Tribological properties of graphene oxide as a lubricating additive in water and lubricating oils

Hiroshi KINOSHITA *, Hideki ONO *, Aidil Azli ALIAS *, Yuta NISHINA ** and Masahiro FUJII *

* Division of Industrial Innovation Sciences,
Graduate School of Nature Science and Technology, Okayama University
3-1-1 Tsushimanaka, Kita-Ku, Okayama 700-8530, Japan
E-mail: kinoshita@mech.okayama-u.ac.jp
**Research Core for Interdisciplinary Sciences, Okayama University
3-1-1 Tsushimanaka, Kita-Ku, Okayama 700-8530, Japan

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Abstract
High-performance lubricating additives are desired in order to improve the properties of lubricating fluids. Recently, carbon nanomaterials such as fullerenes, carbon nanotubes, and carbon onions have been studied as lubricating additives for water and lubricating oils. However, the costs of these carbon nanomaterials are too high for practical use. On the other hand, graphene oxide (GO) is a carbon nanomaterial that consists of single atom thick sheets that possess a large number of oxygen functional groups. Since GO is synthesized from graphite using a chemical liquid process, the cost of GO is significantly lower than other carbon nanomaterials. In this study, the application and tribological properties of GO monolayer sheets as additives in water and poly-alpha olefin (PAO) were investigated. The dependence of the friction coefficient of GO-water dispersions on GO concentration (0.01-1.0 mass %) was investigated. In particular, GO-water dispersions with a concentration of less than 0.1 mass % demonstrated low friction coefficients. In this study, GO was simply dispersed in PAO using surfactant and intermediary solvents without the need for drying treatments. We found that the use of anionic surfactants in the GO-PAO dispersions was better than cationic surfactants in terms of the degree of wear observed. Specifically, GO-PAO dispersions that used an anionic surfactant with a GO concentration of 4 mass % had the smallest wear in this study. Moreover, friction coefficients were not decreased by the addition of GO in PAO. Finally, we found that intermediary solvents did not affect lubrication.

Key words: Graphene oxide, Water, Lubricating oils, Friction coefficient, Wear, Additives

1. Introduction

In order to improve the properties of lubricating fluids, it is desirable to develop high-performance lubricating additives. Recently, many researchers have studied carbon nanomaterials such as fullerenes, carbon nanotubes, and carbon onions as lubricating additives (Martin and Ohmoe 2008). As a result of the need for vacuum and/or plasma processes when synthesizing these carbon nanomaterials and the fact that they are not even widely used in all industrial fields, their costs are currently too high for use in tribological fields. On the other hand, graphene is a two-dimensional, single-atom thick structure that is derived from graphite. Graphene has recently attracted significant attention from various fields owing to its unique properties, including the field of tribology.

Graphene oxide (GO) has been used as a precursor for the large-scale production of graphene (Dreyer et al. 2010) as a result of the low cost of GO. This is due to the fact that the primary material of GO is graphite and only chemical liquid processes are used for its synthesis. The size of GO can be greater than 100 μm² and its thickness is less than 1 nm. GO has many oxygen functional groups (polar groups) even in its basal plane (Dreyer et al. 2010), which allows for dissolution in polar liquids such as water (Paredes et al. 2008). It is likely that GO can be easily adsorbed on steel surfaces owing to its oxygen functional groups, which act like friction modifier additives such as fatty acids. Since the
As mentioned above, since GO has many oxygen functional groups, it is easy to disperse in polar liquids. We carried out tribological experiments between a steel plate and a tungsten carbide ball using GO that was dispersed in water at a concentration of 1 mass % (Kinoshita et al. 2014). The preliminary experimental results indicated that the friction coefficient was very low (approximately 0.05) and surface wear was not obvious. In this study, dependence of the friction coefficient of GO-water lubricants with varying GO concentration (0.01-1.0 mass %) was investigated.

In contrast to water, GO is hard to disperse in non-polar liquids (Paredes et al. 2008). In previous studies, in order to disperse GO in non-polar liquids, GO was either reduced using high-temperature treatments (Eswaraiah, Sankaranarayanan, and Ramaprabhu 2011; Schlüter, Mülhaupt, and Kailer 2014), modified using functional groups with affinity to non-polar liquids (Mungse and Khatri 2014), or dispersed using dispersants (Senatore et al. 2013). However, there is a need to dry GO prior to disperse in a non-polar liquid. This is because GO is typically synthesized as a GO-water dispersion using a modified Hummers’ method. However, when the GO-water dispersion is dried, a large amount of the GO is no longer a monolayer. This is because GO agglutinate strongly during drying. As such, the drying of GO-water dispersions should be avoided. In this study, GO was simply dispersed in poly-alpha olefin (PAO), which is a non-polar liquid, using surfactants and intermediary solutions without the need for drying treatments. Tribological properties of the GO-PAO dispersions were also investigated.

2. Experiments

The GO used in this study was synthesized using a modified Hummers' method, which resulted in an aqueous GO dispersion. Figure 1 shows an atomic force microscopy (AFM) image of the GO that was used in this study. To obtain the image, a drop of the GO-water dispersion was placed on a silicon oxide film, and the drop was allowed to dry. As a result, a single monolayer of GO was adsorbed on the silicon oxide film without the need for centrifugation. This means that the GO sheets were dispersed in water individually. The size of the GO sheets was approximately 1–10 μm, and the height of GO was typically around 1 nm.

To disperse GO in PAO, surfactant was first added to the GO-water dispersion until a surfactant concentration became 1.0 mass %. The GO-water dispersion with the surfactant was then centrifuged to precipitate GO along with the surfactant. The precipitated GO with surfactant was then dispersed in an intermediary solvent. Following this, the

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Table 1 List of the GO-PAO dispersions

<table>
<thead>
<tr>
<th>Intermediary solution</th>
<th>Surfactant</th>
<th>Cationic surfactant</th>
<th>Anionic surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cetyltrimethylammonium bromide (C_{12}H_{25}BrN)</td>
<td>Dimethyldipalmitylammonium Bromide (C_{34}H_{72}BrN)</td>
</tr>
<tr>
<td>Acetone (CH₃COCH₃)</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>1-propanol (CH₃CH₂CH₂OH)</td>
<td>D</td>
<td>E</td>
<td>F</td>
</tr>
</tbody>
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Fig. 1 AFM image of GO used in this study.
intermediary solvent containing the GO dispersion with a concentration of 1.0 mass % was centrifuged and GO was precipitated. This procedure was performed twice to eliminate as much water and excess surfactant as possible. The centrifuged GO was then mixed with PAO. Afterwards, the mixture was centrifuged and the GO was precipitated again. This procedure was also performed twice to eliminate any intermediary solvent. Finally, the precipitated GO was mixed with PAO at a GO concentration of 2 and 4 mass %. Cetyltrimethylammonium bromide (C_{16}H_{33}BrN) and dimethyldipalmitylammonium bromide (C_{34}H_{72}BrN) were used as cationic surfactants and sodium dodecyl sulfate (C_{12}H_{25}NaO_{3}S) was used as an anionic surfactant in this study. Acetone and 1-propanol were used as intermediary solvents. Table 1 lists the compositions of the GO-PAO dispersions, which are labeled from A to F. Thus, for example, the GO-PAO dispersion by the composition of F with the GO concentration of 2 mass % was referred to as “2-F GO-PAO”. A kinematic viscosity of PAO used in this study was 16.8 mm²/s at 40 °C.

A hand-made tribometer with reciprocating sliding configuration by crank mechanism was used in this study. Loads were applied by dead weights, and friction forces were measured by a beam load cell where a ball sample was attached. Table 2 shows friction test conditions using GO-water dispersions and GO-PAO dispersions. Friction test condition using GO-water dispersions included a sliding amplitude of approximately 2 mm, an oscillating rate of 5 Hz, a load of 1.68 N, and a GO concentration of 0.01, 0.1, and 1 mass %. Maximum speed and Hertzian contact pressure were calculated to be approximately 0.031 m/s and 2.1 GPa, respectively. The friction tests were conducted between a stainless steel plates (JIS-SUS304) and φ2 mm tungsten carbide (WC) balls for bearings. The plates had a surface roughness, Ra, of 0.033 μm and a hardness of 196 HV.

For GO-PAO dispersion friction tests, a GO concentration of 2 and 4 mass % was used. In addition, the SUS304 plates and high-carbon steel (JIS-SU12) balls for bearings were used with lubrication and a load was 10.8 N. The estimate Hertzian contact pressure was 3.0 GPa. In this case, a sliding amplitude was 2 mm and an oscillating rate was 8.3 Hz, resulted in a maximum speed of approximately 0.052 m/s. Friction tests were conducted more than two times for each dispersion.

### 3. Results and discussion

#### 3.1 GO-water Dispersions

Fig. 2 shows representative friction coefficients of GO dispersions in water at various concentrations (0.01 ~ 1 mass %). The blue circles indicate the friction coefficients of pure water and the black symbols show the friction coefficients of the GO-water dispersions at various GO concentrations. The 1 mass % GO-water dispersion had a very low friction coefficient of approximately 0.01. The 0.1 mass % GO-water dispersion also had fairly good lubricating properties. In contrast, the 0.01 mass % GO-water dispersion had a friction coefficient of ~ 0.3 and, as such, did not have good lubricating properties. Therefore, decreasing the GO concentration resulted in an increase in the friction coefficient.

Fig. 3 shows representative scanning electron microscopy (SEM) images and cross sections, measured by a stylus profilometer, of the wear on the surfaces after the frictional tests in pure water and the 1 mass % GO-water dispersion.
The width of the wear track that was formed in pure water was approximately 400 μm and that formed in the 1 mass % dispersion was approximately 150 μm, which indicates that the surface wear in the 1 mass % GO-water dispersion was much less than that in pure water. Moreover, the wear track in the 1 mass % GO-water dispersion was much less than that in pure water. Moreover, the wear track in the 1 mass % GO-water dispersion was dark. Energy dispersive X-ray (EDX) analysis indicated that the darker regions had carbon content. This implies that a carbon film from GO was formed on the lubricated surface (Kinoshita et al. 2014). Finally, the wear scar of the WC ball lubricated with pure water was severe. In contrast, the WC ball lubricated with the GO-water dispersion had no wear. This result suggests that the carbon film may decrease the friction coefficient and behave as a protective coating. As such, an increase in the GO concentration would increase the amount of the carbon film, which would decrease the friction coefficient.

3.2 GO-PAO Dispersions

Figure 4 depicts representative friction coefficients of pure PAO and the GO-PAO. The friction coefficient of the pure PAO was high in the running-in period and then decreased to a steady state value. All of the friction coefficients of the GO-PAO mostly remained at a steady state value of 0.10-0.12, which were almost the same as that in pure PAO. Occasional spikes were found in the lubrications with the 2-A, 2-B, 2-D, and 2-E GO-PAO, and occurred until 50,000 sliding cycles. Heights (friction coefficients) of the spikes were not identical for each frictional test even with the same frictional condition. The lubrications with the 2-C and 2-F GO-PAO (both them used an anionic surfactant) did not exhibit a spike. The lubrications provided by the 4-A, 4-D, and 4-F GO-PAO (GO concentration of 4 mass %) remained at steady state values during the friction tests. When we carried out friction tests with different sliding frequency (1Hz-10Hz) for the 2-F GO-PAO, the friction coefficient was unchanged. Thus, boundary lubrication would occur in the friction conditions of this study.
Figure 5 shows the lateral forces measured within a very short time (1000 ms) under the lubrication of pure PAO, and 2-A and 2-F GO-PAO. The lateral forces were obtained at 99,000 sliding cycles. Friction coefficients (µ) were calculated from the low mean lateral force (F_L) and the high mean lateral force (F_H), i.e., µ = (F_H-F_L)/2. The friction coefficients indicated in Fig. 4 are almost of the same value. However, the lateral force data of the pure PAO had large oscillations. In contrast, the lateral forces in the GO-PAO remained very stable.

Figure 6 represents cross sections and optical microscopy images of the wear tracks on the SUS304 plates lubricated using pure PAO, the 2-B, 2-C, and 4-F GO-PAO. The widths of the wear tracks for all the friction conditions are summarized in Figure 7. Blue bars indicate the width of the wear tracks for the GO-PAO using the cationic surfactants and green bars indicate these using anionic surfactants. The widths of wear scars from the counterpart balls that were lubricated in the same conditions almost corresponded to the widths of the wear tracks found on the plates. The depth and width of the plate wear for pure PAO were almost the same as those in the 2-A, 2-B, 2-D, and 2-E GO-PAO (the depths were 6-7 µm and the widths were approximately 450 µm). These GO-PAO used cationic surfactants. Moreover, the spikes of high frictional coefficients shown in Fig. 4 were observed in these GO-PAO. The GO-PAO that used cationic surfactants and had a GO concentration of 2 mass % did not have good lubricating properties. However, as mentioned above, the lateral forces of the 2-A GO-PAO was smooth. This implies that the addition of GO to PAO using the cationic surfactants affects lubrication. The depths and widths of the wear tracks that were lubricated using the 2-D and 2-F GO-PAO were small (the depths were 5 µm and the widths were approximately 400 µm). These GO-PAO used an anionic surfactant, which indicated that anionic surfactants were better to work for the dispersant than cationic surfactants. In Fig. 7, bars with red frame borders show the widths of the wear tracks lubricated with the GO-PAO with the GO concentration of 4 mass %. The depths and widths of the 4-A, 4-D, and 4-F GO-PAO (the depth was 5 µm and the width was 370 µm) were smaller than those with the 2-A, 2-D, and 2-F GO-PAO. In particular, the 4-F GO-PAO (the depth was 4 µm and the width was 270 µm) had the smallest wear track depth and width in this study. We carried out energy dispersive EDS analysis on the wear tracks of the lubrications with the 4-F GO-PAO. However, amount of carbon elements on the wear tracks were not different from those out of the wear tracks. Thus, it is probable that tribofilm was not formed, or very thin. Distinct difference results of the GO-PAO using...
acetone and 1-propanol were not observed.

In conclusion, the GO-PAO using anionic surfactants and with high GO concentrations provide better lubrication, and intermediary solvents such as acetone and 1-propanol have no effect. Since the excess surfactants were eliminated during the GO dispersing process, almost all the surfactants were adsorbed with GO. GO mainly has two surface regions. One is graphitic region (neutral), and another is region where oxygen fictional groups are existed (negatively charged). Thus, as above mentioned, GO is easy to be adsorbed on metal surfaces, like fatty acids. However, GO is difficult to be dispersed in PAO. Since cationic moieties of the cationic surfactant easily interact with oxygen functional groups, the many oxygen functional groups were terminated with the cationic surfactants. Although the adsorption prompted GO to disperse in PAO, adsorption ability of GO on metal surfaces would be decreased. This result in a decrease of the lubrication ability of GO. In contrast, it is difficult for anionic moieties of the anionic surfactant to interact with the oxygen functional groups. Thus, it is likely that number of anionic surfactant interacting with the oxygen functional groups was less than that of the cationic surfactant. Although the GO dispersing ability using the anionic surfactant would be lower than that using cationic surfactants, the GO-PAO using the anionic surfactant had higher lubrication ability. The balance of the dispersing and lubrication abilities using the anionic surfactant might be better than those using the cationic surfactants. The lateral forces obtained using the GO-PAO were smooth, and the wear with the high GO concentration was also better than that using pure-PAO. This indicated that GO (which may be adsorbed on the ball and plate surfaces) got in between the ball and plate and prevented from the direct contact between them, which resulted in smooth sliding and low wear. The reason that GO did not affect the friction coefficients is possibly because shear forces of GO between the ball and plate is relatively high, and/or many GO are broken by friction, which require high energy (high friction). Two different intermediary solvents were used in this study; however, they did not exhibit any difference in their lubrication properties. In particular, during the dispersion process, the intermediary solvents would be mostly removed from the GO-PAO.

4. Summary

In this study, GO was dispersed in water and PAO and their frictional properties were investigated. The friction coefficients of the GO dispersion in water with densities of 0.1 and 1 mass % were very low. GO was simply dispersed in PAO using the intermediary solvents, and the cationic and anionic surfactants without the need for a drying process. For the GO-PAO, lateral forces became stable; however, the friction coefficients were not decreased. It was also found that the GO-PAO using the cationic surfactants were not good lubricants. Specifically, when the GO concentration was 2 mass %, the wear in the GO-PAO when using the cationic surfactants was almost the same as the lubrication provided by pure PAO. Moreover, the high spikes in the friction coefficients were observed. The lowest amount of wear occurred when the lubrication consisted of a GO-PAO dispersion that used an anionic surfactant with the GO concentration of 4 mass %. The anionic surfactant was better to work than the cationic surfactants for the GO-PAO and no difference was observed for acetone and 1-propanol.

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