Modified graphene as novel lubricating additive with high dispersion stability in oil

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Abstract: Graphene is a promising material as a lubricant additive for reducing friction and wear. Here, a dispersing method which combines chemical modification of graphene by octadecylamine and dicyclohexylcarbodiimide with a kind of effective dispersant has been successfully developed to achieve the remarkable dispersion stability of graphene in base oil. The stable dispersion time of modified graphene (0.5 wt%) with dispersant (1 wt%) in PAO-6 could be up to about 120 days, which was the longest time reported so far. At the same time, the lubricant exhibits a significant improvement of tribological performance for a steel ball to plate tribo-system with a normal load of 2 N. The coefficient of friction between sliding surfaces was ~0.10 and the depth of wear track on plate was ~21 nm, which decreased by about 44% and 90% when compared to pure PAO-6, respectively. Furthermore, the analysis of the lubricating mechanisms in regard to the sliding-induced formation of nanostructured tribo-film has been contacted by using Raman spectra and TEM.

Keywords: modified graphene; dispersity; lubricant additives; tribo-film

1 Introduction

Graphene has attracted a great deal of attention in recent years because of its unique structure and remarkable mechanical, electrical, optical and thermal properties [1–5]. In particular, graphene has been proved as an excellent candidate for both solid lubricant and lubricant additive owing to its excellent mechanical strength, low shear strength, high thermal and chemical stability, atomically smooth surface, notable specific surface area, and ultrathin film thickness [6–10].

Friction and wear can lead to energy wastage, material losses and shorter life of moving components in mechanical processes. It is reported that the direct losses from tribological contacts are closed to 23% of total fuel energy lost [11]. In order to save energy as well as to protect the mechanical components, lubrication has been demonstrated as an effective method to reduce friction and wear in multiple industrial applications. Liquid lubricant is one kind of versatile lubricant which has a wide range of uses, and graphene also has gained large interest in recent years as lubricating additives due to their low shear resistance between the layer structure, suitable size to enter the contact areas and good thermal conductivity to dissipate the heat generated during friction process [12–23].

So far, a number of studies have been conducted on the tribological behavior and lubrication mechanism of graphene as lubricating additives. Especially, it is highly necessary to ensure stable dispersion of graphene as lubricating additive in various base lubricants. One of the most effective ways to improve the dispersion stability of graphene is to regulate its physical form.

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Li et al. [16] prepared highly exfoliated reduced graphene oxide by thermal reduction to increase the specific surface area of graphene, and the stable dispersion time of this graphene in PAO-6 could reach 4 days. By adding 0.5 wt% reduced graphite oxide in poly(α-olefin) lubricant oil (PAO-6), the friction coefficient and the depth of wear track decreased by 44% and 90%, respectively. Dou et al. reported a novel crumpled graphene balls as effective lubricant additives in PAO-4 [17]. It could be found that the crumpled graphene balls had better dispersion stability in base oil than graphite, carbon black and commercial reduced graphite oxide. And it was believed that graphene balls could provide ball bearing effect during the friction process, thus improving the friction-reducing and anti-wear properties of PAO-4.

Another commonly used method to improve the dispersibility of graphene is chemical modification. In order to increase the dispersion stability of graphene in water, oxidation methods are employed to graft the oxygen-containing functional group on graphene sheets. Kinoshita et al. [18] investigated the lubrication performance of graphene oxide (GO) when it was added into pure water, and they found that the friction coefficient of water with GO at a concentration of 1 wt% was as low as 0.05 with mild wear on tribo-pairs after friction tests. Lin et al. [19] used stearic and oleic acids as raw materials to graft alkylene chains on graphene sheets by cyclic heating method, thus improving the dispersion stability of graphene in base oil. It was found that the unmodified graphene was heavily agglomerated in base oil in 200 minutes while little precipitation could be observed for modified graphene. And the friction coefficient of base oil with 0.075 wt% modified graphene was about 0.12, which was 33.3% lower than that of pure base oil.

In addition, the use of dispersants is also a feasible means to effectively improve the dispersion stability of graphene in base lubricants. For example, Cai et al. [20] used Span-80 (C₈H₁₆O₈) as dispersant to enhance the dispersibility of graphene in PAO-4. As for PAO-4 with 0.05 wt% graphene and 1 wt% Span-80, the suspension was darker and more turbid than PAO-4 with 0.05 wt% graphene after 3 days, which demonstrated that the Span-80 could effectively improve the dispersion stability of graphene in base oil. However, the longest reported stable dispersion time of graphene in oil-based lubricants is only ~30 days so far. And there still need a lot of efforts in the development of effectively-dispersed solutions of graphene in oil to achieve longer stable dispersion time, thus meeting the imperative demands in practical applications.

Herein, a novel dispersing method is developed to achieve remarkable dispersibility of graphene as lubricant additive in PAO-6. The graphene sheets are modified with octadecylamine through a chemical synthesis process, and an effective dispersant mainly consisting of polyisobutylene succinimide is also added into the lubricant to attain enhanced graphene dispersion. The synergistic effect of chemical modification of graphene and the use of dispersant is quite impressive in terms of the improvement in dispersion stability of lubricating additive. Moreover, the tribological performance of the lubricant is also improved significantly when compared with pure PAO-6. Besides, the effect of additive concentration and the lubrication mechanism were also studied. In a word, the long-term dispersion stability of graphene in lube oil and the high-performance tribological behaviors of the lubricant have great potential to meet practical application needs.

2 Experimental

2.1 Preparation and characterization of material

GO was prepared via a modified Hummer’s method while the graphite powder was used as raw material [21]. The typical preparation process of GO is as follows. Firstly, sulfuric acid was poured into a beaker in an ice bath, and then 2 g graphite powder and 1.6 g sodium nitrate were added into 140 mL sulfuric acid (98 wt%), respectively. The next step was to slowly add 12 g of potassium permanganate to the solution while ensuring that the solution temperature was lower than 15 °C during this process. Then the beaker was placed in a fume hood for 8 hours under magnetic stirring while the temperature of the solution needed to be kept at 35 °C. Then the deionized water was gradually added into the mixture and a dark-brown suspension was obtained. After this step, the 10 mL hydrogen peroxide
solution (30%) was added into the suspension, achieving a brilliant yellow color solution. The solution was centrifuged and the product was washed with hydrogen chloride solution and deionized water. At last, the obtained solid matter was placed in a vacuum oven and dried at 60 °C for 8 hours.

The modified graphene (MG) was then prepared on the basis of GO. The dried GO (0.1 g) was dispersed in deionized water by ultrasonication and mechanical stirring for 30 minutes. Then octadecylamine (0.5 g) and dicyclohexylcarbodiimide (0.1 g) were added to the GO aqueous solution. The mixture was refluxed under the continuous stirring for 12 hours at 120 °C. After the reaction, it could be observed that the supernatant solution in the round bottom flask became clear, and a black solid substance was obtained at the bottom of the flask. The obtained black product was then washed 5 times by deionized water and ethanol, respectively. Finally, the modified graphene was dried in vacuum drying chamber.

Morphology and chemical structural properties of GO and MG were investigated through atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

In addition, the dispersant employed in this work was mainly composed of polyisobutylene succinimide. And the polyisobutylene succinimide was prepared with polyisobutylene, maleic anhydride and polyamine by synthetic reactions.

2.2 Tribological measurements

MG and dispersant were dispersed in PAO-6 by mechanical stirring for 0.5 h and ultrasonication for another 0.5 h, respectively. The tribological properties of the lubricant were investigated by a reciprocating tribotester (UMT-5, Brucker) with a ball-on-disk mode. The plates used in tests were bearing steels (AISI 52100) and the counter balls were also bearing steels (AISI 52100) with 4 mm diameter. The mean roughness of the balls was 20 nm, and the surface of the plates has been polished to a roughness of 5 nm. Balls and plates were cleaned by acetone and ethyl alcohol in ultrasonic cleaner for 10 min before the frictional experiments, respectively. The applied normal load during the experiments was 2 N, resulting in an initial maximum Hertzian contact pressure of about 1.1 GPa. Besides, the average sliding speed was 5 mm/s under reciprocating motion. And the time for each experiment is 900 seconds. All of the friction experiments were conducted in atmospheric environment.

After the tests, the analysis of contact areas was conducted by scanning electron microscopy (SEM), Raman spectroscopy, three dimensional profilometer and transmission electron microscope (TEM).

3 Results and discussion

The morphologies and structures of GO and MG were analyzed by several methods. Figures 1(a) and 1(b) show the dimensions of the prepared GO and MG detected by AFM, and it could be seen that the two-dimensional sizes of GO and MG were 2–5 μm and the thicknesses of GO and MG flakes were about 2.6 and 3.1 nm, respectively. FTIR spectroscopy was also used in order to confirm the existence of alkyl chains. Figure 1(c) is the FTIR result for GO. The peaks appeared at 1,735, 1,624, 1,381, and 1,073 cm–1 represent the C=O, C=C, C–O, and C–O–C, respectively, which are typical peaks of GO sample and have also been reported in previous studies [22]. As for MG sample (Fig. 1(d)), the typical peaks of C-H could be observed at 2,914 and 2,846 cm–1, the peaks appeared at 1,457 and 1,368 cm–1 represent CH 3, and the typical peak of (CH 2)n is at 710 cm–1, these results confirm the existence of long alkyl chains on graphene. Besides, Figs. 1(e)–1(h) show the XPS scan spectra of GO and MG. The C/O atomic percentage of GO and MG was 68.3/30.6 and 89.4/10.2, respectively (Figs. 1(e) and 1(f)). It was believed that the conspicuous increase in carbon atomic percentages for MG is owing to the alkyl chains existed on its surface. Moreover, Figs. 1(g) and 1(h) present the spectra of C1s for GO and MG. The C1s spectra show the presences of C–C at 284.7 eV, C–O at 286.6 eV, and C=O at 288.1 eV.

Dispersion stability of solid additives is quite important for an effective lubricant. Figures 2(a)–2(c) show the photos of MG and MG/dispersant in PAO-6 as a function of time. The MG (0.5 wt%) and MG (0.5 wt%)/dispersant (1.0 wt%) were added in base oil with mechanical stir for 30 min and sonication for 60 min, respectively, thus producing stable dispersed
solutions. It could be observed that the stable dispersion time of MG and MG/dispersant in PAO-6 was 30 days and 120 days, respectively. Moreover, Fig. 2(e) presents the stable dispersion time of graphene reported in the literatures so far when oil was used as the base lubricant [12–14, 20, 23–28]. It could be seen that 120 days obtained in our work were the longest time. And the detailed comparison of these literatures was presented in Table S1 in the Electronic Supplementary Material (ESM). In addition, the variations of stable dispersion time of MG (0.5 wt%) with different concentrations of dispersant were also studied, which was showed in Fig. S1 in the ESM. Besides, as indicated by Fig. S2 in the ESM, the viscosity of PAO-6 with MG/dispersant was 53.1 mPa·s (measured by a Rheometer), which was slightly larger than that of PAO-6 with MG (49.4 mPa·s) and pure PAO-6 (46.2 mPa·s).

It is well known that the solute composed of polar molecules is easily dissolved in a solvent composed of polar molecules, while the non-polar solutes are more soluble in non-polar solvents. Owing to the presence of various polar functionalities like hydroxyl and carboxyl groups, GO is hydrophilic and could be well dispersed in water, but has poor dispersibility in oil. However, many engineering applications have great demands for good dispersion stability of graphene in oil. Here, MG was functionalized with alkylamines to facilitate its well dispersion in PAO-6, and the stable dispersion time could reach ~30 days. It is believed that the interaction between alkyl chains grafted in the graphene nano-sheets and the base oil plays an important role in improving the dispersing performance [29]. Besides, the addition of dispersant could further enhance the dispersion stability of MG in PAO-6, which increased the dispersion time from ~30 to ~120 days. This phenomenon is considered to be due to the fact that the dispersant also contains long alkyl chains, which could be intertwined with the alkyl chain on MG to enhance its dispersion properties.

The tribological properties of PAO-6 with MG were analyzed by UMT-5. The applied normal load was 2 N and the sliding speed was 5 mm/s. Figure 3(a) shows the schematic diagram of frictional experiments. Figure 3(b) presents the friction coefficient for PAO-6 with different MG concentrations. As the content of MG gradually increased, the friction coefficient decreased first and then increased. It could be observed that the lowest friction coefficient was about 0.12 when the amount of MG added was 0.5 wt%, yielding a reduction by about 33.3% when compared to the pure PAO-6 (~0.18). The friction coefficients for PAO-6 with different MG concentrations and 1 wt% dispersant were shown in Fig. 3(c). The variation trend of friction coefficient is consistent with the case in Fig. 3(b), and the lowest friction coefficient was 0.10 for PAO-6 with 0.5 wt% MG and 1 wt% dispersant. Figure 3(d) presents the friction coefficient curves of PAO-6, PAO-6 with MG (0.5 wt%) and PAO-6 with MG (0.5 wt%)/
dispersant (1 wt%), respectively. For the base oil PAO-6, the friction coefficient increased in the beginning of the tests, then decreased and was kept stable at a relatively high value of about 0.18. As for PAO-6 with MG (0.5 wt%) and PAO-6 with MG (0.5 wt%)/dispersant (1 wt%), it is obvious that the friction curves are stabilized at lower levels in the whole tests, which proved that the MG has good friction-reducing effect. Interestingly, the friction coefficient of PAO-6 with MG/dispersant is about 0.10, which is 16.7% lower than that of PAO-6 with MG (~0.12). These results demonstrate that the MG dispersed in base oil has excellent capability of reducing friction.

In addition to the friction reduction, PAO-6 with
MG also provides excellent wear-resistance for the surfaces of tribo-pairs. Figures 4(a)–4(c) show the SEM images of wear tracks on steel plates for three different lubricants. The widths of wear scars were 119, 110, and 114 μm for pure PAO-6, PAO-6 with MG (0.5 wt%), and PAO-6 with MG (0.5 wt%)/dispersant (1 wt%), respectively. More details could be obtained from 3D surface morphologies (Figs. 4(d)–4(f)) and cross-sectional profiles (Figs. 4(g)–4(i)). The wear track depths were 47 nm for PAO-6 with MG and 21 nm for PAO-6 with MG/dispersant, which were 79% and 90% lower than that of pure PAO-6 (221 nm), respectively. In a word, the use of MG and MG/dispersant in PAO-6 could prevent severe wear on the surface of steel plates during the sliding process.

Moreover, the tribological properties of commercial oils with MG and dispersant were also investigated. Figure 5(a) shows the friction coefficient curves of 10W-40 oil and 10W-40 oil with MG (0.5 wt%)/dispersant (1 wt%) when the experimental time was 7,200 s. The friction coefficient of 10W-40 oil with MG/dispersant was about 0.10, which was 9.1% lower than that of pure 10W-40 oil. Figure 5(b) present the depth of wear tracks on the steel plates. It could be observed that the depth of wear tracks for 10W-40 oil with MG/dispersant was about 39 nm, which was

Fig. 4  Scanning electron microscope images, three-dimension surface images and the corresponding surface profiles of wear tracks for (a, d, g) PAO-6, (b, e, h) MG (0.5 wt%), and (c, f, i) MG (0.5 wt%)/dispersant (1 wt%), respectively.

Fig. 5  (a) Friction coefficient curves of 10W-40 oil and 10W-40 oil with MG (0.5 wt%)/dispersant (1 wt%) and (b) corresponding depth of wear tracks.
32.8% lower than that of pure 10W-40 oil. These results proved that MG with dispersant could also improve the tribological behaviors of commercial oil.

Furthermore, since Raman spectroscopy is an effective method for analyzing graphene [30], the lubrication mechanism was studied on the basis of Raman analysis of the wear tracks on steel plates. Figure 6 presents the Raman spectra of GO (Fig. 6(a)), MG before friction tests (Fig. 6(b)), wear track for PAO-6 with 0.5 wt% MG (Fig. 6(c)) and wear track for PAO-6 with 0.5 wt% MG and 1 wt% dispersant (Fig. 6(d)). In all the four cases, there are a D peak at 1,351 cm\(^{-1}\), a G peak at 1,582 cm\(^{-1}\), a weak 2D peak at 2,702 cm\(^{-1}\), and a D + D' peak at 3,081 cm\(^{-1}\). This demonstrates the formation of tribo-film in the contact area, and graphene is one of the components of the tribo-film. Besides, the intensity ratio of D and G peak of MG (\(I_{D}/I_{G} = 1.08\)) is larger than that of pristine GO (\(I_{D}/I_{G} = 0.90\)), which could be on account of the defects induced during the preparation process. After the friction tests, the \(I_{D}/I_{G}\) ratios were 1.39 and 1.34 for PAO-6 with MG and PAO-6 with MG/dispersant, respectively, suggesting that the mechanical action during the friction process could lead to an increase in the defects of graphene.

For more in-depth study of the tribological mechanism of PAO-6 with MG as lubricant additive, the tribo-film formed on contact area of steel plate was further investigated through TEM observation. The TEM-specimen of the tribo-film was prepared by focused ion beam (FIB) method from the contact area. Before the FIB process, the contact area was firstly coated by a protective metal layer of chromium through the ion sputtering technology. Afterwards, the sample was moved to the SEM-FIB chamber and another protective layer of platinum was deposited on the surface of Cr layer. Then the sample was incised and thinned using a Ga\(^+\) ion source accelerated by a voltage of 30–5 kV or 5 kV, and SEM images were delivered for positioning at the same time.

Figure 7(a) presents the TEM image of cross-sectional specimen obtained from the wear track for the PAO-6 with MG (0.5 wt%)/dispersant (1 wt%) under low magnification. It is easy to distinguish the steel substrate, the tribo-film, the Cr and the Pt protective layers. And the thickness of the tribo-film is about 90 ± 10 nm. Figures 7(b)–7(d) show high-resolution TEM images of three typical areas within the tribo-film. The graphene with stacked layer-like structure can be seen in Fig. 7(b), and the \(d\)-spacing value is about 0.498 nm. Figure 7(c) shows the crystal lattice of Fe, and the \(d\)-spacing value is about 0.204 nm, corresponding to the (110) plane of Fe. Another crystal lattice structure with \(d\)-spacing value of about 0.252 is presented in Fig. 7(d), which is believed to be the (110) plane of Fe\(_2\)O\(_3\). The Fe and Fe\(_2\)O\(_3\) particles embedded in the tribo-film could be the wear debris of tribopairs formed during the sliding process. In addition, it can be observed that amorphous regions without an orderly structure exited within the tribo-film (Figs. 7(b)–7(d)), and several possible reasons might explain this phenomenon. Firstly, the preparation process of MG could lead to the amorphization of graphene. Secondly, the Raman pattern confirmed that friction tests would increase the defects in MG (Fig. 6(d)), which probably induced the partial amorphization of the crystal structure of graphene. Besides, the contamination and impurities introduced from preparation process of MG and friction tests might also be amorphous. Figures 7(e)–7(j) show the different elemental mappings of the TEM-specimen. Cr and Pt protective layers are presented in Figs. 7(f) and 7(g), and the tribo-film is mainly composed of C (Fig. 7(h)), Fe (Fig. 7(i)) and O (Fig. 7(j)).

In addition, low magnification TEM image of cross-sectional specimen obtained from the wear track
for the PAO-6 with MG (0.5 wt%) is presented in Fig. 8(a). The thickness of tribo-film is 100 nm ± 5 nm. Steel substrate, Cr and Pt layers could also be clearly found in the image. High-resolution TEM images regarding the detailed microstructures of the tribo-film are shown in Figs. 8(b)–8(d). The layered structure of graphene, the crystal structures of Fe (d-spacing value = ~0.204 nm) and Fe_{2}O_{3} (d-spacing value = ~0.252 nm) are quite similar to that of the tribo-film for PAO-6 with MG/dispersant. Besides, amorphous areas could also be found in the bulk of the tribo-film. Different EDS-elemental mappings of the TEM-specimen are presented in Figs. 8(e)–8(j). C (Fig. 8(h)), Fe (Fig. 8(i)) and O (Fig. 8(j)) are the main components of the tribo-film.

Graphene is a notable two-dimensional material which has been widely used as lubricating additive in both water-based and oil-based lubricants. And many studies have shown that tribo-film would form on the contact area during the friction test when graphene-containing lubricants were applied in the experimental process. Hiroshi et al. [18] investigated the frictional behaviors of GO nano-sheets as additives in water-based lubricants. Tribo-film was formed on the surfaces of tribopairs which was confirmed by SEM images and the corresponding elements mappings, thus enhancing the tribological performance of the lubricant. Researchers also added GO in hydrocarbon base oil to improve the lubricating performance, and tribo-film was detected in the wear tracks after friction process through Raman spectroscopy [31]. When reduced GO was employed as additive in base oil, the formation of tribo-film was proved by Raman spectroscopy and TEM images [14]. In our work, the analysis results of Raman spectra, TEM images and the
corresponding elemental mappings all demonstrate that the tribo-film existed in the wear tracks. It is believed that the tribo-film can prevent the direct contact of steel ball and steel plate, thus promoting the lubrication performances of the lubricant. In addition, graphene could easily enter into contact area during sliding process owing to its unique morphological structure. And shear resistance between the neighboring lamellae of graphene was quite low due to the weak inter-layer van der Waals interactions, which could also contribute to the improvement of tribological performance.

Interestingly, when MG (0.5 wt%) and dispersant (1 wt%) were added into PAO-6 at the same time, not only the dispersion stability of graphene was improved, but also the tribological behaviors of the lubricant were enhanced as compared to PAO-6 with MG (0.5 wt%). Firstly, the dispersant was mainly composed of polyisobutylene succinimide which contained nitrogen groups and long alkyl chains. The polar nitrogen-containing group would adsorb on the surface of the tribo-pairs while the long alkyl chain would form an alkyl chain shear layer (Fig. 9), thus enhancing the friction-reducing and anti-wear abilities of the lubricant [32, 33]. In addition, several studies have shown that the tribological properties of lubricants would also increase with the increase of dispersion stability of lubricating additives [34, 35].
In a word, we combined a chemical modification method with a unique dispersant to successfully increase the dispersion stability of graphene in base oil. In the meantime, the tribological performance of the oil with MG/dispersant was more superior to that of pure oil with MG and pure PAO-6. These results demonstrate that both the dispersion method of graphene in oil and the developed lubricant have great potential in engineering applications.

4 Conclusions

In summary, a novel dispersion method which combines chemical modification of graphene with a kind of effective dispersant has been successfully developed. Remarkable dispersibility of graphene as lubricating additive in PAO-6 is achieved with stable dispersion time up to about 120 days. Besides, the lubricant exhibits a significant improvement in tribological performance when compared to pure PAO-6. It is found that the combination of MG (0.5 wt%) and dispersant (1 wt%) has reduced friction coefficient and wear scar depth by about 40% and 90%, respectively, with respect to the base oil. The excellent performances of MG and dispersant as lubricating additives in PAO-6 can be attributed to (a) the formation of tribo-film preventing the direct contact of tribopair surfaces, (b) weak shear resistance between the lamellas of graphene, and (c) the lubrication effect of dispersant from the polyisobutylene succinimide.

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