Influence of Soot Contamination in API CI-4 Engine Oil on Four-Ball Metallic Wear Using Electron Microscopy Image Analysis

Pitchaporn Oungpakornkaew¹, Panyakorn Rungsritanapaisan¹, Preechar Karin¹, Ruangdaj Tongsri², Dhritti Tanprayoon² and Katsunori Hanamura³

¹Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
²National Metal and Materials Technology Center, Pathumthani 12120, Thailand
³Departments of Mechanical Engineering, Tokyo institute of technology 179-0085, Japan

* Corresponding Author: pitchaporn.oung@gmail.com

Abstract
Engine lubricant has an important role in decreasing friction and the wearing of moving parts in the engine. However, soot contaminated in engine oil could change chemical and physical properties that affect the lubricant oil operation. Soot particles were simulated using carbon black in order to eliminate the effect of metallic ash and unburned hydrocarbon, which contained in particulate matter. The carbon black was blended in CI-4 lubricating oil. The investigation of metallic wear was associated with the use of a four-ball wear test. The amount of wear was compared by measuring the wear scar diameter of the worn surface on the steel balls. Scanning electron microscope (SEM) and confocal laser scanning microscopy were used for characterizing wear scar and surface roughness, respectively. In addition, the evidence of lubricant additive elements was detected on the wear surface by Energy Dispersive X-ray analysis (EDX). This research found that engine oil with soot contamination could lead to increasing amounts of abrasive wear by 83% and has approximately 1.1% larger wear scar diameter.

1. Introduction
An internal combustion diesel engine has been widely used for many decades due to its high torque and power. Contact of moving parts in the engine generates friction force, which decrease the engine efficiency. The lubricant serves several functions in tribological contact. It is crucial to separate the moving part for reducing the friction and avoiding wear and the engine lubricant also removes the frictional heat.² The fuel is combusted under high pressure and temperature. In order to reduce the peak combustion temperature for decreasing the oxides of nitrogen (NOx) emission, exhaust gas
recirculation (EGR) has been used. Therefore, incomplete combustion occurs more easily and causes the particulate matter as a byproduct remaining in the exhaust gas. The combustion products have been recirculated rather than pass out through the exhaust pipe by the recirculation system. The carbon content in the cylinder indicates that soot contamination in the oil effect on increasing piston ring and liner wear and on oil quality. (2) To understand the used lubricant oil contamination P. Karin kept oil samples from 2,000 cc and 2,500 cc diesel engine cars and 7,684 cc trucks. The amount of soot contamination through the end of oil life was less than 1% by weight. The nanostructure of soot was investigated by TEM. The primary particle size was found in the range of 20-80 nm. and the mean size was 30 nm. (3) The effect of soot contamination on engine wear was studied from different kinds of tests. S. George uses a ball-on-flat-disk wear test for testing various soot content in oil. The result showed that wear scar diameter (WSD) due to soot contamination was approximately double the WSD of oil without soot. Meanwhile, at higher soot levels, the oil performance was worsened. (4) Green et al. (2006) suggested that wear mechanisms in soot contamination occur because of the reaction between soot and anti-wear additive producing deteriorated lubricant. Another point of view is the starvation of lubricant in the contact, where the soot agglomeration is greater than oil film thickness and blocks the lubricant enters the contact. The last suggestion wear of surface occurs by three-body abrasion since the soot acts as a third body. (5) Li et al. (2006) have found that hardness of primary soot particles can determine from the correlation between the plasmon energy of a soot particle measured by electron energy-loss spectroscopy (EELS) and soot hardness. The research shows that the primary soot particles are sufficiently hard to abrade diesel engine metal parts. The engine parts wear was observed by SEM and the size of grooves was associated with dimensions of primary particles of diesel engines. The soot particles were a response for abrasive wear in the engine. (6) The soot particles were simulated using carbon black. Supanamok et al. (2016) use an electron microscope to examine the primary soot particles (30-50 nm). It shows small differences between soot and carbon black at the nanoscale. Nevertheless, carbon black creates larger agglomerate diameter than extracted engine soot, greater by approximately 50 nm because of oxygen and hydrogen content on its surface creating a relatively polar surface that interacts with another polar carbon black. Carbon black particles presented higher carbon contents and lower ash and volatile. (7) The wear mechanism of contaminated lubricant is not clearly understood. Hence, carbon black was used for simulating soot contaminating in the CI-4 engine lubricant and a four-ball wear tester was used in this study.

2. Experimental Setup

2.1 Materials and sample preparation

The formulated engine oil, which has been used in this study is CI-4 following API standard. CI-4 is group III base oil adding calcium (Ca), zinc (Zn) and phosphorus (P) as an additive. Calcium contains in detergent or dispersant additive. Zinc and phosphorus are used for anti-wear corrosion inhibitors. The concentration of metallic additives was measured by x-ray fluorescence analyser (XRF) is shown in Table 1 and the oil conditions were tested according to ASTM standard.

| Table 1. Engine oil properties. | Base Oil | Group III SAE15-W40 |
|-------------------------------|---------|---------------------|
| Calcium (Ca) | %wt | ASTM D6481 | 0.3205 |
| Zinc (Zn) | %wt | ASTM D6481 | 0.1349 |
|                          |       | Standard          | Result  |
|--------------------------|-------|-------------------|---------|
| Phosphorus (P)           | %wt   | ASTM D6481        | 0.1254  |
| Total Base Number        | mgKOH/g | ASTM D2896/B-11 |         |
| Viscosity @40°C          | cSt   | ASTM D445-15a     | 112.6   |
| Viscosity @100°C         | cSt   | ASTM D445-15a     | 15.18   |
| Viscosity Index          | -     | ASTM D2270        | 141     |
| Calculated mean oil film thickness at 75°C | Nm |                  | 55.6    |
| Calculated minimum oil film thickness at 75°C | Nm |                  | 34.9    |

(a) Diesel engine soot
(b) Biodiesel engine soot
(d) Primary particle of diesel engine soot
(e) Primary particle of biodiesel engine soot
Figure 1. TEM micrographs of (a) diesel engine soot ultrafine particle, (b) biodiesel engine soot ultrafine particle (c) commercial N330 carbon black at 100000x magnification (d) diesel engine primary particle (e) biodiesel primary particle and (f) N330 carbon black primary particle.

Figure 2. Primary particle size distribution of diesel, biodiesel soot and carbon black (CB N330).

Table 2. Carbon density and hardness comparison of diesel, biodiesel soot and N330 carbon black [8]

|            | Diesel | Biodiesel | N330 CB |
|------------|--------|-----------|---------|
| Carbon density | 2.01   | 1.82      | 1.89    |
| Hardness    | 2,056  | 1,334     | 1,460   |

Commercial carbon black was used instead of a real engine soot. The chemical composition of carbon black mainly contains carbon without ash and unburned hydrocarbon component like the engine soot. Therefore, the carbon black and engine soot have similar particle size and crystallinity at the primary particle size scale as seen in Figure 1. The average primary particle size of carbon black N330, diesel and biodiesel engine soot were measured from TEM images were around 30, 28 and 30 nm, respectively. The distribution of primary particle size is revealed in Figure 2. It also can be seen from the TEM images that carbon black, diesel and biodiesel soot have similar morphology and physical
property at the primary particle level. The TEM image of primary particle diesel, biodiesel soot and N330 carbon black were used for carbon atom density calculation by using image-processing software to convert TEM image to skeletonize image. The lines in skeletonized image represent the crystallite of carbon in soot and carbon black. The hardness of soot and carbon black can be calculated by carbon density and hardness relationship using carbon atom density and hardness data of diamond and diamond like-carbon, which are glassy carbon, amorphous carbon and diamond. The calculated result of carbon atom density and hardness are shown in Table 2. Diesel, biodiesel soot and N330 carbon black were calculated carbon atom density value is nearly the same and calculated hardness is higher than the steel balls of four-ball wear tester, which their harness is 867 kg/mm². The influence of soot contaminating in lubricant on wear was investigated by comparison of wear scar of lubricant without carbon black (CI-4) and with carbon black (CI-4 with CB). The CI-4 engine oil was mixing with carbon black N330 1% by weight to simulate the soot entrainment in the lubricant in a diesel engine.

2.2 Experimental Method
Wear quantity and mechanism are difficult to identify in the engine testing. Therefore, Four-ball test is one of the tribology test methods used to determine the relative wear preventive properties of lubricating fluid in sliding contact under ASTM D4172 standard. The test used four steel balls, three balls were fixed in the oil and another ball on the top rotated at 1,200 rpm and pressed with 392 N. The tested lubricant temperature was 75°C and the test duration was 60 minutes. The chromium alloy steel test balls were extra polished which their surface roughness is 0.005 microns following the AISI B3.12 standard. The hardness of test balls is in range 64-66 HRC. After the test, three balls at the bottom were measured the wear scar diameter using a high-resolution optical microscope to calculate average wear scar diameter of each condition. The surface roughness was measured by confocal laser scanning microscopy, capturing multiple two-dimensional images at different depths in a sample enables the reconstruction of three-dimensional structures of wear scar. The average surface roughness is determined using Ra value. Each ball was measured five times and calculated the average Ra value. In addition, the wear scar surface was characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX).

3. Result and discussion
The worn surface of steel balls (Figure 3) was measured average wear scar diameter is shown in Table 3. The result shows that wear scar diameter gets larger when adding the 1½ wt of carbon black into CI-4 oil; it increases nearly 1.1% from new oil. As a result of carbon black contaminates in the lubricant, it causes more wear in the Four-ball wear test.

The surface roughness measured by confocal microscopy as seen in Figure 4. CI-4 oil with carbon black exhibits lower Ra value than new oil (CI-4) as shown in Table 3. The average primary particle size of carbon black N330 is 30 nm, which smaller than calculated minimum oil film thickness (Table 1). As a result, carbon black can enter into the sliding contact of the tested ball. Moreover, carbon black, which researched to be harder than steel ball, could act as the third body in the wear surfaces, and abrades the ball surface indicated by smoother surface. Thus, the Ra value of contaminated oil declines by 17.2%.
Figure 3. Wear scar diameter images of new oil and oil with carbon black.

(a) CI-4
(b) CI-4 with CB

Figure 4. Surface roughness measurement of (a) CI-4 and (b) CI-4 with CB.

(a) CI-4
(b) CI-4 with CB

Table 3. Wear scar diameter and surface roughness.

|                | Average wear scar diameter (µm) | Ra value (µm) |
|----------------|---------------------------------|--------------|
| CI-4           | 603.31                          | 3.98         |
| CI-4 with CB   | 609.71                          | 3.30         |

(a) CI-4 120x magnification
(c) CI-4 500x magnification
**Figure 5.** SEM micrographs of (a) CI-4, (b) CI-4 with CB at 120x magnification, (c) CI-4 and (d) CI-4 with CB at 500x magnification wear scar.

**Figure 6.** SEM micrographs of (a) CI-4 and (b) CI-4 with CB at 500x magnification with wear analysis criteria.
The wear scars were observed by SEM as well. Figure 5 shows SEM micrographs of wear scar on the ball surface after the four-ball test at 120x and 500x magnification. At low magnification, the wear scar looks similarly between new oil (Figure 5a) and oil with carbon black (Figure 5b). However, the wear scar shows different surface characteristics at high magnification. Both cases exhibit grooves along the sliding direction of the ball where the abrasive wear occurs. The adhesive wear also can be observed in the SEM image as a plastic deformation on the ball surface. The result in the removal of wear debris larger than 20 \( \mu \)m indicates the adhesive wear. \[9\] Lastly, fatigue wear appears as a surface crack on the plastically deformed surface from the cyclic loading in a small section in two cases as shown in Figure 6. In order to analyze the wear mechanism, 24x18 squared blocks were created on the 500x SEM image and distinguish each squared block with different wear mechanism as seen in Figure 7. The blue colored blocks are determined as abrasive wear. Abrasive wear was pointed out by the clear block. Meanwhile, the delamination of the ball surface is defined by the yellow-colored block to specify the fatigue wear. The result of quantitative wear analysis showed the percentage of adhesive wear is highest in CI-4 sample. It shows 62% of the area in SEM image. On the other hand, CI-4 with carbon
black has abrasive wear as a majority wear mechanism for 61% of the area. It demonstrates that the carbon black has a role in roughly increasing abrasive wear in the four-ball wear test by 83% in this research as can be seen in Figure 8.

EDX result of steel ball surface shows iron (Fe), carbon (C) and chromium (Cr) which are the composition of chrome steel ball as was seen in the bar chart in Figure 9. The additive elements are found on the wear surface of both CI-4 and CI-4 with carbon black as can be observed in Figure 9 and 10, which are calcium, zinc, and phosphorus similar to the XRF result in Table 1. It indicates that the additive elements are remaining on the wear surface.

4. Conclusion
This research is aimed to investigate the effect of soot contamination in lubricant on diesel engine wear. New oil and contaminated oil were tested by a four-ball wear test. The N330 carbon black is used as simulated soot contaminate in CI-4 oil. The result of wear scar diameter can represent the quantity of wear which occurs on the ball surface. The measurement from the optical microscope of soot-contaminated oil has a higher amount of wear with approximately 1.1% larger wear scar diameter as a result of soot existence in the lubricant, while the roughness of lubricating oil with soot is 17.2% lower. The carbon black has been investigated that it is harder than the steel ball, therefore carbon black and also small particles that entered into the sliding contact between the wear surface may polish the ball surface. Nevertheless, only the particle size that smaller than oil film thickness can involve in this mechanism. SEM micrographs also illustrate the small groove along the sliding direction, it indicates that the carbon black is abrade the ball surface. Consequently, analyzing the high magnification SEM image of tested oil with carbon black shows a higher percentage of abrasive wear than adhesive wear and fatigue. The adhesive area is increased 83% from the wear scar area of non-contaminating oil which is indicated by the sliding groove along the worn surface. Furthermore, the trace of additive containing in CI-4 oil is presented on the wear surface.

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