# FISEVIER

#### Contents lists available at SciVerse ScienceDirect

#### Wear

journal homepage: www.elsevier.com/locate/wear



## The role of soot particles in the tribological behavior of engine lubricating oils



Enzhu Hu<sup>a</sup>, Xianguo Hu<sup>a,\*</sup>, Tianxia Liu<sup>a</sup>, Ling Fang<sup>a</sup>, Karl D. Dearn<sup>b,\*\*</sup>, Hongming Xu<sup>a,b</sup>

- <sup>a</sup> Institute of Tribology, Hefei University of Technology, Hefei 230009, PR China
- <sup>b</sup> School of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

#### ARTICLE INFO

Article history: Received 22 January 2013 Received in revised form 3 May 2013 Accepted 10 May 2013 Available online 22 May 2013

Keywords: Soot Wear Sliding friction Lubricant Tribochemistry

#### ABSTRACT

This paper describes a study of the influence of soot contamination on the tribological behavior of engine lubricants. The candidate lubricants were a formulated engine lubricant, (CD SAE 15W-40) and a base oil (150SN). Soot particle contamination was simulated using carbon black with friction and wear measured using a four-ball tribometer. The results show that the antiwear and antifriction properties of the CD SAE 15W-40 formulated oil with varying carbon black contents were better than those of 150SN base oil. The antifriction properties of the SAE 15W-40 formulated oil with the addition of 2 wt% carbon black were strengthened. This was ascribed to uniformly dispersed carbon black and the additives in the CD SAE 15W-40. The antifriction properties of the 150SN base oil with 2, 4 wt% carbon black content were upgraded via the addition of 2 wt% dispersant polyisobutylene succinimide. The tribological effect of the carbon black in the lubricants was attributed to absorption and agglomerate effects.

© 2013 Published by Elsevier B.V. Open access under CC BY license.

#### 1. Introduction

Fuels derived from biological sources, such as biodiesel, bioethanol, 2, 5-dimethylfuran and other biomass fuels, have become an established means of reducing exhaust gas emissions and breaking our dependence on fossil fuels. Extensive research on these fuels has been conducted for both spark and compression ignition engines and covers, for example, combustion characteristics, emissions and physical and chemical properties [1–3].

Engines powered by these fuels can benefit from reduced emissions and improved fuel economy, however, the generation of soot is a by-product of the combustion process that cannot easily be eliminated. Most of the soot generated during the combustion process is exhausted however it can also contaminate the lubricating oil within the sump as a result of blow-by gasses. This can be worsened when exhaust gas recirculation (EGR) is employed [4–6]. Soot contamination of the lubricating oil can lead to increased wear in critical components as well as shortening of oil life and increased frequency of oil changes [7]. Hence the importance of understanding the effects of soot contamination on the lubricating oil is highlighted.

Soot contamination therefore presents a potentially serious issue and so is well researched with interest from engine manufacturers and lubrication producers. Engine soot is most damaging

k.d.dearn@bham.ac.uk (K.D. Dearn).

to the engine bearings, camsvalve train, piston rings, cylinder liners, etc. [8]. The nature of contacts nature of the tribological contacts in these components includes of bearings, cams, piston rings and cylinder liners were point-point, rolling/sliding, point and elliptical contact and reciprocating flat-on-flat. The operating lubrication regimes for these components are possible boundary lubrication or liquid full film lubrication and these are dependent on that was decided by the kinematic viscosity of lubricant, applied load, lubricants, surface roughness, etc. As such there are many different theories regarding the properties, formation and effects of soot particulates on the performance of a lubricating oil (i.e. the reduction of friction and the subsequent wear mechanisms). Ryason et al. [9] concluded that soot particles were abrasive based on observed scars and debris generated between metallic test surfaces. However, experiments conducted by Rounds [10] using contaminated oil from a diesel engine showed that the soot reduced the effectiveness of the antiwear additive by preferentially adsorbing the active antiwear additive components before they can form the essential antiwear surface coating. This is rather than removing the surface coatings by abrasion after they are formed. The collection of soot particles to evaluate their tribological properties is very time consuming and difficult, besides the difficulty in producing reliable data lies with reproducing soot with consistent properties for use in contamination tests. To negate these, several studies have been conducted using carbon black, simulating engine derived soot. Ratoi et al. [11] showed that carbon black dispersed in an engine oil rapidly removed ZDDP reaction films by abrasion. However, this removal could be limited (and even eliminated) by the choice of dispersant additive.

<sup>\*</sup> Corresponding author. Tel.: +86 551 6290 1359. \*\* Corresponding author. Tel.: +44 121 414 4190.

E-mail addresses: xghu@hfut.edu.cn (X. Hu),

$W$ Contact load, N $h_{\text{mean}}$ Mean oil film thickness, m $k$ Ellipticity parameter, $k=1.03$ $h_{\text{min}}$ Minimum oil film thickness, m $N_{\text{A}}$ Acidic sites, megg <sup>-1</sup>	<sup>-8</sup> m <sup>2</sup> /N Pa <sup>-1</sup>
$h_{\min}$ Minimum oil film thickness, m $N_{\rm A}$ Acidic sites, meqg <sup>-1</sup>	
$h_{\min}$ Minimum oil film thickness, m $N_A$ Acidic sites, meqg <sup>-1</sup>	
$\eta_0$ Viscosity of the lubricant, $\eta_0 = v\rho$ , Pa s $N_{\rm B}$ Basic sites, megg <sup>-1</sup>	
R Radius of curvature, m $C_{Area}$ Concentration of basic sites per area sites,	
$U$ Entraining surface velocity, m s <sup>-1</sup> $O_{Area}$ Concentration of oxygen atoms per area a	toms, nm <sup>-2</sup>
E Young's modulus, $E=210$ GPa Pa A Specific surface area, $m^2g^{-1}$	

Joly-Pottuz et al. [12] described experiments where carbon black particles were shown to be highly abrasive between steel surfaces with increases in wear and friction. In contrast, they also found that the addition of carbon onions in a lubricant led to a reduction of both friction and wear compared to base oil. Olomolehin et al. [13] found that the combination of an alkyl ZDDP and carbon black produced aggressive wear in test samples. They showed that a lubricant containing carbon black and a ZDDP additive led to considerably more wear than if ZDDP was left out.

Green et al. [14,15] showed that wear of steel contacts either decreased or remained constant when the lubricating oil contained carbon, but this was dependent on the oil formulation. They associated the abundance of amorphous carbon and the amount of antiwear film components on a surface with higher rates of wear. Antuscha et al. [16] found that wear did not depend on the mechanical properties of different soot particles, but was closely related to their reactivity and the amount of defect sites on the

surface of the test specimens. A new wear model for Otto soot was proposed.

The importance of oil additives in the performance of engine oil and the correlation with wear as a result of soot contamination are highlighted above. However, the actual mechanisms of wear induced by the soot, and how these changes in the presence of oil additives are not clear. This paper describes a series of experiments designed to address this deficiency by describing a systematic approach to establish basic wear data and subsequently methods for optimizing engine oil for component durability.

#### 2. Experimental

#### 2.1. Materials and samples preparation

A commercially available carbon black (Cabot N660R) was purchased from Shanghai Cabot Chemical Industry Co., Ltd.,

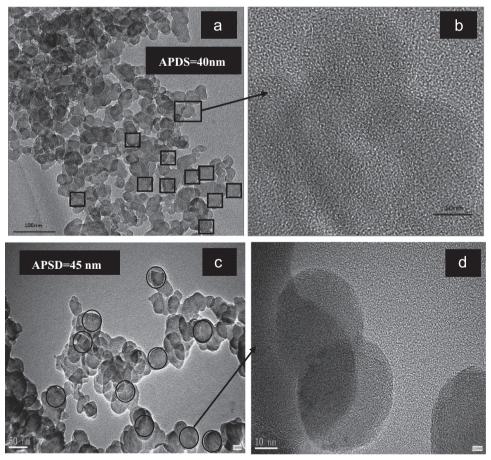


Fig. 1. HRTEM images of the carbon black and engine soot (a) and (b) carbon black, and (c) and (d) engine soot.

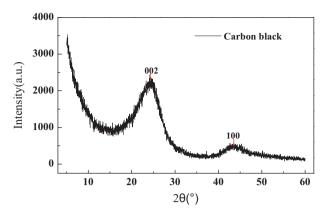


Fig. 2. XRD analysis of carbon black particle

**Table 1**Acidic and basic sites of carbon black.

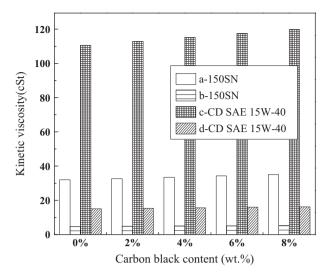
Sample	N <sub>A</sub> (meqg <sup>-1</sup> )	N <sub>B</sub> (meqg <sup>-1</sup> )	C <sub>Area</sub> (sites nm <sup>-2</sup> )	O <sub>Area</sub> (atoms nm <sup>-2</sup> )	A (m <sup>2</sup> g <sup>-1</sup> )
Carbon black	0.0210	0.0216	0.0803	0.5180	162.0046

**Table 2**Physic–chemical properties of base oil and engine oil.

Items	150SN	CD SAE 15W-40
Density (kgm <sup>-3</sup> )	0.90	0.85
Viscosity index	103	142
Sulfur content (wt%)	1.5%	2.5%
Water (m/m)%	Trace	Trace
Pour point (°C)	-15	-24
Basic number (mgKOHg <sup>-1</sup> )	-	10.5

(China) as an engine soot alternative. The efficacy of the carbon black as an engine soot substitute was tested against actual soot generated from the combustion of diesel (purchased from the Hefei Petrochemical Company of China). The mean particulate diameters of each are shown in Fig. 1. The carbon black average particulate diameter was 40 nm and the engine soot was 45 nm. These were measured using a high resolution transmission electron microscopy (HRTEM, JEOL-2010). The XRD analysis results showed that the carbon black was a low graphite-like material, as shown in Fig. 2 [17]. The acidic and basic sites were calculated by titration using the methods suggested by Darmstadt and Roy [18] and Barton et al. [19]. An automatic surface area and pore rate analyzer (TRISTAR II3020-M) was utilized to measure the Brunauer–Emmett–Teller (BET) surface area (A) and pore rate of the carbonaceous materials. The results are shown in Table 1.

A base oil (150SN—Changzhou Qingbang Company) and a formulated engine lubricant (CD SAE 15W-40—Sinopec Lubricant Company) were used for this investigation. A dispersant—Polyisobutylene succinimide (T154 supplied by the Shanghai Demao Chemical Co., Ltd.) was utilized to investigate the behavior of the carbon black agglomerated in base oil. The dispersion phenomenon was also investigated for 4 wt% carbon black in the 150SN base oil during the rubbing process. A dispersant named polyisobutylene succinimide (T154—Shanghai Demao Chemical Co., Ltd.) was utilized to investigate the possibility of carbon black agglomerated behavior in base oil. The dispersion phenomenon of 4 wt% carbon black in the 150SN base oil was also investigated during rubbing process. Their physical and chemical properties are



**Fig. 3.** Variation of kinetic viscosity of two oil samples as a function of carbon black content and temperature (40 and 100  $^{\circ}$ C) (a) 40  $^{\circ}$ C—150SN (b) 100  $^{\circ}$ C—150SN (c) 40  $^{\circ}$ C—CD SAE 15W-40 (d) 100  $^{\circ}$ C—CD SAE 150W-40.

shown in Table 2. The other reagents (such as acetone and ethanol) were of analytical grade. There are three main methods to evaluate the lubrication properties of engine oil viz., the high frequency reciprocating rig (HFRR), scuffing load ball-on-cylinder lubricity evaluator (SLBOLE) and four ball tester. The four ball tester was utilized in this study with the contact geometry simulating the contact of steel ball bearings in an engine [10]. The tribological tests were conducted using a four-ball tribometer. The steel balls (Ø12.7 mm) used were fabricated according to the standard GB T308-2002, using ASTM E52100 bearing steel with a surface roughness (Ra) of 0.032 µm and elastic modulus of 205 GPa. Carbon black was added into the oil and lubricant at mass percentages of 0.0, 2.0, 4.0, 6.0, 8.0 wt%. This was then distributed using an ultrasonic bath (model KQ-300VDE) for 30 min to reduce experimental deviation. The kinematic viscosities of oil samples were measured using a viscosity meter (BF-03A) at 40 °C and 100 °C, and the results are shown in Fig. 3.

#### 2.2. Characterization

The tribological tests were conducted at room temperature (approximately 25 °C) according to ASTM D5183-2005. The wear and friction properties of lubricating oils containing carbon black were investigated at a rotational speed of 1450 rpm and a load 147 N (Maximum Hertzian contact pressure of 2.51 GPa) for 30 min. The effects of load and speed on the tribological behaviors of carbon black contaminated oils were also investigated. The wear scar diameters of the steel balls were observed by optical microscopy (LY-WN-HPCCD). The wear traces and extracted carbon black including wear debris were investigated by scanning electron microscope/energy dispersive X-ray analysis (SEM/EDS, JEOL Model JSM-6490) and Raman spectroscopy (RS, LabRAM-HR; resolution=  $0.6 \text{ cm}^{-1}$ , scanning repeatability =  $\pm 0.2 \text{ cm}^{-1}$ ). The surface roughness  $(R_a)$  of the worn zones was measured using a surface profiler (Model Taylor-Hobson-6). In order to obtain sufficient data to clarify the tribological mechanisms of engine soot, the measurements from the above were combined with oil film thickness calculations according to the following equations [20]:

$$\frac{h_{\text{mean}}}{R} = 2.69 \left(\frac{U\eta_0}{ER}\right)^{0.67} (\alpha E)^{0.53} \left(\frac{W}{ER^2}\right)^{-0.067} (1 - 0.61e^{-0.73k})$$
 (1)

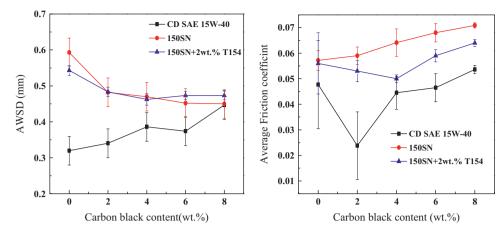


Fig. 4. Variation of the average wear scar diameter and average friction coefficient of the engine lubricant and base oil with increasing contents of carbon black (note: test conditions were 1450 rpm and 147 N for 30 min )

$$\frac{h_{\min}}{R} = 3.63 \left(\frac{U\eta_0}{ER}\right)^{0.68} (\alpha E)^{0.49} \left(\frac{W}{ER^2}\right)^{-0.073} (1 - e^{-0.68k})$$
 (2)

#### 3. Results and discussion

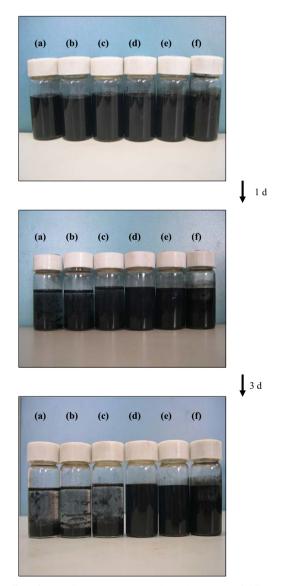
#### 3.1. Effect of soot concentration on wear and friction

Fig. 4 shows the effects of carbon black concentration on the wear (given as the average wear scar diameter (ASWD)) and friction in the test samples.

For the 150SN base oil, the ASWD decreased with carbon black concentration from 0.593 mm at 0 wt% to 0.450 mm at the maximum 8 wt%. When the T154 dispersant (2 wt%) was added to the 150SN base oil, the AWSD showed a similar pattern.

The average friction coefficient increased proportionally with carbon black concentration for the same range of contamination. The average friction coefficient was shown to decrease at a carbon black content of 2 and 4 wt% in the 150SN base oil with 2 wt% dispersant (T154). The results indicate that the dispersion rate of the carbon black has an important role in reducing friction with the 150SN base oil. In all, the variation of AWSD and average friction coefficient of 150SN base oil showed that engine soot increased the wear resistance, but decreased its anti-frictional properties. The increased antiwear property can be attributed to the reduced load carrying capacity of the carbon black during the friction process and the improved antifriction property was attributed to the uniform dispersion.

Fig. 4 shows that for the CD SAE 15W-40 lubricating oil, carbon black contamination had the opposite effect on the AWSD than above, increasing from 0.319 mm (at 0 wt%) to 0.447 mm (at 8 wt%). This increase is the result of carbon black agglomeration and the effects of absorption. The friction coefficient decreased with the addition of carbon black at 2.0 wt%. This effect corresponded to the deduced nano-scale efficacy of the carbon black particle diameter which was uniformly dispersed throughout the lubricant. The friction coefficient decreased when 2 wt% dispersant was added to the 2, 4 wt% carbon black content in 150SN base oil. The results prove that the low content of carbon black can strengthen the antifriction properties of different lubricants. The experimental results show similar trends to the results of Green et al. [14]. Beyond 2 wt% concentration in CD SAE 15W-40, the average friction coefficient increased owing to the agglomeration of carbon black and the resulting abrasion. The agglomerated phenomenon can be indirectly attributed to the effect of the dispersant (T154) on the agglomeration



**Fig. 5.** Effect of 2 wt% dispersant (T154) on the agglomeration of different carbon black contents in the 150SN oil that has been left to stand for 1 day and 3 days. (a) 2 wt% carbon black without dispersant, (b) 1 wt% carbon black without dispersant, (c) 3 wt% carbon black without dispersant, (e) 1 wt% carbon black with dispersant, (e) 1 wt% carbon black with dispersant and (f) 3 wt% carbon black with dispersant.

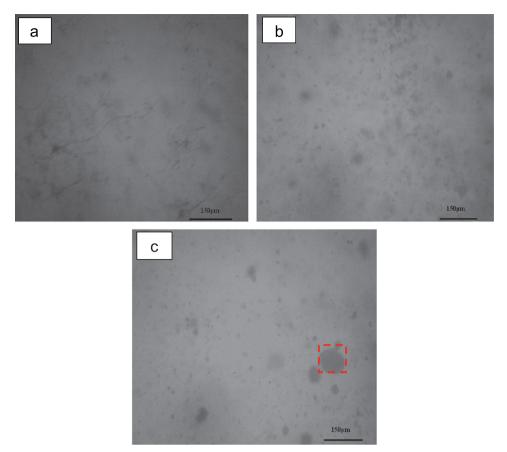


Fig. 6. Optical microscopic images of soot aggregation in 150SN oil with 4 wt% carbon black during the rubbing process (a) initial, (b) 15 min and (c) 30 min.

of 4 wt% carbon black in the 150SN oil. This issue is supported by Fig. 5, which shows the effect of 2 wt% dispersant (T154) on the agglomeration of different carbon black contents in the 150SN stand that has been left to stand for 3 days. It can be clearly seen that the carbon black does not settle at the bottom of the vessels when the dispersant is added.

Fig. 6 shows the soot aggregation in 150SN with 4 wt% carbon black at various stages during the rubbing process. This clearly indicates that the diameter of carbon black particles can increase up to  $100\,\mu m$  due to the agglomeration phenomenon during the tribological process. In addition to these results, the higher kinematic viscosity of engine lubricant compared to the base oil is likely to have contributed to the variation of the AWSD and friction coefficient between the lubricating fluids and the quality of formed oil films [21]. This is further explored in Section 3.4.

#### 3.2. Effect of load and rotation speed on wear and friction

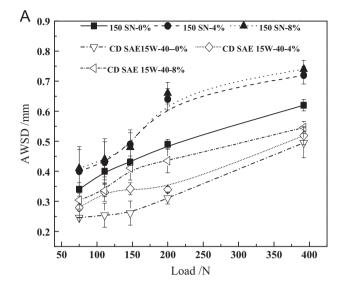
Increasing the load and rotational speed has been shown to effect oil film formation between the contacts [22], which in turn affects the development of friction and wear. Three levels of carbon black concentration (0.0 wt%, 4.0 wt% and 8.0 wt%) were chosen to investigate these effects. Other contamination levels were omitted in order to obtain a good spread of results (based on those given in Fig. 4) between the test oils.

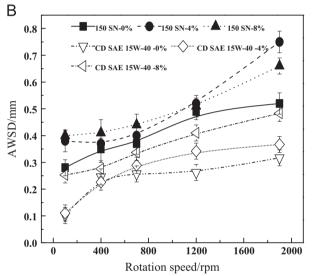
Fig. 7(A) shows that the AWSD increases proportionally with load for the two test oils with the AWSDs of the 150SN base oil larger than those of CD SAE 15W-40 for the same given conditions. This is in agreement with Section 3.1, and is the result of a decrease in oil film thickness with increasing load. The difference

between the oils is also likely to be effected by carbon black absorption and the abrading effect of the contaminants. The elemental composition of the extracted carbon black could be used to expound the absorption effect of contaminants and is shown in Table 3.

Fig. 7(B) shows a proportional increase in AWSD with rotational speed for both oil samples, possibly due to an increasing entrainment force resulting in oil film breakout. For the CD SAE 15W-40, when the carbon black content was over 8.0 wt%, the AWSD increased suddenly under a 147 N load at 2000 rpm. The reason for this is likely to be caused by carbon black abrasion causing the oil film between contacts to breakdown [23]. Generally, for both lubricants the AWSD displayed a proportional relationship with increasing load and rotation speed, and hence oil film thicknesses decreased [24]. The principle wear mechanism observed was that of abrasion caused by the carbon black particles, although the severity of the wear was less for the base oil than the CD SAE 15W-40, a result of formulation.

The effects of increasing rotational speed on the average coefficient of friction are shown in Fig. 8 (with contamination levels of 0.0, 4.0 and 8.0 wt%). It shows that friction was higher in the base oil than that of the formulated lubricant. The variation between the different contamination levels was generally low, except in the case of the CD SAE 15W-40 oil with 8.0 wt% carbon black at a rotational speed of 1200 rpm. In general, the entraining force increases with the increase of rotation speed. At these conditions, the entraining force through the contact may have been strong enough to break the oil film formation. The large increase in friction at 8.0 wt% may also be the result of the carbon black absorbing more lubricant additives, reducing anti-frictional properties.





**Fig. 7.** Effect of load and rotation speed on the wear properties of two oil samples containing different carbon black contents (A: load effect and B: rotation speed effect).

**Table 3** EDS analysis of element contents of extracted carbon black particles.

Items	Addition (wt%)	Element content (wt%)							
	( VV L/0 )	С	0	Fe	Zn	P	S	Mg	Ca
150SN CD SAE 15W-40	4 4		44.42 37.94	-	- 0.52	- 0.50	2.06 1.09	- 0.31	- 0.29
	8	66.05	30.60	-	1.03	-	1.14	0.26	0.66

### 3.3. Morphology, component and structure analysis of frictional surfaces

The morphology, elemental composition, structure of wear scar and wear debris generated as a result of simulated soot contamination was assessed. For the 150SN base oil, 4.0 wt% carbon black contamination was selected for further examination based on the results given in Section 3.1. The results of the SEM examination and EDS analysis are shown in Fig. 9. For CD SAE 15W-40, the carbon black at 8.0 wt% was selected for detailed analysis as this

level of contamination was shown to provide the optimum antiwear benefit. Results of the analysis are shown in Fig. 10.

The surface morphology from the surfaces of the steel test samples shown in Fig. 9 display many furrowed wear tracks indicating significant abrasive wear. The width of the tracks are each approximately 2–3  $\mu m$  wide. When carbon black is added to the oils, it can be seen (Fig. 9(a)) that along with the wear tracks, the morphology of the surface also displays signs of galling. Hence, adhesive wear and plastic deformation on a micro-level had occurred which indicates oil starvation of the contact. This will have resulted in the generation of increased wear debris on the contact surfaces, evident in the EDS analysis. This shows that elemental carbon was elevated on the surface in the contaminated sample. The results given in Fig. 9 help explain why the AWSD of the 150SN base oil decreased with increasing carbon black contamination levels along with increasing friction levels.

The topography and morphological analysis of the CD SAE 15W-40 formulated oil are shown in Fig. 10(a). The wear trace for uncontaminated oil shows some light abrasion. At 4 wt % contamination, abrasive damage increased along with the addition of some debris at the periphery of the wear scar, which may be the result of carbon black or oil deposits. EDS analysis of this area indicated that there were components of carbon black and additives such as ZDDP containing sulfur and phosphor elements. Deposits increased with carbon black contamination as shown in Fig. 10 (c and d), such that the steel ball surface appeared to be polished, with a very low surface roughness ( $R_a = 0.043 \mu m$ ). This phenomenon was ascribed to the packing of carbon black into the wear traces and also being absorbed on the surface. This can be verified by the elevated carbon elements on the wear surface. There was also further surface damage observed in this specimen. Fig. 10(d) shows a large wear scar like chip at the center of the wear trace, which has occurred by fatigue under high rotational speed. The carbon black contamination at this level will also have absorbed many of the components of CD SAE 15W-40 additives. This promotes tribological chemical reactions that degrades the lubricating oil, and enhances corrosion wear [25].

Fig. 11 shows the Raman spectra observed from the wear trace surface of steel ball in the CD SAE 15W-40 formulated oil with  $\lambda_0$ =514 nm. The first-order spectra of carbon generally exhibited two broad and strongly overlapping peaks with intensity maxima at 1350 cm<sup>-1</sup> (D peak) and 1580 cm<sup>-1</sup> (G peak). The D peak (1350 cm<sup>-1</sup>) is attributed to the disordered graphitic lattices, and the G peak (1580 cm<sup>-1</sup>) is attributed to the ideal graphitic lattices. The two peaks were very weak without carbon black, but both were strengthened when carbon black was added to the oil. This was particularly the case for the strength of peak (1580 cm<sup>-1</sup>) in the wear trace generated by the 4.0 wt% carbon black sample. This indicates that the carbon black possessed the necessary lubrication properties that themselves are dependent on the degree of ordered graphite [26,27].

#### 3.4. Tribological mechanism analysis

The most common tribological mechanism of wear in soot contaminated oil is abrasion. However, there will be many other mechanisms present. The abundance of active sites, hardness and chemical bonds of the surface and contaminants will all vary (as is, for example, shown by the acidic and basic sites of the carbon black listed in Table 1). There were few additives in the 150SN base oil so the carbon black could absorb molecules of the oil and were able to react with each other to form suspended agglomerate solids. The uniformly dispersed carbon black particulates were free to reduce friction in the contacting pairs during rubbing. However, the agglomerated carbon black particulates were at times large enough to prevent the oil from entering the friction pairs, enabling

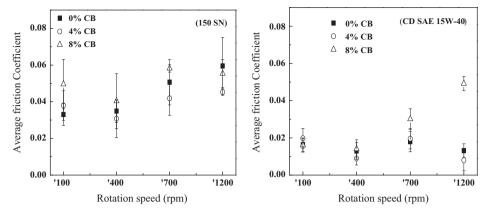


Fig. 8. Effect of rotation speed on average friction properties of two oil samples (load 147N).

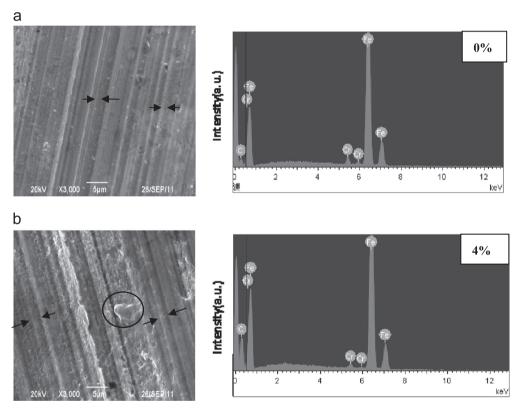


Fig. 9. SEM and EDS analysis of the wear of the steel ball surfaces for 150SN base oil with different carbon black contents (1450 rpm and 147 N for 30 min) (a) 0.0 wt% and (b) 4.0 wt%.

serious abrasive wear to occur. If the carbon black content was low in the oil, it could be uniformly dispersed and hence could play an important role in reducing friction levels. But high carbon black content increased wear as a result of agglomeration and adsorption. The soot should be considered as a third body. In the case of the carbon black used in these experiments, the frictional mechanism could be deduced as a "roller effect" as a result of the carbon black being dispersed throughout the base oil. A schematic diagram of the friction mechanism is shown in Fig. 12.

The CD SAE 15W-40 results indicated that a competitive absorption effect had occurred between the carbon black and additives of lubricating oil including detergent, dispersant, antiwear, anticorrosion, viscosity index improver and other additives. In general, if only soot particles were to be adsorbed on to the rubbing surface instead of the antiwear additive, it would result in agglomerate formation and progressive wear of engine parts. However, Ratoi et al. [11] reported that the selection of an appropriate dispersant played an important role in uniformly

dispersing soot particulates to avoid such agglomerations and allow antiwear additives to be effective.

The variations in the wear scar and friction coefficient of the two oils with different carbon black contamination levels were attributed to the formation and variation of the formed oil film between the contacting surfaces. The minimum oil film thickness ( $h_{\min}$ ), mean oil film thickness and mean carbon black diameter are compared in Table 4. The  $h_{\min}$  of the CD SAE 15W-40 formulated oil was approximately twice than that of 150SN base oil at the same temperature and friction conditions. This is born out in the experimental results where the AWSDs and friction coefficients of the CD SAE 15W-40 formulated oil were lower than those of 150SN base oil. The uniformly dispersed carbon black particulates may have been tribological useful during the initial rubbing [28–30].

The friction coefficient of the 150SN base oil increased at a higher rate than that of the CD SAE 15W-40 formulated oil which was consistent with the experiment results shown in Fig. 4, with the calculated oil film thickness of the 150SN base oil was lower than that

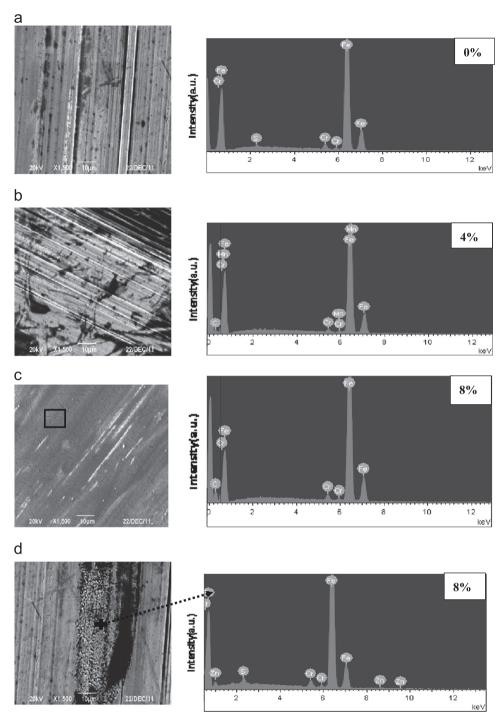


Fig. 10. SEM images and EDS analysis of the wear of the steel ball surfaces for the CD SAE 15W-40 formulated oil with different carbon black contents (1450 rpm and 147 N for 30 min).

of the CD SAE 15W-40 formulated oil. In the formulated oil, the presence of additives promoted an increase in the oil film thickness. When the carbon black content was 2.0 wt%, the friction coefficient decreased, it is at this concentration that the oil film thickness is larger than the diameter of carbon black particles. With the increase in carbon black content in the oil and the subsequent agglomerated effect, the carbon black particle diameter increased such that oil was prevented from entering the contact, increasing the friction coefficient (consistent with the experiment results shown in Fig. 4). The variation of oil film thickness was difficult to observe physically. However, the oil film thickness increased with the kinematic viscosity of lubricating oil [21], as shown in Fig. 13.

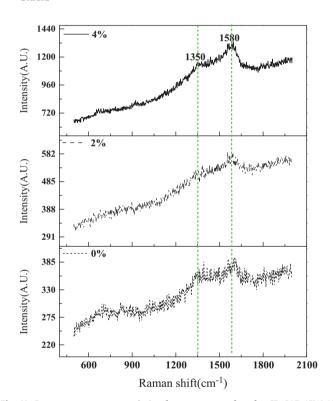
Overall, carbon black particles were shown to play a variety of roles in the wear and friction properties of the lubricants used in these experiments. The tribological mechanisms can be summarized as

- The simulated soot absorbed additives and oil molecules to form mixtures and agglomerates.
- The agglomerates prevented fresh oil entering the contact surfaces resulting in starvation.
- The process can be verified by the oil film thickness.
- The formation of mixtures and agglomerates depended on the components of lubricating oil.

#### 4. Conclusions

This paper describes a series of experiments designed to assess the performance of simulated soot (carbon black) contaminated engine oil, while carbon black is not identical with soot from fired engines, the results reported and discussed here are felt to provide useful insights on the role of such carbon particles in oil. In particular, the mechanisms of wear induced by the soot, and how these changes in the presence of oil additives have been described. A systematic approach has been established to extract basic wear data and this can be used subsequently to optimize engine oils for component durability. The following conclusions can be drawn from this research:

- (1) The antiwear and antifriction properties of the CD SAE 15W-40 formulated lubricant at all levels of contamination were better than those of 150SN base oil. This improvement in tribological terms is a result of the synergetic effect of the additives.
- (2) For the CD SAE 15W-40 formulated lubricant, the friction coefficient decreased to a contamination level of 4 wt%. This phenomenon was ascribed to uniformly dispersion of carbon black.



**Fig. 11.** Raman spectroscopy analysis of wear trace surface for CD SAE 15W-40 formulated oil. (Load 147N, rotation speed 1450 rpm for 30 min).

(3) The wear resistance and frictional properties of the 150SN base oil with 2, 4 wt% carbon black contents were improved by the addition of the T154 dispersant.

**Table 4**The formation of oil film thickness of two oils under different temperatures (load 147 N and rotation speed 1450 rpm).

Items	150SN Temperature (°C)		CD SAE 15W-40 Temperature (°C)	
	40	100	40	100
Kinematic viscosity (cSt)	32.00	4.80	110.60	15.02
Mean oil film thickness (nm)	48.48	13.38	107.1	28.1
Minimum oil film thickness (nm)	30.42	8.26	68.35	17.58
Mean soot diameter (nm)	40.00	40.00	40.00	40.00

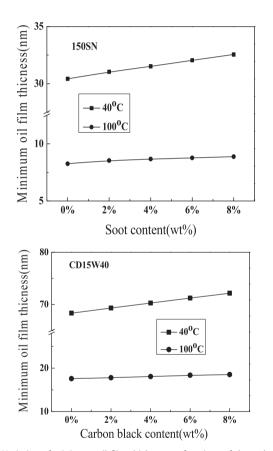


Fig. 13. Variation of minimum oil film thickness as functions of the carbon black content and temperature (40 and 100  $^{\circ}\text{C})$ 

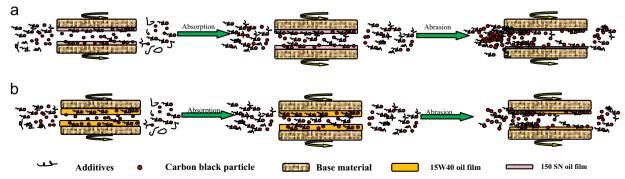


Fig. 12. Schematic of tribological mechanism of simulated engine soot for two oil samples (a) 150 SN and (b) CD SAE 15W-40.

(4) The principal tribological mechanism of the simulated engine soot was attributed to absorption and agglomerate effects with the tested lubricants.

#### Acknowledgments

The authors wish to express their thanks to Professor Xifeng Zhu from University of Science and Technology of China for his helpful discussion in the experimental work. The financial support from the National Natural Science Foundation of China (Grant no. 51275143), National High Technology Research and Development Program of China (863 Program) (Grant no. 2012AA051803), EPSRC Project(Grant no. EP/F061692/1) and The Royal Academy of Engineering—Distinguished Visiting Fellow Scheme are also gratefully acknowledged.

#### References

- E. Hu, X. Hu, X. Wang, Y. Xu, K.D. Dearn, H. Xu, On the fundamental lubricity of 2, 5-dimethylfuran as a synthetic engine fuel, Tribology International 55 (2012) 119–125.
- [2] S.K. Hoekman, C. Robbins, Review of the effects of biodiesel on NOx emissions, Fuel Processing Technology 96 (2012) 237–249.
- [3] D. Nguyen, D. Honnery, Combustion of bio-oil ethanol blends at elevated pressure, Fuel 87 (2008) 232–243.
- [4] S. Aldajah, O.O. Ajayi, G.R. Fenske, I.L. Goldblatt, Effect of exhaust gas recirculation (EGR) contamination of diesel engine oil on wear, Wear 263 (2007) 93–98.
- [5] S.K. Singh, A.K. Agarwal, M. Sharma, Experimental investigations of heavy metal addition in lubricating oil and soot deposition in an EGR operated engine, Applied Thermal Engineering 26 (2006) 259–266.
- [6] K. Ishiki, S. Oshida, M. Takiguchi, M. Urabe, A Study of Abnormal Wear in Power Cylinder of Diesel Engine with EGR-Wear Mechanism of Soot Contaminated in Lubricating Oil, SAE Technical Paper 2000-01-0925.
- [7] D.A. Green, R. Lewis, R.S. Dwyer-Joyce, Wear of Valve Train Components due to Soot Contaminated Lubricant, SAE Technical Paper 2006-01-1098.
- [8] M. Soejima, Y. Ejima, K. Uemori, M. Kawasaki, Studies on friction and wear characteristics of cam and follower: influences of soot contamination in engine oil, JSAE Review 23 (2002) 113–119.
- [9] P. Ryason, I. Chan, J. Gilmore, Polishing wear by soot, Wear 137 (1990) 15-24.
- [10] F.G. Rounds, Soots from Used Diesel Engine Oils: Their Effects on Wear as Measured in Four Ball Wear Tests, SAE Technical Paper 810499, 1981.
- [11] M. Ratoi, R.C. Castle, C.H. Bovington, H.A. Spikes, The influence of soot and dispersant on ZDDP film thickness and friction, Lubrication Science 17 (2004) 25–43.

- [12] L. Joly-Pottuz, N. Matsumoto, H. Kinoshita, B. Vacher, M. Belin, G. Montagnac, J.M. Martinb, N. Ohmae, Diamond-derived carbon onions as lubricant additives, Tribology International 41 (2008) 69–78.
- [13] Y. Olomolehin, R. Kapadia, H. Spikes, Antagonistic interaction of antiwear additives and carbon black, Tribology Letters 37 (2009) 49–58.
- [14] D.A. Green, R. Lewis, Effect of soot on oil properties and wear of engine components, Journal of Physics. D: Applied Physics 40 (2007) 5488–5501.
- [15] D.A. Green, R. Lewis, 2008, The Effects of Soot Contaminated Engine Oil on Wear and Friction: A Review", Proceedings of the Institution of Mechanical Engineers Part D Journal of Automobile Engineering 222 (2008) 1669–1689.
- [16] S. Antusch, M. Dienwiebel, E. Nold, P. Albers, U. Spicher, M. Scherge, On the tribochemical action of engine soot, Wear 269 (2010) 1–12.
- [17] E. Hu, X. Hu, T. Liu, Y. Liu, R. Song, Y. Chen, Investigation of morphology, structure and composition of biomass-oil soot particles, Applied Surface Science 270 (2013) 596–603.
- [18] H. Darmstadt, C. Roy, Surface spectroscopic study of basic sites on carbon blacks, Carbon 41 (2003) 2662–2665.
- [19] S.S. Barton, M.J.B. Evans, E. Halliop, J.A.F. MacDonald, Acidic and basic sites on the surface of porous carbon, Carbon 35 (1997) 1361–1366.
- [20] H. Sato, N. Tokuoka, H. Yamamoto, M. Sasaki, Study on Wear Mechanism by Soot Contaminated in Engine Oil (First report: Relation Between Characteristics of Used Oil and Wear), SAE Technical Paper 1999-01-3573.
- [21] A. Dhar, A.K. Agarwal, V. Saxena, Measurement of dynamic lubricating oil film thickness between piston ring and liner in a motored engine, Sensors and Actuators A: Physical 149 (2009) 7–15.
- [22] K. Manabe, K. Nakano, Breakdown of oil films and formation of residual films, Tribology International 41 (2008) 1103–1113.
- [23] M. Fuller, Z. Yin, M. Kasrai, G.M. Bancroft, E.S. Yamaguchi, P. Ryason, P.A. Willermet, Chemical characterization of tribochemical and thermal films generated from neutral and basic ZDDPs using X-ray absorption spectroscopy, Tribology International 30 (1997) 305–315.
- [24] T.C. Jao, S. Li, K. Yatsunami, S.J. Chen, A.A Csontos, J.M. Howe, Soot characterisation and diesel engine wear. Lubrication Science 16 (2004) 111–126.
- [25] A. Liati, P. Dimopoulos Eggenschwiler, J. Czerwinski, P. Bonsack, S. Hermle, Comparative Studies of Particles Deposited in Diesel Particulate Filters Operating with Biofuel, Diesel Fuel and Fuel Blends, SAE Technical Paper 2011-24-0102.
- [26] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in grapheme, Physics Reports 473 (2009) 51–87.
- [27] C. Jager, T. Henning, R. Schlogl, O. Spillecke, Spectral properties of carbon black, Journal of Non-Cystalline Solids 258 (1999) 161–179.
- [28] A.D.H. Clague, J.B. Donnet, T.K. Wang, J.C.M. Peng, A comparison of diesel engine soot with carbon black. Carbon 37 (1999) 1553–1565.
- [29] L. Joly-Pottuz, N. Matsumoto, H. Kinoshita, B. Vacher, M. Belin, G. Montagnac, G. Montagnac, J.M. Martin, N. Ohmae, Diamond-derived carbon onions as lubricant additives, Tribology International 41 (2008) 69–78.
- [30] G. Jiang, G. Li, Tribological behavior of a novel fullerene complex, Wear 264 (2008) 264–269.