Tribological Properties of a Self-Repairing Material: Functionalized Graphene/montmorillonite Nanosheets Lubricant Additives

Yujunwen Li  
Nanjing University of Science and Technology

Rui Yang  
Nanjing University of Science and Technology

Wu Lei  
Nanjing University of Science and Technology

Qingli Hao (✉ qinglihao@njust.edu.cn)  
Nanjing University of Science and Technology  https://orcid.org/0000-0002-4491-4563

Research Article

Keywords: Graphene, Tribological Properties, Lubricant, Self-repairing

DOI: https://doi.org/10.21203/rs.3.rs-441747/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.  Read Full License
Abstract

The functionalized graphene/montmorillonite (FG/MTT) nanosheets were synthesized through chemically bonding by a simple, green method, which has remarkable dispersion stability in oil and its lubricating performance was evaluated by a four-ball tribometer. The test results show that FG/MTT has a preeminent lubricant property when the concentration is 0.4 mg/ml. Compared with the bare oil sample, its average friction coefficient (FC) and wear scar diameter (WSD) decrease by 50.4 % and 13.2 %, respectively. The synergistic effect between FG and MTT was further explored by comparing the lubricant mechanism of the different additives. After synthetically analyzing worn surface by means of scanning electron microscopy and X-ray photoelectron spectroscopy, the lubrication mechanism of the FG/MTT nanocomposite as oil additive is discussed and postulated: The FG/MTT with weak interlayer adhesion is filled between the friction pairs to avoid contact and clinging of some asperities, and the sliding between the layers plays a role in lubrication. Furthermore, FG/MTT will react with the surface of the friction pair to form a repair layer composed of Fe$_2$O$_3$, SiC, SiO$_2$, and aluminosilicate, mending the grinding surface and promoting the hardness after friction.

1. Introduction

Lubricating oil is widely used in various fields as a lubricant that reduces mechanical loss and improves work efficiency. It consists of base oil and additives. The properties of additives have an important influence on the lubricating performance of lubricating oil. To meet the requirements for lubricating performance in different fields, many lubricating oils containing diverse additives have been produced. Common lubricant additives include the following categories: soft metal nanomaterials (nano copper, nickel, etc.), borate materials (lanthanum borate), carbon nanomaterials (carbon nanospheres), and so on.[1, 2] However, as the performance requirements become multifarious, it is difficult for a single additive to fulfill the requirements. Therefore, the research on composite lubricant additives is becoming crucial. Simultaneously, in addition to ensuring that additives have good lubricating properties, the dispersibility of additives in the base oil is also one of the indicators for evaluating lubricants. Lubricating oil additives with good dispersion stability have better lubricating properties.

Graphene Oxide (GO) is a new type of layered carbon nanomaterial with macroscopic dimensions, which has a nanometer-level thickness, but can be stretched indefinitely on the same plane. Multilayer graphene is prone to sliding between layers, so it has good lubricating properties. Mao et al.[3] analyzed the lubricating properties of three different morphologies of reduced graphene oxide, and the result showed that the morphology of the graphene sheets directly affects its lubrication performance. The lubricity of graphene is not only affected by structural properties such as surface defects and stacking methods but also related the presence of some hydrophilic groups such as hydroxyl and carboxyl groups on the surface, which may cause agglomeration and sedimentation when dispersed in oil. To ameliorate dispersion, domestic and foreign studies have also conducted further investigations on this issue. In addition to being a single-component additive, graphene is compounded with other additives and added to the base oil to further improve the performance of the lubricant. Meng et al.[4] successfully loaded
nano-gold particles on multi-graphene oxide to prepare nano-Sc-Au/GO composites with supercritical carbon dioxide, which has good tribological properties.

As a natural material with abundant reserves and low cost, silicate minerals have been widely developed and used in various fields. In recent years, the research on silicate materials used as lubricant additives has also exploited rapidly. Wang et al. [5] added serpentine nanoparticles as lubricant additives to base oil, and the friction coefficients and wear spot diameters were reduced by 22.8 % and 34.2 %, respectively. Montmorillonite (MTT) is a layered mineral that is composed of a nanometer-thick negative silicate layer on the surface and is accumulated together by the electrostatic action between layers. Its main component is \((\text{Al, Mg})_2(\text{SiO}_10)(\text{OH})_2\cdot n\text{H}_2\text{O}\). The crystal cell in its crystal structure comprises two layers of silicon-oxygen tetrahedron sandwiched with a layer of aluminum oxygen octahedron. Some studies have shown that montmorillonite as a lubricating additive has the excellent self-repairing ability for the surface of friction pair. Still, the repairing effect only will be valid after a long time of friction and wear test[6, 7]. As a natural silicate mineral, even after surface modification, it is still arduous to stably disperse in the oil for a long time. Hence, it has a crucial impact on the tribological properties.

Herein, functionalized graphene oxide (FGO) and its composites with silicates were synthesized, and their tribological properties and abrasion self-repairing performance were systematically investigated. Through simple hydrothermal compounding, the MTT sheets were successfully intercalated and reduced in the surface of FGO to obtain FG/MTT materials that can be stably dispersed in lubricating oil. The prepared nanocomposite of FG/MTT was used as lubricant additive in 15w40 engine oil, and its lubricating performances were evaluated by a four-ball tribometer. After the synergistic effect of the two materials, the material, as a lubricant additive, not only has excellent antifriction, antiwear, and self-healing ability but also can form a self-repairing layer which improves the surface hardness of the friction pair.

2. Experimental Section

2.1 Materials

Montmorillonite was purchased from Zhejiang Fenghong Chemical Co., Ltd (Zhejiang, China). Silane coupling agent (KH550, chemically pure) was purchased from Shanghai Alading Biochemical Technology Co., Ltd. Ethanol (analytically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The GO was synthesized according to a modified Hummers method in our laboratory as previous report[8].

2.2 Synthesize of the Functionalized graphene oxide

The GO was modified with a silane coupling agent (KH550) to get the functionalized graphene oxide (FGO). Firstly, 0.025 wt % GO suspension was prepared in 160 g water under ultrasonication, then 6 mL KH 550 was added slowly in the GO suspension. The mixture was kept stirring for 60 min at room temperature, and was transferred into the flask and stirred for 2 h at 80 °C to get the FGO. After
centrifugation, the solid was kept in the Falcon centrifuge tube and washed in deionized water three times.

2.3 Synthesize of the functionalized graphene/montmorillonite

1.6 g montmorillonite was ground by wet grinding of 25 ml ethanol in mortar for 30 min and was dispersed into 50 ml water by ultrasonication for 2 h. The montmorillonite suspension was added slowly into the FGO aqueous suspension and stirred for 2 h at room temperature. The mixture was transferred into hydrothermal reactor kettle for 2 h at 120 °C to get the functionalized graphene/montmorillonite (FG/MMT). The solid was kept in the Falcon centrifuge tube and washed in ethanol three times by centrifuge to get the wet sample of FG/MMT.

2.4 Characterization of FG/MMT

Morphology analyses of samples were performed on a transmission electron microscope (TEM, JEOL JEM-2100) and the field emission scanning electron microscopy (SEM, Quant 250 FEG) with energy-dispersive spectrum (EDS). For the TEM observation, the samples were firstly dispersed in ethanol by ultrasonic treatment and then dropped on carbon copper grids. Fourier transform infrared spectroscopy (FTIR) was recorded on Nicolet IS10 (ThermoFisher) with Ever G10 optical source. The powder X-ray diffraction pattern (XRD) analyses were carried out on a Bruker D8 Advance diffractometer with a Cu Kα radiation (λ = 1.5406 Å), whose scanning angle ranged from 5° to 80° of 2θ. Additionally, X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Escalab 250 (U.K.) at the monochromatic Al Kα (150 W, 500 μm and 1486.6 eV) radiation.

2.5 Tribological Test

The tribological properties were performed on an MRS-10G four-ball tribometer (Jinan Yongce Industrial Equipment Co., Ltd., China.) under 197 N with a rotary velocity of 600 rpm at room temperature for 3600 s. The friction pair consists of four identical balls, one rotating on the top while the other three fixed beneath. The balls were composed of GCr15 bearing steel with a diameter of 12.7 mm (Shanghai Steel Ball Plant CO., Ltd., China.). All test-section components were cleaned ultrasonically in petroleum ether for 3 min and dried in the air before tests. The friction coefficient was recorded automatically by a strain sensor, and the wear scar diameter was measured by a 15J optical microscopy (Shanghai Optical Instruments Sixth Factory Co., Ltd., China). Each scar was surveyed at least five times to guarantee the standard deviations less than 5%.

2.6 Analysis of Worn Steel Surfaces

The surface morphology and composition of the steel balls after the tribological test were analyzed with SEM (Quant 250 FEG) with energy-dispersive spectrum (EDS) and XPS (Thermo Escalab 250).

3. Results And Discussion
3.1 Characterization of Materials.

FG/MMT was produced with MMT and FGO by the hydrothermal method, and the synthesis process of FGO and FG/MMT is shown in Fig.1. Fig.2 (a) and (b) show the TEM diagram of FG/MMT composites with different magnifications. From the image, it can be seen that montmorillonite layers are uniformly loaded on the large folded graphene oxide layers.

The FTIR spectra of the samples in Figure 3(a) show that the typical peaks of GO appear at 3300, 1720, 1600, and 1050 cm\(^{-1}\), corresponding to the presence of hydroxyl, carboxyl and epoxy groups, respectively. Compared with GO, the disappearance of the peak at 1720 cm\(^{-1}\) and the new peaks at 1560 cm\(^{-1}\) (N-H stretching vibration) and 1460 cm\(^{-1}\) (C-N stretch of amide) of FGO indicate the formation of C-N-C bands in the FGO sample, intensely supporting the presence of the amide groups on the FGO, which means that the amino group on the silane coupling agent reacts with the carbonyl group on GO to form an amide bond[9, 10]. The disappearance of the bands near 1150 cm\(^{-1}\) (symmetrical stretching vibration peak of the epoxy group) demonstrates the reaction of amino groups of KH550 with the epoxy group on GO. In the case of FGO, the bands near 1100 cm\(^{-1}\) correspond to the stretching vibration peaks of Si–O of Si-OH. The asymmetric peaks at 2920 and 2850 cm\(^{-1}\) are assigned to the C-H stretching vibrations of the alkyl group (-CH\(_2\), -CH\(_3\)), derived from the alkyl chain of the silane coupling agent KH550. It is proved that the KH550 molecules successfully bonded to the graphene oxide surface to form the functional graphene oxide. As the infrared spectrum of MMT exhibits, the peak at 3610 cm\(^{-1}\) corresponds to the stretching vibration peaks of –OH groups, and the peak near 980 cm\(^{-1}\) is assigned to the stretching vibration peaks of Si–O of Si–O-Si, which could serve as a hydrogen-bonding sites for the functional groups of FGO[11]. Compared with the infrared spectra of single FGO and MMT, the FG/MMT composite shows the blue-shifts of asymmetric peaks at 2990 and 2900 cm\(^{-1}\) and the blue-shift of the stretching vibration peak of Si-O bond at 1010 cm\(^{-1}\), revealing that the FG/MMT composites were successfully synthesized[12, 13].

The TEM images of composites shown in Fig.1 also demonstrate this.

The XRD patterns of the GO, FGO, MMT, and FG/MMT are shown in Fig.3(b). There is a strong (001) diffraction peak at \(2\theta = 11.45^\circ\)in the XRD pattern of GO, indicating that the layer spacing is 0.77nm. In the XRD pattern of FGO, the strong peak at \(2\theta = 11.45^\circ\) almost disappears, and a relatively broad peak appears at \(2\theta =23.52^\circ\), which corresponds to the characteristic peak of graphene (002)[14, 15]. It shows that the carbon structure of FGO becomes more disordered due to the graft of silane coupling agent on it. The layer spacing of (001) can be calculated to be 1.296 nm based on the (001) diffraction peak of MMT at \(2\theta = 7.117^\circ\) according to Bragg's law[16]:

\[
2dsin \theta = n\lambda
\]  

(1)

The typical diffraction peak of MMT also can be found in FG/MMT composite, and the (001) diffraction peak at \(2\theta = 5.79^\circ\) indicates the layer spacing is 1.58 nm according to Eq. (1). It means that the MMT is successfully intercalated into FGO layers[13].
After graphene oxide was treated with a silane coupling agent, the functionalized graphene oxide (FGO) was produced. The grafting of KH550 with GO makes its crystal plane spacing increase. After MMT is introduced into FGO during the hydrothermal reaction, the MMT sheets are inserted between the graphene oxide sheets to make the crystal plane spacing larger. The enhancement and leftward shift of the diffraction peak of the MMT (001) crystal plane in the composite products also prove that the montmorillonite lamellae are intercalated successfully between graphene lamellae. From these results, it can be concluded that the FG/MMT composite gets a larger interlayer spacing after intercalation.

The Raman patterns of the GO, FGO, and FG/MMT are shown in Fig.3(c). The D band at around 1340 cm⁻¹ shows the vibrations of disordered sp³ carbon atoms; the G band at 1585 cm⁻¹ reflects the vibrations of sp² carbon atoms in the hexagonal lattice of graphene. The ratio of the intensity of the D and G band (I_D/I_G) is in direct proportion to the disordered degree of the graphene lattice[17]. The I_D/I_G of FGO (1.081) is higher than the I_D/I_G of GO (I_D/I_G = 0.986), indicating that the FGO is more disordered with more defects in the surface. The I_D/I_G of FG/MMT (0.920) is lower than that of FGO and GO, indicating that the surface defect of FG/MMT decreases due to the reduction of FGO and the MTT chemically bonded with KH550 to form FG/MMT composite during the hydrothermal process.

3.2 Friction and Wear Performance

The images of FG/MMT composite dispersed in the 15w40 engine oil after 30 and 120 days are presented in Fig.4. The dispersion stability of additives in lubricating oil is a considerable standard to evaluate the performance of additives[18, 19], which affects the tribological properties of oil samples. After 30 days of sedimentation experiment, it is obvious that the FG/MMT composite can be well-dispersed without sediments at 0.4 and 1.0 mg/ml. While after 120 days, the upper color of the two concentrations FG/MMT oil sample is similar, which is deeper than the 15w40 oil sample. However, there is a little sediment on the bottom of the bottle for the oil sample at 1.0 mg/ml, but can be re-mixed uniformly by a slight shake. It means the composite materials have excellent dispersion stability in oil. Moreover, the dispersion stability of the composite is more remarkable at a lower concentration of 0.4 mg/ml.

According to the conclusion of the sedimentation experiments, the oil samples of FG/MMT at 0.4mg/ml with good dispersion were prepared. For comparison, the bare oil and oil samples of MMT, GO, and FGO were also prepared. The tribological tests were carried out under the same conditions, and the results are shown in Fig.5. It presents the variation of friction coefficient (FC) of different oil samples overtime in the tribological test. It can be seen from Figure 5a that the FC values of several oil samples except for FG/MMT basically increase first and then decrease gradually. This may be explained as follows: During the process of friction, some large particles are squeezed by the asperities and broken into tiny particles by the action of mechanical motion, resulting in the increased FC. With the increase of time, the small particles could uniformly fill the friction surface to form a lubricant layer, thereby decreasing the FC.
The FC curve of the bare 15w40 oil sample reached its peak at 890s, about 0.129, and dropped to 0.120 at the end of 3600 s. For the oil samples containing GO, FGO, MTT, and FG / MTT, the friction coefficient declines to 0.090, 0.095, 0.105, and 0.051 at 3600 s, respectively, indicating that each oil sample has a certain lubricating effect with antiwear and antifriction properties for each additive, due to the special two-dimensional layered structure of the above additives. The layers could make relative slides easily with each other, which has the effect of reducing friction. However, when only MTT or GO is added, the oscillation of FC is relatively immutable, but the lubrication performance of the base oil is slightly elevated.

Compared to bare oil sample, GO oil sample has the same initial FC and the analogous ascent trend as bare oil in the first 600 s but shows the fast decrease rate of FC during the long-term test. It means GO shows some antiwear and antifriction properties as reported[20, 21]. GO and FGO oil samples demonstrate a similar fluctuation tendency of FC over time. Still, FGO presents a lower FC over the time range of the experiment, which indicates FGO oil exhibits more advantageous antiwear and antifriction properties than GO oil. It might be due to the better dispersion in the presence of KH550 modification. In the case of MMT oil sample, its long-term tribological property surpasses that of bare oil but worse than the GO and FGO oil samples.

As for FG/MMT oil sample, it shows the lowest initial FC value; moreover, the FC continues to decrease from the beginning and end to the lowest value of 0.051 at 3600s compared to the rest samples. Therefore, the FG/MMT oil sample shows the best property compared to GO, FGO, MMT, and bare oil samples. Moreover, the excellent tribological performance of FG/MMT reflects the different mechanism from the test, which will be investigated further.

Fig.5(b) shows the average FC values calculated from the tribological test in 3600s of oil samples containing different additives. It can be seen from the figure that the average FCs of 15w40 oil and oil samples containing MTT, GO, FGO, and FG/MMT are 0.121, 0.109, 0.106, 0.080, and 0.060, respectively. Wherein the average friction coefficient of FG/MMT is 50.4 % lower than that of 15w40 base oil, which proclaims the intense enhancement of the lubricating properties. It was confirmed that the prepared FG / MTT as the additive material is excellent in friction reduction.

The wear scar diameter (WSD) is also one of the common indexes to evaluate the lubrication performance[22]. The WSD of the steel ball after the four-ball tribometer test was measured, and the average WSD of the steel balls in different oil samples was calculated. The result is shown in Fig.5(b). When no additives are added, the average WSD of the steel ball tested in the 15w40 oil sample is 0.333mm, and after adding different additives, the WSD becomes smaller, indicating that the addition of different additives promotes the 15w40 oil lubrication properties. Moreover, the average WSD of FG/MMT oil sample is at least 0.289 mm, which is 13.2 % lower than that of base oil sample, proving FC/MMT as an additive with the eximious ability to reduce friction.

The FC and WSD for the FG/MMT oil sample with different concentration (0, 0.2, 0.4, 0.8, 1.0 and 1.6 mg/mL) tested at 197 N and 600 rpm for 3600s are shown in Fig.5(c). The change range of the FC can be
seen from the figure. The fluctuation range of the 15w40 engine oil is the largest, and that of the FG/MMT oil sample is relatively smaller, which reveals that the composite material has preeminent anti-friction ability. When the concentration of FG/MMT is 0.2 mg/mL, the additive can effectively reduce the FC, but the anti-friction and anti-wear ability is not as good as that of the 0.4 mg/mL sample. The reason is the deficiency of material in the oil sample, and it cannot be evenly covered on the wear surface during the friction and wear process so that there are vacancies in some places. The curves of FC and WSD with concentration are concave, and both of them reach the lowest value at 0.4 mg/ml. The FC and WSD reduce 50.4 % and 13.2 % compared to the base oil, respectively. The FC and WSD increase gradually with concentration rising to 0.8~1.6 mg/mL, which declares that the higher concentration of the composite hurts improving the lubricating performance. It would be resulted in the agglomerate of the composite at a high concentration.

FG/MMT composite not only has excellent lubrication performance of antifriction and antiwear but also contains oil-friendly functional groups to promote dispersion. Through the bonding and intercalation of two functional materials, the agglomeration between the composite materials can be effectively reduced, and the composite materials can be more stable and evenly dispersed in the lubricating oil for a long time.

Fig.6 shows the SEM images of the worn surface of friction pair in different oil samples after tested for 1 h. With comparison, the WSD of the 15w40 oil samples (Fig.6a and b) is the largest, and the wear surface is rough with a small amount of wear traces. In contrast, the wear scars formed in the FGO oil sample (Fig.6c and d), MTT oil sample (Fig.6e and f), FG/MMT oil sample (Fig.6g and h) become smaller in sequence. Although the WSD of the MTT oil sample is reduced compared with that of the 15w40 oil sample, there are more apparent scratches on the friction surface of MTT oil sample. This is probably because the particles of MTT material are relatively large and stiff, which damage the friction surface in the initial wear process. Both the wear surfaces in FGO and MTT oil samples still show scratches. However, it is worthy to note that the surface of wear scar in FG/MMT oil sample becomes much smoother, even no evident scratches observed in Fig.6 (g and h). It indicates that FG/MMT exhibits good antiwear property and self-repairing function, which can also be proved by further lubrication properties. As carefully observed, the grooves and valleys of this worn surface seem to be filled with the uncharacterized materials (Fig.6g and h).

During the sliding process, all the additives including FGO, MTT, and the synthesized FG/MMT composites are easily deposited on the contact pair surfaces and thus form a protective film, which can smooth the surfaces and reduce friction and wear effectively. Compared to FGO and MTT additive, the self-repairing performance of FG/MMT is the best.

Fig.7(a-d) are the EDS diagrams of the selected areas in Fig.6(b, d, f, h) of the wear scars in the FGO, MTT, and FG/MMT oil samples, respectively. Compared with the bare oil sample, the FGO sample exhibits the increase in the contents of carbon and oxygen and the presence of silicon from the anchored KH550 on GO, which means a friction film formed from FGO additive. The wear surface of the MTT sample is rich in
C, O, Na, Si, and other elements. The Na element must come from the MTT additive, implying MTT additive also has a self-repairing effect. The content of C, Na, and Si elements on the worn surface of FG/MTT oil sample is significantly higher than those for FGO and MTT oil samples, which proves the presence of a self-repairing layer and its repair capacity is far greater than that of a single material.

Fig. 8 shows the micro indentation hardness test results of the steel ball surfaces and wear spots for bare oil, FGO, MTT and, FG/MTT oil samples. Compared to the hardness results in the bare 15w40 oil, it can be clearly seen that MTT additive almost hardly improves the hardness of the worn surface, although it can reduce the FC value. However, both FGO and GO additives can make the worn surface harder than the bare steel ball surfaces with 10.04 % and 6.91 % higher value of HV0.5. Most importantly, for FG/MTT composite oil sample, the hardness of the worn surface is 22.4 % higher than that of the steel ball surface. It reflects that under the action of FG/MTT composite additive, the worn scar in the process of friction and wear test becomes harder due to a repairing “coating” film generated from FG/MTT, whose hardness is much higher than that of the original steel ball material. Moreover, this repairing film should be different from the physical mixture of FGO and MTT due to the synergistic effect between two components of FG/MTT, which is prepared by chemical reaction.

To further reveal the friction-reducing and antiwear mechanism of the FG/MTT dispersed oil, the valence states of several typical elements on the wear scar of the steel ball are examined by XPS measurements. Fig. 9 shows the full spectrum from the binding energy of 0 to 1200 eV and the curve-fitted XPS spectra of C1s, O1s, Si2p, Fe2p, Na1s, and Cr2p on the wear scar surface. The C1s spectrum shows the peak at 285.2 eV, which can be attributed to the carbon atoms in the functional group: C-C.[23, 24]. It proves that FGO is attached to the wear scar surface, which can also be seen from the silane bond in FGO corresponding to the peak at 101.2 and 102.1 eV in the Si2p spectrum. Existing studies have shown that silicate minerals will generate SiO2 after friction[25]: In the FG/MTT wear scar XPS spectrum, the Si2p peak at 103.8 eV and the O1s peak at 532.8 eV also reveal that the FG/MTT tribochemical reaction occurred during the friction process to generate SiO2. The peak of O1s at 531.9 eV indicated the formation of metal carbonates[26], which is accorded with the emergency of the C1s peak at 288.2 eV[27]. The peak at 530.7 eV can be attributed to -Fe(III)-O-, interpreting the formation of Fe2O3 during the friction process. The Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> peaks appearing at 710.8 and 724.6 eV were matched with Fe2p of Fe2O3[19, 28, 29]. The formation of the layer containing Fe2O3 could be beneficial to the improvement of the performance[28]. The Si2p peak at 102.9 eV and 100.7 eV are ascribed to chemical bonds of aluminosilicate and SiC, respectively[27]. These may be formed owing to the flash temperature and pressure during the friction process.

The chemical bond in FG/MTT is broken by mechanical force, releasing active groups (O-, Si-, -Mg-OH[30]) and chemically reacting with the substances on the surface of the friction pair to form the aluminosilicate, SiC, Fe2O3, and SiO2. SiO2 and SiC have good mechanical properties and creep resistance, filling the defects of the grinding surface to improve the surface hardness[31]. The peaks at 1071.6 eV of Na 1s originate from the FG/MTT composite, which testifies the destruction of the chemical
bonds between the layers of MTT during the friction process. The peaks at 586.8 and 576.9 eV of Cr2p originated from Cr2O3, a product of the tribology reaction, which also protects the friction surface[32].

3.3 Lubricating Mechanism Analysis

According to the experimental results, the lubrication mechanism of FG/MTT can be explained as follows: Fig.10(a) and (b) are microscopic schematic diagrams of the surface of the friction pair. During the friction process, the FG/MTT nanosheets are uniformly distributed on the surface of the friction pair under the action of mechanical force to form a "lubricating layer", which avoids some asperities of the friction pair directly contact with each other and reduces the wear of the workpiece. FG/MTT is a two-dimensional lamellar structure, and its interlayer bonding force is weak, which makes the layer slide easily, thereby playing a lubricating effect and reducing the coefficient of friction, and form a self-repairing layer as the SEM and EDS images of the worn scars exhibit.

Fig.10(c) explains the metal elements contained in the friction pair are ionized on the surface to form Fe3+, which would react with the O2- generating between electrons and O2 to produce Fe2O3. The MTT structure is shown in Figure 10(e). The Mg/Al atoms in MTT can be replaced by other metal atoms[33], and the collapse of asperities will release energy by friction, resulting in flash temperature, which make the Mg/Al atoms in the MTT exchange with Fe atoms in the friction pair, and aluminosilicate and SiO2 are produced in the tribochemical reaction[25].

XPS energy spectrum analysis shows the existence of SiC and Fig.10(d) illustrates the generation principle. The flash temperature engendered by the energy released from the disintegration of the asperity provides the reaction conditions. The reaction equation is as follows:

\[
\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}
\]  

(2)

The formula of FC in the friction energy model proposed by Heilmann and Rigney is as follows[34]:

\[
\tau_f = \frac{\tau_{max}}{W} f \left( \frac{\tau_s}{\tau_{max}} \right)
\]  

(3)

\(\tau_f, W, \tau_{max}\) and \(\tau_s\) mean furrow friction coefficient, load, ultimate shear force, and average shear force of grinding surface, respectively. Since the real contact area \(A_r\) is more difficult to determine, analogous to the definition of hardness \(H\) as load/contact area, using \(1/H\) instead of \(A_r/W\). Eq. (3) can be transformed into the following form:

\[
\tau_f = \frac{\tau_{max}}{H} f \left( \frac{\tau_s}{\tau_{max}} \right)
\]  

(4)
According to the Eq. (4), it can be seen that the FC is inversely proportional to the hardness, and the hardness test shows that the hardness elevates after adding FG/MTT, the FC will also decrease accordingly, thus providing lubrication.

In general, FG/MTT not only avoids the contact of some asperities, but its special two-dimensional structure also plays an eminent role in declining friction and ameliorates the surface hardness of the friction pair, thereby reducing the friction coefficient. As a result of the frictional flash temperature and high pressure, complex tribological reactions may among MMT, FGO, and metal elements on the surface of the friction pair, to generate SiC, SiO$_2$, aluminosilicate, and Fe$_2$O$_3$. The above substances could cover the metal surface to form a repair layer to protect and repair the surface.

4. Conclusion

In this work, the FG/MTT lubricant additive was successfully prepared, After that, the structure and morphology is characterized and the tribological properties is tested. According to the characterization results of XRD, TEM, FT-IR, and Raman spectroscopy, and infrared absorption spectroscopy, it can be proved that FG/MTT was successfully prepared. By analyzing the consequences of the tribological test and the settlement experiment, the following conclusions are drawn:

- FG/MTT can be evenly dispersed in oil. After comparing the test results of GO, MTT, FGO, and FG/MTT four-ball friction tester, it can be concluded that the lubrication performance of the above four substances has been improved. The performance of FG/MTT is the best one, whose the test final FC is 57.5 % lower than that of 15W40 simple oil. After exploring the lubrication performance of different concentrations of FG/MTT, it is certificated that the performance is best when the concentration is 0.4 mg/ml, and the average friction coefficient and wear scar diameter are reduced by 50.9 % and 19.1 %, respectively.
- The hardness test shows that after adding GO, FGO, and FG/MTT, the hardness of the grinding surface has been increased by 6.9 %, 10.0 %, and 22.4 % respectively, which improves the bearing capacity of the grinding surface.

To analyze the lubrication mechanism of FG/MTT, the grinding surface after the friction experiment was analyzed by EDS and XPS, and the lubrication repair mechanism was explained as follows:

- FG/MTT is a two-dimensional layered composite material. During the friction process, its micro-nanosheets fill between the asperities on the contact surface of the friction pair to form a lubricating layer and avoid direct contact of some asperities.
- The flash temperature generated during the friction process makes the FG/MTT and the friction pair carry out a tribological reaction. Owing to its special structure, FG/MTT will release the active group in the interlayer domain during the interlayer sliding process, which may react with the surface of the
friction pair to form a repair layer composed of the SiC, SiO₂, aluminosilicate, and Fe₂O₃, declining the wear of the grinding surface.

Declarations

Acknowledgement

The work was supported by the program for Science and Technology Innovative Research Team in Universities of Jiangsu Province, and the ‘333 program’ BRA2019262 of Jiangsu Province, China. We also thank the support of the Analysis and Test Center, Nanjing University of Science and Technology, for XRD and Raman data collection.

Ethical Declarations

The authors would like to declare that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part, and they declare no competing financial interest.

References

[1] Abdel-Rehim, A.A., Akl, S., Elsoudy, S. Investigation of the Tribological Behavior of Mineral Lubricant Using Copper Oxide Nano Additives. 9:16 (2021).

[2] Singh, A., Chauhan, P., Mamatha, T.G. A review on tribological performance of lubricants with nanoparticles additives. Materials Today: Proceedings 25:586-591 (2020).

[3] Mao, J., Zhao, J., Wang, W., He, Y., Luo, J. Influence of the micromorphology of reduced graphene oxide sheets on lubrication properties as a lubrication additive. Tribology International 119:614-621 (2018).

[4] Meng, Y., Su, F., Chen, Y. Au/Graphene Oxide Nanocomposite Synthesized in Supercritical CO₂ Fluid as Energy Efficient Lubricant Additive. ACS Applied Materials & Interfaces 9:39549-39559 (2017).

[5] Wang, X., Wu, J., Wei, X., Liu, R., Cao, Q. The effect of serpentine additive on energy-saving and auto-reconditioning surface layer formation. Industrial Lubrication and Tribology 69:158-165 (2017).

[6] Martín-Alfonso, J.E., Martín-Alfonso, M.J., Valencia, C., Cuberes, M.T. Rheological and tribological approaches as a tool for the development of sustainable lubricating greases based on nanomontmorillonite and castor oil. Friction 9:415-428 (2021).

[7] Zhang, Y., Cao, Y., Ma, X., Xu, S., Wang, M. Influence of Dispersion Stability of Modified Montmorillonite Particles in Lubricating Oil on Their Tribological Properties. Lubrication Engineering 45:36-42 (2020).

[8] Wang, H.L., Hao, Q.L., Yang, X.J., Lu, L.D., Wang, X. Graphene oxide doped polyaniline for supercapacitors. Electrochem Commun 11:1158-1161 (2009).
[9] Choudhary, S., Mungse, H.P., Khatri, O.P. Dispersion of alkylated graphene in organic solvents and its potential for lubrication applications. Journal of Materials Chemistry 22:21032-21039 (2012).

[10] Zhang, M.M., Yan, H.X., Yang, X.W., Liu, C. Effect of functionalized graphene oxide with a hyperbranched cyclotriphosphazene polymer on mechanical and thermal properties of cyanate ester composites. RSC Adv 4:45930-45938 (2014).

[11] Bai, L.H., Yan, H.X., Yuan, L.X., Liu, C. Synthesis of functionalized GO for improving the dielectric properties of bismaleimide-triazine resin. J Polym Res 23:10 (2016).

[12] Ouhaddouch, H., Cheikh, A., Idrissi, M.O.B., Draoui, M., Bouatia, M. FT-IR Spectroscopy Applied for Identification of a Mineral Drug Substance in Drug Products: Application to Bentonite. Journal of Spectroscopy 2019 (2019).

[13] Yadav, M., Ahmad, S. Montmorillonite/graphene oxide/chitosan composite: Synthesis, characterization and properties. International Journal of Biological Macromolecules 79:923-933 (2015).

[14] Rao, C.N.R., Sood, A.K., Subrahmanyam, K.S., Govindaraj, A. Graphene: The New Two-Dimensional Nanomaterial. Angewandte Chemie-International Edition 48:7752-7777 (2009).

[15] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J.W., Potts, J.R., et al. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Advanced Materials 22:3906-3924 (2010).

[16] Jauncey, G.E. The Scattering of X-Rays and Bragg's Law. Proceedings of the National Academy of Sciences of the United States of America 10:57-60 (1924).

[17] Kudin, K.N., Ozbas, B., Schniepp, H.C., Prud'homme, R.K., Aksay, I.A., Car, R. Raman spectra of graphite oxide and functionalized graphene sheets. Nano Letters 8:36-41 (2008).

[18] Meng, Y., Su, F., Chen, Y. Effective lubricant additive of nano-Ag/MWCNTs nanocomposite produced by supercritical CO2 synthesis. Tribology International 118:180-188 (2018).

[19] Song, W., Yan, J., Ji, H. Tribological Study of the SOCNTs@MoS2 Composite as a Lubricant Additive: Synergistic Effect. Industrial & Engineering Chemistry Research 57:6878-6887 (2018).

[20] Qian, Y., Gong, H., Zhao, X., Cao, L., Shi, W., He, J. Experimental investigation on the tribological property of functionalized graphene lubricant against steel. Industrial Lubrication and Tribology 72:307-314 (2020).

[21] Wei, X.Y., Zhao, Y., Zhang, L.X., Wang, J.H., Wang, L.Y., Xi, D.Y. Effects of ionic liquid on the dispersion and tribological property of graphene lubricant. Lubr Sci 32:415-423 (2020).

[22] Gao, Y.J., Sun, R., Zhang, Z.J., Xue, Q.J. Tribological properties of oleic acid - modified TiO2 nanoparticle in water. Materials Science and Engineering a-Structural Materials Properties Microstructure
and Processing 286:149-151 (2000).

[23] Chen, Z., Yan, H., Liu, T., Niu, S. Nanosheets of MoS2 and reduced graphene oxide as hybrid fillers improved the mechanical and tribological properties of bismaleimide composites. Composites Science and Technology 125:47-54 (2016).

[24] Yan, H., Li, S., Jia, Y., Ma, X.Y. Hyperbranched polysiloxane grafted graphene for improved tribological performance of bismaleimide composites. RSC Adv 5:12578-12582 (2015).

[25] Qi, X., Jia, Z., Yang, Y., Fan, B. Characterization and auto-restoration mechanism of nanoscale serpentine powder as lubricating oil additive under high temperature. Tribology International 44:805-810 (2011).

[26] Wang, W., Zhang, G., Xie, G. Ultralow concentration of graphene oxide nanosheets as oil-based lubricant additives. Applied Surface Science 498 (2019).

[27] Wagner, C.: NIST X-ray photoelectron spectroscopy (XPS) database. NIST X-ray photoelectron spectroscopy (XPS) database, pp. 68 pp-68 pp. Place (1991)

[28] Meng, Y., Su, F., Chen, Y. A Novel Nanomaterial of Graphene Oxide Dotted with Ni Nanoparticles Produced by Supercritical CO2-Assisted Deposition for Reducing Friction and Wear. Acs Applied Materials & Interfaces 7:11604-11612 (2015).

[29] Meng, Y., Su, F., Chen, Y. Supercritical Fluid Synthesis and Tribological Applications of Silver Nanoparticle-decorated Graphene in Engine Oil Nanofluid. Scientific Reports 6 (2016).

[30] Bai, Z.M., Yang, N., Guo, M., Li, S. Antigorite: Mineralogical characterization and friction performances. Tribology International 101:115-121 (2016).

[31] Lu, G., Qiao, S. Influence of Si-O-C Interlayer on Mechanical Properties and Thermal Expansion Properties of C/SiC-N Composites. Journal of Materials Engineering 46:83-87 (2018).

[32] Cetinel, H., Celik, E., Kusoglu, M.I. Tribological behavior of Cr2O3 coatings as bearing materials. Journal of Materials Processing Technology 196:259-265 (2008).

[33] Bhattacharyya, K.G., Sen Gupta, S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Advances in Colloid and Interface Science 140:114-131 (2008).

[34] Heilmann, P., Rigney, D.A. An energy-based model of friction and its application to coated systems. Wear 72:195-217 (1981).

Figures
Figure 1

The synthesis process of FGO and FG/MMT

Figure 2

(a,b) TEM images of FG/MMT with different magnification;
Figure 3

(a) FTIR spectra of GO, FGO, MMT, and FG/MMT. (b) XRD patterns of GO, FGO, MMT, and FG/MMT with drop lines corresponding to standard XRD patterns in JCPDS card No.43-0688. (c) Raman patterns of GO, FGO, and FG/MMT
Figure 4

Images of the oil samples of the FG/MMT composite with different concentration after standing for 30 and 120 days. (a) 1.0mg/ml; (b) 0.4 mg/ml

Figure 5

(a) the relationship of friction coefficient (FC) with time, (b) average FC and wear scar diameter (WSD) for different samples. (c) average FC and WSD values of the FG/MMT at different concentration.
Figure 6

SEM images of the worn scars with various oil samples. (a, b) 15w40 oil; (c, d) FGO; (e, f) MTT; (g, h) FG/MTT
Figure 7

EDS images of the worn scars with various oil samples. (a, b) 15w40 oil; (c, d) FGO; (e, f) MTT; (g, h) FG/MTT
Figure 8

Microhardness of steel ball surface and wore surface

22.4%
Figure 9

(a) XPS full-spectrum and curve-fitted XPS spectra of (b) C1s, (c) O1s, (d) Fe, (e) Si2p, (f) Na1s and (g) Cr on the wear scar surface of the ball lubricated with 0.4 mg/mL FG/MTT dispersed oil after sliding for 60 min at 197 N and 600 rpm.
Figure 10

Schematic diagram of lubrication mechanism.