302 cm^{-1} are associated with CH_2 bending mode and CH_2 twisting, respectively [29]. Fig. 1 b shows the Raman spectrum of GNP, where the typical G, D, and 2D bands of graphene can be detected at ~ 1580, ~1364, and ~ 2713 cm^{-1}, respectively [30]. The Raman spectrum of MSNP has been obtained from the literature [31], which shows two prominent peaks: around 383 and at 407 cm^{-1}.

2.2. Sliding tests

The sliding tests were performed using an UMT-3 tribometer (from former CETR Corporation) in a reciprocating ball-on-disc configuration. The balls (Ø = 6 mm, 58–66 HRC and R_a = 0.05 µm) and discs (Ø = 10 mm, 225 HV_{30} and R_a = 0.018 µm) were manufactured from AISI 52100 steel. The tests were performed under the following test conditions: temperature of 363.15 K (optimum operating temperature of an internal combustion engine), a 20 N-load (corresponding to 1.8 GPa of maximum contact pressure), 3.18 Hz-frequency, a stroke length of 5 mm of and 180 m of sliding distance (Fig. 2). The lubricant volume used to perform the sliding

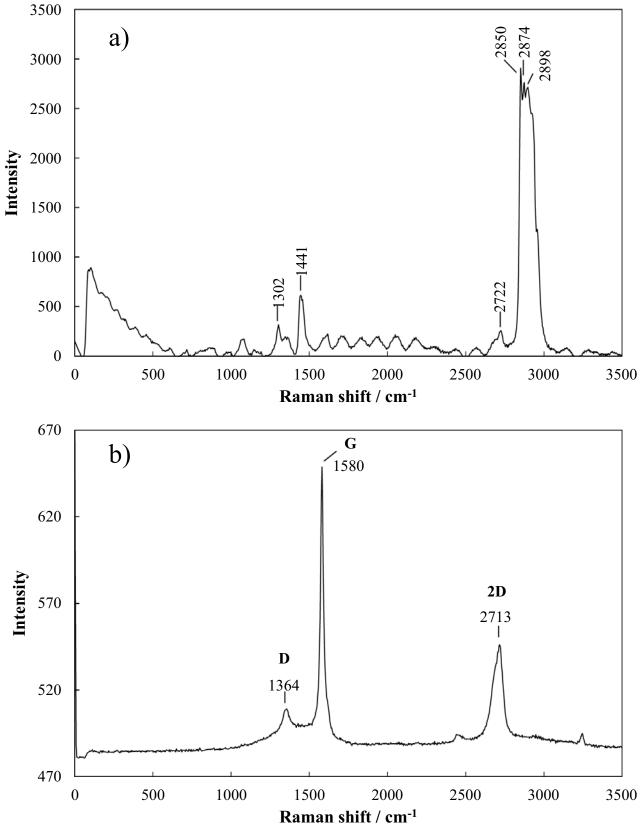

Fig. 1. Raman spectrum of both a) 5W-30 engine oil and b) graphene nanoplatelets.

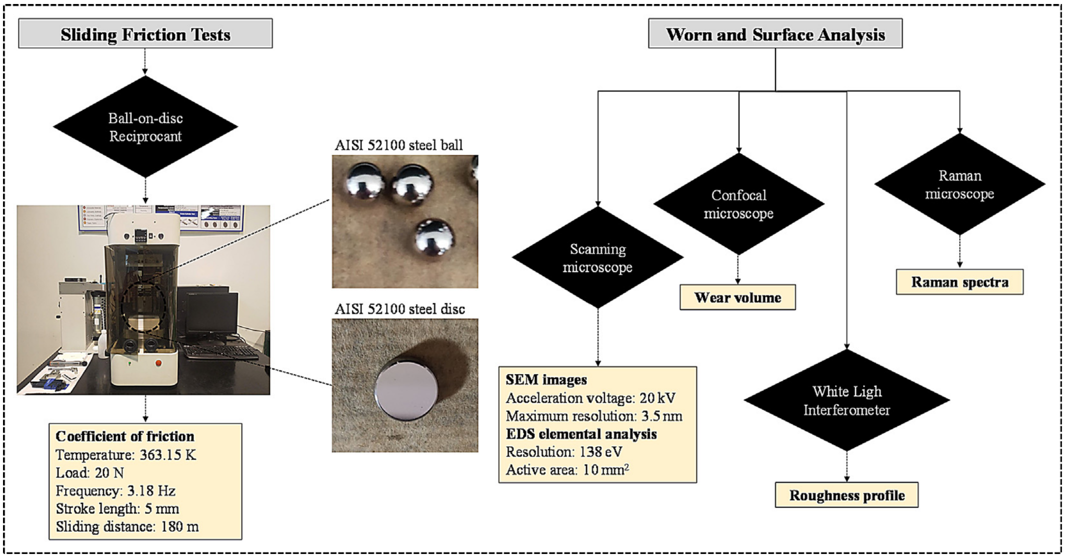

Fig. 2. General scheme of the experimental procedure.

tests was 4 mL. Three replicates were conducted for each nanolubricant and for the engine oil, and the average coefficient of friction (COF) and its standard deviation was calculated.

2.3. Worn surface analysis

After sliding reciprocating ball-on-disc tests, the wear volume on the disc surface, the roughness profiles of the wear scar on the discs and on the balls and the possible chemical interaction of the nano additives with the steel surface were evaluated. The wear volume was obtained with a confocal microscope (Leica DCM 3D), and the wear rate was determined using a Sartorius MC 210P high precision balance. The roughness profiles of the specimens were obtained using a Zygo White Light Interferometer. For the wear surface characterisation, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques were employed. Both specimens were cleaned ultrasonically before and after sliding tests with petroleum ether for 5 min and then air-dried. Furthermore, confocal Raman microscopy (WITec alpha300R +) was employed to detect any possible tribofilm formation on the worn surface of the steel discs. Raman spectra were performed at a wavelength of 532 nm.

2.4. Rolling/sliding tests

A MTM2 (Mini Traction Machine tribometer from PCS Instruments) in a ball-on-disc configuration was used to complete the tribological behaviour investigation of the nanolubricants under different lubrication regimes (see Fig. 3). The Stribeck curves of the nanolubricants were recorded under a slide-to-roll ratio (SRR) of 50%, a 30 N-load (equivalent to 0.95 GPa of maximum contact pressure), a mean entrainment speed between 2500 and 10 mm·s^{-1}, and temperatures of 303.15, 333.15 and 363.15 K. The volume of lubricant used for each test was 10 mL. The mean entrainment speed was calculated as the mean between the sliding speed at the point contact of the disc (u_d) and of the ball (u_b):

$$u = \frac{u_d + u_b}{2} \tag{1}$$

Thus, the slide-to-roll ratio (SRR) is defined as the ratio of sliding speed to mean speed:

$$SRR(\%) = \frac{2(u_d - u_b)}{u_d + u_b} \times 100 \tag{2}$$

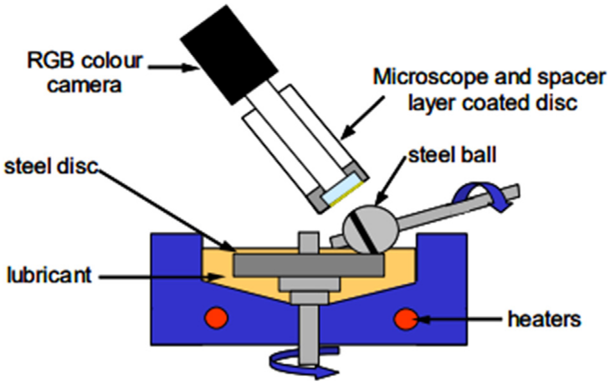

Fig. 3. Diagram of the MTM2 tribometer set-up [32].

The specimens used in these tests were: balls (Ø = 19.05 mm, 800–920 HV and $R_a \le 0.02$ μm) and discs (Ø = 46 mm, 720–780 HV and $R_a \le 0.02$ μm) manufactured from AISI 52100 steel. The specimens were cleaned with petroleum ether in an ultrasonic bath for 5 min and then dried with hot air.

3. Results and discussion

3.1. Sliding tests

The coefficient of friction from the sliding tests with the engine oil and various nanolubricants measured at 363.15 K is shown in Fig. 4. The nanolubricants with the lowest concentrations show better antifriction behaviour than the engine oil. However, when the concentration of additives increases, the COF worsens compared to the base oil. Both nanolubricants, GNP and MSNP, showed very similar behaviour at low and high loading, but differed significantly at 0.1 wt% loading. At this concentration, the MSNP nanolubricant presented a reduced performance in tribological behaviour than the same concentration of GNP and even than the engine oil. The nanolubricants containing 0.05 wt% loading of GNP and MSNP achieved a decrease in the COF of around 7% and 4%, respectively. The friction results are consistent with those obtained from the wear analysis also shown in Fig. 4. The nanolubricants with low loading showed a better antiwear behaviour,

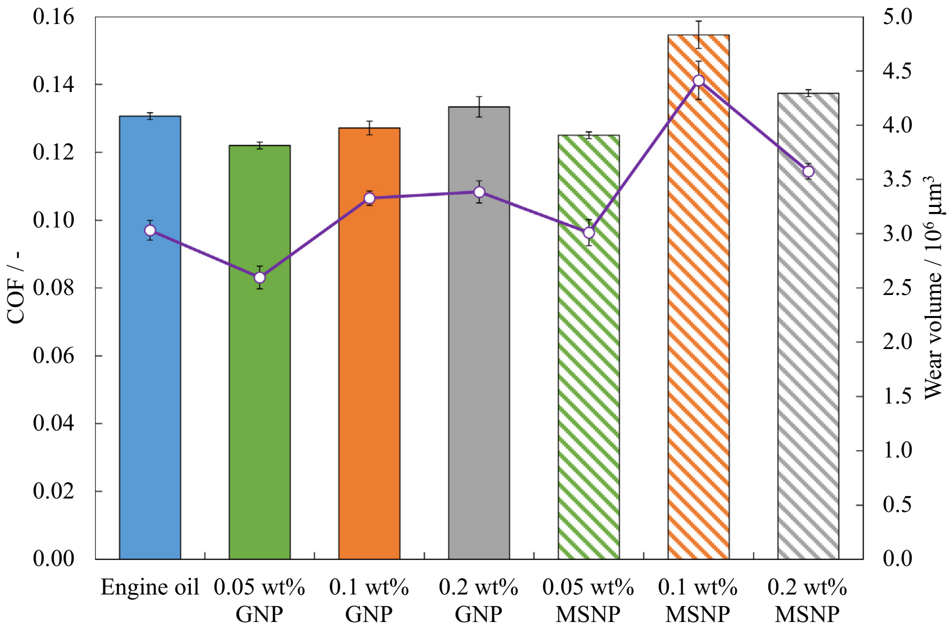

Fig. 4. Coefficient of friction (COF) and wear volume on the disc surface of sliding tests for the engine oil and six different nanolubricants at 363.15 K.

achieving a wear volume less than that of the engine oil by 14% and 7% for GNP and MSNP at 0.05 wt%, respectively. A similar trend was observed by Zhang et al. [33] for dispersions of graphene sheets in a polyalphaolefin-9 (PAO9). A significant increase in the wear scar volume was found with the nanolubricant containing 0.1 wt% of MSNP, which is consistent with the COF results.

Tribological results obtained in this work have been compared with those previously reported [27] under the same test conditions (temperature, sliding distance and load) but at different contact configuration (maximum Hertzian contact pressure). It is noticeable that the contact configuration clearly affects the coefficient of friction. Unidirectional sliding tests showed a 6% reduction in the COF when used with the 0.1 wt% MSNP nanolubricant compared to the engine oil [27]. However, for the reciprocanting sliding friction tests, this nanoparticle loading (0.1 wt% MSNP) provokes the opposite effect, an 18% increase in COF compared to engine oil (Fig. 4). This may be attributed to the fact that by increasing the maximum Hertzian contact pressure (from 1.1 GPa in rotational/unidirectional motion to 1.8 GPa in reciprocating motion), more nanoplatelets were ejected from the wear tracks, thus reducing their mechanical effect or the possible formation of tribofilms. This phenomenon was also observed by Kalin et al. [34] for a PAO lubricant containing nanotubes. However, this is not the case for the wear results. For unidirectional motion, the highest reductions were obtained with the lowest nanoparticle concentrations (0.05 wt% GNP and MSNP) as in the current work (reciprocating motion). Moreover, the friction and wear results reveal that the increase of nano additives loading above 0.05 wt% leads to a significant reduction in the nanolubricants tribological performance, in agreement with previous studies under rotational configuration [27]. It is worth mentioning here that the enhanced tribological performance of low GNP-loaded nanolubricants is due to the slightly better dispersion of the graphene nanoplatelets in commercial engine oil, resulting in an improvement in the strength of the tribofilm [35].

The wear rate was determined from the mass loss in the steel discs and calculated using the following equation [36,37]:

$$W = \frac{\Delta V}{F_n S_s} \tag{3}$$

where W is the specific wear rate ($mm^3 \cdot N^{-1} \cdot m^{-1}$), ΔV is the volume loss (mm^3), F_n is the applied load (N), and S_s is the sliding distance (m). The volume loss can be determined using equation (4):

$$\Delta V = \frac{1}{\rho}(\Delta W) \tag{4}$$

where ρ is the AISI 52100 steel density and ΔW is the mass loss. The tests were carried out at least three times under the same conditions and then the average results were taken to minimize measurement error.

Fig. 5 shows the change in the wear rate with the nano additives loading measured after 180 m of sliding distance. It can be seen that the addition of GNP and MSNP nanoparticles at a lower concentration significantly improved the wear resistance as compared to the engine oil, reaching a maximum improvement of 53% for the 0.05 wt% GNP-containing nanolubricant. These wear measurements are in agreement with those previously obtained for the total wear volume. Fig. 4 and Fig. 5 also show that the influence of the nano additives on the antiwear behaviour of the engine oil was correlative with the COF variation. The highest values of wear volume and wear rate were found at 0.1 wt% MSNP loading, the same loading that gave the highest COF value.

3.2. Worn surface analysis

Nanoparticles can reduce friction and wear through different mechanisms, such as rolling, polishing and mending effects, and/or the formation of a protective film [38]. Determining the exact mechanism of the protection helps to understand the role of the nano additives in the tribological system. The cross-section profiles of the worn scar on the AISI 52100 steel discs lubricated with the 5W-30 oil and nanolubricants are shown in Figure S1. The cross-section areas for the nanolubricants with 0.05 wt% of GNP (Figure S1b) and MSNP (Figure S1 e) present a smaller depth of the wear scar compared to the profile for the commercial engine oil (Figure S1 a). This result confirms the friction and wear results, with both loading nanolubricants showing the best antifriction and antiwear performance. It is important to note that the rough-

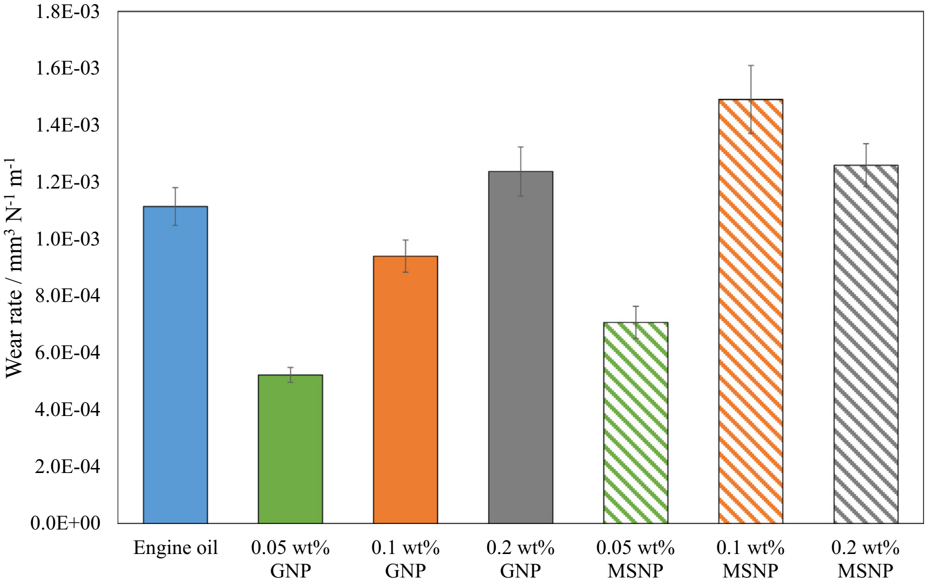

Fig. 5. Wear rate from the sliding tests for the engine oil and six different nanolubricants at 363.15 K.

ness profiles of the wear surface on the steel discs reveal that the wear tracks are not uniform.

Figure S2 shows the images obtaining with the Zygo scanning light microscope for the upper counterparts, the steel balls. The images were captured using an objective of 10X for all cases. A similar wear scar can be observed for the samples lubricated with the nanolubricants containing 0.1 wt% (Figure S2 c) and 0.2 wt% (Figure S2 d) of GNP compared to that for the contact lubricated only with formulated engine oil (Figure S2 a). However, the other nanolubricants produced a larger wear scar compared to unadditivated engine oil. These results are in agreement with the roughness profiles obtained for the wear surface on the steel discs (Figure S1). Thus, the narrower wear track width was produced by the nanolubricants formed by the same GNP concentrations (0.1 and 0.2 wt%).

Furthermore, from the cross-section profiles, the arithmetic mean surface roughness, R_a, was determined according to ASME B46.1 standard [39] using the following equation:

$$R_a = \frac{1}{L}\int_0^L Z(x)dx \tag{5}$$

where L is the evaluation length, Z(x) the profile height function, and R_a is the arithmetic mean of the absolute values of the deviations of the profile height from the mean line, recorded within the evaluation length. Table 1 presents the mean roughness surface, R_a, on the cross-section area of the wear scar after using different nanolubricants. For surface roughness on the steel discs, the maximum reduction (28%) regarding the engine oil was obtained with the loading of 0.05 wt% GNP. The second maximum reduction, which is up to 22% compared to the engine oil, was recorded for the 0.05 wt% MSNP/5W-30 nanolubricant. These results suggest that the polishing wear mechanism takes place for these loadings of nano additives. It is known that the nanoparticles smooth the worn surface by polishing in the polishing mechanism [40]. This wear mechanism is favoured by the shape of the 2D nano additives since they offer excellent sliding and delamination properties, which results in a smoother worn surface [41]. When the variation of surface roughness on the steel balls is analysed (Table 1), an opposite effect can be observed. The balls' surface roughness increases when they are in contact with the nanolubricant, even at the optimum loading, with respect to the balls in contact with the 5W-30 engine oil. This is because the steel balls have a much higher hardness than the steel discs, 58–66 HRC vs 225 HV30, respectively. Therefore, the nanoparticles are not hard enough to produce the same polishing effect on the surface of the steel balls.

The role of GNP and MSNP nano additives on the wear mechanism was further investigated by SEM and EDS analysis of the wear surfaces. Fig. 6 a), b), and c) show the morphology of the worn AISI 52100 steel discs used as a lower specimen lubricated with the engine oil with no additives at three different magnifications (10X, 100X and 1000X). The morphologies of the worn surfaces of the disc lubricated with the engine oil doped with 0.05 wt% of GNP and with 0.05 wt% of MSNP are shown in Fig. 6 d)- f) and

Table 1
Mean roughness surface, R_a, on the cross-section area of the wear scar and its standard deviation on the steel disc and ball for the different analysed nanolubricants.

Lubricant	Steel disc		Steel ball	
	Ra / µm	σ / µm	Ra / µm	σ / µm
5W-30	1.196	0.037	0.708	0.012
+ 0.05 wt% GNP	0.859	0.006	1.576	0.021
+ 0.1 wt% GNP	1.195	0.017	0.606	0.014
+ 0.2 wt% GNP	1.156	0.019	0.696	0.011
+ 0.05 wt% MSNP	0.937	0.035	1.232	0.019
+ 0.1 wt% MSNP	0.974	0.055	1.761	0.023
+ 0.2 wt% MSNP	1.166	0.019	1.152	0.017

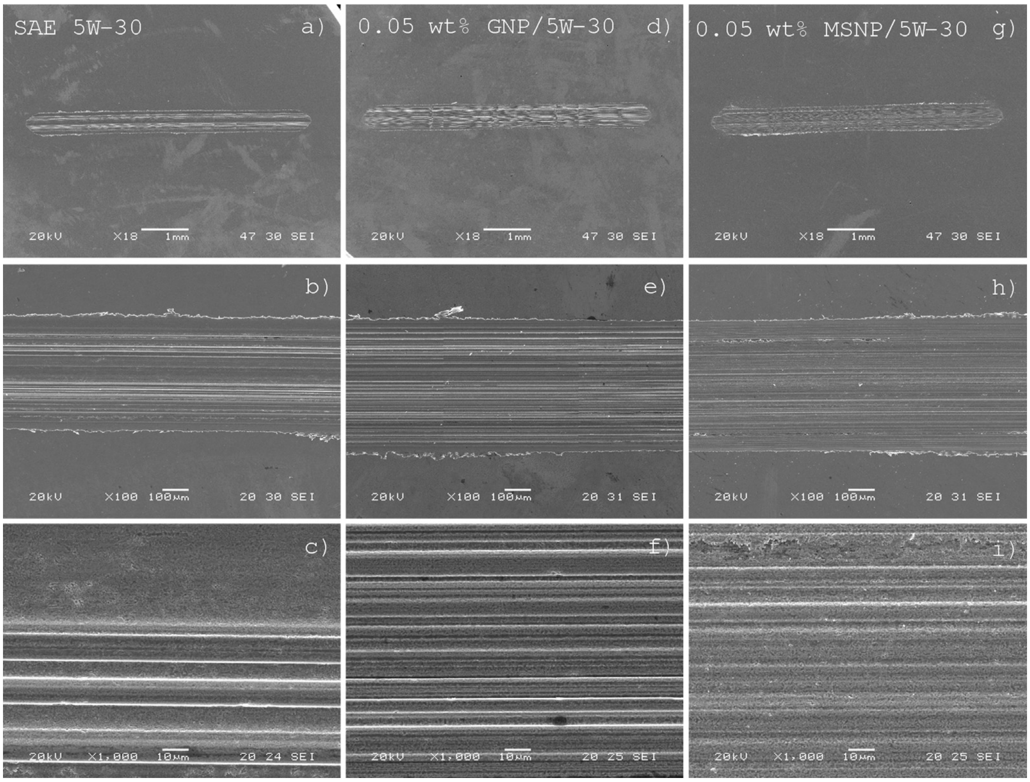

Fig. 6. SEM images of the wear scars on the steel discs from the test with: (a, b, c) 5W-30 engine oil, (d, e, f) 0.05 wt% GNP and (g, h, i) 0.05 wt% MSNP.

Fig. 6 g)- i), respectively. The high magnification images in Fig. 6 c), f), and i) show parallel grooves typical of abrasive wear in all tests. These grooves are smoother for the surface lubricated with 0.05 wt% of MSNP (Fig. 6 i), suggesting better antiwear ability than the other tested lubricants. This reveals the influence of the MSNP on minimising the sliding contact between both specimens, which results in the observed reduction of friction and wear for this nanoparticle loading. However, this effect has not been observed clearly in the GNP case (Fig. 6 f). A slight exfoliation effect can also be observed on the wear track lubricated with 0.05 wt% MSNP nanolubricant (Fig. 6 i), which is not visible on wear tracks lubricated with the 5W-30 engine oil (Fig. 6 c) and with 0.05 wt% GNP nanolubricant (Fig. 6 f).

Table 2 gathers the EDS results of the elemental chemical analysis on the steel discs after the sliding test using commercial engine oil and the optimum loading of the nanolubricants (0.05 wt% of GNP and MSNP). The elemental analysis has been performed within the wear scar of the steel discs in the marked area in Figure S3. While EDS is a semi qualitative analysis and is not considered reliable when it comes to light elements, the increases in the Fe on the surface when GNP and MSNP are used to support this hypothesis. It is also worth noting from Table 2 that no deposition of the nano additives was detected on the wear surfaces, only those chemical elements present in steel (Fe, C, Cr and Mn) and in the engine oil as antiwear additives (P, S and Zn) could be found. This may be since the estimated detection depth of EDS into AISI 52100 steel with 20 kV accelerating voltage is about 0.6 μm and the nanoparticles behaved as a third body, and the amount of the deposit was too low to be detected in the wear track by this technique, as reported in other works [42].

To further investigate the possible role that nanoparticles play in the contact area, Raman spectra and elemental mapping analysis were collected for the surface of the steel disc after the sliding tests. Figs. 7 and 8 show the elemental mapping of the tribofilms formed with the commercial engine oil and the 0.05 wt% GNP- and 0.05 wt% MSNP-containing nanolubricants, respectively. This technique has a detection depth at a wavelength of 532 nm around 500 nm in AISI 52100 steel, revealing that the nanoparticles are concentrated on the peaks of the grooves. This fact suggests the formation of stable GNP and MSNP tribofilms (red colour) on the wear surface, located mainly along several grooves, protect the rubbing surfaces from severe wear through the mending effect [16]. The Raman spectra taken for each tribofilm reveal the presence of amorphous carbon with its typical peaks at 1300–1600 cm^{-1} [43,44]. In summary, the results obtained for both Raman and roughness allow concluding that the mechanisms played by nanoparticles as lubricant additives are the formation of tribofilm, as a result of tribochemical reactions, mending effect because of the nanometric size, and polishing effect [45]. These findings agree with a recent theoretical study of poly-α-olefins-based lubricant [46], which suggests that the tribofilm formation is influenced by the presence of 2D MoS_2.

Table 2
EDS element analysis in wt.% on the wear scar.

Lubricant	C	O	P	S	Cr	Mn	Fe	Zn	Total
5W-30	4.2	7.7	0.7	1.2	1.9	0.6	83.0	0.7	100.0
0.05 wt% GNP	3.7	7.9	0.7	0.9	1.4	0.6	84.0	0.8	100.0
0.05 wt% MSNP	3.1	7.9	0.4	0.6	1.5	0.5	85.6	0.4	100.0

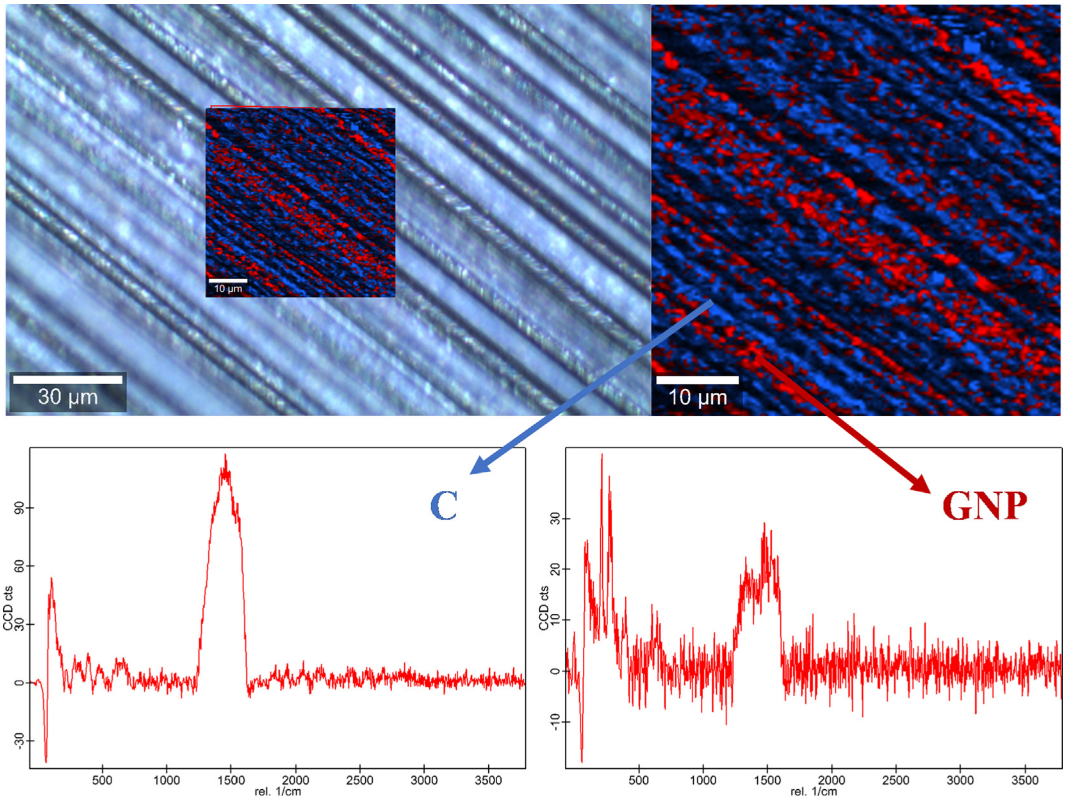

Fig. 7. Raman spectra mapping of the wear surface lubricated with the nanolubricant of GNP.

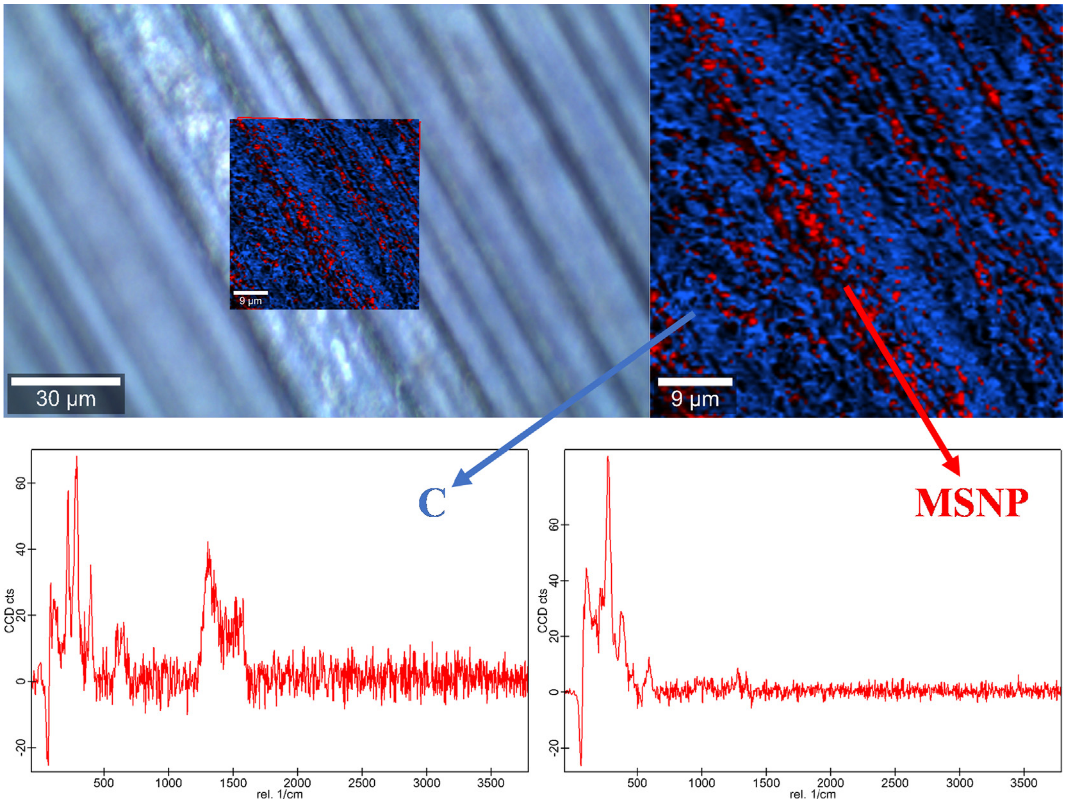

Fig. 8. Raman spectra mapping of the wear surface lubricated with the nanolubricant of MSNP.

3.3. Rolling/sliding tests

The Stribeck curves were recorded for the engine oil and for all nanolubricants at three different temperatures (303.15, 333.15 and 363.15 K) and a slide-to-roll ratio (SRR) of 50%. As expected, Figs. 9 and 10 show that all the nanolubricants changed to ML regime at lower speeds and to EHL at high speeds under all tested temperatures. The traction behaviour of the GNP nanolubricants was similar under the EHL regime for all loading because the measured kinematic viscosities of the samples were almost identical [27]. However, the COF of the GNP nanolubricants is not better than that of the commercial engine oil under a mixed lubrication regime. A decline in the tribological performance of the engine oil is observed when the GNP loading increases. One possible explanation for this is that while at low speeds (mixed lubrication), the GNP flakes are trapped in the wear tracks and preventing metal–metal contact, their high mechanical strength [18,47] promote friction. Thus higher COF is observed for the increased loading nanolubricants than for the engine oil. On the other hand, the temporal stability of the nanolubricant could be affected by the rolling/sliding of the steel ball, so weakening the dispersion of the GNPs and intensifying their aggregation [48]. Consequently, the formation of an adsorption film is unlikely to occur, which is detrimental to the lubrication performance of these dispersions.

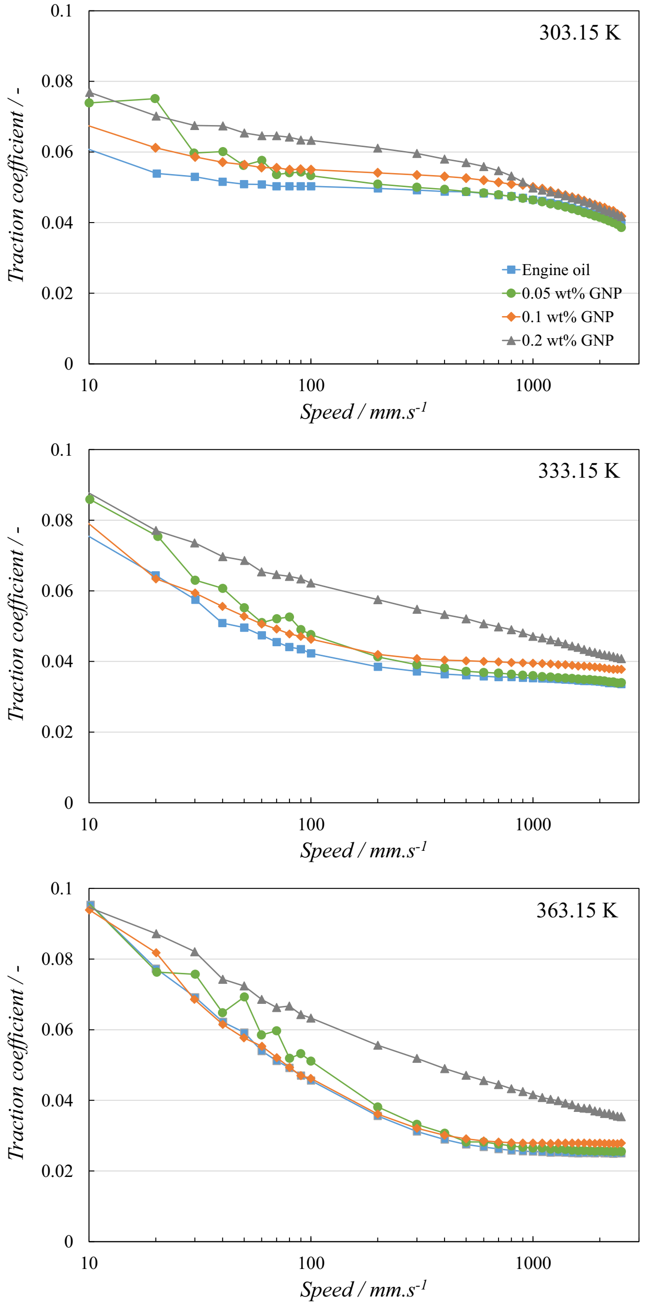

Fig. 9. Stribeck curves of the engine oil and the different nanolubricants of GNP at different temperatures during rolling/sliding friction tests.

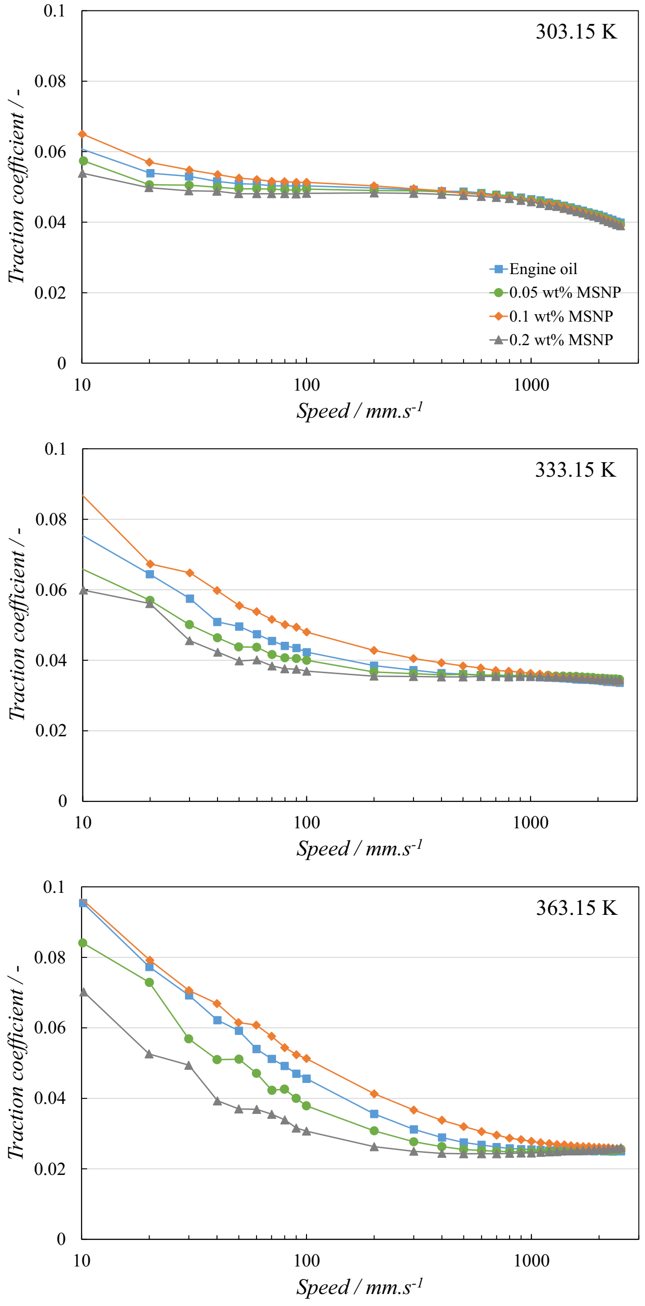

Fig. 10. Stribeck curves of the engine oil and the different nanolubricants of MSNP at different temperatures during rolling/sliding friction tests.

In contrast, Fig. 10 shows the Stribeck curves for the MSNP-based nanolubricants measured at 303.15, 333.15 and 363.15 K. A noticeable reduction of the traction coefficient has been observed for nanolubricants of 0.05 and 0.2 wt% MSNP concentration, both under mixed and elastohydrodynamic lubrication regimes. The decline in friction increases as the temperature rises. Thus, at 303.15 K and a velocity of 10 mm s^{-1}, a decrease of 6% and 11% in the traction coefficient compared to the commercial engine oil are observed for a MSNP loading of 0.05 and 0.2 wt%, respectively. While at 363.15 K and under the same testing conditions, the recorded traction coefficient for 0.05 and 0.2 wt% of MSNP nanolubricants is 12% and 26% less than the engine oil, respectively. It is worth mentioning that only the 0.1 wt% MSNP loading does not confer better traction behaviour to commercial motor oil. This phenomenon coincides with that observed in pure sliding friction tests, where this concentration of nano additives revealed the worst antifriction and antiwear behaviour (Fig. 4).

From rolling/sliding tests, the MSNP presented a better friction reduction than the GNP. This fact is because MoS_2 nanoparticles exhibit weak Van der Waals forces between the S-Mo-S layers and pure positive charge on the surface favouring the propagation of electrostatic repulsion [49]. All this leads to slipping the adjacent molybdenum disulfide layers against each other and provides better lubrication properties.

4. Conclusions

The use of two different 2D nanomaterials (GNP and MSNP) as lubricant additives has been studied for a steel-steel contact in two different testing configurations (pure sliding and rolling/sliding). The main conclusions extracted from the obtained results are:

1. The sliding tests revealed a friction and wear reduction for the lower nano additive loading (0.05 wt%). Both nano additives (GNP and MSNP) showed similar tribological behaviour in friction and wear when used as lubricant additive of the engine oil (5W-30).
2. SEM surface analysis revealed a smooth effect on the wear scars lubricated with the lower GNP and MSNP concentrations. Besides, the EDS analysis showed mainly the steel disc elements composition.
3. Tribofilm formation and mending and polishing mechanisms produced by both nano additives were detected by Raman and roughness analysis.
4. The rolling/sliding friction tests confirmed a friction reduction for the nanolubricants containing 0.05 and 0.2 wt% of MSNP, making the addition of that nano additive more suitable than GNP for improving the tribological performance of commercial engine oil.
5. A remarkable tribological improvement of the formulated oil modified with GNP and MSNP as an antifriction and antiwear additive at low concentrations (0.05 wt%) was revealed under pure sliding and rolling/sliding conditions, respectively.
6. Friction and wear enhancements have been obtained with stable nanolubricants without the use of surfactants or functionalisation of nano additives.

CRediT authorship contribution statement

María J.G. Guimarey: Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Jose Luis Viesca:** Conceptualization, Supervision, Validation, Writing - review & editing. **Amor M. Abdelkader:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing. **Ben Thomas:** Writing - review & editing. **A. Hernández Battez:** Conceptualization, Supervision, Validation, Writing - review & editing. **Mark Hadfield:** Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.116959.

References

[1] K. Holmberg, P. Andersson, A. Erdemir, Global energy consumption due to friction in passenger cars, Tribol. Int. 47 (2012) 221–234, https://doi.org/10.1016/j.triboint.2011.11.022.

[2] H. Spikes, Friction Modifier Additives, Tribol. Lett. 60 (2015) 1–26, https://doi.org/10.1007/s11249-015-0589-z.

[3] D. Berman, A. Erdemir, A.V. Sumant, Approaches for Achieving Superlubricity in Two-Dimensional Materials, ACS Nano 12 (2018) 2122–2137, https://doi.org/10.1021/acsnano.7b09046.

[4] Z. Tang, S. Li, A review of recent developments of friction modifiers for liquid lubricants (2007–present), Curr. Opin. Solid State Mater. Sci. 18 (2014) 119–139, https://doi.org/10.1016/j.cossms.2014.02.002.

[5] W. Dai, B. Kheireddin, H. Gao, H. Liang, Roles of nanoparticles in oil lubrication, Tribol. Int. 102 (2016) 88–98, https://doi.org/10.1016/j.triboint.2016.05.020.

[6] A. Elagouz, M.K.A. Ali, H. Xianjun, M.A.A. Abdelkareem, M.A. Hassan, Frictional performance evaluation of sliding surfaces lubricated by zinc-oxide nano-additives, Surf. Eng. 36 (2020) 144–157, https://doi.org/10.1080/02670844.2019.1620442.

[7] V. Eswaraiah, V. Sankaranarayanan, S. Ramaprabhu, Graphene-Based Engine Oil Nanofluids for Tribological Applications, ACS Appl. Mater. Interfaces 3 (2011) 4221–4227, https://doi.org/10.1021/am200851z.

[8] L. Joly-Pottuz, F. Dassenoy, M. Belin, B. Vacher, J.M. Martin, N. Fleischer, Ultralow-friction and wear properties of IF-WS2 under boundary lubrication, Tribol. Lett. 18 (2005) 477–485, https://doi.org/10.1007/s11249-005-3607-8.

[9] V. Zin, S. Barison, F. Agresti, L. Colla, C. Pagura, M. Fabrizio, Improved tribological and thermal properties of lubricants by graphene based nano-additives, RSC Adv. 6 (2016) 59477–59486, https://doi.org/10.1039/C6RA12029F.

[10] N. Rajendhran, S. Palanisamy, P. Periyasamy, R. Venkatachalam, Enhancing of the tribological characteristics of the lubricant oils using Ni-promoted MoS_2 nanosheets as nano-additives, Tribol. Int. 118 (2018) 314–328, https://doi.org/10.1016/j.triboint.2017.10.001.

[11] R. Chou, A.H. Battez, J.J. Cabello, J.L. Viesca, A. Osorio, A. Sagastume, Tribological behavior of polyalphaolefin with the addition of nickel nanoparticles, Tribol. Int. 43 (2010) 2327–2332, https://doi.org/10.1016/j.triboint.2010.08.006.

[12] A. Hernandez Battez, J.E. Fernandez Rico, A. Navas Arias, J.L. Viesca Rodriguez, R. Chou Rodriguez, J.M. Diaz Fernandez, The tribological behaviour of ZnO nanoparticles as an additive to PAO6, Wear 261 (2006) 256-263. https://doi.org/10.1016/j.wear.2005.10.001

[13] J.L. Viesca, A. Hernández Battez, R. González, R. Chou, J.J. Cabello, Antiwear properties of carbon-coated copper nanoparticles used as an additive to a polyalphaolefin, Tribol. Int. 44 (2011) 829–833, https://doi.org/10.1016/j.triboint.2011.02.006.

[14] W.K. Shafi, A. Raina, M.I. Ul Haq, Tribological performance of avocado oil containing copper nanoparticles in mixed and boundary lubrication regime, Ind. Lubr. Tribol. 70 (2018) 865–871, https://doi.org/10.1108/ILT-06-2017-0166.

[15] A. Hernández Battez, R. González, J.L. Viesca, J.E. Fernández, J.M. Díaz Fernández, A. Machado, R. Chou, J. Riba, CuO, ZrO2 and ZnO nanoparticles as

antiwear additive in oil lubricants, Wear 265 (2008) 422-428. https://doi.org/10.1016/j.wear.2007.11.013

[16] J.M. Liñeira del Río, E.R. López, M. González Gómez, S. Yáñez Vilar, Y. Piñeiro, J. Rivas, D.E.P. Gonçalves, J.H.O. Seabra, J. Fernández, Tribological Behavior of Nanolubricants Based on Coated Magnetic Nanoparticles and Trimethylolpropane Trioleate Base Oil, Nanomaterials 10 (2020) 683, https://doi.org/10.3390/nano10040683.

[17] P. Uzoma, H. Hu, M. Khadem, O. Penkov, Tribology of 2D Nanomaterials: A Review, Coatings 10 (2020) 897, https://doi.org/10.3390/coatings10090897.

[18] H. Xiao, S. Liu, 2D nanomaterials as lubricant additive: A review, Mater. Des. 135 (2017) 319–332, https://doi.org/10.1016/j.matdes.2017.09.029.

[19] M.K.A. Ali, H. Xianjun, M.A.A. Abdelkareem, M. Gulzar, A.H. Elsheikh, Novel approach of the graphene nanolubricant for energy saving via anti-friction/wear in automobile engines, Tribol. Int. 124 (2018) 209–229, https://doi.org/10.1016/j.triboint.2018.04.004.

[20] S. Qiu, G. Liu, W. Li, H. Zhao, L. Wang, Noncovalent exfoliation of graphene and its multifunctional composite coating with enhanced anticorrosion and tribological performance, J. Alloys Compd. 747 (2018) 60–70, https://doi.org/10.1016/j.jallcom.2018.03.007.

[21] W. Shang, T. Cai, Y. Zhang, D. Liu, S. Liu, Facile one pot pyrolysis synthesis of carbon quantum dots and graphene oxide nanomaterials: All carbon hybrids as eco-environmental lubricants for low friction and remarkable wear-resistance, Tribol. Int. 118 (2018) 373–380, https://doi.org/10.1016/j.triboint.2017.09.029.

[22] L. Liu, M. Zhou, X. Li, L. Jin, G. Su, Y. Mo, L. Li, H. Zhu, Y. Tian, Research Progress in Application of 2D Materials in Liquid-Phase Lubrication System, Materials 11 (2018) 1314, https://doi.org/10.3390/ma11081314.

[23] R. Rosentsveig, A. Gorodnev, N. Feuerstein, H. Friedman, A. Zak, N. Fleischer, J. Tannous, F. Dassenoy, R. Tenne, Fullerene-like MoS_2 Nanoparticles and Their Tribological Behavior, Tribol. Lett. 36 (2009) 175–182, https://doi.org/10.1007/s11249-009-9472-0.

[24] C.P. Koshy, P.K. Rajendrakumar, M.V. Thottackkad, Evaluation of the tribological and thermo-physical properties of coconut oil added with MoS_2 nanoparticles at elevated temperatures, Wear 330–331 (2015) 288–308, https://doi.org/10.1016/j.wear.2014.12.044.

[25] P. Rabaso, F. Ville, F. Dassenoy, M. Diaby, P. Afanasiev, J. Cavoret, B. Vacher, T. Le Mogne, Boundary lubrication: Influence of the size and structure of inorganic fullerene-like MoS_2 nanoparticles on friction and wear reduction, Wear 320 (2014) 161–178, https://doi.org/10.1016/j.wear.2014.09.001.

[26] Q. Wan, Y. Jin, P. Sun, Y. Ding, Rheological and tribological behaviour of lubricating oils containing platelet MoS_2 nanoparticles, J. Nanoparticle Res. 16 (2014) 2386, https://doi.org/10.1007/s11051-014-2386-2.

[27] M.J.G. Guimarey, A.M. Abdelkader, M.J.P. Comuñas, C. Alvarez-Lorenzo, B. Thomas, J. Fernández, M. Hadfield, Comparison between thermophysical and tribological properties of two engine lubricant additives: electrochemically exfoliated graphene and molybdenum disulfide nanoplatelets, Nanotechnology 32 (2020), https://doi.org/10.1088/1361-6528/abb7b1 025701.

[28] A.M. Abdelkader, I.A. Kinloch, R.A.W. Dryfe, Continuous Electrochemical Exfoliation of Micrometer-Sized Graphene Using Synergistic Ion Intercalations and Organic Solvents, ACS Appl. Mater. Interfaces 6 (2014) 1632–1639, https://doi.org/10.1021/am404497n.

[29] K. Czamara, K. Majzner, M.Z. Pacia, K. Kochan, A. Kaczor, M. Baranska, Raman spectroscopy of lipids: a review 46 (2015) 4–20, https://doi.org/10.1002/jrs.4607.

[30] Y. Wang, X. Liang, G. Tang, Y. Chen, L. Dong, G. Shu, Impact of lubricating oil combustion on nanostructure, composition and graphitization of diesel particles, Fuel 190 (2017) 237–244, https://doi.org/10.1016/j.fuel.2016.11.021.

[31] H. Li, Q. Zhang, C.C.R. Yap, B.K. Tay, T.H.T. Edwin, A. Olivier, D. Baillargeat, From Bulk to Monolayer MoS_2, Evolution of Raman Scattering 22 (2012) 1385–1390, https://doi.org/10.1002/adfm.201102111.

[32] P. Instruments, PCS Instruments. MTM (Mini Traction Machine). Retrieved,

[33] W. Zhang, M. Zhou, H. Zhu, Y. Tian, K. Wang, J. Wei, F. Ji, X. Li, Z. Li, P. Zhang, D. Wu, Tribological properties of oleic acid-modified graphene as lubricant oil additives, J. Phys. D Appl. Phys. 44 (2011), https://doi.org/10.1088/0022-3727/44/20/205303 205303.

[34] M. Kalin, J. Kogovšek, M. Remskar, Mechanisms and improvements in the friction and wear behavior using MoS_2 nanotubes as potential oil additives, Wear 280–281 (2012) 36–45, https://doi.org/10.1016/j.wear.2012.01.011.

[35] G. Paul, H. Hirani, T. Kuila, N.C. Murmu, Nanolubricants dispersed with graphene and its derivatives: an assessment and review of the tribological performance, Nanoscale 11 (2019) 3458–3483, https://doi.org/10.1039/C8NR08240E.

[36] N. Zawawi, W. Azmi, A. Redhwan, S. Mohd Zaki, Coefficient of friction and wear rate effects of different composite nanolubricant concentrations on Aluminium 2024 plate, IOP Conf. Ser. Mater. Sci. Eng. 257 (2017) 012065. https://doi.org/10.1088/1757-899X/257/1/012065

[37] F. Motamen Salehi, A. Morina, A. Neville, The effect of soot and diesel contamination on wear and friction of engine oil pump, Tribol. Int. 115 (2017) 285–296, https://doi.org/10.1016/j.triboint.2017.05.041.

[38] A. Singh, P. Chauhan, T.G. Mamatha, A review on tribological performance of lubricants with nanoparticles additives, Mater. Today: Proceedings 25 (2020) 586–591, https://doi.org/10.1016/j.matpr.2019.07.245.

[39] ASME, Surface texture, surface roughness, waviness and lay., B46.1: 2019.

[40] J.P. Ewen, C. Gattinoni, F.M. Thakkar, N. Morgan, H.A. Spikes, D. Dini, Nonequilibrium Molecular Dynamics Investigation of the Reduction in Friction and Wear by Carbon Nanoparticles Between Iron Surfaces, Tribol. Lett. 63 (2016) 38, https://doi.org/10.1007/s11249-016-0722-7.

[41] I. Khan, K. Saeed, I. Khan, Nanoparticles: Properties, applications and toxicities, Arab. J. Chem. 12 (2019) 908–931, https://doi.org/10.1016/j.arabjc.2017.05.011.

[42] A. Hernández Battez, J.L. Viesca, R. González, D. Blanco, E. Asedegbega, A. Osorio, Friction reduction properties of a CuO nanolubricant used as lubricant for a NiCrBSi coating, Wear 268 (2010) 325–328, https://doi.org/10.1016/j.wear.2009.08.018.

[43] D. Uy, R.J. Zdrodowski, A.E. O'Neill, S.J. Simko, A.K. Gangopadhyay, M. Morcos, F. Lauterwasser, G. Parsons, Comparison of the Effects of Biodiesel and Mineral Diesel Fuel Dilution on Aged Engine Oil Properties, Tribol. Trans. 54 (2011) 749–763, https://doi.org/10.1080/10402004.2011.597545.

[44] D. Uy, S.J. Simko, R.O. Carter, R.K. Jensen, A.K. Gangopadhyay, Characterization of anti-wear films formed from fresh and aged engine oils, Wear 263 (2007) 1165–1174, https://doi.org/10.1016/j.wear.2006.12.026.

[45] J.M. Liñeira del Río, E.R. López, J. Fernández, Synergy between boron nitride or graphene nanoplatelets and tri(butyl)ethylphosphonium diethylphosphate ionic liquid as lubricant additives of triisotridecyltrimellitate oil, J. Mol. Liq. 301 (2020), https://doi.org/10.1016/j.molliq.2020.112442 112442.

[46] L. Maritsa, S. Martel, R. Barros, A. Bol, S. Aparicio, Additivation of MoS_2 nanosheets to synthetic poly-alpha-olefins base oils: A theoretical study of nanolubrication, J. Mol. Liq. 332 (2021), https://doi.org/10.1016/j.molliq.2021.115881 115881.

[47] J. Spear, B. Ewers, J. Batteas, 2D-nanomaterials for controlling friction and wear at interfaces, Nano Today 10 (2015) 301–314, https://doi.org/10.1016/j.nantod.2015.04.003.

[48] T. Gao, C. Li, Y. Zhang, M. Yang, D. Jia, T. Jin, Y. Hou, R. Li, Dispersing mechanism and tribological performance of vegetable oil-based CNT nanofluids with different surfactants, Tribol. Int. 131 (2019) 51–63, https://doi.org/10.1016/j.triboint.2018.10.025.

[49] S.B. Mousavi, S.Z. Heris, P. Estellé, Experimental comparison between ZnO and MoS_2 nanoparticles as additives on performance of diesel oil-based nano lubricant, Sci. Rep. 10 (2020) 5813, https://doi.org/10.1038/s41598-020-62830-1.