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Tribofilm formation and characterization of lubricating oils with biofuel soot and inorganic fluorides

Enzhu Hu[a,b], Karl Dearn[c,*], Bingxun Yang[b], Ruhong Song[b], Yufu Xu[b], Xianguo Hu[b,*]

[a] Department of Chemical and Materials Engineering, Hefei University, 99 Jinxiu Road, Hefei 230601, China
[b] Institute of Tribology, Hefei University of Technology, Hefei 230009, China
[c] Department of Mechanical Engineering, School of Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

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ABSTRACT

A series of tribological experiments have been conducted to characterise and study the formation of tribofilms derived from TiF_3 and FeF_3 catalysts impregnated in soot-contaminated lubricants. Results showed that inorganic fluorides reduced friction and wear in the specimen contaminated lubricants. With the best results observed when TiF_3 was used. There were also indications that the frictional process, when coupled with the fluorides induced a structural change in the soot particles within the contact zones, contributing to the improved tribological performance. The key contributors to the formation of robust tribofilms were adsorption and tribochemical reactions. The better tribological response leads to a method for the design of engine lubricants to mitigate against the effects of soot contamination.

1. Introduction

Biomass pyrolysis fuel is receiving increasingly more attention because of several potentially beneficial characteristics that include a low sulfur content and environmental-friendliness. Refined biomass can be used to prepare emulsified biomass fuel (biofuel), which has been used in diesel engines [1–3]. When used as a combustible fuel, soot is generated, and this can have a negative effect on the tribological surfaces within the engine. Eliminating biomass fuel soot particles (biofuel soot, BS) in diesel engines is extremely difficult. Soot particles can contaminate lubricating oils within the sump through blow-by gases, which can be further worsened by exhaust recirculation systems [4,5]. Engine soot particulates can increase the kinematic viscosity and acid number of a lubricant, as well as promote the appearance of oily slurry in the engine sump, which combined leads to a shortened oil life [6,7]. Moreover, soot particulates can result in an increased wear of critical components, thus indicating the importance of investigating the tribological impact of BS contamination of lubricating oils.

Soot contamination is a serious issue that has been extensively investigated the engine and lubricant industry and academia. Studying soot however is challenging not least because the collection of soot particles from the engine sump is a time-consuming and laborious task. Researchers therefore tend to simulate the soot by using simulated particulates generated from, for example, a diffusion flame or carbon black. These substitute engine soot particles can then be used to study the effects of contamination on the lubrication properties of lubricating oils. However, the differences in the nanostructure, composition and surface functional groups among engine soot [8], carbon black [9] and flame soot [10,11] are likely to result in morphological changes in a state of agglomerates in a lubricant [12], and so may result in a different tribological response of lubricating oils [13]. For example, in previous research, the graphite degree, composition and surface function group (-OH) content of BS particles were higher than those of commercial carbon black [14].

There have been many studies of the tribological mechanisms of soot particles in lubricating oils that have been conducted on a variety of different tribometers, with a variety of lubricants, soot contents and soot types. Green and Lewis [15,16] used carbon black particles as a substitute for engine soot and presented abrasion effects and variations in the lubrication conditions that determined the wear mechanism dominating in specific situations. Others studies also indicated that carbon black rapidly removed tribological films by abrasion [17]. Rounds et al. [18] postulated that the adsorption role mechanism of carbon black resulted in reducing antiwear components in lubricants. These studies indicate that a large number of different wear mechanisms can be observed when carbon black is as a substitute for engine soot when investigating the tribological behaviors of lubricating oils. Antusch et al. [19] measured the mechanical properties of different soot particles and found that they were closely related to their reactivity and the amount of defect sites. George et al. [20] indicated that base

* Corresponding authors.
E-mail addresses: k.d.dearn@bham.ac.uk (K. Dearn), xghu@hfut.edu.cn (X. Hu).

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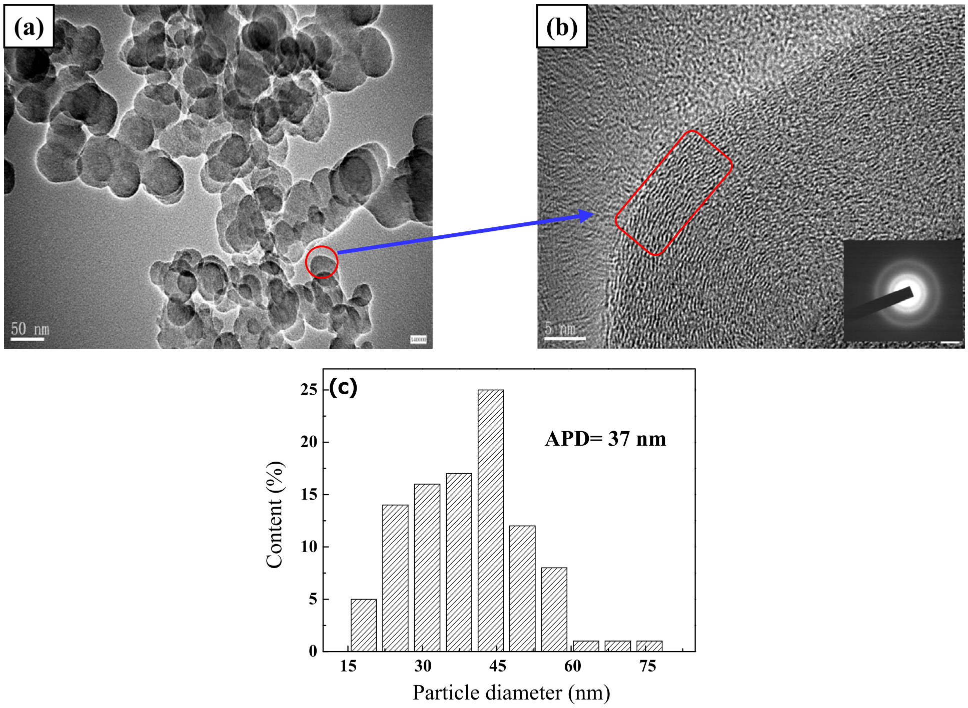

Fig. 1. Morphology and distribution diagram of BS average particle diameter: (a) morphology, (b) diffraction pattern, and (c) distribution diagram of BS particles.

Table 1
Physicochemical properties of liquid paraffin and CD SAE 15W-40.

Item	Liquid paraffin	CD SAE15W-40	Methods
Density (kg/m^3, 20 °C)	880	850	ASTM D4052
Kinematical viscosity (mm^2/s, 40 °C)	100	110.6	ASTM D445
Viscosity index	98	142	ASTM D2270
Sulfur content (wt%)	No	2.5%	ASTM D4294
Phosphorus content (wt%)	No	0.1%	ASTM D1091
Water (m/m) %	Trace	Trace	ASTM D6304
Pour point (°C)	−15	−24	ASTM D9
Flash point (°C)	210	220	ASTM D93
Acid number (mgKOH g^{-1})	0.014	0.035	ASTM D664

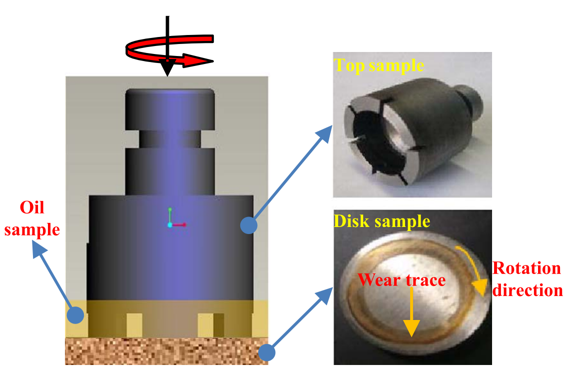

Fig. 2. Schematic diagrams of friction pairs of end-face tribometer.

stock and soot content were the most significant variables affecting wear. However, interestingly some researchers have found that low levels of soot particles can have a beneficial effect on the tribological performance of lubricating oils. Hu et al. [21] revealed that low levels (1 wt%) of carbon black enhanced the antifriction properties of engine lubricating oils using a four-ball tribometer. Liu et al. [22] also indicated that soot (3 wt%) in certain engine oils appeared to act as a friction modifier. Wei et al. [23] prepared candle soot and obtained similarly beneficial tribological results.

The structure and composition of BS particles are different to traditional diesel engine-derived soot particles because of the complicated composition of biomass fuels. There have been few studies to date that have investigated the tribological effect of self-prepared BS and low BS contamination levels on the tribological behaviors of engine oils. The effects of TiF_3 and FeF_3 catalyzing tribofilms in contacts lubricated with different lubricants has been investigated by Nehme [24–26]. They focused on the investigation of the efficacy of TiF_3 and FeF_3 particles, along with polytetrafluoroethylene to zinc dialkyldithiophosphates (often referred to as ZDDP), in promoting the formation of robust anti-wear films, using a sliding ball-on-ring tribometer. Robust material transfer layers and tribochemically formed films are responsible for improving the wear resistance and friction reduction of engine lubricating oils [27]. Mourhatch and Swathe [28,29] used different contact loads and performed several chemical characterization studies to differentiate between tribofilms of lubrication oils with and without FeF_3. Parekh et al. [30] examined the chemical interactions between ZDDP and FeF_3. A new chemical species was detected and was shown to be responsible for improved wear performance. TiF_3 and FeF_3 catalysts are both known to reduce gas emissions and promote ZDDP degradation [31], which could improve the antiwear and antifriction properties of engine oils, as well as reduce sulfur and phosphorous levels.

At present, studies on the use of inorganic fluorides with low content BS contaminated Liquid Paraffin (BS-LP) and fully formulated engine oil are limited. Previous work [32] has shown that TiF_3 can promote anti-wear and anti-friction properties of carbon black contaminated-LP and CD SAE 15W-40 using a four-ball tribometer. This paper describes a study on the formation and characterization of tribofilms from TiF_3 and FeF_3 catalysts (0.5 wt%) on the tribological behaviors of low-content (3 wt%) BS contaminated LP and fully formulated engine oil (CD SAE 15W-40). A series of tribological experiments were conducted using an end-face tribometer to assess the tribological properties of 3 wt% BS-contaminated LP and CD SAE15W-40 with and without 0.5 wt% TiF_3 or FeF_3. A systematic approach was used to establish basic wear data and then a detailed design methodology for the development of optimized engine oil that is