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DEVELOPMENT OF NANOLUBRICANT BASED ON IMPREGNATED MULTILAYER GRAPHENE FOR AUTOMOTIVE APPLICATIONS: ANALYSIS OF TRIBOLOGICAL PROPERTIES

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ABSTRACT

This paper shows novel formulations of nanolubricants added with multi-layer graphene (MLG), multi-layer graphene impregnated with copper (MLG-Cu), and multi-layer graphene impregnated with polyaniline (MLG-PANI) for applications in automotive engines. These nanofluids were prepared using commercial motor oil as the base fluid. The tribological properties were measured at 100 °C, and significant reductions were found in the coefficient of friction and wear. The concentrations used were 0.5% and 2% by weight, obtaining reductions in the friction coefficient and wear of up to 43% and 63%, respectively, in the case of motor oil with copper-impregnated graphene. All formulations of MLG, MLG-Cu, and MLG-PANI did not show any sedimentation when dispersed in engine oil, even three months after being produced.

Keywords: Impregnated Graphene, PANI, Nanofluid, Tribology.

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1. Introduction

Lubricants are mainly used to eliminate contact between two parts in a sliding movement. The main applications of lubricants are focused in internal combustion engines, vehicle and industrial gearboxes, compressors, turbines, and hydraulic systems, where engine oil applications represent approximately 50% of the global market [1]. Engine oils contain many additives in order to effectively and efficiently accomplish their functions. Some commonly used additives are antioxidants, detergents, dispersants, friction modifiers, anti-wear, viscosity modifiers, pour point depressants, tackifiers and antimisting, corrosion inhibitors, etc. [2]

Because conventional additives fail at high temperatures (> 200 °C) and pressures (> 5000 psi), extreme pressure (EP) and anti-wear (AW) additives are needed. However, these types of materials are expensive and environmentally hazardous. In addition, EP additives have many technical limitations, such as ineffectiveness at slow speeds and low temperatures, high reactivity and corrosivity in contact with water, very limited operation at high temperatures, etc. [3] Due to the above reasons, there is a need to find new types of additives that are cost-effective and environmentally friendly [3]. Recently, it has been reported that metallic nanoparticles added to lubricant oils (nanolubricants) are able to act as anti-wear additives under extreme pressure [4]. These metallic nanoparticles are non-corrosive and are capable of working at very high temperatures. Therefore, they are very promising for establishing a new era of AW and EP additives [5, 6].

The main advantage of using nanoparticles as additives is that they are not degraded or modified with the temperature. Moreover, due to the small size of these particles, clogging problems are avoided in lubrication systems [5].

Friction and wear, i.e., two of the main causes of material failure, have attracted more and more attention all over the world. Advances in nanotechnology have allowed the dispersion of nanoparticles in fluids without encountering sedimentation problems [5,7, 8]. Numerous studies have been conducted on improving the tribological properties of certain lubricant fluids by the addition of nanoparticles. Nanoparticles that have been used include graphite [9,10]; nickel [5]; nanodiamond [11]; boron nitride [12]; CuO [13]; fullerene [14]; silica, titanium dioxide, alumina, tin dioxide, magnesium oxide, cerium oxide, zirconia, and mixtures thereof [15]; molybdenum disulfide, tungsten disulfide, and calcium oxide [16]. In particular, carbonaceous nanoparticles, such as graphene, CNTs, fullerenes, etc., are the most studied [9-11, 14, 15, 17] due to large improvements in the wear and a friction coefficient reduction [18].

Some of the recently published articles and patents related to nanolubricants are listed in Table 1.

Gulzar et al. [6] improved the anti-wear (AW) and extreme pressure (EP) abilities of chemically modified palm oil (CMPO) by adding CuO and MoS_2 nanoparticles at low filler contents (1 wt. %). The morphology of the CuO nanoparticles was fairly spherical, with particle sizes between 50 and 300 nm. The particles of the MoS_2 powder had larger sizes, ranging from 50 to 2000 nm. The AW/EP properties of the formulations were evaluated by four-ball and sliding wear tests. The wear scar diameter reductions at 120 kg loading were 6.65% and 11% for CMPO + 1% MoS2 and CMPO + 1% CuO, respectively. An average reduction of 16.6% at loads higher than 80 kg was achieved with the wear scar diameters. This reduction was higher than that achieved (10%) at a lower load range.

Chen et al. [17] presented a study of a nanofluid based on multi-wall carbon nanotubes (MWCNTs) dispersed in pure liquid paraffin at a concentration of 0.45 wt.% MWCNTs, where the nanotubes were surface modified by means of oxidation via refluxing in stearic acid (SA). The maximum friction and wear reduction reported were approximately 10% and 40%, respectively.

Madhusree et al. [20] experimented with a nanofluid in order to improve the viscosity behavior. They used spherical CuO nanoparticles with diameters of 40 nm and gear oil as the base fluid. The CuO volume fraction was between 0.005 and 0.025, and the prepared nanofluids were stabilized by adding oleic acid (surfactant). The prepared nanofluids did not show any visual sedimentation of CuO nanoparticles, even after keeping the fluids stationary for more than 30 days. By increasing the CuO nanoparticle content to more than 0.025 wt. % at 30 °C, the nanofluid viscosity was enhanced by nearly three times compared to the gear oil viscosity.

Chou et al. [21] presented a study of a nanofluid based on Ni nanoparticles dispersed in polyalphaolefin (PAO6) as the base oil. Ni nanoparticles were dispersed in the lubricant at concentrations of 0.5, 1, and 2 wt. %. The suspension with 0.5 wt. % exhibited the best tribological behavior, i.e., 54% wear reduction, and the worst performance was found for the 2 wt. % suspension, which gave a 5% wear reduction.

Hernández et al. [13] and Madhusree et al. [22] reported a nanofluid formulation using spherical CuO nanoparticles dispersed in gear and PAO oil for improving lubrication properties. CuO nanoparticles were evaluated in the range between 0.005 and 2 wt. % of the filler content.

Zhamu et al. [18] patented a nanolubricant-based multi-layer graphene (MLG) dispersed in the lubricant fluid. The content of MLG ranged from 0.001 to 75 wt. %, with an average thickness less than 10 nm and length or width less than 500 nm. Compared with graphite or carbon nanotube-modified lubricants, MLG-modified lubricants exhibited much better thermal conductivity, friction-reducing capability, anti-wear performance, and viscosity stability.

Most of the earlier studies focused on thermophysical properties of nanofluids based on single nanoparticles, and in particular, graphene-based nanofluids provided the best results [23]. However, the synthesis of hybrid nanofillers and the preparation of nanofluids based on hybrid nanofillers to evaluate their synergistic effects are still very new areas of research. Two examples of the preparation of water-based nanofluids with hybrid nanofillers are the addition of graphene-copper oxide (GNP-CuO) [23] and graphene-silver (GNP-Ag) [24]. In both types of nanofluids, water was the base fluid, and only thermal and rheological properties were evaluated. Therefore, it will be interesting to analyze the behavior of hybrid nanofillers dispersed in oil to evaluate their capabilities as nanolubricants.

In this work, the tribological properties of metallic nanoparticles with a spherical shape (Cu) and polymer nanoparticles with a tubular shape (PANI), in synergy with multi-layer graphene, dispersed in a commercial engine oil (EO), were evaluated. All experiments were conducted at 100 °C because this is very close to the temperature at which vehicle engines work. Morphology analyses of multi-layer graphene (MLG), multi-layer graphene impregnated with copper (MLG-Cu), and multi-layer graphene impregnated with polyaniline (MLG-PANI) were conducted. Moreover, characterization of worn surfaces using MLG and hybrid nanofillers (MLG-PANI and MLG-Cu) was conducted. Finally, the stability of nanoparticles in the base fluid was analyzed.

2. Experimental details

2.1 Materials

Commercial graphite powder (<20 μm) was utilized as the graphene precursor. The base fluid was a commercial engine oil (SAE 25 W-50).

Sulfuric acid with a purity of 95-98%, nitric acid with a purity of 68.0-70.0%, potassium chloride with a purity ≥ 99.0%, aniline with a purity of 99.5%, ammonium persulfate with a purity of > 98%, hydrochloric acid with a purity of 37%, tetraamminecopper (II) sulfate monohydrate, and ammonium hydroxide solution were used as reagents.

2.2 Materials Preparation

Synthesis of MLG. Graphite powder was oxidized using a modified Staudenmaier's method to produce graphite oxide (GO) [27, 28]. In this work, graphite (5 g) was first mixed with sulfuric acid (87.5 mL) and nitric acid (45 mL), and the mixture was stirred for 15 minutes. When graphite was dispersed uniformly, potassium chlorate (55 g) was added slowly and stirred for over 96 h. Once the oxidizing reaction was finished, the mixture was added to deionized water and then filtered. The GO was rinsed repeatedly and re-dispersed several times in a 5% solution of HCl. It was then washed continuously with deionized water until the pH of the filtrate was neutral. The GO slurry was dried and pulverized twice. Finally, the GO was heated to 1050 °C in an inert atmosphere for 1 min to form MLG. A summary of the entire MLG chemical exfoliation process described above is represented in Figure 1.

Fig. 1 MLG chemical exfoliation process.

Synthesis of MLG-Cu. To obtain MLG-Cu nanoparticles, a natural graphite powder was first oxidized using the same modified Staudenmaier's method described before. Then, the GO (0.20 g) was dispersed into an NH_3 solution (pH 9.5) using ultrasonic sonication for 15 min. Then, $[Cu\ (NH_3)_4]$ SO4 (0.07 g) was added to the solution and stirred for 24 h. The obtained compounds of Cu complexes and GO (Cu–GO) were calcined gradually by putting them into a furnace at room temperature and then heating them to 400 °C at a rate of 5 $°Cmin^{-1}$. The specimens were kept for 30 min at the heating temperature to obtain MLG-Cu nanoparticles [25]. The synthesis of MLG-Cu is shown in Figure 2 below.

Fig. 2 Synthesis of MLG-Cu nanoparticles.

Synthesis of MLG-PANI. The preparation of MLG-PANI nanoparticles was based on the process described by Li and colleagues [28]. Briefly, the process employed for the preparation of MLG-PANI is as follows: (1) 0.94 g of aniline was added to 30 mL of deionized water, with 2 wt. % to 5 wt. % of MLG; (2) a sonotrode was used to agitate the solution for 30 minutes at 24 KHz, followed by magnetic stirring at 100 rpm; (3) a solution containing 5.705 g of ammonium persulfate and 2.5 mL of hydrochloric acid was prepared, followed by the addition of 30 mL of deionized water; (4) the two solutions were mixed and magnetically stirred at 100 rpm for 12 h; (5) the solution was washed by adding 200 mL of deionized water and then filtered; and (6) the obtained product was vacuum dried at 60 °C for 12 h.

2.3 Measurements

Morphology

The morphology of the wear scar was analyzed by optical microscopy using an OLYMPUS microscope (model BX63) containing an UIS2 optical system.

The transmission electron microscope (TEM) used in this study was a JEOL JEM-1230 with an electron gun at 120 kV. Samples were prepared on a copper grid (200 mesh) and coated with Formvar/carbon film.
In addition, energy dispersive X-ray spectroscopy (EDX) analysis was conducted. All elements were analyzed, and peaks at 8.036 and 8.899 keV, corresponding to the copper cells, were omitted. The quantification method used was the Cliff Lorimer thin ratio section, with only one iteration.

Production of nanolubricants

In the first stage of the production process of nanolubricants, the nanoparticles were mixed in the engine oil (EO) for 10 to 15 min using magnetic stirring. Subsequently, the mixture was placed in an ultrasonic bath for 60 min at 25 ºC. Finally, the mixture was sonicated for 1 hour in a UP200S sonicator (200 W, 24 kHz) in an ice-water bath. The device parameters were set to a cycle of 0.5 and amplitude of 80%. In the preparation process of these samples, pH adjustment and the addition of surfactants were removed from the general two-step method used to prepare nanofluids without MLG. This was because the purpose of these steps was to ensure the stability of nanoparticles in the base fluid, as MLG had intrinsic stability in EO.

Tribological testing

The tribometer used was a T05-block-on-ring wear tester (Figure 3) for the evaluation of lubricants and engineering materials [5, 13]. The machine was manufactured by the Institute for Terotechnology in Poland. Experiments were carried out in accordance with the ASTM D 2981, D 3704, G 77, and D 2714 standards.

Fig. 3 Block on ring T05 tribology tester.

The geometry and measurements of the block and ring (Figure 4), as well as the procedure of the wear test employed, were based on the ASTM G77 standard. The ring was manufactured from carbon steel with a hardness of 62 HRC, while the block was manufactured from AISI-1045 steel with a hardness of 48 HRA. The outer diameter and concentricity with the inner diameter are the critical parameters of the ring. The inner diameter is optional depending on the machine design during the test; the friction force, lubricant temperature, and vertical displacement of the block were recorded.

Fig. 4 Block and ring lay out according ASTM G77 standard

Calculation of Block Scar Volume (WEAR)

In order to obtain the block scar volume, three repetitions of each experimental combination were conducted, and the scar in each block was analyzed by optical microscopy. The preferred method for calculating block scar volume is via a geometric equation approach, which can be programmed on a calculator or computer. In this work, the wear scar volume was calculated geometrically according to Equation 1 and is represented in Figure 5.

$$Wear\ (\mathrm{mm}^3) = \left[\left(\pi r^2 \cdot \frac{\alpha}{360°}\right) - (cos\theta \cdot r \cdot b)\right] t \qquad (1)$$

where r = disc radius, b = scar width, and t = specimen width.

Fig. 5 Schematic drawing of the wear calculation.

The radius of the disk was 17.5 mm and the block width was 6.35 mm, both of them were constant for all the experiments. For the determination of the scar width, the scar was measured along three points (Figure 6), and the values were averaged. Finally, the averaged scar width values were substituted into Equation 1 to obtain the volumetric wear.

Fig. 6 Sketch of the measuring method of scar width

Coefficient of friction

The coefficients of friction were calculated from the friction force values according to Equation 2 as follows:

$$\mu = F / W \qquad (2)$$

where μ = coefficient of friction, F = measured friction force (N), and W = normal force (N).

The friction force was measured by a load cell and was graphed in real time during each experiment. The magnitude of the force corresponds to the force exerted by the arm for holding the block in contact with the ring and moving in normal direction to the load cell. The normal force was constant for all the experiments and corresponds to the load applied under the block.

Test parameters

The parameters of the block-on-ring test were as follows:
load of 200 N; speed of 300 rpm; distance of 1000 m; and chamber temperature of 100 °C.

The parameters were selected according to a literature review [5, 31, 32], which allows for a comparison between all formulations versus engine oil without nanoparticle additives. The temperature of the test (100 °C) was selected because the temperature that is reached in the engine is very close to this temperature.

3. Results and discussion

3.1 Morphology analysis

The morphology of MLG was observed by transmission electron microscopy (TEM). The TEM micrograph obtained is shown in Figure 7. The analysis of the TEM micrographs showed that the MLG obtained (< 10 layers of thickness) exhibited an average area of 0.5 μm x 1.5 μm. The shape of the MLG was irregular and folded because of the exothermic reaction in the last stage of synthesis. Finally, the MLG was observed to be free from impurities.

Fig. 7 TEM micrograph of synthesized MLG at a magnification of 20,000 X.

The TEM micrograph of MLG-Cu is depicted in Figure 8. The Cu nanoparticles on graphene sheets were distributed with sizes <100 nm and a density ranging between 50-80 Cu nanoparticles for each MLG. A nonhomogeneous morphology with both well-dispersed areas and aggregated areas was observed.

Fig. 8 TEM micrograph of synthesized MLG-Cu at a magnification of 20,000 X.

Table 2 shows the EDX analysis of the MLG-Cu sample, from which we can observe that Fluor existed as a trace element, which was used during the process of copper reduction.

The TEM micrograph of MLG-PANI particles is shown in Figure 9. The polyaniline morphology on the MLG was hollow-tubular with an average size of 40 nm width x 150 nm length. The polyaniline form observed was emeraldine, which was doped with the imine nitrogens protonated by ammonium persulfate in the presence of MLG. This molecular structure of dopant was responsible for the length and diameter values of the nanotubes. Emeraldine is regarded as the most useful form of polyaniline due to its high stability at room temperature, and the emeraldine salt obtained from the synthesis of polyaniline is highly electrically conducting.

Fig. 9 TEM micrograph of synthesized MLG-PANI at a magnification of 15,000 X.

Table 3 shows the EDX analysis of the MLG-PANI sample. From the EDX analysis, we can see that MLG-PANI was composed of carbon, oxygen, and nitrogen. The presence of oxygen was due to the carboxylic groups on the surface of MLG, while the presence of nitrogen was due to the polymeric chain of polyaniline.

3.2 Coefficient of friction

The coefficients of friction for MLG and MLG-Cu and MLG-PANI formulations with 0.5 wt. % and 2 wt. % concentrations were evaluated and measured (Table 4). The results of the friction coefficient versus distance are plotted in Figure 10.

Fig. 10 Average friction coefficient from 1000-m sliding tests at 95% confidence level (Cl) as a function of the nanoadditive type, i.e., MLG, MLG-PANI, or MLG-Cu. The base fluid was engine oil with 0.5 wt.% and 2 wt. % loading tested at 100 °C.

The friction reduction behaviors of the MLG formulations evaluated were related to the fact that the nano-sheets can be piled up on wear tracks forming a tribo-film between contact junctions, thus protecting sliding surfaces. For the case of MLG-Cu and MLG-PANI, these nano-sheets piled up below and above Cu and PANI nanoparticles [19]. On the other hand, similar to the work reported by Li et al. [30], the MLG could become a mono-layer because it can be mechanically peeled off. Based on these reports, it was speculated that a tribo-film may have been formed by repeated exfoliation and deposition of MLG. Therefore, MLG, MLG-Cu, and MLG-PANI sheets can reduce friction due to the layered structure and the continuous exfoliation between them, allowing for easier surface sliding. This mechanism can allow for the generation of a tribo-film even at an infinitesimal amount of MLG, which can be enough to protect sliding surfaces [19]. Details of the reductions in the friction coefficient with respect to the engine oil without nanoadditives for all evaluated formulations are shown in Figure 11.

Fig. 11 Average friction coefficient reduction percentage as a function of nanoadditive type, i.e., MLG, MLG-PANI, and MLG-Cu.

For the case of engine oil added with MLG at 0.5 wt. and 2 wt. %, the reductions in the coefficient of friction were approximately -2.8% and 4.8%, respectively. The negative decrease in friction coefficient using MLG may be due to its low concentration (0.5 wt. %) and the thinness (<10 nm) of the nano-sheets dissolved, i.e., there may not have been enough material to form a tribo-layer between contact junctions. This was improved by using a higher concentration (2 wt. %) of MLG, allowing the formation of a tribo-layer that was slightly thinner than the mixed and boundary lubrication regimes (< 250 nm). In addition, the mechanical exfoliation of the MLG during the sliding also contributed to the friction reduction.

For the case of engine oil filled with MLG-Cu at 0.5 wt. % and 2 wt. %, the friction reductions were approximately 33% and 43%, respectively. These large reductions may be due to the copper nanoparticles acting as spacer elements between the tribo-layers formed by graphene. This allowed the formation of a tribo-layer that was thicker than the mixed and boundary lubrication regimes.

Finally, for the case of engine oil filled with MLG-PANI at 0.5 wt. % and 2 wt. %, the friction reductions were approximately 30% and 20%, respectively. Similar to Cu, PANI nanotubes acted as spacers between the tribo-layers. However, because polymers have a lower hardness than metals, a lower resistance between the contact junctions was produced, causing the reductions in the friction to be less than that achieved by MLG-Cu. On the other hand, it was observed that as the concentration of MLG-PANI increased (2 wt. %), a lower decrease in the coefficient of friction was achieved. This may be due to the formation of inhomogeneous morphologies produced by the entanglement of PANI nanotubes.

It is important to remark that the above reductions were achieved at 100 °C, i.e., a temperature at which the viscosity of the lubricant suffered a substantial decrease. Thus, a proportional reduction in its carrying capacity can lead us to infer that the nanofillers used can serve as additives for high temperatures. Moreover, the high temperature may also have contributed to the process of tribosinterization of the nanoparticles.

3.3 Wear

The average wear for the engine oil was approximately 1.28 mm^3. For the case of engine oil added with MLG at 0.5% wt. % and 2 wt. %, the wear values were approximately 1.02 mm^3 and 0.89 mm^3, respectively. For the case of engine oil added with MLG-Cu at 0.5 wt. % and 2 wt. %, the wear values were approximately 0.47 mm^3 and 0.46 mm^3, respectively. Finally, for the case of engine oil added with MLG-PANI at 0.5 wt. % and 2 wt. %, the wear values were approximately 0.93 mm^3 and 0.84 mm^3, respectively (Figure 12).

Fig. 12 Average wear from the two repeated measurements with a) the standard error of the mean (SEM) and b) 95% confidence levels as a function of nanoadditive type, i.e., MLG, MLG-PANI, and MLG-Cu. The base fluid was engine oil with 0.5 wt. % and 2 wt. % loading tested at 100 °C.

In general, the most common anti-wear mechanism of MLG, MLG-Cu, and MLG-PANI additives is the tribosinterization of nanoparticles on the wear surface. When tiny particles are used, the process of sinterization begins immediately after room temperature is reached [33], forming boundary films with excellent mechanical properties on the rubbed surfaces.

The greater wear reductions achieved using the MLG-Cu formulations were mainly due to the presence of copper nanoparticles on the wear surface. From the mechanism of colloidal solid dispersion and taking into account that the lubricant film thickness for mixed and boundary lubrication regimes was thinner (< 0.025 μm) than the Cu nanoparticle diameter (100 nm), it can be inferred that nanoparticles were blown and contacted by the surface, achieving an improvement in the tribological behavior of the engine oil. In addition to the colloidal effect, Cu nanoparticles can also behave as tiny bearings, increasing the load carrying capacity by surface hardness effects of the lubricant and leaving the contact surface later on [33].

Details of the reductions in wear with respect to engine oil without nano-additives for all of the evaluated formulations are shown in Figure 13.

Fig. 13 Average wear reduction percentage as a function of nanoadditive type, i.e., MLG, MLG-PANI, and MLG-Cu.

The wear reductions of engine oil added with MLG at 0.5 wt. % and 2 wt. %, were approximately 20% and 30%, respectively. Smaller degree of wear was observed with increasing concentration of MLG, which may be due to the fact that when the concentration of nano-sheets in the lubricant increased, there was a higher amount of tribo-sinterized nanoparticles protecting the wear surface.

For the case of engine oil added with MLG-PANI at 0.5 wt. % and 2 wt. %, the wear reductions were approximately 27% and 35%, respectively. These reductions achieved were slightly higher than that obtained by adding only MLG. This result indicated that the tribosinterization of PANI nanotubes contributed marginally in reducing the wear of contact junctions and that the predominant effect in reducing the wear was the MLG tribosinterization on the wear surface.

Finally, for the case of engine oil added with MLG-Cu, both concentrations offered almost the same wear reduction (> 60%), i.e., the largest reduction achieved among all evaluated formulations. Thus, we can speculate that the effect of MLG tribosinterization on the wear surface, in combination with the ball-bearing effect of copper nanoparticles, led to a positive synergistic effect in the wear reduction. Additionally, the fact that almost the same reduction in wear was observed for both concentrations may indicate that the ball-bearing effect of copper nanoparticles was predominant in reducing the wear. That is, regardless of the concentration of MLG-Cu, the size and physical properties of copper nanoparticles did not change, which offered the same spacing and load capacity between contact junctions.

3.4 Surface characterization: Atomic Force Microscopy (AFM)

To analyze the topography of the worn surfaces, atomic force microscopy (AFM) was conducted in peak force tapping mode using NanoScope Analysis Version 1.40. The AFM was equipped with a SCANASYST-AIR cantilever with a nominal spring constant K= 0.4 N/m and a resonant frequency between 50 and 90 kHz. The mean roughness (Ra) was used as a parameter for the analysis, and peaks were removed to calculate the Ra values. The Ra values of the worn surfaces using engine oil without nanoparticles, engine oil added with 2 wt. % of MLG-PANI, and engine oil added with 2 wt. % of MLG-Cu as lubricants were 658 nm, 109 nm, and 40.8 nm, respectively (Figures 14 and 15).

Fig. 14 AFM 3D topographic images of the worn surfaces using the following lubricants: a) Engine oil (EO), b) EO+MLG-PANI at 2 wt. % loading, and c) EO+MLG-Cu at 2 wt. % loading. For the MLG-PANI and MLG-Cu samples, the scanning rate was 0.250 Hz, and 256 samples per line were recorded; the scan size was 70.0 μm, the amplitude setpoint was 250 mV, and the drive amplitude was 122.38 mV. For the engine oil sample, the scanning rate was 0.500 Hz, and 256 samples per line were recorded; the scan size was 25.0 μm, the amplitude setpoint was 357.79 mV, and the drive amplitude was 122.38 mV.

Fig. 15 Peak force error and deflection error of the AFM 3D topographic images of the worn surfaces using the following lubricants: a) Engine oil (EO), b) EO+MLG-PANI at 2 wt. % loading, and c) EO+MLG-Cu at 2 wt. % loading.

From the AFM analysis, we can observe a more polished surface when using engine oil added with MLG-Cu at 2 wt. % loading. This may be due to the ball bearing effect of the Cu nanoparticles, which was also responsible for the friction reduction.

3.4 Stability

All formulations of MLG, MLG-Cu, and MLG-PANI did not show any sedimentation when dispersed in engine oil, even three months after being produced. This stability may be due to the aspect ratio and surface functionalization (chemical affinity) of the MLG.

The aspect ratio (length/thickness) of MLG was very high because its length was approximately 0.5-2 μm and its thickness was approximately 1-10 nm. Wohner et al. [33] reported the influence of compactness on the stability of MLG in a base fluid and chose rectangular shapes with different aspect ratios. They found that the cohesive energies increased significantly at higher aspect ratios.

Surface functionalization accomplished during graphite oxidation can be another way to improve the stability in the fluid. In this stage, hydroxy and carboxylic functional groups were linked on the graphite oxide surface, which remained until MLG exfoliation [33]. When the modified MLG was dispersed in the engine oil, the long hydrocarbon segment stretched very easily into the base lubricant, resulting in the formation of steric hindrance force. The steric hindrance force was able to conquer the van der Waals interaction between MLGs, thereby separating them from each other. At the same time, the steric hindrance force was able to conquer gravity and prevent MLG agglomeration and sedimentation [17].

4. Conclusions

Engine oil added with MLG and MLG impregnated with nanomaterials showed the ability to integrate a friction modifier with an anti-wear modifier in a single lubricant, even at temperatures up to 100 °C, i.e., the typical working temperature of the conventional engine vehicles.

The TEM micrographs showed that the MLG obtained (< 10 layers of thickness) had an average area of 0.5 μm x 1.5 μm, which exhibited an irregular shape and was folded due to the exothermic reaction in the last stage of synthesis. Regarding MLG-Cu, the TEM micrograph showed that Cu nanoparticles (<100 nm) were distributed on graphene sheets with a density ranging between 50-80 Cu nanoparticles for each MLG. Finally, the TEM micrograph of MLG-PANI showed that the acquired polyaniline morphology was tubular, with an average size of 40 nm width x 150 nm length. The polyaniline form observed was emeraldine.

Regarding the coefficient of friction, engine oil added with MLG-Cu and MLG-PANI nanoparticles showed higher reductions in comparison with MLG fillers without decoration. Engine oil added with MLG-Cu and MLG-PANI showed the best results at 2 wt. % and 0.5 wt. %, achieving average reductions of 45% and 30%, respectively, which may be because copper and PANI nanoparticles acted as fillers between the tribo-layers created by graphene nanosheets, allowing the formation of a tribo-layer that is thicker than the mixed and boundary lubrication regimes. In this case, because PANI nanotubes were formed by polymers (with lower hardness than metals), they opposed less resistance between contact junctions, causing reductions in friction with values lower than that achieved by MLG-Cu.

Regarding the wear, all formulations showed significant reductions. However, the MLG-Cu formulations showed the highest reduction of approximately 60%, which may be due to the synergistic effect of MLG tribosinterization on the wear surface with the ball-bearing effect of copper nanoparticles. For the case of engine oil added with MLG and MLG-PANI, the wear reductions were very similar, ranging between 25-35%. In this regard, it can be concluded that the tribosinterization of PANI nanotubes contributed marginally in the wear reduction and that the predominant effect in reducing the wear was the MLG tribosinterization on the wear surface.

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Table 1
Nanofluids used in lubricant applications.

Nanoparticle	Base fluid	Size(nm)	Wear reduction (%)	Friction reduction (%)	Concentration	
CuO	GO, PAO	40		45	0.005-2 vol. %	[2,5,13]
Graphene	LO	500	20-68	40-70	0.001-30 wt. %	[18]
Graphite	LO	500			1-30 wt. %.	[9,10,16]
CNT MWNT, fullerene, Diamond	EO, GO	200	40-50	10-55	0.001-30 wt. %	[9-11,14, 15, 17]
BN h-BN	PAO, GO	150	15	20	1 wt. %	[1,7,12, 19]
TiO2, Al2O3, SiO2, MoO2	LO, EO	40-100			0.01-10 wt. %	[10,15,16]

GO = Gear oil; LO= Lubricant oil; EO = Engine oil; PAO = polyalphaolefine

Table 2
EDX analysis of the MLG-Cu nanoparticles.

Element	Atomic %
C	69.8
F	2.12
Cu	28.04

Table 3
EDX analysis of the MLG-PANI nanoparticles

Element	Atomic %
C	53.94
N	36.43
O	9.63

Table 4
Average Friction Coefficient with the standard error of the mean for different nanoadditives.

Nanoadditive	Mean friction coefficient	Standard error of the mean (SEM)
Engine Oil	0.128	0.0064
MLG, 0.5 wt. %	0.132	0.0058
MLG, 2 wt. %	0.122	0.0063
MLG-Cu, 0.5 wt. %	0.086	0.0061
MLG-Cu, 2 wt. %	0.073	0.0049
MLG-PANI, 0.5 wt. %	0.090	0.0051
MLG-PANI, 2 wt. %	0.102	0.0045

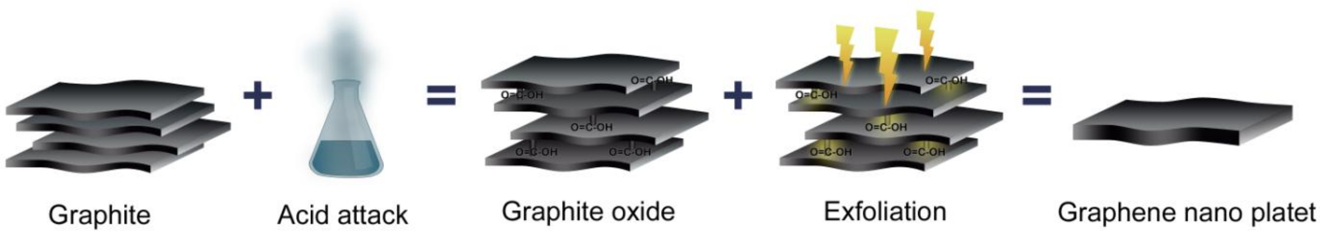

O=C-OH
Graphite
Acid attack
Graphite oxide
Exfoliation
Graphene nano platet

Figure 1

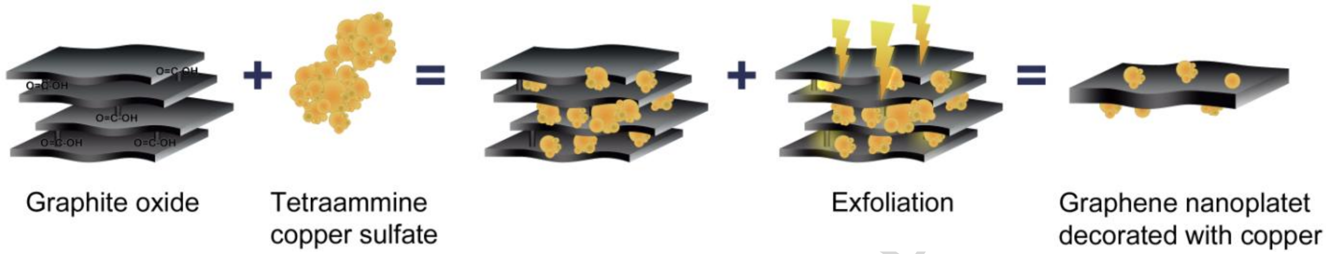
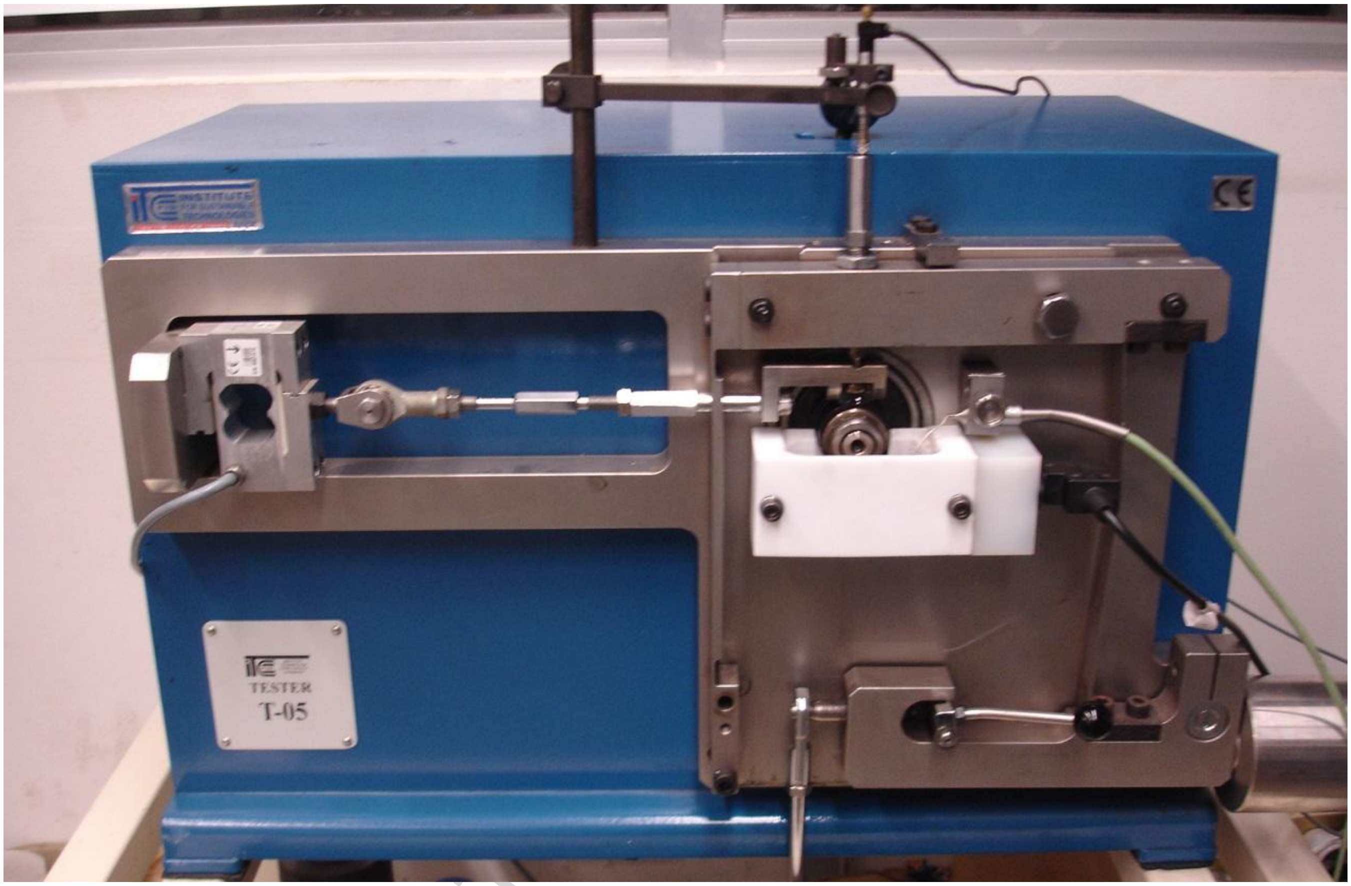

O=C-OH
O=C-OH
O=C-OH
O=C-OH
O=C-OH
Graphite oxide
Tetraammine
copper sulfate
Exfoliation
Graphene nanoplatet
decorated with copper

Figure 2



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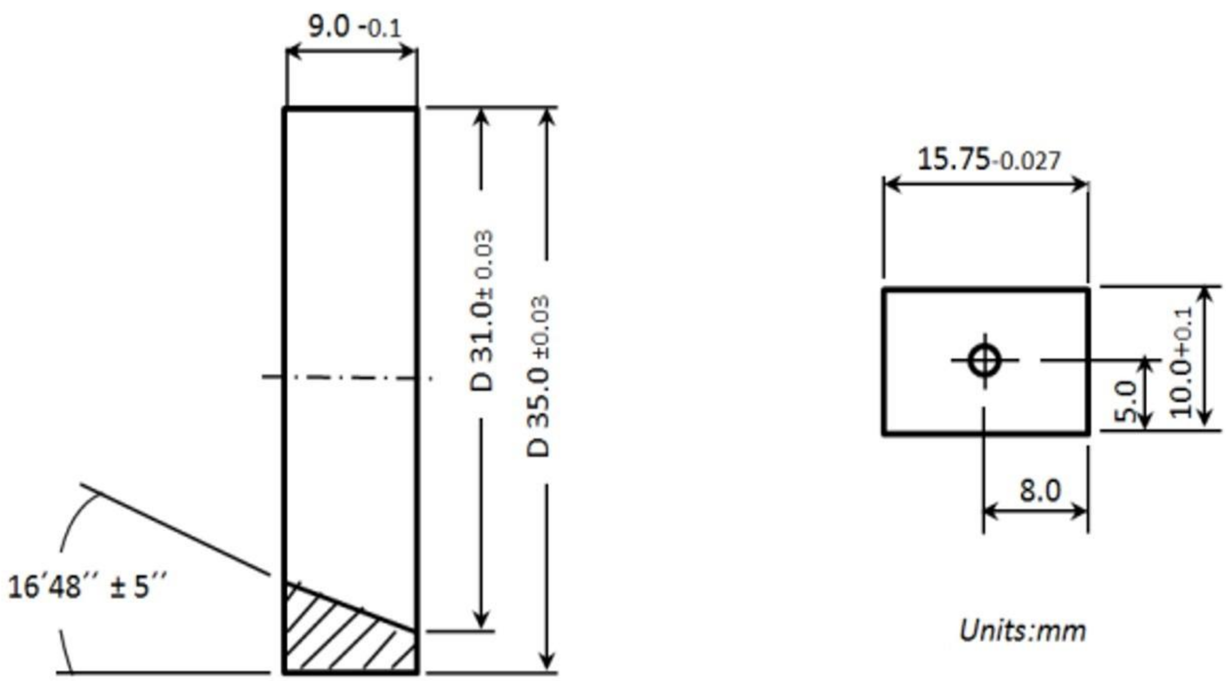


Figure 4

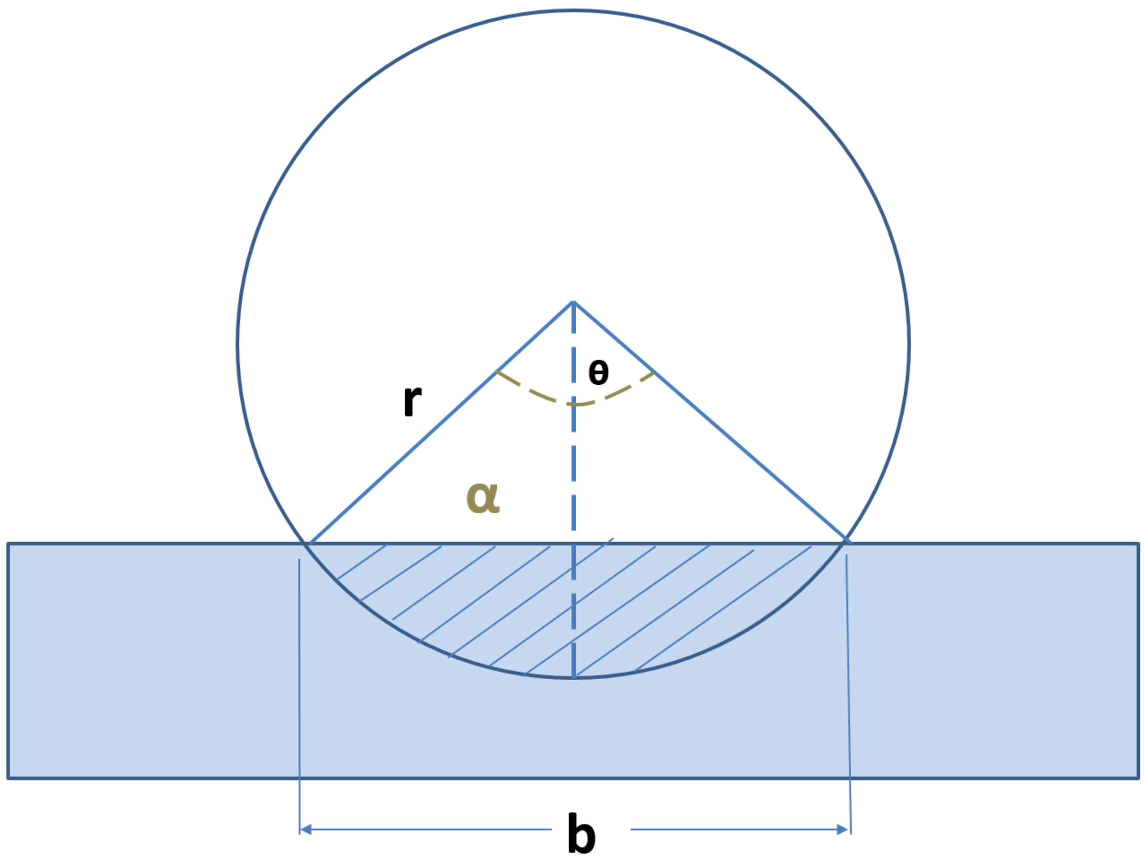


Figure 5

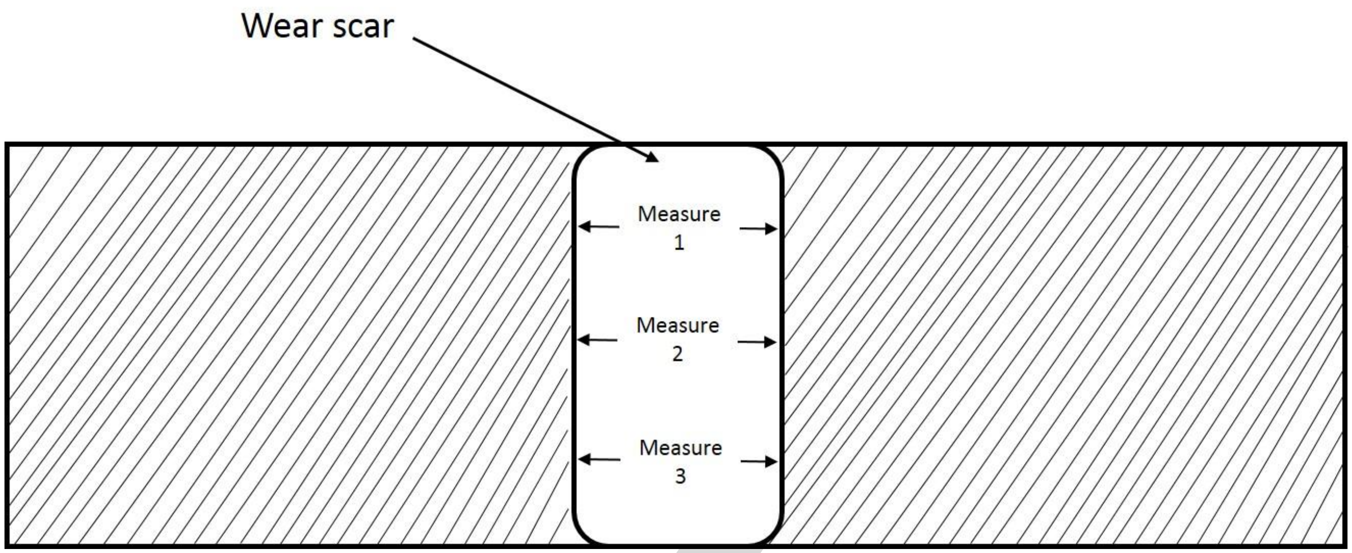


Figure 6

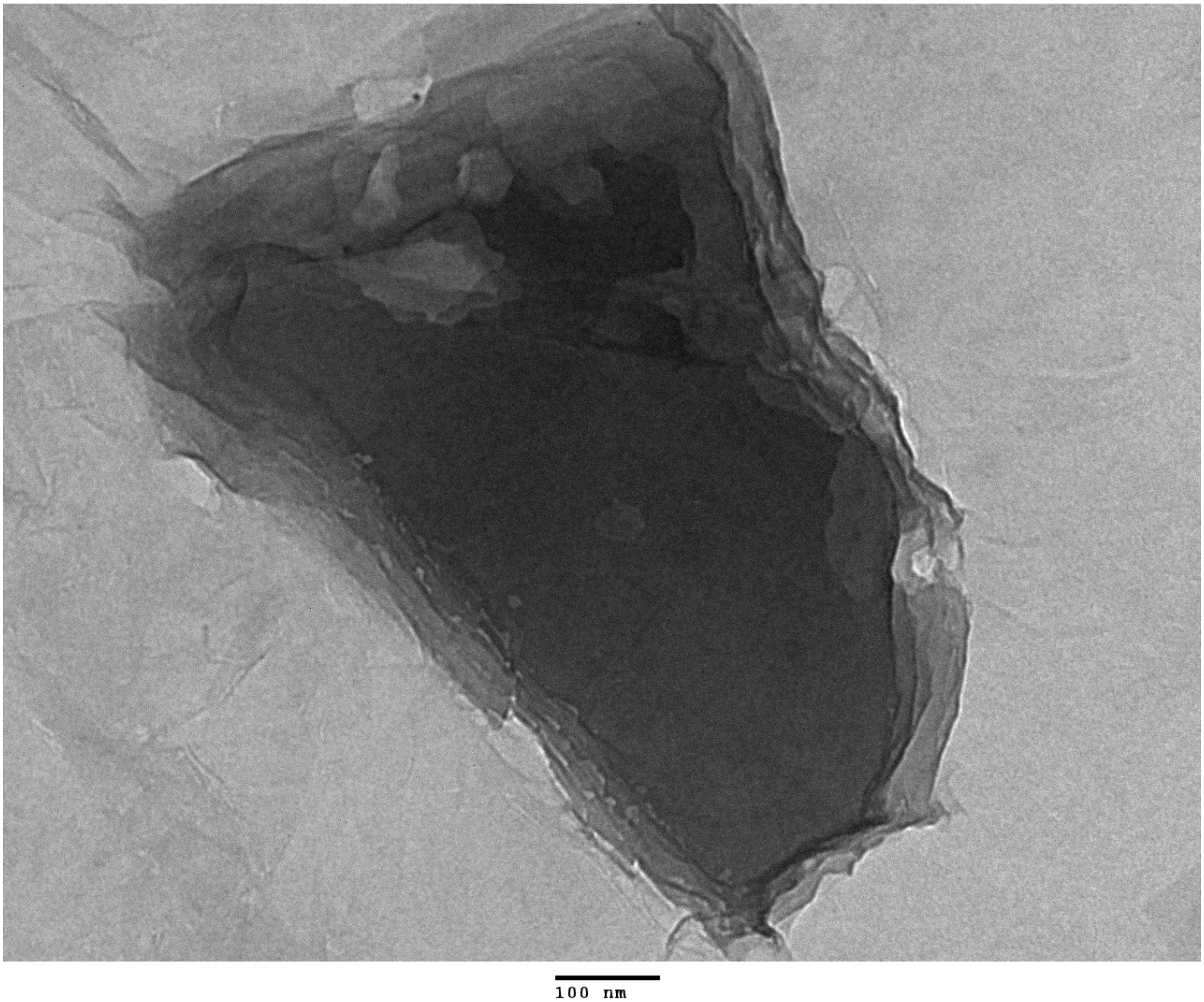


Figure 7

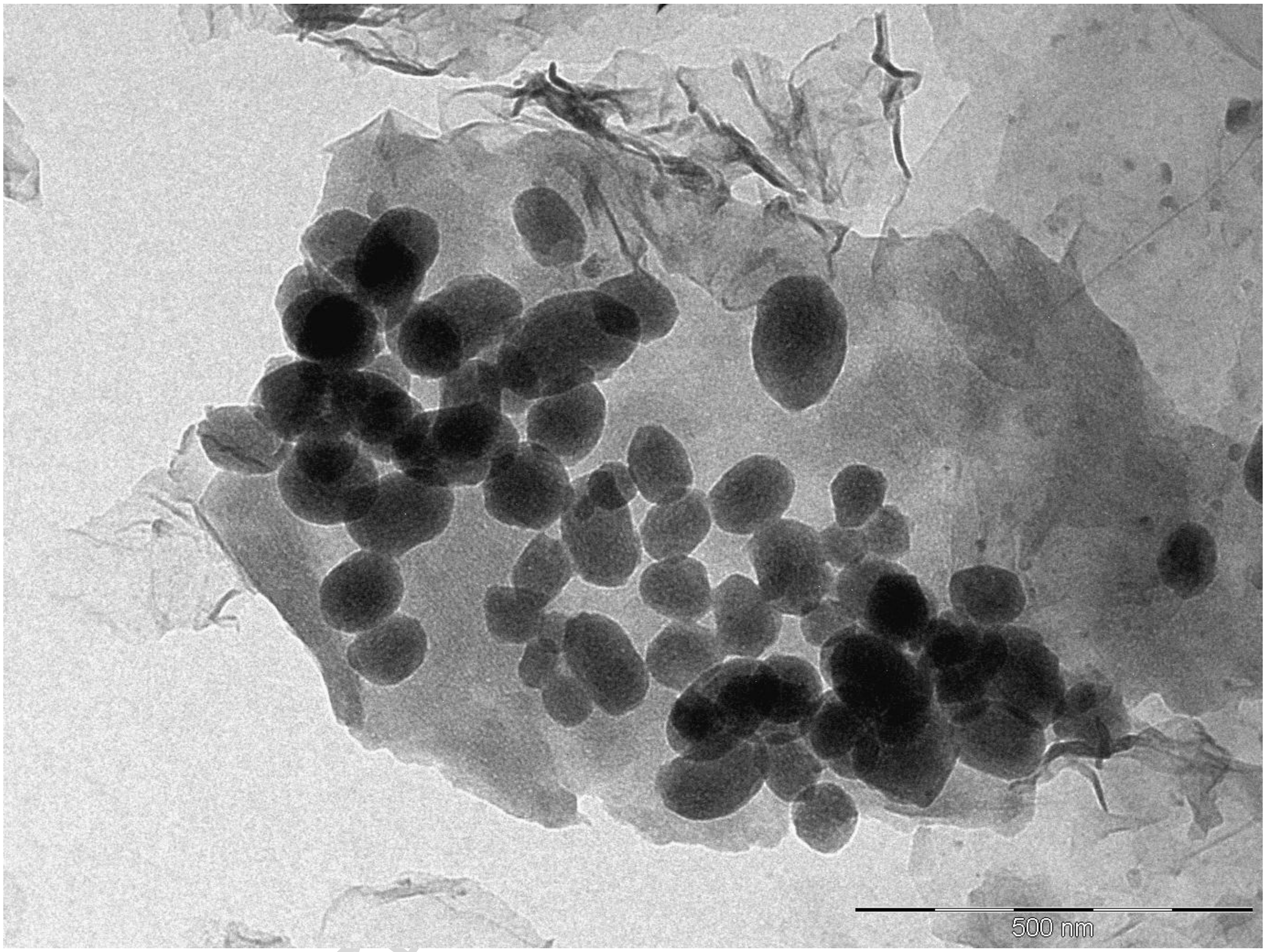


Figure 8

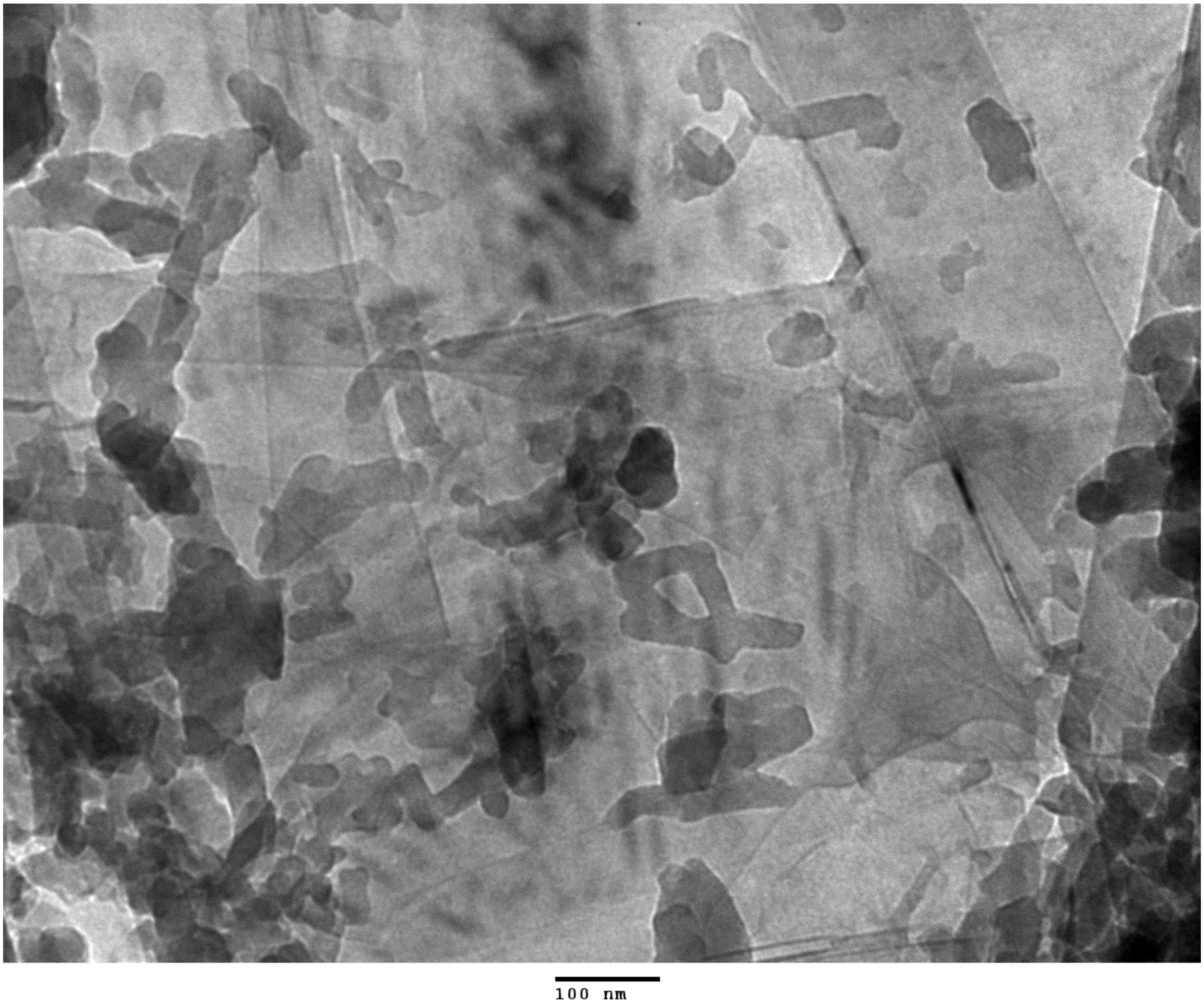
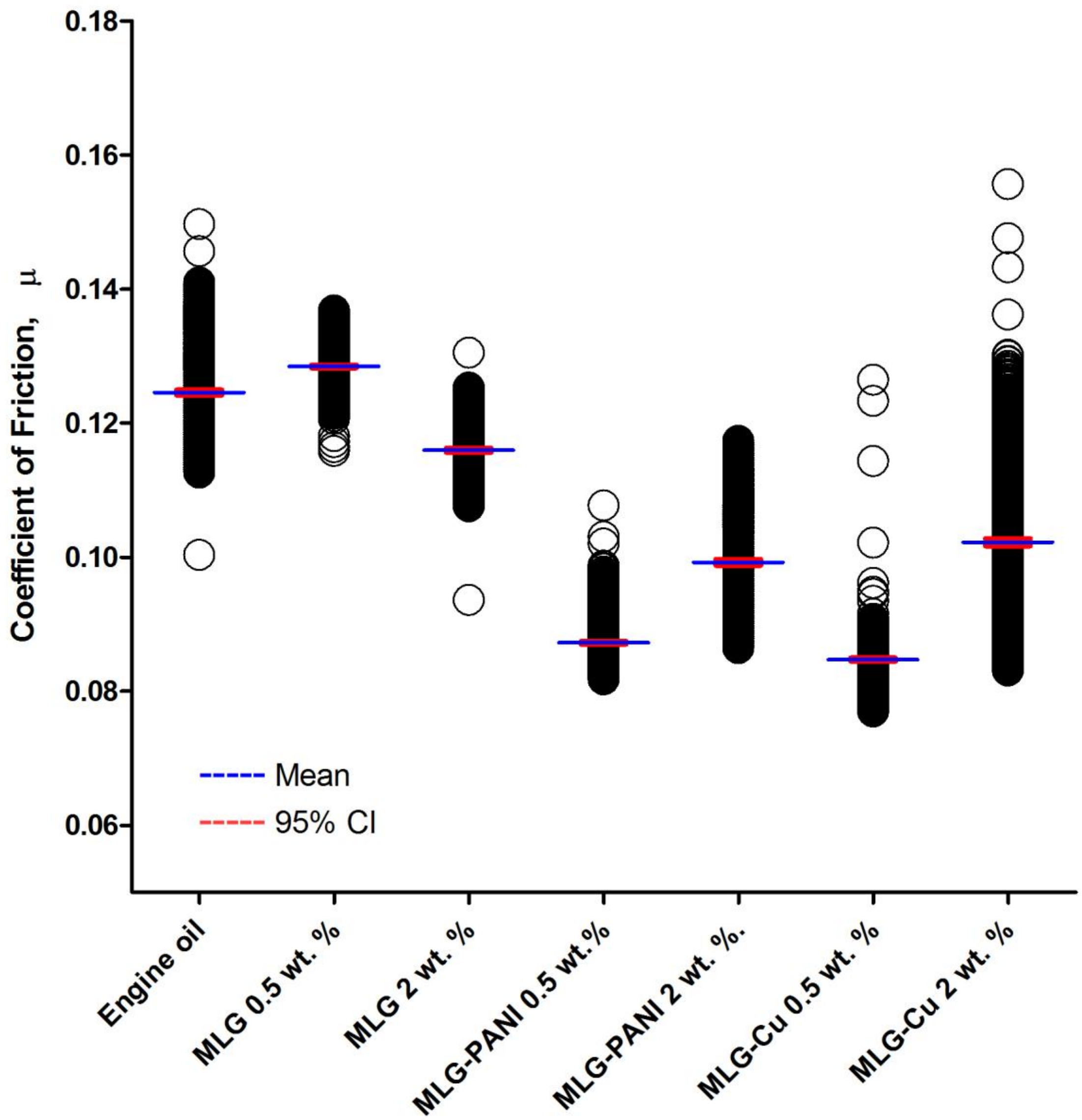


Figure 9



0.18
0.16
0.14
0.12
0.10
0.08
0.06
Coefficient of Friction, μ
Mean
95% CI
Engine oil
MLG 0.5 wt. %
MLG 2 wt. %
MLG-PANI 0.5 wt.%
MLG-PANI 2 wt. %.
MLG-Cu 0.5 wt. %
MLG-Cu 2 wt. %

Figure 10

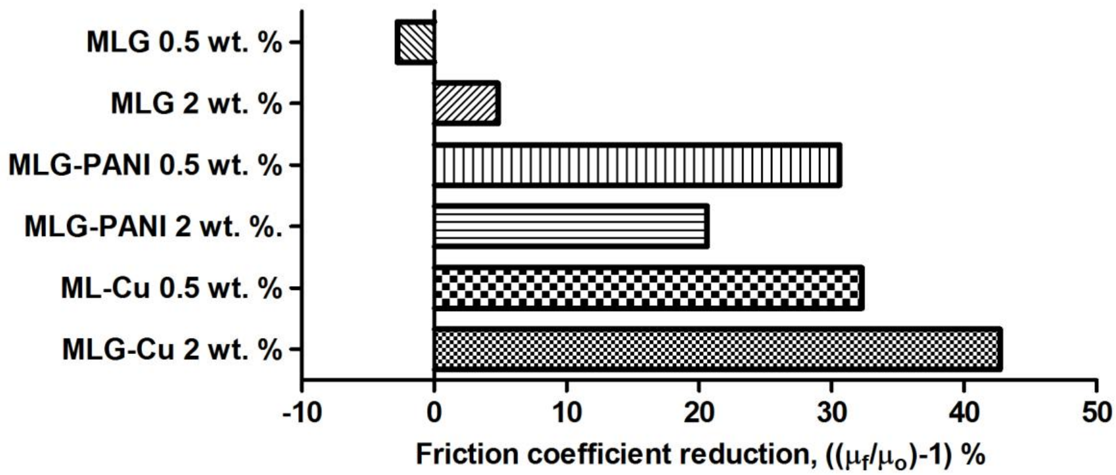

MLG 0.5 wt. %
MLG 2 wt. %
MLG-PANI 0.5 wt. %
MLG-PANI 2 wt. %.
ML-Cu 0.5 wt. %
MLG-Cu 2 wt. %
-10
0
10
20
30
40
50
Friction coefficient reduction, ((μf/μo)-1) %

Figure 11

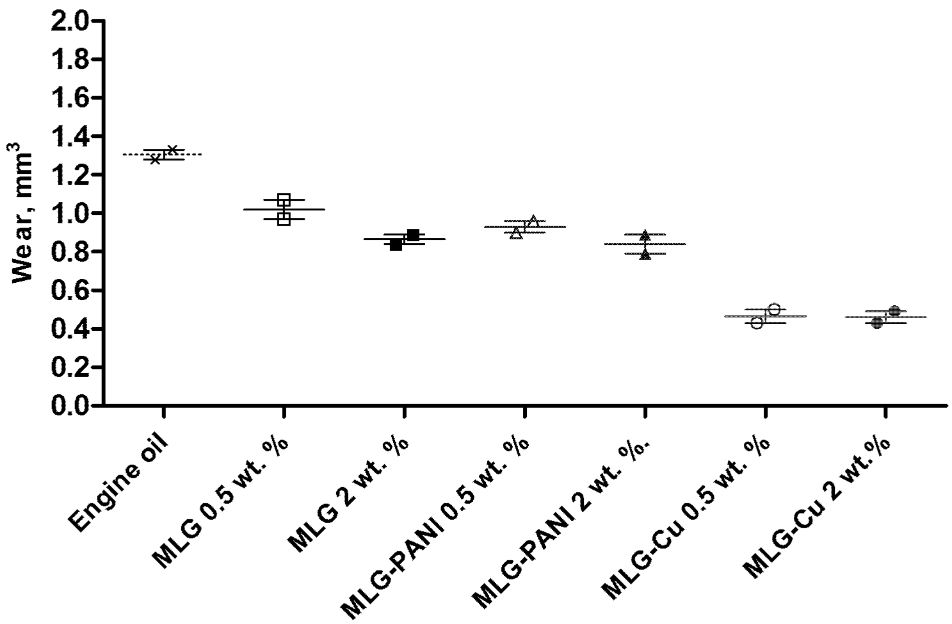
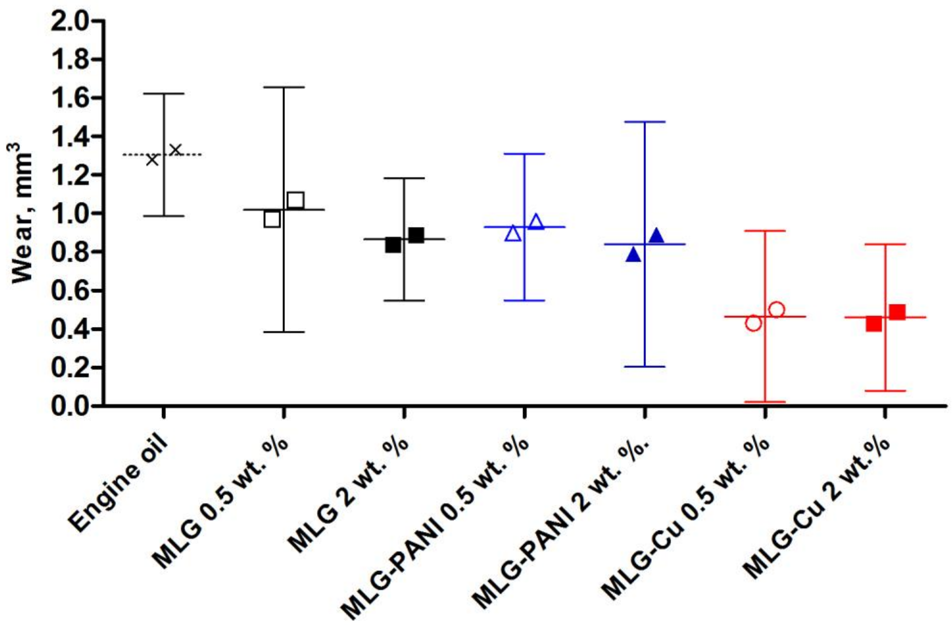

Wear, mm^3
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Engine oil
MLG 0.5 wt. %
MLG 2 wt. %
MLG-PANI 0.5 wt. %
MLG-PANI 2 wt. %.
MLG-Cu 0.5 wt. %
MLG-Cu 2 wt.%

Figure 12a



Wear, mm^3
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Engine oil
MLG 0.5 wt. %
MLG 2 wt. %
MLG-PANI 0.5 wt. %
MLG-PANI 2 wt. %.
MLG-Cu 0.5 wt. %
MLG-Cu 2 wt.%

Figure 12b

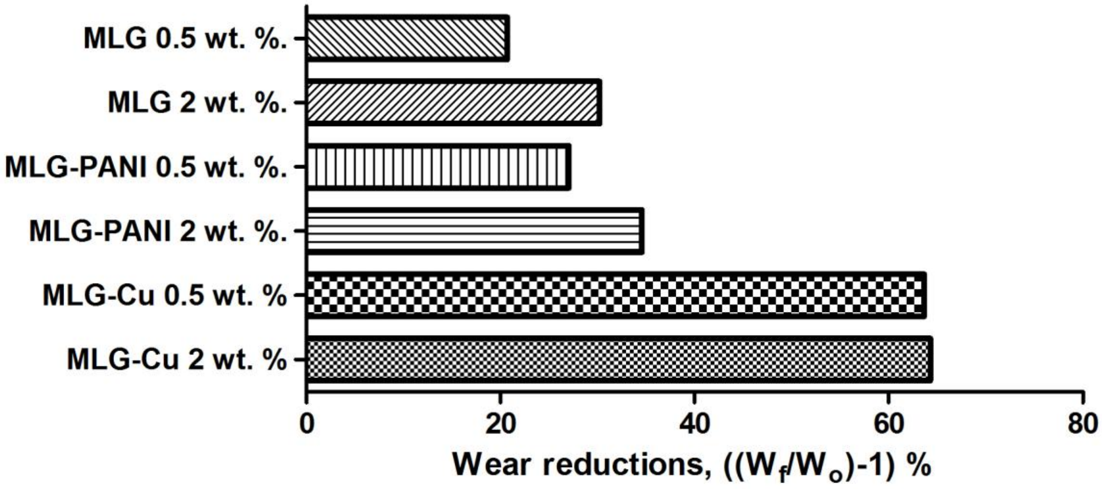

MLG 0.5 wt. %.
MLG 2 wt. %.
MLG-PANI 0.5 wt. %.
MLG-PANI 2 wt. %.
MLG-Cu 0.5 wt. %
MLG-Cu 2 wt. %
0
20
40
60
80
Wear reductions, ((Wf/Wo)-1) %

Figure 13

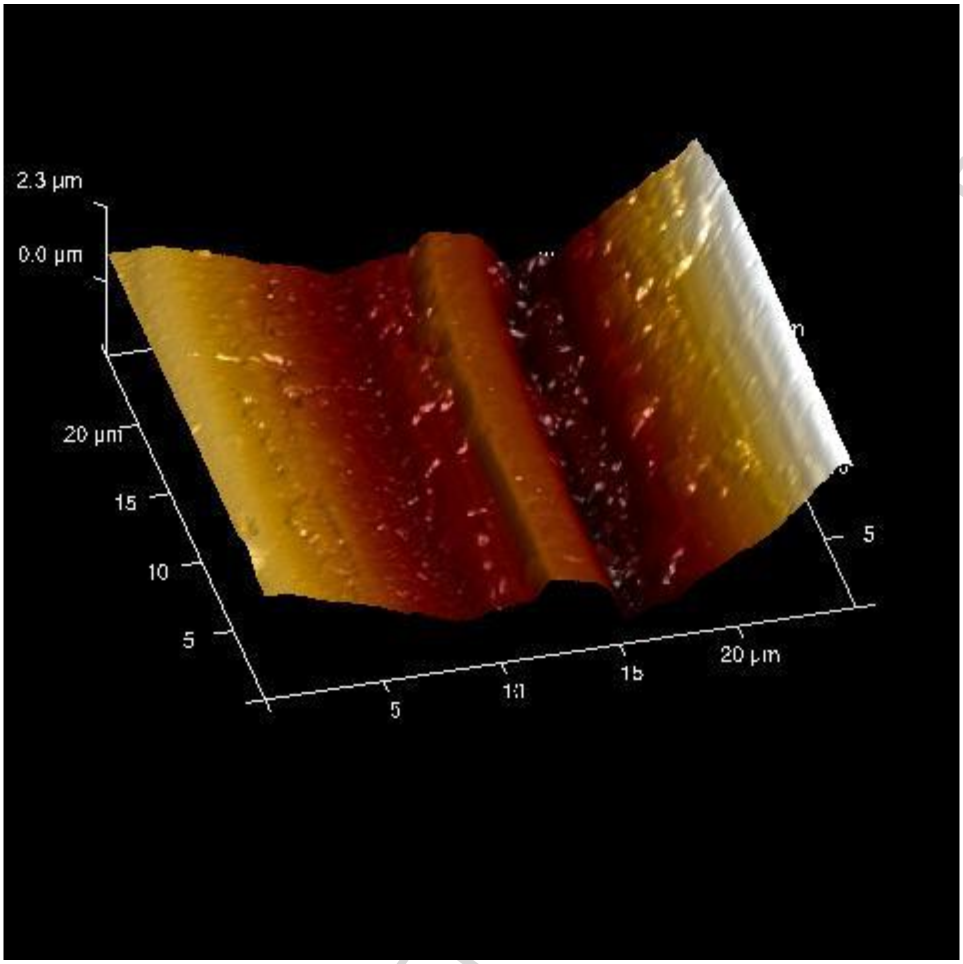


Figure 14a

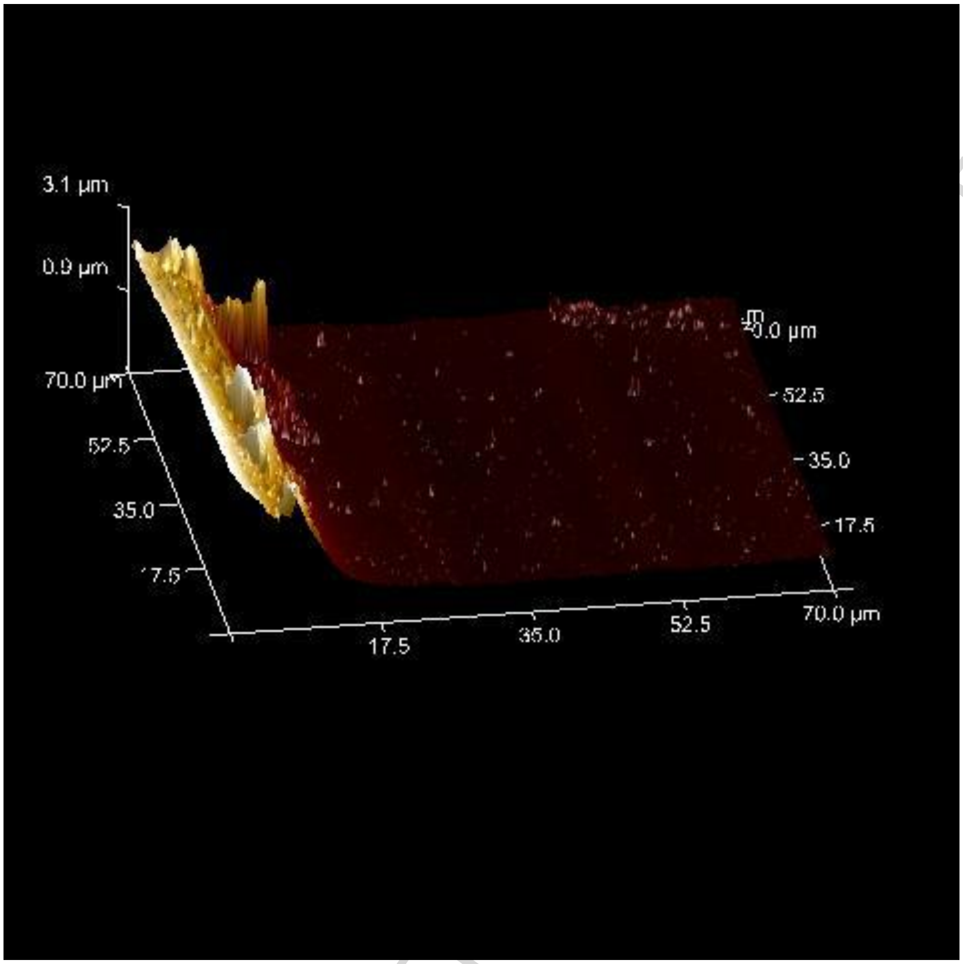


Figure 14b

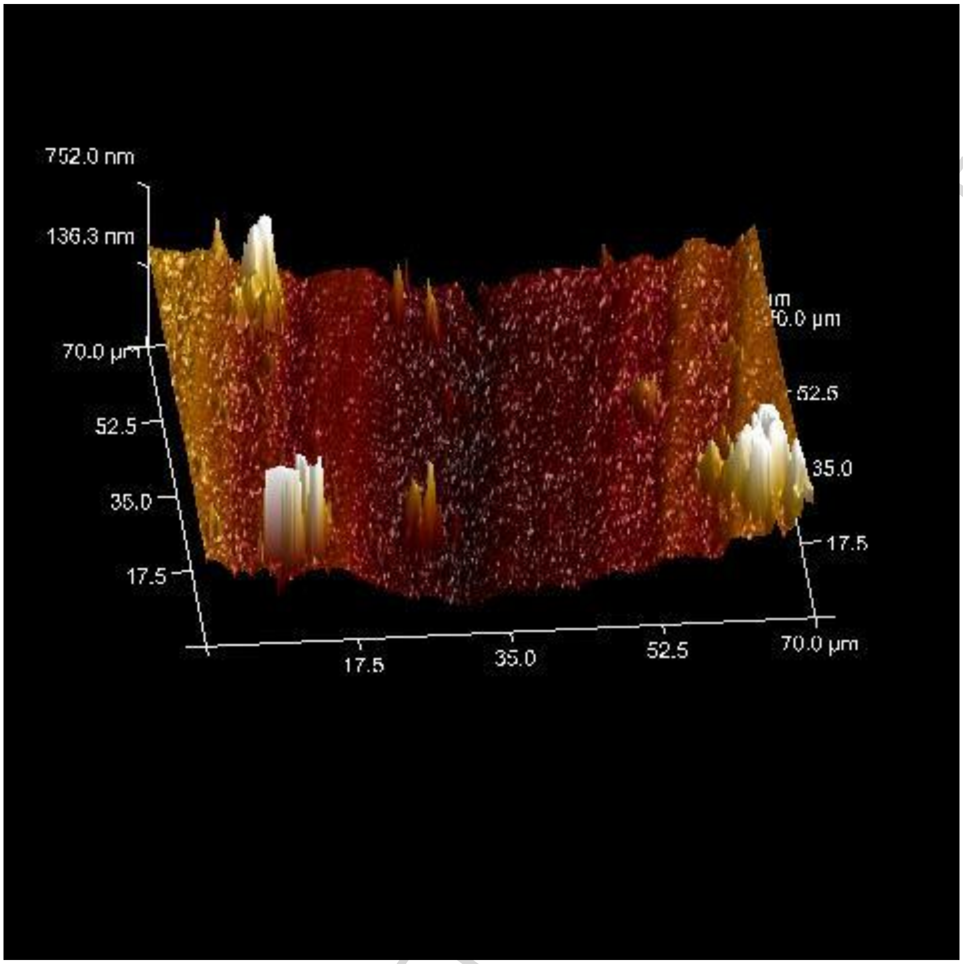

752.0 nm
136.3 nm
70.0 µm
52.5
35.0
17.5
70.0 µm
52.5
35.0
17.5
17.5
35.0
52.5
70.0 µm

Figure 14c

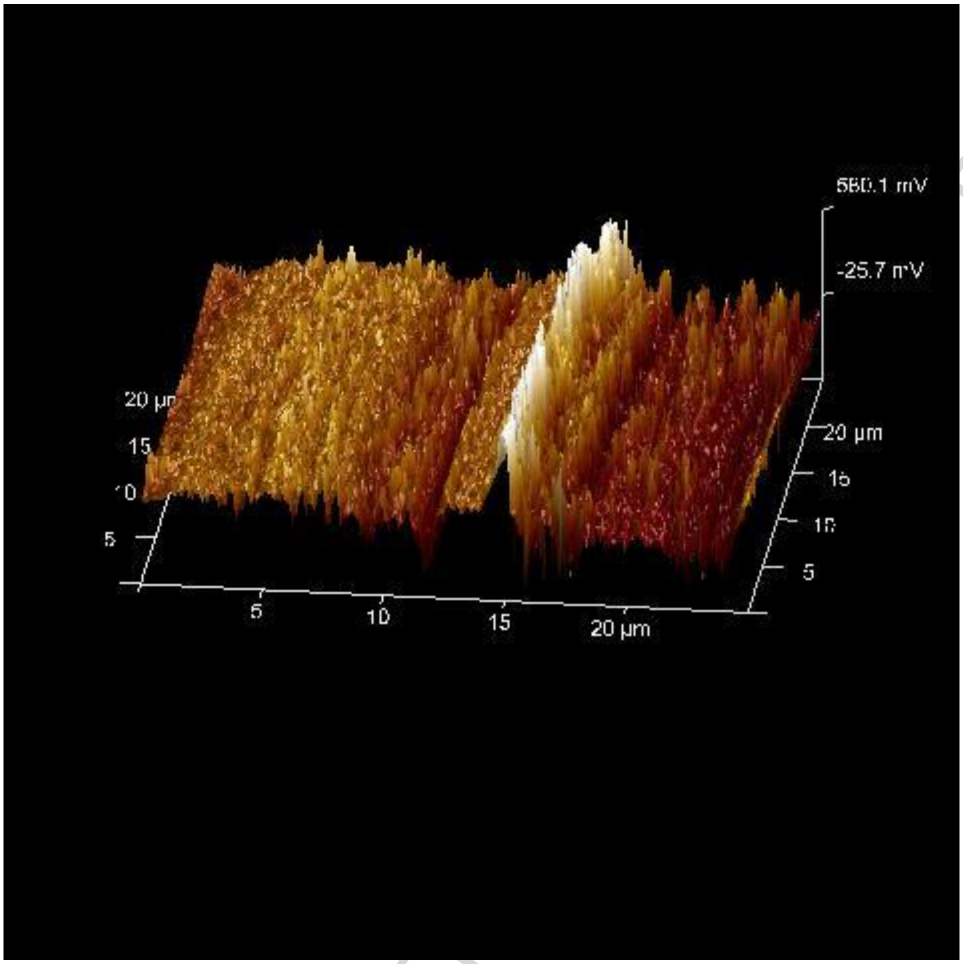


Figure 15a

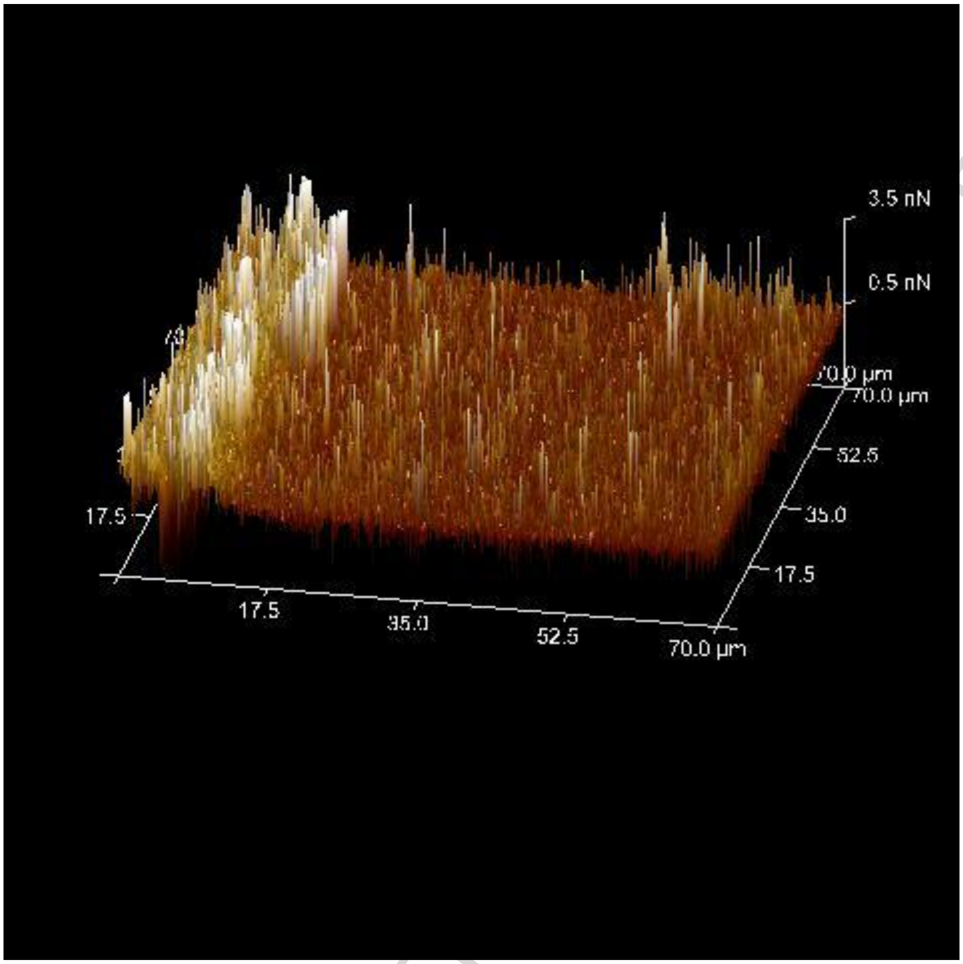


Figure 15b

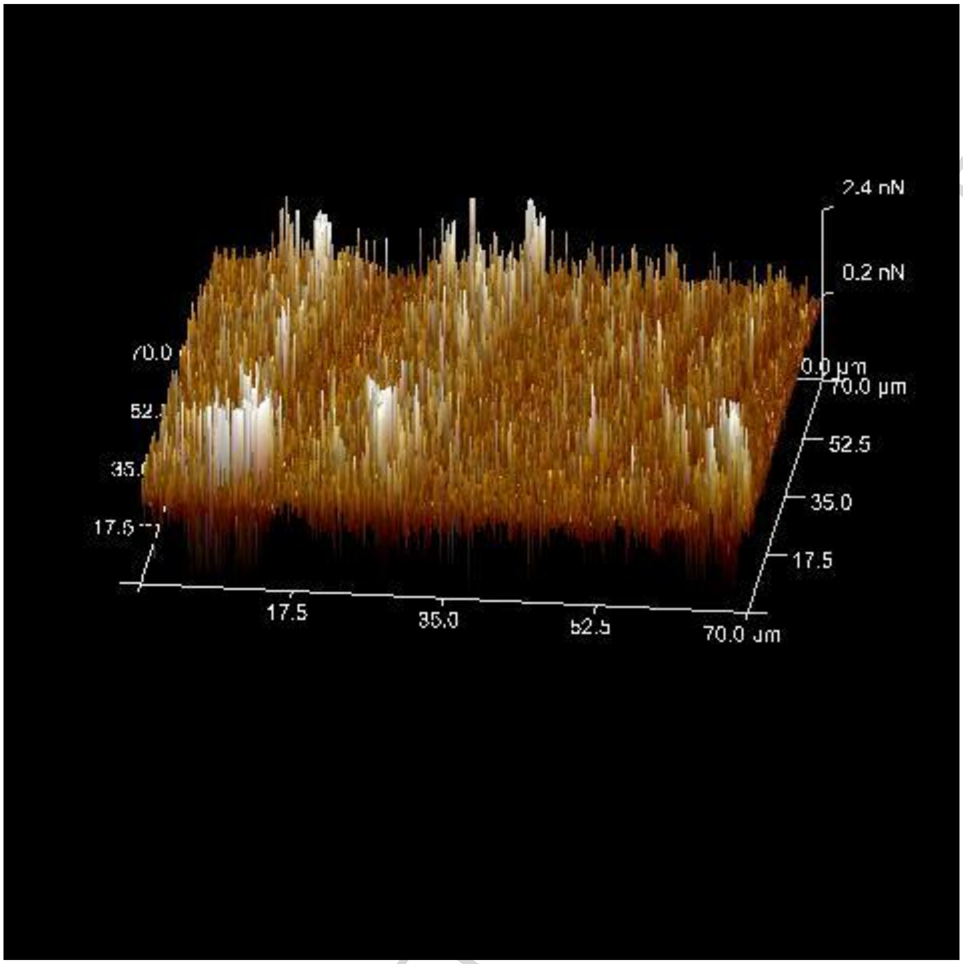
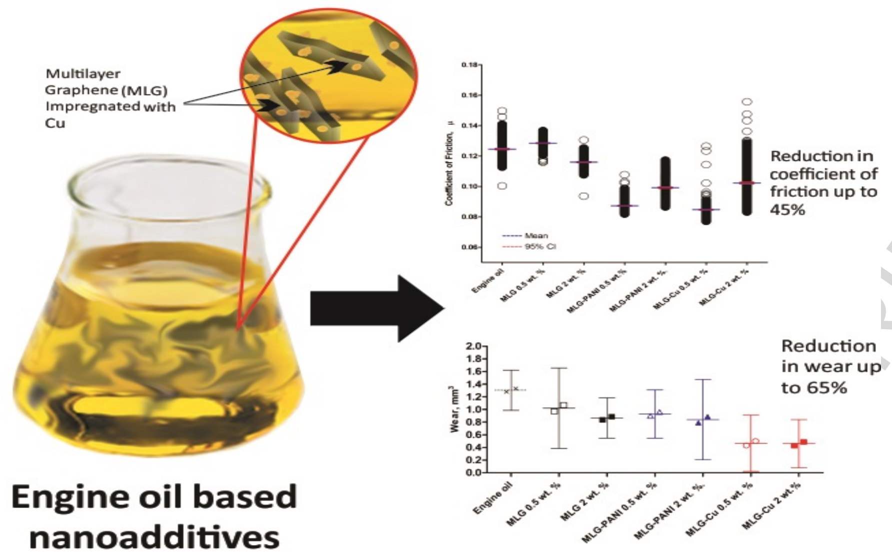


Figure 15c



Graphical abstract

Highlights

- Nanolubricants based on functionalized multilayer graphene were developed.
- Important reductions in friction and wear were obtained for the nanolubricants.
- Tribological properties of engine oil with nanoparticles were improved even at 100°C.
- Nanolubricant formulations remain stable even after three months of being prepared.