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Chemical and Physical Assessment of Engine Oils Degradation and Additive Depletion by Soot

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Abstract

Soot contamination in engine oil causes a significant increase in wear of engine components. Presence of soot in the engine oil is one of the most common reasons leading to an increase in oil change intervals. There are several mechanisms that affect the performance of engine oil such as oil degradation, additive decomposition and additive adsorption on soot particles. It is recommended that removal of soot contamination from engine oil can reduce wear of engine components and extend the service life of engine oil. However, removing soot particles from the engine oil can diminish the efficiency of additives in engine oils as some additives adsorbs on these particles. There is still no census on this area. Thus, this experimental study aims to investigate how removing different levels of Carbon Black Particles (CBP), commonly used as surrogate for soot, from aged engine oil influences the engine oil performance. The study reveals three main mechanisms that influence the tribological performance of the engine oil expressed as additive depletion, additive adsorption and degradation products. Removal of CBP from engine oil is expected to reclaim the oil performance. However, the results demonstrate that the performance of oil after removal of CBP is still not as good as the fresh oil. These results confirms that reclaiming the oil performance can not be achieved by just removing the CBP. Other mechanisms such as oil degradation and additive adsorption on CBP adversely affect the engine oil performance during the removal of CBP.

Keywords/Phrases
Soot, Wear, Oil degradation, Additive depletion, Oil reclamation

1. Introduction

Engine manufacturers are facing greater demands to increase the oil change period and consequently reduce the total costs on customers over the engine service life. The major factors that adversely affect the performance of engine oil and accelerate oil degradation are oxidation, nitration, contamination, additive depletion, etc. [1–3]. Used engine oils are replaced regularly in machinery and vehicles to reduce the effect of various contaminants including the dirt, salt, water, incomplete products of combustion and other materials. These contaminants accelerate the chemical breakdown of additives, the base oil and subsequent chemical interactions producing corrosive acids and other harmful substances [4]. Soot forms due to incomplete combustion of hydrocarbons and is one of the most common reasons for changing the engine oil [5]. Soot causes an increase in wear [6] and continuously accelerates oil degradation [7]. The longer the engine working hours are, the higher levels of soot are produced. This continues until a certain level where the lubricant is no longer fit for continued service. Consequently, engine oil with a high level of soot causes a decrease in oil drain interval.

There has been a lot of research on the effect of soot on the engine oil performance [8,9] and oil degradation [10]. The contact type, soot content level and additives are considered as key factors affecting the friction performance in a controlled tribology test. In general, soot could act as a friction modifier and reduce the friction coefficient [11]. Soot is certainly shown to increase the wear of engine components significantly [6,9,12]. High concentration of soot contamination in the engine oil causes oil starvation due to a blockage of soot particles in the inlet of contact surfaces [13,14]. Sato et al.[14] revealed that starvation occurred due to the agglomeration of soot particles with a diameter larger than the oil film thickness leading to high wear. To minimise the starvation problem, more dispersant is added to reduce the soot agglomeration and its effect on the wear. It is worth mentioning that using dispersant additive, on the other hand can also promote corrosion [15,16]. Abrasive wear is the most common surface damage in the presence of soot contamination. This leads to a decrease in the engine oil performance and hence engine failure [17–19]. The effect of abrasive wear varies depending on the film thickness and soot particles diameter [14].

Oil degradation, as an irreversible chemical deterioration process, is used to monitor the changes in the chemical structure of oil, for instance oil oxidation, the formation of degradation products and additives depletion [20]. Fourier-Transform Infrared Spectroscopy (FTIR) technique is used to monitor the contaminants including soot, water, fuels, sulfonation, oxidation and nitration of base stocks of oils [21,22]. Oil oxidation is accelerated in the presence of soot. Motamen Salehi et al.[10] demonstrated that ageing oil containing CBP increased the oil oxidation compared to oil aged with no CBP. The study on the effect of soot level on oil oxidation has shown that a higher level of soot in the engine oil causes a higher oxidation rate [23]. Also, combustion by-products formed during the combustion process such as unburnt hydrocarbons, carbon monoxide, oxides of nitrogen and carbon dioxide can be detected in a used oil [24]. Presence of these by-products in the used oils causes an increase in the rate of oxidation, nitration and sulfation due to their interactions between oil, soot and additives [25]. Fundamentally, It is believed [25] that if soot particles are removed from the used oil, the lubricant service life would then be influenced mainly by oil degradation and not by soot dependant factors. Consequently, the improvement in oil function and extending the oil drain intervals are expected after soot removal.

Additive adsorption on soot particles is another concern when soot contamination presents in the engine oil. Soot particles have a reactive surface that additives in the engine oil can be adsorbed on these particles. FTIR technique is used to justify the change in ZDDP content or degradation in $P = S$ and $P - O - C$ bands at the area around the wavenumbers $650\mathrm{cm}^{-1}$ and $978\mathrm{cm}^{-1}$respectively [26]. Several studies [10,27–29] monitored the additive depletion using the FTIR method especially for oils containing the ZDDP antiwear additive. The results monitored the adsorption of ZDDP on soot using the FTIR method, however the researchers did not consider the change in FTIR peaks could also come from the decomposition of ZDDP compounds [30] to the chemical structure which is difficult to be detected using FTIR. Inductively coupled plasma (ICP) and X-ray fluorescence (XRF) are the most quantitative techniques that can be used to monitor the additive elemental concentration in oils. Thus, ICP technique has been used in the current study. Motamen Salehi et al. [10] studied the adsorption of ZDDP additive on CB particles (1wt% and 5wt%). The results showed a significant reduction in zinc and phosphorous concentration due to additive adsorption on CB particles. It is worth nothing that they have used base oil in their study. There are several studies [10,27–29] that have investigated the additive adsorption on soot particles, however none of them studied the effect of the increased soot surface area on the additive adsorption and, if the additive is adsorbed on soot particles, what will be the effect of removing these soot particles on the tribological performance of the resulting oil.

This study aims to understand the effect of soot removal on additive concentration and engine oil performance. Filtration or centrifugation system can potentially remove soot particles from the engine oils, however there is still unknown whether engine oil can perform as a fresh oil after reclamation or not. This is because other contaminants such as degradation products are difficult to remove by filtration and can also influence the oil functionality.

2. Experimental Methodology

2.1 Materials and Methods

A commercial Fully Formulated Oil (FFO) of passenger car with a viscosity grade 10W-40 was used in this study. Table 1 shows the physical and chemical properties of FFO. Monarch 120 Carbon Black Particles (CBP) used to simulate the soot particles in engine oil. Monarch 120 was purchased from Cabot Corporation, Massachusetts, USA. The crystal structure of CB particles consists of core and shell as shown in **Error! Reference source not found.**. In the current study, the size distribution of CBP in aged oil containing 5wt%CBP varies between 150 nm to 1.5 µm, as shown in Figure 2: TEM images show CBP size distribution in oils containing 5 wt% CB a) CBP agglomerates with size distribution(≤1 µm), b) CBP agglomerates in large size distribution (≤1.5 µm).
a and b. The chemical analysis of CBP consists of carbon (C), oxygen (O) and sulphur (S) as shown in **Error! Reference source not found.**. The engine oil has been artificially aged oil in the lab in accordance to ASTM D4636-99 standard [31]. This method is used to simulate the engine oil in vehicles that are working in severe conditions. As shown in Figure 4, 250ml of mixed oil is placed in a beaker covered

with a three-neck lid. The beaker containing oil is placed on the hot plate in a constant temperature at 160°C. The first open neck allows the airflow (2 L/h) through the oil providing a source of oxygen to imitate the real oxidation process. The middle neck-led is equipped with a condenser to prevent the evaporation of the oil. The last neck is used to monitor the temperature during the ageing process. Metal samples (grey cast iron material) are placed in beaker to provide catalytic reactive surfaces. Blended oil is stirred at the speed of 500 rpm to keep lubricating liquid homogeneously over the ageing period. The ageing process is applied for oils containing different levels of carbon black (0, 0.75, 1.5, 3 and 5 wt %) for 96 hrs. The ageing period is chosen according to D4636 standard [32], which allows measurable results (i.e. oxidation) to be obtained in a reasonable time [32]. The aged oils samples before and after removing CBP are used for the subsequent experiments. The oil degradation and additives depletion are detected using FTIR technique. FTIR spectra within the range of 650 to 4000cm^{-1} are applied and the resolution of collected spectra is 4cm^{-1}. Inductively Coupled Plasma (ICP) is used to quantify the additive concentration in the engine oil at Oil Check Laboratory Services Ltd, UK. KINEXUS rheometer is also used to measure the viscosity of the oils. Viscosity measurements are conducted at 40°C and 100°C according to ASTM D2270 standard [33].

Table 1: Physical and chemical properties of fresh engine oil (FFO)

Details	**Parameters**
Density at 15°C	0.961 g/ml
Kinematic viscosity at 40 °C	80.6 mm^2/s
Kinematic viscosity at 100 °C	11 mm^2/s
Flash point	135°C
Total base number	77 mgKoH/g
Zn concentration	1115 ppm
P concentration	1065 ppm
S concentration	4140 ppm

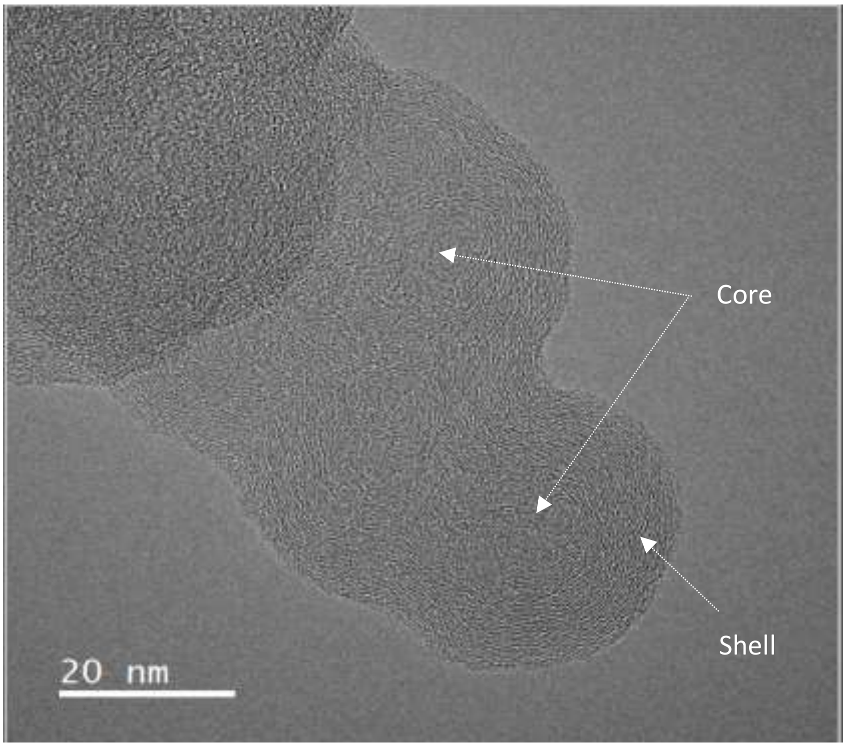


Figure 1: TEM image shows CB particles at a high magnification level.

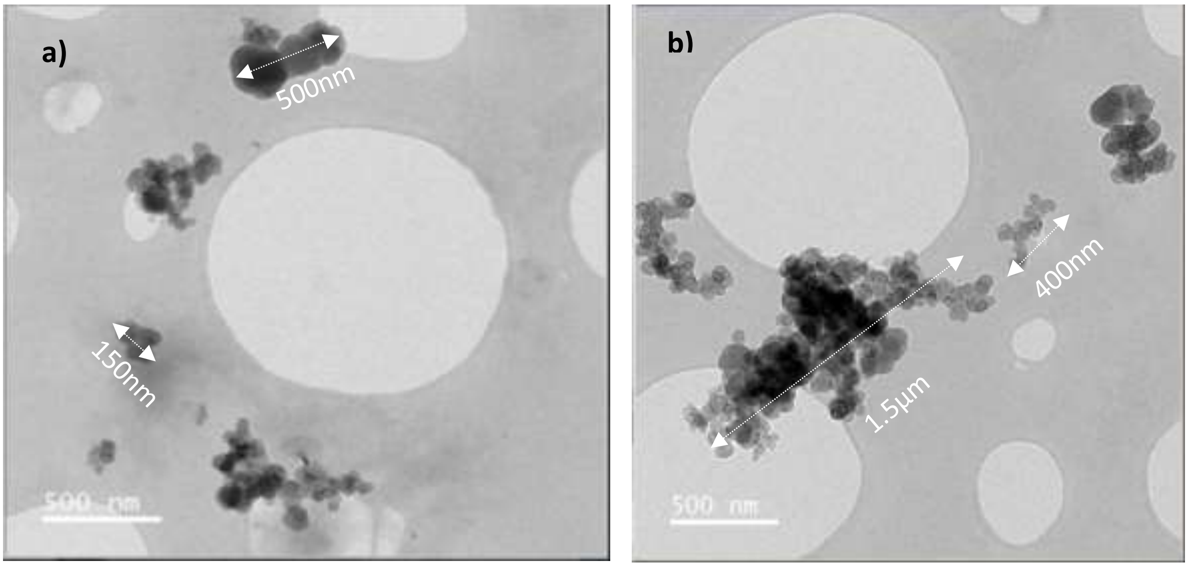


Figure 2: TEM images show CBP size distribution in oils containing 5 wt% CB a) CBP agglomerates with size distribution(≤1 µm), b) CBP agglomerates in large size distribution (≤1.5 µm).

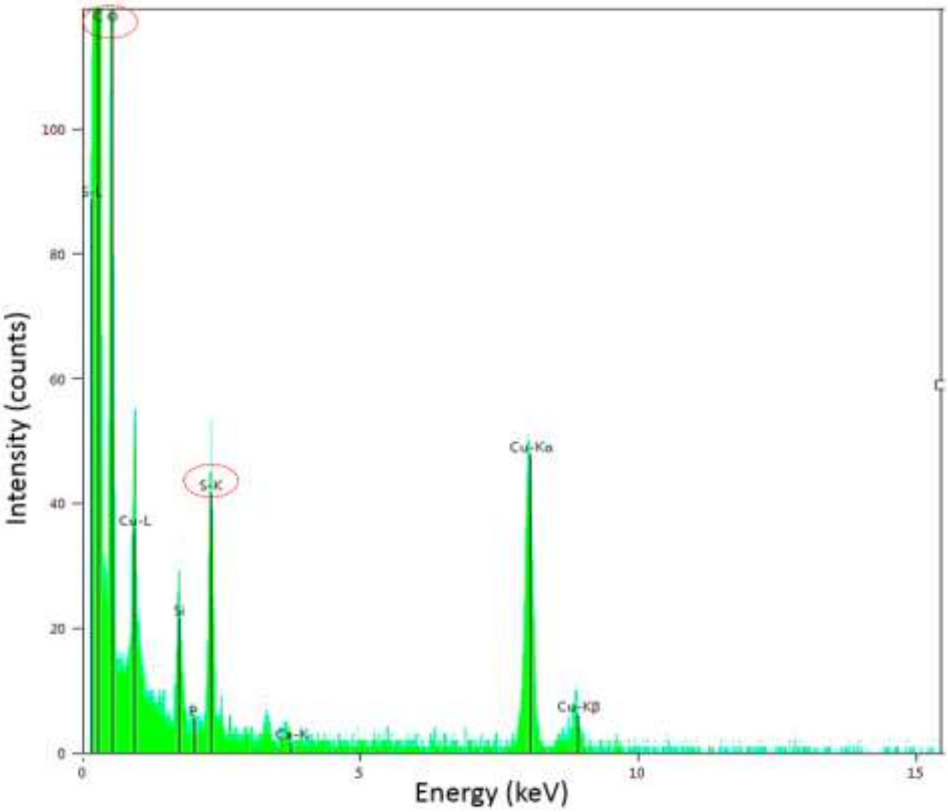


Figure 3*:* TEM spectra of fresh carbon black particles

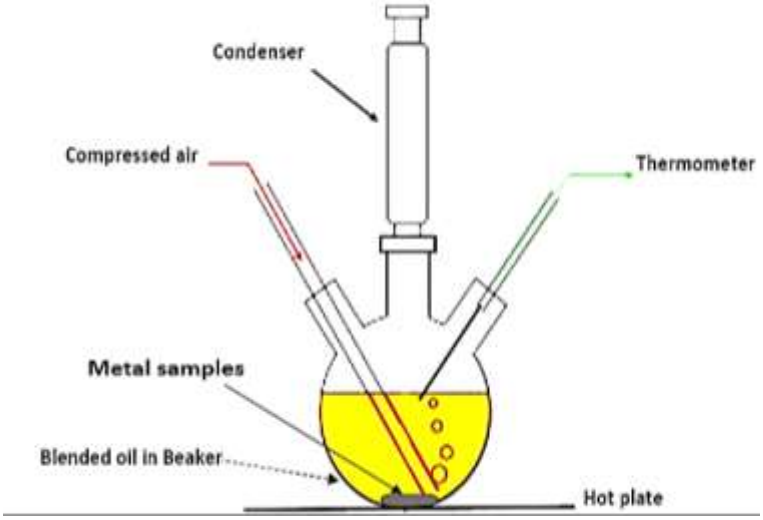


Figure 4: Schematic set-up of the artificial ageing process [34]

2.2 Tribological Tests

TE77 tribometer is used to simulate reciprocating sliding condition in an engine according to ASTM G 181 [35]. A 3D diagram of TE77 is shown in Figure 5a. Dimensions and material properties of specimens are described in Table 2. Experiments are carefully designed to investigate wear and friction in a boundary lubrication regime (Lambda of FFO $\lambda=0.27<1$). The maximum contact pressure is calculated using the Hertzian contact theory. The test temperature used to replicate the real working condition in the engine as shown in Table 2. The electric motor applies a reciprocating motion through the gearbox on the pin holder arm. The force transducer is used to measure the friction force which is used to calculate the friction coefficient. The normal load is applied by a cantilever system through the contact interface as shown in Figure 5b.

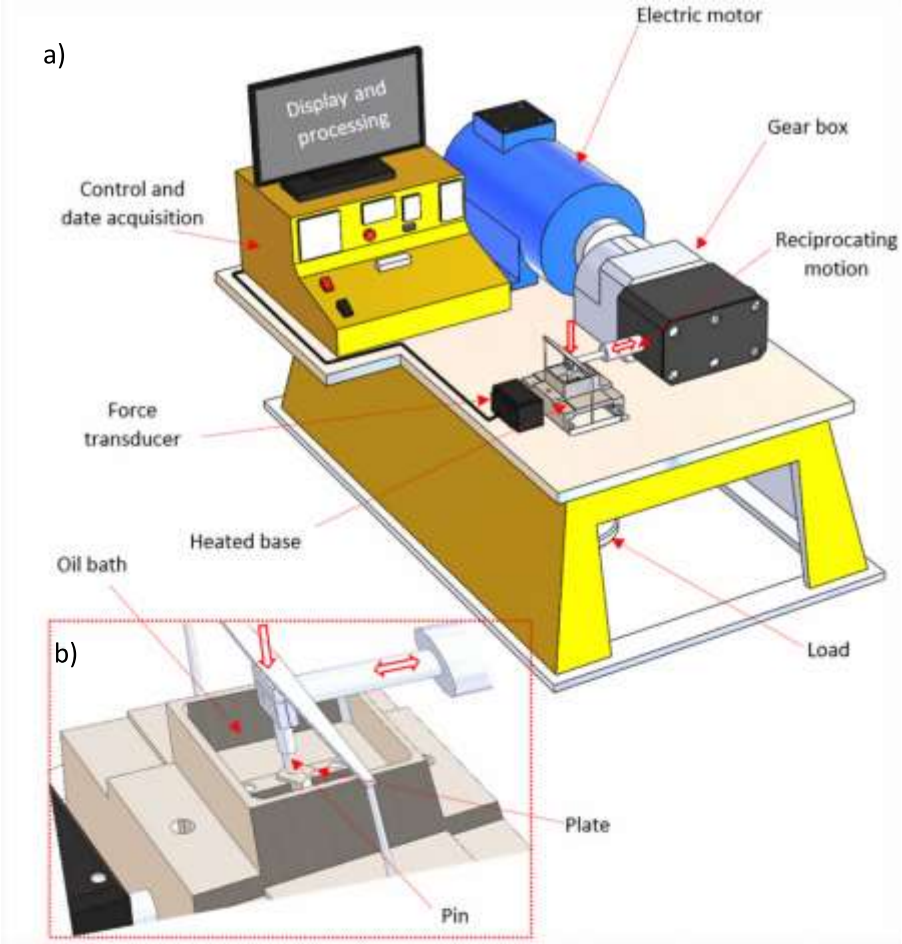


Figure 5: 3D schematic of TE77 experimental set up (a), the contact interface between pin and plate (b).

For all oil samples containing CBP, a magnetic stirrer is used at speed 500rpm for 1hr to disperse the CBP in oil before TE77 tests. This has been conducted to ensure that the CBP are homogeneously dispersed in the oils to reduce the deviation in results. 10ml of oil sample is used for each tribological test. The experiments are repeated at least twice to ensure the repeatability of tests. After all the tribological tests, pins and plates are rinsed with heptane to remove the contaminated oil from the surfaces.

Table 2: TE77 set up parameters and materials properties of specimens.

Material Properties	Pin	Plate	TE77 Parameters	Value
Material	Steel EN31	Steel EN31	Temperature °C	100
Dimensions (mm)	10 radius	7x7x3	Contact pressure (GPa)	1.26
Hardness (HRC)	58-62	58-62	Load (N)	22.1
Roughness (nm)	30-50	400-600	Frequency (Hz)	25
Elastic modulus (GPa)	190-210	190-210		
Poisson's ratio	0.28	0.28	Test duration (min)	120

An optical white light interferometer (NPFLEX) is used to measure wear volume loss on pins after tribometer tests. Scanned images of pin surface that are measured by NPFLEX have been investigated using Vision64 software from Bruker Corporation. Wear volume loss (spherical cap volume) on pin is calculated using the equations (1) and (2) as follows:

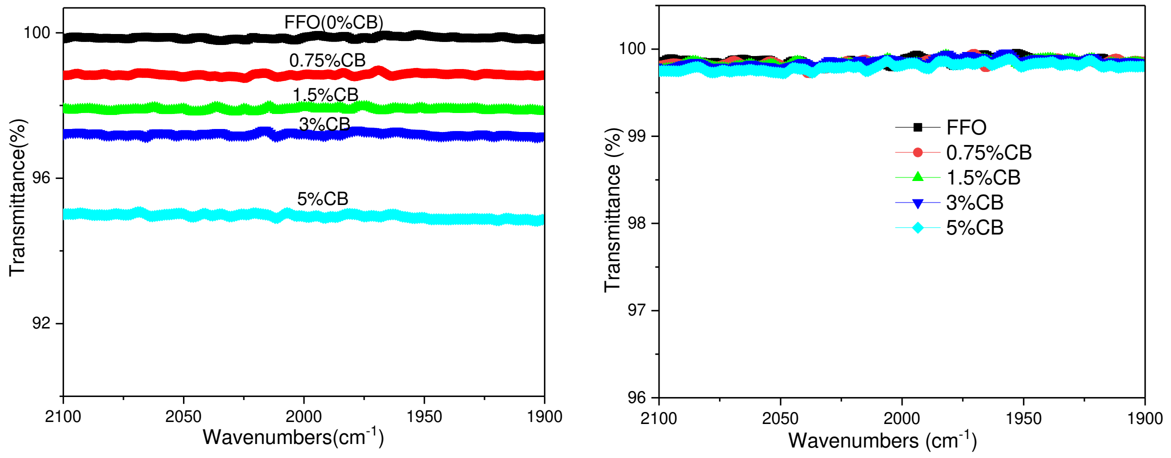
$$V_{pin\ volume\ loss} = \frac{\pi.h^2.(3R-h)}{3} \quad (1) \qquad ; \ h = R - ((R^2 - r^2))^{0.5} \quad (2)$$

Where,

h: Spherical cap height (µm), R: sphere radius (µm), r wear scar radius (µm).

2.3 CBP Removal from Oils

A centrifuge process is used to remove the CBP from the aged oil samples for post analysis to identify the interactions between the CBP, additives and oil. Oil samples are centrifuged at 12000rpm and at $40°\text{C}$ to remove the CBP from oil. This process is repeated four-times to ensure the removal of CBP as much as possible. FTIR determines the change in soot concentration in the engine oil at the region around 2000cm^{-1} [22]. Figure 6 demonstrates the CBP concentration before and after centrifugation with various CBP percentage in the oil. After centrifugation as shown in Figure 6b, the results show that all FTIR spectra have no shift at the region around 2000cm^{-1} similar to fresh FFO. This determines that almost all CBP were removed from oils by the centrifugation process explained above. It is worth noting that there is a limitation on the FTIR technique since this method does not detect a small amount of CBP (less than 0.1%) in the engine oil [22]. However, Berbezier et al.[36] investigated the effect of low levels of CB (<0.1wt%) on the engine oil performance, the results showed that the CBP concentration lower than 0.1% in oil does not influence the wear.



a) Before centrifugation **b) After centrifugation**

Figure 6: FTIR spectra of aged oil samples in the region around 2000cm^{-1} to determine the CBP level before and after using the centrifuge compared to fresh oil (FFO) a) before centrifuge b) after centrifuge

3. Results and Discussion

3.1 Chemical Structure of Oil

Chemical structure of bulk oils is investigated using FTIR technique. Figure 7 displays the overall FTIR spectra of aged oil samples containing CB before and after centrifugation. FTIR detects the change in soot concentration in the engine oil at the region around 2000cm^{-1} [22]. However, the existence of soot in engine oil causes a shift in overall FTIR spectra depending on the level of soot [22]. Figure 8 shows that FTIR spectra shifted down with an increase in the CBP levels in the aged oils as expected. FTIR spectra after removing CB shifted up and three influenced regions explained in Figure 8. The $\mathrm{P-O-C}$ band around 978cm^{-1} corresponds to the antiwear additive (ZDDP) [37–39] as shown in Figure 8a. The oil samples after ageing have no peak at 978cm^{-1} as can be seen in Figure 8a. This means that the antiwear additive could have either been depleted or decomposed during the ageing process. These results are in line with other studies [10,40], showing that ageing the oil at high temperature causing decomposition or depletion of antiwear additive and as a result the $\mathrm{P-O-C}$ peak disappears in the FTIR at 978cm^{-1} region. The $\mathrm{S-O}$ and $\mathrm{S=O}$ bands in FTIR spectra, as shown in Figure 8b, are identified in regions around 1150 and 1250cm^{-1} respectively [23,38]. The $\mathrm{S-O}$ and $\mathrm{S=O}$ bands are referred to the formation of sulphate by-products as an increase in FTIR intensity (shift down) in the presence of CBP in the oils. Oxidation of oils, the formation of carboxylic by-products, is indicated in $\mathrm{C=O}$ peak around 1720cm^{-1} [37] as shown in Figure 8c. These results are in agreement with other studies that showed the formation of sulphate by-products [40] and oil oxidation [15] during the ageing process. In general, the intensity of FTIR spectres (shifting down) increases with increasing CBP levels in the oils. In the current study, the effect of CBP on degradation products during the ageing process has been observed as seen in Figure 8b and c. The results confirm that existence of CBP in the oil during the ageing process affects oil degradation and induce the formation of degradation products in the oil. There are complex chemical interactions between the additives themselves and the CBP in existence of oxygen at high temperature. CB surface chemistry contains chemical bonds such as carbon-oxygen and sulphur-oxygen bonds. As CB level increases in the oil, higher density of carbon-oxygen and sulphur- oxygen bonds exist in the aged oil. This can cause higher chemical interactions between released chemical bonds from soot and the additives hence catalysing the formation of degradation products.

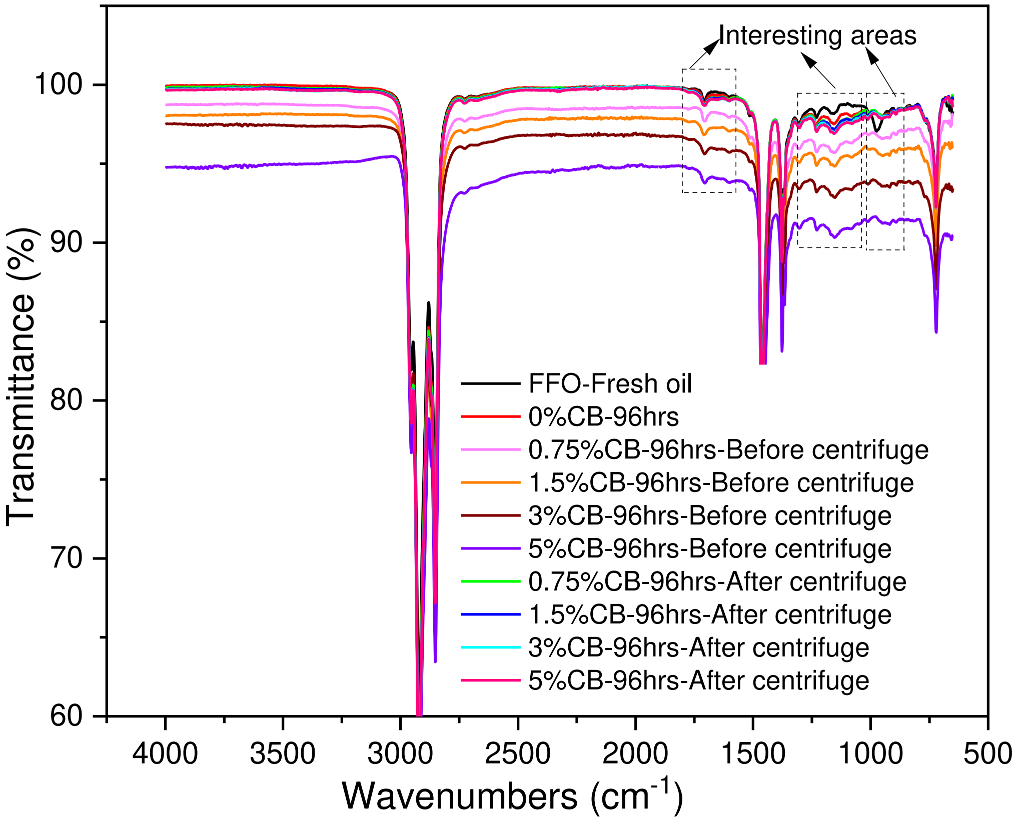
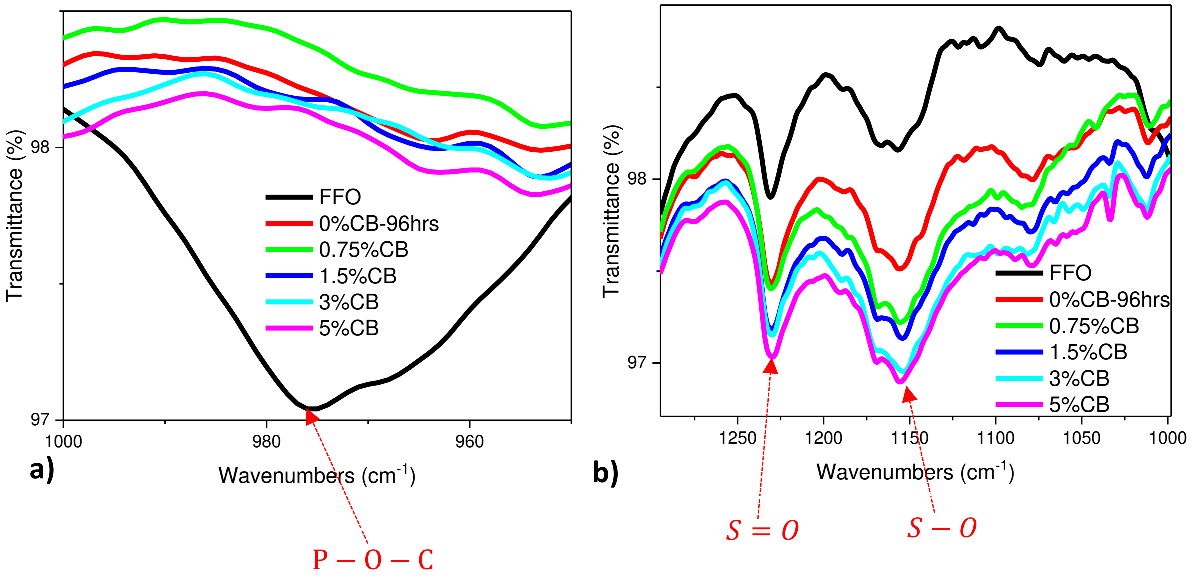


Figure 7: FTIR spectra for aged oil samples before and after removing CB.



c)

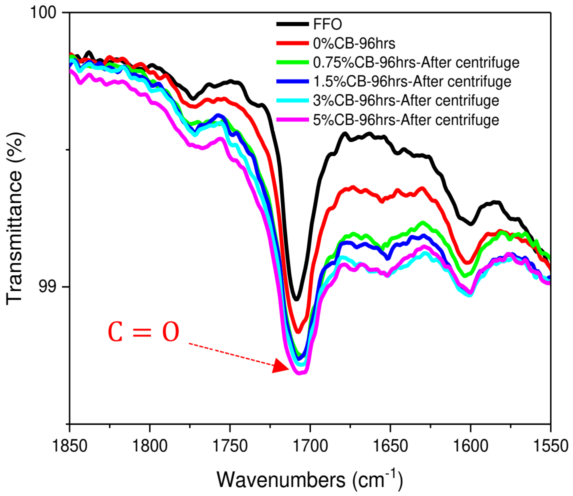


Figure 8: FTIR measurements of aged oils after removal of CBP at a) 978cm^{-1} point represents the $P-O-C$ antiwear additive b) around 1150 and 1250cm^{-1} points represent the $S-O$ and $S=O$ respectively c) around 1720cm^{-1} point represents $C=O$ band.

3.2 Physical Properties of Oils

Viscosity is one of the most important physical properties which is used to identify signs of oil contamination and oil degradation [42]. Figure 9: a displays the effect of the ageing process on the viscosity of the oils containing CBP. In both ageing and no-ageing conditions, the results show an increase in viscosity with increasing the level of CBP in the oils as expected [43,44].These results are in line with other studies [43,44] in terms of the effect of CB level on oil in viscosity. In general, the results show an increase in the viscosity after the oils are being aged compare to the fresh oil mixed with the same level of CBP. Since both oils (aged and non-aged) contain the same levels of CBP, this increase in viscosity is related to the ageing process and formation of degradation products. To investigate the effect of degradation products on viscosity, CBP were removed from aged oil. Figure 9: b displays the viscosity of oils at 40°C and 100°C after removal of CB from aged oils samples. Viscosity of oils samples decreases after removing the CBP as expected. However, these values are still higher than the viscosity of fresh oil. This is probably due to the formation of degradation products in oils. The results are in line with different studies that have confirmed the effect of degradation products [42,45,46] on the physical property of oils. The current study shows how the oil degradation can influence the increase in viscosity even after soot removal as demonstrated in Figure 9: b.

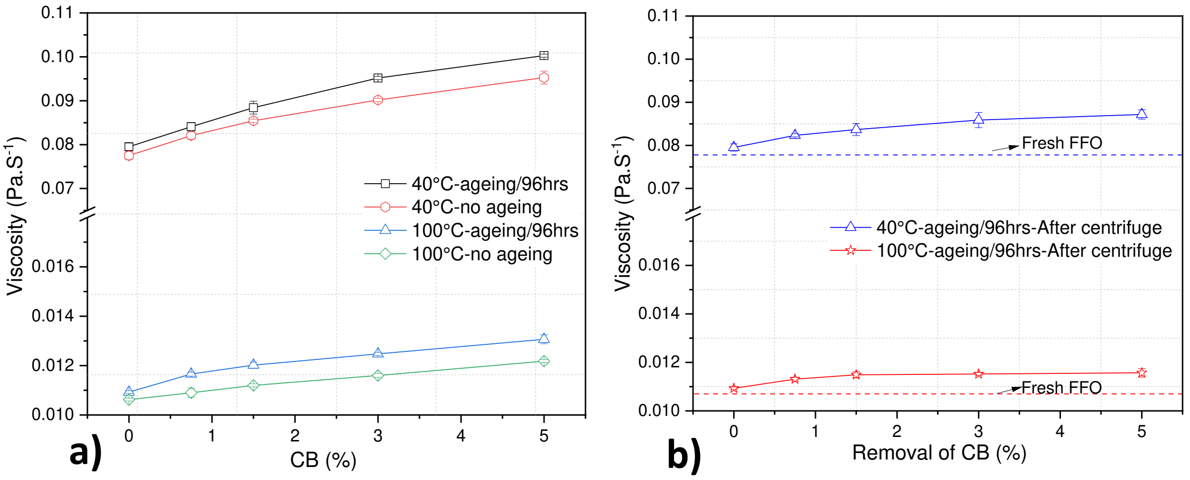


Figure 9: Viscosity of oils at 40°C and 100°C a) with increasing the CBP levels after ageing the oil for 96hrs compared to non-aged oil samples containing the same level of CB b) after removing the CB from aged oil samples.

3.3 Additives Adsorption on CBP

FTIR results showed the antiwear decomposition or depletion in oils with no CBP and oils containing CBP as explained in Figure 8a. It is not possible to detect the changes in additive concentration of oils using FTIR technique. Therefore, ICP analysis was conducted on the oil samples to determine the additive concentration after centrifugation. ICP results in Figure 10 indicate the change in the concentration of S, P and Zn elements in aged oils and after removing different levels of CBP from the aged oils. The reduction in additives concentration in engine oils classifies into two types: additive depletion [47] when there is no CBP in oil and additive adsorption [10] when the CBP exists in the oils. The S, P and Zn elements come from antiwear additives, for instance, Zinc dialkyldithiophosphates (ZDDP) and Zinc dithiophosphate (ZDP), while the S and P elements could also come from dispersant/or detergent compounds such as sulfonates and phosphonates [48].

The concentration of S decreased significantly in aged oil with no CB due to additive depletion as shown in Figure 10. ICP analysis was conducted on the aged oils containing various levels of CB after centrifugation. The results confirm the phenomenon of additive adsorption on CBP. Moreover, the results show a lower concentration of S, P and Zn in the oils containing higher levels of CB. This is due to the higher active surface area with higher CB levels in the oil leading to more additive adsorption on CB particles. This is in agreement with the function of dispersant/detergent additives with polar groups to attract the organic contaminants which are expected to be removed by CBP [49].

Additive adsorption on CBP was previously studied by Motamen Salehi et al [10] at the same conditions. However, they used the base oil+1wt% ZDDP to investigate the additive adsorption on CBP, instead of FFO. The results showed full adsorption of ZDDP compound on 5wt% CB after ageing the oil [10]. In the current study, however, lower levels of additives adsorption on CBP is observed in FFO compared to the base oil and ZDDP. This could be due to interactions between the additives in the presence of antiwear, dispersant and detergent which may reduce the antiwear additive adsorption on CBP. The decomposition of additive (as shown in Figure 8a) could also be another factor that affects the additive adsorption on CBP.

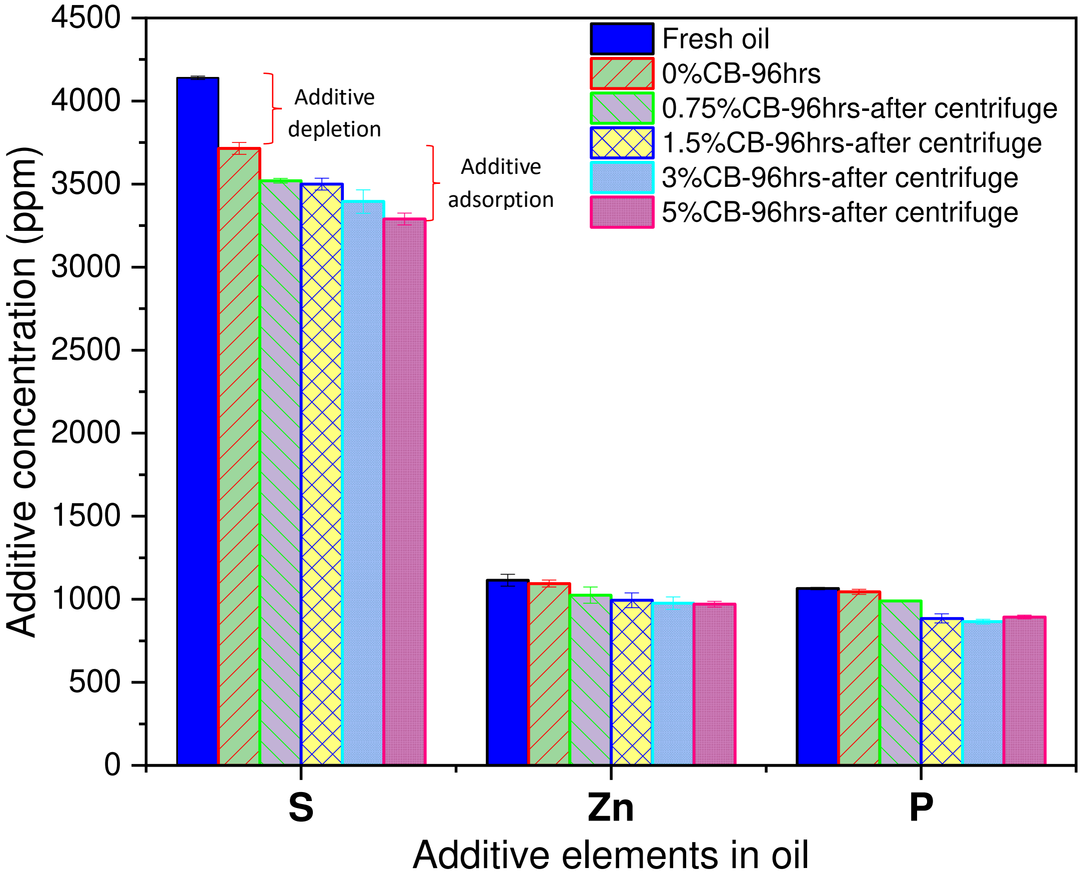


Figure 10: ICP results of oils after removing CBP.

Figure 11 shows Energy Dispersive X-ray (EDX) results on CBP extracted from the aged oil to confirm the existence of additive adsorption on CBP. The extracted CBP from oil containing 5wt% by centrifugation indicated the presence of constituents of an antiwear additive such as Zn, P and S due to adsorption of these elements on CBP. The results are in the line with other studies showing the existence of engine oil additive elements on the soot particles using EDX [10,47,50].

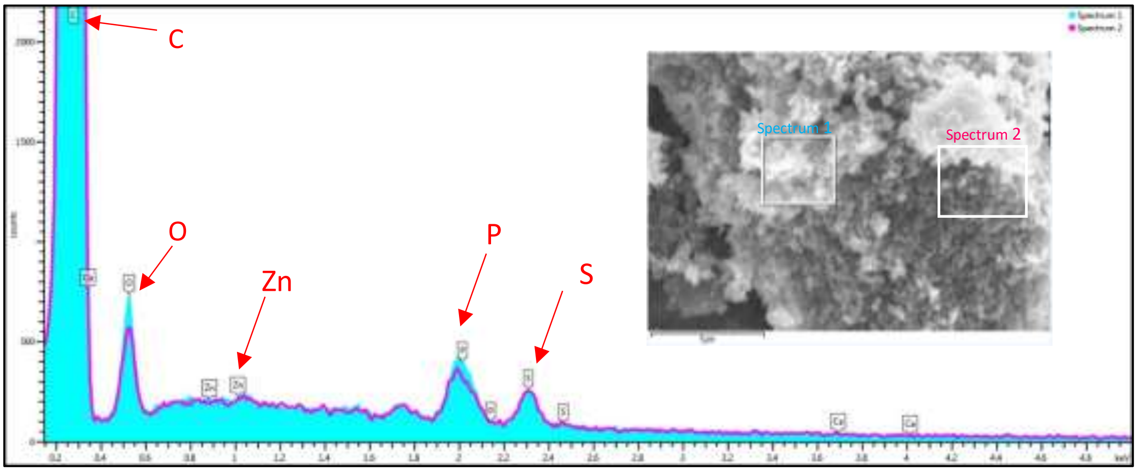


Figure 11: EDX chemical analysis of extracted CBP from aged oil containing 5%wt CBP after 96hrs ageing.

3.4 CBP Effect on Tribological Performance

The effect of CBP on friction coefficient is determined over two hours of tribological tests as shown in Figure 12. It can be observed that the friction coefficient decreases gradually with rubbing time in the samples containing CB. For oils containing 1.5, 3 and 5wt% CBP, the friction coefficient was high (higher than fresh oil) at the beginning of the tests and then gradually decreased over time. The length of the high friction period was increased with increasing CBP level in the oil. This can be explained by the small contact area between pin and plate (as shown in Figure 12) and high levels of CB which causes oil starvation at the beginning of the test. Over time, this contact area increases in size and becomes a larger flat area due to high wear. In this case, there is a possibility of moving towards a mixed lubrication regime that explains the lower coefficient of friction observed in tests with high levels of CB. The increase in friction coefficient at the initial period and decrease over time due to starvation has also been observed in the previous studies [9,51]. While the results show that CB at level 0.75% act as a friction modifier [52,53] and reduce the friction coefficient between the contact surfaces over time. CBP at low concentration has less ability to form the large agglomeration and does not affect the oil starvation. This is due to dispersant ability to disperse the particles at a low CB level preventing the coalescence into large agglomeration [54].

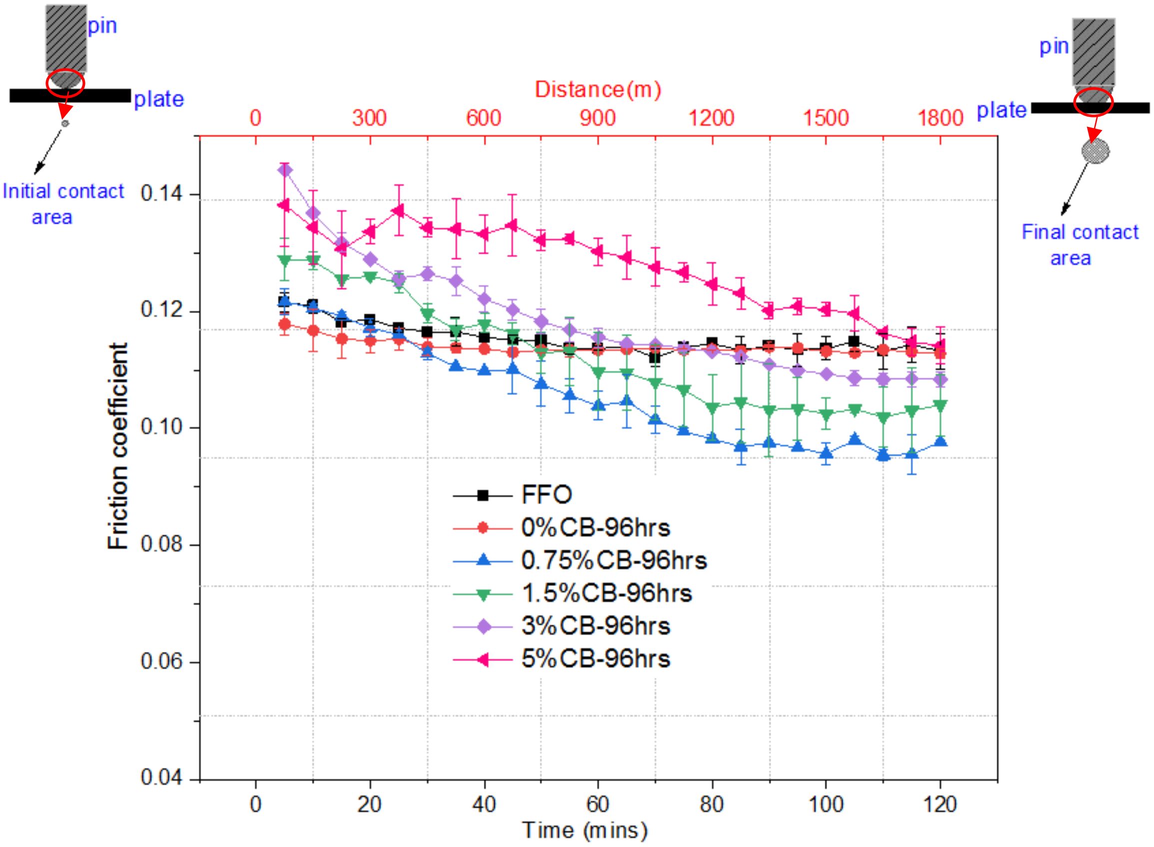


Figure 12: Friction coefficient of aged oils containing CBP (before centrifugation) over 2hrs period of the test with schematic images of the contact area.

The effect of CBP on wear before centrifugation is investigated as shown in Figure 13. Wear increases with increasing the CBP level as expected. This is because more CBP and large clusters of particles exist in the oils. The increase in wear by increasing CB levels in the oil is in agreement with other studies [25,55] as higher level of CBP forms large clusters leading to starvation as shown schematically in Figure 14b. There is also another factor of increasing wear with higher CBP as dispersant becomes less effective to disperse the particles preventing them from approaching and coalescing into large agglomerates [54]. The correlation between wear and friction, as illustrated in Figure 13 depends on the CB level in the oils. With low CB level as shown in Figure 14a, the particles act as a friction modifier producing low friction during the test in contradiction with wear. However, as the CB level increased causing the starvation (as shown in Figure 14b), both wear and the average of friction coefficient over the whole test increased as shown in Figure 13.

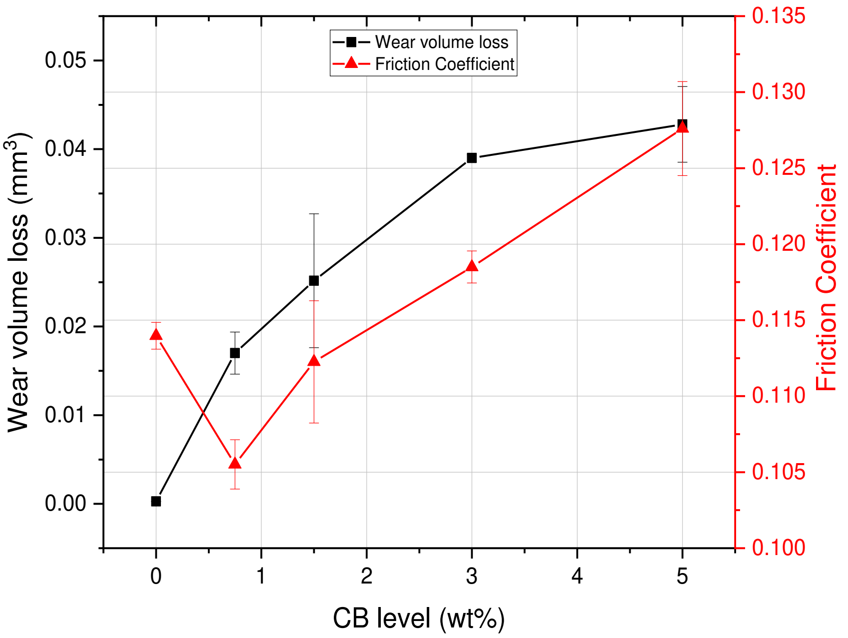


Figure 13: Wear volume loss with different levels of CBP correlated to the mean of the coefficient of friction over the whole test of each sample.

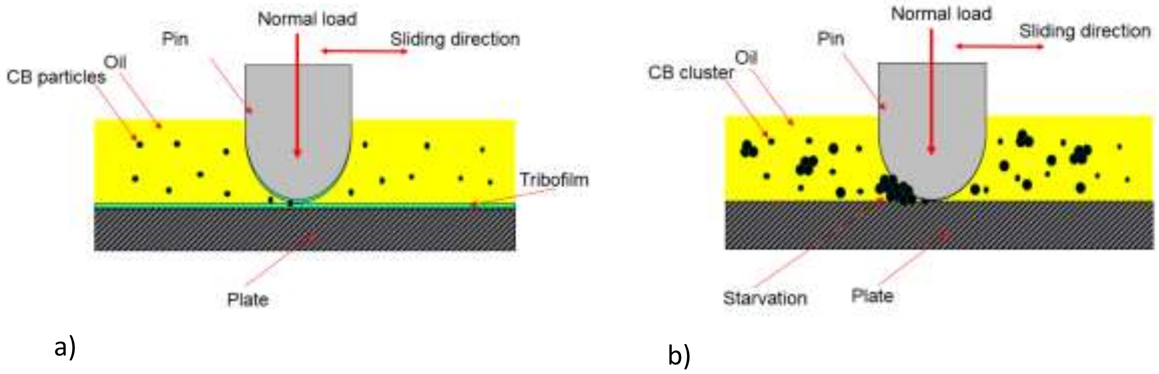


Figure 14: 2D-schematic explains the pin-on-plate contact with oils containing a) low CBP level b) high CBP level.

3.5 Effect of Oil Degradation on Wear

Removing CBP from oils has a significant effect on decreasing the wear compared to the oil-containing CBP as shown in Figure 15. The increase in wear after CBP removal compared to fresh oil could potentially due to three main mechanisms. Firstly, the increase in the additive adsorption such as Zn, P and S on CBP (as shown in Figure 10) leading to a reduction in antiwear additive. Secondly, the formation of sulphate by-products due to the interactions between CBP and additives during the ageing process. Thirdly, oil oxidation (carboxylic by-products). The results show that the engine oil after removing CBP does not perform as good as the fresh oil. This is due to the oil degradation and additive adsorption. However, a significant improvement in wear is expected after CBP removal as shown in Figure 15.

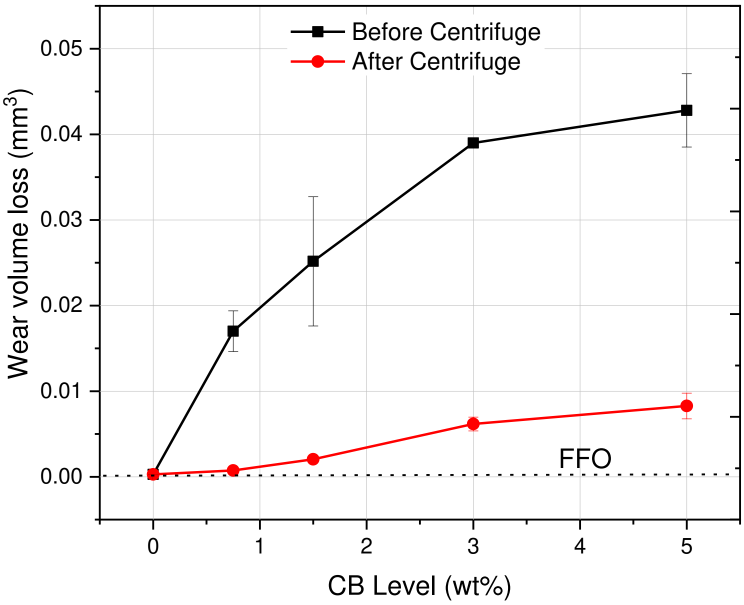
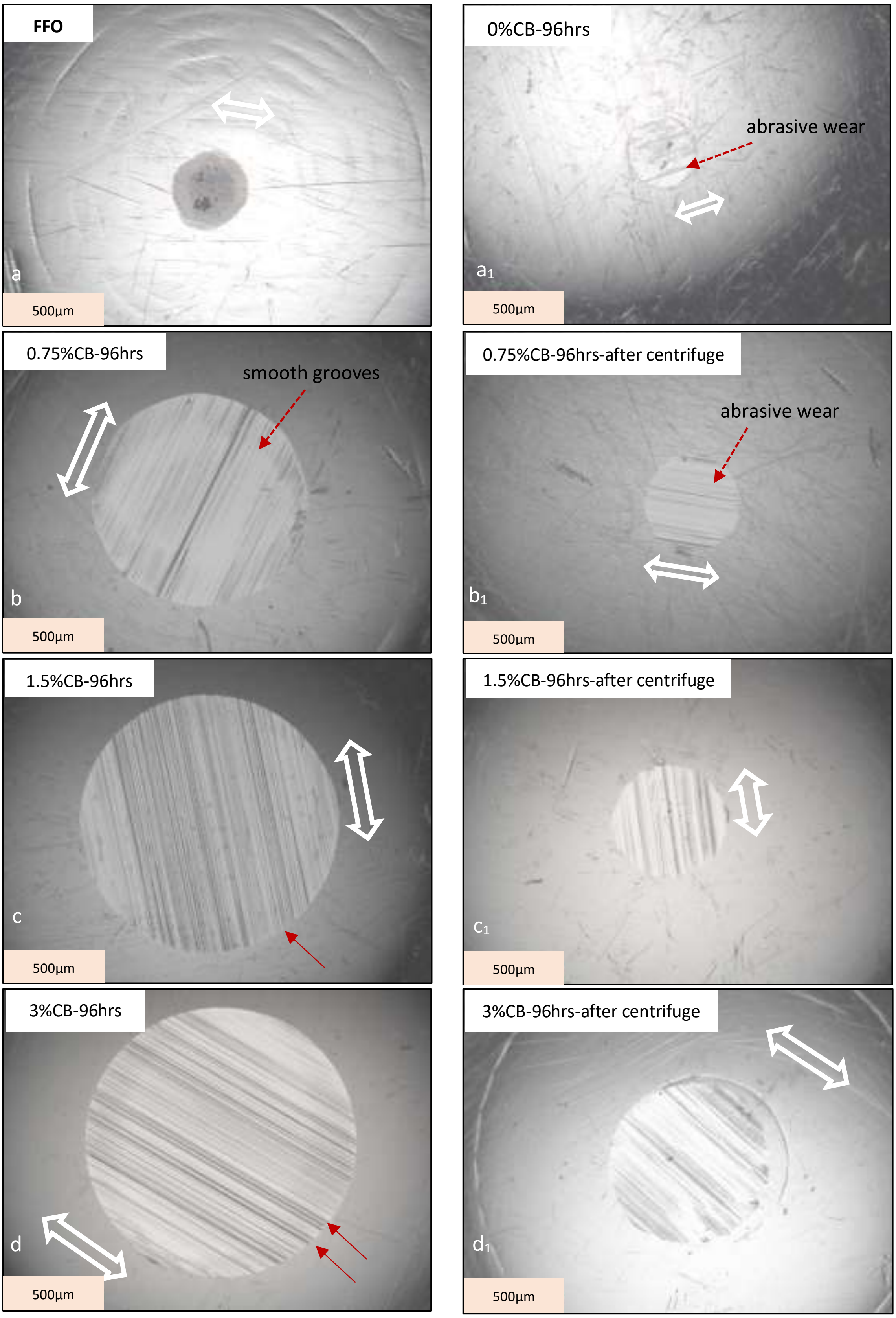


Figure 15: Wear with different levels of CBP in aged oil before and after centrifuge.

3.6 Surface Characterisation

Figure 16 shows microscopic images of wear scars on pins for oils containing CBP and after CBP removal. The arrow on the image refers to the sliding direction of pin-on-plate. The wear scar of fresh FFO shows no abrasive wear with full coverage of tribofilm is observed on the surface as shown in Figure 16a. Oil samples containing CBP demonstrate the sign of abrasive wear on the surface and more CB particles producing higher wear as expected. The wear scars showed a constant increase in the width of grooves with a higher concentration of CBP as shown in Figure 16b, c, d, and e in comparison to fresh oil in Figure 16a. This can be attributed to higher CBP concentration in oils producing more and larger CB agglomerates causing the plastic deformation by these particles. These results are in line with other studies [53,56–58] showing the effect of soot particles on the contact surfaces causing the abrasive wear. Figure 16a_1 demonstrates abrasive wear on wear scar after ageing the oil with no CB due to additive depletion. The wear scars are significantly smaller after removing CBP (Figure 16b_1, c_1, d_1 and e_1) compared to the oils samples before removing CBP as shown in Figure 16b, c, d, and e. It is worth noting that there is still signs of abrasive wear on the wear scars after removal of CBP, this is due to additives adsorption on CBP and oil degradation during the ageing process.


FFO
a
500μm
0%CB-96hrs
abrasive wear
a1
500μm
0.75%CB-96hrs
smooth grooves
b
500μm
0.75%CB-96hrs-after centrifuge
abrasive wear
b1
500μm
1.5%CB-96hrs
c
500μm
1.5%CB-96hrs-after centrifuge
c1
500μm
3%CB-96hrs
d
500μm
3%CB-96hrs-after centrifuge
d1
500μm

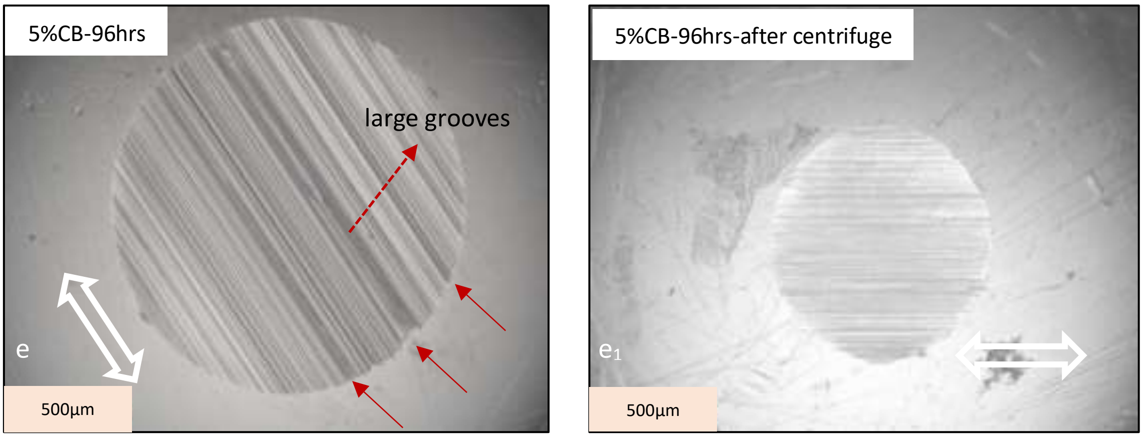
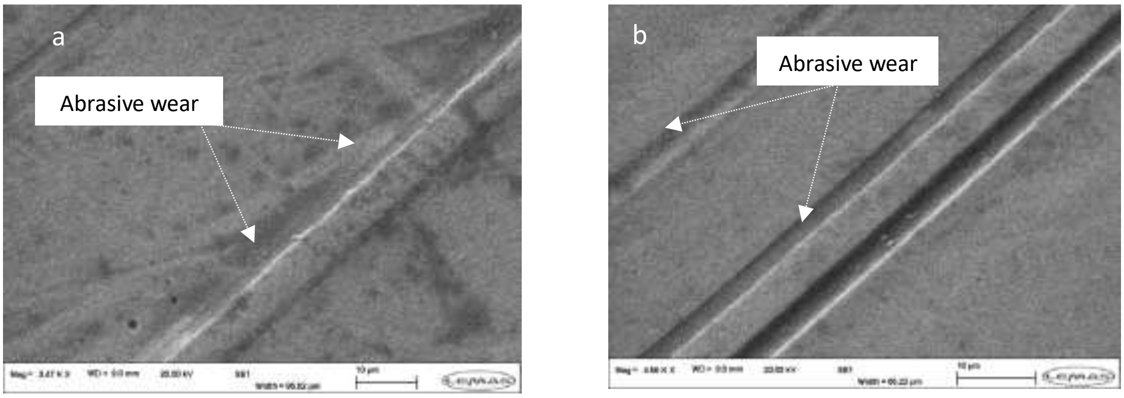


Figure 16: Microscope images show wear scars on pins of oils containing CBP before and after centrifuge, arrows indicate sliding direction.

Several studies [53,56–58] showed the presence of CB or soot particles influences the contact surfaces causing abrasive wear. SEM images at high magnification as shown in Figure 17a and b confirm that abrasive wear occurs also after ageing the oil with no CBP and for aged oil containing 0.75%CB after centrifuge. The chemical and physical changes in oils due to additive depletion and oil degradation can affect the contact surfaces and cause hard abrasive wear on surfaces.



a) 0%CB-96hrs

b) 0.75%CB-96hrs-after centrifuge

Figure 17: SEM images with high magnification a) abrasive wear of the oil after ageing with no CBP b) abrasive wear of aged oil containing 0.75%CB after centrifuge.

3.7 Chemical Composition of Tribofilm

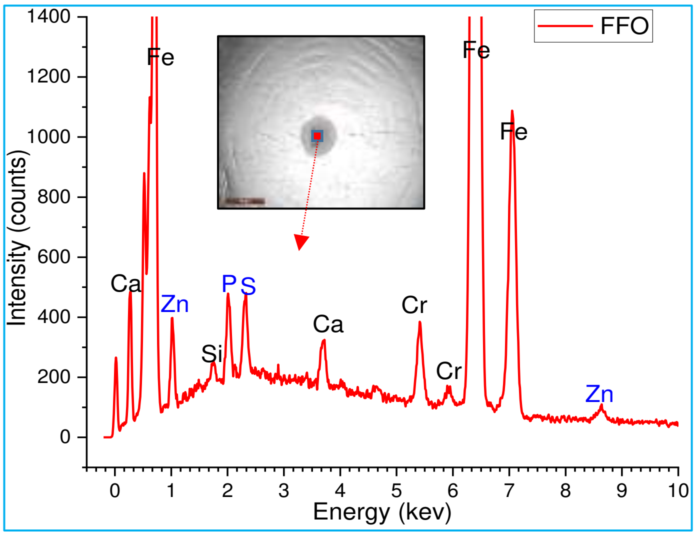
Scanning Electron Microscope SEM/EDX is conducted on pin samples to verify the observation from wear results and optical microscope images. It is believed that when CBP exists in the oil, the tribofilm is removed by CB particles causing abrasive wear [18]. Figure 18 demonstrates the change in the chemical composition of tribofilm inside the wear scar. In this current study, EDX analysis is conducted to assess if the additive depletion during oil ageing, additive adsorption on CBP and oil degradation can affect the chemical composition of tribofilm. Figure 18a$_1$ of the fresh oil sample shows the presence of antiwear additive elements (Zn, P and S) on the tribofilm which are originated from ZDDP.

The effect of ageing oil with no CBP on tribofilm chemistry is demonstrated in Figure 18a$_2$, the result shows a significant reduction in P and S atomic concentration with the absence of Zn on tribofilm. This correlated to additive depletion and oil degradation during the ageing process at high temperature. The result from the aged oil with 0.75wt%CBP after centrifugation in Figure 18a$_3$ indicates the absence of all elements of tribofilm. This result confirms that both additive adsorption on CB particles and oil degradation reduce the ability of lubricant to protect the contact surfaces.

Elements/Wt% **EDX**

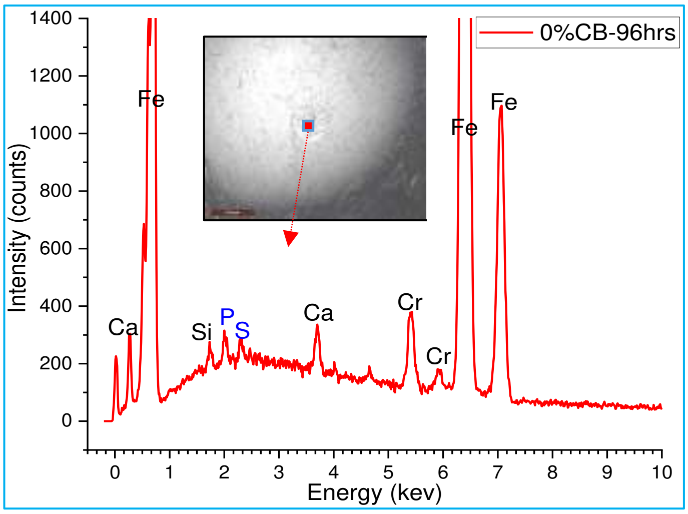
a$_1$

Element	Wt.%
Fe	71.38
O	5.83
Si	4.29
P	3.04
S	3.85
Ca	2.52
Cr	5.01
Zn	4.08
Total	100



a$_2$

Element	Wt.%
Fe	89.84
O	3.81
Si	0.94
P	1.03
S	0.85
Ca	1.52
Cr	2.01
Zn	0
Total	100



a_3

Element	**Wt.%**
Fe	93.55
O	2.61
Si	0.71
P	0
S	0.02
Ca	2.52
Cr	0.59
Zn	0
Total	100

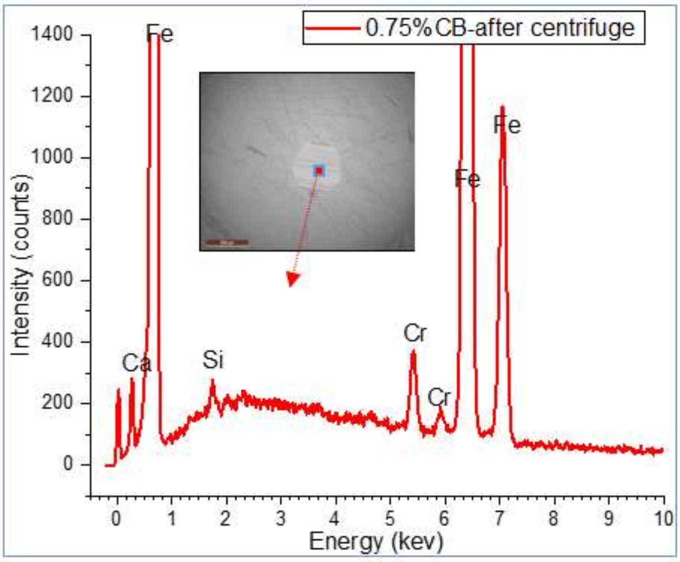


Figure 18: SEM/EDX to identify the chemical composition of tribofilm of wear scar on pins a_1 fresh oil, a_2 aged oil for 0wt% CB-96hrs, a_3 aged oil containing 0.75wt% CB-after centrifuge

4. Conclusions

In the current study, the effect of CBP contaminant at varying levels has been investigated. It was observed that adding CBP to FFO at ageing condition affected the engine oil performance as expected. The results proved that removing the CBP from oils will certainly improve the performance of the oil and reduce the wear caused by CBP significantly. It is worth noting that the oil performance after the removal of CBP is still not as good as the fresh oil. This is due to the fact that the aged oil after removing the CB is experiencing other problems such as additives depletion, additive adsorption and degradation products in oils that influence the performance of the oil. The main conclusions are:

- Ageing the oil results in the decomposition of antiwear additive as shown in the FTIR results.
- Chemical analysis of oils using FTIR revealed the formation of degradation products depending on the amount of CBP presented in the oil.
- Additives are adsorbed on CBP. ICP analysis of the oil shows a reduction in the elemental concentration of additives that originate from antiwear and detergent/dispersant additives.
- Friction, in the presence of a high level of CBP, increases at the beginning of the tests due to the high impact of oil starvation on the inlet of contact surfaces and then decreases over the remaining duration of the test.
- Wear increases with an increase in the CBP level in aged oil. However, the oils after removing CBP show a significant reduction in wear. The aged oils after removing CB perform higher wear compare to the wear of fresh oil due to additive adsorption and oil degradation.

- Chemical composition of tribofilm shows a significant decrease in antiwear elements' concentration after the oil was aged for 96hrs. Whilst the chemical composition of tribofilm of aged oils after centrifuge 0.75wt%CBP demonstrates the absence of antiwear elements.

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6. Declaration of Interest Statement

There were no conflicts of interest.

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