Effects of Graphene Nanoadditive on the Lubrication Performance of Lithium Grease

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Abstract. In this study, graphene nanoplatelets were blended with lithium base grease in the range of 0 wt%-1 wt% amount, and lubrication behaviors were examined by means of four-ball friction test system. First, the graphene and grease materials were observed by scanning electron microscope (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Friction and wear tests were carried out at ambient temperature with 392 N normal load and 1200 rpm speed. Results show that the grease containing 0.5 wt% of graphene reached to the optimum lubrication behavior with minimum friction and wear. Based on the friction test results and wear surface microscopy analysis, the mechanism of lubrication was discussed for better understanding the grease element interactions during frictional shearing actions. It is concluded that the graphene nanoplatelets promote the formation of protective tribofilm in the contact interface, as indicated by EDS and Raman spectroscopy, which is crucial to the improvement of anti-friction and anti-wear behavior.

Keywords: Graphene; Lithium Grease; Characterization; Friction; Wear

1. Introduction

Strong friction forces between rubbing parts result in wear of components, followed by the break-down of the equipment. It is important to fully comprehend the phenomenon of friction, and to control the frictional properties of mating parts in order to save energy and lower CO_2 emission, in the same time prolonging the lifetime of mechanical parts. According to Luo and Zhou [1], friction reduced by 18% results in about $90 billion savings and CO_2 emissions reduction by 290 million tons per year, with an associated huge decline in PM2.5 emissions. Hence, the research and development of new cutting-edge tribological means has become a paramount purpose for scientific community so as to better the environment, reduce pollution and to save energy. Superlubricity could be useful in solving the wear problem, particularly in bearings and heavy-duty pin-bushing joints. Often malfunctions take place due to the wear and fatigue of sliding and rolling bearings which limits the lifetime of bearing parts. 2D materials are the most suitable nanoadditive materials for lubricants due to their low coefficient of friction and great load-carrying capability. Superlubricity behaviors of graphene is superior than other nanomaterials as it forms protective coating on the frictional surface by covering surface roughness, healing wear pits, carrying loads, preventing direct metal-to-metal contacts, endowing low shear stress between adjacent layers, and finally causing inter-laminar sliding [2].

Since its discovery in 2004, graphene has been explored extensively, because it has unique easy shearing layer structure, outstanding mechanical and electrical properties. By possessing these distinctive features, graphene stands out as a novel candidate for tribological challenges [3]. In science, graphene is known as the thinnest and strongest material with about 0.35 nm layer thickness, and composed of hexagonal (sp^2) carbon atoms looks like honeycomb with Young's modulus of about 1 TPa [4]. In opposite, frail Van der Walls forces attach the adjacent graphene layer structure, so the layers can effortlessly slip to each other with low strength of shear. Moreover, the specific surface area of the graphene is larger rather than other remaining 2D materials which is preferred to cover more frictional wear surfaces by absorbing and mitigating the probability of metal-metal contacts, and facilitating the antiwear [5]. Thus, it is often favored by many scholars to utilize in the field of superlubricitive technology.

Grease lubricants are very prevalent and widely employed in the mechanical engineering to prevent the excessive friction and wear of the contact pairs [6]. Yet, with the fast growth of industry equipment, grease lubrication is insufficient to perform well, and breaks-down between harsh contact conditions. Meanwhile, the oil release capability of the grease thickener is not often adequate to endure the compressive forces. So, over decades nanoadditives were incorporated to the grease lubricants to increase the tribology properties and to boost the extreme pressure (EP) capacities [7, 8]. However, several factors should be considered on the amount when it is synthesized into the colloid grease. The graphene is effective as an additive only when its kind and amount is controlled in the lubricant, otherwise the small and large portion of it can cause negative tribological effects. Small amount of graphene in grease network can serve to the proper rheological process, while the large amount may disturb the grease soap fibers and result in agglomeration in the direction of lubrication inlet. Ren et al. [9] suggested the right amount of nanoadditive concentration between 02 wt% to 2 wt% in base oil, while four-ball friction tests by Wu et al. [10] indicated the concentration of 0.075 wt% few-layered graphene to be optimum lubricating performance by reducing wear in 43% and friction in 27% considerably. Liang et al. [11] fabricated the graphene by chemical modification and ultrasonic-assisted ball milling method to evenly disperse in the lubricating grease. In their case, 0.2 wt% graphene-modified grease improved the antiwear and antifriction performance, while the graphene concentration of 0.3 wt% was best for corrosion resistance. However, these findings should be further assured to amplify the lubricating process involving the actions of various interrelated forces in grease than a simple base oil. Thus, it has been a major task to research the effects of graphene concentration on the molecular mechanism of grease lubrication, and to obtain the tribological optimal additive amount in base lubricant.

This work attempts to explore the effects of graphene nanoplatelets as an additive on the lubricating behavior of grease. Graphene-PAO 6 dispersion oil was produced with dissimilar concentration and synthesized with lithium grease by high-shear mixing and homogenizing methods. Before friction and wear tests, grease and graphene material characteristics were conducted by microscope tools to find out the layer thickness, lateral dimensions and grease soap microstructure. Tribology evaluations were made by employing four-ball friction machine where one steel ball rotates against three fixed steel balls in the presence of grease lubricants. Wear surface condition of the steel ball specimens were carefully observed by SEM and Raman spectroscopy to reveal possible lubrication and wear mechanisms.

2. Experimental Details

2.1 Materials

Graphene nanoplatelets (GNP) material with 99.5% purity and 31.65 m^2/g surface area was bought from XFNano Materials Tech (Nanjing, China). The lateral size and thickness of the graphene sheets are described by the manufacturer as 1-3 μm and 1-5 nm, respectively. NLGI 1 grade lithium grease with drop point temperature 200°C was utilized as a base grease. Work penetration is about 310 mm^{-1} at ambient air for this grease which is widely used in rolling and sliding bearing applications from -45°C to 150°C.

2.2 Characterization Techniques

Microstructure of the pristine graphene powder morphology was captured by scanning electron microscope (HITACHI, Japan) at 15 kV. Nanostructure of the graphene is analyzed by transmission electron microscope (Thermo Scientific, USA) with probe at 200 kV current. Raman spectroscopy (Renishaw plc, Wotton-under-Edge, UK) with 532 nm excited laser was used to examine the quality features of graphene.

Washed base grease thickener microstructure was also observed by SEM. Small amount of grease sample was put into n-heptane and sonicated for 1 hour to completely dissolve the base oil, followed by high-speed centrifugation (Tdl-500, China) at 20,000 rpm for 20 min. Then the achieved white sample was vacuum dried at 90°C for 45 min prior to the SEM analysis.

2.3 Graphene and Grease Dispersion

Particular amount of graphene powder is added into PAO 6 base oil and dispersed using magnetic stir at 80°C and ultrasonic probe for 3 hours to develop fine exfoliation and dispersion. Then, prepared solution was blended with base grease at 0.05 wt%, 0.1 wt%, 0.5 wt% and 1 wt% concentrations through high-speed mixer (Flacktek SpeedMixer, USA). Speed mixer was set to 3500 rpm and 15 min to produce a uniform dispersion. Afterwards, the nanogreases went through three-roll grinding mill for final homogenous graphene-modified grease.

2.4 Friction and Wear Test

Tribological properties of the nanogrease lubricants were tested in four-ball friction and wear machine (MS-10A, Xiamen Tenkey Automation, China) as shown in Figure 1. GCr15 high chromium steel balls in 12.7 mm diameter, 62 HRC hardness and 0.02 µm (Ra) surface roughness were used as sliding parts with prepared nanogreases. Steel balls were cleaned before each test in ethanol with ultrasonic bath. Standard test method (ASTM D2266) is employed for wear preventive characteristics of the available greases to confirm the coefficient of friction and wear scar diameter (WSD). The applied normal load was 392 N with 1200 rpm sliding speed, and run for 1 hour at 75°C. All tests were repeated three times for reproducibility. Once the friction test was completed, the fixed lower balls were taken to measure the average wear scars on the embedded microscope with 10 µm accuracy. Samples were cleaned in ethanol to remove the oil residuals, then wear scar topographical data was evaluated in 3D profiler platform (NexView, Zygo Corporation, USA). Finally, the worn surface morphologies were examined by SEM/EDS and Raman spectroscopy to conclude the possible mechanisms of wear and lubrication.

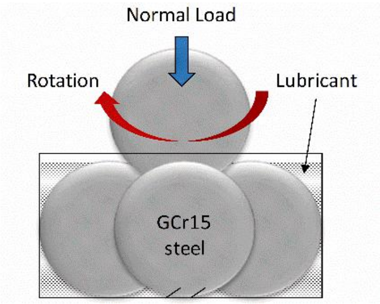

Figure 1. Four-ball Friction Test Method

3. Results and Discussion

3.1 Microstructure Characterization

Figure 2a shows SEM morphology of as-received pristine graphene sheets where the thin nano-flakes are exfoliated and overlapped each other. For better morphology results, small amount of graphene is dispersed in ethanol with ultrasonic process. TEM sample in Figure 2b was further refined with non-polar solution, resulting in transparent and ultra-thin nanostructure. Overlapped graphene layers are visible in darker zones as curving or folding with each other. Inset picture in Figure 2b indicates the SAED (Selected Area Electron Diffraction) spots in orderly position which means that graphene multilayer nanostructure is well-organized in crystalline network.

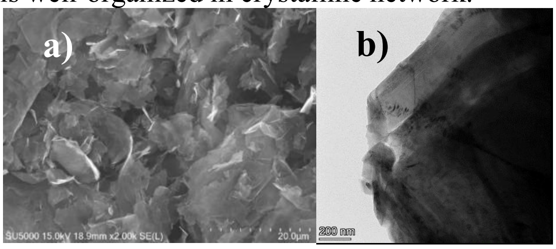

Figure 2. SEM Morphology of As-Received Graphene (a), TEM Characterization with SAED Pattern Inset (b)

Raman spectroscopy results provide more detail to distinguish the graphene structural characteristics whether it is ordered or disordered position as in Figure 3. Well known D and G bands are respectively situated at 1350 cm^{-1} and 1580 cm^{-1}. It is known from the literature that D peak represents unstructured carbon disorder deriving from symmetrical A1 k-mode phonons, while G band ordain extended Sp^2 hybrid vibration of carbon atoms in hexagonal lattice [12]. The lattice disorder can be estimated by the intensity of D peak to G as a ratio (for example I_D/I_G=0.31 in our work). Thus, the flaws and deficiency in the graphene structure rise as the ratio of intensity increase. Moreover, wide-ranging 2D peak prevails at 2715 cm^{-1} as an indicator of secondary order 2-phonon, demonstrating well-built frequency dominion by the spectrum laser excitement.

Figure 4 shows the microstructural SEM morphology of lithium thickener after the base oil is washed out. It is obvious that lithium soap fiber is long and entangled as a sponge with many gaps inside. It is assumed that the base oil is kept inside the fibers by nano-mechanical absorption, preventing the free oil flow. The size of the thickener fibers is seen a few microns long with tube-like 70-90 nm diameter.

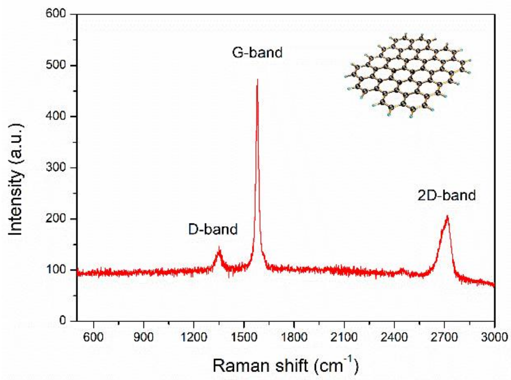

Figure 3. Raman Spectrum of Pristine Graphene

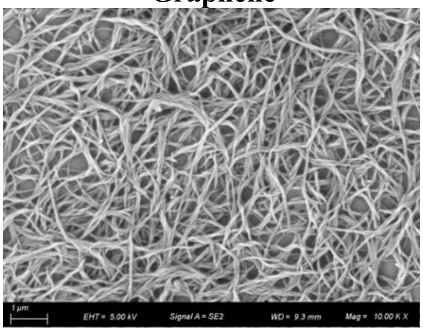

Figure 4. SEM Morphology of Lithium Soap after Base Oil Extraction from Thickener Material

Czarny suggested that roughly 75% amount of base oil is kept inside the thickener fibers by capillary forces while the remaining (about 25%) is linked by inter-molecular attractive forces [13]. This mechanism of sponge-like thickener structure is crucial for frictional interfaces as it provides lubricity by releasing oil under the shear forces.

3.2 Tribological Properties

Friction coefficient curves as a function of time, the average coefficient of friction (COF) and WSD are given in Figure 5 under various graphene concentration. Results indicate that the COF and WSD are reduced considerably in the presence of graphene nanoplatelets by boosting the anti-wear and anti-friction properties of the lubricant. It is noteworthy that when the graphene amount is reached to 0.5 wt%, the lowest COF is experienced (0.062) by reducing 30% down, thus endowing the grease lubricant with its most optimum tribological state. When the additive concentration exceeds this value, friction and wear increases again due to the extra graphene agglomeration. Similarly, the size of WSD is in the same trend with the average COF in all cases. Wear is experienced 20% reduction in 0.5 wt% graphene additive.

Three-dimensional topographical surfaces and two-dimensional cross-section profiles for wear scars lubricated by base grease and 0.5 wt% GNP consisting grease are given in Figure 6. The overall worn area became smaller in size with grease consisting GNP 0.5 wt%, and having shallow depth of 0.9 μm. In this condition, the graphene lubricant is considerably mitigated the serious abrasion by the friction asperities. It is clear that GNP nanomaterials alleviate the wear streaks and irregular surfaces compared to the lithium grease without GNP additive.

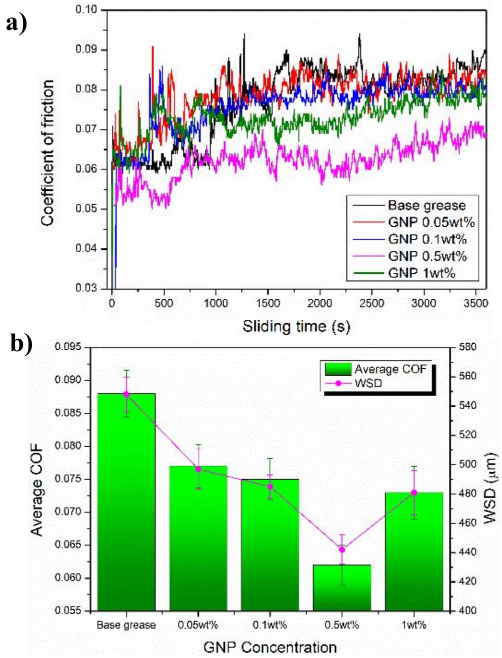

Figure 5. Friction Coefficients as a Function of Time (a), Average COF and WSD (b) for Various GNP Concentration.

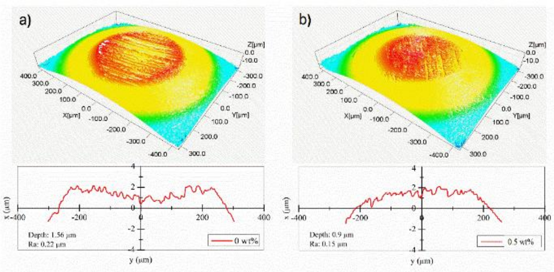

Figure 6. Worn Surface Topographies of Steel Balls Lubricated by 0 wt% Grease (a), and 0.5 wt% GNP Concentration (b), with Corresponding Cross-sectional Profile

3.3 Wear Surface Analysis

Wear and lubrication mechanisms are studied to further understand the effects of the nanogrease on wear and friction behaviors by SEM, EDS and Raman spectrum. Figure 7 displays SEM morphologies of wear scars under 0 wt% and 0.5 wt% GNP lubrication, and corresponding magnification spots and C element in wt%. The frictional surfaces shown in Figure 7a and b display abrasive scratches and seriously plowed resulting in an irregular roughness under the base grease lubrication. Wear delamination and micro-pits can be observed owing to severe lubrication starvation and direct steel contact. In Figure 7d, graphene adsorption on the wear surface is obvious as a dark spot, suggesting that with the lubrication of GNP additive, graphene deposits and forms as an anti-wear protection against the steel counterface. This might be the key responsibility of the graphene to play as main tribology enhancement. Especially, some of the severe wear surfaces seems to be covered by graphene film deposition. From these examinations and performances, it can be assumed that the GNP layers avoid the direct metal-metal contact as it builds tribo-chemical layer in contact interface, therefore tremendously ameliorating anti-wear capability [14]. Additionally, it can be noted that easy-shearing behavior of GNP is prone to inter-layer sliding because of weak bonds under shearing force, encouraging anti-friction capability of grease [2].

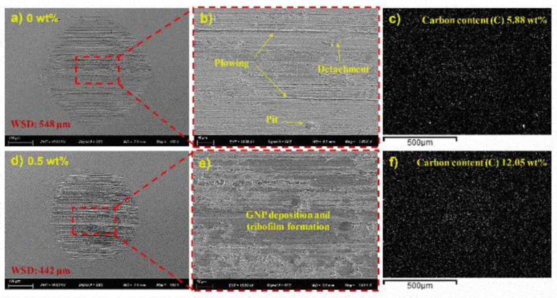

Figure 7. SEM Wear Scar Morphologies and EDS for C Element for Rubbing Parts under Base Grease (a, b, c), and Optimal GNP Concentration (d, e, f)

Energy dispersive spectroscopy analysis in Figure 7c and f gives the C content in wt% for the wear scars inside the rectangle dashes in red. It assures our previous discussions about the existence of tribo-film deposition on the wear interface by GNP particles. Even under the grease lubricant without GNP additives, there is some content of carbon elements because of the steel base composition and carbonization during the rubbing and tearing process. It is interesting that C elements are detected with more agglomeration when steel balls are slid with 0.5 wt% GNP additive (Figure 7f). As a matter of fact, extra amount of graphene particles could result in more coagulated networking in colloid grease owing to the tendency of re-stacking [10].

Additionally, Raman spectrum in Figure 8 provides supplementary information about the lubricating mechanism by exposing the residual peaks of GNP spectrum on the wear scar. Raman spectrum captured on the wear scar of friction contacts with GNP 0.5 wt% grease. It is confirmed that the prominent peaks of D and G bands are confirmed at 1331 cm^{-1} and at 1593 cm^{-1}, respectively. This concludes that the GNP particle absorption film is strongly attached to the wear surface during the test. As we mentioned before, the ratio of intensity I_D by I_G have seen a significant rise at 1.23, which can be attributed to the serious disorder and layer flaws of the graphene structure [5, 12]. It is because the tearing and re-stacking of GNP nanoparticles lead to a greater amount of Sp^3 carbon formation. Extra increase in the intensity ratio would cause the graphitization on the wear scar due to the more agglomeration and shear tearing [2, 9, 14]. According to the above findings, we can provide the fact that GNP adsorbed on the wear surface and acted as a shield against the frictional counterface. Due to its tremendous mechanical strength, it can endure and inhibit the adhesion and abrasion.

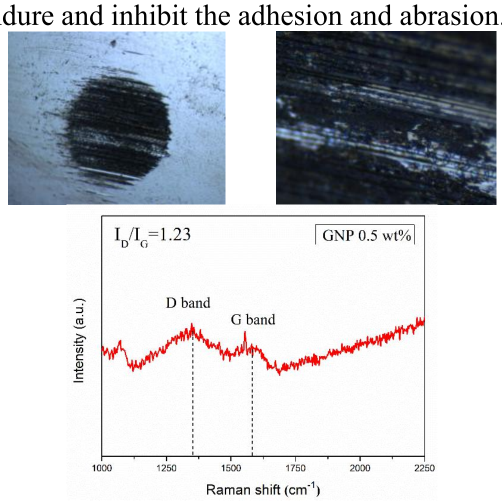

Figure 8. Raman Spectrum of Wear Surface with Optimal GNP 0.5 wt% Concentrated Lubricant

4. Conclusion

According to the obtained results, we can conclude that, the graphene nanoplatelets demonstrated exceptionally well in the lithium grease lubricating behavior as an additive. Microstructural characterizations of lubricant materials were evaluated by microscopy equipment which is very important to understand the nature of lubricating process and wear mechanism. Four-ball friction and wear tests were carefully carried out with prepared nanolubricants. Results showed that the friction and wear is significantly mitigated by 30% and 20% respectively, with GNP 0.5 wt% dose. Post-friction test surface analysis provides the solid evidence of wear-protective film formation by GNP nanoparticles, therefore, improving the anti-wear performance of grease. This study can serve to the academic and industry community to comprehend the lubrication process behind the graphene along with grease soap fiber and base oil in the contact interface, and to use it in right amount in many tribology cases.

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