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Tribological Properties of Few-layer Graphene Oxide Sheets as Oil-Based Lubricant Additives

CHEN Zhe, LIU Yuhong, and LUO Jianbin*

State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

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Abstract: The performance of a lubricant largely depends on the additives it involves. However, currently used additives cause severe pollution if they are burned and exhausted. Therefore, it is necessary to develop a new generation of green additives. Graphene oxide (GO) consists of only C, H and O and thus is considered to be environmentally friendly. So the tribological properties of the few-layer GO sheet as an additive in hydrocarbon base oil are investigated systematically. It is found that, with the addition of GO sheets, both the coefficient of friction (COF) and wear are decreased and the working temperature range of the lubricant is expanded in the positive direction. Moreover, GO sheets has better performance under higher sliding speed and the optimized concentration of GO sheets is determined to be 0.5wt%. After rubbing, GO is detected on the wear scars through Raman spectroscopy. And it is believed that, during the rubbing, GO sheets adhere to the sliding surfaces, behaving like protective films and preventing the sliding surfaces from contacting with each other directly. This paper proves that the GO sheet is an effective lubricant additive, illuminates the lubrication mechanism, and provides some critical parameters for the practical application of GO sheets in lubrication.

Keywords: tribological properties, graphene oxide sheets, lubricant additive, hydrocarbon base oil

1 Introduction

Friction is very common in our daily activities. However, enormous amount of energy is consumed by friction. According to the researches of HOLMBERG, et al[1–2], in most vehicles, about one third of the fuel energy is used to overcome friction. Moreover, if friction is not controlled effectively, severe wear will occurred and further result in machine part failures, which may lead to fatal mechanical accidents[3]. Considering the facts that the energy and resources are becoming increasingly precious but the demand for them is rising sharply, the pursuit of reducing or even eliminating friction and wear with new technology and new materials still continues[4].

The discovery of mono-layer graphene opened up a new world of ultrathin two-dimension materials[5]. Compared with bulk materials, ultrathin materials possess many specific properties and have many potential applications in various fields[6–10]. And this kind of material has attracted a lot of attention among the tribologists all over the world.

GO sheet is one of the ultrathin two-dimension materials and it is being investigated as a friction-modifier in many different ways. It has been investigated as surface coatings and three kinds of deposition methods have been reported. LIANG, et al[11], fabricated GO films on silicon wafer through a green electrophoretic deposition approach. KIM, et al[12], deposited GO sheet coatings on silicon substrates with an electrodynamic spraying process. PENG, et al[13], used suspension deposition to prepare GO sheets on silicon dioxide. All the GO coatings can largely reduce the COF and wear at the same time. The reported lowest COF is about 0.05 achieved by LIANG, et al[11] using electrophoretic deposition with the working voltage at 20 V.

Besides the use as surface coatings or solid lubricants, GO sheets are also considered to be green lubricant additives. Because GO only contains C, H and O instead of N, S, P and heavy metal elements, no toxic particles or ashes will be produced when it is burned and exhausted.

Due to the excellent dispersibility in water without any surfactants or dispersants, GO sheets are widely studied as additives in water-based lubricants with different rubbing surfaces. SONG, et al[14], investigated the tribological properties of GO sheets solution between steel surfaces. ELOMAA, et al[15], also used steel surfaces, but they deposited DLC films on one of the surfaces. KINOSHITA, et al[16], used WC and steel as the material of surfaces. And LIU, et al[17] changed the rubbing surfaces into Si_3N_4 and Al_2O_3. Among all the researches, significant reduction in both COF and wear has been accomplished. Especially, KINOSHITA, et al[16], reported that no obvious wear was found on the rubbing surfaces after 60 000 cycles of

* Corresponding author. E-mail: luojb@tsinghua.edu.cn
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friction. COF in the order of one percent is obtained when the lubricant is used in the situations of DLC or WC versus steel and Si_3N_4 versus Al_2O_3. But the COF would be larger than 0.1 when the rubbing surfaces are both made of steel. In addition, SARNO, et al[18], and SENATORE, et al[19], studied the GO sheets as additives in oil-based lubricants. In this case, although the reduction in COF was not remarkable, the anti-wear property of the lubricant was largely improved. Moreover, KINOSHITA, et al[20], dispersed GO sheets into ionic liquid and found that corrosion wear on the rubbing surfaces became lower.

Therefore, it can be concluded that GO sheet can be both a very good solid lubricant and a lubricant additive. However, among all the researches mentioned above, especially those, in which the GO sheets are used as lubricant additives, the size of the GO sheets is at least about tens of micrometers. Usually, it is considered that smaller size will make the entrance of additives into the contact area much easier and result in better tribological properties[21–22]. Moreover, oil-based lubricant is the most commonly used lubricant. Therefore, in this paper, GO sheets with a lateral size in the range from hundreds of nanometers to a few micrometers are added into hydrocarbon base oil forming lubricants. And the lubricant is investigated systematically with a series of tribological tests. Firstly, focusing on the COF and wear, the lubricant is tested under different loads at various temperatures. Then the effect of rubbing speed on the COF and the wear is investigated. After this, an optimized concentration of GO sheets is determined. Finally, the wear scars are analyzed with Raman spectroscopy. This work enriches the investigation of ultrathin 2D materials as lubricant additives and has important guiding significance for practical application.

2 Materials and Methods

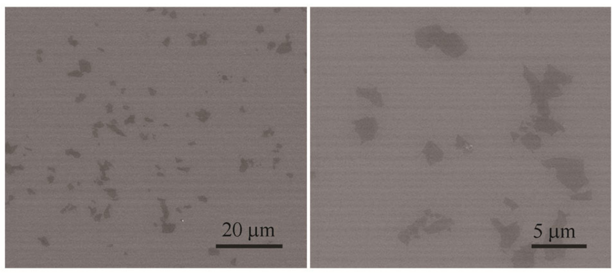
Both the few-layer GO sheets and the hydrocarbon base oil(GTL8, Shell) are commercial products. The lateral size and the thickness of the GO sheets were determined with a scanning electron microscope(SEM, FEI Quanta 200 FEG) and an atomic force microscope(AFM, Veeco diDimension V). The viscosity of the base oil was measured with a standard rheometer(Anton Paar Physica MCR301) and it is found to be 23.1 mPa • s at 50℃, 6.16 mPa·s at 100℃ and 2.77 mPa·s at 150℃. A certain amount of GO sheets were added into the base oil to form lubricants with the concentration in the range from 0.01 wt% to 5 wt%.

The tribological tests were performed with a commercial tribotester(Optimal SRV4) and the mode of the test is reciprocating ball-on-disk. The material of both balls and disks are bearing steel(AISI 52100). The ball is a commercial product with a diameter of 10 mm and a surface roughness(*Ra*) of about 18.5 nm. The surface of the disk was grinded with SiC paper(Struers #1200) and its final surface roughness(*Ra*) is about 40 nm. The surface roughness was measured by a commercial surface mapping microscope(ADE PHASE SHIFT MicroXAM). Before the test, the ball and disk were washed ultrasonically with petroleum ether and acetone. The lubricant was ultrasonicated for about 3600 s to make the GO sheets dispersed. Then 30 μL lubricant was placed between the ball and the disk. During the test, the disk was fixed and the ball was pressed onto the disk with reciprocating motion. The reciprocating stroke was set at 2 mm. The reciprocating frequency would vary from 10 Hz to 50 Hz in steps of 10 Hz among different tests. The load was in the range from 50 N to 150 N. Three temperatures, which are 50℃, 100℃ and 150℃, were selected. At the beginning of the test, there would be a 30-second running period at 50 N. Then the load would rise to the set value and keep constant until the test ended. The number of the rubbing cycles under the set load in one test was 30 000, so the duration of the test would depend on the reciprocating frequency. All the tribological tests were repeated at least three times. For each test, a new ball and an un-rubbed area on the disk were put into use.

After the test, the ball and disk were ultrasonically cleaned with petroleum ether and acetone. The wear scars were observed with an optical microscope(Olympus BX60). The wear degree can be determined from the optical images by observing the grinding traces on the disks. Raman spectroscopy(HORIBA Jobin Yvon HR800) was used for the analysis of the wear scars. Raman spectra with the resolution of 0.7 cm^{-1} was taken under ambient condition. The spectrometer used the 514 nm line of an argon ion laser at 12 mW of power on the sample, which was focused on the wear scar with a specimen depth of 1 μm. The scattered radiation was analyzed using an 1800 g/mm grating with a liquid-nitrogen-cooled 1024×256 pixel array CCD detector. The system was calibrated with the Si peak at 520.7 cm^{-1}.

3 Results and Discussion

Fig. 1 shows the SEM images of the GO sheets deposited on SiO_2 wafer. It can be seen that the lateral dimension of most of the GO sheets is in the range from hundreds of nanometers to a few micrometers.



(a) Magnification: ×3 000 (b) Magnification: ×10 000

Fig. 1. SEM images of GO sheets

The AFM image(Fig. 2) supports the lateral dimension data obtained from the SEM images, and the thickness of the GO sheets are found to be about 1.8 nm thick, indicating that the sheets are of few layers.

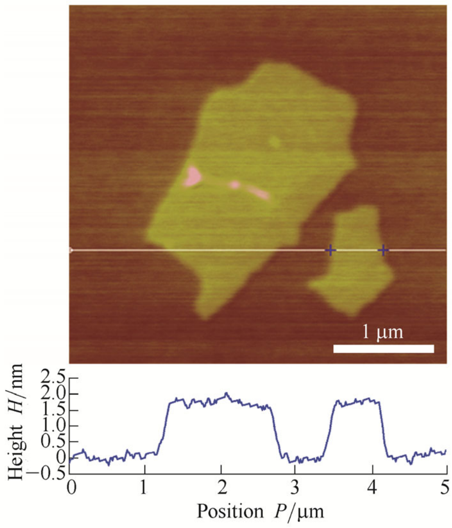
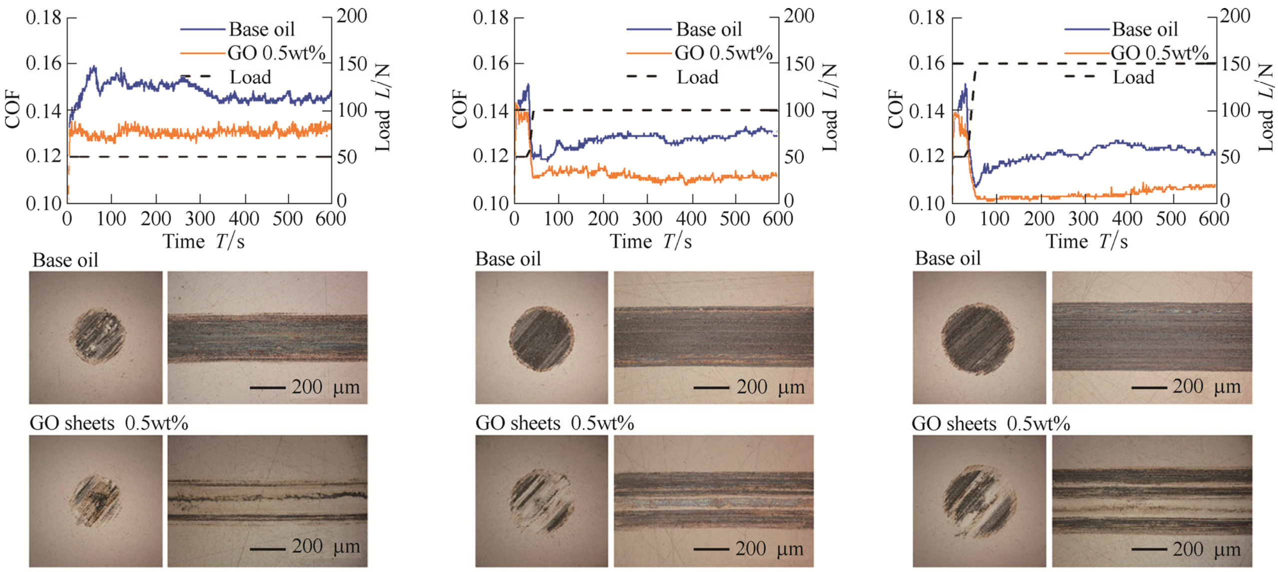


Fig. 2. AFM image and height of GO sheets

After the GO sheets were dispersed in the hydrocarbon base oil forming lubricants, the lubricants were put into a series of tribological tests. Firstly, the lubricant containing 0.5 wt% GO sheets was compared with hydrocarbon base oil under different loads at various temperatures. The reciprocating frequency was fixed at 50 Hz. The results of the tests operated at the temperature of 50℃ are presented in Fig. 3. It can be seen that, under all the selected loads, the COF of the lubricant containing 0.5 wt% GO sheets is about 10 % to 20 % smaller than that of pure hydrocarbon base oil. As for the wear scars, although the size of the wear scars under each load for the two samples are similar, the wear degree was largely reduced with the addition of GO sheets. Especially, it can be seen that when the load is 50 N, most of the grinding traces on the disk are recognizable after the test, indicating that an ultralow wear was achieved.



(a) 50 N (b) 100 N (c) 150 N

Fig. 3. The COF and wear scars of the tests at 50 ℃

The test results at a temperature of 100℃ are provided in Fig. 4. It can be found that, at this temperature, the hydrocarbon base oil has become so thin that it can not bear the load of 50 N. At the beginning of the test, the COF rose dramatically over 0.6(the part over 0.24 is not shown in Fig. 4), indicating that the ball and disk contacted directly and seizure between them took place. Thus the wear was very severe. As for the lubricant containing 0.5 wt% GO sheets, under all the selected loads, the COF was relatively stable. And according to the wear scars, effective lubrication had been provided by the lubricant. Therefore, it can be concluded that the upper limit of the operating temperature range of the base oil can be enhanced to at least 100℃.

Then the COF and wear scars at 150℃ under the load of 50 N are displayed in Fig. 5. It is found that, at this temperature, the viscosity of the base oil further decreases and both the lubricant containing GO sheets and the base oil can not bear the load of 50 N. For both samples, the COF was high at the beginning of the tests and the wear was severe. Based on the test results under 50 N, it is believed that there is no need to perform the tests under higher loads.

The effect of rubbing speed on the tribological properties of the GO sheets contained lubricant was then investigated. The rubbing speed can be controlled through the reciprocating frequency. And five frequencies in the range from 10 Hz to 50 Hz were selected. The load was chosen at 100 N and the temperature was set at 50 ℃. The concentration of GO sheets was 0.5 wt%. The COF of these tests are summarized in Fig. 6 and the wear scars are shown in Fig. 7. It can be seen that the COF would decrease as the frequency rose. And the wear also became lighter under higher frequency. This phenomenon can be explained by the hydrodynamic effect[23]. Higher frequency leads to higher sliding speed and further results in thicker lubricant film when the pressure is constant. Therefore, more GO sheets can enter the contact area and offer better lubrication under higher rubbing speed.

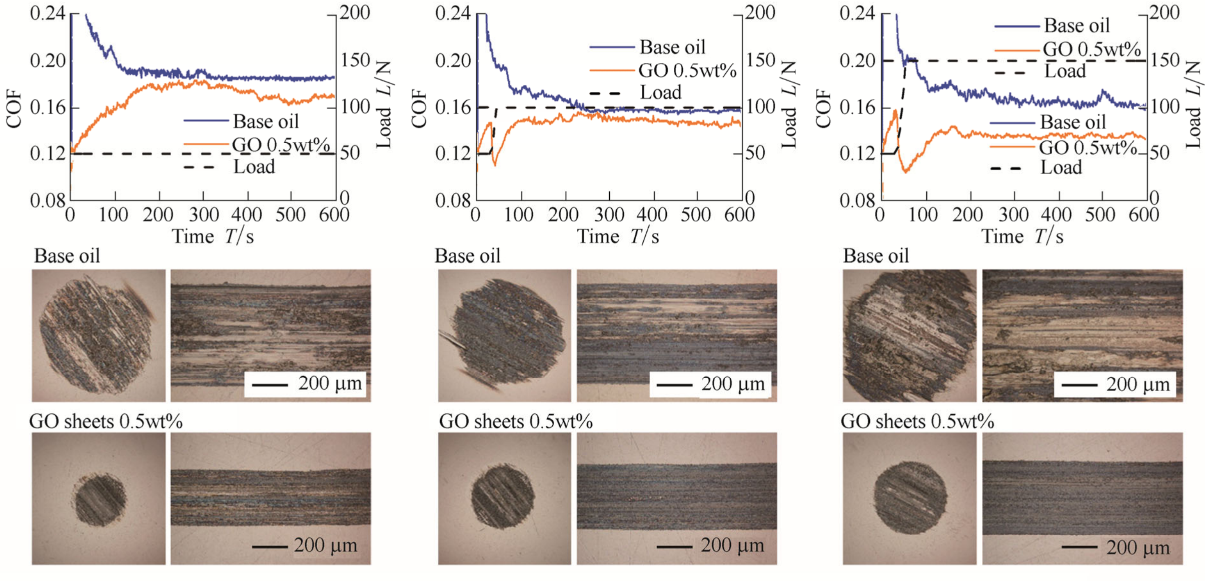


Fig. 4. COF and wear scars of the tests at 100℃

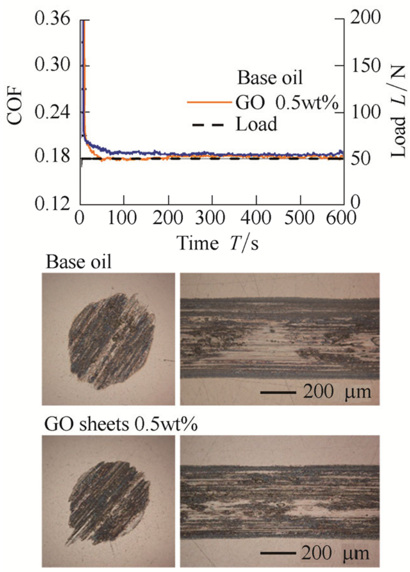


Fig. 5. COF and wear scars of the tests at 150℃

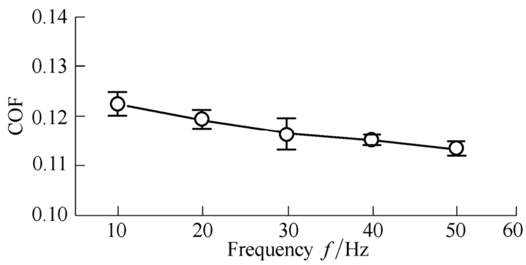


Fig. 6. COF of the tests under various frequency

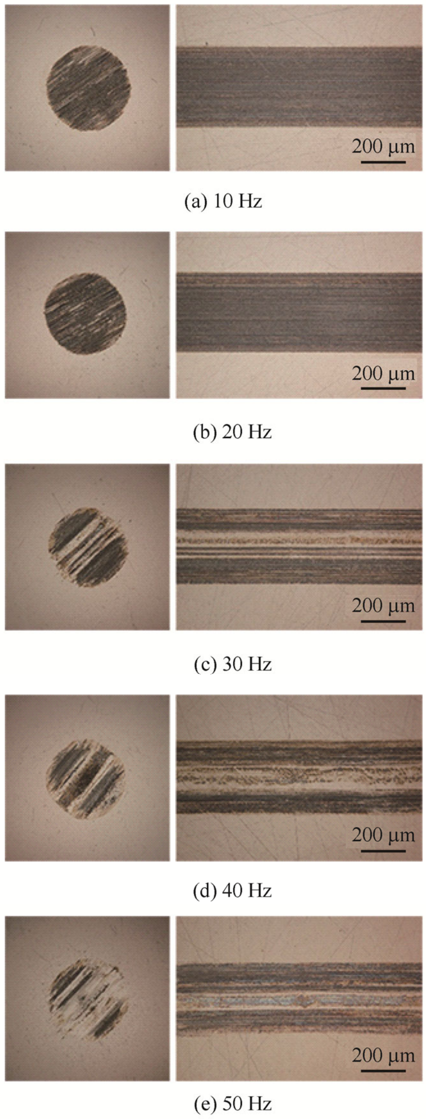


Fig. 7. Wear scars of the tests under various frequency

Moreover, the concentration of the GO sheets in the lubricant was studied. Several concentrations in the range from 0.01 wt% to 5 wt% were selected. And the tests were conducted with the reciprocating frequency of 50 Hz, the load of 100 N and the temperature of 50℃. The COF of the tests are summarized in Fig. 8. And a typical portion of the wear scars are displayed in Fig. 9. It can be found that the COF would decrease as the concentration increased until the concentration reached 1 wt%. After that, the COF would increase very slightly. However, it can be seen that when the concentration is no less than 0.5 wt%, the difference among the tests are almost negligible. Meanwhile, similar trend can be found from the wear scars. When the concentration was smaller than 0.5 wt%, the grinding traces on the disk in the contact area would be removed due to the wear. But when the concentration was no less than 0.5 wt%, many grinding traces in the contact area can still be observed, indicating that very limited wear was caused. Therefore, it can be concluded that 0.5 wt% is the optimized concentration.

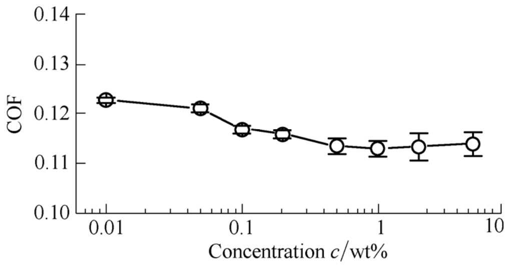
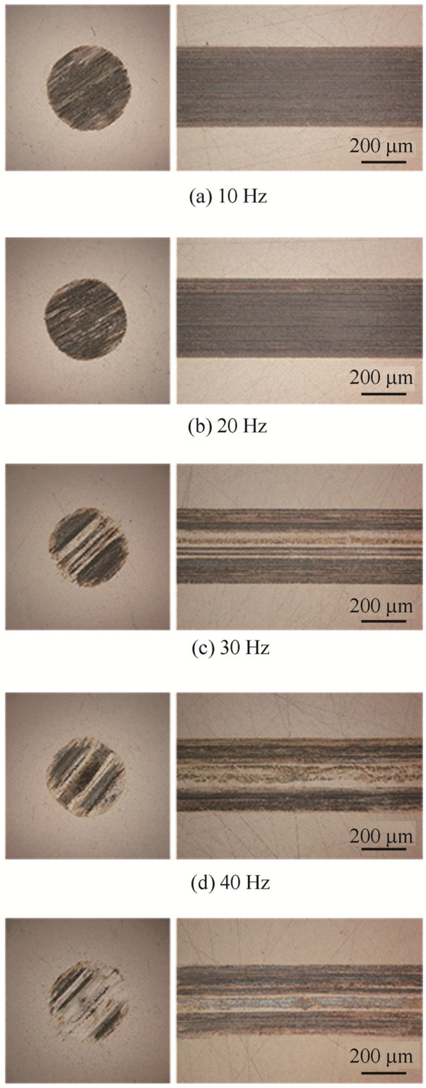


Fig. 8. COF of the tests with different concentration

After the test, the ball and disk were ultrasonically cleaned for the analysis of the wear scars. Because carbon and its compounds exist in the rubbing steel surfaces, it is very difficult to distinguish the source of the detected carbon through common elements analysis techniques, such as EDS and XPS. Therefore, Raman spectroscopy, which can provide the information of chemical bonds, was used. The Raman spectrum obtained from the surface of the wear scars lubricated with GO sheets is displayed in Fig. 10. And the Raman spectrum of the powders of GO sheets is also shown in Fig. 10 for comparison. It can be seen that both the D band and G band are very clear in the spectrum of the wear scar[24], indicating that GO sheets had adhered to the rubbing surfaces forming a tribofilm.

In addition, it is reported that ultrathin 2D materials can be excellent coatings for low friction and wear in the load scenarios where the coating itself is not damaged[25]. Therefore, the strength of the 2D materials is of crucial importance. However, the measurement of the breaking strength of GO sheets has not been reported. But the value of the breaking strength of the GO sheets can be obtained through computational studies according to the work of PACI, et al[26]. They reported that, compared to that of graphene, the strength was reduced by 46% due to oxidation. The breaking strength of chemically derived single graphene sheets measured through AFM is about 130 GPa[27]. So it can be estimated that the breaking strength of GO sheets is in the scale of decades of GPa, which is two orders larger than that of steel[28]. Therefore, it is considered that the GO sheets, which enter the contact area, can working as protective films preventing the direct contact between the opposite asperities and reducing friction and wear at the same time.



(a) 10 Hz

(b) 20 Hz

(c) 30 Hz

(d) 40 Hz

(e) 50 Hz

Fig. 9. Wear scars of the tests with different concentration

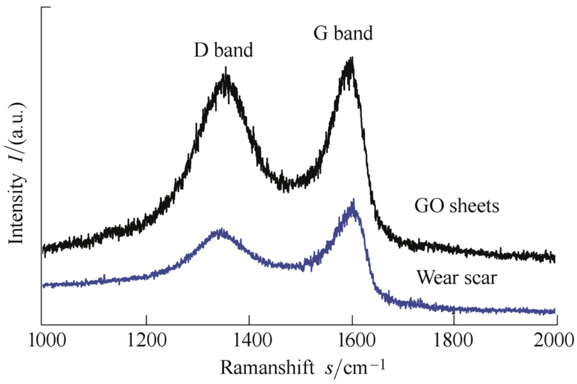


Fig. 10. Raman spectra of the GO sheets and the surface of the wear scar

4 Conclusions

(1) The tribological properties of few-layer GO sheets, whose lateral size is from hundreds of nanometers to a few micrometer, as additives in oil-based lubricant are investigated systematically. Both COF and wear are reduced with the addition of GO sheets.

(2) The working temperature range of the lubricant is expanded in the positive direction with GO sheets.

(3) The performance of lubricant containing GO sheets is better under higher rubbing speed.

(4) The optimized concentration of GO sheets in lubricant is determined to be 0.5wt%

(5) GO is detected inside the wear scars after tests and thus the lubrication mechanism is revealed.

References

[1] HOLMBERG K, ANDERSSON P, NYLUND N, et al. Global energy consumption due to friction in trucks and buses[J]. *Tribology International*, 2014, 78: 94–114.

[2] HOLMBERG K, ANDERSSON P, ERDEMIR A. Global energy consumption due to friction in passenger cars[J]. *Tribology International*, 2012, 47: 221–234.

[3] WEN S Z, HUANG P. Principles of tribology[M]. New York: John Wiley & Sons, 2012.

[4] LUO J B, LU X C, WEN S Z. Developments and unsolved problems in nano-lubrication[J]. *Progress in Natural Science*, 2001, 11(3): 173–183.

[5] NOVOSELOV K S, GEIM A K, MOROZOV S V, et al. Electric field effect in atomically thin carbon films[J]. *Science*, 2004, 306(5696): 666–669.

[6] GEIM A K, NOVOSELOV K S. The rise of graphene[J]. *Nature Materials*, 2007, 6(3): 183–191.

[7] STANKOVICH S, DIKIN D A, DOMMETT G H B, et al. Graphene-based composite materials[J]. *Nature*, 2006, 442(7100): 282–286.

[8] ZHU Y, MURALI S, CAI W, et al. Graphene and graphene oxide: synthesis, properties, and applications[J]. *Advanced Materials*, 2010, 22(35): 3906–3924.

[9] HWANG H, KIM H, CHO J. MoS_2 nanoplates consisting of disordered graphene-like layers for high rate lithium battery anode materials[J]. *Nano Letters*, 2011, 11(11): 4826–4830.

[10] CHEN Z, LIU X, LIU Y, et al. Ultrathin MoS_2 nanosheets with superior extreme pressure property as boundary lubricants[J]. *Scientific Reports*, 2015, 5: 12869.

[11] LIANG H, BU Y, ZHANG J, et al. Graphene oxide film as solid lubricant[J]. *ACS Applied Materials & Interfaces*, 2013, 5(13): 6369–6375.

[12] KIM H, PENKOV O V, KIM D. Tribological properties of graphene oxide nanosheet coating fabricated by using electrodynamic spraying process[J]. *Tribology Letters*, 2015, 57(273).

[13] PENG Y, WANG Z, ZOU K. Friction and wear properties of different types of graphene nanosheets as effective solid lubricant[J]. *Langmuir*, 2015: 1279897608.

[14] SONG H, LI N. Frictional behavior of oxide graphene nanosheets as water-base lubricant additive[J]. *Applied Physics A-Materials Science & Processing*, 2011, 105(4): 827–832.

[15] ELOMAA O, SINGH V K, IYER A, et al. Graphene oxide in water lubrication on diamond-like carbon vs. stainless steel high-load contacts[J]. *Diamond and Related Materials*, 2015, 52: 43–48.

[16] KINOSHITA H, NISHINA Y, ALIAS A A, et al. Tribological properties of monolayer graphene oxide sheets as water-based lubricant additives[J]. *Carbon*, 2014, 66: 720–723.

[17] LIU Y, WANG X, PAN G, et al. A comparative study between graphene oxide and diamond nanoparticles as water-based lubricating additives[J]. *Science China-Technological Sciences*, 2013, 56(1): 152–157.

[18] SARNO M, SENATORE A, CIRILLO C, et al. Oil lubricant tribological behaviour improvement through dispersion of few layer graphene oxide[J]. *Journal of Nanoscience and Nanotechnology*, 2014, 14(7): 4960–4968.

[19] SENATORE A, D'AGOSTINO V, PETRONE V, et al. Graphene oxide nanosheets as effective friction modifier for oil lubricant: materials, methods, and tribological results[J]. *ISRN Tribology*, 2013, 2013: 1–9.

[20] KINOSHITA H, KONDO M, NISHINA Y, et al. Anti-wear effect of graphene oxide in lubrication by fluorine-containing ionic liquid for steel[J]. *Tribology Online*, 2015, 10(1): 91–95.

[21] RABASO P, VILLE F, DASSENOY F, et al. Boundary lubrication: Influence of the size and structure of inorganic fullerene-like MoS_2 nanoparticles on friction and wear reduction[J]. *Wear*, 2014, 320(1–2): 161–178.

[22] DONG L, SHU G, LIANG X, et al. Effect of lubricating oil additives on particle size distribution and total number concentration in diesel engine[J]. *Lubrication Science*, 2012, 24(7): 325–338.

[23] HAMROCK B J, DOWSON D. Isothermal elastohydrodynamic lubrication of point contacts 1. theoretical formulation[J]. *Journal of Lubrication Technology-Transactions of the ASME*, 1976, 98(2): 223–229.

[24] KUDIN K N, OZBAS B, SCHNIEPP H C, et al. Raman spectra of graphite oxide and functionalized graphene sheets[J]. *Nano Letters*, 2008, 8(1): 36–41.

[25] KLEMENZ A, PASTEWKA L, BALAKRISHNA S G, et al. Atomic scale mechanisms of friction reduction and wear protection by graphene[J]. *Nano Letters*, 2014, 14(12): 7145–7152.

[26] PACI J T, BELYTSCHKO T, SCHATZ G C. Computational studies of the structure, behavior upon heating, and mechanical properties of graphite oxide[J]. *Journal of Physical Chemistry C*, 2007, 111(49): 18099–18111.

[27] GOMEZ-NAVARRO C, BURGHARD M, KERN K. Elastic properties of chemically derived single graphene sheets[J]. *Nano Letters*, 2008, 8(7): 2045–2049.

[28] BERTOLAZZI S, BRIVIO J, KIS A. Stretching and breaking of ultrathin MoS_2[J]. *ACS Nano*, 2011, 5(12): 9703–9709.

Biographical notes

CHEN Zhe, born in 1988, is currently a PhD candidate at *State Key Laboratory of Tribology, Tsinghua University, China*. He received his bachelor degree from *Northwestern Polytechnical University, China*, in 2011. His research interests include nanotribology and 2D nanometerials.
Tel: +86-10-62788309;
E-mail: zhe-chen11@mails.tsinghua.edu.cn

LIU Yuhong, born in 1978, is currently an associate professor at *State Key Laboratory of Tribology, Tsinghua University, China*. She received her PhD degree from *Instituent of Chemistry, CAS, China*, in 2005. Her research interests include nanotribology and 2D nanometerials.
Tel: +86-10-62792449;
E-mail: liuyuhong@tsinghua.edu.cn

LUO Jianbin, born in 1961, is a member of *Chinese Academy of Sciences* and a professor at *State Key Laboratory of Tribology, Tsinghua University, China*. He has long been engaged in nanotribology research and nanomanufacturing.
Tel: +86-10-62781379;
E-mail: luojb@tsinghua.edu.cnering