Alkyl Titanate-Modified Graphene Oxide as Friction and Wear Reduction Additives in PAO Oil

Lei Zhang,* Xin Sun, Xiang Liu, Yuanhua He, Yonggang Chen,* Zhenwei Liao, Han Gao, and Shuo Wang

ABSTRACT: Diacetoxy-stearoxytitanium-modified graphene oxide (Titanate-GO) was successfully prepared using titanium tetraisopropanolate, stearic acid, acetic acid, and graphene oxide (GO). The morphology and structure of the as-prepared materials were tested by FT-IR, Raman, TG/DSC, SEM, and TEM instruments. The results indicate that long alkyl titanium chains have been grafted on the surface of a GO sheet, which guaranteed the dispersibility of Titanate-GO in PAO10 base oil. Then, the lubrication properties of Titanate-GO as a lubricating additive in PAO10 base oil were evaluated on a four-ball machine. The results show that the average coefficient of friction and wear scar diameter were reduced by 49.5 and 28.2%, respectively, compared with bare PAO10 base oil. Finally, the lubrication mechanism was discussed based on the Raman analysis, which was carried out on the worn surface of the steel ball.

1. INTRODUCTION

In 2004, the novel graphene was first prepared by Geim and Novoselov. The one-atom-thick graphene was found to possess great talent in several properties such as high thermal stability, low surface energy, excellent mechanical strength, superconductivity, good transmittance, and so on. Therefore, graphene-related materials have brought wide interest and research. In the last two decades, numbers of researches have been focusing on the several application fields, macroscopic preparation techniques, and industrial production. Furthermore, great technological breakthroughs have been made in many terminal application products.

As is known to all, friction and wear play a very important role in energy consumption and materials losses. Using friction reduction and anti-wear additives is an effective method to formulate high-performance lubricants. Owing to the ultrathin lamellar structure, low shear stress, ultimate mechanical strength, and high thermal stability, graphene and modified graphene possess potential application prospect as a lubricant additive. The challenge of graphene dispersion in oil has been solved in many research reports. Thus, many researchers have reported their work focusing on the lubricating properties of modified graphene. Khatri et al. have reported that octadecylamine-functionalized graphene oxide improves the performance of hexadecane by 26 and 9% reduction in the friction coefficient and wear scar diameter, respectively. Cheng et al. developed an oleic diethanolamide borate-modified graphene oxide (ODAB) possessing good dispersibility and transparency in oil. Furthermore, the friction coefficient and wear scar diameter of base oil with 0.02 wt % ODAB was decreased by 38.4 and 42.0%, respectively. The maximum non-seizure load increased by 46.2%. Recently, they reported an eco-friendly expansion—reduction exfoliation method to prepare graphene from graphene oxide (GO) with the aid of oxalic acid (H₂C₂O₄). The test results showed that the friction reduction and wear-resistant properties were improved by 35.8 and 32.8%, respectively.

The alkylated graphene (AGN) was prepared and shown to possess excellent anti-wear and friction reduction properties in our previous work. However, the boundary lubrication performance of AGN was not outstanding. Hu et al. synthesized organic titanate (STAE) via an in situ method with soybean oil, diethanolamine, and isopropyl titanate. The as-synthesized STAE exhibits excellent anti-wear and load-carrying capacities as well as good anti-wear synergism with zinc dialkyldithiophosphate (ZDDP) in poly-α-olefin. It deserves to be mentioned that titanium complex grease is a kind of lubricant with excellent properties. Although it contains less additives, titanium complex grease possesses better...
tribological property, high- and low-temperature property, shear stability, and biodegradability.27

Boundary friction is very common in mechanical motion under large load. When the oil film between friction pairs breaks down, a boundary lubrication film is important to protect the surfaces of friction pairs. Thus, boundary lubrication performance of a lubricant additive is undoubtedly important. According to the previous research, graphene additive modified with non-polar alkyl showed a poor boundary anti-wear property.25

In this paper, we report a mild method to prepare diacetoxy-stearoyloxy-titanium-modified graphene oxide (Titanate-GO) and the application of Titanate-GO as friction reduction and anti-wear additive in PAO10 base oil. The structure of Titanate-GO was characterized using FT-IR, Raman, TG/DSC, SEM, and TEM. The results show that the long alkyl titanium chains have been successfully grafted on the surface of the GO sheet. Then, the lubrication performance of PAO10 containing different concentrations of Titanate-GO was evaluated on a four-ball machine. The testing results indicated significant enhancement in lubrication performance of base oil by adding a small-dose Titanate-GO additive, showing promising application potential as an oil-based lubricant additive. Finally, the lubrication mechanism is further discussed on the basis of Raman shift analysis on the worn surfaces of steel balls.

2. RESULT AND DISCUSSION

2.1. Characterization of Titanate-GO. 2.1.1. FT-IR Analysis. The FT-IR analyses of GO and Titanate-GO are displayed in Figure 1. The peaks around 1735 cm⁻¹ in all spectra are attributed to the C=O on the surface of GO and Titanate-GO. As for GO, the wide band around 3191 cm⁻¹ is assigned to the stretching vibration of O–H. The same band in the Titanate-GO spectrum is around 3195 cm⁻¹. The new peak in Titanate-GO around 754 cm⁻¹ is the in-plane vibration of –CH₂–. Meanwhile, the peaks at 1417 and 1379 cm⁻¹ are attributed to the –CH₃– groups, indicating that the long-chain alkyl groups have been grafted on the surface of Titanate-GO. The peak at 1512 cm⁻¹ is assigned to the vibration of –COO– of carboxylate. According to the FT-IR analysis, we may

| Table 1. Quantitative Composition of GO and Titanate-GO |
|-----------------|---------------|---------------|
| element        | mass fraction (wt %) | atom ratio (%) |
| C              | 55.37         | 62.32         |
| O              | 44.63         | 37.68         |
| Ti             | 0             | 10.58         |
conclude that the long alkyl titanium chain has been successfully grafted on the surface of the GO sheet.

2.1.2. XPS Analysis. The XPS spectra of GO and Titanate-GO are shown in Figure 2. As shown in the C1s spectrum of GO, C and O were detected: C−C/C≡C (284.8 eV), C−O (286.7 eV), and C≡O (287.2 eV). In the wide-scan XPS survey spectrum of Titanate-GO (Figure 2c), there is a new signal of Ti2p detected in Titanate-GO: Ti−C (458.8 eV) and Ti−O (464.6 eV). We can also observe that the intensity of the C1s peak increased in the Titanate-GO survey spectrum. The quantitative composition of GO and Titanate-GO attributed to the XPS analysis is shown in Table 1. The C/O atomic ratio increases from 1.65 in GO to 1.99 in Titanate-GO, suggesting that long-chain alkyl was introduced into the structure of Titanate-GO.

2.1.3. TG/DSC Analysis. The thermal decomposition properties of GO and Titanate-GO were evaluated from 30 to 800 °C under flowing N2 using the TG/DSC method. In Figure 3, the curve of GO shows a small amount of loss of adsorbed water in the sample around 100 °C. Then, the loss of GO around 200 °C can be attributed to the vigorous release of pyrolysis gas from labile functional groups, which results in a thermal expansion of the modified graphene. The thermal weight loss analysis of GO has been reported in our previous work. However, the thermal weight loss of Titanate-GO was much less than GO, showing that the thermal stability of Titanate-GO was better than GO. According to the comparison of thermal weight loss and heat flow of GO and Titanate-GO, the heat flow of GO was always higher than Titanate-GO (Figure 3).

2.1.4. Morphology Analysis of Titanate-GO. The morphology of GO and Titanate-GO sheets were investigated on SEM and TEM instruments, and the images are shown in Figure 4. The images in Figure 4 clearly show the layer structure of GO and Titanate-GO. The SEM (a–d) and TEM (e, f) images present the ultrathin structure and smooth surface of GO and Titanate-GO, respectively. This is important to guarantee the interposition of Titanate-GO nanosheets into the gap between friction pairs. The inset images of EDS analysis show the new emergence of Ti element in Titanate-GO, indicating the introduction of alkyl titanate on the GO surface.

2.2. Lubrication Characterization of Titanate-GO. The tribological performance of Titanate-GO was evaluated on a four-ball machine. The wear scar diameter (WSD) of Titanate-GO in PAO10 base oil was tested on a four-ball machine as per standard ASTM D4172 (75 °C, 1200 rpm, 392 N, 60 min). Meanwhile, the coefficient of friction (COF) between the top ball and lower three balls was recorded. The results are shown in Figure 5. The COF curves shown in Figure 5a illustrate the fluctuation of the COF. The COF of bare PAO10 kept climbing from 0.07 to 0.12 throughout the test. However, the PAO10 with different concentrations of Titanate-GO all display lower COF. When the concentration of Titanate-GO was 0.1 mg/mL, the COF declined significantly with drastic fluctuation. The COF of PAO10 containing 0.5 mg/mL fluctuated more drastically than the others throughout the testing process and increased with the time. The lowest and most stable COF was found at the concentration of 0.3 mg/mL. According to Figure 5b, the average COF decreased with

Figure 3. TG curves of (a) GO and (b) Titanate-GO. DSC curves of (c) GO and (d) Titanate-GO.

Figure 4. SEM images of (a, c) GO and (b, d) Titanate-GO. TEM images of (e) GO and (f) Titanate-GO. EDS spectrum of (h) GO and (i) Titanate-GO.
the increasing of concentration during the early period and increased later. The lowest COF (~0.055) at the concentration of 0.3 mg/mL is reduced by 49.5% compared to pure PAO10.

Wear scar diameter (WSD) results measured by a four-ball machine are shown in Figure 6. The results show that the concentration of Titanate-GO blended in PAO10 base oil. Test condition: 75 °C, 1200 rpm, 392 N, 60 min.

Figure 8. Raman shifts of (a) Titanate-GO sample and worn surface lubricated (c) without and (b) lubricated with Titanate-GO. Test condition: 75 °C, 1200 rpm, 392 N, 60 min.

Figure 7. SEM images of the wear scar of steel balls lubricated by PAO10 with and without Titanate-GO. (a–d) 0, 0.2, 0.3, and 0.5 mg/mL, respectively. (a’–d’) Magnified images of panels (a–d), respectively.
WSD decreased with the increment of Titanate-GO concentration to the lowest value 585.5 μm. It is about a 28.2% decline compared to 710.0 μm of the bare PAO10 base oil. Then, there is an increment as the concentration of Titanate-GO increases.

The SEM images of wear scar shown in Figure 7 nicely confirm the results above.

The microscopy image in Figure 7a shows serious adhesive wear with many deep hollows, which was lubricated by bare PAO10. Meanwhile, metal exfoliation can be clearly observed under higher magnification in Figure 7a’. However, as shown in the other images, the wear scar diameter was significantly reduced with smoother features, and no evidence of abrasive wear was detected in the presence of Titanate-GO.

Furthermore, to understand the role of Titanate-GO as a lubricating additive during the friction procedure, Raman shift was performed on worn surfaces in the presence and absence of lubricating additive during the friction procedure, Raman shift of Titanate-GO, which represent the defects and characteristic bands of graphene were also detected on the worn surface of the steel ball used in the lubrication property test, which was lubricated by PAO10 with 0.3 mg/mL Titanate-GO. However, there is no Raman signal detected on the worn surface lubricated with bare PAO10 base oil. These comparison results indicate that the Titanate-GO sheets have entered the gap of friction pairs. Combining with the result of the lubrication property test, we consider that the Titanate-GO sheets formed an effective lubricating film on the steel balls.

(b) with 0.3 mg/mL Titanate-GO.

3. CONCLUSIONS

In this research, the GO was modified with alkyl titanate through facile procedures, and a kind of effective lubricating additive was prepared. The followed characterizations using FT-IR, XPS, Raman, TG/DSC, SEM, and TEM confirmed that the alkyl titanate was successfully grafted on the surface of GO, which guaranteed the stable dispersibility of Titanate-GO in PAO10 base oil. The tribological properties tests of Titanate-GO performed on a four-ball machine in terms of friction coefficient and wear scar diameter indicate its promising application potential as friction reduction and anti-wear additive in oil.

4. EXPERIMENTAL SECTION

4.1. Materials. The self-made GO was prepared by modified Hummer’s method.31 The procedure details were reported in a previous work.31 The 10St polyalpaholefin (PAO10) base oil was purchased from Shenyang Hongcheng Fine Chemical Plant. The specifications of PAO10 are tabulated in Table 2. The other chemicals were purchased from Aladdin and used without any further treatment.

4.2. Preparation and Characterization of Titanate-GO. The alkyl titanate-modified graphene dioxide (Titanate-GO) was prepared by three steps (Scheme 1). The reaction procedures were carried out in the atmosphere of nitrogen. Briefly, 372 mg of titanium tetraisopropanolate and 40 mL of THF was mixed in a 250 mL flask followed by 10 min of stirring at room temperature. Then, 220 mg of GO was dispersed in 40 mL of THF by 5 min ultrasonic treatment and added into the flask dropwise followed by 1 h of stirring at 60 °C. Furthermore, 746 mg of steric acid and 358 of mg acetic acid were added as the lipophilic group modifier followed by 2 h of stirring and reflux, respectively. The solvent and as-formed isopropanol were removed by evaporation. Finally, the target product was washed with ethyl acetate and tetrahydrofuran and dried at 50 °C in a vacuum oven. The samples of GO and Titanate-GO were characterized by FT-IR, XPS, Raman, TG/DSC, SEM, and TEM.

Fourier transform infrared (FT-IR) spectra of GO and Titanate-GO samples were characterized by infrared spectroscopy (PerkinElmer Spectrum Two) with KBr pellets as the sample matrix. X-ray photoelectron spectroscopy (XPS, Escalab 250XI, Thermo Fisher Scientific) was used to analyze the binding energy of the samples. Raman spectroscopy (Dxi, Thermo Fisher Scientific) was also used with a 633 nm laser excitation. Thermostability of samples was tested on a thermal analyzer (PerkinElmer TGA4000) from 30 to 800 °C with a heating rate of 10 °C/min. The morphology was observed on SEM (FEI Inspect F50, 10 kV) and TEM (JEM-2100, 200 kV) instruments.

Table 2. Specifications of PAO10 without and with 0.3 Mg/mL Titanate-GO

| sample ID          | density (20 °C) (kg/m³) | viscosity (40 °C) (mm²/s) | viscosity (100 °C) (mm²/s) | viscosity index | pour point (°C) |
|--------------------|------------------------|--------------------------|----------------------------|-----------------|-----------------|
| PAO10              | 833.9                  | 65.23                    | 10.07                      | 140             | −57             |
| PAO10 + Titanate-GO| 834.0                  | 65.30                    | 10.05                      | 139             | −57             |
4.3. Lubrication Properties Test. Different concentrations of compounded lubricating oil with Titandate-GO in PAO10 base oil were prepared using an ultrasonic method. Then, the tribological properties of compounded lubricating oil were evaluated in terms of frictional coefficient (COF) and wear scar diameter (WSD) on a four-ball test machine according to the standard ASTM D4172 (75 °C, 1200 rpm, 392 N, 60 min). Meanwhile, the coefficient of friction (COF) between the top ball and three lower clamped balls was recorded once a second. Finally, the wear scar diameter was observed and measured on an SEM instrument.

ACKNOWLEDGMENTS

This work was financially supported by the Scientific Research Foundation (J2020-109) and the Student’s Research and Innovation Fund of Civil Aviation Flight University of China.

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