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Influence of the micromorphology of reduced graphene oxide sheets on lubrication properties as a lubrication additive

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A R T I C L E I N F O

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A B S T R A C T

The microstructures of graphene sheets have been widely researched, but few studies have been conducted on the influence of their micromorphology on lubrication properties. In this paper, the lubrication properties of three types of reduced graphene oxide sheets with different micromorphologies—regular edges (RG), irregular edges (ir-RG), and both irregular edges and wrinkles (ir-RWG)—were investigated. RG lubricant has the best lubrication properties and its friction coefficient and wear-scar depth remarkably decrease to 27.9 and 14.1% of that of base oil, respectively, whereas ir-RWG has the worst. The morphological regularity of the graphene sheets has a direct influence on their lubricant properties. The more regular, the better the properties. The results provide an efficient method for researchers to prepare suitable graphene sheets as lubrication additives.

1. Introduction

Low friction and low wear have been the development trend of the machine industry to decrease energy consumption and prolong service life. Also, the effectiveness of lubrication oil for decreasing friction and wear diminishes with gradually increasing working speeds and pressure conditions. Therefore, in recent years, carbon materials [1] especially graphene, a 2D laminated material, has been explored extensively as a lubrication additive to furtherly improve the properties of lubrication oil [2–11]. However, many factors affect the lubrication properties of graphene, for example, interlayer distance between sheets [12], 2D size of sheets [13], in-sheet defects [14,15], disorder of stacked sheets [16], number of layers [15,17], thickness [13,18], micro-hardness [19], and wrinkle of sheets [17]. Graphene that is small in 2D size or with sheets of small thickness can lead to lower friction because it is easier for such graphene to enter the contact region. A large interlayer distance between the sheets can be beneficial to lubrication for a low interlayer interaction between the sheets [12], whereas graphene with many wrinkles can directly cause strong sliding resistance between the graphene layers. Although much research has been conducted on the microstructures of graphene sheets, few have investigated the influence of their micromorphology on lubrication properties, which is a dramatically important factor for a lubrication additive. Generally, particles with onion or sheet micromorphologies demonstrate better lubrication properties than those of granular and tubular particles [20]. The onion-like particle will roll along the rubbing interface if it is stable, just like a sphere; otherwise, the particle would exfoliate and result in a sheet-like micromorphology [21–23]. The sheet-like particle can easily slide between the adjacent layers under a shear force if it exhibits a relatively weak interlayer Van der Waals force [24–26]; otherwise, the particle would reduce the fluid drag according to the comprehensive roles of particles and fluids [20,27,28]. Nevertheless, these studies have addressed the influence of the overall shape of a particle on the lubrication mechanism.

The micromorphology of graphene sheets is directly influenced by the preparation methods [29]. Mechanically exfoliated graphene exhibits perfect graphitic micromorphology with relatively few defects [30]. Chemical vapor deposition (CVD) can be expected to control the ripples and the dopping levels of the graphene layers [29]. However, the reduced graphene oxide based on the Hummers method [31] has attracted greater attention for research [32,33] because of its low cost, simple process, and high yield. Through different synthesis processes [34,35], the reduced graphene oxide might exhibit diverse micromorphology, such as obvious folds, wrinkles, and large holes, on its sheets, which could possibly affect the lubrication properties when used as a lubrication additive. Therefore, it is relevant to investigate and determine the influence of the micromorphologies of graphene sheets on lubrication properties as a lubrication additive.

In this study, for the first time, the lubrication properties and additive potential of three types of graphene sheets with various micromorphologies were investigated and discussed. The micromorphologies of these

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graphene sheets include regular edges (RG), irregular edges (ir-RG), and both irregular edges and wrinkles (ir-RWG). To determine the possible underlying mechanism for the tribological enhancements, graphene lubricants were tested in a ball-on-disk tribometer with reciprocating sliding conditions. Scanning electron microscopy (SEM) and high revolution transmission electron microscopy (HRTEM) were used to observe the micromorphologies of graphene sheets. Furthermore, TEM was used to observe the micromorphology of graphene wear debris on the rubbing interface to investigate the tribofilm formed by the graphene sheets. The results provide an efficient method for researchers to prepare suitable graphene sheets with regular edges, but few wrinkles, as lubrication additives.

2. Experiment

2.1. Materials

Three types of reduced graphene oxide were prepared by ball milling commercially purchased reduced graphene oxide (The Sixth Element Materials Technology Co., Ltd., Changzhou, China). The base oil used in the experiments was hydraulic oil (Kunlun Lubricant, China) with a kinematic viscosity of 13.2 mm^2/s at 40 °C and 4.9 mm^2/s at 100 °C. The friction pair consisted of commercially available bearing steels and brass, and the composition and mechanical properties of the friction pair is shown in Table 1.

2.2. Preprocessing by grinding

A ball-milling process is used extensively to reduce the 2D size of particles [36–39] and to protect the graphene in-plane crystal from destruction at a low rotary speed [39]. In this experiment, the grinding process was performed to reduce the 2D size of the commercially reduced graphene oxide so that the graphene sheets could enter the lubrication contact region more easily [40]. The grinding experiments were carried out in a planetary mill with four vials (inside volume 100 ml, for a diameter of 10 cm) made of zirconia. The three types of purchased reduced graphene oxide powders were introduced with zirconia balls of different diameters, 1–10 mm, into three vials by medicine spoons. A ball-to-powder mass ratio of 230 to 1.5 was used for a rotation duration of 5 h, at rotation speeds 300–500 rpm. All of the parameters in the three vials were completely identical, and the fourth vial with the same weight as the others was used to balance the centrifugal force during rotation. Fig. 1 shows the SEM micromorphology of RG and its corresponding initial condition before the ball-milling process; the reduced size of the 2D graphene sheets is clearly evident.

2.3. Experiment

The tribological experiments were conducted on a friction and wear tester (UMT-3, CETR) with a reciprocating ball-on-disk mode (Fig. 2). The load and the reciprocating frequency were fixed at 3 N and 0.5 Hz, respectively, with a maximum Hertzian pressure of approximately 1 GPa on the rubbing surfaces. Graphene sheets (1 wt%) were firstly fully mixed in the hydraulic oil by magnetic stirring for 30 min, and then fully dispersed by ultrasonic for 30 min at 40 °C.

Table 1
Composition and mechanical properties of the friction pair.

Friction Pair	Composition	Hardness /HV	Young's Modulus /GPa (20 °C)	Poisson's Ratio (20 °C)	Tensile Strength /MPa
H62	Cu (62%)+Zn (38%)	110–130	100	0.36	410
GCr15	Fe (97%)+C (1%)+ Cr (1.5%)+ Trace amount of Mn, Si, S, P and Mo et al.	650–700	210	0.3	861.3

2.4. Characterization

The micromorphologies of the graphene sheets were observed through an environmental scanning electron microscope (FEI Quanta 200 FEG, Netherlands) and a high revolution transmission electron microscope (JEM-2010, Japan) with an accelerating voltage of 120 KV. The X-ray Diffraction (XRD) from a Bruker D8 Advance diffractometer (Bruker, USA) over a 2θ range of 10–90° was used to identify the crystallinity and crystallographic orientation of the graphene sheets. The Raman spectra of the graphene sheets were measured by using a Jobin Yvon HR800 confocal Raman system with 632.8 nm diode laser excitation at −70 °C. A three-dimensional white-light interferometer (Zygo Nexview, America) was used to measure the wear loss after the experiments.

3. Results

3.1. Micromorphological characterization

As shown in Fig. 3(a)–(c), the three types of graphene sheets exhibit similar distributions of 2D size, no more than 2 μm, and completely different micromorphologies. Fig. 3(a) shows a regular laminated micromorphology for the RG sheets, whereas Fig. 3(b) and (c)—especially Fig. 3(c)—shows obviously irregular micromorphologies, respectively, for ir-RG and ir-RWG. To more clearly observe the micromorphology of the graphene sheets, Fig. 3 (d)–(f) show them characterized by TEM analysis. The edge of RG is regular and smooth without any obvious wrinkles; whereas the ir-RG displays irregular edge, and the ir-RWG shows irregular edge and wrinkles in the sheets. Therefore, these graphene sheets indeed exhibit different micromorphologies.

As shown in Fig. 4, long stacked atomic layers can be seen in the three images, indicating good crystallinity of graphene sheets [33]. But the atomic layers of RG and ir-RWG are more clearly visible than those of ir-RG, indicating relatively ordered graphene sheets for the former two types of graphene.

As is shown in Fig. 5, the strong (002) diffraction peaks at $2\theta = 21.5°$, 22.5° and 25.8° for RG, ir-RG and ir-RWG respectively, while the weak diffraction peaks at 2θ interval of 40–50 are due to (100) and (101) reflections [41]. The average out-of-plane grain sizes (to estimate the average height of graphene sheets) can be determined from the (002) full width at half maximum (FWHM) values [41,42]. According to the Scherrer's equation ($D = K\lambda/\beta\cos\theta$, where $\beta = \pi\cdot\mathrm{FWHM}/180$, $K = 0.9$) [43], the average out-of-plane grain sizes (denoted as D) are 1.11 nm, 0.88 nm and 1.09 nm for RG, ir-RG and ir-RWG respectively, which are shown in Table 2. Furthermore, crystallinity of graphene is related to FWHM value [44,45]. As the values shown in Table 2, the FWHM values of RG and ir-RWG are nearly the same, and are a little higher than that of ir-RG, indicating relatively high crystallinity for the former two types of graphene [45]. Meanwhile, as shown in Fig. 5, the (002) diffraction peaks of RG and ir-RWG are nearly the same sharper than that of ir-RG, also indicating better crystallinity for the former two types of graphene sheets [46]. All of these results gotten from XRD patterns are consistent with that from HRTEM.

According to the Raman spectra of the RG, ir-RG, and ir-RWG powders in Fig. 6, the two intense features are the D band at approximately 1330 cm^{-1} and the G band at approximately 1590 cm^{-1}. The presence of defects in sp^2 carbon network give rise to D band in the Raman spectra, namely containing the sp^3 carbons in the graphene lattices, and the G peak is attributed to the in-plane vibration of sp^2 atoms and the doubly degenerate zone center E_{2g} mode [47,48]. The relatively higher intensities of D band compared to that of G band in the Raman spectra of the three types of graphene in Fig. 6 show some defects on the surfaces and edges of the three types of graphene sheets. According to the literature [49–52], the intensity of the D band relative to the G band (ID/IG) can reveal the defects in any sp^2-carbon material. The ID/IG ratios of RG (1.26) and ir-RG (1.31) are nearly the same, and much lower than that of