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The pH-dependent structural and tribological behaviour of aqueous graphene oxide suspensions

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The pH-dependent structural and tribological behaviour of aqueous graphene oxide suspensions

Abstract

In this study, the tribological characteristic of aqueous dispersions of single-layer graphene oxide (GO) sheets was assessed as a function of pH. The flexible and large GO sheets were broken down and chemically reduced upon increasing the pH from 3.10 to 9.70. By using the 0.06 wt% GO suspension, the noise and vibration in tribological tests were eliminated, at the same time, the coefficient of friction (COF) and wear mark radius were reduced by 44.4% and 17.1%, respectively, compared with baseline water. While the increase of pH of the GO suspensions increased COF and wear significantly. The difference of the lubricating mechanism of the GO suspensions was attributed to the change of morphological and physicochemical properties of the GO sheets.

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The pH-dependent structural and tribological behaviour of aqueous graphene oxide suspensions

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Abstract

In this study, single-layer graphene oxide (GO) sheets were uniformly dispersed in water, and the effects of pH modification on the structure and morphology of the GO sheet were investigated. The flexible and large GO sheets were broken down and chemically reduced, caused by the increase of pH value from 3.10 to 9.70. The tribological performance of the GO suspensions of different pH values was characterised using a ball-on-three-plate tribometer with a steel on steel contact. It was found that using the GO suspension of pH 3.10, the coefficient of friction (COF) and wear mark radius were reduced by 44.4% and 17.1%, respectively, compared with baseline water, whereas neutral and basic GO suspensions increased COF and wear significantly. The effect of pH value on the lubrication was attributed to morphology change of the GO sheets in suspensions.

Keywords: Graphene oxide, water-based lubricant, lubrication, pH value, tribology.

1. Introduction

Water-based lubricants have recently attracted great academic and industrial attention as they have high thermal conductivity and are environmentally friendly [1]. Water itself is not a good lubricant because of its relatively low lubricity, low viscosity and weak load-carrying capacity. However, the addition of nano-structures into water could improve the tribological performance of water-based lubricants [2, 3]. Carbon-based nanomaterials, such as the single-layer and few-layer graphene oxide (GO) sheets, are potentially such candidates, owing to their superior tribological behaviours, unique mechanical properties, and most importantly, self-lubricating ability [4-10].

Previous studies were concerned with the feasibility of using GO sheets as water-based lubricant additives. The friction and wear in the steel to steel sliding contacts can be effectively reduced by the addition of GO sheets into water [11-13]. For example, Song and Li [11] reported that the addition of well-dispersed GO improved the friction and wear properties of the water-based suspension compared with those of water in a steel-steel ball-on-plate tribological test. The most commonly applied lubrication mechanism for GO in water-based lubricants was that the unique one-atom-thick layer structure of GO sheets and weak van der Waals force between adjacent GO layers made the entrainment of GO sheets into the contact area and inter-layer sliding easy for friction reduction. The GO sheets could also cover the contact surfaces during lubricating processes, preventing the surfaces from corrosion and oxidation [6, 14].

Nevertheless, the GO structures and morphology are very sensitive to the solvent properties such as ionic strength and pH value [15-17], and the relationship between physicochemical change and pH value are still unclear because of the complex functional group attached on GO sheets. For example, Bosch-Navarro *et al.* [17] demonstrated that during the hydrothermal reduction process of GO, acidic conditions induce larger amount of defects, leading to the reduced GO (r-GO) with smaller sizes, compared to those produced under the basic conditions. However, Wu *et al.* [18] reported that due to the protonation of carboxyl groups and the partial removal of oxygen-containing functional groups, both high and low pH values resulted in GO sheets with small lateral sizes, while in neutral and alkaline environment the GO sheets appear to be large. Till now, little has been reported on how solvent acidity/alkalinity may affect the GO structural properties and functional groups, and hence the tribological performance and lubrication mechanism [19].

In this study, the effect of pH values on the GO microstructures was systematically investigated. The tribological behaviour of the GO water-based lubricants with different pH values was evaluated by using the tribological testing with steel-steel ball-on-three-plate sliding contact. Eventually, a link between the change of the structure and morphology of GO sheets and their effects on the lubricating mechanism of GO water-based suspensions was revealed.

2. Experimental details

2.1. Materials

GO sheets in powder form (analytical grade with a purity of > 97 wt.%) were commercially available (supplied by Henqiu Graphene Tech. Co. Ltd, China). The sheets have a lateral size varied from 10 to 50 μm and a thickness of 1-2 nm. The XRD spectrum of the GO sheets is shown in Fig. 1(a). A dominant (002) diffraction peak is found at 11.2° , indicating a large interlayer spacing of approximately 7.95 Å. A much weaker peak is located at 20.9° , corresponding to an interlayer spacing of approximately 4.24 Å. The results indicate that a small amount of graphite exists in the GO powder, but the majority of the powder is well-exfoliated single layered. Fig. 1(b) shows the atomic force microscopic (AFM) image of the GO sheets deposited on freshly cleaved mica substrate. Typical GO morphologies, such as wrinkles and folding, can be observed. The edges of the GO sheets are well defined without sharp corners. From the line profile shown in Fig. 1(c), it is seen that the thickness of the GO sheets is approximately 1.04 nm, indicating that the GO sheets have single-layer structure.

2.2. Preparation of GO suspensions

A mechanical de-agglomeration process was used to prepare GO suspensions. In this process, 0.5 wt.% of GO powders were added into Milli-Q deionised (DI) water. The suspension was stirred for 30 minutes, followed by ultrasonic bathing (Hwashin Tech. Co., Korea) for 15 minutes. The suspension was then agitated using an ultrasonic probe (Branson Digital Sonifier 450, USA), wherein a high intensity ultrasonic agitation of 400 watts was applied for 10 minutes with a 5-second on/off interval. Circulated chilled water bath was used to maintain suspension temperature during the agitation process. The suspension was further diluted to a weight content of 0.06 wt.%. The pH value of the pristine GO suspension was at 3.10, measured using a digital calibrated pH meter (Mettler-Toledo International Inc., Switzerland). Finally, 0.1 M of NaOH was added into the suspension, at mass fractions of

0.725, 1.1, 1.375 and 2.1 wt.%, respectively, so the GO suspensions with different pH values of 3.10, 5.41, 6.62, 8.80 and 9.70 were prepared. For comparison purpose, water with corresponding pH values was also prepared by addition of 0.1 M of NaOH and HCl.

2.3. Materials characterisation

The morphology of the GO sheets was examined using a field emission scanning electron microscope (FE-SEM, JSM-7001F, JEOL, Japan) and a transmission electron microscope (TEM, JEM2100, JEOL, Japan) operated at 200 kV. For FE-SEM, the suspensions were directly deposited on oxygen-plasma treated silicon wafers, which were cleaned with ethanol in ultrasonic bath for 10 minutes beforehand. After drying, the residual was uniformly deposited over the substrate. For TEM, the suspensions were further diluted in DI water to 0.006 wt.%. The suspension appears to be gold in colour. Then a pipet was used to transfer the suspension onto a TEM copper grid for observation. The chemical composition of GO was analysed using an X-ray photon spectroscopy (Axis Ultra XPS, Kratos, UK). The Raman spectra of the GO suspensions at different pH values were measured using a Renishaw microscope with a 514 nm laser excitation.

The Z-average particle size distribution, which is the representation of the GO lateral size distribution, was measured using a dynamic light scattering (DLS) method using a Zetasizer nanosystem (Malvern Instruments Ltd., UK). DLS is commonly used to measure the diameter of spherical particles, but it was a promising method to estimate the lateral size distribution of GO sheets in this case. According to the Beer-Lambert Law [20], the change of concentration of the supernatant fluid of a GO suspension over time can be characterised by the absorbance change, which was used to investigate the colloid stability of the suspension [21]. In this work, a UV-vis spectrophotometer (V-650, JASCO Inc., USA) was used to measure the absorbance of the GO suspensions. At first, the suspensions were aged at room temperature for designated time interval. Then the supernatant fluid was extracted using a high precision pipet. The suspension was diluted at 1:100 (suspension to water) before testing. The absorbance of the wavelength of 286 nm for all GO suspensions was used for comparison. A linear calibration was confirmed (not shown here) between absorbance and GO concentration. Each data point was the average of three repeated measurements to ensure repeatability.

The contact angles of the GO aqueous suspensions were measured using an optical capturing method. In this method, 10 μ L of sample was dropped onto a stainless steel plate substrate (with $R_a=37 \pm 6$ nm) from 5 mm above. The image of the droplet shape was immediately

taken using a camera with a macro lens and the contact angle was then measured from the image.

2.4. Tribological characterisation

The tribological performance of GO aqueous lubricants was tested using a Modular Compact Rheometer (or MCR, Anton Paar, Auatria) with a ball-on-three-plate testing configuration. In this configuration, a Cr alloy steel ball (AISI 52100, grade 10) was rotated in contact against three AISI 304 stainless steel plates. The three plates were fixed at 45° angle to the loading axis. The plate holder was suspended horizontally so that the loading axis and the centre of the three plates could be self-aligned when a small normal load was applied. A fixed sliding speed of 50 mm/s and sliding distance of 7.5 m were applied for all the tests. A normal load of 20 N was used, corresponding to an average Hertzian contact pressure of 689 MPa. The detailed specifications of the ball and the plates used are summarised in [Table 1](#)~~Table 1~~. During the tribological test, the torque experienced by the ball was recorded, and was used to calculate the coefficient of friction (COF). Every testing condition was repeated for three times and the results were averaged.

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Table 1. Specifications of the ball and plates used in the tribological tests.

	Material	Surface treatment	Surface roughness (nm)	Hardness
Ball	AISI 52100 alloy steel	Polished	11.1 ± 0.4	64 HRC
Plate	AISI 304 stainless steel	Lapped	37.0 ± 6.2	92 HRB

Fig. 2 shows the typical cross-sectional profile of a wear mark on the plate after testing, measured by a stylus profiler (DektakXT Stylus Profiler, Bruker, USA). The profile symmetric and has a circular curvature, indicating that most of the wear occurred on the plate and the ball remained its spherical shape after the test. Visual examination also confirmed that the ball experienced little wear because its hardness is much greater than that of the plates. Therefore, the plate wear was used to represent the total wear in this work. The wear marks on the plates were examined using a confocal microscope (LEXT OLS4100, Olympus, Japan). The wear surfaces were also examined using SEM with Energy-dispersive X-ray spectroscopy (EDS) module (JSM 6610, JEOL, Japan). The Raman spectra of wear surfaces were used to analyse the characteristics of the GO residue.

3. Results and discussion

3.1. Morphology

Fig. 3 shows the TEM images of the GO sheets in the suspensions of different pH values. The GO sheets in acidic conditions show typical wrinkled morphologies, as shown in Fig. 3(a) and (b). This indicated that the GO sheets are thin and flexible. The GO sheets in alkaline conditions have slightly different morphologies with sharp and localised edge puckering, as shown in Fig. 3(c) and (d). In the suspension of the highest pH value of 9.70, the GO sheets were broken into smaller pieces with sharp edges, as marked by the white arrows in Fig. 3(e).

SEM images of the GO suspensions of different pH values are shown in Fig. 4. Fig. 4(a) and (b) shows the GO sheets in the acidic suspensions with pH values of 3.10 and 5.41, which appear flexible and have apparent wrinkles, demonstrating typical morphologies of GO sheets. When pH value in the suspension was higher, the GO sheets became smaller with sharper corners and less wrinkles, as shown in Fig. 4(c) to (e). Interestingly, nano pores were observed on the sheet surfaces.

3.2. Chemical properties

XPS analysis was performed to investigate the bonding structural change of the GO suspensions. The survey scan spectrum of the GO suspension at pH 3.1, as shown in the inset of Fig. 5(a), demonstrates there are two large peaks at approx. 532 eV and 286 eV representing oxygen (31 at.%) and carbon (68 at.%), respectively. Small traces of sulphur and chlorine are found in the enlarged spectrum at 168.5, 201 and 233.0 eV, whose atomic content is 1 at.% in total, which are likely the impurities of the potassium chlorate and sulphuric acid left from the synthesis process. As a result, the pristine GO suspension without pH modification is acidic, as indicated in Section 2.2. Figs. 5(a) and 5(c) show the high-resolution O 1s and C 1s spectra and their corresponding fitting curves, respectively. The O 1s spectrum clearly indicated that most of the oxygen is chemically bonded to the carbon by single and double bonds, reflected by the prominent peak at 532.3 eV, while small portion of oxygen is bonded with sulphur to form sulphate ions (SO_4). The C 1s spectrum has two strong peaks at 284.6 and 298.0 eV, corresponding to the carbon-carbon bonds (C-C) and single carbon-oxygen bonds (C-O and C-O-C), respectively. Functional groups such as carbonyl (C=O), epoxy bridges (C-O-C), hydroxyl (-OH) and carboxyl (-COOH) are attached on the basal plane and the edges of the sheet, as shown by the respective peaks of relatively

smaller intensities. These oxygen based groups are hydrophilic, which would help the GO sheets disperse in water. Oxygen based groups might also bind to metal ions through both electrostatic interactions and coordination bonds [22].

The survey scan of the GO suspension of pH 9.7 is shown in the inset of Fig. 5(b). The peak of sodium at 1071 eV (3.20 at.%) should be attributed to the addition of small amount of NaOH for pH adjustment. Quantitative calculation showed that the oxygen and carbon contents were 25.93 and 70.87 at.%, respectively. As shown in Fig. 5(b), the O 1s spectrum of the GO suspension at pH 9.7 is somehow different from that at pH 3.10 shown in Fig. 5(a). It contains two extra peaks at 535.2 and 530.8 eV, which are attributed to sodium Auger signal and the oxygen in NaOH, respectively. Fig. 5(d) shows the C 1s spectrum with corresponding fittings. It can be found that the ratio of C-O to C-C peaks is distinctly different from that of the pristine GO suspension. Calculated from the fittings in the C 1s peaks shown in Fig. 5(c) and (d), the ratios of atomic percentage of total carbon-oxygen to carbon-carbon bonding for the GO sheets in acidic and basic conditions are 1.41 and 0.60, respectively. This strongly suggests that the GO sheets in the suspension at pH 9.7 were chemically reduced, which is highly likely due to the breakage of carbon-oxygen bonds [23]. The evidences for the breakage of GO sheets were observed in the TEM and SEM images of the suspensions shown in Figs. 3 and 4.

3.3. Physical properties

Fig. 6(a) shows the relative concentrations of the supernatant fluids of the suspensions plotted as a function of the aging time. It is seen that the relative concentrations decreased and reached a stable status in the first two days, and were approximately 80% after 5 days of aging. The GO suspensions show uniformly dark colour, and no difference could be observed for the suspensions with different aging times, as shown in Fig. 6(b) and (c). Apparently, the suspensions at different pH values retained similar relative concentrations in the aging tests. This is because the change of pH did not change the single layered structure of GO sheets, and the surface charge remained at a similarly high value (Zeta potential was approx. -45 mV for all GO suspensions).

The light absorbance at 286 nm wavelength of the GO suspensions with different pH values is shown in Fig. 7(a). The absorbance value increased linearly from 1.25 to 1.43 for pH values from 3.10 to 9.70, indicating that the increase in pH value resulted in the darkening of suspension, though it could not be observed visually. Such darkening might be attributed to

the breaking of GO sheets at higher pH values. Similar darkening phenomena were observed in the previous studies [22, 23].

The effect of pH value to the Z-average particle size distribution is shown in Fig. 7(b). The Z-average was reduced by approx. 77% when the pH value increased from 3.10 to 6.62. The further increase in pH value led to insignificant reduction in Z-average. This trend is a good indication of the lateral size reduction of the GO sheets in a suspension. The reason was because that hydroxyl and epoxide groups are mainly on basal planes, and ionisable carboxylic acid groups are mostly at the edges of GO sheets. Therefore, the change of pH varied the edge chemical condition and caused GO to break down. As the pH modification resulted in the breakage of GO sheets, which in turn caused the reduction in Z-average [15, 16].

The contact angles of the GO suspensions measured on the polished stainless steel substrate are shown in Fig. 8. For the pristine GO with the pH of 3.10, the measured contact angle was $53.5 \pm 1.9^\circ$, which was a reduction of 13% compared with that of the benchmark water. However, after the pH was increased to 5.49 and above, the contact angle increased to around 64° . The results indicate that the pristine GO could enhance the wetting of the GO suspension onto a steel substrate. However, the increase in pH value caused the contact angle to increase, which indicated that the GO sheets were chemically reduced and the suspension become less hydrophilic.

Fig. 9(a) shows the Raman spectra of the GO suspensions at different pH values. All GO suspension samples show comparable D band and G band with wavenumbers of 1410 cm^{-1} and 1595 cm^{-1} , respectively. In general, the peak intensity ratio of the D band and G band (I_D/I_G) suggests the amount of disordered defect and oxidation. The I_D/I_G of GO with different pH is shown in Fig. 9(b). An increasing trend was found from 0.44 at pH 3.10 to 0.53 at pH 9.70. This result indicates that the increase in pH value resulted in more of defects in the GO sheets, thus weakened the integrity in the lateral direction. Therefore, the GO sheets tend to break into smaller pieces. The change in size and wettability of GO sheets are thus attributed to their morphology change.

3.4. Tribological performance

Fig. 10(a) shows the curves of COF plotted as a function of sliding distance obtained from the tribological tests using water and the GO suspensions of different pH values. For water, the COF is 0.4 with ± 0.02 fluctuation. For the GO suspension of pH 3.10, the COF decreased

from 0.29 to 0.2 in the initial 0.3 meters of test, and reached a stable value of 0.25. When the GO suspensions with neutral and high pH values were used, the values of COF are in between those of water and the GO suspension of pH 3.10. The COF curves of the GO suspensions have less fluctuation than that of water.

Fig. 10(b) shows the effect of pH value of water and GO suspensions on the averaged COF from the tribological tests. The pH values of water were adjusted to approximate those of the corresponding GO suspensions. For water, the averaged COF was not stable, reflected by the large standard deviation. The tests were accompanied by large high pitch noise, which caused the real-time COF to fluctuate. Overall, the COF decreased from 0.45 to 0.33 for pH 3.25 to pH 4.86. When the pH was further increased, the COF remained on the same level of 0.35. For GO suspensions, the COF increased from 0.24 to 0.28 for pH 3.10 to pH 5.41, and then remained at the same value for the rest of the pH values. It is noticeable that there was no longer noise during the tribological test, hence the stable COF values. Notably, the GO suspensions at pH 3.10 showed a reduction of averaged COF of 44.4% compared with that of unmodified DI water.

Fig. 11(a) to (f) shows the wear marks on the plates after the tribological tests using water and the GO suspensions of different pH values. It is seen in Fig. 11(a) that the wear mark surface lubricated with water exhibited had some dark residues accumulated on the entry side. EDS mapping confirmed that the dark residues are iron oxide, which were most likely left from the testing due to severe rubbing and tribo-corrosion. For all the wear marks with GO suspensions, the surface was covered with scratches in the sliding direction and the boundary of the wear mark is well-defined without obvious residue accumulation. As shown in Fig. 11(b) and (c), the surfaces of the wear marks after the tribological tests using GO suspensions of pH 3.10 and 5.41 are covered with coarse scratches. While Fig. 11(d) shows a combination of fine scratches, which distributed along the sliding direction across the centre, and coarse scratches on the two sides on the wear mark after the test using the GO suspensions of pH 6.62. Moreover, the scratches on the wear marks after the tests using the GO suspensions of pH 8.80 and 9.70 shown in Fig. 11(e) and (f) are fine and dark, possibly resulting from high density and deposition of GO residue.

Fig. 11(g) shows the radii of wear marks plotted as a function of pH value for both water and GO suspensions. It can be seen that for water the change of pH showed insignificant effect on wear mark radius. The pH value of GO suspensions, however, has effect on the wear radius.

The GO suspension of pH 3.10 resulted in an averaged wear mark radius of $159 \pm 3 \mu\text{m}$. The increase of pH value to 5.41 significantly increased the wear mark radius.

Fig. 12 shows the low and high magnification back-scattered electron SEM images of the wear mark surfaces lubricated using water and the GO suspensions at pH 3.10 and pH 9.70, and their corresponding Raman spectra at different locations. The contrast observed in the SEM images indicates the different chemical compositions.

When water was used as lubricant, the wear surface was mostly smooth, indicating plastic adhesive wear via asperity contact and formation of metallic junctions [24]. Residues were found being accumulated at the entry side of the wear mark, as shown in Fig. 12(a), and some relatively shallow scratches were observed in the enlarged image shown in Fig. 12(d). The Raman spectra for the reference surface and light scratches demonstrates no trace of oxide, whereas iron oxide peaks exist in the spectrum of the dark scratches, as can be seen in Fig. 12(g). The two strong peaks at 1580 cm^{-1} and 1360 cm^{-1} is attribute to the typical Raman peaks of Fe_2O_3 [25], and that at 688 cm^{-1} belongs to Fe_3O_4 [26]. This result indicates that the harder iron oxide debris (compared to the stainless steel substrate) induced fracturing and scratches.

The morphology of the wear marks from the tribological tests with the GO suspensions shown in Fig. 12(b) and (c) are different from that in Fig. 12(a). Apparent scratches along the sliding direction covered the entire wear mark, but the scratch density on the wear mark with the GO suspension of pH 3.10 in Fig. 12(e) is lower than that of pH 9.70 shown in Fig. 12(f). The corresponding Raman spectra shown in Fig. 12(h) and (i) present small GO D and G bands on the light scratches and strong ones of the dark scratches, but no trace of GO on the reference surface. The iron oxide peaks were not found in the spectral analysis. The evidences and analytical results strongly suggest that a thin GO layer might be deposited on the wear surface. As shown in Fig. 12(h) and (i), for the wear mark of GO suspension of pH 3.10, the I_D/I_G is 0.90, and that of pH 9.70 is 1.0. The difference between their I_D/I_G values indicates that the GO sheets residue on the dark scratches in the two cases could have different amount of defects. The GO sheets under basic conditions appear smaller and have more defects and sharper edges, as can be seen in Fig. 4. These should contribute to the making of denser scratches shown in Fig. 12(f). In contrast, the GO suspension under the acidic condition maintained its structural integrity, which was expected to reduce friction and wear within the contact pair during sliding. It should also be noted that compared with the

I_D/I_G values of the GO suspensions before testing (as shown in Fig. 9), those measured on the wear mark increased significantly. This indicates that during testing the rubbing might introduce defects on the GO sheets and cause them to break down. This result also explains the increasing trend of COF for GO suspensions of pH 3.10 as shown in Fig. 10(a).

4. Discussion on lubrication mechanism

Based on the wear mark surface characteristics and the related chemical and physical properties of the GO suspensions at different pH values, the lubricating mechanisms of GO suspensions could be depicted using the schematic illustration shown in Fig. 13.

For water, as well-documented [27], adhesive wear via plastic deformation is the predominant mechanism. Because of the low viscosity of water, the contact between the ball and the plate was via direct asperity contact under the testing condition used in this study. As shown in Fig. 13(a), at the contact points, large pressure induced micro welding, which could bind the contact pair well. During sliding, the re-breaking of the welded contact pairs could cause vibration and noise, accompanied with tribo-corrosion. The resultant iron oxide debris was partially carried away by adjacent fluid, but some might accumulate at the entry side of the wear mark. Some debris might be trapped into the contact, which produced scratches unevenly distributed on the wear mark. The combined effect of micro welding and breakage of contact pair during sliding caused severe friction and wear. This is why water produced significantly greater COF than the GO suspensions, as can be seen in Fig. 10.

Comment [ZJ1]: It is better if a mechanism name can be generated here.

The tribological performance of the GO suspensions was apparently affected by their pH values. Geometrically, the GO sheets are thin, flexible and can be easily folded or wrinkled. Their edges are well-defined without sharp corners. Under acidic conditions, the GO sheets could maintain their structural integrity, which enabled them to have relatively low degree of defects and large lateral surface area. From the chemical point of view, the surfaces of GO sheets were highly oxidised and therefore very hydrophilic, resulting in good wetting property, as shown in Fig. 8. Therefore, during tribological testing the GO sheets could cover the contact pair well through forming a thin tribofilm, as illustrated in Fig. 13(b). The tribofilm effectively separated the contact between the ball and plate and thus avoided the asperity contact. It is anticipated that the tribofilm could also help protect the steel substrate from tribo-corrosion. As GO sheets have relatively low shear strength along lateral direction, the interlayer sliding was quiet and no vibration was observed. The shallow scratches

scarcely distributed on the wear mark should be attributed to the existence of the few GO sheets of small lateral sizes in the GO suspension.

At neutral and basic conditions where $5.41 \leq \text{pH} \leq 9.70$, the GO sheets started to break down and were chemically reduced. The GO sheets in the suspension became stiffer and their edges were relatively sharp, as shown in Fig. 4. Those GO sheets would adhere onto the valleys of the plate surface randomly, being unable to cover the contact pair, as shown in Fig. 13(c). As a consequence, the GO sheets scratched the steel substrate during sliding, rather than protecting it from wear. Such a process is similar to abrasive machining, where hard particles tend to remove the work material via three-body abrasion [6]. Under this circumstance, abrasive wear was predominant, where the frictional force was small, but the wear was considerably high.

5. Conclusions

The effect of pH in GO suspensions on their microstructure and tribological performance was systematically understood. The acidic GO suspension (pH 3.10) effectively reduced COF by 44.4% and wear mark radius by 17.1%, in comparison with water. The vibration and noise that usually occur in the sliding test with water was almost eliminated by use of the acidic GO suspension. Nevertheless, the increase of pH in the GO suspension to the basic level resulted in a greater COF and significantly increased wear.

The lubrication mechanisms of GO the suspensions and water were revealed. With water, adhesive wear through repetitive welding and breaking of contact pairs was predominant and iron oxide debris also enhanced such wear. For the acidic GO suspension, relatively large flexible GO sheets tended to cover the contact pair, forming a thin tribofilm to separate contact pairs. This thus reduced friction and wear. The GO suspensions under basic conditions caused the GO sheets to break down, which affected the formation of a tribofilm to protect the contact pair. The relatively small GO sheets thus entered the contact area and caused significantly high density of scratches during sliding, hence greater wear.

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Fig. 1. (a) The XRD spectrum, (b) AFM image of the GO sheets, and (c) the profile of a GO sheet sectioned at the location marked by the red line shown in (b).

Fig. 2. The surface profile of the wear mark after a tribological test using water as a lubricant.

Fig. 3. TEM images of graphene oxide sheets in the suspensions with pH values of (a) 3.10, (b) 5.41, (c) 6.62, (d) 8.80, and (e) 9.70.

Fig. 4. SEM images of graphene oxide sheets deposited on silicon wafer with pH values of (a) 3.10, (b) 5.41, (c) 6.62, (d) 8.80, and (e) 9.70.

Fig. 5. XPS O 1s spectrum with a survey scan as the insert for (a) pristine GO (pH 3.10) and (b) GO suspension with pH 9.70; C 1s spectrum of the (c) pristine GO (pH 3.10) and (d) GO with pH 9.70.

Fig. 6. (a) The relative concentration of the supernatant fluid of the GO suspensions with different pH values over 5 days; photographs of the (a) as prepared GO suspensions, and (b) GO suspensions after 7 days of aging.

Fig. 7. (a) The light absorbance at 286 nm, and (b) Z-average particle size of GO suspensions with different pH values.

Fig. 8. Wetting angles of the GO suspensions with different pH values.

Fig. 9. (a) Raman spectra, and (b) the ratio of D band to G band of GO samples dispersed in deionised water with different pH values.

Fig. 10. (a) COF-distance curves, and (b) averaged COF obtained from the tribological tests using water, GO suspensions with pH values ranged from 3.10 to 9.70.

Fig. 11. Confocal microscope images of wear marks after the tribological tests using (a) water, GO suspensions with pH values of (b) 3.10, (c) 5.41, (d) 6.62, (e) 8.80, (f) 9.70, and (g) the averaged wear mark radius of water and GO suspensions with different pH values.

Fig. 12. (a, b, c) Low magnification back-scattered electron SEM images, (d, e, f) high magnification back-scattered electron SEM images of the squared location, and (g, h, i) RAMAN spectrum performed on the arrow-indicated locations of wear mark tested with water, GO suspension at pH 3.10 and GO suspension at pH 9.70.

Fig. 13. Schematic of the contacts during tribological tests using (a) water, (b) acidic GO, and (c) basic GO suspensions as lubricants.