coatings

Article

Investigation of Graphene Platelet-Based Dry Lubricating Film Formation in Tribological Contacts

Florian Pape

Institute of Machine Design and Tribology (IMKT), Leibniz University Hanover, An der Universität 1, 30823 Garbsen, Germany; pape@imkt.uni-hannover.de; Tel.: +49-511-7621-3392

Abstract: Dry lubricants used in highly loaded rolling bearings are in the focus of current research. In previous studies, graphene platelets applied as dry lubricants on the surfaces of angular contact ball bearings demonstrated superior properties. These specific bearings, experiencing both rolling and spinning motion, create more severe conditions for dry lubricants. To gain deeper insights into the lubrication effects, micro-tribological studies were carried out on the respective film formation and running behavior effects. In the tests, a fixed steel ball slid against an oscillating counterpart under a defined load. During the measurements, the applied load and tangential forces on the ball were recorded to calculate the friction. Comparative investigations included nano-graphite particles and fullerene as dry lubricants, in addition to graphene platelets of various staple thicknesses. To increase the adhesion of the films to the surfaces, a pre-rolling process was implemented. Afterwards, the friction on the compressed films was measured. The results indicate that the pre-rolling process effectively reduces the friction of the system. After testing, the surfaces underwent analysis using laser scanning microscopy to assess the formed films, wear, and material transfer. It has been demonstrated that the pre-rolling process leads to the formation of a very thin compacted film with surface protective properties. With the ball as a counterpart, the graphene platelets generate a transfer film on the contacting surface.

Keywords: graphene platelets; fullerene; nano-graphite; dry lubrication; tribological contact; transfer film

check for updates

Citation: Pape, F. Investigation of Graphene Platelet-Based Dry Lubricating Film Formation in Tribological Contacts. *Coatings* **2024**, *14*, 360. https://doi.org/10.3390/coatings14030360

Academic Editor: José Carlos Fonseca

Received: 22 December 2023
Revised: 1 March 2024
Accepted: 11 March 2024
Published: 18 March 2024

1. Introduction

1.1. Introduction to Dry Lubrication

Lubricants play a crucial role in minimizing friction and wear between components in relative motion. However, conventional lubricants may not always be the optimal choice, particularly under extreme environmental conditions (e.g., when freezing or under hot conditions where oil evaporates) or sporadic usage. The current research emphasizes the exploration of lubricants with enhanced extreme pressure and anti-wear properties to address these challenges. Carbon nanomaterials have attracted much attention as lubricant additives due to their unique nanoscale structure and extremely high thermal conductivity and mechanical strength. As research progresses, distinctions in the lubricating properties of carbon nanomaterials have been identified under varying conditions.

Graphene, as an allotrope of carbon, is a two-dimensional (2D) layer consisting of covalently bonded carbon atoms. Compared to graphite, graphene offers better sliding properties and improved thermal conductivity, which is important for the transfer of heat from the tribological contacts [1]. In addition, graphene has a higher electrical conductivity [2]. When applying graphene in journal bearings, chemical vapor deposition (CVD) coatings were employed, yielding a noteworthy reduction in both friction and power consumption [3]. To study a graphene additive film in n-hexadecane lubricating oil, Zhang et al. performed pin-on-disk tests and molecular dynamic studies. It was found that the adsorption of the lubricant could be increased by adding graphene, and shear stresses on the surface were reduced [4]. Wu et al. studied graphene oxide nanoplatelets as a lubricant additive for the contact of Si_3N_4 ceramic/GCr15 steel in a four-ball tester. They demonstrated not only a reduction in friction but also enhanced wear resistance and load-carrying capacity through the incorporation of graphene oxide additives [5]. The lubrication of dry sliding contacts by graphene oxides with regard to adhesion was investigated by Samanta et al. and they were able to demonstrate the formation of films with beneficial tribological properties for particles with good adhesion to the substrate [6]. Goti et al. investigated the tribological behavior of graphene coatings as dry lubricants for copper substrates. It was shown that wear and friction could be reduced, but that the adhesion of the graphene has a major influence on the coating resistance [7].

Initially, nanomaterials found application exclusively in specific conditions like elevated temperatures and vacuum environments, where traditional organic lubricants were unsuitable. Nanotechnology enables precise tuning of nanoparticle shape, size, and surface groups, enhancing their potential for applications in various fields, including colloidal systems like lubricating greases, oil recovery, and biomedicine [8]. The addition of nanoparticles to lubricating oil can effectively reduce the boundary friction and increase the wear resistance of the lubricating oil. Carbon nanomaterials, like graphene and its derivatives, carbon nanospheres, fullerenes, etc., serve as vital components of nanoparticles and find diverse applications in contemporary research. Another emerging material is $Ti_3C_2T_x$ nanosheets (MXene), which have advantageous sliding planes for dry lubrication [9]. Graphene exhibits distinctive physical and chemical properties, combining high chemical inertia, exceptional strength, and low shear strength. As an additive to liquid lubricants, such as lubricating and cutting oil, it can improve lubrication, friction reduction, and anti-wear properties [10,11].

Studies of graphene platelets as a grease additive could prove the outstanding effect as a 2D nanomaterial in reducing friction and wear, as shown by Pape et al. [12], as well as by Nassef et al. [13–15]. Kim et al. achieved good lubricating conditions for reduced graphene oxide (rGO) coatings on AISI 440C stainless-steel balls sliding against a silicon specimen under water lubrication conditions [16]. At the same time, the gas and liquid impermeability of graphene can effectively delay the corrosion and oxidation process of the friction surface, and its distinguished thermal conductivity can lower the temperature generated on the surface. This reduces the decomposition process of the surfaces during tribological contact. A molecular dynamics study on the interlayer sliding behavior of a few layers of graphene was conducted by Xu et al. Coherent sliding at several interfaces and a periodic layer transition were demonstrated [17]. Restuccia et al. demonstrated the chemisorption of graphene on an iron substrate, while the bonding was enhanced by reactive protruding bonds. The surface–surface mechanism of interaction changes from chemical to physical due to the passivation effect caused by graphene, which reduces adhesion and friction [18]. In the case of hot rolling, Wang et al. proved the ability of graphene nanoplatelets to serve as a dry lubricant up to 960 °C [19]. Regarding the thickness and particle size of graphene platelets as a lubricant additive, Kong et al. demonstrated that thicker layers and a smaller particle size have a better positive effect on the tribological performance as a lubricant additive [20].

Fullerene has been explored in numerous studies as a dry lubricant, displaying superior friction conditions to graphite, particularly in very dry air (<35% relative humidity). Its friction coefficient exhibits minimal temperature dependence, providing advantages over traditional dry lubricants, especially in extreme conditions [21]. In composite materials, such as when embedded in epoxy resin, fullerene has the potential to improve the mechanical properties [22].

Graphite, employed as a dry lubricant, exhibits favorable properties and finds widespread use in tribological contacts with low-contact pressures. While predominantly applied as a thicker coat, it has not gained prominence in bearing applications. In the study of Suparno et al., the authors highlighted graphite's effective dry lubrication potential in the tribological rail-wheel contact, where it adhered to the wheel surface and permeated fissures, resulting in minimal wear [23]. Morstein et al.'s investigation into the frictional properties of graphite in reciprocating sliding tests yielded a compressed thin carbon film with low friction [24].

The application of graphene platelets on bearing surfaces allows for significantly thinner coatings, contributing to extended running times in bearing applications. Graphene platelets, consisting of a few layers of graphene with a diameter in the μm range, can be efficiently produced on a large scale through graphite exfoliation [25,26]. When used as an additive to grease, graphene platelets can form protective films between sliding surfaces, particularly effective under lubricant-starved conditions as encountered in oscillating motion. Pape and Poll have demonstrated this effect in the case of graphene platelets used as dry lubricants [12].

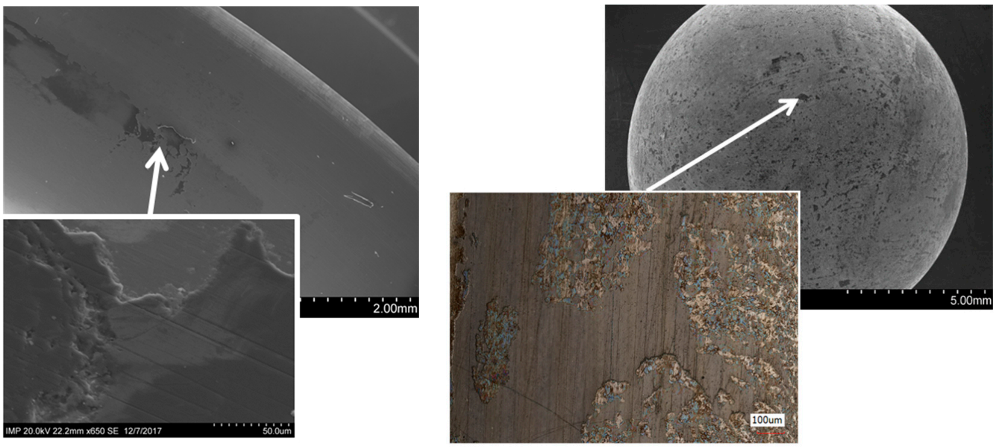
1.2. Introduction to Graphene Platelet Dry-Lubricated Angular Contact Ball Bearings

In a previous study, thin layers of graphene platelets were subjected to a Hertzian pressure of 1.5 GPa in angular contact ball bearings [12]. These bearings, characterized by both rolling and spinning motion, along with Heathcote slip, revealed that the layer thickness of the platelets significantly influences the frictional torque. It is inferred that the rolling motion contributes to the formation of a compressed graphene platelet-based layer with a thickness of a few tens of nanometers. These layers exhibit superior tribological properties and can withstand high tribological loads encountered in rolling bearing contacts.

To advance and understand the lubrication effect of graphene platelet-based dry lubricants, the bearings were analyzed via scanning electron microscopy (SEM) and Raman spectrometry. In addition to this, microtribological studies were performed to determine the effects acting on the angular contact ball bearings. Figure 1 illustrates the SEM images of the raceway and a bearing ball after testing on a rig (1.3 million cycles tested under 48% degree of reciprocating motion), with detailed information available in [12]. A thin, dry lubricant film based on graphene platelets formed on the surface. On the counterpart, including the ball itself and the outer bearing ring, a transfer film developed, resulting in low friction and prolonged running time. The hardness was assessed using a Hysitron/Bruker nanoindenter (TriboIndenter TI 950, Bruker Corporation, Billerica, MA, USA) as described in [27]. Prior to the test, the hardness of the uncoated bearing surface was 9.2 GPa; after the pivoting test, the hardness of the raceway dropped to 7.3 GPa. The hardness of the accumulated graphene platelets was approximately 0.3 GPa.

Furthermore, the graphene layers underwent examination using Raman spectroscopy (Figure 2). For the measurement, an alpha300 RA Raman-AFM microscope was used (Oxford Instruments, Abingdon, UK). The 2D peak around 2690 cm^{-1}, with a half-width of 105 cm^{-1} (half-width of the monolayer $\approx$ 24 cm^{-1}), indicates stacked graphene. The measurement before and after exposure reveals a distinct G peak at 1591 cm^{-1}, typical for graphene, which splits into the G and two D peaks when it has defects. The intensity of the D peak at 1351 cm^{-1}, signifying defects in the graphene structure, notably increased after the panning experiment. These defects may manifest as fractures in the graphene or as charged particles (e.g., metal ions) embedded in the graphene structure. It is plausible to assume that the graphene undergoes wear during the endurance test.

To validate these effects, studies were conducted on the frictional properties under sliding conditions. Graphene platelets were applied as thin layers on bearing steel, undergoing both pre-rolling compaction and direct deposition without compaction. By applying graphene platelets of various staple thicknesses, the respective influence on adhesion and wear resistance was investigated. The graphene platelets were compared to nano-graphite powder and fullerene, which feature less or no sliding planes.



(**a**) (**b**)

Figure 1. SEM micrograph after endurance test as described in [12] of (**a**) graphene platelet film on angular contact ball bearing raceway and (**b**) roller of the angular contact ball bearing.

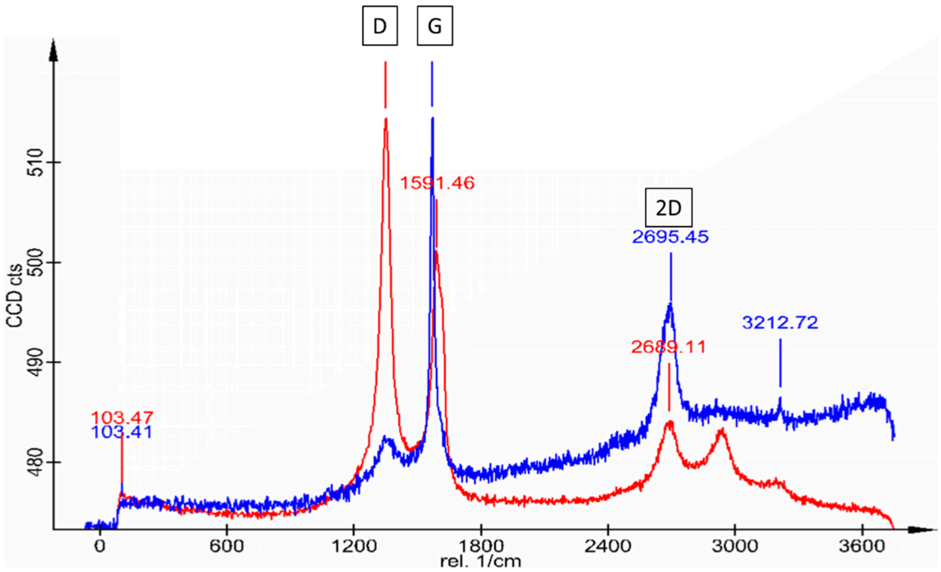


Figure 2. Raman spectroscopy (wavelength 520 nm, intensity 0.1 mW) of a graphene platelet-lubricated bearing before loading (blue) and after the endurance test (red) as described in [12]. The typical G-peak for graphene is clearly visible in the dry lubrication layer before loading. After loading in the pivoting test, the increase in the intensity of the D peak indicates the occurrence of defects in the graphene structure. The 2D peak shows how many layers of graphene are on top of each other.

2. Materials and Methods

For the experiments, the graphene nanoplatelets that were utilized were sourced from IOLITEC (IoLiTec-Ionic Liquids Technologies GmbH, Heilbronn, Germany), with staple thicknesses of 2 nm, 6–8 nm, and 11–15 nm. Nano-graphite powder (3–4 nm diameter) and fullerene (C60/C70 bucky balls) were employed to assess their impacts in the tribo-contact (also purchased from IOLITEC). The graphene platelets, nano-graphite, and fullerene were precisely weighed and combined with dimethylformamide. To mitigate agglomeration and achieve a well-dispersed suspension, the mixtures underwent ultrasonic treatment, as a first step, in an ultrasonic bath for 1 h.

As a second step, the mixtures underwent a 10 min treatment in an ultrasonic homogenizer (Bandelin SONOPULS, BANDELIN electronic GmbH & Co. KG, Berlin, Germany) directly before the application onto the substrates. Bearing washers, specifically, type WS81102 (manufactured by Schaeffler, Herzogenaurach, Germany), crafted from bearing steel AISI 52100 were then coated by brushing them with the prepared mixtures. To secure the applied coating, the bearings were placed in an oven at 120 °C for 15 min. A Tribotechnic MILLI TRIBOtester (Tribotechnic, Clichy, France) was employed to qualify the coatings.

In this setup, a plate undergoes linear reciprocating motion against a fixed pin. To elucidate the mechanism of the beneficial effect for angular contact ball bearings, the investigations were conducted in two steps, as shown in Figure 3. In the first step, a movable mounted ball travels in oscillating motion along the graphene platelet-covered sample to achieve a compressed film of graphene platelets with parameters as shown in Table 1. The setup of the tribometer is shown in Figure 4. The second step involves examining the frictional properties of the film using a sliding test with parameters shown in Table 2. For comparison, measurements were performed with uncompressed dry lubricants. The test setup allows the application of normal pressure by a carbon fiber cantilever arm with a frictionless cardan bearing system. An integrated sensor records the arm's tangential elongation in order to calculate the friction. For the rolling process, a movable mounted ball with a diameter of 5 mm made of AISI 52100 was used, while the sliding tests employed AISI 52100 balls with a diameter of 6 mm. Therefore, the material of the counterpart and pin is the same as that found in real bearing applications. The tracks resulting from sliding on the bearing washers were observed using a Keyence laser scanning microscope (KeyenceVK-X200, Keyence, Osaka, Japan).

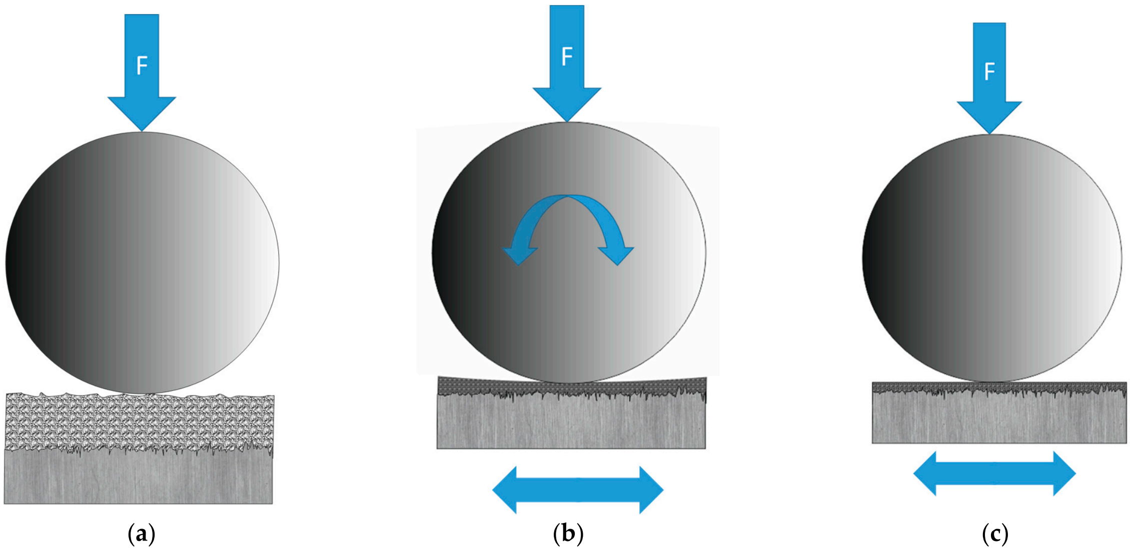


Figure 3. Test principle: (**a**) loading the dry-coated sample, (**b**) pre-rolling under load and subsequent compacting with movable mounted ball, (**c**) sliding test with fixed ball on compacted dry lubricant coating.

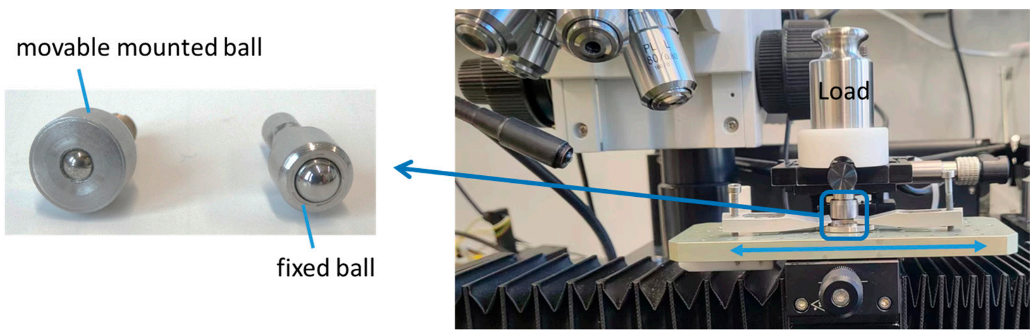


Figure 4. Setup for pre-rolling in milli tribometer: on the left, the movable mounted ball for the pre-rolling process and the fixed ball for sliding tests are shown.

Table 1. Setup of pre-rolling conditions.

Diameter of the Ball	5 mm (100Cr6/AISI 52100)
Track length	2 mm
Sliding speed	1 mm/s
Sliding length	1 m
Normal load	3 N
Pressure	1073 MPa
Duration	15 min

Table 2. Sliding test conditions.

Diameter of the Ball	6 mm (100Cr6/AISI 52100)
Track length	2 mm
Sliding speed	1 mm/s
Sliding length	4 m
Normal load	1 N, 2 N
Pressure	660 MPa, 830 MPa
Duration	1 h

3. Results

3.1. The Effect of Pre-Rolling on the Lubricating Properties

In the initial stage, the dry lubricant coatings were examined in the tribometer without the pre-rolling process. For this investigation, the normal load was set to 1 N (660 MPa contact pressure), the sliding speed was 1 mm/s, and the track length was 2 mm. The measured friction force on the sample for using the five dry lubricants is depicted in Figure 5.

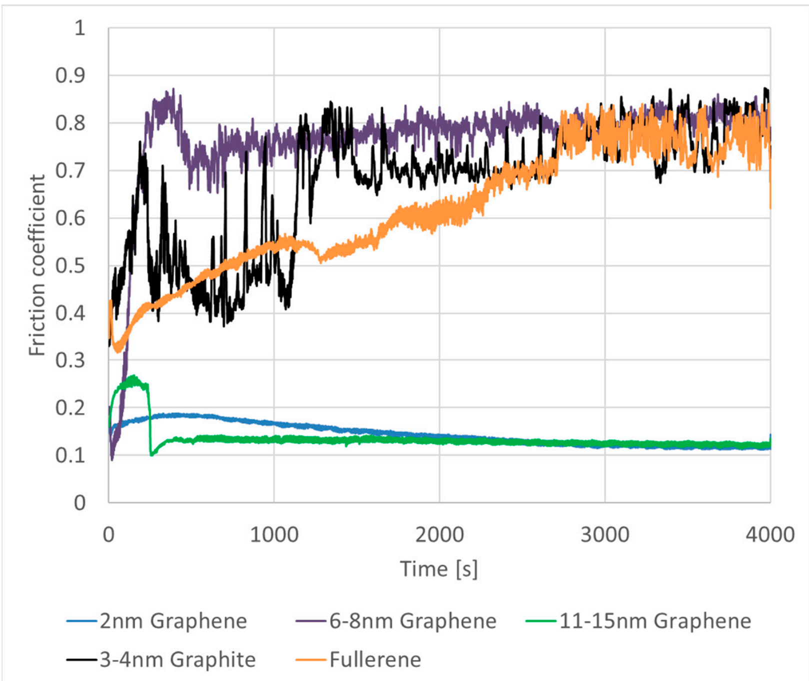


Figure 5. Friction coefficient on steel coated with graphene platelets, nano-graphite, and fullerene without pre-rolling, tested under 660 MPa.

It is evident that the nano-graphite, 6–8 nm graphene platelets, and fullerene did not exhibit friction reduction under these test conditions. During the test, these dry lubricants were displaced from the contact area, leading to steel–steel contact and resulting in high friction. Conversely, in the case of the 2 nm graphene platelets and 11–15 nm graphene platelets, a film was formed, featuring a low coefficient of friction (COF). In these instances, a compact film could be established, while the other dry lubricants were removed from the raceway.

Before repeating the test, a pre-rolling step was performed on a freshly coated surface. By employing this method, a rolling ball with a diameter of 5 mm was utilized, oscillating at 1 mm/s, covering a track length of 2 mm along a racetrack for a duration of 15 min, with a load of 3 N applied, equal to approx. 1 GPa contact pressure. Subsequently, a compressed film was attained on the surface. The sliding test was then conducted directly on this compacted film as the second step.

The friction coefficient after the pre-rolling step was measured under the same conditions as before at a sliding speed of 1 mm/s, a normal load of 1 N, and track length of 2 mm. From Figure 6, it can be seen that the COF using the 11–15 nm graphene platelet dry lubricant recorded the lowest value, followed by that using the 6–8 nm graphene platelet dry lubricant. However, the COF was the highest in the case of fullerene while the COF of the nano-graphite could be decreased but still remained in the range of 0.4 to 0.5, a value much higher than that observed for the graphene platelets, which ranged from below 0.1 to below 0.2.

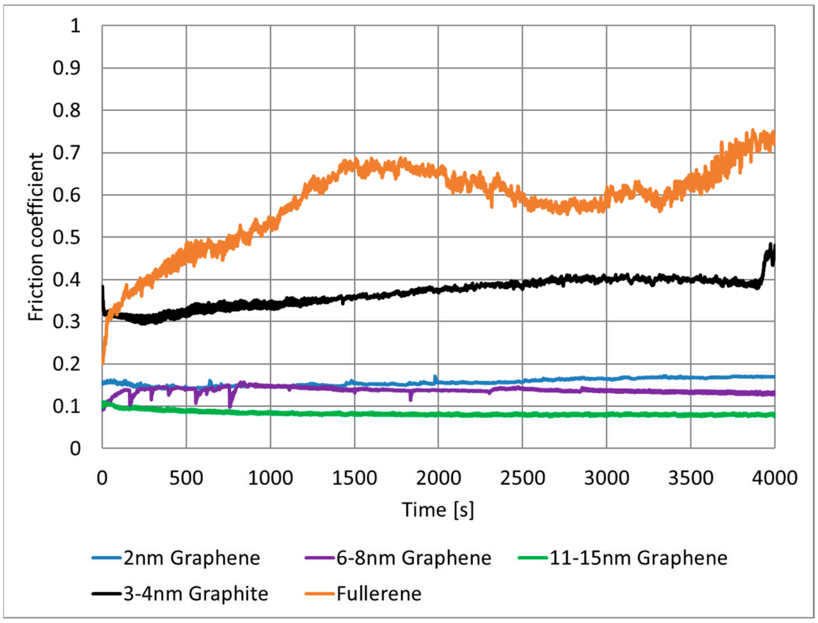


Figure 6. Friction coefficient on steel coated with graphene platelets, nano-graphite, and fullerene with pre-rolling, tested under 660 MPa.

Through the comparison above, it can be determined whether or not pre-rolling has the greatest effect on the friction coefficient of the samples using 6–8 nm graphene platelets and 3–4 nm graphite dry lubricant. In addition, the curves for the dry lubricants feature lower fluctuations due to the compressed and more stable dry lubrication film.

3.2. The Effect of Sliding Contact Pressure on the Lubricating Properties (with Pre-Rolling)

To investigate higher contact pressure, the tests were repeated under 2 N load (830 MPa contact pressure). In this case, a new sample was pre-rolled with a rolling ball of 5 mm diameter. For the sliding tests, the sliding speed and the track length were 1 mm/s and 2 mm, respectively. The measured COF values for the five dry lubricant cases are shown in Figure 7. As the load increased to 2 N, the COF of both the graphene platelets and nano-graphite samples is considered almost the same.

Under these challenging conditions, the COF of samples using 3–4 nm graphite dry lubricant is the lowest among the group. Conversely, the friction coefficient measured by the sample using fullerene dry lubricant is significantly higher than that of the other dry lubricants, indicating that no compacted dry lubricant film could be achieved. This highlights the poorer lubricating property of fullerene dry lubricant under these conditions. In this case, stiction through physical surface effects, such as adhesion and bonding, results in a friction coefficient higher than 1. In conclusion, when the normal load is 2 N, the sliding speed is 1 mm/s, and the track length is 2 mm, the lubricating properties of 3–4 nm nano-graphite and graphene platelets are nearly comparable to typical lubricated contacts, with a COF between 0.1 and 0.15 under similar test conditions [28].

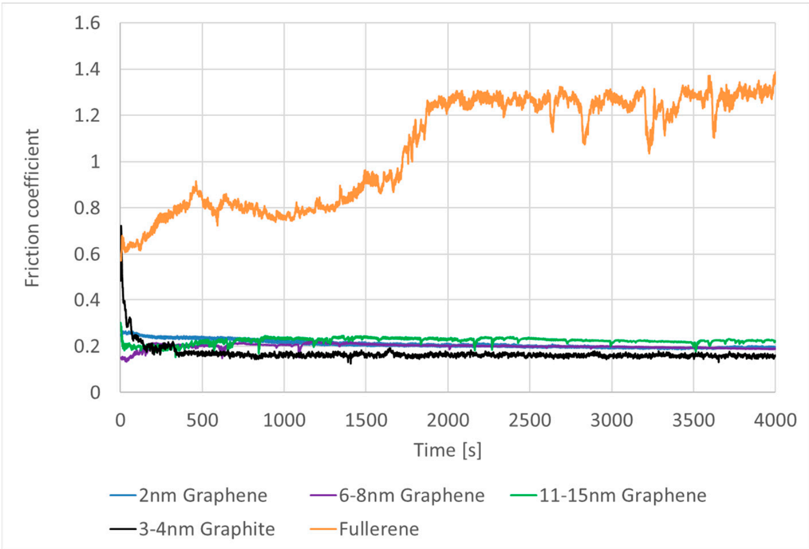


Figure 7. Friction coefficient on steel coated with graphene platelets, nano-graphite, and fullerene with pre-rolling, tested under 830 MPa.

3.3. Investigations on Wear Volume of the Sliding Ball

The balls and raceways were investigated via laser scanning microscopy (KeyenceVK-X200). To conclude, on the wear of the respective balls, the wear spots were measured using Keyence Analyzer software (VK Analyzer Version 3.8.0.0). Figure 8 shows the comparison of the balls' wear spots after the sliding test with a pressure value of 660 MPa without the pre-rolling process. In this test, the graphene platelets with thicknesses of 2 nm and 11–15 nm feature the smallest wear spot area, while the wear spot area on the balls for the other lubricants is increased.

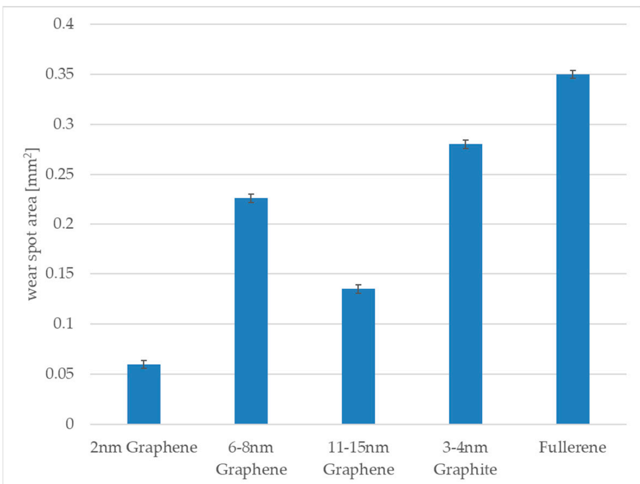


Figure 8. Wear spot areas of steel balls measured under 3D laser scanning microscope tested against dry lubricants under 660 MPa contact pressure after sliding test.

For the test with the pre-rolling process and investigation under a contact pressure of 660 MPa, Figure 9 shows the balls' wear spots. It is significant that in all cases, the wear spot area is reduced. In the case of the graphene platelets, no wear could be measured.

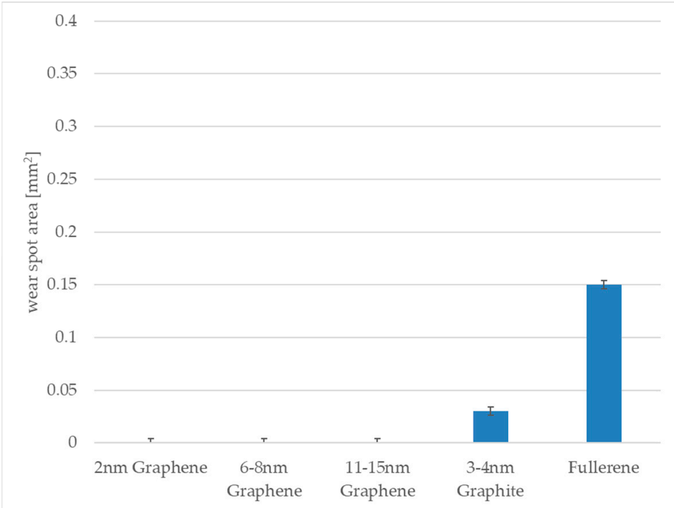


Figure 9. Wear spot areas of steel balls measured under 3D laser scanning microscope tested against pre-rolled dry lubricants under 660 MPa contact pressure after sliding test.

In comparison, the wear spot areas for experiments under increased contact pressure are shown in Figure 10 (the balls' wear spots are compared after the sliding test under pre-rolling with a pressure value of 830 MPa).

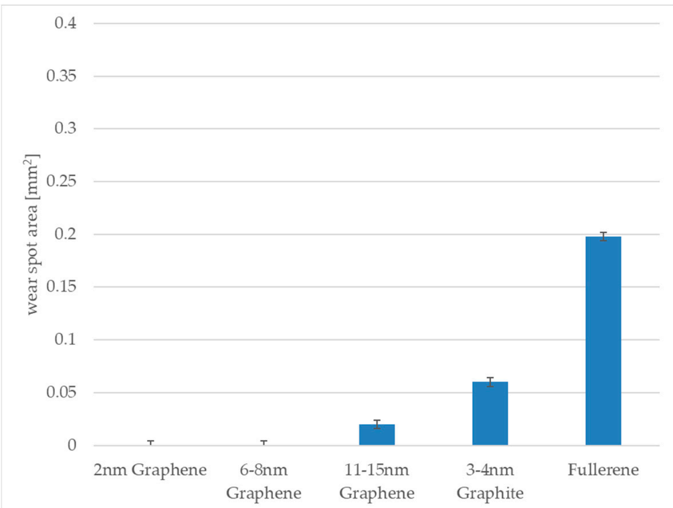
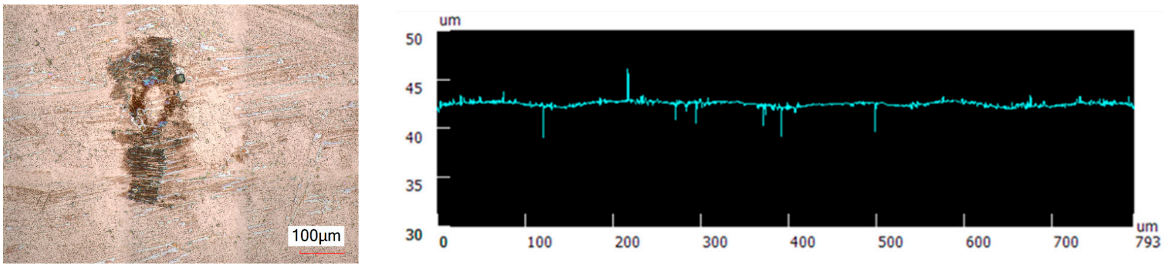


Figure 10. Wear spot areas of steel balls measured under 3D laser scanning microscope tested against pre-rolled dry lubricants under 830 MPa contact pressure after sliding test.

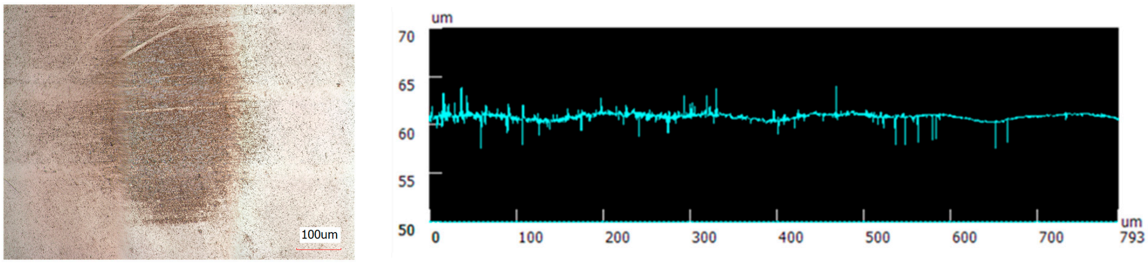
In case of the 2 nm and 6–8 nm thick graphene platelets, it was not possible to measure any wear; for the 11–15 nm thick graphene platelets, only a very slight wear scar was visible; and for the nano-graphite and fullerene, a significant wear spot could be measured, which is increased in comparison to the lower contact pressure of 660 Mpa.

3.4. Investigation of the Transfer Film Formation for Pre-Rolled Dry Lubricants under Increased Load

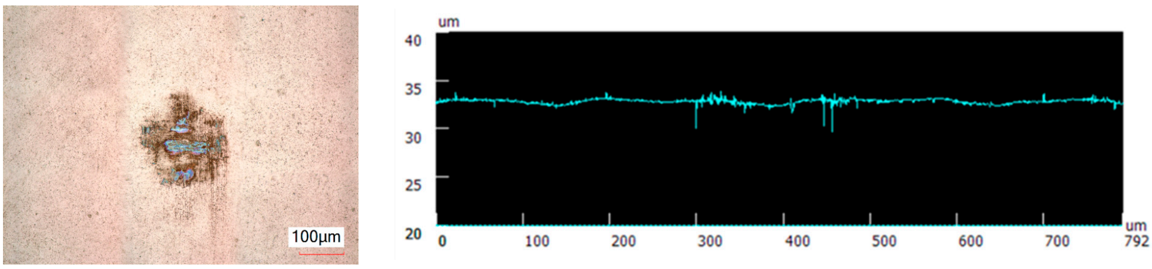
For the balls tested on the pre-rolled lubricant film under a higher load, the respective ball surfaces are shown in Figure 11. The tests under increased load show an increased wear volume and visualize the film formation, which provides a deeper insight into the positive and negative wear. The comparison of the wear spot area on the steel ball surface when using different types of lubricants proves the formation of a wear protective film by the graphene platelets. As depicted in Figure 11, under identical load (830 MPa contact pressure), speed, and track length conditions, the wear spot area on the steel ball surface is not visible or is smallest when using graphene platelets as a dry lubricant. Due to the graphene platelets, a black-colored zone on the contact point is visible with nearly no thickness. The figure reveals the surface image on the left and the respective profile on right in order to determine the ball wear. In comparison, the fullerene dry lubricant resulted in significant wear on the balls' surface. Regarding nano-graphite, a slight amount of wear can be found on the surface. The steel ball using fullerene dry lubricant indicates the largest wear spot area, which is roughly consistent with the variation of the wear degree under microscope.



(**a**)

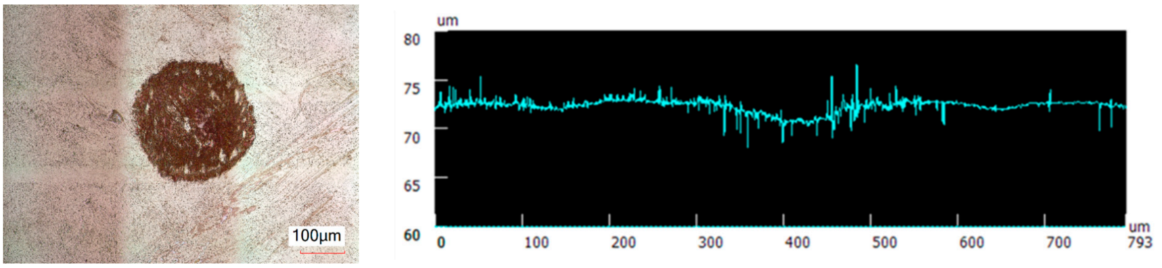


(**b**)

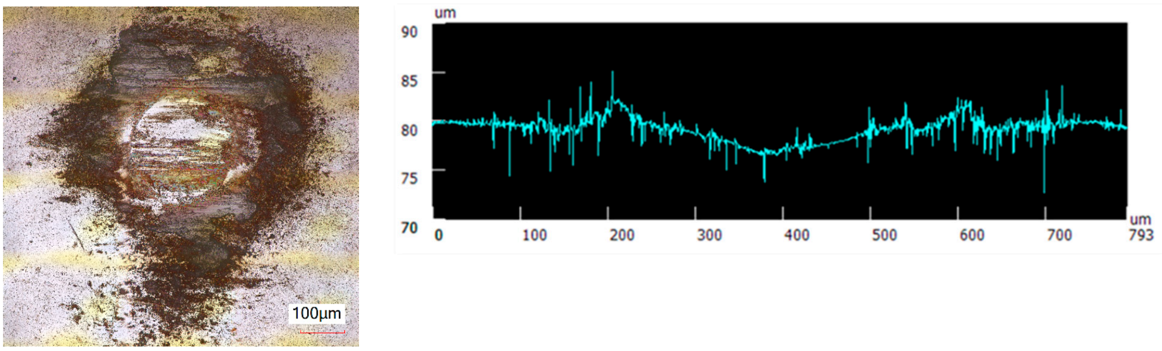


(**c**)

Figure 11. *Cont.*



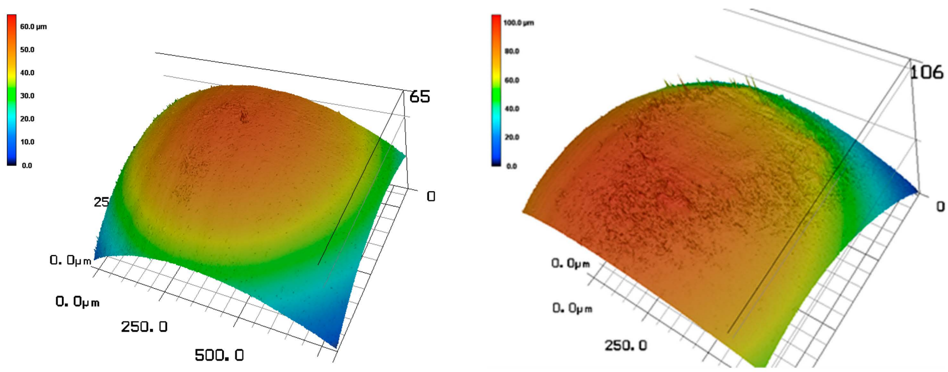
(**d**)



(**e**)

Figure 11. Wear spot of steel balls under 3D laser scanning microscope tested against pre-rolled dry lubricants under 830 MPa contact pressure after sliding test for (**a**) 2 nm thick graphene platelets, (**b**) 6–8 nm thick graphene platelets, (**c**) 11–15 nm thick graphene platelets, (**d**) 3–4 nm nano-graphite, and (**e**) fullerene.

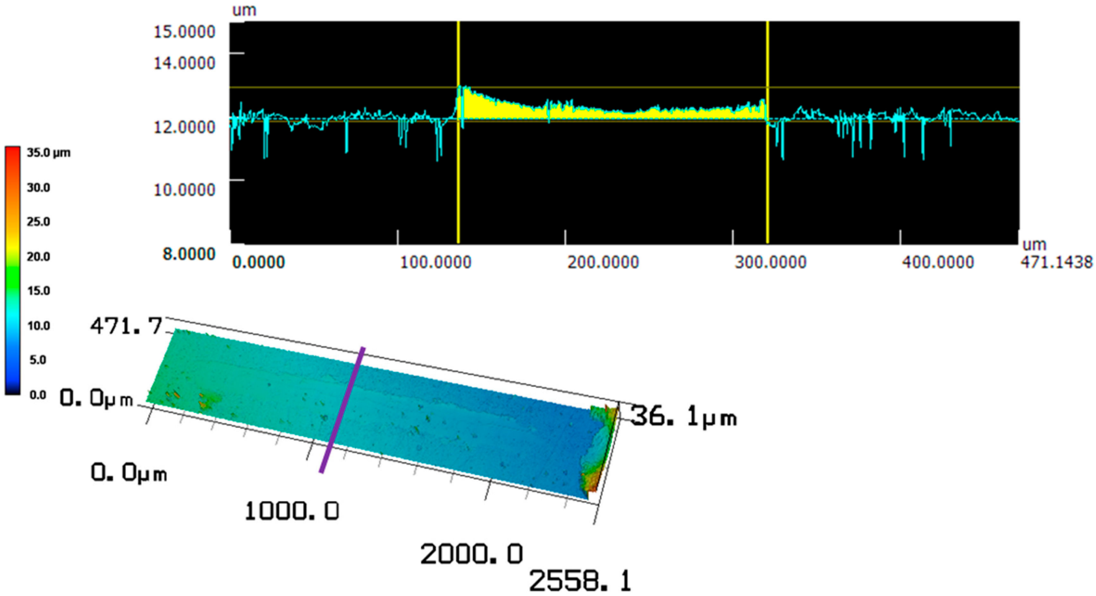
The contrast between graphene platelets as dry lubricant (in this case, 2 nm staple thickness) and fullerene is also visualized in Figure 12. A plateau is formed on the surface of the steel ball in the case of the fullerene dry lubricant, while for the graphene platelets, no wear can be found. The images prove that a small portion of graphene platelets were transferred to the balls' surface and can feature a significant enhancement as dry lubricant.



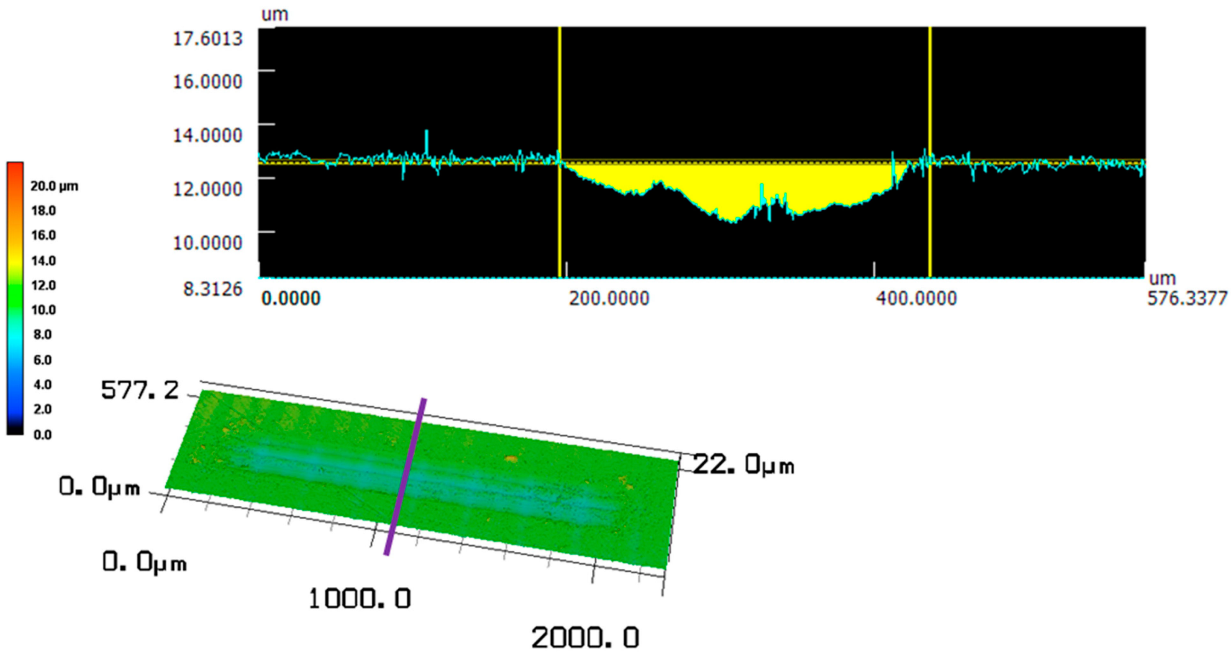
(**a**) (**b**)

Figure 12. Comparison of the surface after the sliding test (830 MPa contact pressure) for the ball tested against pre-rolled (**a**) 2 nm graphene platelets and (**b**) fullerene.

The respective dry-lubricated racetracks for the graphene platelet dry lubricant (6–8 nm graphene platelets) and fullerene are illustrated in Figure 13. The surfaces were analyzed by laser scanning microscopy. It can be seen that the graphene platelets form a dense film on the surface with a thickness of approx. 150 to 200 nm in the central contact zone. In contrast, for the fullerene on the surface, wear is evident, with the base material being removed to a depth of up to 2.5 μm.



(**a**)

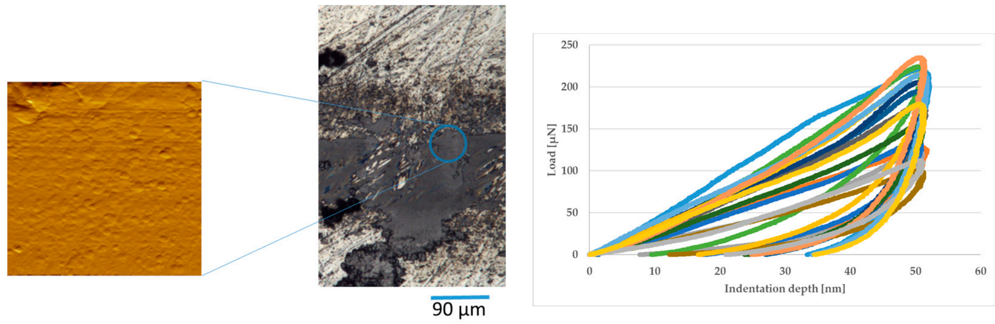


(**b**)

Figure 13. Comparison of the bearing washers' surface coated with pre-rolled (**a**) 6–8 nm graphene platelets and (**b**) fullerene after the sliding test (830 MPa contact pressure).

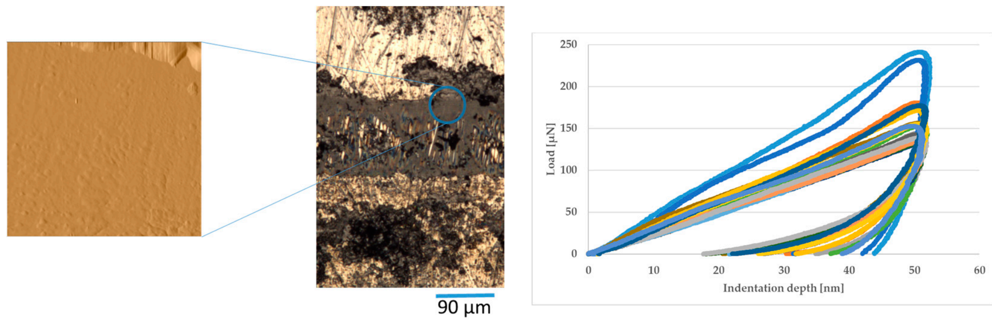
3.5. Nanoindentation Studies on the Transfer Film for Pre-Rolled Dry Lubricants

In the case of the compacted graphene platelet-based track, for the sample run with 6–8 nm thick graphene platelets, nanoindents were performed with an indentation depth of approx. 50 nm. For the measurements, a Bruker Hysitron TriboIndenter TI 950 (Bruker Corporation, Billerica, MA, USA) with a Berkovich tip was used. The compacted graphene film used for the measurements is shown in Figure 14a (on the left is the scanning probe image with measurement points, and on the right is a microscopic view of the surface) for the test performed under 660 MPa contact pressure. Figure 15a depicts the surface for the nanoindentation tests for a track that was pre-rolled and investigated under the contact pressure of 830 MPa. The load-displacement curves for the nanoindents are shown for the test at 660 MPa in Figure 14b and for the contact pressure of 830 MPa in Figure 15b. The scanning probe microscopy (SPM) images prove surface smoothening and a fine surface structure for both cases. A slightly higher hardness, as compared to the compacted graphene platelets on the angular contact ball bearings was achieved. A hardness of approx. 0.6 GPa and a Young's modulus of approx. 30 GPa were achieved in both cases. The compacted graphene platelets feature elastoplastic material behavior (Figures 14b and 15b). In the case of the higher contact pressure, the load-displacement curves feature less derivation.



(**a**) (**b**)

Figure 14. Nanoindentation study on pre-rolled 6–8 nm thick graphene platelets under 660 MPa: (**a**) surface for nanoindentational study after test (on the left: scanning probe microscopy of the surface 25 × 25µm; on the right: light microscopic view) and (**b**) nanoindents on surface after test with pre-rolled 6–8 nm thick graphene platelets under 660 MPa.



(**a**) (**b**)

Figure 15. Nanoindentation surface study on pre-rolled 6–8 nm thick graphene platelets under 830 MPa: (**a**) surface for nanoindentational study after test (on the left: scanning probe microscopy of the surface 25 × 25µm; on the right: light microscopic view) and (**b**) nanoindents on surface after test with pre-rolled 6–8 nm thick graphene platelets under 830 MPa.

4. Discussion

In this study, the formation of a compacted dry lubricant film on steel surfaces was demonstrated. This film exhibits mechanical properties similar to the film identified on angular contact ball bearings tested with graphene platelets as a dry lubricant.

When used in oscillating angular contact ball bearings, the graphene platelet layer is compacted by the rolling process. This protects the surface and achieves long running times with low friction. In comparison, the graphene platelets also form lubricating layers, which adhere firmly to the substrate in dependence of the graphene staple thickness. The film adhesion can be improved through compaction by rolling. When a compact film forms on the surface, it introduces a fine roughness, contributing to improved sliding conditions. The asperities of the steel surface are covered, and direct steel–steel contact can be avoided. When it comes to spherical nanoparticles, such as those found in fullerene, no compacted film is formed. Consequently, the surfaces are more susceptible to wear. It can be inferred that carbon-based nanoparticles help inhibit surface oxidation, thereby mitigating increased friction. An interesting alternative is the utilization of nano-graphite. Under higher pressure, specifically, 830 MPa, a lower coefficient of friction (COF) was attained. In this scenario, favorable sliding planes contribute to enhanced frictional properties. The presence of a stable, compacted film on the surface suggests that, owing to the thin film with a reduced Young's modulus, the contact pressure is likely slightly diminished. This reduction in contact pressure mitigates the occurrence of pressure peaks on roughness asperities. A secondary effect is the formation of a transfer film on the steel counterpart, preventing oxidation and smoothing the counterpart surface. The pre-rolling process can affect the friction under sliding significantly. This could be shown especially in the case of the 6–8 nm graphene platelets.

Figure 16 shows the comparison of the sliding friction for the samples with and without pre-rolling. It is obvious that in the case of the nano-graphite and 6–8 nm graphene platelets, the sliding friction experienced a significant reduction. As for the 11–15 nm thick graphene platelets, this effect becomes a little visible, but is not that distinctive. Regarding the 2 nm graphene platelets, the sliding friction remained nearly at the same level of low COF.

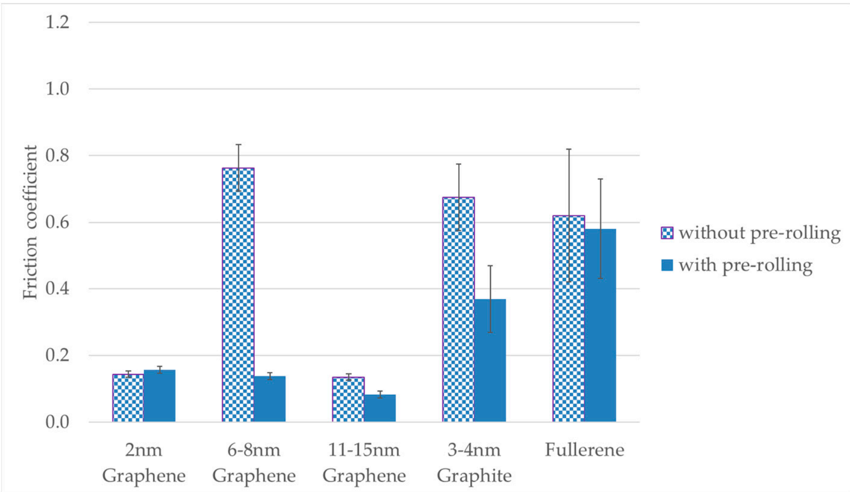


Figure 16. Comparison of frictional coefficients for dry lubricants with and without pre-rolling.

As illustrated in Figure 17, with an increase in load to 2 N, the COF for the graphene platelet-coated samples with pre-rolling slightly rose to approximately 0.2. However, when employing the 3–4 nm nano-graphite dry lubricant, a substantial reduction in the friction coefficient was observed. In this instance, additional compaction may contribute to the formation of an improved sliding surface. Conversely, the use of fullerene resulted in a significant increase in COF with an escalating load.

As depicted in the aforementioned figures, it is evident that the utilization of dry lubricants, specifically, 2 nm graphene platelets and 11–15 nm graphene platelets, exhibits minimal variation in the friction coefficient under different parameter conditions. Contrastingly, when employing the dry lubricants, 3–4 nm graphite and 6–8 nm graphene platelets, alterations in the parameter conditions exert a more pronounced influence on the friction coefficient.

In comparison to contacts lubricated with oil and grease, dry lubricants can exhibit nearly identical lower coefficients of friction (COF) under sliding conditions. This observation was initially demonstrated in the comparison between grease-lubricated angular contact ball bearings and their dry-lubricated counterparts [12] and has now been confirmed through tribometer investigations.

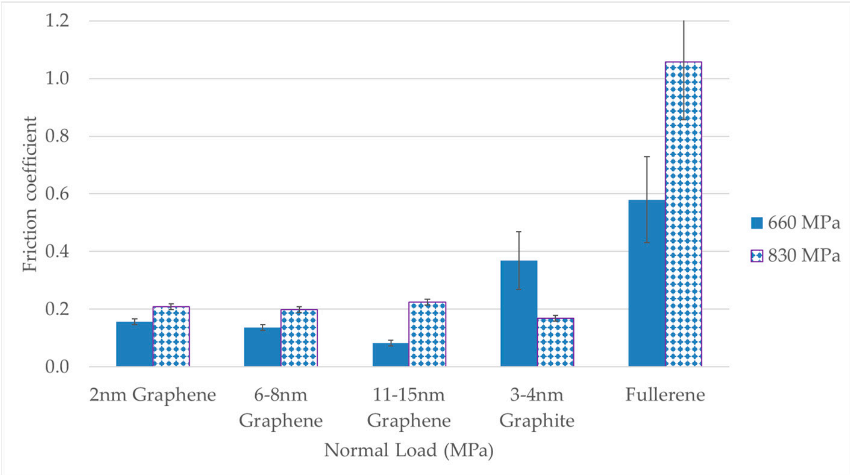


Figure 17. Comparison of frictional coefficients for pre-rolled dry lubricants under 660 MPa and 830 MPa pressure, after pre-rolling.

5. Conclusions

Graphene platelets show good properties as a dry lubricant. Since the requirements can be produced with a layer thickness in the nm range by mechanical exfoliation processes, the production of dry lubricants is economical. With further scaling, more favorable prices can also be expected here.

In this study, five various dry lubricants were prepared, namely, 2 nm graphene platelets, 6–8 nm graphene platelets, 11–15 nm graphene platelets, 3–4 nm nano-graphite, and fullerene (C60/C70). The friction under reciprocating motion was investigated to draw conclusions on the film formation and lubrication mechanism. It was found from microscopic observations that the graphene dry lubricant had the best anti-wear and anti-friction properties. In the absence of pre-rolling, the 2 nm and 11–15 nm graphene platelets demonstrated the most effective lubricating properties, forming a compact film. In contrast, the other dry lubricants were displaced from the raceway.

During sliding contact, adjustments to corresponding parameters can influence the lubricating properties of the aforementioned dry lubricants to some extent. Generally, graphene exhibits better lubrication effects compared to graphite and fullerene. The amount of dry lubricant adhered to the friction surface decreases with friction movement, and thicker layers result in a higher remaining amount, thereby optimizing the lubrication effects. The transfer of graphene platelets to the sliding ball has been substantiated. Pre-rolling the dry-lubricant coating establishes a friction coefficient in a range comparable to oil- or grease-lubricated sliding contacts. This study proved previous investigations on angular contact ball bearings showing the ability of graphene platelets as dry lubricants to protect tribological contacts, especially under reciprocating motion. It is helpful to perform compaction of the respective dry lubricant film to achieve low friction and nearly no wear on the contacting surfaces. First insights could be obtained. The formed film should be investigated in future studies in more detailed nanoindentation and nanoscratch studies.

Research into the long-term durability and stability of the graphene platelet-based dry lubricating film under various operating conditions, such as the influence of moisture, water, or oil, should be considered in further research. The positive influence of graphene platelets mixed with oils and grease showed that positive effects can be expected here. Restrictions due to changed environmental conditions can lead to new findings in the application. The application of graphene platelets as dry lubricant on rotating bearings has to be regarded in further studies. It is expected that, in contrast to oscillating use, it will be more difficult to build up a compact lubricating layer.

It can be concluded that graphene platelets, as 2D materials with excellent sliding properties, offer significant advantages as dry lubricants over fullerene, which acts as a nanoparticle in the contact zone. Graphite nanoparticles exhibit slight wear on the surface, while maintaining good frictional properties. This study validates previous investigations on angular contact ball bearings, demonstrating the efficacy of graphene platelets as dry lubricants in protecting tribological contacts, especially under reciprocating motion. The compaction of the respective dry lubricant film is crucial to achieving low friction and minimal wear on the contacting surfaces. This type of lubricant showcases promising properties, and given the ease of production of graphene platelets through mechanical exfoliation, it is anticipated to gain traction in the market. Potential applications include bearings under reciprocating motion.

Funding: The publication of this article was partially funded by the Open Access Fund of Leibniz Universität Hannover. This research was partially funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), grant number 524080913.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets of the study can be requested from the author.

Acknowledgments: The author would like to thank B.-A. Behrens and N. Mohnfeld from Leibniz University Hanover, Institute of Forming Technology and Forming Machines and Glasmacher and S. Knigge from Leibniz University Hanover, Institute for Multiphase Processes for their support in researching the dry lubrication mechanism of graphene platelets. The author would also like to thank G. Poll (IMKT, Leibniz University Hanover) for supporting these investigations and H.-H. Gatzen (Institute of Micro Production Technology (former Institute for Microtechnology) Leibniz University Hanover) for initiating the investigations on carbon-based nanoparticles. The results presented in this paper were obtained partially within the scope of the project "Dry lubrication and transfer lubrication of rolling contacts by self-regenerating molybdenum oxide coating systems", funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG))—524080913. The author gratefully acknowledge the German Research Foundation for their financial support of this project.

Conflicts of Interest: The author declares no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E.P.; Nika, D.L.; Balandin, A.A.; Bao, W.; Miao, F.; Lau, C.N. Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. *Appl. Phys. Lett.* **2008**, *92*, 151911. [CrossRef]
2. Marinho, B.; Ghislandi, M.; Tkalya, E.; Koning, C.E.; De With, G. Electrical conductivity of compacts of graphene, multi-wall carbon nanotubes, carbon black, and graphite powder. *Powder Technol.* **2012**, *221*, 351–358. [CrossRef]
3. Wang, X.B.; Zhang, Y.F.; Yin, Z.W. Frequent start-stop test study of graphene coatings on journal bearings. *Key Eng. Mater.* **2020**, *841*, 26–35. [CrossRef]
4. Zhang, L.; Lu, B.; Wu, Y.; Wang, J.; Zhang, X.; Wang, L.; Xi, D. Molecular dynamics simulation and experimental study on the lubrication of graphene additive films. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* **2020**, *234*, 1957–1972. [CrossRef]
5. Wu, L.; Xie, Z.; Gu, L.; Song, B.; Wang, L. Investigation of the tribological behavior of graphene oxide nanoplates as lubricant additives for ceramic/steel contact. *Tribol. Int.* **2018**, *128*, 113–120. [CrossRef]
6. Samanta, S.; Singh, S.; Sahoo, R.R. Lubrication of dry sliding metallic contacts by chemically prepared functionalized graphitic nanoparticles. *Friction* **2020**, *8*, 708–725. [CrossRef]
7. Goti, E.; Mura, A.; Wang, H.; Ji, X.; Kong, J. Comparison of the tribological behaviour of various graphene nano-coatings as a solid lubricant for copper. *Appl. Sci.* **2023**, *13*, 8540. [CrossRef]
8. Gu, Y.K.; Cao, L.; Wan, Y.; Gao, J.G. Tribological performance and lubrication mechanism of carbon microspheres as oil-based lubricant additive on aluminum alloy substrate. *Wuji Cailiao Xuebao/J. Inorg Mater* **2017**, *32*, 625.
9. Marian, M.; Song, G.C.; Wang, B.; Fuenzalida, V.M.; Krauß, S.; Merle, B.; Tremmel, S.; Wartzack, S.; Yu, J.; Rosenkranz, A. Effective usage of 2D MXene nanosheets as solid lubricant–Influence of contact pressure and relative humidity. *Appl. Surf. Sci.* **2020**, *531*, 147311. [CrossRef]
10. Nassef, B.G.; Pape, F.; Poll, G. Enhancing the Performance of Rapeseed Oil Lubricant for Machinery Component Applications through Hybrid Blends of Nanoadditives. *Lubricants* **2023**, *11*, 479. [CrossRef]
11. Berman, D.; Erdemir, A.; Sumant, A.V. Graphene: A new emerging lubricant. *Mater. Today* **2014**, *17*, 31–42. [CrossRef]

12. Pape, F.; Poll, G. Investigations on graphene platelets as dry lubricant and as grease additive for sliding contacts and rolling bearing application. *Lubricants* **2020**, *8*, 3. [CrossRef]
13. Nassef, M.G.; Soliman, M.; Nassef, B.G.; Daha, M.A.; Nassef, G.A. Impact of graphene nano-additives to lithium grease on the dynamic and tribological behavior of rolling bearings. *Lubricants* **2022**, *10*, 29. [CrossRef]
14. Nassef, M.G.; Hassan, H.S.; Nassef, G.A.; Nassef, B.G.; Soliman, M.; Elkady, M.F. Activated Carbon Nano-Particles from Recycled Polymers Waste as a Novel Nano-Additive to Grease Lubrication. *Lubricants* **2022**, *10*, 214. [CrossRef]
15. Nassef, B.G.; El-Labban, H.; Al-Oufy, A.; Daha, M.A. Effect of Graphene Addition to Lithium-Based Grease on the Performance of Rolling Element Bearings. *Key Eng. Mater.* **2022**, *913*, 279–284. [CrossRef]
16. Kim, H.J.; Shin, D.G.; Kim, D.E. Frictional behavior between silicon and steel coated with graphene oxide in dry sliding and water lubrication conditions. *Int. J. Precis. Eng. Manuf.-Green Technol.* **2016**, *3*, 91–97. [CrossRef]
17. Xu, L.; Ma, T.B.; Hu, Y.Z.; Wang, H. Molecular dynamics simulation of the interlayer sliding behavior in few-layer graphene. *Carbon* **2012**, *50*, 1025–1032. [CrossRef]
18. Restuccia, P.; Righi, M.C. Tribochemistry of graphene on iron and its possible role in lubrication of steel. *Carbon* **2016**, *106*, 118–124. [CrossRef]
19. Wang, L.; Tieu, A.K.; Ma, M.; Li, J.; Hai, G.; Zhu, H. Potential application of graphene nanoplatelets as a high temperature lubricant for hot rolling. *Friction* **2022**, *10*, 1810–1823. [CrossRef]
20. Kong, S.; Wang, J.; Hu, W.; Li, J. Effects of thickness and particle size on tribological properties of graphene as lubricant additive. *Tribol. Lett.* **2020**, *68*, 1–10. [CrossRef]
21. Vijayaraghavan, A.; Iliut, M. Graphene. In *Springer Handbook of Nanotechnology*; Bhushan, B., Ed.; Springer Handbooks; Springer: Berlin/Heidelberg, Germany, 2017. [CrossRef]
22. Kausar, A. Fullerene Nanofiller Reinforced Epoxy Nanocomposites—Developments, Progress and Challenges. *Mater. Res. Innov.* **2021**, *25*, 175–185. [CrossRef]
23. Suparno, J.; Halim, D.A.; Junaidi Setiawan, A.; Effendy, M.; Jamari, J. Graphite as Dry Lubricant to Reduce Rail Wheels Wear Level. In *Materials Science Forum*; Trans Tech Publications, Ltd.: Stafa-Zurich, Switzerland, 2019; Volume 961, pp. 126–133. [CrossRef]
24. Morstein, C.E.; Dienwiebel, M. Graphite lubrication mechanisms under high mechanical load. *Wear* **2021**, *477*, 203794. [CrossRef]
25. Wen, Y.; Liu, H.; Jiang, X. Preparation of graphene by exfoliation and its application in lithium-ion batteries. *J. Alloys Compd.* **2023**, *961*, 170885. [CrossRef]
26. Yi, M.; Shen, Z. A review on mechanical exfoliation for the scalable production of graphene. *J. Mater. Chem. A* **2015**, *3*, 11700–11715. [CrossRef]
27. Pape, F. *Mikrotribologische Untersuchungen an Wälzlagern mit Polymeradditivierter Fettschmierung*; PZH, Produktionstechn. Zentrum: Garbsen, Germany, 2011.
28. Pape, F. Nano-and Micro-Tribological Investigations of Boundary Layers on Axial Bearing Washers Tested under WEC Critical Conditions. *Lubricants* **2022**, *10*, 198. [CrossRef]