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Tribo-thermo-electrical investigation on lubricating grease enriched with graphene nano-platelets as an additive

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ABSTRACT

Many efforts are being made in recent years to boost the performance of traditional lubricants with innovative nano-additive, like graphene. In this paper, long-term lubricated pin-on-disc tests were performed with four grease compounds filled with 0.5 %–5 % graphene nano-platelets. Severe contact conditions were explored to investigate the impact of graphene on the performance and thermal properties of grease. The temperature of the sliding contact and the in-situ electric contact resistance were monitored and correlated to friction and wear. Results of the tribo-thermo-electrical tests indicated that a moderate quantity of graphene reduce both friction and wear because graphene strengthened the lubricating film against scuffing. However, an excessive quantity was detrimental and interfered with lubrication. Graphene also affected the thermal properties of grease, but it did not directly affect the overall thermal behaviour of the tribopair.

1. Introduction

Wear is one of the primary reasons for reduced operational efficiency and replacement of components in engineering systems. Degradation due to wear usually appears when a contact interface between any two bodies is subjected to relative motion. Sliding wear, together with the inherent frictional effect, is responsible for the dissipation of mechanical energy and lead mechanical systems to failure unless properly controlled. Liquid or semi-solid lubricants such as oils and grease apply to reduce friction and wear of rolling and sliding parts, as a way to reduce the adhesion energy between solid surfaces and, possibly, also the area of direct solid-solid contact [1]. Although there exists a lot of wear processes that can severely impair the serviceability of components, e.g. rolling wear in bearings, fretting wear in couplings and others, sliding wear may be a major issue in some applications like mechanical systems for railroad [2,3].

Many efforts are being made to replace traditional liquid and semi-solid lubricants with more environmental-friendly solid lubricants, such as carbon-based [4] or MoS_2-based materials [5]. For instance, Babuska et al. [6] proved the high wear performance of a high-density sputtered pure MoS_2 solid lubricating. Solid lubricants offer the advantage of avoiding mechanical power waste due to viscous effects. However, liquid or semi-solid lubricants are hardly replaceable in many industrial applications, i.e., where they serve as debris conveyor or when their cooling-down effect at the contact site is invaluable, e.g. in machining and cutting. Among others 2D coatings like graphene [7] and graphene-like MXenes have attracted a lot of interest in research [8].

Several researchers have been evaluating the effect of graphene as an additive to improve the tribological performance of lubricating oils and greases [9–22]. Besides, it was also claimed by previous investigation [23,24] that graphene, like other carbon solid additives such as carbon nanotubes [25] or graphite, is able to affect the thermal conductibility of the lubricant with a beneficial effect on the contact temperature and related temperature-induced wear damages. Fu et al. reported an increment of 55 % of thermal conductivity by enriching grease with 4 % graphene [26]. Thermal conductivity is crucial especially for greases because it is the only mechanism to shed heat in a grease lubricated contact. Their consistency makes them unable to remove heat from the contact site by convection, like oils can do. Greases may lead to failure in application where speed is overly high, also because their consistency may contribute decisively to the overheating of the system. Conductive solid lubricants added to greases as performance modifiers may improve the stability of greases by protecting them from thermal degradation and therefore extend their life or the time-to-relubrication.

In boundary lubrication regime, typical of sliding grease-lubricated contacts [27,28], the separation between the surface asperities is ensured by a molecular adsorbed layer of lubricant, while the mechanical action of the liquid phase of the lubricant is limited [29]. Zhou et al.

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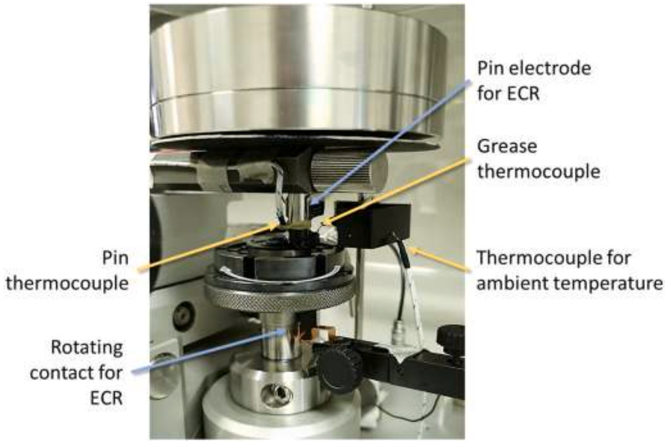

Fig. 1. Experimental layout for the tribological tests.

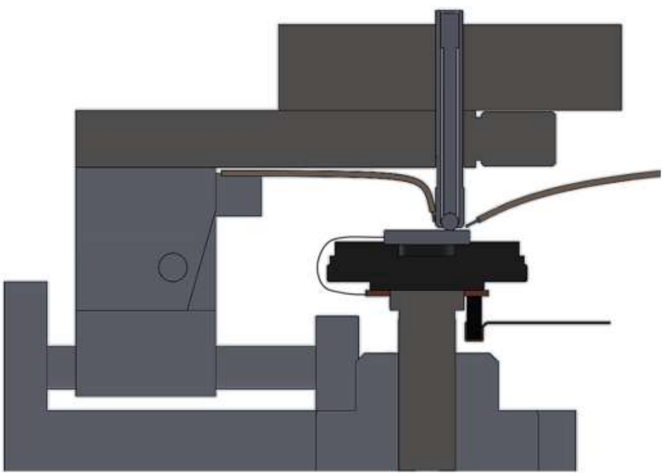

Fig. 2. Cross-section view of the modified test layout of the tribometer.

Table 1
Surface mechanical properties of the samples for tribological tests.

	AISI 52100 discs	6 mm AISI 52100 spheres
Roughness *Ra*	0.673 μm	0.086 μm
Hardness	68 HRC	62 HRC

[30] argued that the bleed base oil from grease is able to provide a thin film that separates friction surfaces at the start-up phase and under light load and low speed, but soon the film breaks down and the lubricant carries no load by itself. Its cooling effect is also drastically reduced since the lubricant flow through the interface is poor. The probability of localized desorption of the lubricant molecular layer due to scraping effects and direct solid-to-solid contact spots increases , especially under high loads or limited sliding speed [27], and friction heat generates as the working condition becomes increasingly harsh. This mechanism may involve some thickener to deposit onto the rubbing surface, acting as a boundary film, and the increase of the active nascent surface and friction heat contributes to the generation of the tribo-chemical reaction film involving the thickener and wear debris [27,30].

Solid additives like graphene flakes can be particularly effective in reducing friction in these extreme conditions. According to Niu et al. [27] the optimum quantity of graphene flakes can be evenly incorporated in the fibrous network of the grease and deposit onto the surface forming a layered structure that promotes the sliding of the asperities without adhesion. Experimental evidence proves that such a quantity strongly depends on the formulation of greases [7–18]. Wang et al. [28] pointed out that, while the increase of the contact load favours the deposition of this protective film rich in graphene on the contact surface, the graphene-rich boundary layer is destroyed as soon as the contact load becomes overly high.

Previous investigations presented experimental methods to investigate the lubrication mechanism and to monitor or infer the lubricant film thickness by monitoring the electrical properties of lubricants, for instance Refs. [31–34]. Thermal analyses during tribological tests have been also extensively exploited to get information about the friction and wear mechanisms and their transitions, for instance Refs. [35–38]. However, the augmentation of tribological results with auxiliary thermal and electrical signals acquired synchronously were rarely performed in the previous research. An example is the paper by Gama et al. who investigated traction in lubricated rolling contacts by monitoring the electrical potential at increasing temperature; however, they did not provide a direct correlation of all the acquired curves to characterize the tribological response of the system [39].

In this paper grease-lubricated pin-on-disc tests were carried out in sliding conditions. Grease compounds filled with an increasing amount of graphene nano-platelets (GNPs) were prepared based on a commercially formulated grease and tested. Friction curves were correlated with the thermal response of the contact and the accumulation of wear to investigate the impact on the grease performance related to the quantity of additive and the possible improvement of the grease thermal properties. Augmentation of the tribological data was also performed by monitoring the in-situ electric contact resistance (ECR) of the sliding interface, synchronously to the others signals, in order to assess the effectiveness of lubrication. Long-term tests were performed to highlight the effect of the carbon nano-additive on the evolution of the tribological behaviour due to accumulation of wear and ageing of the grease. The tribo-thermal-electrical analysis allowed to get useful information about the evolution of the lubrication regime and the role of the additive with increasing the cumulated wear damage and sliding time.

2. Materials and methods

Lubricated sliding friction tests were performed in ambient conditions by means of a ball-on-disc tribometer (Anton Paar TriTec, TRB) consistently to some previous investigation on lubricating greases, for instance Refs. [40–42]. Fig. 1 shows the overview of the experimental layout for the tribo-thermo-electrical tests, and the cross-sectional view in Fig. 2 highlights how the test method was modified. The ball-on-disc testing method produces pure sliding motion at the interface like the four-ball method does (as per ASTM D-2266). However, ball-on-disc method was preferred over four-ball, although the latter is the standard for lubricant testing, because monitoring the thermal and electrical properties of the contact site is easier.

Ball-on-disc tests (with point contact geometry) were performed on 5 mm thick and 30 mm wide flat cylindrical steel samples of quenched AISI 52100 chromium steel. Samples were prepared by CNC milling, quenched, and then finished to ensure the parallelism of the upper and lower flat sides within the tolerance of 0.05 mm. The friction counterpart was a 6 mm AISI 52100 (100Cr6) chromium steel ball for rolling bearings. The amount of grease spread onto the contact surfaces was about 1 g, and it was arranged to cover the whole surface of the sample at the beginning of each test. All the tests ran under 30 N load and 0.9 m/s speed, and the total sliding distance was 23 km (about 7 h tests). A very long test duration was chosen to detect any evolution of the grease performance due to ageing or stress degradation. One new sample was used for every test to keep constant the radius of the wear track equal to 11 mm, and the average Hertzian contact pressure was 1290 MPa. Each graphene compound was tested at least three 3 times to account for the natural scattering of the tribological phenomena. Table 1 summarizes roughness and hardness values for the flat samples and the spheres. Roughness was measured through a contact-stylus roughness tester (SM

Table 2
Technical sheet of MULTEMP ET-C high-performance grease from Kyodo Yushi Co. Lt.

	MULTEMP ET-C
Base oil	ADE + polyol ester
Thickener	di-urea
Base oil viscosity	81.6 mm^2/s at 40 °C 10.8 mm^2/s at 100 °C
NLGI Class (DIN 51818)	2
Dropping point (ISO 2176)	>260 °C
Temperature range	−40 °C–200 °C
Worked penetration (ISO 2137)	280

Instruments, RTP80).

The base grease selected for this investigation is MULTEMP ET-C by Kyodo Yushi Co. Ltd. This lubricant is a fully synthetic heat-resistant, anti-flaking and low-noise urea grease for bearings featuring a specific package of additives for working in a wide temperature range. As per Table 2, the Low Temperature Performance Limit (LTPL) is −40 °C, i.e., where oil separation practically stops, and the High Temperature Performance Limit (HTPL) is 200 °C, i.e., the point where the grease matrix loses its structure, and excessive leakage occurs. The reason for choosing a high-quality grease is to assess if this innovative carbon nano-additive can outperform the conventional molecular additives currently used by lubricant manufacturers to boost the performance of their greases.

Three grease compounds with increasing content in Graphene Nano-Platelets (GNPs) were prepared in-house and compared with base grease, i.e., 0.5 % wt. GNPs, 1 % wt. GNPs, and 5 % wt. GNPs.

Commercial Graphene Nano-Platelets (Cometox Srl, Milan, Italy) with grade C-500 were added to the base grease. GNPs are characterized by a nominal thickness of 2 nm, a maximum diameter of 2 μm and an average specific surface area of 500 m^2/g. The defined amount of graphene was gradually incorporated into the grease by mechanical stirring at room temperature using a Heidolph Hei Torque Precision 400 homogenizer. The compounds were mixed for 30 min at room temperature to achieve uniform nano-particle dispersion into the grease. Fig. 3 compares the appearance of the graphene-enriched grease with the pure one. The grease compounds were prepared by mechanical mixing at room temperature. The solid nano-additive was added into the grease by gradually increasing the quantity to the defined percentage to give the solid particles time to spread evenly into the grease. Fig. 4 shows the images of the graphene-grease compounds taken under the optical microscope in transmission mode.

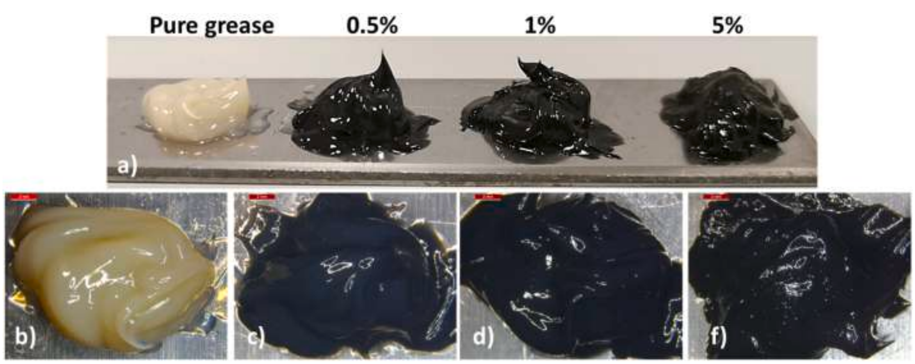

Fig. 3. (a) Overview of the four grease compounds, the black ones are those functionalized with GNP. Inspection under the microscope of the (b) the pure grease; (c) 0.5 % graphene grease; (d) 1 % graphene grease; (e) 5 % graphene grease. Interestingly, the addition of 5 % wt of graphene makes the grease grainy, meaning that the nano platelets cannot disperse evenly.

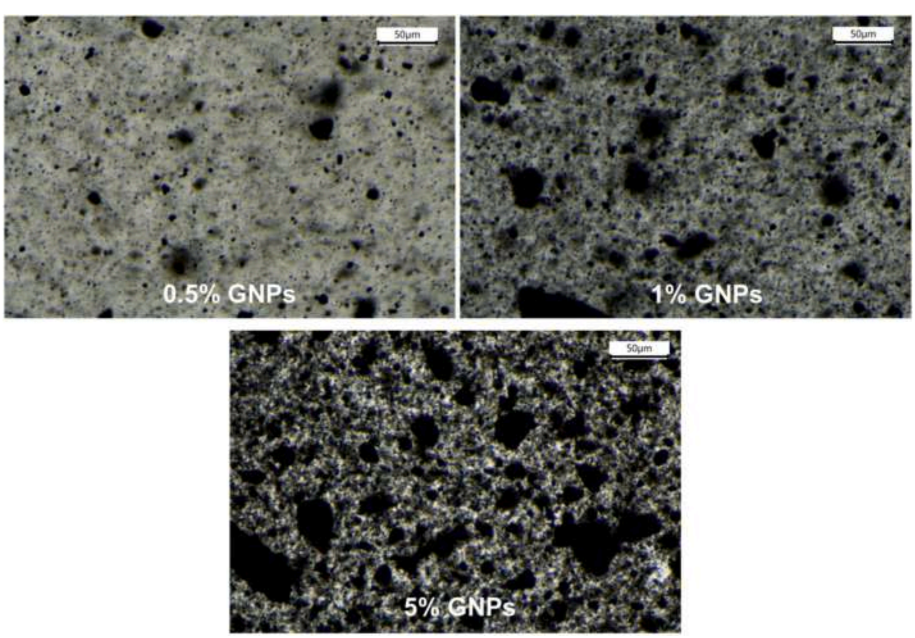

Fig. 4. Transmission optical microscope image of the graphene-grease compound prepared for this research. Some clustering of the nanoplatelets in larger carbon particles is visible in transmitted light microscopy.

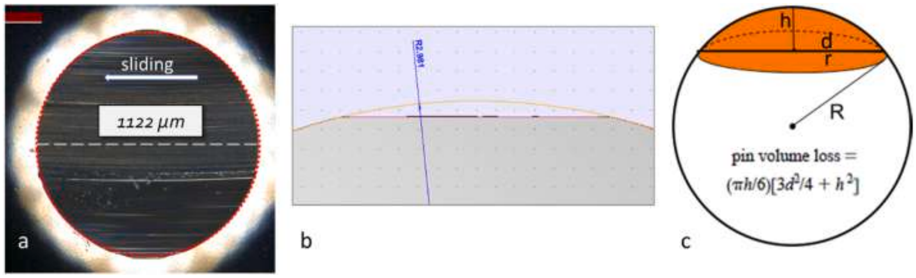

Fig. 5. Wear damage on the sphere. (a) Example of a spherical cap diameter measurement under the microscope at the end of a test lubricated with the base grease (the grey dashed line is the location of the profilometric inspection); (b) Profilometric inspection of the flattened region on the sphere; (c) Calculation of the spherical cap volume as per ASTM G99-17.

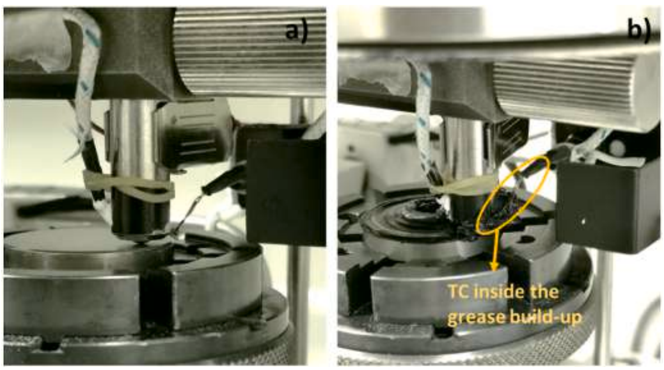

Fig. 6. Position of the two thermocouples (a) before greasing, (b) after grease build-up is formed. The pin thermocouple was installed with thermo-conductive paste to improve the accuracy of the measured value and protect the sensing region of the probe from convective effect.

At the end of each test, the pin and the sample were inspected under a digital microscope (Leica Z16 APOA) after the tests, both before and after cleaning with acetone. The material loss was restricted to the sphere only because the quenched sample was harder than the sphere. The wear trace on the spheres was shaped as flattened regions with an almost circular shape (Fig. 5a), whose diameter was measured under the microscope. Stylus profilometry (SM Instruments, PGS200) on the spheres confirmed that the worn-out region was flat; therefore, the amount of material lost by the system was approximated to a spherical cap with a known base diameter, as per the ASTM G99-17 guidelines. SEM inspection (Tescan VEGA, CZ) of the worn surfaces and EDS analysis were carried out at the end of the test after cleaning the samples with acetone and isopropyl alcohol.

Two type-K thermocouples (0.5 mm diameter) were installed close to the contact point to monitor the thermal state of the system. One thermocouple was placed in contact with the pin (the ball-holder) as close as possible to the spherical tip; the other was placed inside the grease build-up accumulated at the leading edge of the sliding contact. Both thermocouples were connected to the acquisition card of the tribometer; therefore, the temperature signals were sampled at the same rate. The ambient temperature inside the testing chamber was traced by placing another type-K thermocouple close to the contact site to sense the air temperature in that region. A thin metallic lamina was used to shield the tip of the thermocouple from direct exposure to the whirlwinds caused by the rotating spindle. The trend of the ambient temperature was then subtracted from the temperature values measured by the two thermocouples to compensate for the unavoidable temperature fluctuations inside the testing chamber. Fig. 6 provides a detailed view of how the thermocouples were positioned close to the contact point.

The electric contact resistance (ECR) across tribological contact was also measured during the tests. The ball holder and the rotating sample were connected to the digital multimeter (DMM) board of a National Instruments VirtualBench VB-8012 device. The electric resistance was measured with the 2-wire method to obtain the broadest measuring range out of the DMM, i.e. from 0.001Ω to 100 MΩ, with auto-ranging enabled by the control software of the instrument. The ECR values were acquired via a dedicated NI LabView routine. The ball holder and the rotating sample were insulated from the tribometer frame using a high-performance insulating varnish to avoid disturbances due to electric dispersion through the ground. A slip ring system made of a flat copper ring and a carbon brush was installed onto the tribometer spindle, and the copper ring was soldered to the steel sample with an external wire. The electrical circuit of the ECR was closed via the carbon brush pressed against the rotating copper ring by a leaf spring. The carbon-copper sliding pair minimizes the disturbances on the electrical signal at the level of the sliding electrical contact. The schematic of the electrical circuit is shown in Fig. 7.

Measuring the ECR value provides an indirect average thickness measurement of the lubricating film interposed between the solid surfaces under sliding motion. The more the boundary film increases its thickness the more the steel surfaces are separated by a non-conductive layer of lubricant and, thus, the more the ECR value is expected to be high. When the lubrication film fails, i.e., when it is completely scraped off, a direct metal-to-metal contact establishes which opposes low

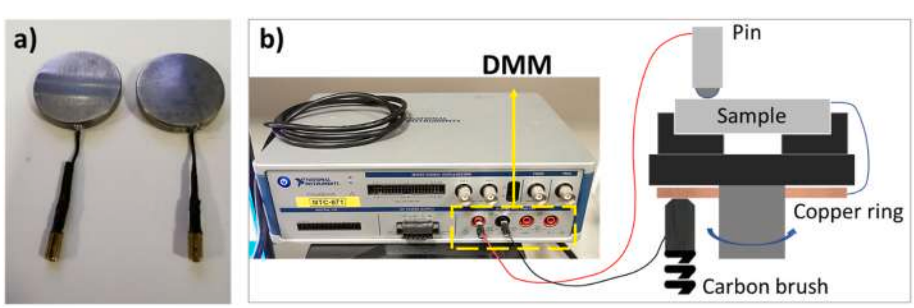

Fig. 7. (a) Samples prepared for ECR measurements with an external wire welded on the side for connection to the rotating copper ring; (b) Schematic of the ECR measurement circuit.

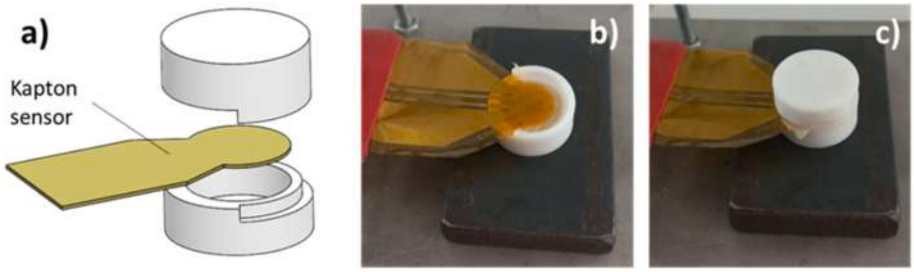

Fig. 8. (a) Special device for Hot Disk Test with grease; (b, c) Experimental setup.

Table 3
Thermal conductivity (k) estimated with Hot Disk method.

Grease type	k [$W/m/K$]
Pure grease	0.166 ± 0.005
0.5 % GNPs	0.166 ± 0.005
1 % GNPs	0.168 ± 0.005
5 % GNPs	0.182 ± 0.005

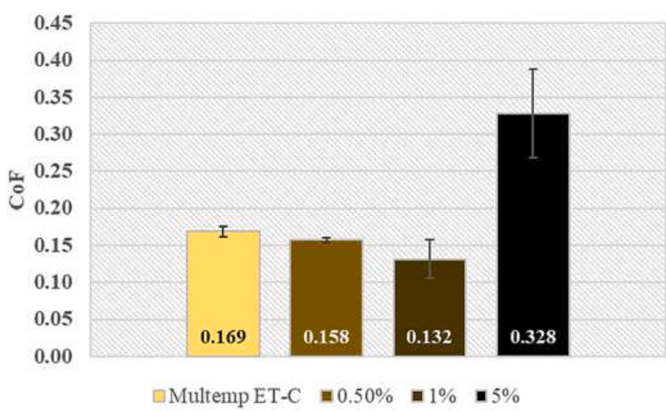

Fig. 9. Comparison among the average friction value measured with the four grease compounds. The error bars represent the 95 % confidence level for the estimated average values.

resistance to the electric current flow. This (sudden) drop in the ECR value marks the point of lubrication failure.

The ECR value measured through this setup also includes the bulk resistance of the sample, the resistance of the electrical line, and that of the rotating carbon-copper contact. The contributions read as per equation (1).

$$R_{ECR} = R_{samples} + R_{cables} + R_{connectors} + R_{weldings} + R_{slip\ ring} + R_{pin-sample} \quad (1)$$

However, any other terms except $R_{pin-sample}$ were deemed to have negligible fluctuations during the tests. The preliminary investigation carried out without lubrication showed that the stationary resistance of the carbon-copper sliding contact $R_{pin-sample}$ measured remained stable while increasing the rotating speed of the spindle. This evidence suggests that R_{ECR} would vary during the tribological tests according to the evolution of the lubrication and wear regime at the pin-sample sliding interface only.

Previous research proved that the addition of conductive particles into the grease increases the bulk electrical conductivity of the lubricant [43]. This aspect should be taken into account. It is therefore necessary to identify, at least in a qualitative way, to what extent the measured values of ECR are affected by the bulk conduction of the grease. Appendix A explains how the qualitative characterization of the bulk electrical conductivity of the grease compounds was carried out.

The thermal conductivity of the grease compounds was experimentally determined through the transient plane source (TPS) technique, also called the Hot Disk method, as per ISO 22007–2. A special container consisting of two parts (case and cover) was manufactured on purpose to accommodate grease and keep the Kapton sensor in place during the test. The shape and dimension of the container were optimized to allow the thermal wave to propagate uniformly inside the grease. Both the parts were manufactured by 3D printing in PLA. Fig. 8 shows the details of the special grease container and the Hot Disk experimental setup.

3. Results and discussion

3.1. Thermal conductivity of grease compounds

Table 3 summarizes the measured values of thermal conductivity for each grease compound obtained by the Transient Plane Source method through the special setup presented in Section 2. The estimated experimental error was about 0.005 W/m/K; therefore, the most appreciable thermal conductivity variation was observed for the 5 % GNPs grease compared to the pure MULTEMP ET-C.

3.2. Pin-on-disc tests

Fig. 9 compares the results regarding the average friction coefficient over the whole duration of tribological tests. The lowest friction was achieved with 1 % GNPs into grease, which exhibited a 22 % reduction compared to base grease. The compound with 0.5 % GNPs performed better than the base grease, but the CoF decreased by just 6.5 %. On the contrary, a detrimental 94 % increase in the average CoF was exhibited by the grease compound with the highest GNPs content, revealing a critical performance loss due to the excess of carbon nano-additive.

Fig. 10 shows, as an example, the results of four tests that the author deemed representative of the characteristic tribological response with each grease compound. The diagrams report the set of experimental curves acquired synchronously, including the CoF curve, the thermocouples curves and the online wear depth curve (corresponding to the vertical displacement of the pin). The diagrams give more details on the effect of graphene on the tribological and thermal response of the system. Interestingly, the friction and thermal curves always followed an extraordinarily similar trend due to an obvious cross-correlation.

When pure Multemp ET-C grease was applied to the contact, the frictional behaviour of the tribological system was divided into two phases. After the wear-in, which lasted approximately 700 *m* of sliding, the friction curve stabilized at about 0.13 with a very low scattering of values. According to Wang et al. [28], a flat, stable friction curve hints that a stable boundary lubrication regime exists at the interface. Boundary lubrication could not rely on any hydrodynamic separation of surfaces, and considerable asperity contact occurs through a thin molecular film adsorbed on surfaces [44], but the thickener fibers play a fundamental role increasing the thickness of the lubrication film and contributing to the tribo-chemical film on the metal surfaces [22]. The corresponding ECR values presented in Fig. 11a are relatively low in this first phase and indicate that conduction through the nanometric film is

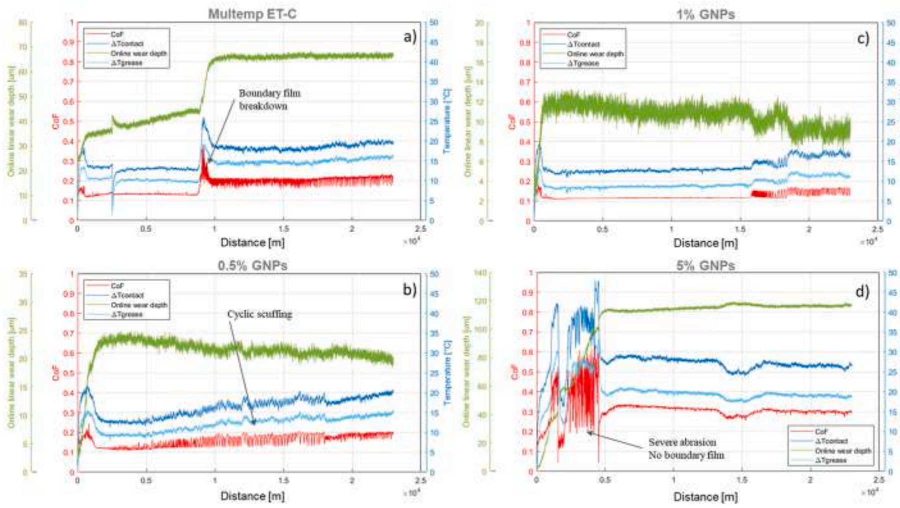

Fig. 10. Friction and thermal curves were recorded during four tests to compare the tribological performance of the four graphene-rich grease compounds. The values recorded by the pin thermocouple close to the contact region are labelled ΔTcontact; those recorded by the thermocouple inside the grease build-up are labelled ΔTgrease.

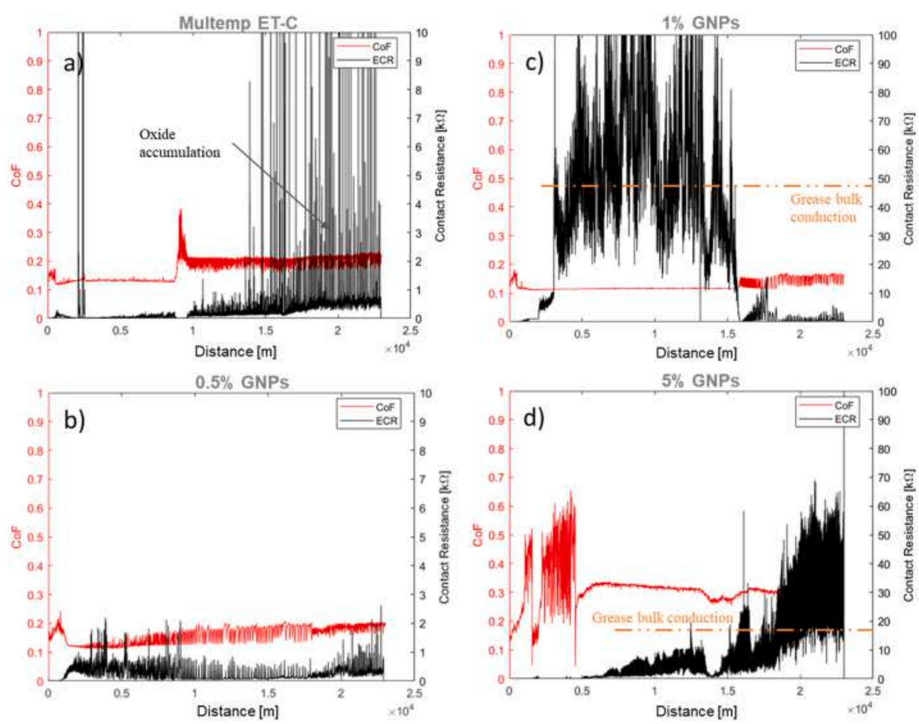

Fig. 11. ECR curve recorded during four tests lubricated with different graphene-grease compounds. Additional information about the grease ECR limit of inset (d) is reported in Section 5.1.2.

relatively easy. Although the test ran smoothly, wear accumulated in this first phase since the linear wear curve increased. Asperities probably scraped off the boundary film, but it was continuously restored steadily [22]. After a given time, which varied from test to test, this lubrication mechanism ran into instabilities, and a lubricant shortage event occurred.

A peak of the CoF, a steep increase of the linear wear curve and a transient drop of the contact resistance to conduction marked the failure of the boundary film after about 10 km. Lubricant shortage events after some stable running with a boundary film were also reported by Wang et al. in reciprocating pin-on-plate tests with pure lithium grease [28]. A boundary film grew again in the remaining part of the test but was less stable, and sliding was harsher. The CoF stabilized to a higher level, and the friction curve was more scattered than before. Temperature also rose by 10 °C. The ECR curve slowly increased up to the end of the test with localized peaks of reduced conduction. This trend may be evidence of the accumulation of oxides from tribo-oxidation.

Oxide particles were found at the trailing edge of the contact (see Fig. 15a) and into the waste grease at the border of the wear track. Tribo-oxidation may have been triggered during the lubrication shortage. The linear wear curve was considerably stabilized and increased very gently up to the stop of the test. This trend may indicate that the oxides interacted with the newly formed boundary film and contributed to carrying part of the applied load.

The addition of 1 % GNPs produced an improvement in the frictional performance of the grease. Results suggested that 1 % GNPs allowed the

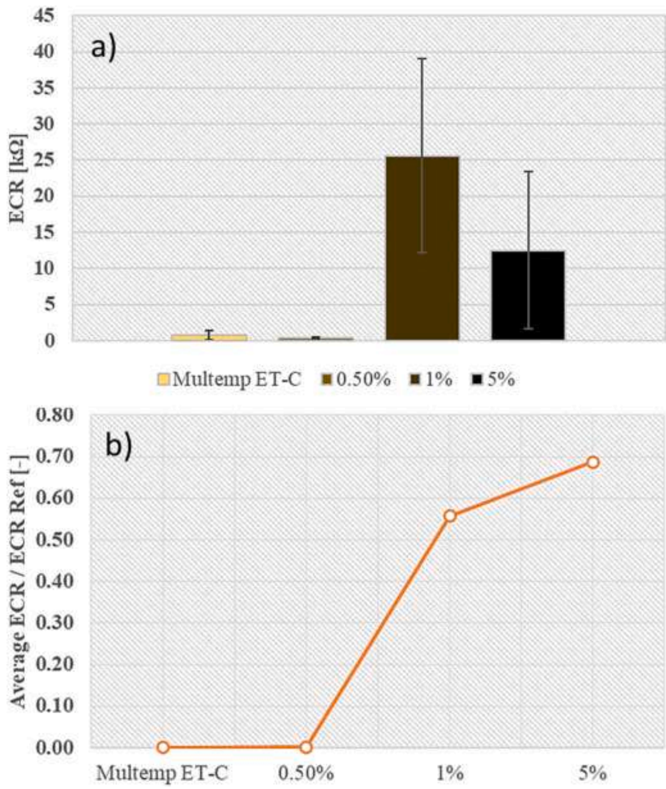

Fig. 12. *(a) Average ECR values recorded during pin-on-disk tests; (b) Ratio between the average ECR value and the grease bulk conduction value.*

system to run with a stable and low scattered friction curve for an extended time. Wang et al. [45], which reported a similar result by reciprocating pin-on-plat tests, argued that graphene increases the strength of the boundary film when the optimum quantity of graphene is added to grease. As a result, the film is denser [22], more stable and withstands friction longer without failure. This scenario was precisely the case of the test reported in Figs. 10c and 11c. Therefore, 1 % GNPs can be considered close to the optimum quantity for Multemp ET-C grease. The very smooth running of the test matched high values of the ECR in the first 15,000 *m*. The ECR values of the same order as the characteristic bulk conduction of 1 % GNPs grease (see Table A1 in Appendix A) corroborated the inference that a boundary film settled. Since a small quantity of oxidized debris was found in the waste grease (see Fig. 15c), oxides were not likely to cause such a high contact resistance. High ECR may indicate that graphene embedded into the adsorbed boundary film according to the interaction mechanism with the fat molecules proposed by Niu et al. [27] and promoted the absorption of a thicker film. The thickening of the boundary film would explain why the linear wear curve followed a decreasing trend, which would be otherwise illogical. No dramatic lubrication shortage occurred, but cyclic fluctuations of the CoF appeared in the last 7000 *m* of sliding. Localized scuffing with the formation of a few oxides probably started here, and ECR was correspondingly reduced by 10 times due to the less uniform boundary film. The linear wear curve kept decreasing, indicating that the boundary film was probably still growing, although less uniformly.

However, 1 % GNPs could not always prevent dramatic film breakdown events from occurring in other tests. In one test, a friction curve similar to that of Fig. 10a was observed. Yet, if the film breakdown occurred, graphene could alleviate the transient period of severe sliding with an additional solid lubrication action. Moreover, it always regularized the friction curve, it reduced scattering and promoted the fast restoration of the boundary film after any film breakdown. More repetitions of these tests are needed in the future to investigate deeper this

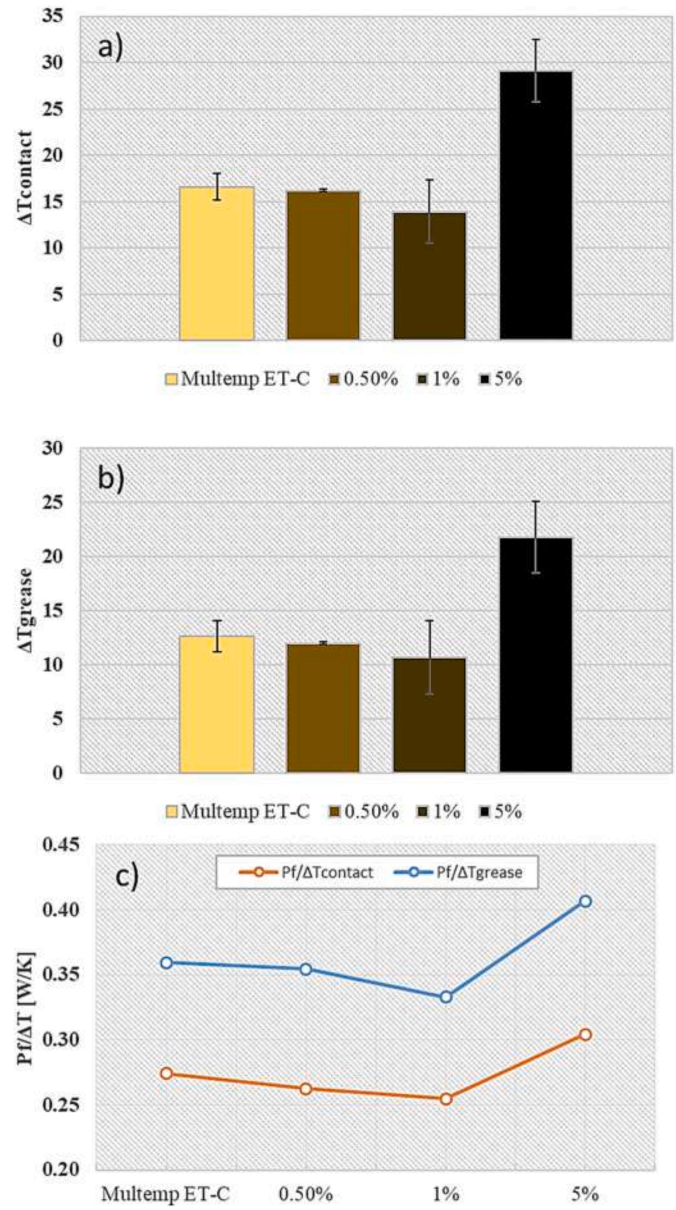

Fig. 13. (a) Average temperature rise on the pin; (b) average temperature rise inside the grease build-up; (c) $P_f/\Delta T$ ratio.

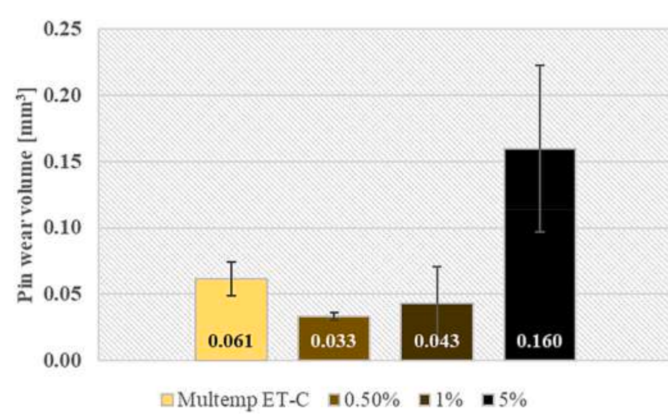

Fig. 14. The volume of removed material from the pin due to wear with the four grease compounds.

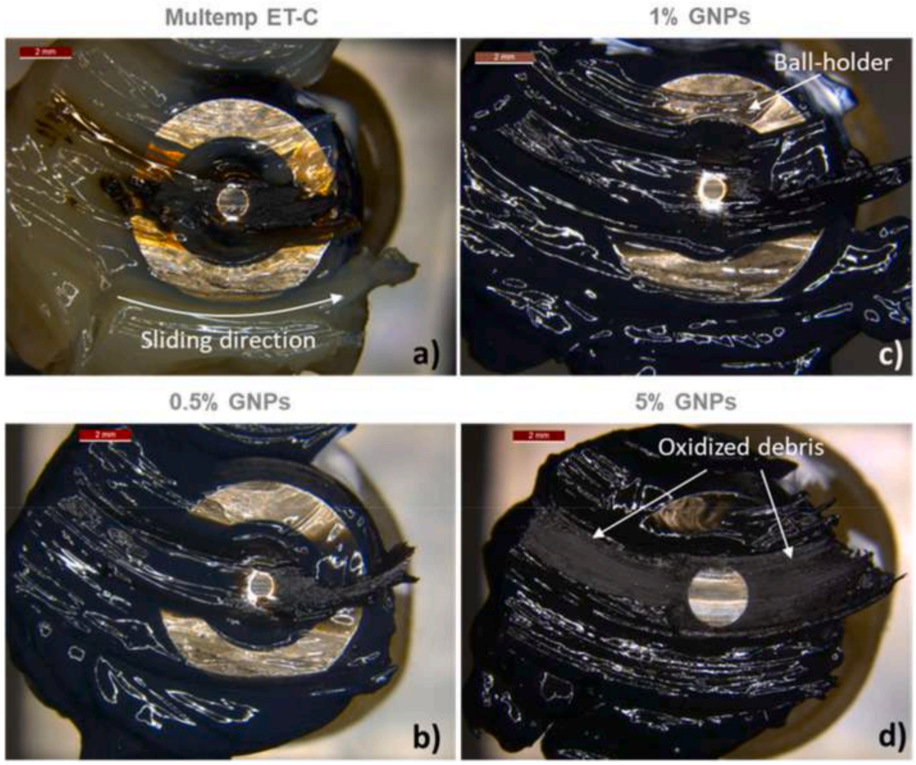

Fig. 15. The worn region and waste grease on the steel sphere right after the tribological tests with the four grease compounds.

aspect.

The 0.5 % GNPs grease had a somewhat similar behaviour to 1 % GNPs but suffered a long period of cyclic scuffing and repeated fluctuations of friction which started after just 4000 *m*. The CoF increased continuously throughout the test, but its value never exceeded 0.2. This behaviour contributed positively to limiting the average friction value. The linear wear curve replicated the trend observed with 1 % GNPs and decreased after the wear-in. The wear loss measured on the sphere was probably lost in the wear-in phase only. ECR remained throughout the test at a similar value to part 2 with 1 % GNPs (Fig. 11c) and base grease (Fig. 11a), where oxides were supposed to accumulate. Fig. 15b reports a higher quantity of oxides in the waste grease than Fig. 15c, which leads to thinking that oxide formation started earlier as soon as the curved started fluctuating. However, less oxides are detected than in Fig. 15a and no spikes of the ECR were recorded, as with base grease. Noteworthy, 0.5 % GNPs grease also exhibited the highest repeatability over the three repetitions of the tests.

Fig. 10d shows that grease struggled to give rise to a stable lubrication mechanism at the onset of sliding when the amount of additive rose to 5 % GNPs. The CoF underwent huge fluctuations up to 0.6 in the first 5000 *m* of sliding, a value dramatically close to the typical values measured in dry sliding contacts of steel [1]. This scenario was in line with the results reported by Singh et al. who argued that the excess of graphene let the nanometric flakes clump together. Larger carbon particles struggled to enter the contact zone and interfered with the feed of lubricant to the contact, thus hindering the formation of a boundary film [15]. Niu et al. argued that agglomerates of additives particle may disrupt the fibrous network of greases, thus affecting its flow behaviour, so that the contact is starved of both fresh grease and nanoparticles [27]. The contact suffered severe wear in this first phase, and the noise level was high. Although a lot of oxidized debris was found in the grease accumulated on the pin and at the borders of the track (Fig. 15d), oxides did not appear to play a significant role at the interface since ECR indicated metal-to-metal conduction. The wear rate was so high that debris was readily ejected from the contact, and the accumulation into a reaction layer proceeded slowly in the presence of fat molecules. Some stabilization of the friction curve was suddenly observed after 5000 *m*. At that point, the degree of coverage of the sliding track by oxidized matter was such that wear was mitigated and friction considerably stabilized. The lubricious effect of the reaction layer (visible in Fig. 16) and the thermal softening of grease may have fostered more lubricant flow through the contact and the eventual formation of some boundary layer rich in graphene. ECR grew and reached values similar to the characteristic bulk conduction of 5 % GNPs grease compound reported in Table A1. This trend may hint that a layer of grease was settling. However, mild abrasion went on at a reduced rate until the end of the tests because the linear wear curve kept growing.

Let us compare the characteristic values of the bulk electrical conduction presented in Appendix A and the ECR values averaged across the tribological tests. Average ECR values are presented in Fig. 12a, while the ratio of the average ECR to the bulk ECR of greases is presented in Fig. 12b. ECR in tests with 1 % GNPs and 5 % GNP grease was of comparable magnitude to the bulk conduction of grease. In both cases, a boundary film was present for most of the testing time. 1 % GNPs grease was the most effective in providing lubrication and its average ECR was the highest. With 5 % GNP the relatively thick boundary film (the value is the highest in Fig. 12b) formed too late when the system had already suffered severe wear damage and high friction. The very low values associated to 1 % GNPs and 0.5 % GNPs in Fig. 12a and b suggest that metal-to-metal and metal-oxides-metal contact prevailed during the testing time.

Regarding the thermal behaviour, the blue curves in Fig. 10 represent the heating-up of the pin and the grease accumulated at the leading edge of the sliding contact. The data are plotted as increments above the ambient temperature signal. The two temperature trends were firmly cross-correlated with the trend of the friction curve, as was expected because the energy loss due to friction caused the temperature at the contact interface to rise. This correlation showed that the effect of graphene on the thermal behaviour of the system was indirect. Temperature rise lowered if graphene could mitigate its cause, i.e., friction. However,

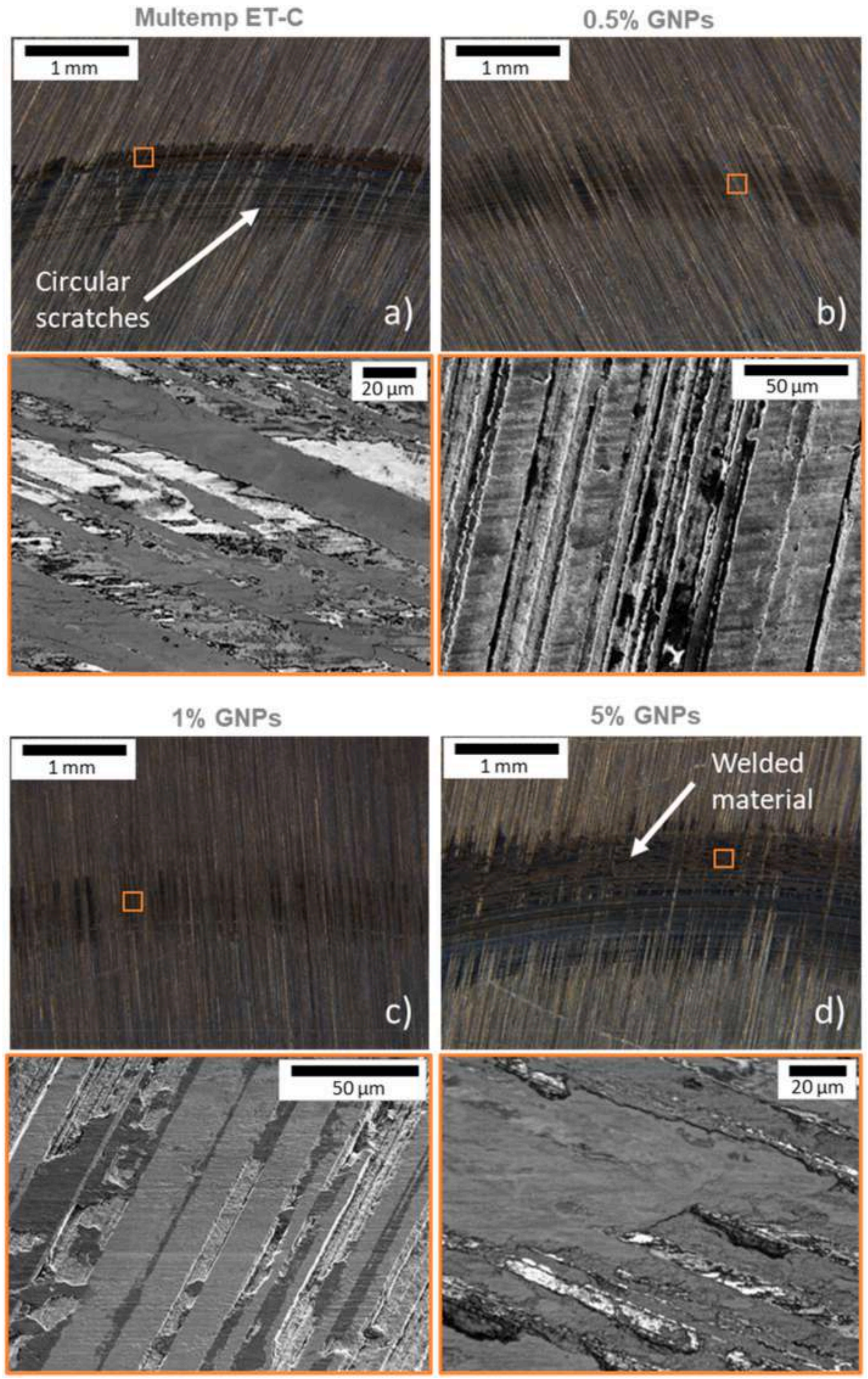

Fig. 16. The appearance of the wear traces on the AISI 52100 flat sample under the optical microscope. Insets show the micro topography visible with SEM analysis corresponding to the position in the wear track highlighted by the white squares.

a direct beneficial effect could not be identified. It would be there only if the high-conductive additive affected the average conduction of the tribological interface. It is interesting to consider the ratio between the average friction power P_f and the average temperature increase ΔT. Friction power is calculated as per equation (2) and is converted almost entirely to heating power [1].

$$P_f = \frac{F_N}{t_{TOT}} \bullet \int_0^{d_{TOT}} \mu(x) \bullet dx \tag{2}$$

The ratio $P_f/\Delta T$ represents a global thermal conductivity of the tribological interface, including grease. Fig. 13c suggests that only 5 % GNPs could be responsible for a direct beneficial effect on the thermal behaviour of the system because the $P_f/\Delta T$ ratio is higher than the corresponding ratio estimated with base grease. Unfortunately, frictional heating from the unfavourable lubrication regime prevailed, and the average temperature with 5 % GNPs (Fig. 13a) was almost double as high as base grease (Fig. 13b).

The addition of graphene also impacted wear, which was in line with friction. Fig. 14 shows that graphene reduced the volume of material lost

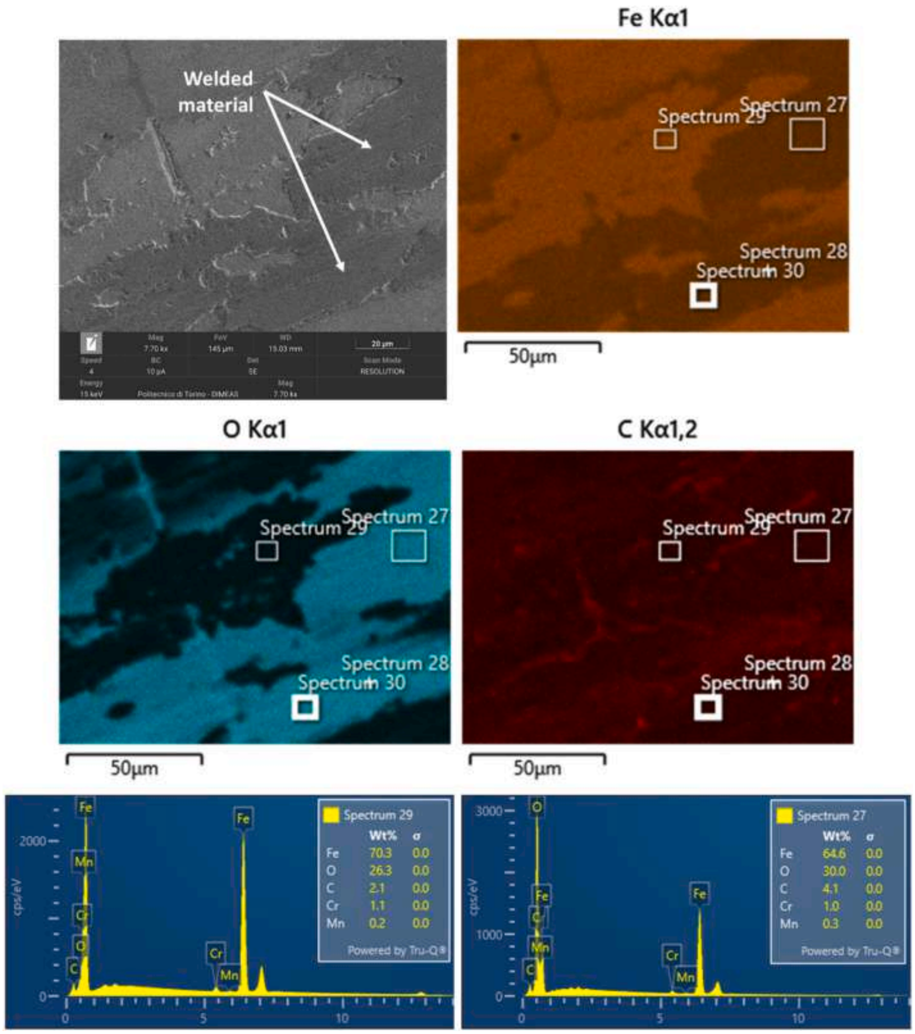

Fig. 17. EDS mapping inside the wear track of a sample tested with 5 % GNPs grease. Before the elemental analysis, samples were soaked into a bath of acetone and a bath isopropanol for some hours to remove any trace of grease, dust and other organic contaminants from the sample surface.

by the system, except with 5 % GNPs, where the wear damage was about three times higher on average. 0.5 % GNPs grease exhibited the best performance in terms of wear, and the average wear volume decreased by 46 % w. r.t base grease. With 1 % GNPs, the average wear reduction was 29 %, but the scattering of the results was relatively high. The related confidence interval is superposed to that of base grease and 0.5 % GNPs; therefore, it is hard to distinguish the performance of this compound from the statistical point of view.

Fig. 15 shows the appearance of the worn sphere right after the tribological test corresponding to the results presented in Fig. 10. Wear debris was found in the grease build-up, mainly at the trailing edge of the contact. A notably high quantity of debris was observed at the end of the tests with 5 % GNPs grease, whereas a little debris was generated during the tests with 0.5 % GNPs. This evidence correlates very well with the results of Fig. 14, the friction curves in Fig. 10 and the ECR values in Fig. 11.

Fig. 16 shows the worn region on the sample under the optical microscope and SEM. Even if the sliding path was visible on the flat sample, the amount of wear was overly tiny to be measured by surface profilometry. The wear damage was essentially limited to modifications of the surface roughness pattern because the samples were harder than the sphere. The sliding path featured a series of relatively deep circular abrasion scratches with pure grease and 5 % GNPs and a reaction layer formed in the outer region of the track where speed was maximum.

According to some researchers, among others, Singh et al. [15] and Niu et al. [27], the improvement of the anti-wear properties of the grease involves many physical aspects. Niu et al. argued that graphene does not only participate in boundary lubrication, thus promoting a thicker carbon-rich boundary layer, but in the presence of wear, it can be incorporated into a chemical reaction layer rich in oxides and carbides welded to the steel surfaces. If this occurs, graphene may promote the formation of lubricious carbides, e.g., F_3C, and may play a role as a solid lubricant, offering planes of easy sliding between the asperities [27].

The results of the EDS mapping inside the wear tracks produced with 5 % GNPs grease indicate that where residuals of a transferred chemical reaction layer are observed, a significantly and generalized higher oxygen content and a slightly higher carbon content are detected from the elemental analysis. Compare, for instance, spectrum 27 and spectrum 29 in Fig. 17. This suggests that the chemical reaction layer is composed of oxides and may have encapsulated structures rich in carbon or some of graphene flakes.

With the other two graphene-enriched grease compounds, a light crushing of the roughness ridges and some shallow scratches were visible after the test. Boundary lubrication film protected the steel surface during the tests here, thus limiting the deposition of a reaction layer (sporadic traces are visible in the inset of Fig. 15c). The EDS analysis performed with these samples indicated that the composition of the very few traces of welded material inside the wear tracks was essentially oxides.

4. Conclusions

The research presented in this paper aimed to set up a dedicated tribo-thermo-electrical analysis to investigate the tribological performance of graphene-enriched grease under sliding motion. Standard pin-on-disc tests were augmented with synchronous acquisition of temperature and ECR data. Long-term tests were carried out to assess whether graphene can serve as a solid nanoadditive for the selected grease in heavy-duty sliding conditions where the entrainment of lubricant into the contact is difficult.

A high-quality fully synthetic grease was selected to point out whether graphene can outperform the traditional molecular additive packages currently used in high-performance greases. Graphene-grease compounds were prepared with an increasing percentage of GNPs, i.e. 0.5 %, 1 % and 5 % (wt.), and the performance of these compounds was compared to that of the base grease.

The pin-on-disc test results proved that graphene positively affects sliding wear and friction if its concentration in the selected grease does not exceed 1 %wt. A moderate percentage of graphene in the grease reduced the average CoF and the contact temperature compared to base grease and suppressed most of the fluctuations of the friction curves related to micro-scuffing events. Data augmentation by ECR measurement further confirmed the outcome of tribological tests and suggested that in pure sliding, the nano-additive made the boundary lubrication regime of grease more effective by strengthening the boundary layer. Graphene also reduced the amount of wear, and as such, it acted as an additional solid lubricant at the interface. 5 % GNPs of additive seemed to interfere with the lubrication mechanism causing high friction and a high wear rate in the initial part of the tests.

From the thermal point of view, 0.5 %–1 % of GNPs improved the thermal state of the systems indirectly. Graphene reduced the heat source by reducing the frictional energy dissipation but could not affect the thermal diffusivity at the interface. On the other hand, a concentration of 5 % GNPs increased the measured thermal conductivity of grease significantly, but such a high concentration turned out to be detrimental to the system in terms of wear and frictional energy dissipation. Consequently, any direct correlation between the improvement of the thermal properties of grease by graphene and the tribological behaviour of the system cannot be inferred based on the results presented.

Only 3 repetitions with each grease compound were carried out in this exploratory work because a long time was needed to prepare the special setup and each test was time consuming (about 7 h tests). The authors are planning more repetitions of the tests, especially with the most promising grease compounds, to corroborate these results and take into account the scattering related to the inherent chaotic behaviour of grease lubrication. It would be interesting to investigate the effect of roughness and speed on graphene-grease compounds in the future. Roughness may interact with the additive promoting or discouraging some carbon deposits on the surfaces; speed may affect the feed of melted lubricant towards the contact site, thus highlighting the degree of intervention of the nano-additive as a solid lubricant.

CRediT authorship contribution statement

Edoardo Goti: Conceptualization, Data curation, Methodology, Validation, Writing – original draft, W. **Luca Corsaro:** Conceptualization, Data curation, Writing – review & editing, Methodology. **Francesca Maria Curà:** Project administration, Resources, 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.

Data availability

Data will be made available on request.

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Appendix A. Static electrical conductivity tests on greases

Previous research proved that adding conductive particles to the grease increases the bulk electrical conductivity of the lubricant [43]. As a carbon material, graphene plays a role [46]. Sometimes this effect is desired, for instance, in the case of greases for electrical motors. In the case of monitoring the lubricating film via the electrical contact resistance value, it is necessary to characterize the bulk electrical conductivity of grease to properly analyze the data obtained during tests, i.e., to identify when the measured ECR values indicate conduction through a film of grease.

In order to measure the characteristic value of the electrical conductivity of the four grease compounds, static ECR measurements were performed by exploiting a unique setup. A flat-ended pin was placed 8 μm above the steel sample, and a small quantity of grease was added to fill the gap. Figure A1 shows the measurement setup. A calibrated 8 μm lamina was used to separate the pin and the disc.

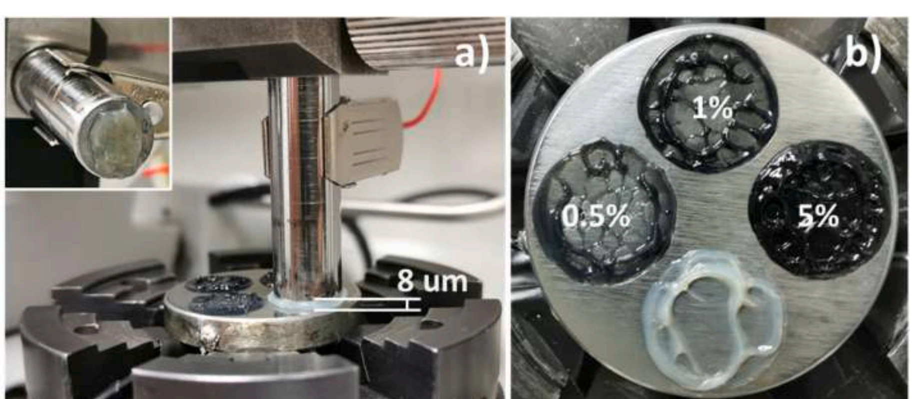

Fig. A1. (a) Experimental setup for the static non-contact ECR measurement with the four grease compounds. (b) Overview of the grease contact sites after the static ECR tests on the same sample.

Grease was applied on the pin surface, and the pin moved downward to the desired pre-set distance from the sample so that grease could fill the interspace. The pin was held in place for 10 min, and the ECR values were sampled at 0.5 Hz. The average and standard deviation values were estimated across the whole measuring time. The same sample was used to characterize the four grease compounds to make the measured values comparable (Figure A2). The average values and related confidence intervals are summarized in Table A1 and Figure A2.

Table A1
Static non-contact ECR measurement across an 8 μm thick film of grease

	MULTEMP ET-C	0.5 % GNPs	1 % GNPs	5 % GNPs
Electrical resistance	>100 MΩ	265.2 kΩ	45.9 kΩ	18.2 kΩ

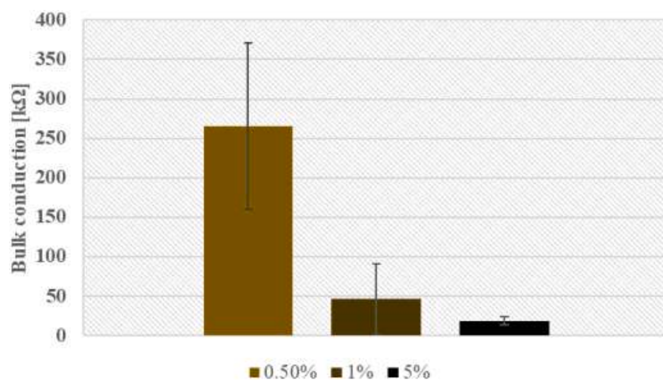

Fig. A2. Average values of bulk electrical resistance across an 8 μm thick film of grease with confidence intervals. Adding 0.5 % wt. Of graphene flakes increased the electrical conductivity significantly. The value related to pure MULTEMP ET-C is not displayed because the measuring range of the DMM (100 MΩ) was saturated.

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