Tribological behavior of nanocarbon materials with different dimensions in aqueous systems

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Received: 02 November 2017 / Revised: 08 April 2018 / Accepted: 24 July 2018

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Abstract: Due to the widespread use of nanocarbon materials (NCMs), more researchers are studying their tribological performances. In this work, the tribological behaviors of the following five types of NCMs with different geometric shapes were evaluated in a novel oil-in-water system: spherical fullerenes (C60, 0D), tubular multi-walled carbon nanotubes (MWCNT, 1D), sheet graphene oxide (GO, 2D), sheet graphene oxide derivative (Oct-O-GO, 2D), and lamellar graphite (G, 3D). Among these, GO with two types of oxidation degrees, i.e., GO(1), GO(2), and Oct-O-GO(1) were synthesized and characterized using Fourier-transform infrared spectroscopy, Raman spectroscopy, x-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and contact angle measurements. The load-carrying capacity of the NCM emulsions were evaluated using a four-ball test machine, and the lubrication performances were investigated using a high-frequency reciprocating friction and wear tester with a sliding distance of 1,800 mm under different loads (50 N and 100 N) at 0.5 Hz. The results revealed that the Oct-O-GO(1) emulsion exhibited the best load-carrying capacity, and the best friction-reducing and anti-wear properties compared to other emulsions. Moreover, the anti-wear advantage was more prominent under high load conditions, whereas the other emulsions exhibited a certain degree of abrasive or adhesive wear. The lubrication mechanism was determined through the analysis of worn surfaces using scanning electron microscopy/energy-dispersive x-ray spectroscopy, micro-Raman spectroscopy, and x-ray photoelectron spectroscopy. The results revealed that during frictional sliding, the ingredients in the emulsion can absorb and react with the freshly exposed metal surface to form surface-active films to protect the surfaces from abrasion. Moreover, it was found that the higher the amount of ingredients that contain alkyl and O-H/C=O, the better was the lubrication performance in addition to an increase in the carbon residue in the tribofilm generated on the metal surface.

Keywords: nano-carbon materials; tribological behavior; modified graphene oxide; oil-in-water emulsion

1 Introduction

Graphene has attracted significant attention in recent years. One of its most desirable properties is its super-low-friction characteristic, which expands the concept of zero wear [1–4]. Other nanocarbon materials (NCMs) with the same skeleton structures, such as fullerene (C60), multi-walled carbon nanotubes (MWCNTs), graphite (G) and graphene oxide (GO) also exhibit

remarkably low friction and wear [5–9]; thus, they demonstrate a high potential for application as lubricant additives.

Moreover, C60 has been applied to lubricant oil, ionic liquids [10, 11], solid films [8] and other solutions [12–14] (i.e., ethanol and water, etc.) to study their tribological properties. Lei et al. reported that when 0.5 wt.% of fullerene-styrene sulfonic acid copolymer was added to base stock, it exhibited the maximum

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P_B value and minimum wear scar diameter (WSD) [14]. When used as oil additives, alkylated C60 exhibits a remarkable anti-wear property by reducing the areas of the worn surfaces and smoothing the scuffing. Liu et al. applied alkylated C60 to paraffin oil [15]. The results revealed that the addition of the alkylated C60 reduces the friction coefficient both at 25 °C and 90 °C, where it exists as aggregates and monomers, respectively. This can be attributed to the presence of the aliphatic chains, thus leading to an improved solubility and dispersibility of the target compound in lubricating oils.

Huang et al. utilized MWCNT/minimum quantity lubrication (MQL) in the milling of SKD11 die steel as a cutting fluid [16], which can effectively prevent tool wear, due to the increased wear resistance yielded by the carbon nanotubes, thus increasing the tool-life. Moreover, it allows for a lower cutting temperature environment, resulting in the superior thermal conductivity of MWCNTs [17]. A 1.0 wt.% addition of MWCNTs can improve the anti-wear, friction coefficient (COF), and load-carrying capacity of the base lubricant when used in Mobilgear 627 and paraffinic mineral oils [18]. The results of the morphology analyses revealed that the addition of MWCNT nanoparticles decreases wear, resulting in a relatively smooth surface with fewer scars, thus indicating that the presence of the MWCNTs significantly reduces metal contact. The mechanism of anti-wear is attributed to the deposition of MWCNT nanoparticles on the worn surface, which may decrease the shearing stress, thus improving the tribological properties [19].

As a conventional solid lubricant, graphite has been extensively studied and applied in industry for more than 40 years [20, 21]. It was reported that graphitic tribofilms can form *in vivo* on the rubbing surfaces of metal-on-metal hip replacements, which are made of cobalt, chrome, and molybdenum [22]. Moreover, Erdemir et al. found that carbon-based tribofilms with catalytically active $\text{MoN}_x\text{-Cu}$ coatings enable base oils (PAO10 and all formulated 5W30) to provide solid tribofilms that protect sliding surfaces against friction and wear [23].

Graphene oxide (GO) is regarded as the precursor in the production of graphene (reduced GO) by chemical and thermal reduction, due to its abundant oxygen-based groups [24]. Moreover, not only can

it be obtained easily from the oxidation of graphite, but it can also be readily exfoliated to nanosheets using ultrasonic devices. In recent times, several GO derivatives such as GO-based composites [25, 26], GO-based coating [27, 28], thin films [29], and GO-based nanoparticles have emerged as functional materials for lubrication applications [30–33]. Cheng et al. reported that when using 0.02 wt.% MGO in base oil, the COF and WSD decreased to approximately 38.4% and 42.0%, respectively [34]. Moreover, He et al. found that 0.06 wt.% GO suspensions can reduce the COF by 37% and WSD by 19.1%, when compared with water [35]. It was also reported that GO aqueous dispersion can reduce friction between diamond-like carbon and stainless steel. When the GO concentration was increased from 0 to 1.0 wt.%, there was a continuous decrease in the COF from 0.14 to 0.06 [30].

In summary, graphene-based additives in the lubrication medium can effectively reduce the friction and improve the wear resistance of the contacting surfaces [36–38]. However, the abovementioned researches that considered carbon materials as lubricating additives mostly focused on single carbon materials or their composites instead of systematically comparing the tribological behaviors of different carbon materials. To address this, in this study, the tribological behaviors of five types of NCMs with different dimensions, i.e., zero-dimensional C60, one-dimensional MWCNT, two-dimensional (2D) GO, n-Octanol modified graphene oxide (Oct-O-GO), and three-dimensional (3D) graphite were investigated. A simple and low-cost chemical method was used to prepare n-Octanol functionalized graphene oxide. Given that the hydrophilicity of different NCMs are different, it is difficult to disperse them in the same solvent. To solve this problem, a novel oil-in-water (O/W) emulsion system was designed to incorporate the different NCMs in the same system, to obtain stable NCM lubricants. The corresponding tribological properties were then evaluated, and the worn surfaces were analyzed to clarify their lubricating mechanisms.

2 Experiment

2.1 Materials

The following materials were used as received: flake

graphite (500 mesh, J&K Scientific Ltd., 99%); fullerene (C60, Aldrich, 98%); multi-walled carbon nanotubes (MWCNT, J&K Scientific Ltd., 95%); n-Octanol (Sinopharm Chemical Reagent Co. Ltd., 98%); thionyl chloride (SOCl_2 , Sinopharm Chemical Reagent Co. Ltd., 96%); methyl formamide (DMF, Sinopharm Chemical Reagent Co. Ltd., 98%); dimethylsulfoxide (DMSO, Sinopharm Chemical Reagent Co. Ltd., 98%); hydrochloric acid (HCl, Sinopharm Chemical Reagent Co. Ltd., 35%); sulphuric acid (H_2SO_4 , Sinopharm Chemical Reagent Co., Ltd., 98%); phosphoric acid (H_3PO_4 , Sinopharm Chemical Reagent Co., Ltd., 85%); potassium permanganate (KMnO_4 , Sinopharm Chemical Reagent Co., Ltd., 98%); hydrogen peroxide (H_2O_2 , Sinopharm Chemical Reagent Co., Ltd., 30% w/w); Tween 20 (TW 20, Haian petrochemical, 99%); Carbomer 20 (U 20, Guangzhou Shi Ming Chemical Co., Ltd., 98%); MethocelTM 40-202 (Shanghai Qianfei Chemical Co., Ltd., 99%); poly α -olefins (PAO8, Shanghai Naco Lubrication Technology Co., Ltd., 98%); triethanolamine (TEA, Sinopharm Chemical Reagent Co., Ltd., 97%). The water used was Wow Haha pure water.

2.2 Synthesis of GO and Oct-O-GO

Graphene oxide was prepared from flake graphite using the modified Hummers method [39], due to the advantages of a short reaction time, high oxidation degree, less environmental pollution, and high security. For GO synthesis, a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (400 mL) was added to a round bottom flask with graphite powder (3.0 g) under ice-cold conditions. Thereafter, KMnO_4 (18.0 g) was slowly added to the mixture and stirred at a low speed. After all the KMnO_4 was added, the mixture was heated to 50 °C and stirred for 12 h. The mixture was then cooled to room temperature and poured into 800 mL ice water with 30% H_2O_2 (~6 mL) and left for one night. The resultant product was centrifuged, and the supernatant was decanted. The remaining slurry mixture was washed using 400 mL of pure water followed by 200 mL of 37% HCl. The solution was washed using water, and centrifuged until the pH value of the supernatant was 7. It was then dried in a vacuum oven at 45 °C to obtain graphite oxide powder. After ultrasonication, the graphene oxide was obtained and labeled as GO(1). In this study, a higher oxidation degree graphene oxide

GO(2) was also synthesized according to the steps above by changing the amount of KMnO_4 to 12 g [40].

To prepare Oct-O-GO(1) [41], 200 mg of GO(1) powder was dispersed in a 20:1 mixture of SOCl_2/DMF (64 mL) by ultrasonication for 30 min. The solution was then heated under 70 °C for 24 h in the sealing tube. After the completion of the reaction, the precipitate was filtered, washed with water and methanol, then dried in a vacuum oven at 45 °C for 18 h to obtain GOCl(1) powder. In the next step, GOCl(1) was dispersed in 20 mL of dimethyl sulfoxide (DMSO) after ultrasonication for 0.5 h, and n-Octanol (7.1 mL) was dropped into the dispersion. The solution was then heated at 80 °C for 23 h (monitored by GC). Thereafter, the precipitate was filtered, washed, and dried in the vacuum oven at 60 °C for 24 h. The n-Octanol modified graphene oxide, i.e., Oct-O-GO(1) powder, was then obtained. The synthesis route is presented in Scheme 1.

2.3 Preparation of tribological study samples in aqueous systems

To prepare the O/W emulsion system, the NCMs were separately added to a 500 mL beaker with U20 and Methocel40-202 in water, and stirred at 50 °C for 10 min. The oil phase (PAO8 and TW20) was then added to the water phase with stirring at 800 rpm for 30 min. Thereafter, triethanolamine was used to adjust the pH of the emulsion to 7, and the emulsion was cooled to room temperature with stirring. The formulation of the emulsions is presented in Table 1.

Scheme 1 Synthetic route of GO and Oct-O-GO.

Table 1 The formulation of the emulsions.

Trade name	Description	Content (wt.)
NCMs	Nano carbon materials	100 ppm
U20	Acrylates/C10-30 alkyl acrylate crosspolymer	0.15%
Methocel™ 40-202	Hydroxypropyl methyl cellulose	0.50%
H ₂ O	Pure water	92.35%
TW20	Polyoxyethylene (20) sorbitan monolaurate	4.00%
PAO8	Hydrogenated polydecene	3.00%
TEA	Triethylamine	q. s.

Moreover, emulsions without any NCMs were selected as the base sample for comparison with those containing NCMs. Images of the emulsions are presented in Fig. 1.

2.4 Characterization

The FTIR spectra were obtained by a Paragon 1000 FTIR spectroscope (Perkin Elmer, Inc., USA) with the attenuated total reflectance (ATR) attachment scanning from 650–4,000 cm^{-1} .

The Raman spectra of the nanocarbon materials were obtained using a Raman spectroscope (Senterra R200-L) in the range of 50–3,500 cm^{-1} with a laser source wavelength of 532 nm.

The XRD spectra were obtained using a D-MAX 2200/PC x-ray diffractometer (Japan Rigaku Corp.) operating under the condition of $2\theta = 5^\circ\text{--}60^\circ$ at a speed of $4^\circ\cdot\text{min}^{-1}$ with Cu K α radiation ($\lambda = 0.154$ nm).

Thermostability was achieved using Q600 (TA Instruments, USA) under an N₂ atmosphere at 100 mL/min with 10 °C/min temperature programmed from room temperature to 800 °C.

The microtopography of the NCMs were obtained by a Phenom Pro scanning electron microscope (Phenom World, Holland).

Fig. 1 Images of O/W emulsions with NCMs.

The water static contact angle was tested using an optical contact angle measuring instrument (DSA30, Kruss, Germany) by injecting one drop of 30 μL of H₂O on the surface of the tablet made of NCMs, which was made from a ~1 g sample under 25 MPa for 6 min using a desktop electric powder tablet presser (Tianjin Sichuang Technology Development Co. Ltd., China).

The viscosity test was carried out using a rheometer AR-G2 (TA, USA) under various shear speeds that ranged from 0.01–30 rad/s for 240 s at 25 °C. The droplet size of the emulsions was monitored using an optical microscope with measuring software (CK-330C, Caikon, China), and the droplet size was taken as the average value of ten measurement sets.

2.5 Tribological test

The tribological performances of the lubricants with different NCMs were evaluated using a high-frequency reciprocating friction and wear tester (Rtec, USA). The upper ball (5 mm in diameter, 304 stainless steel) rubbed against the stationary lower steel plate (50 mm $\times$ 25 mm $\times$ 2 mm, 304 stainless steel, roughness Ra = 0.8 ± 0.3 μm). Before the test, all the balls and plates were washed twice. They were first ultrasonicated with a mixture of petroleum and ethanol (v:v = 1:9) for 5 min, then ultrasonic washed with petroleum for 3 min. Thereafter, 5 mL of lubricant was applied to the ball-plate contact area for the tests, which were conducted with a stroke of 10 mm under a frequency of 0.5 Hz with reciprocating sliding for 3 min. The applied nominal pressure was approximately 1.73 GPa with a normal load of 50 N, and 2.18 GPa for 100 N. The sliding distance of each test was 1,800 mm. All the samples were tested three times under each experimental condition, and the COF was recorded automatically by the tribotester.

The load-carrying capacity (maximum non-seized load P_B and the weld load P_D of all the NCM emulsions) was tested using a four-ball test machine (MS-10A, Xiamen Tenkey Automation Co., Ltd., China). The test standard used was GB/T 3142-82, and the ball used in the four-ball tests was a 304 stainless steel ball with a diameter of 12.7 mm.

2.6 Worn surface analysis

After the tribological tests, the tested balls and plates

were ultrasonic washed with petroleum for 1 min and 4 min. The wear volumes of the worn balls and plates were measured using a non-contact 3D surface interferometer (Bruker, Contour GT, USA) after the tribological test. The worn surface morphologies of the plates were also examined using a 3D color confocal laser scanning microscope (Keyence, VK-9700K, Japan) with a magnification of 10 $\times$. The micro-Raman spectra of the worn scars on the balls after the four-ball tests under a load of 660 N were obtained using a DXRTM xi Raman imaging spectroscopy (Thermo Fisher Scientific, USA) in the range of 50–3,500 cm⁻¹, with a laser source wavelength of 532 nm. The SEM images were captured and the EDS analysis of the worn balls after the tribological tests under 100 N was performed using an EVO18 (ZEISS, Germany). The chemical composition on the wear tracks was determined using XPS with Al K α radiation as the exciting source. The binding energies of the target elements were determined at the pass energy of 29.35 eV with a resolution of approximately 70.3 eV, using the binding energy of contaminated carbon (C 1s: 284.8 eV).

3 Results and discussion

3.1 Characterization of GO and Oct-O-GO

The infrared (IR) spectrum as one of the four spectrums of organic structure analysis can be used to effectively identify structure and functional groups in compounds. The FTIR spectra of GO(1), GO(2), and Oct-O-GO(1) are presented in Fig. 2(a). From the 1,053 cm⁻¹ (C-O vibration), 1,225 cm⁻¹ (C-O-C), 1,384 cm⁻¹ (C-O bonds of carboxyl), 1,621 cm⁻¹ (skeletal vibration of C=C bonds in GO) [42], 1,736 cm⁻¹ (C=O stretching of carboxylic acid), and 3,400 cm⁻¹ (O-H vibration) in the FTIR spectra, it is confirmed that the GO prepared in

this work contained carboxyl groups, carbonyl groups, hydroxyl groups, and epoxy groups. Moreover, the oxidation degree of GO(2) was higher than that of GO(1) with respect to the intensity of transmission (C-O-C, C-O and O-H vibration). The FTIR spectrum of Oct-O-GO(1) revealed the characteristic bands of the alkyl groups corresponding to the modification with n-Octanol. In particular, the peaks at 2,853 cm⁻¹ and 2,924 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibration of the alkyl groups, respectively [43]. Moreover, there were several characteristic bands of epoxy groups and no carboxyl groups in the FTIR spectrum of Oct-O-GO(1), which indicates that the carboxyl groups in Oct-O-GO(1) reacted with n-Octanol.

By unscrambling the XRD spectra, the composition and internal information such as atomic or molecular structure of the materials can be speculated; thus, it is also an important analysis method for carbon materials. Figure 2(b) displays the XRD spectra of GO(1), GO(2), and Oct-O-GO(1). Both GO(1) and GO(2) exhibited the characteristic diffraction peak of graphene oxide (2 θ ~10°), whereas that of Oct-O-GO(1) shifted to 24.031° (Fig. 2(b)). According to the Bragg Law [31] ($n\lambda = 2d\sin\theta$) and Scherrer equation [44] ($D = k\lambda/\beta\cos\theta$) (where n is the diffraction series, λ is the X-ray wavelength, d is the interlayer spacing, D is the mean diameter of the crystalline grain, k is the shape factor, and β is the fullwidth at half maximum), an approximate calculation of the interlayer distance [36, 45] in different materials was performed, as shown in Table 2. Compared with the characteristic peak of graphite at approximately 26.58° [46], the diffraction peak of GO shifted to the left. The disappearance of the characteristic peak of graphite indicates that GO(1) and GO(2) were successfully prepared. From Table 2, it can be seen that the interlayer distance of GO(2) was

Fig. 2 FTIR, XRD, and TG analysis of GO(1), GO(2), and Oct-O-GO(1).

larger than that of GO(1), which further confirmed that the oxidation degree of GO(2) was higher than that of GO(1). In comparison with GO(1), the 2θ peak of Oct-O-GO(1) was wider and weaker, and the interlayer distance was smaller. This may be due to the decrease in the number of oxygen-containing groups after its modification with octanol. The decrease in the number of oxygen-containing groups reduced the hydrogen-bond interaction between layers; thus, the interlayer spacing decreased [36].

The results of the thermostability of GO(1), GO(2), and Oct-O-GO(1) are presented in Fig. 2(c) and Table 3. For GO(1) and GO(2), two clear gravity gradients were present, namely, (1) the first decrease in mass due to a small number of free water or combined water in molecules from 50 °C to 130 °C [47], and (2) the second gravity gradient between 130 °C and 300 °C, which was mainly due to the decomposition of oxygen-containing functional groups on the surface and edge of the graphite oxide. Moreover, the process may generate CO, CO₂, and H₂O [48]. From the TGA curve, it can be seen that GO(2) was easier to decompose than GO(1), which may contribute to the higher content of oxygen groups. However, the remaining mass of GO(1) and GO(2) rapidly approached to zero after decomposition, which was probably due to the energy released by degradation. Furthermore, this had a temporary effect on the balance of the measuring

instrument, thus decreasing its sensitivity [49]. From the results, it can be seen that the thermostability of Oct-O-GO(1) is better than that of GO, which can be attributed to the n-Octanol modified carboxyl. It is common knowledge that the thermostability of ester is better than that of carboxylic acid. After 500 °C, most of the oxygen-containing functional groups on the layers were removed; however, there was still a decrease in mass, which was possibly due to the destruction of the carbon skeleton [50].

Raman spectroscopy is a useful technique for the characterization of sp² and sp³ hybridized carbon atoms, including those in graphite, fullerenes, carbon nanotubes, and graphene [51]. The G band corresponds to the in-plane vibration of sp²-bonded carbon in a hexagonal lattice, and the D band associated with various types of disorder in the sp² lattice. Figure 3 presents the Raman spectra of the nanocarbon materials used in this study. For C60 (Fig. 3(a)), the highest peaks were located at 1,457.17 cm⁻¹ and 491.76 cm⁻¹, and consisted of the Ag symmetry assignment for this mode [52, 53]. The observed Raman characteristics of MWCNT (Fig. 3(b)) were very similar to those of commercial MWCNT, which was analyzed by Santangelo et al. [54]. In particular, the D and G bands were at 1,337.60 cm⁻¹ and 1,573.73 cm⁻¹, respectively. From the Raman spectrum of graphite, it can be inferred that the graphite used contained defects and disorder, as indicated by the D band at 1,354.82 cm⁻¹ (Fig. 3(c)) [55].

Furthermore, GO(1), GO(2), and Oct-O-GO(1) exhibited D and G bands at approximately 1,340 cm⁻¹ and 1,580 cm⁻¹, respectively (Fig. 3(d)) [56]. Origin 8.0 was used to fit the points in the Raman spectra after peak processing, for the calculation of the area ratio of the G and D peaks (I_D/I_G : D and G peak relative strengths). It can be used to estimate the content between the sp³ and sp² hybridization of carbon atoms, which can distinguish the disorder of the graphite crystal structure. In the oxidation process, the sp² hybridization of the graphite carbon atoms in the network structure converts to sp³ hybridization for the destruction of the carbon network. The I_D/I_G ratio of GO(1), GO(2), and Oct-O-GO(1) was 1.793, 2.409 and 2.481, respectively. This meant a decrease in the size of in-plane sp² domains, as well as an increase in the number density of grain boundaries that contained

Table 2 Theoretical calculation of the interlayer distance.

Samples	2θ (°)	Interlayer distance (nm)
G	26.580	0.340 ¹⁷
GO(1)	10.545	0.747
GO(2)	10.035	0.785
Oct-O-GO(1)	24.031	0.326

Table 3 Thermo gravimetric analysis (TGA).

Sample	Temperature (°C)	Mass remaining (%)
GO(1)	124.50	83.78
	187.49	65.82
	190.66	3.34
GO(2)	108.28	83.01
	136.88	77.37
	140.04	2.23
Oct-O-GO(1)	533.12	77.10
	713.09	9.66

Fig. 3 Raman spectra of (a) C60; (b) MWCNT; (c) G; (d) GO(1), GO(2) and Oct-O-GO(1).

various defects in GO(2) and Oct-O-GO(1). This confirmed that under the H_2SO_4 and H_3PO_4 mixed acid condition, GO(2) exhibited a more disordered crystal structure, which implies that the oxidation degree of GO(2) was higher [57]. In particular, Oct-O-GO(1) exhibited an increased D/G intensity ratio in comparison with GO, thus indicating a decrease in the average size of the sp^2 domains upon reaction with $-COOH$. The 2D band at $2,690\text{ cm}^{-1}$ is attributed to transverse optical phonon modes near the high symmetry point of the Brillouin zone (K point), which arises due to

a two-phonon double-resonance process. This peak was poorly developed, which indicates disordered graphene layers and stacking faults. The D+G peak is a combination mode of the D and G bands, and it appears in the graphite lattice with a high defect density [58].

The microtopography of the NCMs are presented in Fig. 4. The particle size distribution of C60 was not uniform, MWCNT appeared fluffy, and the graphite was layered. Multi-layer fold sheets could be clearly observed in GO(1), GO(2), and Oct-O-GO(1), which was the characteristic appearance of the graphite oxide prepared by Hummers' method [59]. This is because the oxidation group mostly exists on the surface and edges of the pieces, which can give rise to the thin film structure with curls and folds due to van der Waals forces, i.e., hydrogen-bond interactions and Π - Π stacks [60]. The wrinkles of Oct-O-GO(1) were less than that of GO(1) and GO(2), as it had been modified with n-octanol, which decreased the hydrogen-bond interaction to a certain extent.

3.2 Surface wettability test

The water static contact angle reveals the surface wetting characteristics. The wettability differs for different microstructures and functional groups. From Fig. 5, it can be seen that both GO(1) and GO(2) had

Fig. 4 SEM images of (a) C60; (b) MWCNT; (c) Graphite; (d) GO(1); (e) GO(2); (f) Oct-O-GO(1).

Fig. 5 The schematic overview of surface wettability test and the static contact angles of NCMs.

a better wettability than the pristine graphite, due to the oxygen-containing functional groups. Moreover, GO(2) was more hydrophilic in comparison with GO(1), which further confirmed that a larger amount of oxygen-containing functional groups were present on GO(2) than on GO(1). With respect to organic modification, Oct-O-GO(1) revealed a higher static contact angle at approximately 62.6° , thus resulting in decreased hydrophilicity.

3.3 Characterization of the emulsions

Viscometry is one of the most widely used investigation methods for colloidal solutions, which can effectively reflect the stability and rheological properties of emulsions [61]. Figure 6 presents the viscosity curves and size changes of the emulsions. From the viscosity curves of the emulsions in Fig. 6(a), it can be inferred that all the emulsions were shear-thinning liquids, which belonged to non-Newtonian fluids. Moreover, all the emulsions exhibited similar viscosities. From Fig. 6(b), it can be seen that there was a slight general

decrease in the size of the emulsion droplets in all the samples over time, suggesting that all the emulsions had good stabilities.

3.4 The tribological performance

3.4.1 The load-carrying capacity

The results of the tribological tests are presented in Fig. 7. The emulsions with NCMs exhibited better load-carrying capacities with respect to the P_B values (Fig. 7(d)), when compared with the base emulsion. Moreover, the Oct-O-GO(1) emulsion yielded a prominent P_D value, whereas those of other NCM emulsions were similar to that of the base emulsion.

3.4.2 The friction-reducing property

For the same sample tested under the same frequency, the average COF under 100 N was smaller than that under 50 N during the relatively stable period (70–180 s) (Fig. 7(c)). This was because within a certain load range, with an increase in pressure, the emulsion droplet was more easily broken, and the released oil phase and emulsifiers could quickly form lubrication films to reduce the COF. Emulsions with different NCMs demonstrated different friction-reducing performances, and the COFs when the load was 50 N can be ranked as follows: Oct-O-GO(1) emulsion < GO(2) emulsion < MWCNT emulsion < C60 emulsion < base emulsion < GO(1) emulsion < G emulsion; whereas when the load was 100 N, it can be ranked as Oct-O-GO(1) emulsion < GO(1) emulsion < C60 emulsion < GO(2) emulsion < MWCNT emulsion < base emulsion < G emulsion. The emulsion with Oct-O-GO(1) demonstrated a better friction reducing performance than that with the other NCMs under 50 N and 100 N. This

Fig. 6 (a) The viscosity curve of emulsions and (b) the size change of emulsion droplets over time.

Fig. 7 Friction profile of emulsions during the whole test period (0–180 s) under (a) 50 N & (b) 100 N; (c) the average COF of emulsions during relative stable period (70–180 s) under 50 N and 100 N; (d) the P_B and P_D values of NCMs emulsions.

may be because of its increased solubility in PAO8, due to the alkyl chains of graphene oxide. Therefore, during sliding, when the oil droplets of the emulsions were broken, the hydrophilic region of Oct-O-GO(1) interacted with the metal surface, whereas the alkyl chain of Oct-O-GO(1) stretched out in the PAO8 base oil to form a compact and well ordered thick interfacial film. This resulted in a better friction reducing performance. However, the friction reducing properties of other NCMs were similar, which was probably because they held the same carbon skeleton structure. When compared with the base emulsion, almost all the emulsions with NCMs played the role of friction-reducing, with the exception of that with graphite. This may be because it is difficult for graphite to be dispersed in oil or water. Other NCMs were more easily dispersed in the aqueous or oil phase, and emulsions with other NCMs as lubricants demonstrated better friction reducing performances than the base emulsion. In terms of the friction profiles, the Oct-O-GO(1) emulsion had the lowest COF and shortest running-in period. This was possibly because the alkyl chains on graphene oxide can arrange rapidly and directionally to form a protective film on the friction pairs, especially under a higher load (100 N).

3.4.3 The anti-wear property

The anti-wear performances of the NCM emulsions were studied using 3D surface interferometer analysis and confocal surface analysis, and the results are presented in Table 4, in which the colored images are from the interferometer analysis, and the grey images are from the confocal surface analysis. From the 3D surface interferometer analysis, the wear volume could be obtained, and the corresponding wear rate could be calculated. The wear rates of the worn balls and plates after the tribological tests under 100 N are presented in Fig. 8. For all the emulsions, the scratches under 100 N were more severe than those under 50 N (see Table 4). This suggested that at the same condition, a larger load resulted in more severe wear.

The 3D contour images revealed that the Oct-O-GO(1) emulsion exhibited a better anti-wear performance when compared with the other emulsions, regardless of whether the load was 50 N or 100 N, and this advantage was more prominent under the high load condition. The surface of the rubbing pair lubricated with the Oct-O-GO(1) emulsion was smooth, and no significant furrows were observed, whereas that lubricated with other emulsions was rough, and different-sized furrows were present. The wear rates

Table 4 3D contour and confocal (50×) pictures of scratches on balls and plates after tribological tests under 50 N and 100 N.

	Ball		Plate	
	50 N	100 N	50 N	100 N
Base emulsion
C60 emulsion
MWCNT emulsion
GO(1) emulsion
GO(2) emulsion
Oct-O-GO(1) emulsion
G emulsion

of worn plate surfaces after the tribological tests under 100 N, as shown in Fig. 8, can be ranked as follows: Oct-O-GO(1) emulsion < G emulsion < MWCNT emulsion < GO(1) emulsion < C60 emulsion < GO(2) emulsion < base emulsion. The results further indicated that the Oct-O-GO(1) emulsion exhibited the best anti-wear property.

Compared with white-light interference, laser

confocal scanning offers a higher resolution, and can achieve a narrow-range evaluation to obtain true color images. When the load was 100 N, the scratches on the plates lubricated with the Oct-O-GO(1) emulsion and base emulsion were the shallowest and the deepest, respectively, which is consistent with the results of the 3D interferometer analysis. In addition, there was a certain degree of abrasive wear and adhesive wear

Fig. 8 Wear rate of balls, plates and total wear rate of ball & plate after the tribological tests under 100 N with different NCM.

for all the emulsions, with the exception of that with Oct-O-GO(1). This was probably because the emulsion with Oct-O-GO(1) formed a uniform and stable lubricating film due to the combined effect of the alkyl chains and oxygen-containing functional groups on the GO skeleton.

3.5 The lubrication mechanism

To determine the lubrication mechanism of the NCM

emulsions, surface analyses including SEM-EDS, Raman spectroscopy, and XPS were conducted.

3.5.1 SEM-EDS analysis

To better observe the surface topography, SEM was conducted, and several black fractions on the worn surfaces (Fig. 9) were detected. Consequently, EDS analysis was employed to investigate the composition of the fractions on the worn surfaces. According to Table 5, C, O, Fe, Cr, Ni, and several other elements were detected in the magnifying region of the worn scars. The fresh surface of the friction pairs mainly contained Fe, Cr, Ni, and small amounts of C and Si, whereas the lubricants (NCM emulsions) contained C and O. Compared with the EDS data of the worn surface lubricated by the base emulsion, it can be inferred that the presence of C was mainly due to the residual NCM materials, whereas O was derived from the oxygen-containing ingredients. From the results of the EDS analysis, the order of the C and O contents from high to low was as follows: Oct-O-GO(1) emulsion ~ C60 emulsion > MWCNT emulsion > GO(1) emulsion ~ GO(2) emulsion ~ G emulsion. In Fig. 8,

Fig. 9 SEM images (150×) of scratches on balls after tribological tests under 100 N.

Table 5 EDS analysis of scratches on balls after tribological tests under 100 N.

Element content (%)	Base emulsion	C60 emulsion	MWCNT emulsion	GO(1) emulsion	GO(2) emulsion	Oct-O-GO(1) emulsion	G emulsion
C	—	78.70	49.03	39.72	39.21	76.92	23.26
O	43.69	10.60	32.39	36.34	38.72	10.16	55.96
Na	—	0.71	0.92	0.87	—	0.62	—
Si	—	—	0.26	0.29	0.22	0.30	0.56
Cl	—	0.71	0.16	0.28	1.68	0.19	0.52
K	—	0.13	0.15	0.22	—	0.12	0.30
Ca	—	—	—	—	—	0.20	0.21
Cr	13.09	2.16	4.33	5.12	2.89	2.51	5.60
Fe	39.34	6.68	11.63	15.67	15.76	8.01	12.20
Ni	3.88	0.64	1.13	1.49	1.53	0.96	1.38

the rank of the wear rates of the worn ball surfaces was Oct-O-GO(1) emulsion < C60 emulsion < MWCNT emulsion < GO(1) emulsion ~ GO(2) emulsion < G emulsion. This implied that an increase in the C and O contents in the film on the worn surface can result in an improved anti-wear property.

3.5.2 Raman analysis

Raman spectroscopy is commonly used to provide a structural fingerprint by which molecules can be identified. For Raman micro-spectroscopy (micro-Raman), sampling is non-destructive, and water, media, and buffers typically do not interfere with the analysis. Therefore, to better understand the lubricating mechanism of NCM emulsions, the Raman responses of the worn surfaces after four-ball tests were investigated. The micro-Raman results (Fig. 10) revealed six main peaks, which corresponded to alkyl chains (840 cm^{-1} and $2,220\text{ cm}^{-1}$), a carbon aggregation ($1,250\text{ cm}^{-1}$), a D peak ($1,370\text{ cm}^{-1}$), a G peak ($1,540\text{ cm}^{-1}$), and a 2D peak ($2,760\text{ cm}^{-1}$), respectively [62–64]. This demonstrated that all the NCM had residue on the worn surfaces when compared with the base. However, the micro-Raman spectra of the ball surfaces lubricated with GO(1), GO(2), G, and MWCNT emulsions were similar, which only presented signals of the D, G, and 2D peak. Although they had similar Raman responses, the intensities of their response peaks varied. First, the total intensity of the D and G peaks for GO(1) or GO(2) was higher than that of MWCNT, thus indicating differences in amounts of residue. Moreover, this was consistent with the SEM-EDS analysis. Second, for

GO(1) and GO(2), the intensity of the D peak was smaller than that of the G peak, whereas for MWCNT, the intensity of the D peak was a slightly higher than that of the G peak. This indicates a higher sp^3 hybridization of carbon atoms in the MWCNT residual film. From Section 3.4.3, it was confirmed that the anti-wear performance of MWCNT was superior to that of GO(1) and GO(2), thus indicating that the carbon residue contributed to the anti-wear performance. As for that lubricated with the C60 and Oct-O-GO(1) emulsions, signals were similar except alkyl chains for Oct-O-GO(1). The worn surfaces of the balls lubricated with the C60 and Oct-O-GO(1) emulsions exhibited a certain degree of amorphous carbon agglomeration, which may be why their load-carrying capacities were more prominent than that of the other emulsions (Fig. 7(d)). This further indicated that the accumulation of carbon was beneficial to

Fig. 10 Micro-Raman spectra of worn scars on balls after four-ball tests under 660 N.

lubrication. The micro-Raman results of the Oct-O-GO(1) emulsion presented two additional wide peaks (840 cm^{-1} and $2,220\text{ cm}^{-1}$), which can be attributed to alkyl chains. It indicated that the alkyl chains grafted onto GO sheets could be sheared during friction, and that the regions containing decomposed alkyl chains can be absorbed onto the freshly exposed metal surface, in addition to the carbon residue. Consequently, the Oct-O-GO(1) emulsion exhibited

the best lubrication properties.

3.5.3 XPS analysis

X-ray photoelectron spectroscopy is mainly used to determine the binding energy of electrons and to identify the chemical properties and composition of sample surfaces. The main elements on the worn ball surfaces lubricated with NCMs emulsions after the tribological tests under 100 N are presented in Fig. 11,

Fig. 11 XPS spectra of the typical elements on the worn balls after tribological test under 100 N.

as obtained using XPS analysis. Table 6 presents the contents of corresponding binding energies, obtained using theoretical calculations. Moreover, the peak area of every binding energy was obtained through peak fitting, and the percentage contents of corresponding bonds were estimated. As can be seen in Fig. 11, the C element on the worn surface mainly exists in three forms: non-oxygenated ring carbon (C-C/C=C, ~285 eV), hydroxyl and epoxy carbon (C-OH/C-O-C, ~286 eV), and carboxyl carbon (C=O, ~289 eV). In these forms, C-C/C=C corresponded to the basic bond of the NCMs, the C-O and C=O bonds were the oxygen-containing functional groups in the NCMs (such as GO(1) and Oct-O-GO(1)), or were produced by the friction process when the fresh metal surface was exposed to emulsions and air. The O element was present as iron oxides (i.e., FeO, FeOOH, Fe₃O₄, ~530 eV), C=O (~531 eV), and C-OH/C-O-C (~532 eV). The Fe element was present in the form of Fe(C₅H₅)₂ (~710 eV), Fe (~720 eV), and iron oxides (~730 eV) [65, 66]. The presence of iron oxides and Fe(C₅H₅)₂ indicated that the NCM emulsions had reacted with the metal surface and formed the tribochemical reaction film.

From the summary in Table 6, it can be seen that the compositions of the lubricating films formed by all the emulsions were similar; however, the content of each component was different. The ball surface lubricated with the Oct-O-GO(1) emulsion yielded the highest O-H/C=O content, whereas that lubricated with G emulsion was the lowest. As previously discussed, when the load was 100 N, the average

COF and the surface wear rate of the friction pairs lubricated by the Oct-O-GO (1) emulsion were the lowest, whereas those of friction pairs lubricated by the G emulsion were the highest. This suggested that the higher composition of O-H/C=O on the worn surface contributed to the superior lubricating properties. Moreover, less iron oxides formed on the surface lubricated by Oct-O-GO(1), thus indicating that the surface was well protected by a thick layer of complex (organic and inorganic) tribochemical reaction film. On the surface lubricated by G emulsion, the content of iron oxides was very high, which indicated that more iron had reacted, thus resulting in severe wear, as suggested in Table 4. It was speculated that because the alkyl chains on the GO edges increased the inter-distance between layers and weakened the inter-molecular forces, the interfacial strength during frictional sliding could be reduced, resulting in less friction. Moreover, after sliding, the well exposed oxygen-containing functional groups of the molecular structure would interact with the freshly exposed metal surfaces, quickly forming a protective lubricating film with high oxygen containing compounds. The results suggested that the different contents of the components in the lubricating film formed on the sliding surfaces were the main cause of the different tribological performances of the NCM emulsions. Furthermore, the alkyl and O-H/C=O containing ingredients, in conjunction with the carbon residue, were beneficial to the lubrication performance.

Table 6 Element on worn balls lubricated with emulsions after tribological test under 100 N by XPS analysis.

Element	C 1s				O 1s		Fe 2p		
Binding energy (eV)	~285	~286	~289	~530	~531	~532	~710	~720	~730
Corresponding bond content (%)	C-C C=C	C-OH C-O-C	C=O	FeO FeOOH Fe ₂ O ₃ Fe ₃ O ₄	C=O O-H	C-OH C-O-C	Fe Fe(C ₂ H ₅) ₂ FeO FeOOH	Fe	Fe ₃ O ₄
C60 emulsion	79.59	10.98	9.43	35.03	51.29	13.68	28.44	28.45	42.22
MWCNT emulsion	56.11	37.85	6.05	50.15	49.85	—	44.76	24.95	27.89
G emulsion	42.28	46.38	11.34	66.47	9.21	24.32	65.98	26.94	7.07
GO(1) emulsion	56.10	34.61	9.29	61.93	35.39	—	44.18	19.79	36.03
Oct-O-GO(1) emulsion	46.50	41.37	12.13	—	96.15	3.85	35.11	52.18	10.68

4 Conclusion

In this work, two types of GOs with different oxidation degrees (GO(1) and GO(2)) were successfully prepared using the modified Hummers' method, and one n-octanol functionalized GO (Oct-O-GO(1)). Their structures were confirmed using FTIR spectroscopy, Raman spectroscopy, XRD, TGA, and SEM analysis. The tribological behaviors of five types of NCMs with different dimensions in an O/W system, including zero dimensional C60, one-dimensional MWCNT, 2D GO, n-octanol modified graphene oxide (Oct-O-GO), and 3D graphite were studied, and the following conclusions can be drawn:

(1) The stabilities indicated that all the NCMs can be well dispersed in the same oil-in-water system. Moreover, the prepared NCM emulsions exhibited good stabilities.

(2) The tribological tests revealed that the Oct-O-GO(1) emulsion exhibited the best load-carrying capacity, in addition to the best friction-reducing and anti-wear properties.

(3) The lubrication mechanism was investigated using SEM-EDS, micro-Raman spectroscopy, and XPS. The results indicated that during frictional sliding, the ingredients in the emulsion can react with the freshly exposed metal surface and be absorbed by it, thus forming surface-active films to protect the surfaces from abrasion. Moreover, the ingredients containing alkyl and O-H/C=O, in addition to the carbon residue in the tribofilm generated on the metal surface, improved the lubrication performance.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (Nos. 21703279, and 21506064), Shanghai Natural Science Foundation (No. 17ZR1442100) and the Shanghai Municipal "Science and Technology Innovation Action Plan" International Cooperation Project (No. 15540723600) for financial support.

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