Graphite oxide tribo-layer formation under boundary lubrication of diesel fuel

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Abstract. Friction and wear of mechanical components (such as engines) is controlled by some kind of boundary films (also referred to as tribo-layer). In some cases, such boundary film is formed on the contact interface due to a tribo-chemical process in the presence of liquid media. In this paper, we demonstrate the formation of graphite oxide tribo-layer on the contact interface of steel in the presence of diesel fuel liquid media. A Raman spectrometer was used to analyse the tribo-layer structure. Although the intensity is low, it is shown that the tribo-layer has a structure of graphite oxide, demonstrated by the presence of D band peak at approximately 1350 cm\(^{-1}\) and G band peak at approximately 1550 cm\(^{-1}\) in the Raman spectra. Such graphite solid films on the sliding surfaces have ability to control friction and wear. This finding demonstrates the possibility of in-situ formation of solid protective film of a tribo-pair components using the working fluid where the use of lubricants is restricted as they contaminate the working fluid.

1. Introduction

Due to environment and sustainability issues, the use of diesel fuels from renewable resources are continuously increasing. Biodiesel fuels are converted from vegetable oils or animal stocks by transesterification process. They can be used directly in diesel engines or mixed with petroleum diesel fuel at certain volume percentages. Palm methyl ester is one of the biodiesel fuel sources available in large amount due to high annual production of crude palm oil. The use of methyl ester as mixture in diesel fuel has several implications to the tribological behaviour of the mechanical systems such as fuel system and piston-ring component. Particularly, the oxygen contain in the methyl ester makes it corrosive in nature, compensating the material stability and integrity [1]. However, biodiesel also has several beneficial effects on the tribological properties of the materials, such as friction and wear reduction [2].

In order to control the friction and wear, additives are commonly used in lubricants as friction modifier. The wear protection is achieved by the formation of third body layer, or also called as tribo-layer/tribo-film on the contact interface during friction. Additives such as ZDDP, MoS\(_2\), and PTFE protect the wear of material by forming a protective tribo-layer on the interacting surfaces, reducing direct material contact among bulk material asperities to prevent seizure and abrasion [3]–[6]. MoS\(_2\), PTFE, and graphite belongs to the group of solid lubricants. They have lamellar structure interconnected by weak Van der Waals force, enabling they to withstand high load bearing capacity. The lamellar structures are deposited on the interacting surfaces during friction, acting as a protective layer.
Besides additives, solid coatings are also used to control friction and wear of mechanical components, such as diamond-like carbon DLC coatings [7]. Such solid coatings, as it is worn out during friction, produced a transfer layer of graphitic structure to the adjacent surface. The lamellar structure of graphite can easily slide among each other due to weak Van Der Waals force, resulting in low friction and wear of the bulk material [8]. Nowadays, carbon nanoflakes such as graphene are used as nano additives in lubricant because they produce similar effect to those achieved by solid carbon-based coatings.

The formation of protective tribo-layer on the contact interface that has carbon-based structure can also be achieved by in-situ tribo-chemical process [9]–[12] with the presence of hydrocarbon liquid media. The protective layer formation is assisted by high shear force on the contact interface during friction, which promotes decomposition of carbon from the material or liquid media, resulting in thin film of carbon structure on the contact interface.

In this study, we investigated the formation of tribo-layer on the contact interface by in-situ tribo-chemical process involving diesel fuels as the liquid media. The wear tests were conducted using a pin-on-disk tribometer at boundary lubrication regime. The objective of this study is to demonstrate possibility of forming a graphite oxide layer on the contact interface using in-situ tribo-chemical process using diesel fuel media. Such in-situ process can be used in tribological application in which lubricant cannot be used because it will contaminate the working fluid. In this study, the properties of tribo-layer was analysed using Raman spectroscopy method.

2. Methodology

A ball on disk tribometer was used in the investigation, as schematically shown in Figure 1. The tribometer consists of a ball and disk holder, which is rotated by a motor. The normal force is applied using a gravitational load lever, equipped with a load cell to measure the friction force. The contact interface was submerged in a media chamber filled with liquid. An 8 mm diameter ball specimen and a 5 mm thick with a 5 mm diameter disk were used as the specimens.

![Figure 1. Schematic illustration of ball-on-disk tribometer](image)

In order to simulate the severe contact condition between the material, the tests were conducted at boundary lubrication regime. The condition was achieved by applying a 12 N normal force, which resulted in approximately 1.2 GPa initial Hertzian contact pressure to the contact combination. The tests were conducted at ambient temperature of 27°C. The wear tests were conducted at sliding speed of 12 mm/s for a sliding distance approximately 750 meters.
In order to investigate the boundary film formation on the contact interface at various material and fluid media combinations, several materials and fluid media combinations were used. The material for the ball specimen is stainless steel SUS304 and the materials for the disk are stainless steel SUS 304 and grey cast iron. The materials are commonly used as materials for engines components. Particularly, SUS304 is a low carbon steel considered having high resistant to oxidative nature of palm methyl ester. Both the ball and disk specimen were polished to a roughness approximately Ra = 0.03 μm. For the fluid media, two compositions were prepared, i.e. petroleum diesel fuel and a mixture of 7.5% palm methyl ester in the petrol diesel fuel. The four material and fluid combinations are summarized in Table 1. The palm methyl ester was achieved from a transesterification process while the petrol diesel fuel was acquired from a commercial gas station. The mixture of the palm methyl ester and the petrol diesel fuel was prepared by direct mixture of the liquid using a physical mixing process.

**Table 1. Material combinations for the wear tests**

| No | Material                  | Fluid Media                      | Temp., °C | Initial Contact Pressure, GPa |
|----|---------------------------|----------------------------------|-----------|-------------------------------|
| 1  | SUS 304 ball vs Cast Iron Disk | Petrol diesel fuel               | 27        | 1.2                           |
| 2  | SUS 304 ball vs Cast Iron Disk | 7.5% palm methyl ester mixed petrol diesel fuel | 27        | 1.2                           |
| 3  | SUS 304 ball vs SUS 304 disk | Petrol diesel fuel               | 27        | 1.2                           |
| 4  | SUS 304 ball vs SUS 304 disk | 7.5% palm methyl ester mixed petrol diesel fuel | 27        | 1.2                           |

**Figure 2.** Raman shift reference of graphite and graphite oxide

The properties of boundary film on the contact interface were evaluated by using Raman spectroscopy method. The evaluation was conducted only to the ball’s worn surface because the ball specimen was in static contact position whereas the disk was in constant rotation. Thus, the possibility of boundary film formation is higher on the ball’s worn surface compared to that on the disk surface.

Figure 2 provides the reference Raman spectra for graphite (G) and graphite oxide (GO) [13]. The GO is characterized by the appearance of two peaks; D band and G band, also referred to as sp3 peak and sp2 peak, respectively, in the Raman spectra. D band peak appears at approximately 1355 cm⁻¹ and G band peak appears at approximately 1593 cm⁻¹. Pure graphite has only one peak, which is Sp3, at approximately 1580 cm⁻¹. This reference was used for analysing the properties of boundary films in this study.
3. Results and discussion

In this paper, the main discussion is focused on the tribo-layer properties forming on the contact interface. Since the ball is in static position during the sliding test, there is a greater possibility that the tribo-layer is formed and accumulated on the ball’s contact interface rather than that of the disk. Therefore, the investigation was conducted on the worn scar of the balls. Here, the worn track on the disk was not shown. Fig. 3 shows the results of wear test indicated by condition No. 1 and No. 2 in Table 1; condition No. 1 shown in (a), (b), and condition No. 2 shown in (c), (d). Figure 3(b) indicates the three-dimensional view of Figure 3(a), so as Figure 3(d) to Figure 3(c).

![Figure 3. Worn scar of SUS304 ball sliding against cast iron disc; under petrol diesel fuel, (a) and (b), and under 7.5% palm methyl ester mixed petrol diesel fuel (c) and (d).](image)

It can be observed in the Fig. 3 that the worn scar area of SUS304 ball is slightly larger in the case of condition No. 1, Fig. 3(c), than that in the case of condition No. 2, Fig. 3(a). In the case of condition No. 1, the width of the worn scar is 600 μm while in that of condition No. 2 it is 500 μm. This indicates some wear reduction of the material due to the presence of palm methyl ester components in the petrol diesel fuel, as reported in several previous works [10], [14], [15]. As given in Table 1, the fluid media in condition No. 2 contained 7.5% palm methyl ester while that of fluid media in condition No. 1 has no contain of palm methyl ester. Despite the wear difference, it should be noted that there were no significant difference in the friction coefficient in the two cases. The average friction coefficient of the case in condition No. 1 was 0.3 while that in the case of condition No. 2 was 0.28.

In both case No. 1 and No. 2, the worn scar of the ball indicates a uniform wear mode in the form of worn grooves along the direction of sliding. Such regular grooves indicate abrasive wear which is commonly caused by counter surface having higher hardness. In this case, the cast iron is harder than SUS304 with a hardness of 294 (Brinell) [16] compared to 123 (Brinell) [17]. Thus, it can be concluded that the worn grooves on the SUS304 ball was abrasive wear. Some blackish mark along the sliding direction can be observed on the contact interface, indicated some tribo-layer had been formed on the contact interface during the friction process.

The worn scar area on SUS304 balls in the case of condition No. 3 and No. 4 are given in Fig. 4; Fig. 4(a) and (b) for condition No. 3 and Fig. 4(c) and (d) for condition No. 4. Figure 4(b) indicates the three-
dimensional view of Fig. 4(a), so as Fig. 4(d) to Fig. 4(c). It can be observed from the Figure that the width of the wear track in both conditions are relatively similar, i.e. 500 μm. In both cases, the average value of coefficient of friction was relatively similar at 0.3.

Figure 4 illustrates that the wear behaviour of the SUS304 ball in the cases of condition No. 3 and No. 4 consists of two different wear modes. The first wear mode can be classified as abrasive wear and the second one as catastrophic wear due to the presence of pits and transferred material. Abrasive grooves is indicated by ploughing of the material sliding direction, similar to those occurred in condition No. 1 and No. 2. For condition No. 3 and No. 4, abrasive wear occurred for about 50% of the worn area. The second wear mode, catastrophic wear, involved the material transferred from the counter surface. In this case, it seems that the material was removed due to friction and reattached to adjacent location or to the counter surface. Such wear behaviour could be caused by material weakening due to some tribo-chemical reaction involving manganese and carbon [10]. In this case, the manganese came from the bulk material and rich carbon came from petrol diesel fuel fluid. The tribo-layer is formed on the worn surface of the SUS304 ball in both wear modes area; abrasive worn area and catastrophic worn area.

Figure 4. Worn scar of SUS304 ball sliding against SUS304; under petrol diesel fuel, (a) and (b), and under 7.5% palm methyl ester mixed petrol diesel fuel (c) and (d).

Figure 5 shows the Raman spectra taken on several positions on the contact interface of SUS 304 ball of condition No.1. In these cases, the SUS ball was sliding against cast iron disk under lubrication of petrol diesel fuel fluid. As shown in the Figure, position no. 1 is located in the middle of sliding track. A more detailed worn surface of position no. 1 reveals a visible tribo-layer, seen as blackish layer. The Raman spectra indicates two peaks of D band and G band at about 1350 cm\(^{-1}\) and 1550 cm\(^{-1}\), respectively. These peaks are quite close to the sp\(^3\) and sp\(^2\) reference value, as indicated by the vertical lines. The appearance of D band and G band peaks can also be observed for Raman spectra taken at position no. 2, as indicated by the inset Figure, although the intensity is not as high at those taken at position no. 1. Similar to that in position no. 1, the tribo-layer in this position is also visible as blackish layer. Position no. 3 is outside the sliding track. It can be seen that in this position there is no trace of visible tribo-layer.
comparable to those in the other two positions. As expected, the Raman spectrogram on position no. 3 shows no peak, indicating that the surface contains no such tribo-layer of carbon structure.

**Figure 5.** SUS ball vs Cast iron disc at 12 N normal load sliding under petrol diesel fuel

**Figure 6.** SUS ball vs Cast iron disc at 12 N normal sliding under 7.5% palm methyl ester mixed petrol diesel fuel
The Raman analysis results for condition No. 2 is given in Figure 6. In this case, the SUS304 ball was sliding against cast iron disk under petrol diesel fuel containing 7.5% palm methyl ester. As seen in the figure, the Raman analysis conducted to position no. 1 and no. 2 indicates the D band and G band peaks, although the intensity is quite low compared to those shown in Figure 5. For position no. 1, the D band peak occurred at about 1350 cm\(^{-1}\) and the G band peak occurred at about 1550 cm\(^{-1}\). For position no. 2, the D band and G band peaks occurred at about 1345 cm\(^{-1}\) and 1600 cm\(^{-1}\), respectively. As it is observed on the inset Figures for position no. 1 and no. 2, there are visible tribo-layer, which is blackish in colour, on the contact interfaces. Here, position no. 3 is outside the sliding track, provided for the purpose of comparison, thus no peak in reference to the sp\(^2\) and sp\(^3\).

The results of Raman analysis for test condition No. 3 is summarized in Figure 7. In this condition, the SUS304 ball was sliding against SUS304 disk under lubrication fluid of petrol diesel fuel. As mentioned previously, the worn scar of the ball in this condition consists of two wear modes. The Raman analysis were conducted on the part of worn surface of abrasive mode because the tribo-layer in this part is more visible than in the part of catastrophic wear mode. The blackish layer of tribo-film is visible at location no. 1 and no. 2, as given in the inset Figures of Figure 7. The Raman spectra of location no. 1 shows 2 peaks, occurred at about 1320 cm\(^{-1}\) for D band and about 1550 cm\(^{-1}\) for G band. For location no. 2, the resulted Raman spectra indicates the D band peak at about 1320 cm\(^{-1}\). For G band, the peak is less visible, although still traceable at about 1580 cm\(^{-1}\). Similar to other condition, location no 3 was taken outside the sliding track for comparison purpose.

Figure 8 shows the results of Raman analysis for test condition No. 4. In this case, the SUS304 ball was sliding against SUS304 disk under lubrication fluid of petrol diesel fuel mixed with 7.5% palm methyl ester. From the microscopic observation, the tribo-film on the contact interface is also visible as blackish layer, as given in inset Figure 1 and 2 of Figure 8. In location no. 1, the Raman spectra indicates the D band peak at about 1350 cm\(^{-1}\) and G band peak at about 1580 cm\(^{-1}\). However, the Raman spectra taken at location no. 2 shows no traceable peaks of either D band or G band, despite visible trace of blackish layer of tribo-film on the contact interface. Among possible explanation is that the tribo-film in this specific location has a different structure, which requires further investigation. Location no. 3, as also mentioned in other test condition, was taken outside the sliding track.

Raman analysis conducted to all four condition reveals the existence of graphite oxide tribo-layer on the contact interface, evidenced from the occurrence of peaks of D band and G band comparable to those in Figure 1. The blue graph in Figure 1 refers to the Raman spectra of a highly ordered graphite, indicated by narrow G band (graphite lattice) at 1575 cm\(^{-1}\) and the weak disorder band caused by D band at approximately 1355 cm\(^{-1}\) [18]. The black graph refers to the Raman spectra of Graphite Oxide, indicated by the presence of D band peak at 1340 cm\(^{-1}\) and G band peak at 1593 cm\(^{-1}\). The D band and G band experienced changes in the frequency due to amorphization of graphite as amorphous carbon, which contains a fraction of sp\(^3\) carbon [19]. A broader G band and D band is an indication of highly disordered graphite [13], which resulted in the shift of D band and G band frequency.

In reference to this, the D band’s peak of the tribo-layer occurred on SUS304 balls in this analysis have frequency ranging from 1320 cm\(^{-1}\) (test condition No. 3) to 1350 cm\(^{-1}\) (test condition No. 1, No. 2, and No. 4) while that of G band’s peak occurred at frequency ranging from 1550 cm\(^{-1}\) (test condition No. 1, No. 2, and No. 3) to 1600 cm\(^{-1}\) (test condition No. 4). Thus, it can be concluded that, since both D band and G band have a broad frequency band, the tribo-layer formed on the contact interface is graphite oxide with high disorder graphite. Here, the possibility of graphite oxide tribo-layer formation is higher in the case of SUS ball sliding against Cast iron disk rather than in the case of SUS ball sliding against SUS disk. This is evidenced from the presence of D band and G band peaks in all four locations selected on the case of SUS ball sliding against Cast iron. Whereas for the case of SUS ball sliding against SUS disk, only two of four selected locations show the occurrence of the D band and G band peaks.
Figure 7. SUS ball vs SUS disk at 12 N normal Load 200 rpm under petrol diesel fuel

Figure 8. SUS ball vs SUS disk at 12 N normal Load sliding under 7.5% palm methyl ester mixed petrol diesel fuel

The higher possibility of graphite oxide formation in the case of SUS ball sliding against Cast iron disk is caused by the content of graphite flake in grey cast iron. Graphite flake is found easily deformed when shear force is involved, such as in tribological application [20]. Such formation of interlayered
distorted graphite involves mechanical action and chemical reaction [21], [22], or also known as tribo-chemical reaction, with or without the presence of liquid lubricant media [9]. In the case of test condition No. 1 and No. 2, the graphite flake from cast iron disk could be transferred to the SUS ball during the tribo-chemical process, forming a layer of distorted graphite oxide.

Other source of carbon that was involved in the formation of graphite oxide is the lubricant fluid, which in this case is the diesel fuel. With high contact pressure and shear force at boundary lubrication condition, it is possible for the carbon to be decomposed during the tribo-chemical process leading to the formation of graphite oxide tribo-layer on the contact interface [10]. Therefore, in contact condition No. 3 and No. 4, the graphite oxide layer can still be found on the contact interface although the material does not contain graphite flake.

The mixture of palm methyl ester in the diesel fuel have not resulted in significant change in the property of tribo-layer in all four test conditions, at least for the volume percentage of 7.5%. However, the mixture has led to some reduction of material’s wear, although not significant. Here, the purpose of adding palm methyl ester in petrol diesel fuel is to increase the renewable portion of diesel fuel. Therefore, this study has demonstrated that the graphite oxide tribo-layer can also be formed with the presence of palm methyl ester in the fuel.

Such tribo-chemical formation of graphite oxide tribo-layer provide a possibility for in-situ lubrication process of a mechanical system using the working fluid such as fuel system, hydraulic system, and combustion system. In such system, conventional lubricant fluid cannot be used because it will contaminate the working fluid. However, the formation of such carbon-based tribo-layer on the contact interface, which is beneficial for wear protection of the material, requires a suitable combination between the material and the working fluid. Therefore, further researches for understanding the optimal condition for such tribo-layer formation and its mechanism are required.

4. Conclusion
In this study we have demonstrated that tribo-layer having a structure similar to that of graphite oxide can be formed on the contact interface of metallic material under boundary lubrication using diesel fuel as the fluid lubricant. The structure is shown by the appearance of D band and G band in the Raman spectra at approximately 1350 cm\(^{-1}\) and 1550 cm\(^{-1}\) for all four test conditions conducted. The formation of the graphite oxide tribo-layer is assisted by a tribo-chemical process involving both the material and fluid media. Here, the role of palm methyl ester in the solid film formation is still not clear.

The formation of graphite-oxide tribo-layer on the contact interface during the friction process provide a possibility for an in-situ lubrication method using the working fluid. In order to achieve such lubrication process, it is necessary to conduct further investigation to find out the necessary condition as well as the formation mechanism.

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