The emulsifying and tribological properties of modified graphene oxide in oil-in-water emulsion

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ABSTRACT

Graphene oxide (GO) was asymmetric chemically modified with myristyltrimethylammonium bromide (TTAB) to get modified graphene oxide (MGO). This MGO was used as an emulsifier and additive in oil-in-water emulsion. The emulsifying tests showed MGO greatly improved the stability of base emulsion and decreased its droplets size. Tribological test results showed that under the boundary lubrication condition with MGO-emulsion, the friction coefficient (COF) and the wear rate of the steel ball were decreased by about 18% and 48% respectively, comparing with base emulsion lubrication. The tribological mechanism of MGO-emulsion could be explained by the strong film-forming ability on the metal surface; the good lubricity of its small droplets; the formed adsorption film, transfer film and tribofilm between the contact surfaces.

1. Introduction

Water as a lubricating fluid has many advantages such as low cost, environmental compatibility and high thermal conductivity, in comparison with oil based lubrication. However, water shows poor lubricating properties for steel and related materials, which are commonly used as contacting surfaces in industrial applications. Oil-in-water (O/W) emulsions could bridge the gap between water and oil based lubrication as they consist of a large amount of water and a small proportion of oil, thus potentially combining the cooling and environmental benefits of water with the lubrication performance of oil based lubrication. The latter effect can be created based on “plate-out” of oil droplets onto the contacting metal surfaces [1]. As such an oil film is formed which, assuming full coverage, could well attribute to the tribological performance of the sliding contact. O/W emulsion lubrication could be even more promising by selecting a vegetable oil instead of a mineral oil for the environmental benefit.

In an emulsion, the emulsifier can be aligned on the water-oil interface and significantly decrease the surface tension. Compared with traditional emulsifiers, nanoparticles are used as emulsifiers in Pickering emulsions. Emulsions prepared by nanoparticles show a high stability because they are less susceptible to the effects of temperature, pH value, and ion concentration [2]. Besides, the separation of those solid particles is simple in the subsequent treatment of the emulsion. Therefore, nanoparticles have great prospects in the field of emulsion. Due to the special amphiphilic structure (chemical anisotropy), Janus particles are expected to be accumulated more easily than isotropic particles at the oil-water interface. As a special kind of surfactant, amphiphilic Janus particles combine advantages of solid particles and amphiphilic surfactant molecules, hence provide better emulsifying properties. Glaser et al. [3] reported that Janus particles can effectively reduce the tension of a liquid/liquid surface, twice compared to homogeneous particles. Rodriguez [4] also experimentally proved that Janus particles exhibited a higher interfacial activity than homogeneous particles. Arditty et al. [5] pointed out that even if the amount of solid particles was insufficient to completely cover the surface of the droplet, the aggregation of droplets was significantly decreased. Binks et al. [6] found the surface activity of Janus particles in oil-water interface was three times higher than that of the corresponding homogeneous solid particles. Compared with homogeneous particles, Janus particles have the potential to produce smaller and more stable emulsion droplets.

Among all known materials, graphene is considered the strongest material with a Young’s modulus of 1TPa and it can be mechanically stretched 25% without breaking [7]. In graphene, each carbon atom has four valence electrons and its ground state electron configuration is $1s^22s^22p^2$. By the hybrid of $2S$, $2P_x$ and $2P_y$ orbits, σ bonds are formed between the adjacent carbon atoms. These σ bonds are the main reason...
of the high binding energy and elastic properties of graphene. The remaining 2p\textsubscript{z} orbits overlap each other to form π bonds, which is the main reason for its adsorption capacity onto the metal surface. Besides, the shearing strength between the graphene layers is small. Kim et al. [8] used the method of chemical vapor deposition to create multilayered graphene on a SiO\textsubscript{2}/Si surface. This graphene film was tested by an atomic force microscope (AFM). The results showed that the friction coefficient (COF) between graphene layers can reach 0.03. The high Young’s modulus and low shearing strength made graphene and its derivative have attracted a lot of attention in tribology. Fan et al. [9] used modified graphene oxide as an additive and found this significantly improved the tribological performance of pure multialkylated cyclopentanes. The COF and wear were reduced about 27% and 74% respectively. Jia et al. [10] used a four-ball tribometer to investigate the tribological behaviour of graphene sheets which were modified by oleic acid and calcium borate and subsequently dispersed in poly alpha olefin (PAO). Their results showed that the friction-reducing and anti-wear properties of PAO were both improved by the formation of a graphene-related lubricating boundary layer.

This work combines the potential emulsifying properties of Janus GO nanosheets, which were also called modified graphene oxide (MGO) in this work, and their potential tribological properties in Pickering emulsions. MGO was expected to act as an emulsifier to stabilize the O/W emulsion, and also act as an additive to improve the tribological properties of O/W emulsions. In order to get Janus GO nanosheets, long chain quaternary ammonium (TTAB) was grafted to one side of the GO surface. Through this way, the solubility of GO nanosheets in oil was increased, and their emulsifying properties were improved. The emulsifying and tribological properties of MGO nanosheets were investigated and compared with base emulsion with classical emulsifiers and Pickering GO-emulsion. Tribological properties of water and base emulsion were also studied for the comparison of friction-reducing and anti-wear capacities of MGO-emulsion. Fig. 1 shows the schematic diagram of emulsion droplets stabilized by classical emulsifier, nanoparticles and graphene derivative respectively.

2. Experimental part

2.1. Raw material

A commercial rapeseed oil, provided by Grease Factory of China was used as the base oil without any further treatment. The main chemical ingredients of the rapeseed oil are: palmitic acid (C\textsubscript{16}H\textsubscript{32}O\textsubscript{2}) 4.8%, stearic acid (C\textsubscript{18}H\textsubscript{36}O\textsubscript{2}) 5.0%, oleic acid (C\textsubscript{18}H\textsubscript{34}O\textsubscript{2}) 58.5%, linoleic acid (C\textsubscript{18}H\textsubscript{32}O\textsubscript{2}) 22.8%, linolenic acid (C\textsubscript{18}H\textsubscript{30}O\textsubscript{2}) 10.2%, erucic acid (C\textsubscript{22}H\textsubscript{40}O\textsubscript{2}) 0.8%, and behenic acid (C\textsubscript{22}H\textsubscript{44}O\textsubscript{2}) 0.1%. A nonionic surfactant polyoxyethylene (20) sorbitan monooleate (Tween 80) [11] was used as an emulsifier to prepare the base emulsion. Tween 80 was purchased from Sigma-Aldrich. Graphite powder (8000 mesh) and Myristyltrimethylammonium bromide (C\textsubscript{17}H\textsubscript{38}BrN, TTAB) were purchased from Aladdin. Paraffin wax and other used reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All raw materials were used without additional treatment. The water used in the experiments was deionized water.

2.2. Synthesis

Graphene oxide (GO) used in this study was synthesized from graphite by using the modified Hummers’ method [12]. Then, MGO was synthesized according to reference [13]. The process is shown in Fig. 2. Firstly, graphite oxide was synthesized from graphite powder. Next, the bulk graphite oxide was exfoliated by sonication to gain a GO aqueous solution. Lastly, GO was modified by TTAB to obtain the final product, which was referred to as MGO in this work. The specific method for the modification of GO with TTAB was as follows.

Paraffin wax (50g) was added to deionized water (200g) under a 60 °C water bath until wax was melted, then 200g GO solution (0.5 wt %) was added, followed by stirring for 2 h to form a wax-in-water emulsion. Hydrophilic oxygen-containing groups and a hydrophobic basal plane endow GO with amphiphilicity to act as Pickering stabilizer. Next, the wax-in-water emulsion was cooled to room temperature and GO-coated microparticles as shown in photograph can be obtained, the diameter of these microspheres was about 0.5–1 mm as shown in the SEM image in Fig. 2. Then microspheres were cleaned in deionized water and sonicated for 10 min to remove the GO nanosheets which physically adsorbed on the microspheres surface. After that 50g GO-coated microparticles and 1g TTAB were dispersed in aqueous-ethanol solution (1/1, V/V), followed by mild stirring at 30 °C for 12 h. Lastly wax microspheres were dispersed and dissolved in chloroform, washing with ethanol several times by using the centrifugation and sonication until bromide ions can’t be detected. The collected solid was dried at 40 °C under vacuum to obtain Janus GO and coded as MGO.

2.3. Emulsion preparation

The O/W base emulsion was prepared by mixing rapeseed oil (6.0 wt%), Tween 80 (3.0 wt%) and water. Emulsification usually does not happen spontaneously, and some extra energy is required to produce emulsion droplets [14]. For that, stirring and homogenization was employed. In this work, each emulsion sample was stirred (800 r/min) for 30 min and then homogenized 10 min (2000 r/min). The MGO-emulsion was prepared by the same steps, using rapeseed oil (6.0 wt%), Tween 80 (3.0 wt%), MGO nanosheets (0.5 wt%) and water. GO-emulsion was prepared with the same substance ratio and the same preparation steps for comparison.

2.4. Test methods

The micro-structure of graphite, GO and MGO were taken by a S-2150 Scanning Electron Microscope (SEM, Hitachi High-Technologies Corp., Japan), a JEM-2100 transmission electron microscope (TEM, Jeol, Japan) and a nanosurf C3000 atomic force microscope (AFM, Nanosurf AG, Switzerland). X-ray diffraction (XRD) measurements

![Fig. 1. Schematic diagrams of emulsion droplets stabilized by emulsifier, nanoparticles [2] and graphene derivative respectively.](image-url)
were performed by using a D-MAX 2200/PC X-Ray diffractometer (Japan Rigaku Corporation) under the condition of 2θ=5–60° and 6° min⁻¹. Cu Kα radiation (λ=0.154 nm) for the XRD analysis. GO and MGO nanosheets were dried at 40 °C for 24 h before XRD characterization. The chemical structures of GO and MGO were analyzed using a Paragon 1000 FT-IR Spectrometer (Perkin Elmer, Inc., USA).

The viscosities of emulsions were measured by a Brookfield DV-I digital viscometer. Microscopic images of large emulsion droplets were taken by an optical microscopy (Leica Map). The nanoparticle size distributions (1–1000 nm) of emulsions were measured by a NANOflex®-180° DLS Particle Analyzer.

The tribological properties of the emulsions were studied with a ball-on-ring tribometer as shown in Fig. 3(a), which was manufactured by CSM-instruments. Friction force and the corresponding COF were recorded automatically. The wear volume of the ball can be calculated by the formula in literature [15], which was also shown in Fig. 3(b).

Using k=V/(FN×l), the wear rate (k, mm³ N⁻¹ m⁻¹) can be calculated. V is the wear volume (mm³), l is the total sliding distance (m), F_N is the applied load (N). AISI 52100 bearing steel flat rings and bearing steel balls with a diameter of 25.4 mm were selected for the tests and purchased from SKF. The hardness of balls and rings was 65 HRC. The tribological behaviour of water, base emulsion, GO-emulsion and MGO-emulsion were investigated under a wide range of velocities from 20 mm/s to 200 mm/s. Before friction test, the rings and the balls were ultrasonically cleaned in acetone, isopropanol, and finally in water for 5 min each. Each test was repeated 3 times. The volume of lubricant used for the friction experiments was 30 ml. Based on the theory outlined in [16] and the initial test conditions, the lubrication regime was estimated to be in the boundary lubrication. An overview of the test conditions was given in Table 1. The contact pressure was calculated according to the Hertz equation for a point contact.

The roughness of the balls and the rings, as well as the 3D...
The prepared dispersions were stored in room temperature for 30 days. Ether solution (1/1, V/V) respectively with a concentration of 0.2 wt%. GO solutions in concentrations of 1 wt%, 0.5 wt% and 0.1 wt% were obtained.

3. Polarity and surface activity of GO and MGO

3.1. Hydration property of graphite oxide

The basic unit of graphite oxide has a typical two-dimensional plane structure. Carbon atoms in the same layer are linked by covalent bonds. However, carbon atoms between adjacent layers are connected by weak hydrogen bonds formed between the oxygen-containing functional groups. Graphite oxide contains a large amount of -C-OH, -C-O-C- and -COOH groups, thus having a very strong polarity. Also due to the presence of these polar groups, small molecules can insert into the layers of graphite oxide, such as water molecules. This means that graphite oxide can be hydrated and swollen in water. Fig. 4 shows the different swollen state of graphite oxide during the washing process. Each time the part above the dotted line was removed, the part below di

3.2. Polarity and surface activity of GO and MGO

GO nanosheets were dispersed in deionized water by ultrasound to get GO solutions in concentrations of 1 wt%, 0.5 wt% and 0.1 wt%. MGO nanosheets were ultrasonically dispersed in water and water-ether solution (1/1, V/V) respectively with a concentration of 0.2 wt%. The prepared dispersions were stored in room temperature for 30 days. Fig. 5 shows their dispersion photographs after the 30 days storage. Fig. 5(a1), (a2), (a3) are the aqueous solution of GO. It can be seen GO can be dispersed well in water, the aqueous solution of 1 wt% GO was brownish yellow and the color gradually faded with the decrease of GO concentration. Li et al. [17] proposed that some carboxyl and hydroxyl groups on GO surface can be ionized, hence the GO nanosheets in water were negatively charged, resulting in electrostatic repulsion. Meanwhile, the oxygen containing groups C-OH, -C-O-C- and COOH possess strong polarity. They can form hydrogen bonds with water. Electrostatic repulsion and strong polarity both contribute to the good water-solubility and stability of GO in water medium.

Fig. 5(b1) and (b2) show the dispersion results of 0.2 wt% MGO in water and in water-ether solution (1/1, V/V) respectively. From Fig. 5(b1), it can be seen that the solubility of MGO in water was poor, a part of the MGO nanosheets were deposited to the bottom, another part was concentrated in the upper side of the water. This is explained by the fact that one side of MGO nanosheets was covered with TTAB chains which is hydrophobic, whereas the basal plane of MGO is hydrophobic. Therefore, the hydrophilicity caused by the oxygen-containing groups was suppressed in MGO. MGO nanosheets tended to concentrate in the water-air interface to reduce the interfacial free energy, indicating that MGO nanosheets possess a high surface activity. This can be confirmed by Fig. 5(b2), where MGO nanosheets were concentrated in the water-ether interface.

To a certain extent, this indicated that the preparation of MGO was successful, and the non-polarity of MGO was stronger than that of GO due to the modification of the GO surface. MGO possesses a higher adsorption energy than GO at the oil-water interface due to its amphiphilic structure. It was expected that most of the MGO nanosheets would be located at the oil-water interface to stabilize the droplets in the emulsion instead of floating in the water phase like GO.

3.3. SEM analysis

Fig. 6 shows the SEM images of pristine graphite ((a) and (b)), GO ((c) and (d)) and MGO ((e) and (f)) nanosheets. We can see that the pristine graphite showed a stacking layered structure. From the SEM images of GO and MGO, we can see that they both show a flexible film structure with folds. For GO, this is explained by the oxygen-containing groups on the GO nanosheets. The inside areas contain hydroxyl and epoxy groups, the edge areas contain carboxyl groups. These oxygen-containing groups attracted to each other through hydrogen bond or polar adsorption, resulting in folds in GO sheets. For MGO, one side was modified with TTAB, therefore folds in MGO were less than that of GO, which means MGO nanosheets were smoother than GO nanosheets. This can be confirmed through SEM images of MGO (e) and (f).

3.4. TEM analysis

TEM images of GO and MGO are shown in Fig. 7. It can be seen

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Friction test conditions in this work.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test-related</td>
<td>Instructions</td>
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<tr>
<td>Equipment:</td>
<td>Ball-on-ring</td>
</tr>
<tr>
<td>Diameter of the ball:</td>
<td>25.4 mm</td>
</tr>
<tr>
<td>Normal load:</td>
<td>0.5 N</td>
</tr>
<tr>
<td>Contact pressure:</td>
<td>130 MPa</td>
</tr>
<tr>
<td>Velocities:</td>
<td>20–200 mm/s</td>
</tr>
<tr>
<td>Sliding distance:</td>
<td>100 m</td>
</tr>
<tr>
<td>Rs surface roughness (ball):</td>
<td>30 ± 10 nm</td>
</tr>
<tr>
<td>Rs surface roughness (ring):</td>
<td>100 ± 50 nm</td>
</tr>
<tr>
<td>Velocities:</td>
<td>200 mm/s</td>
</tr>
<tr>
<td>Contact pressure:</td>
<td>130 MPa</td>
</tr>
<tr>
<td>Normal load:</td>
<td>0.5 N</td>
</tr>
<tr>
<td>Sliding distance:</td>
<td>100 m</td>
</tr>
<tr>
<td>Rs surface roughness (ball):</td>
<td>30 ± 10 nm</td>
</tr>
<tr>
<td>Rs surface roughness (ring):</td>
<td>100 ± 50 nm</td>
</tr>
</tbody>
</table>

Fig. 4. Photographs of graphite oxide during the washing process.
that GO and MGO films were both translucent. The edge areas of MGO had less folds comparing with GO, which further confirmed the effect of oxygen-containing functional groups on the folds. From the SEM and TEM images, it can be inferred that the folds of GO and MGO may be associated with their oxidation degrees. The higher oxidation degree resulted in more folds.

3.5. XRD analysis

The results of XRD tests are shown in Fig. 8. It can be seen that a strong diffraction peak of GO appeared at around 10.34°, which was the characteristic peak of GO. Compared with the characteristic peak of graphite at about 26.58°, the diffraction peak of GO was shifted to the left. Besides, the X-diffraction characteristic peaks corresponding to (002), (101) and (004) crystal planes of graphite all disappeared in the XRD pattern of GO. The disappearance of the characteristic peak of graphite meant that graphite powder had been fully oxidized. Meanwhile, compared with graphite, the diffraction intensity of GO was reduced. This can be explained from the following two aspects. On one hand, after the oxidation process of graphite, the distance between the adjacent layers became larger, the original structure was destroyed and the crystallinity was decreased, which may lead to a smaller diffraction peak. On the other hand, during the oxidation process, the original graphite plate may have been divided into several smaller pieces. The smaller plane size may also lead to the smaller diffraction peak.

The 20 peak of MGO was weaker comparing with GO. It may be ascribed to TTAB chains, which prevented the aggregation and re-stacking of MGO nanosheets. Two peaks at 8.85° and 10.34° can be seen from the XRD pattern of MGO. The peak at 8.85° may correspond to the interlayer spacing between two modified sides of MGO, and the peak at 10.34° may be ascribed to the distance between two unmodified sides [13]. According to Bragg’s law: 2d sin θ = nλ [18], the distance between two neighboring sheets in graphite was around 0.335 nm, in GO it was 0.855 nm, and in MGO it mainly was 0.999 nm. This indicated that the interlayer spacing of GO crystals was increased about 0.144 nm after the modification with TTAB, which means the effect length of TTAB chains after drying was about 0.144 nm.

3.6. AFM analysis

Fig. 9 shows the AFM images and the corresponding height curve of MGO. For AFM's nanometer resolution, surface morphology and the three-dimensional structure information can be obtained, such as surface area, thickness, width and volume. It can be seen that the thickness of MGO was about 0.8–1.4 nm (Line 1). Based on the report of De Silva [19], the monolayer thickness of GO was around 0.8–1.2 nm, and the aforementioned XRD result that the effect length of TTAB chains after drying was about 0.144 nm, it can be inferred that the prepared MGO was about one layer.

3.7. FT-IR analysis

The IR spectra of TTAB, GO and MGO are shown in Fig. 10, the corresponding IR absorption peak are shown in Table 2. From the 1053 cm⁻¹ (C=O vibration in C=O-H), 1225 cm⁻¹ (C-O-C), 1384 cm⁻¹ (C-O bonds of carboxyl), 1621 cm⁻¹ (skeletal vibration of C=C bonds in GO) [20], 1736 cm⁻¹ (C=O stretching of carboxylic acid) and 3400 cm⁻¹ (O-H vibration) in the FT-IR spectrum of GO, it can be seen that GO prepared in this work contained carboxyl, hydroxyl and epoxy groups. Because of these oxygen-containing groups, GO has a good hydrophilicity. The FT-IR spectrum of MGO showed the characteristic peaks of alkyl groups which are ascribed to TTAB chains. The peaks at 2853 cm⁻¹ and 2924 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibration of alkyl groups, respectively. Meanwhile, characteristic bands corresponding to oxygen functional groups also can be found in the FT-IR spectrum of MGO. It indicated that there were a certain amount of epoxy groups and carboxyl groups on the MGO nanosheets which did not interact with TTAB. To a certain extent, FT-IR results proved that the MGO preparation was successful.

4. The emulsifying and tribological properties of the emulsion containing GO and MGO

4.1. Emulsifying property

The nanoparticle size distributions and average particle diameter of the prepared emulsion droplets (1–1000 nm) at the 1st day and 30th day are presented in Fig. 11. Normally, emulsions are thermodynamically unstable and droplets tend to merge with each other to form bigger droplets. Fig. 11(b) shows that the mean particle sizes of the base emulsion, the GO-emulsion and MGO-emulsion were respectively around 410 nm, 230 nm and 110 nm one day after preparation. 30 days later, the mean particle size changed to around 800 nm, 350 nm and 140 nm, respectively. The average particle size of MGO-emulsion was smaller than that of the others. Fig. 11(a) shows that the particle size of MGO-emulsion only slightly changed after 30 days of storage, comparing to the other emulsions, indicating the highest stability of MGO-emulsion. From the contrast of GO-emulsion and MGO-emulsion, it can be inferred that the emulsifying property of MGO
Fig. 6. SEM images of graphite (a), (b), GO (c), (d) and MGO (e), (f)

Fig. 7. TEM images of GO (a) and MGO (b).
nanosheets was stronger than GO nanosheets.

Fig. 12 shows optical microscopy images of base emulsion, GO-emulsion and MGO-emulsion at the 1st and 30th day after preparation. Compared with the method of dynamic light scattering (DLS), optical microscopy can be used to visually observe the morphology of large droplets in emulsion. Fig. 12 shows that, incorporating GO or MGO into base emulsion led to the formation of smaller droplets with higher stability. MGO’s effect was particularly noticeable. After 30 days storage, the particle size of the MGO-emulsion was virtually unaffected. This suggested that the emulsifying property of MGO was better than that of GO, and MGO can efficiently improve the stability of the base emulsion.

Figs. 11 and 12, from the micro and macro point of view, show the variation of the emulsion droplets. It can be seen that, MGO-emulsion possessed the smallest droplets and the best stability. After 30 days storage, the droplet size of MGO-emulsion hardly changed. However, both GO and MGO nanosheets possess the ability to reduce the droplet size, and increase the stability of the base emulsion. This can be explained by the fact that, compared to the traditional emulsifier, Tween 80, nanoparticles films are capable of withstanding physical shocks and maintaining stability. Moreover, for GO- and MGO-coated droplets, the carboxyl groups and hydroxyl on the hydrophilic side of the droplets may be ionized to be negatively charged, resulting in electrostatic repulsion. The stable nanoparticles film and electrostatic repulsion might be the main reasons for the increased stability of base emulsion after the addition of GO or MGO.

Long-term stability of emulsions mainly depends on the thickness and strength of the adsorbed emulsifier film at the oil-water interface [21]. Generally the thicker the interfacial film, the greater the interfacial strength and the more stable the emulsion droplets. Compared with GO, MGO possessed TTAB chains (C17), resulting in the thicker interfacial film. Moreover, rapeseed oil contained various long-chain fatty acid (C16–C22), which means TTAB chains can be well dispersed in rapeseed oil, resulting in a higher affinity of MGO towards oil phase than that of GO. The thicker interfacial film and the better solubility of MGO in the oil phase provide MGO-emulsion droplets a more effective barrier against coalescence. This explains why MGO showed better...
emulsifying property than GO.

### 4.2. Tribological property

The COF and the 3D topographies of the corresponding wear scars lubricated with water, base emulsion, GO-emulsion and MGO-emulsion at a sliding velocity of 40 mm/s are shown in Fig. 13(a)–(d) respectively. It can be seen that, under water lubrication the COF was the highest, with an average value of 0.136 and an increasing trend over 100 m. In the situation of water lubrication, it was difficult to form a sufficiently thick boundary lubrication film due to the low viscosity of water. Convex points on the friction surface were easy to contact and scratch the counter friction surface, deep grooves and some large abrasives can be produced. This metal-metal contact led to the higher COF, abrasive wear and more grooves in the subsequent friction process. This can be confirmed from the 3D topography of the corresponding worn surface, which showed the biggest wear scar diameter (WSD) about 413 µm and the deepest wear scar about 87.5 µm with obvious furrows on it.

The base emulsion lubrication maintained a COF of approximately 0.120, the WSD and wear scar depth on the corresponding wear scar were about 380 µm and 57.6 µm respectively. Compared with water lubrication, base emulsion showed the improved friction-reducing and anti-wear capacities. This is due to the "plate-out" process, which creates a boundary oil-film with better lubricity, compared to the water-film in water lubrication.

GO-emulsion lubrication resulted a COF about 0.114, the WSD and wear scar depth on the corresponding wear scar were about 362 µm and 37.6 µm respectively. Compared with base emulsion lubrication, GO-emulsion showed the reduced friction-reducing and anti-wear capacities. This is due to the critical surface tension of GO nanosheets, which might create a solid lubrication film on the rubbing surface and effectively reduce friction and wear.

MGO-emulsion lubrication showed the lowest COF of 0.098 with a slight decreasing trend. This may be because, with the continuous sliding more and more MGO nanosheets were adsorbed on the metal surfaces creating a more compact MGO layer between the two contact surfaces, resulting in a decreasing COF and the smallest WSD about 323 µm. Meanwhile, the worn surface lubricated with MGO-emulsion showed the minimum roughness with a wear scar depth of 31.2 µm.

The anti-wear capacity of lubricant can be reflected from the 3D topography of the wear scar. The wear rate of the ball can be calculated from the WSD. In the 100 m test with an applied load of 0.5 N and a sliding velocity of 40 mm/s, the wear rates of the balls lubricated by water, base emulsion, GO-emulsion and MGO-emulsion were $2.25 \times 10^{-6}$, $1.61 \times 10^{-6}$, $1.33 \times 10^{-6}$ and $8.41 \times 10^{-7}$ mm$^3$ N$^{-1}$ m$^{-1}$ respectively. Fig. 13 shows that the MGO-emulsion has better friction-reducing and anti-wear properties than the GO-emulsion. This may be due to the following three reasons. First, droplets in the MGO-emulsion are relatively stable, stable droplets may be more conducive to the reduction of COF, and let it vary in a small range which can be confirmed in Fig. 13(d). Second, the long TTAB chains and the better solubility of MGO in oil phase make MGO and rapeseed oil form thick adsorption film together between two rubbing surfaces, which would result in a relative small COF and wear rate. Third, the TTAB chain can provide a big steric hindrance to prevent the restacking of the "graphene basal plane", which has been proved by the XRD analysis. This means it is difficult for MGO nanosheets to form large solid particles. Compared with GO, MGO nanosheets are more inclined to keep the loose state, which may also contribute to the smaller COF and lower wear rate. These three reasons can be used to explain why MGO-emulsion showed better friction-reducing and anti-wear properties than GO-emulsion.

Fig. 14(a) compares the COF of the contact surfaces lubricated with deionized water, base emulsion, GO-emulsion and MGO-emulsion respectively at a sliding velocity of 40 mm/s. Fig. 14(b) shows the variations of the COF as a function of velocity. Considering the sliding velocities of 20–200 mm/s, initial boundary lubrication conditions were expected to occur in the friction experiments [16]. From Fig. 14, it can be seen that the friction-reducing capacity of the used lubricants can be ranked as MGO-emulsion > GO-emulsion > base emulsion > deionized water under the same test conditions. MGO-emulsion showed the best friction-reducing performance. However, it can be seen that with the increase of velocity, the COF created by the four lubricants all showed the decreasing tendency. This may be because, as a result of the wear, the contact area was increased which means the contact pressure was reduced under the constant applied load, coupled with the increased velocity, the lubrication regime may be transferred from boundary lubrication to mixed lubrication. Based on the Stribeck curve, the COF of mixed lubrication is lower than that of boundary lubrication. This could be the reason of why COF of the contact surfaces lubricated by these four lubricants all showed the decreased trend as the velocity increased.

A summary of the fluid viscosity, COF, WSD and specific wear rate

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**Table 2**

<table>
<thead>
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<th>Absorption peak (cm$^{-1}$)</th>
<th>Vibration functional group</th>
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<tr>
<td>3400</td>
<td>OH</td>
</tr>
<tr>
<td>1736</td>
<td>C=O in COOH</td>
</tr>
<tr>
<td>1621</td>
<td>C=C</td>
</tr>
<tr>
<td>1384</td>
<td>C-O in COOH</td>
</tr>
<tr>
<td>1225</td>
<td>C-O-C</td>
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<tr>
<td>1053</td>
<td>C-O in C-OH</td>
</tr>
<tr>
<td>875, 2924</td>
<td>CH$_2$</td>
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</tbody>
</table>

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**Fig. 11.** (a) The size distribution and (b) mean particle size of emulsion droplets in the 1st and 30th day after preparation.
of the ball is given in Table 3. From this table it can be seen that, with an average contact pressure of 130 MPa and a velocity of 40 mm/s at room temperature, the average COF and wear rate of the ball lubricated with MGO-emulsion were decreased by about 18% and 48% respectively compared to base emulsion lubrication, and about 14% and 37% respectively, comparing to GO-emulsion lubrication. MGO can effectively improve the friction-reducing and anti-wear properties of the base emulsion. However, it should be noticed that the viscosity of base emulsion only increased slightly by adding MGO, which suggests that the reduction of COF and wear rate after the addition of MGO was not due to the change of fluid viscosity. Different COF and wear rate could be due to the different boundary lubrication films on the rubbing metal surfaces [22].

5. Surface analysis

5.1. Raman analysis

Raman spectroscopy is one of the most powerful tools for the analysis and characterization of carbon materials. Fig. 15 shows the Raman spectra of graphite, GO, MGO, and the worn surface after lubricating with MGO-emulsion. The used excitation wavelength was 532 nm. It can be seen, Raman spectrum of graphite showed two peaks located at about 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\), corresponding to the D bond and G bond, respectively. G peak in the spectrum of graphite was narrow and high, which meant the crystalline form of graphite was good and the sp\(^2\) hybrid was dominant. In the graphite family, G peak represents the in-plane C-C stretching vibration (sp\(^2\) hybridization) of carbon atoms. D band can tell the information of introduced defects, including the presence of sp\(^3\)-sp\(^2\) impurities, the clustering of the sp\(^2\) phase, and so on [23].

The R value (R=\(\text{I_D}/\text{I_G}\)) represents the disorder degree of carbon material, and can be obtained by peak fitting and integral strength calculation. The higher the R value, the higher the disorder degree. We can see that the R value of graphite, GO, MGO and the worn surface were 0.08, 0.95, 1.09 and 1.2 respectively. The GO crystal layer has a large amount of oxygen-containing functional groups which can be viewed as lattice defects. Compared with graphite, the sp\(^3\) hybrid of GO was decreased but the sp\(^2\) hybrid was increased, resulting in an increased D band. After the modification of GO nanosheets, the \(\text{I_D}/\text{I_G}\) ratio increased from 0.95 to 1.09, which further confirmed that TTAB chains had been successfully grafted onto GO surface, as TTAB chains can be viewed as sp\(^3\) impurities.

Compared with MGO, the spectrum of the worn surface showed improved D band intensity, the R value increased from 1.09 to 1.2, which firstly proved the existence of MGO nanosheets on the wear scar surface. Since D band contains the information of possible defects, the increased R value of the worn surface implied that some MGO nanosheets may have been destroyed during the sliding process, and some defects may have been formed. By Raman analysis, it can be concluded that a thin MGO film was formed on the contact surface.

5.2. XPS analysis

Fig. 16(a)–(c) show the XPS spectra of the main elements on the cleaned ball surface before friction test, worn surfaces after friction test with base emulsion and MGO-emulsion respectively. Table 4 shows the binding energies corresponding to worn surfaces lubricated with MGO-emulsion. The corresponding substance of each separated peak was queried from the NIST XPS Database [24].

Fig. 16(a) showed that the major substances on the pristine ball surface were C, SiO\(_2\), H\(_2\)O and FeOOH. C may exist in the bearing steel ball, SiO\(_2\) could be some pollution, H\(_2\)O might be due to the moisture in the air, FeOOH was some minor oxidation. Fig. 16(b) indicated that after the friction test with the base emulsion, the main compounds on the worn surface were organic matters and iron oxides. Organic matters were originated from rapeseed oil and emulsifier. Most of the iron oxides were produced during the friction test due to the tribochemical reaction.

From Fig. 16(c) and Table 4, it can be seen that after the friction test with MGO-emulsion, C element on the worn surface mainly existed in the form of graphite C, C-H, C-O and C=O. Wherein, graphite C corresponded to the basal plane in MGO. C-O and C=O bonds might be oxygen-containing groups on MGO surface. O element on the worn surface mainly existed in the form of iron oxide Fe\(_{x}\)O\(_{y}\), C-O and C=O. Fe element mainly existed in the form of Fe\(_{x}\)O\(_{y}\), Fe(CO)\(_{5}\), Fe(C\(_{5}\)H\(_{4}\)COOH)\(_{2}\) and Fe(C\(_{5}\)H\(_{4}\))\(_{2}\). The existence of Fe(CO)\(_{5}\), Fe(C\(_{5}\)H\(_{4}\)COOH)\(_{2}\) and Fe(C\(_{5}\)H\(_{4}\))\(_{2}\) denoted that MGO had reacted with the metal surface, and the tribochemical reaction film (tribofilm) had been formed.
Fig. 13. COF and 3D topography of wear scars on the balls lubricated with (a) deionized water, (b) base emulsion, (c) GO-emulsion and (d) MGO-emulsion (X 50, sliding velocity 40 mm/s).
studied the strong adsorption ability onto the metal surface. Cambiella et al. surface exhibited a better film-forming ability of emulsions. Their results showed that the adsorption interactions between the metal surface and the emulsifier molecules played a key role in the mechanism of emulsion lubrication. For MGO-emulsion, the polar sides of MGO nanosheets which contained oxygen functional groups made MGO-coated droplets have strong adsorption ability onto the metal surface. Meanwhile, the π bond in the basal plane of MGO was also helpful for the adsorption ability. The adsorption ability of MGO-coated droplets was stronger than droplets in base emulsion. Hence the film-forming ability of MGO-emulsion was stronger than that of base emulsion. Strong film-forming ability could be one of the reasons of why MGO-emulsion showed better tribological performances than the base emulsion though it also exhibited better stability with smaller droplets.

Second, MGO-emulsion results in good lubricity due to its small droplets. Kumar et al. [26] suggested that the smaller droplets played a more important role in lubricity than the bigger droplets, and the smaller droplets in an emulsion aided lubricity. In their work, the average particle size of the base emulsion, GO-emulsion and MGO-emulsion were respectively around 410 nm, 230 nm and 110 nm in the nanotribometer. Their study showed that the smaller droplets were situated much closer to the substrate than the bigger droplets. In this work, the average particle size of the base emulsion, GO-emulsion and MGO-emulsion were respectively around 410 nm, 230 nm and 110 nm in the first day after the preparation. This meant that those small MGO-coated droplets could be easily brought into the small grooves and filled in the micro-pits on the contact surfaces. As a result, the roughness of the rubbing surfaces was decreased, the COF and the wear rate were reduced. The small droplet size could be another reason of why MGO-emulsion showed better tribological properties than base emulsion and GO-emulsion.

Third, MGO-emulsion can form the adsorption film, transfer film and tribofilm between the contact surfaces. After the breakup of MGO-coated droplets, the flexible thin film structure of MGO nanosheets endows them easily be transferred into the contact surfaces, and further adsorbed and deposited on the friction surfaces. Raman spectroscopy confirmed that MGO-emulsion can form a MGO film on the rubbing surface. MGO nanosheets not only can inlay in the micro-pits and smooth the rubbing surfaces, but also can be attached tightly to the metal surfaces, enhancing the hardness of the rubbing surfaces because of the high Young’s modulus of their basal plane. Moreover, due to the TTAB chains and their good solubility in oil phase, MGO and rapeseed oil can form a relative thick and strong adsorption film between two contact surfaces, which reduces wear. Some MGO nanosheets may adhere directly with the metal surface, some MGO nanosheets may overlap irregularly. The overlapped MGO nanosheets can be slipped easily for their low shearing strength, thus can be viewed as transfer films. MGO transfer films with self-lubricity had the ability to reduce the COF and improve the wear resistance of the steel balls. Moreover, through XPS analysis, it can be seen that some MGO nanosheets had reacted with the rubbing surfaces, and a tribofilm had been formed. Hence, MGO nanosheets can be bound more tightly

6. Tribological mechanism of MGO-emulsion

Tribological test results told us that MGO-emulsion had the friction-reducing and anti-wear capacities. Based on the worn surface analysis, the tribological mechanism of MGO-emulsion can be proposed as the following three aspects.

First, MGO-emulsion possesses the strong film-forming ability for its strong adsorption ability onto the metal surface. Cambiella et al. [25] studied the film-forming ability of O/W emulsions, and they found the adhesion ability of oil droplets onto metal surfaces can be used to predict the film forming ability of emulsions. Their results showed that those emulsion droplets with a strong adsorption capacity at the steel surface exhibited a better film forming ability. Macroscopic characteristics of emulsions such as stability and droplet size distribution didn’t seem to affect the lubrication performance. Cambiella et al. claimed that the adsorption interactions between the metal surface and the
with the metal surfaces through the formation of chemical bonds. Adsorption film, transfer film and tribofilm may work together to reduce COF and wear of the contact surfaces.

In summary, during the friction process, MGO-coated droplets can be quickly adsorbed onto metal surface, forming adsorption film and transfer film between the rubbing surfaces. Those shortened the “running in” period \[22\] and the initial COF. With subsequent sliding, a more compact and continuous oil-containing transfer film may be formed by the mixture of MGO and rapeseed oil. Meanwhile, MGO nanosheets can react with the rubbing surfaces to bind more tightly with the metal surfaces. The formed adsorption film, transfer film and tribofilm possessed the friction-reducing and anti-wear capacities.

### 7. Conclusions

(1) In this work, graphene oxide (GO) was obtained by Hummer’s method, GO nanosheets were asymmetric modified with TTAB. Successful grafting of TTAB chains was proved by using XRD, FT-IR and Raman spectroscopy.

(2) SEM and TEM results showed that the original graphite had a stacking layered structure, but GO and MGO both showed the flexible thin film structure with folds. By AFM, it can be suggested that the prepared MGO was about one layer.

(3) The changes of nanoparticle size distributions and optical microscopy images of the emulsion were used to value the emulsifying properties of GO and MGO. The results showed that MGO contributed to the better emulsification performance comparing to GO. MGO-emulsion exhibited smaller droplets with higher stability, hardly changed within 30 days storage.

(4) MGO-emulsion possesses high friction-reducing and anti-wear performances. Compared with base emulsion lubrication, COF

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### Table 4

<table>
<thead>
<tr>
<th></th>
<th>(C_1s) E (eV)</th>
<th>(O_1s) E (eV)</th>
<th>(Fe_{2p3/2}) E (eV)</th>
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<tr>
<td>C-O</td>
<td>288</td>
<td>533.3</td>
<td>Fe(_2O_3), Fe(_3O_4) 715.7</td>
</tr>
<tr>
<td>C-H</td>
<td>285.7</td>
<td>532.6</td>
<td>Fe(OH)(_2), Fe(_2O_3) 711.3</td>
</tr>
<tr>
<td>C-O</td>
<td>284.83</td>
<td>531.4</td>
<td>Fe(CO)(_3), FeO 709.6</td>
</tr>
<tr>
<td>Graphite</td>
<td>284.3</td>
<td>530</td>
<td>Fe(C(_5)H(_4)COOH)(_2) 708.4</td>
</tr>
</tbody>
</table>

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Fig. 16. XPS spectra of the typical elements on the ball surfaces.
and wear rate of the ball were decreased by 18% and 48% respectively. Compared with GO-emulsion lubrication, the reduction of COF and wear rate of the ball were about 14% and 37% respectively.

(5) Raman spectra results confirmed the existence of MGO film on the worn surface, and some MGO nanosheets may have been destroyed during the sliding process. XPS results indicated that MGO had reacted with the metal surface, and the tribofilm was formed on the rubbing surface.

(6) Tribological mechanism of MGO-emulsion may be due to the following three aspects: The strong film-forming ability of MGO-emulsion; the excellent lubricity of the small droplets in MGO-emulsion; the formed adsorption film, transfer film and tribofilm between the two rubbing surfaces. These three aspects may work together to reduce COF and wear of the contact surfaces.

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References


