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## Tribological effects of nano-based engine oil diluted with biodiesel fuel

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**Abstract:** The aim of this study was to investigate the tribological effects of nano-based engine oil diluted with biodiesel fuel. The nano-oil was prepared by disperse an optimal composition 0.5 vol.% of 70 nm hexagonal boron nitride (hBN) nanoparticles in diesel engine oil using sonication technique. Sample was diluted by difference percentages of B100 biodiesel fuel in range of 5–20 vol.%. The tribological test was performed using a four-ball tribometer. It was found that the addition of biodiesel fuel increases the coefficient of friction (COF) and seizure wears as compared with nano-oil. However, there is no significant effect on the extreme pressure (EP) properties, where the seizure for all tested samples starts to occur at 981 N.

**Keywords:** nanoparticles; additives; biodiesel fuel; friction coefficient; extreme pressure.

**Reference** to this paper should be made as follows: Abdullah, M.I.H.C., Abdollah, M.F.B., Amiruddin, H., Tamaldin, N. and Mat Nuri, N.R. (2017) 'Tribological effects of nano-based engine oil diluted with biodiesel fuel', *Int. J. Surface Science and Engineering*, Vol. 11, No. 1, pp.12–22.

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## 1 Introduction

Nowadays, many diesel engine manufacturers have implemented what is called post-injection, the introduction of fuel late in the combustion cycle, as part of an advanced control strategy to reduce emissions. However, post-injection of biodiesel blends facilitates dilution of engine oil while interacting with oil additives to potentially accelerate engine wear (Herdan, 2000). Through the slapping motion of the pistons and oil rings, the unburned fuel from post-injection can make its way through the tight, hot quarters between the piston, rings and cylinder walls. The fuel accumulates in the

crankcase and dilutes the oil, which is a major concern regarding engine wear and longevity. With conventional diesel fuel, it can boil out of the lube oil, minimising long-term dilution effects. However, this effect is accentuated with biodiesel because of its high boiling point relative to petroleum diesel, which can lead to a disproportionate amount of fuel being retained in the lube oil.

Wear properties of mineral and fossil-oil lubricant contamination with biofuels have been recently studied using pin-on-disc tribometer by Shanta et al. (2011) and Jech et al. (2008). They tested the effect of different biodiesels on the wear characteristics of biodiesel-contaminated oil. They consistently found that any degree of mineral and fossil-oil dilution by the tested biodiesels can reduce the wear protection properties of the engine oil and subsequently can affect the lubricity of such mixture. According to Yamane et al. (2001), diluted engine oil will weaken lubricant detergency by disrupts the oil film strength causing metal asperities to contact each other which promoting surface wear. This dilution also may affect the oil film thickness which can lead to lubricant regime phase changes. Most of cases happened due to decreases of lubricant thickness/lubricant phase changes will cause catastrophic surface failure. Undesirables wear type and mechanism may occur due to this situation such as abrasive, adhesive or abrasive wear with surface-initiated fatigue.

Besides, some studies have also investigated the chemical and physical properties for biodiesel in mineral oil mixtures, since it can affect engine performance and tribological behaviour. According to Agarwal (2005), the viscosity of the lubricating oil decreased with engine runtime mainly due to increasing fuel dilution by the biofuels. Thornton et al. (2009) evaluated the biodiesel blend effects in oil dilution and on the associated engine performance. They concluded that biodiesel in the engine oil led to enhanced oxidation inside the mixture. It was believed that by using advance additives or nano-oil, problems correspondent to dilute side effect can be monitored and controlled.

Currently, many types of additives including methyl ester and nanoparticle additive (Hasan and Yunus, 2014; Wu et al., 2007; Zhang et al., 2009; Zulkifli et al., 2013; Liew and Dayou, 2014) are introduced in lubricating oil. The presence of these additives in the lubricating oil reduced the friction coefficient, severity of welding and increased the critical load for welding to occur. Besides, the potential of the nano size particle in maintaining the heat stabilising and reduce wear between the engine component has dominantly suitable as friction modifier and antiwear additive, which can boost the performance and increases the engine efficiency.

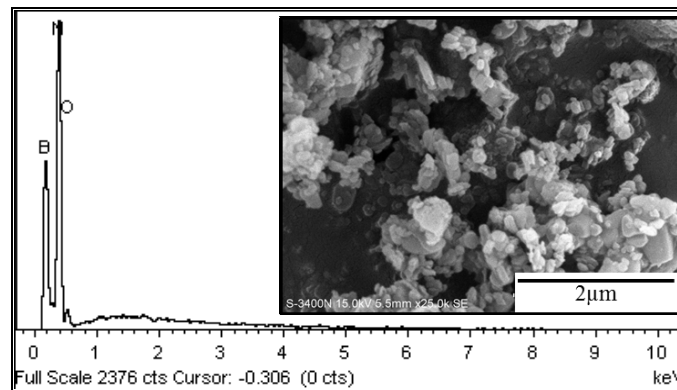
As discussed above, there were only limited laboratory investigations on the tribological properties of typical engine material contacts when they are lubricated by mineral oils contaminated with biofuels. However, the use of nanoparticles as lubricating oil additives to address engine oil dilution caused by biodiesel fuel has not been study yet. Since the engine oil enhanced with boron-based nanoparticles particularly hexagonal boron nitride (hBN) additive work well in preventing the wear and reduce the coefficient of friction (COF) (Abdullah et al., 2014), thus in this study, further investigation of tribological effects of nano-based engine oil diluted with biodiesel fuel were discussed.

## **2 Experimental procedure**

The nano-oil was prepared by dispersing an optimal composition 0.5 vol.% of 70 nm hBN nanoparticles (Figure 1) in 15W40 diesel engine oil using ultrasonic homogeniser

(Sartorius Labsonic P) for 20 minutes. The physical and chemical properties of the hBN nanoparticles are shown in Table 1. The optimal composition was determined from the previous work of Abdullah et al. (2013). Samples were stabilised using a surfactant (oleic acid) to prevent sedimentation of nanoparticles. The surfactant shows no significant effect on the tribological performance of lubricants (Abdullah et al., 2014). Samples were then diluted by four difference percentages of 5%, 10%, 15% and 20% of B100 biodiesel fuel. The viscosity of diluted samples was measured by viscometer.

**Figure 1** The EDX spectrum and SEM image of hBN nanoparticles

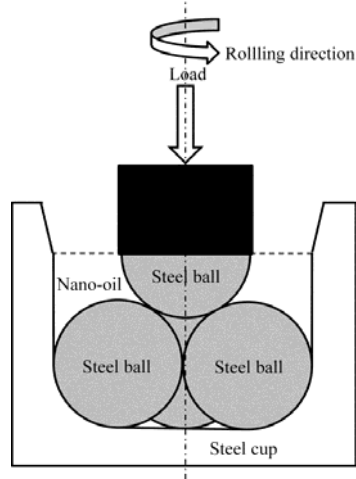


**Table 1** Physical and chemical properties of hBN nanoparticles

Properties <sup>a</sup>	hBN nanoparticles
Appearance	White powder
Chemical formula	BN
Crystal structure	Hexagonal
Melting point, °C	3,000 dissociates
Average diameter particle size, nm	70
Density, kgm <sup>-3</sup>	2.3
Hardness, HRC	40
Maximum use temperature in air, °C	1,000
Thermal conductivity, Wm <sup>-1</sup> K <sup>-1</sup>	27
Thermal expansion coefficient @25°C–1,000°C	1 × 10 <sup>-6</sup> /°C (parallel to press dir.)

Note: <sup>a</sup>From manufacturer.

Tribological tests were performed using a four-ball tribometer (TR 20) according to the ASTM D4172 and D2783 standards (ASTM, 2010, 2009). The schematic diagram of the four-ball tribometer is shown in Figure 2. The COF was measured at the constant speed of 1,200 rpm, load of 392.4 N, time of 3600 secs, and temperature of 75°C. Besides, the series of extreme pressure (EP) tests of 10 sec durations were conducted at increasing load from 196 N to 1,570 N at the constant speed of 1,760 rpm and temperature of 35°C.

**Figure 2** Schematic diagram of a four-ball tester

The four-ball tribometer incorporated three 12.7 mm diameter carbon chromium steel balls, clamped together, and covered with lubricant for evaluation. A fourth steel ball of the same diameter (referred to as the top ball), held in a special collet inside a spindle, was rotated by an AC motor. The top ball was rotated in contact with the three fixed balls that were immersed in the sample oil. The COF was recorded using a data terminal processing system. The wear scar diameter was measured by microscope. The detailed mechanical properties of the balls are shown in Table 2.

**Table 2** Mechanical properties of the ball material

<i>Properties<sup>a</sup></i>	<i>Ball bearing (carbon chromium steel)</i>
Hardness ( <i>H</i> ), HRC	61
Density ( $\rho$ ), g/cm <sup>3</sup>	7.79
Surface roughness ( $R_a$ ), $\mu\text{m}$	0.022

Note: <sup>a</sup>From laboratory measurements.

The surface morphology of worn surfaces was observed and analysed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

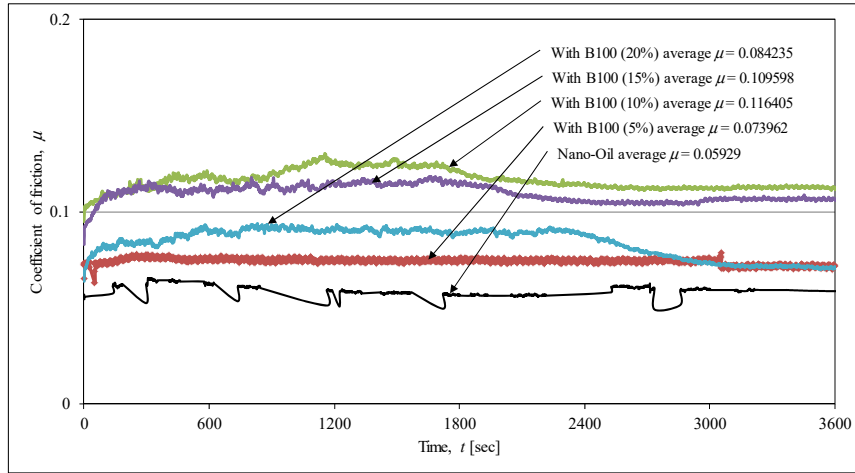
### 3 Results and discussion

#### 3.1 Effect of dilution on COF

From Figure 3, the average COF of nano-oil is the lowest value compared to nano-oil diluted with B100 biodiesel fuel. This might be due to the formation of a tribofilm, which probably arises because this additive can form a boron (B)-containing complex stable surface film with low shear strength under boundary lubrication conditions. The detailed discussion is in Section 3.1.3. However, the COF gradually increases when the nano-oil diluted with certain percentages of B100 biodiesel fuel in the range of 5–20 vol.%. This is due to the oil starvation was suspected to take place. These results are consistent with

Shanta et al. (2011), where any degree of mineral oil dilution by the biodiesels increases the friction coefficient and reduces the wear protection of engine oil even at small mixture percentages.

**Figure 3** Average COF over time for all tested samples (see online version for colours)



### 3.2 Effect of dilution on EP properties

The data in Table 3 shows the tabulated results for EP test of lubricating oils. The data in Table 3 is extracted and represented in Figure 4. It was found that there is no significant effect on the EP properties, where the immediate seizure for all tested samples start to occur at load of 981 N before reach the weld point. From Figure 5, the wear scar diameter at the beginning of seizure of diluted nano-oil with 5 vol.% of B100 biodiesel fuel increases by 9.68%, while for 10, 15 and 20 vol.% increases rapidly about 19.38%–19.50%, as compared with nano-oil. At the weld point of 1,570 N, the wear scar diameter of diluted nano-oils drastically increases, between 9.98 and 62.29%. The details of wear types will be discussed in Section 3.1.3.

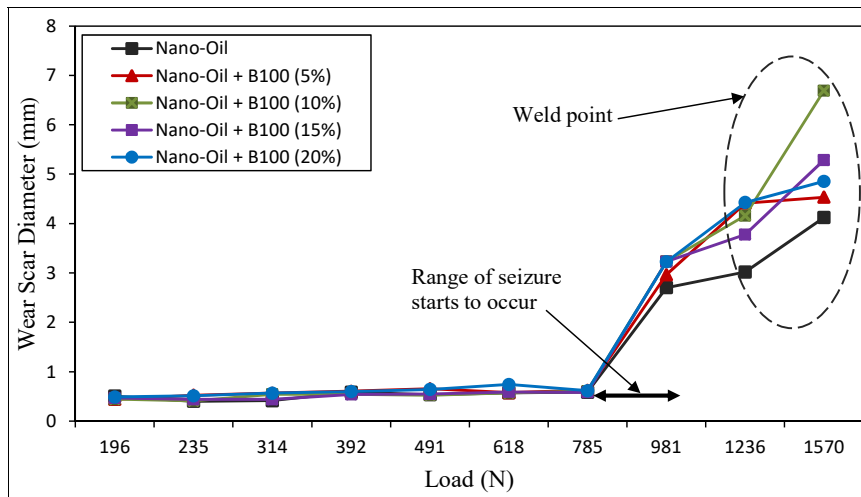
**Table 3** Collected data for the extreme pressure test of lubricating oils using a four-ball tribometer

Applied load (N)	Average wear scar diameter (mm)					
	SAE15W40	Nano-oil	Nano-oil + B100 (5%)	Nano-oil + B100 (10%)	Nano-oil + B100 (15%)	Nano-oil + B100 (20%)
196	0.403	0.504	0.442	0.444	0.468	0.487
235	0.491	0.401	0.523	0.410	0.438	0.511
314	0.582	0.415	0.565	0.543	0.437	0.567
392	0.587	0.586	0.604	0.544	0.540	0.599
491	0.604	0.533	0.656	0.523	0.546	0.641

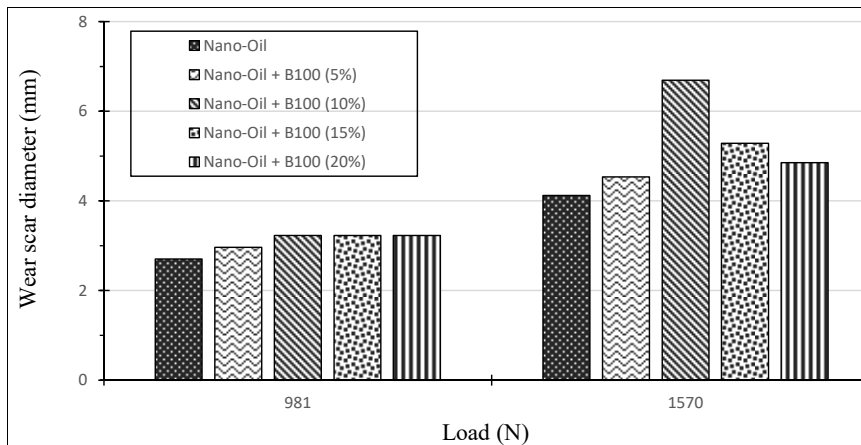
**Table 3** Collected data for the extreme pressure test of lubricating oils using a four-ball tribometer (continued)

Applied load (N)	Average wear scar diameter (mm)					
	SAE15W40	Nano-oil	Nano-oil + B100 (5%)	Nano-oil + B100 (10%)	Nano-oil + B100 (15%)	Nano-oil + B100 (20%)
618	0.620	0.573	0.575	0.570	0.588	0.742
785	0.549	0.586	0.625	0.605	0.584	0.615
981	0.621	2.703	2.965	3.230	3.229	3.227
1,236	1.781	3.018	4.412	4.159	3.777	4.427
1,570	5.304	4.122	4.534	6.690	5.284	4.854

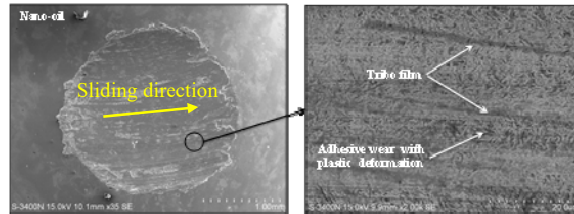
**Figure 4** Wear scar diameter versus applied load for tested samples (see online version for colours)



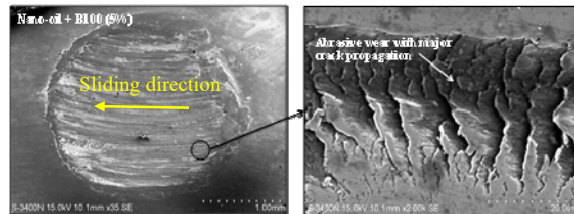
**Figure 5** Wear scar diameter versus applied load at the starting seizure of 981 N and weld point of 1,570 N



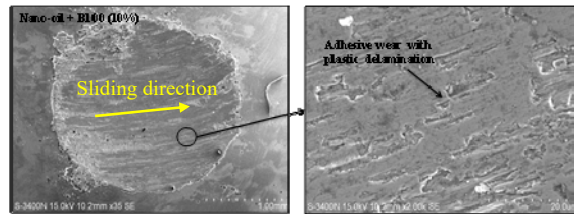
**Figure 6** SEM image of worn surfaces at weld point of 1,570 N tested by, (a) nano-oil (adhesive wear with plastic deformation) (b) diluted with 5% B100 (abrasive wear with cracking surfaces) (c) diluted with 10% B100 (adhesive wear with plastic delamination) (d) diluted with 15% B100 (abrasive with surface crack) (e) diluted with 20% B100 (adhesive wear with scarring surfaces) (see online version for colours)



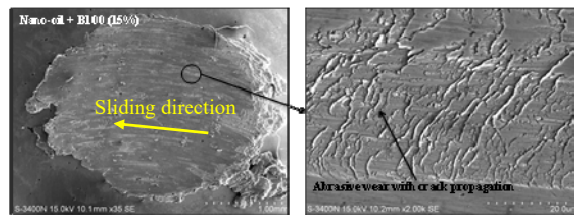
(a)



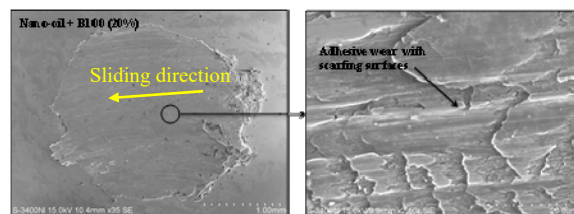
(b)



(c)



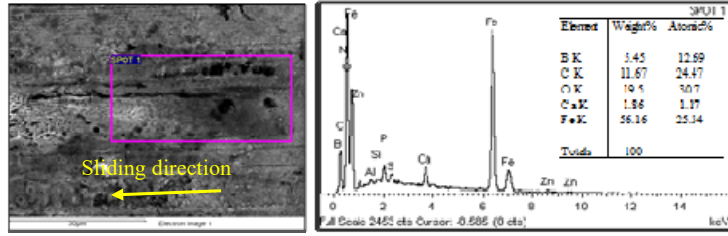
(d)



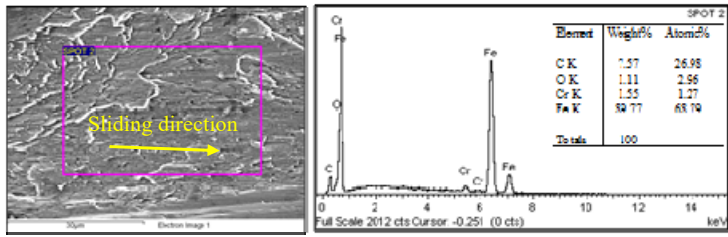
(e)



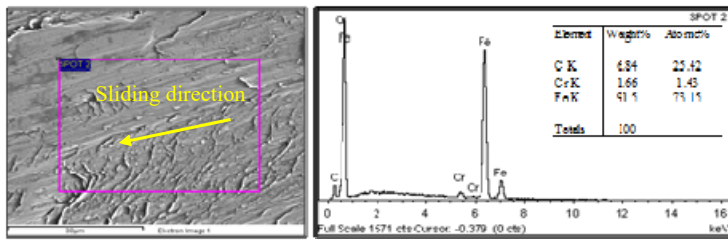
**Figure 7** SEM image and EDX analysis of worn surfaces at weld point of 1,570 N tested by, (a) nano-oil (b) diluted with 5% B100 (c) diluted with 10% B100 (d) diluted with 15% B100 (e) diluted with 20% B100 (see online version for colours)



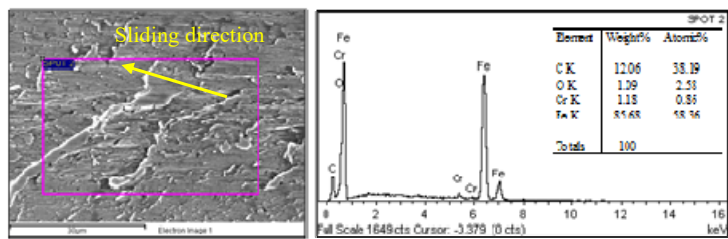
(a)



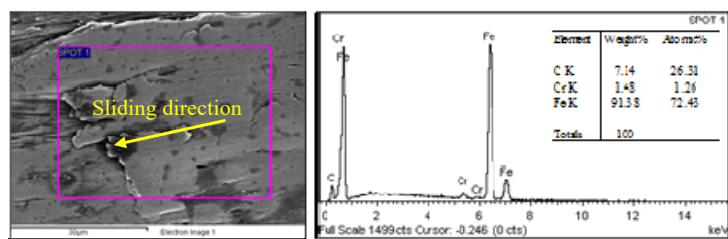
(b)



(c)



(d)



(e)

### 3.3 Surface morphology of worn surfaces

The SEM micrograph of worn surfaces that occur on the tested sample is shown in Figure 6. Most of the catastrophic surface failure are due to unable lubricated (lubricant thinner) the asperities because of higher load been applied.

Figure 6(a) shows the worn surface of the tested sample of nano-oil, where the adhesive wear type with plastic deformation was identified. Besides, the tribofilm, mainly dominated by boron, oxygen and carbon elements [Figure 7(a)], was formed due to the local high contact pressure and flash temperature caused by the collision and rupture of the asperities between the mating surfaces. It was believed that the tribofilm is boron oxide ( $B_2O_3$ ), which is when expose to the atmosphere it slowly absorbs water, reverting to boric acid ( $H_3BO_3$ ) as in equation (1); and consequently reducing the COF. The boric acid is one of the most popular solid lubricants and has excellent lubrication properties.



As contrast, the diluted nano-oil shows several typical wear types occur compared to nano-oil. Figure 6(b) and Figure 6(d) show abrasive wear by lateral cracking occur on the sample tested by nano-oil diluted with 5% and 15% of B100 biodiesel fuel. According to Lawn and Marshall (1979), at low loads, a sharp asperity contact will cause only plastic deformation and wear occurs by plastic deformation. Above a threshold load, brittle fracture occurs, and wear occurs by lateral cracking at a sharply increased rate. This lateral crack was developed from the residual stresses associated with the deform material. Figure 6(c) and Figure 6(e) show adhesive wear type occur on sample tested by nano-oil diluted with 10% and 20% of B100 biodiesel fuel. This wear occurs due to plastic shearing of successive layers at an asperity interface resulting in detachment of wear fragment which resulting in higher ferum (Fe) element on the worn surfaces shown by Figure 7(c) and Figure 7(e).

## 4 Conclusions

As summary of this study, it was found that the addition of the B100 biodiesel fuel into the nano-oil as a diluted nano-oil increases the COF and seizure as compared with nano-oil. This was believed due to the oil starvation was suspected to take place. However, there is no significant effect on the EP properties, where the seizure for all tested samples starts to occur at 981 N. Some adhesive and abrasive wear types with lateral cracks were identified on the worn surfaces.

## Acknowledgements

The authors also gratefully acknowledge contributions from the members of the Green Tribology and Engine Performance (G-TriboE) research group. This research was supported by grants from the World Academy of Sciences (TWAS) [Grant No. GLUAR/2013/FKM(2)/A00003], Ministry of Higher Education Malaysia [Grant Nos. FRGS/2013/FKM/TK01/02/1/F00163 and FRGS/2013/FTK/TK06/02/3/F00166], and Universiti

Teknikal Malaysia Melaka (UTeM) [Grants No. PJP/2012/FKM(40A)/S01044 and PJP/2012/FKM(11A)/S01086].

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