Performance Evaluation of Palm-Olein TMP Ester Containing Hexagonal Boron Nitride and an Oil Miscible Ionic Liquid as Bio-Based Metalworking Fluids

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ABSTRACT

Bio-based lubricants from vegetable oils are seen as a great potential alternative to the ever declining petroleum oil sources. Vegetable oils are highly biodegradable and non-toxic, pose good lubricating properties and do not require high production costs. Palm oils as the main renewable oil sources in Southeast Asia are being widely used as cooking oils. Researches have been conducted to expand their potential usage as lubricants for manufacturing applications. In this study, a chemically modified palm olein trimethylolpropane (TMP) ester (MRPO) containing various additives has been tested for their tribological characteristics. Two types of additives; hexagonal boron nitride (hBN) nanoparticles as solid lubricants and phosphonium-based ionic liquid (PIL) as an oil-miscible liquid additive were added into the MRPO to enhance its physical and tribological properties. Four ball wear tests were performed on steel/steel contacts lubricated with each of the lubricant samples. The experimental results presented improved physical properties as well as good antiwear and antifriction performances of the lubricant mixtures compared to the base oil. A minute quantity of PIL (1 wt. %) and hBN nanoparticles (0.05 wt. %) are found to increase the tribological performance of the MRPO, as well as when they are mixed together as lubricant additives into the base oil. The tribological improvements posed by the MRPO+PIL1% revealed better than or comparable results to the conventional synthetic ester and therefore is seen suitable for the use as a new advanced renewable bio-based metalworking fluid for manufacturing activities that corresponds to the energy saving benefits and environmental concerns.

Keywords: *Bio-Lubricant, Hexagonal Boron Nitride, Ionic Liquid, Renewable Sources, Sustainable Machining*

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Introduction

Bio-based lubricants have gained increased interest worldwide due to the consideration of renewable energy sources. The usage of environmental friendly lubricants in machining process seems to be an outstanding method to reduce the negative effect of mineral-based lubricant [1]. The latter is composed of petroleum-based oil, which is toxic and can cause serious environmental deficiency and health issues. Vegetable-based lubricants portrays excellent lubricity, biodegradability and renewability. They have higher viscosity indices and are effectively economical. Recently, palm oil has been discovered as an alternative to the production of coolant or industrial lubricant [2]. Globally, Malaysia accounted for 42.3% of worldwide production and 48.3% of the world's total exports of palm oil [3]. Due to this matter, it is a great intention to expand the usage of palm oil for various applications in lubricant industry. During machining process, metalworking fluids (MWFs) act as a lubricant and coolant to improve the workpiece quality by reducing friction and heat generation between tool and workpiece. MWFs contribute to the prevention of thermal damage of the workpiece material and reduction of tool wear, which will subsequently prolong the tool life [4]. In addition, MWFs also helped evacuate chips out of the cutting zone.

The application of vegetable oils as MWFs has great influence in improving machining performances by reducing the cutting force, producing least surface roughness and longer tool life. The lubricant viscosity strongly affects the capability of the oils to maintain lubrication film. Rahim and Sasahara [5] initiated that the highly viscous palm oil provides effective lubricating capability by reducing the friction at the tool-chip interfaces, thus reducing the tool wear rate. The high viscosity of palm oil contributes to the lower coefficient of friction due to strong bonding of intermolecular hydrogen bonds between –OH group in the oil molecule, which promotes stable and high boundary lubrication effect. Palm oil contains high palmitic acid that composed of long carbon chains and a high degree of saturation, which attributed to the increase of the lubricant viscosity. Li et al. [6] found that castor oil formed a layer of dense boundary film on the sliding surface due to its high viscosity level. The lubrication film exhibits a high anti-friction ability, thus reduces friction between grinding wheel and the workpiece and generates low grinding force. Quinchia et al. [7] also found that high viscous castor oil formed a thicker lubrication film, resulting in a low friction coefficient. The friction force is promoted by the tribochemical process during the rubbing action between a steel ball and a flat polished steel disc surface.

However, Shashidhara and Jayaram [8] identified that vegetable oil had major performance issues such as poor thermal-oxidative stability, high pour points, and inconsistent chemical composition. They addressed three methods; (1) chemical modification, (2) additive reformulation and (3) genetic modification of oil seed crop, in order to develop new bio-based MWFs. Zulkifli et al. [9] found that trimethylolpropane (TMP) ester (jatropha and palm oil) showed better lubricity in preventing metal-to-metal contact compared to the mineral oil, resulting in small wear scar diameter and low coefficient of friction. This is due to high polarity of TMP ester that creates a strong affinity on the metal surface by one end of the molecules and allows a nonpolar hydrocarbon to extend out and provide a barrier between the surfaces. They also stated that the viscosity decreases as temperature drops, thus decreases the lubrication thickness. Salih et al. [10] stated that the chemical modification of bio-based lubricant increases the viscosity index due to the increased molecular weight of the synthesized compounds; and decreases friction coefficient due to the increasing number of polar functional groups in the chemical structures of the synthesized compounds. The chemical modification also eliminated the double bonds together with the attachment of mid- and end-chain ester groups, which corresponds with the excellent physicochemical and tribological properties of the synthesized products. These changes led to a strong adsorption film onto the metal surface and enhanced the surface protective layer.

Green solid lubricant and ionic liquid are being added in the vegetable oil-based lubricants in order to enhance their tribological performances. Hexagonal boron nitride (hBN) is a type of green solid lubricant that has a lamellar crystalline structure, whereby the chemical bonding among the molecules within each layer is covalent, but the bonding between layers is determined by the weak van der Waals forces [11]. Talib et al. [12] found that the addition of 0.05 wt. % of hBN particles in modified Jatropha oil posed excellent anti-friction ability. They indicated that the presence of 0.05 wt. % of hBN nanoparticles in the vegetable oil tended to reduce friction at the sliding surfaces due to the change in the type of friction; from metal sliding to rolling effects due to the presence of the hBN nanoparticles on the sliding surfaces. Further, the hBN particles filled the asperity valleys, reducing the exposed area of worn surfaces thus resulted in small wear scar diameter and low coefficient of friction compared to the surface lubricated by synthetic ester. Reeves et al. [13] indicated that hBN particles filled the asperity valleys, established a thin lubrication film that allowed the particles to align themselves parallel to the relative motion. The particles slid over one another, thus reducing the stress concentration at the contact surfaces and contributes to a low amount of forces that decreases the friction coefficient.

Ionic liquids (ILs) are organic salts, identified as an advanced chemicals which poses low molten temperatures with unique lubricating characteristics. They have been suggested as potential friction and wear-reducing additives in the lubricants industry [14–16]. A recent review work on ionic liquid as sustainable lubricant [17] has outlined the impressive ability of phosphonium based ILs that do not emit volatile organic compounds into the environment. The ability of the anionic moieties of the ILs which can quickly adsorb on the sliding metal surfaces via strong electrostatic interactions even at high temperature and load working conditions has become an attractive contribution towards the formation of tenacious lubricant films that reduces friction and wear [17]. Yu et al. in 2012 [18] reported a phosphonium-based IL, trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate, $[P_{6,6,6,14}]$[Phosphinate], that was fully miscible in both mineral oil-based and synthetic lubricants. This IL is composed of three-dimensional quaternary structures with long hydrocarbon chains, which enables it to easily dissolve into non-polar base oils. As a highly viscous lubricant, $[P_{6,6,6,14}]$[Phosphinate] (596.4 mm^2/s at 40 °C) will still be able to retain its load carrying capacity in extreme temperature working condition compared to conventional lubricants [17]. As a neat chemical, it displayed non-corrosive behaviour when exposed on a cast iron and cast aluminium 319 surfaces at 135 °C for seven days. Several authors [15,19,20] have proposed the usage of 1 wt.% of phosphonium-based IL as additive in non-polar base oils considering their good to excellent tribological performance during the sliding tests. Their results indicate that minimum quantity of phosphonium-based ILs enhanced the antifriction performance of the base oil, especially under a high load. Wear volumes of sliding steel discs lubricated with the lubricant mixture on the other hand, remain significantly lower at all loads compared with the neat lubricant.

In this study, newly formulated bio-based MWFs were developed to get a better understanding on the effect of various type of additives mixed in the bio-based lubricant through physical properties tests and tribology experiments. Modified refined, bleached and deodorized (RBD) palm olein was chosen as the oil-based lubricant with the addition of minute quantity of hBN nanoparticles and ionic liquid, PIL. RBD palm oils are mainly used for cooking oil and industrial frying of processed food. The usage of RBD palm oil as a lubricant is still not widespread. Therefore, the aim of this study is to investigate the effect of different types of additives being mixed at small quantities into the modified RBD palm olein in order to discover their potential as an environmentally benign MWF that promotes cleaner production and as feasible and economical alternatives to traditional lubricants.

Methodology

In this section, the experimental methodology are discussed. The chemicals used in this work were of analytical reagent (AR) grades, which can be obtained from various laboratory chemical manufacturers. The synthesis process of the modified palm oil TMP ester (MRPO) has also been discussed in details in various published articles [21–23]. The experimental setup, standards and procedures are carried out in accordance to the American Society for Testing and Materials (ASTM).

Samples preparation

A chemically modified palm olein trimethylolpropane (TMP) ester (MRPO) has been formulated as a renewable bio-based lubricant for machining applications. A two steps modification process was used on a refined, bleached and deodorized palm olein (RBDPO) during the conversion process into a vegetable oil-based TMP ester. Fatty acid methyl ester (FAME) was initially produced via transesterification process at a molar ratio of methanol to RBDPO of 6:1. Further, the second transesterification process was performed by mixing the FAME with the TMP following the molar ratio of 3.3:1. A conventional cutting fluid, synthetic ester was purchased from local market and was used as the benchmark lubricant in this study [21].

An oil miscible ionic liquid, trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate, (PIL) and hexagonal boron nitride nanopowder (hBN) were purchased from Iolitec GmbH, Germany and local market respectively. Both were used directly from their packaging without further purification. PIL which has three-dimensional quaternary structure with long hydrocarbon chains has high steric hindrance making it possible to dissolve in a non-polar vegetable oil. The hBN nanopowder is a ‘green’ solid nanoparticle with average particle size of approximately 3.5 x 10^3 nm [21]. It will create an emulsion type of mixture with the non-polar base oil.

The additives were mixed into the MRPO to create three different types of blended bio-based lubricants. A weight of additive to weight of base oil ratio was used in preparing the mixtures. Small amount of additives; 1 wt. % of PIL and 0.05 wt. % of hBN were selected respectively as the minute quantity of additives and being mixed separately in the base oil to create the first two mixtures. Then, both of them with the same weight quantity were mixed in another base oil to create the third mixture. Mixing processes were carried out by heating the base oil at about 70 °C and by using a magnetic stirrer, the additives were blended rigorously for thirty minutes. The samples used in this work are summarized in Table 1.

Table 1: List of lubricant samples

Samples	Remarks
SE	Synthetic Ester
MRPO	Modified Palm Olein TMP Ester
MRPO+PIL1%	MRPO mixed with 1 wt.% of phosphonium based IL
MRPO+hBN0.05%	MRPO mixed with 0.05 wt.% of hBN nanoparticles
MRPO+PIL1%+hBN0.05%	MRPO mixed with 1 wt.% of PIL and 0.05 wt.% of hBN nanoparticles

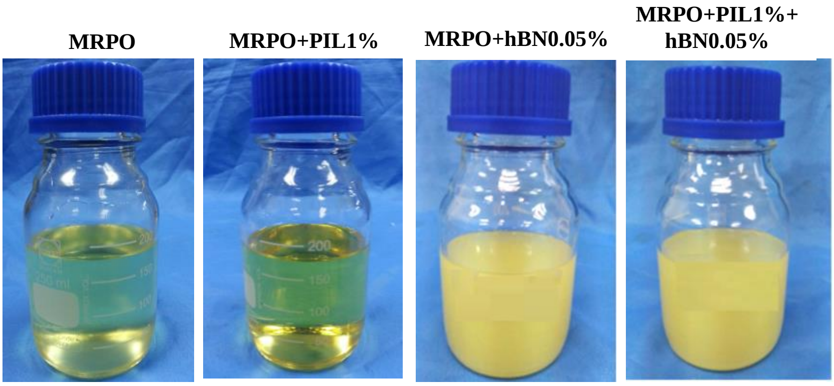

Figure 1: Samples of newly modified bio-based cutting fluids.

The homogeneity of the samples being blended with PIL can be shown by monitoring the liquid after the mixing process. The mixture appears to have no cloudy liquid and no precipitation is present even after many months of storage. The emulsion produced with hBN mixture on the other hand, has a cloudy liquid appearance with hBN particles deposited on the bottom of the bottle when stored after a period of time. This is also present when mixing both additives into the base oil as shown in Figure 1.

Physical Properties

The physical properties of the newly formulated lubricant samples were determined in terms of their kinematic viscosity and viscosity index. The kinematic viscosity of the newly formulated lubricants were measured in laboratories based on ASTM D445 standard. A viscometer's probe (Viscolite 700) was submerged into the lubricants at temperature of 40 °C and 100 °C to measure its kinematic viscosity, v. The viscosity index (VI) of each lubricants is then determined following the ASTM D2270 method using their kinematic viscosities measured at 40 °C and 100 °C.

Tribology Test via Four Ball Wear Test

The lubricity performance of the new lubricant mixtures are investigated on their tribological behavior in terms of wear and friction. The tests were conducted on a four ball wear test machine according to the ASTM D4172-94 method. The test was selected as a preliminary evaluation of the anti-wear properties of the lubricant mixtures in sliding contact [24]. The relationships between wear mechanisms on the steel ball surface and the tribological interactions of the lubricant samples interposed between the steel surfaces are investigated. A schematic diagram of the four ball assembly located in the tribology test machine is shown in Figure 2. Each test utilized a new set of four steel ball bearings (AISI 52100) with a diameter of 12.7 mm and a hardness value of 62 HRC. The arithmetic average surface roughness (R_a) of the steel balls was approximately 0.02 µm.

By applying approximately 10 ml of each lubricant samples, three stationary balls were submerged in the lubricant while being clamped together in a pot. A rotating spindle was used to hold a single steel ball on a collet and was pressed against the three stationary balls with a load of 40 kg (392N). According to the standard, the initial test temperature of the lubricant was set at 75 °C and the top ball was rotated at a constant speed of 1200 rpm for 1 hour. After the experiment, friction torque, coefficient of friction and the mean wear scar diameter of the stationary steel balls were recorded to determine the relative wear preventive properties of the lubricant samples in sliding contact under the aforementioned test conditions.

The wear scar diameters of the stationary steel balls were analysed and the images were captured underneath an optical microscope embedded with a digital camera. The diameter of the scars were measured directly by an image acquisition system based on the average lengths of horizontal and vertical scars. The wear scar diameter (WSD) was then calculated from those average scar diameter. The friction coefficient (COF) was determined from the average tangential load from the values of friction torque sampled at 30 readings per minute. The average friction torque at the steady state was recorded and the COF was calculated using Equation (2) according to IP-239 standard [9,25,26]:

$$Friction\ torque, T = \frac{\mu \cdot 3W \cdot r}{\sqrt{6}} \qquad (1)$$

Where, μ is the friction coefficient; W is the applied load in N and r is the distance from the center of the contact surface on the lower balls to the axis of rotation, which is 3.67 mm.

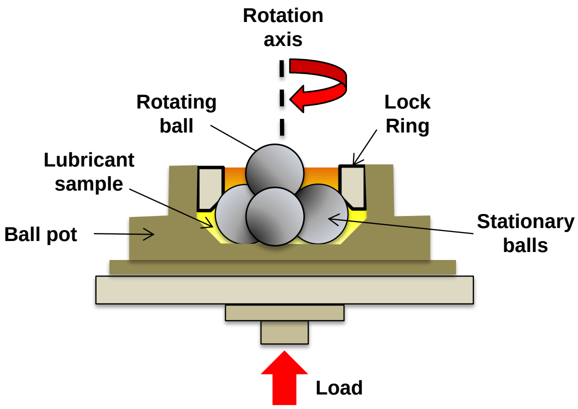

Figure 2: Schematic view of the four ball assembly in the tribometer.

Results and Discussion

Viscosity and Viscosity Index

Figure 3 shows the viscosity values of the newly developed lubricants at both 40 °C and 100 °C. The benchmark lubricant's kinematic viscosity is shown by SE which has a minimum value of about 21 mm^2/s at 40 °C. The neat MRPO, on the other hand, exhibits a value of kinematic viscosity above the benchmark lubricant of about 23.2 mm^2/s. The viscosity of MRPO at 100 °C is also found to be higher than SE (approximately 12.7% increment). This is due to the presence of longer carbon number between 16 and 18, compared to SE that has only between 8 and 10 [12,22]. The long carbon chain length increases the viscosity value of the neat vegetable-based lubricant [27].

The viscosity value increases with the addition of 0.05 wt. % hBN nanoparticles, while the addition of PIL1% exhibits the lowest kinematic viscosity at 40 °C compared to others. This may be caused by a formation of thick film from the hBN particles inside the base oil. By mixing both 1 wt. % PIL and 0.05 wt. % hBN particles in the base oil, the viscosity at 40 °C shows a decrement of about 5% from MRPO.

The calculated Viscosity Index values denote the temperature range that a lubricant can withstand during operation. MRPO+PIL1% shows the highest VI, which corresponds to the properties of PIL that has low-volatility and nearly non-flammable nature of PIL. The long alkyl chain length of PIL is also responsible to its viscosity increase [17]. Thermal conductivity of PIL has very small dependence on temperature and pressure, hence, the high thermal stability. It also retains a high evaporation temperature, therefore attains a high VI value for the lubricant mixture [18].

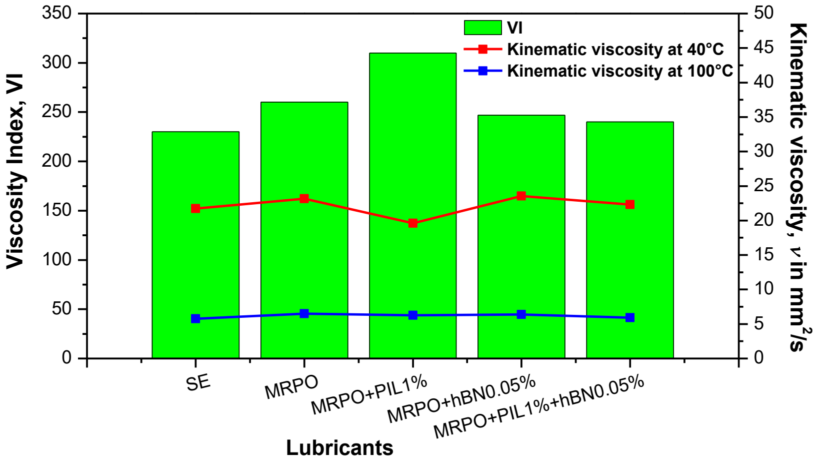

Figure 3: Viscosity and viscosity index values of the tested lubricants with SE as the benchmark oil.

Friction Torque

The friction torque after the tribology test is depicted in Figure 4. It shows an interesting result, whereby the addition of additives clearly lower the frictional torque compared to the conventional synthetic ester (SE) and base oil (MRPO). The neat MRPO contains fatty acids that help the lubricant molecules to form lubricant film by adsorption on the ball bearing surface. The presence of a thin protective layer between the steel ball surfaces minimized the material transfer and adhesion of the two metal surfaces. This makes MRPO have lower friction torque compared to SE [28].

Sample mixture of 0.05 wt. % hBN shows the lowest frictional torque during the metal to metal sliding contacts of about 8.6 % difference from MRPO. Similar findings by Talib et al. [12] and Reeves et al. [13] indicated that, the hBN additives established a thin lubrication film by filling the particles in the asperity valleys which allowed them to align in parallel to the relative sliding motion. These particles slid over one another, thus reducing the real contact area of worn surfaces which subsequently reduces stress concentration on the contact surfaces and contributes to reduced frictional forces that decreases the friction coefficient.

The addition of 1 wt. % PIL does lower the frictional torque of the base oil corresponding to the reduction of friction coefficient. The formation of a triboactive layer that has high load carrying capacity by the PIL molecules with the metal substrate provides a boundary film that separates the metal contacts [29]. The adsorption process of the IL molecules on the metal surface decreases the direct contacts of metal asperities and thus reduces the friction torque [30].

Low friction torque with low values of COF implied a good lubricity of the lubricant [12]. From the result in Figure 4, it is shown that 0.05 wt. % hBN poses superior ability in reducing the frictional torque during the steel sliding process compared to 1 wt. % PIL. While 1 wt. % PIL improved the base oil performance, the addition of both additives in the base oil (MRPO+PIL1%+hBN0.05%) shows a comparable trend with the base oil, MRPO. Nevertheless, all mixtures show a decreasing trend of frictional torque compared to the benchmark oil, SE.

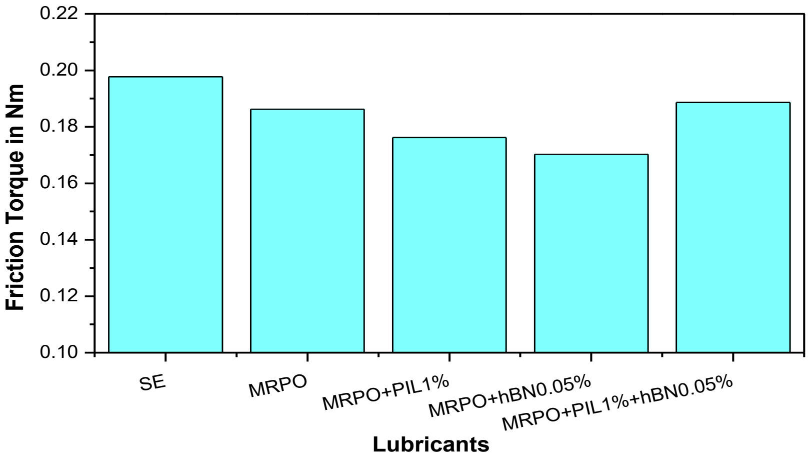

Figure 4: Frictional torque of the lubricant samples after the tribology test.

Wear Scar Diameter and Friction Coefficient

The average diameter of the worn out area on the steel balls are presented in Figure 5. The conventional MWF, SE shows the lowest worn out area on the steel ball despite of its high coefficient of friction (COF). Similarly, it is shown that the addition of each type of additives reduces the friction coefficient of the base oil which is consistent with the results in many published articles [11–13,18,31]. However, the amount of additive being mixed in the base oil does play an important measure affecting the friction reduction ability [31]. This can be the explanation on the increased friction coefficient of the MRPO+PIL1%+hBN0.05% sample.

The mean wear scar diameter (WSD) of the steel ball lubricated with MRPO+PIL1% shows a good reduction of approximately 2% compared to MRPO which corresponds with its low COF value. By adding 0.05 wt. % hBN particles, the WSD decreases only about 1.1 % from the base oil. The addition of both additives on the other hand, shows an improvement of WSD reduction of about 3.4 % from the base oil.

SEM images of the worn out surface of the steel ball bearings are shown in Figure 6. It is seen that the wear surfaces present circular shape patterns which indicates the continuous rotation (sliding operation) of the top ball. Different wear mechanism can be seen on the surface lubricated with SE, in which abrasive wear with parallel grooves covered the worn surface area. MRPO which shows the highest WSD presents a trace of abrasive wear and shallow groove pattern with traces of surface oxidation (dark lines). The addition of PIL1% enhances the base oil antifriction and antiwear properties by reducing the scuffing effect and the abrasive wear mechanism. This is also shown by the result from MRPO+hBN0.05%. Smooth worn area with traces of shallow grooves are shown by the surface lubricated with MRPO+PIL1%+hBN0.05%.

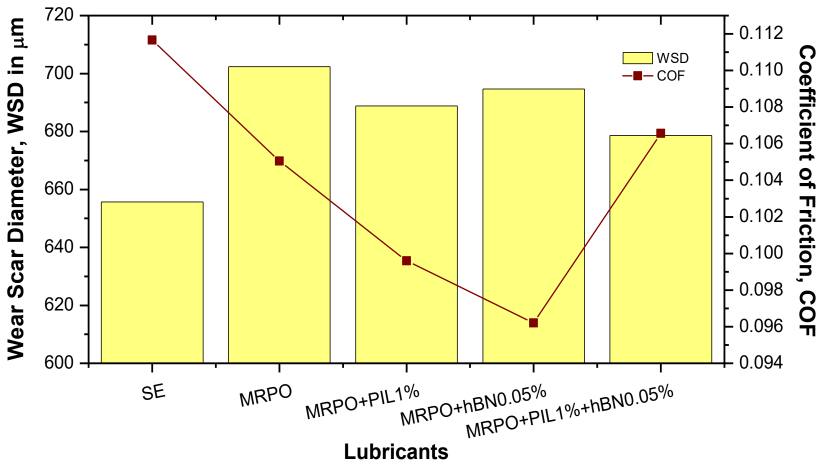

Figure 5: WSD and COF values of the tested lubricant samples.

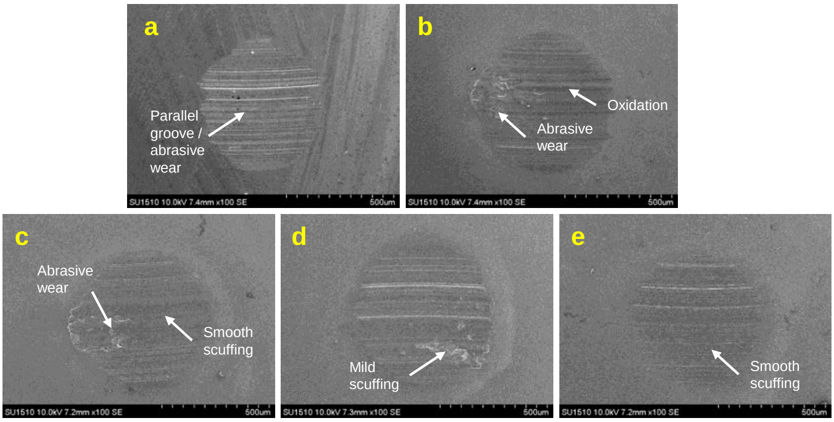

Figure 6: SEM images of the worn area on the steel ball bearings lubricated with (a) SE, (b) MRPO, (c) MRPO+PIL1%, (d) MRPO+hBN0.05% and (e) MRPO+PIL1%+hBN0.05%. Magnification of the images is at 100X.

PIL interact with the base oil and the steel surface during the tribotest to create a protective boundary film by the chemical adsorption of the PIL anion on the steel surface that reduces the friction and wear [18]. The ability of the hBN nanoparticles to interact with the friction surfaces and form a thin protective film on the surfaces also causes the reducing effect on both friction and wear [12]. Mixing both additives presents a different explanation, whereby both additives are competing with each other during the adsorption process of hBN particles and PIL anions on the steel surfaces to create the boundary film. Overall, the addition of both additives has successfully reduces the friction coefficient and wear scar diameter of the steel ball compared to the base oil, MRPO and is comparable to or better than the antifriction and antiwear ability of the conventional synthetic ester.

Conclusions

The conclusions that could be made from this work are as below:

- The addition of additives in the base oil, MRPO increases the antiwear and antifriction performance by modifying the viscosity value of the base oil.
- The phosphonium based ionic liquid poses better antifriction and antiwear ability than the green solid lubricant of hBN nanoparticles by reducing the friction coefficient of about 11% and WSD of about 2% from the base oil, MRPO.
- The addition of both types of additive in minute quantities (1 wt.% PIL and 0.05 wt.% hBN) increases the antiwear ability of the base oil (approx. 3.4% reduction) with good antifriction performance compared to the conventional synthetic ester (approx. 5% reduction), which leads to the improvement of the modified palm olein ester as a bio-based MWF.
- A new advanced bio-based metalworking fluid is therefore developed in this work for future metalworking application and testing that corresponds to the energy saving benefits and environmental concerns for manufacturing activities.

Acknowledgments

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References

[1] N.W.M. Zulkifli, M.A. Kalam, H.H. Masjuki, M. Shahabuddin and R. Yunus, “Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant”, *Energy*, 54, 167–73 (2013).

[2] M.I. Izhan, A.K.M. Rafiq and S. Syahrullail, “Friction Resistance of Refined, Bleached and Deodorized (RBD) Palm Olein Using Modified Pin-on-disk Tribotester”, *J. Teknologi*, 60, 27–33 (2013).

[3] A. Zhou and E. Thomson, “The Development of Biofuels in Asia”, *Appl. Energy*, 86, S11–20 (2009).

[4] E. Brinksmeier, D. Meyer, A.G. Huesmann-Cordes and C. Herrmann, “Metalworking fluids - Mechanisms and performance”, *CIRP Ann. - Manuf. Technol.,* 64, 605–28 (2015).

[5] E.A. Rahim and H. Sasahara, “A study of the effect of palm oil as MQL lubricant on high speed drilling of titanium alloys”, *Tribol. Int.,* 44 (3), 309–17 (2011).

[6] B. Li, C. Li, Y. Zhang, Y. Wang, D. Jia and M. Yang, “Grinding temperature and energy ratio coefficient in MQL grinding of high-temperature nickel-base alloy by using different vegetable oils as base

oil", *Chinese J. Aeronaut.*, 29 (4), 1084–1095 (2016).

[7] L.A. Quinchia, M.A. Delgado, T. Reddyhoff, C. Gallegos and H.A. Spikes, "Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers", *Tribol. Int.,* 69, 110-7 (2014).

[8] Y.M. Shashidhara and S.R. Jayaram, "Vegetable oils as a potential cutting fluid-An evolution", *Tribol. Int*., 43(5-6), 1073–81 (2010).

[9] N.W.M. Zulkifli, M.A. Kalam, H.H. Masjuki, K.A.H. Al Mahmud and R. Yunus, "The Effect of Temperature on Tribological Properties of Chemically Modified Bio-Based Lubricant", *Tribol. Trans.,* 57(3), 408–15 (2014).

[10] N. Salih, J. Salimon, E. Yousif and B.M. Abdullah, "Biolubricant basestocks from chemically modified ricinoleic acid", *Chem. Cent. J.,* 7(128), 1–13 (2013).

[11] Z. Pawlak, T. Kaldonski, R. Pai, E. Bayraktar and A. Oloyede, "A comparative study on the tribological behaviour of hexagonal boron nitride (h-BN) as lubricating micro-particle-An additive in porous sliding bearings for a car clutch", *Wear*., 267(5-8), 1198–202 (2009).

[12] N. Talib, R.M. Nasir and E.A. Rahim, "Tribological behaviour of modified jatropha oil by mixing hexagonal boron nitride nanoparticles as a bio-based lubricant for machining processes", *J. Clean. Prod.,* 147, 360-78 (2017).

[13] C.J. Reeves, P.L. Menezes, M.R. Lovell and T.C. Jen, "The size effect of boron nitride particles on the tribological performance of biolubricants for energy conservation and sustainability", *Tribol. Lett.,* 51(3), 437-52 (2013).

[14] P. Waara, J. Hannu, T. Norrby and Å. Byheden, "Additive influence on wear and friction performance of environmentally adapted lubricants", *Tribol. Int.,* 34(8), 547-56 (2001).

[15] I. Otero, E.R. López, M. Reichelt, M. Villanueva, J. Salgado, J. Fernández, "Ionic liquids based on phosphonium cations as neat lubricants or lubricant additives for a steel/steel contact", *ACS Appl. Mater. Interfaces.*, 6(15), 13115-28 (2014).

[16] Z. Cai, H.M. Meyer, C. Ma, M. Chi, H. Luo and J. Qu, "Comparison of the tribological behavior of steel–steel and Si3N4–steel contacts in lubricants with ZDDP or ionic liquid", *Wear*., 319(1-2), 172-83 (2014).

[17] S.A.S. Amiril, E.A. Rahim, S. Syahrullail, "A review on ionic liquids as sustainable lubricants in manufacturing and engineering: Recent research, performance, and applications." *J Clean Prod.*, 1–19 (2017), http://dx.doi.org/10.1016/j.jclepro.2017.03.197.

[18] B. Yu, D.G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich and D.J. Smolenski, "Oil-miscible and non-corrosive phosphonium-based ionic liquids as candidate lubricant additives", *Wear.,* 289, 58-64 (2012).

[19] J. Qu, H. Luo, M. Chi, C. Ma, P.J. Blau, S. Dai, M.B. Viola, "Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive", *Tribol. Int.,* 71, 88-97 (2014).

[20] M. Cai, Y. Liang, M. Yao, Y. Xia, F. Zhou, W. Liu, "Imidazolium ionic liquids as antiwear and antioxidant additive in poly(ethylene glycol) for steel/steel contacts", *ACS Appl. Mater. Interfaces.,* 2(3), 870-6 (2010).

[21] E.A. Rahim, N. Talib, S.A.S. Amiril, S. Syahrullail, Z. Mohid, "Tribological Evaluation on Various Formulation of Modified RBD Palm Olein as Sustainable Metalworking Fluids for Machining

Process", *Mater. Sci. Forum.*, 882, 13-17 (2017).

[22] E.A. Rahim, S.A.S. Amiril, Z. Mohid, S. Syahrullail, "Tribological evaluation on vegetable oils based trimethylolpropane (TMP) ester as sustainable metalworking fluids in machining applications", *Proceeding of 7th Int. Conf. Mech. Manuf. Eng.* (unpublished manuscript), Jogjakarta, Indonesia, 1-8 (2016).

[23] N. Talib, E.A. Rahim, "Performance Evaluation of Chemically Modified Crude Jatropha Oil as a Bio-based Metalworking Fluids for Machining Process", *Procedia CIRP*., 26, 346-50 (2015).

[24] T.C. Ing, A. K Mohammed Rafiq, Y. Azli, S. Syahrullail, "The Effect of Temperature on the Tribological Behavior of RBD Palm Stearin", *Tribol. Trans.*, 55, 539-548 (2012).

[25] M.A. Fazal, A.S.M.A. Haseeb, H.H. Masjuki, "Investigation of friction and wear characteristics of palm biodiesel", *Energy Convers. Manag.*, 67, 251-256 (2013).

[26] N.A.M. Aziz, R.Yunus, U. Rashid, N.W.M. Zulkifli, "Temperature effect on tribological properties of polyol ester-based environmentally adapted lubricant", *Tribol. Int.*, 93, 43-49 (2016).

[27] L.A.T. Honary, E. Richter, "Biobased Lubricants and Greases: Technology and Products", 1st ed. (John Wiley & Sons, United Kingdom 2011), pp 41 – 45.

[28] T.C. Ing, A.K.M. Rafiq, Y. Azli, S. Syahrullail, "Tribological behaviour of refined bleached and deodorized palm olein in different loads using a four-ball tribotester", *Sci. Iran.*, 19, 1487-1492 (2012).

[29] M. Kronberger, V. Pejakovic, C. Gabler, M. Kalin, "How anion and cation species influence the tribology of a green lubricant based on ionic liquids", *Proc. Inst. Mech. Eng. Part J. J. Eng. Tribol.*, 226, 933–951 (2012).

[30] A.E. Somers, B. Khemchandani, P.C. Howlett, J. Sun, D.R. MacFarlane, M. Forsyth, "Ionic Liquids as Anti-wear Additives in Base Oils: Influence of Structure on Miscibility and Wear Performance for Steel on Aluminium", *ACS Appl. Mater. Interfaces.*, 5(22), 11544−11553 (2013).

[31] Z. Tang, S. Li, "A review of recent developments of friction modifiers for liquid lubricants (2007-present)", *Curr. Opin. Solid State Mater. Sci.*, 18(3), 119-39 (2014).