Tribological Improvement Using Ionic Liquids as Additives in Synthetic and Bio-Based Lubricants for Steel–Steel Contacts


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ABSTRACT
This study investigates the performance of three ionic liquids (ILs), trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, trihexyl(tetradecyl)phosphonium decanoate, and 1-butyl-3-methylimidazolium tetrafluoroborate, as lubricant additives in synthetic oil polyalphaolefin (PAO8) and bio-based oil trimethylolpropane trioleate (TMPTO). The ILs were added at 0.5, 1.0, and 1.5 wt% concentrations and evaluated in terms of their miscibility with base oils as well as friction- and wear-reducing abilities. Four-ball and high-frequency reciprocating rig (HFRR) tribotesters were employed to evaluate the tribological performance under a boundary lubrication regime. Worn steel surfaces were characterized using optical microscopy, profilometry, scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) analysis. The results suggested that the addition of trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate and trihexyl(tetradecyl)phosphonium decanoate improved the tribological performance of both PAO8 and TMPTO at an optimum concentration of 1 wt%. They showed good friction reduction, lower overall surface wear, and improved surface finishing. 1-Butyl-3-methylimidazolium tetrafluoroborate managed to improve the tribological performance of both base oils only at 0.5 wt%. A further increase in 1-butyl-3-methylimidazolium tetrafluoroborate concentration caused detrimental effects on the steel surface due to the formation of halogenic compounds.

Introduction
The increase in environmental awareness in recent years has demanded more environmentally friendly lubricants for use in certain applications. In addition to being readily biodegradable and renewable, bio-based lubricants are known to possess good lubricity, a high flash point, a high viscosity index, and good resistance to shear compared to mineral-based oils (Salimon, et al. (1); Soni and Agarwal (2)). However, their antiwear capability and extreme pressure characteristics are still debatable when compared to those of conventional petroleum-derived lubricants with antiwear additives (Syahir, et al. (3)).

Bio-based lubricants contain triglyceride molecules, which means that they have a higher polarity than mineral oils. Higher polarity means that they have a higher affinity to metallic surfaces (Prado, et al. (4)). Due to this special property, vegetable oils and their derivatives show superior tribological performance and therefore are suitable for lubrication applications. Oils containing polar groups such as esters and carboxylic acids have a greater tendency to adsorb and react with metallic surfaces, resulting in boundary lubrication effects (Schmidt, et al. (5)). It is well known that a lubricating film or tribofilm with strong surface attraction and enough cohesive interaction among lubricant molecules can effectively reduce friction and wear on interacting surfaces. Such a tribofilm must be able to withstand severe variations in temperature and shear degradation and sustain boundary-lubricating properties during operation in order to maintain low friction and wear. However, the physicochemical properties and lubrication performance of bio-based materials are affected by their free fatty acid composition (Syahir, et al. (3); Silitonga, et al. (6)).

Lubricant additives are needed to further increase the performance of base oils. Ionic liquids (ILs) are room-temperature molten salts that possess unique physical properties, including high thermal stability, very low volatility, low melting point and nonflammability (Lei, et al. (7); Amiril, et al. (8)). Therefore, ILs have shown immense potential in many applications, with lubrication as one of the latest. The lubricating performance of ILs has been associated with their ability to form a thin lubricant layer during contact by the fast formation of an IL-derived tribofilm that may prevent asperity contact in the boundary lubrication regime.

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An IL tribofilm is composed of densely packed and oriented molecules that adsorb on friction surfaces (Zhou and Qu (9)). The properties of such a tribofilm depend on the anion and cation structures of the ILs. However, some ILs possess major drawbacks such as corrosion to metal surfaces, high production cost, low hydrolytic stability, and poor miscibility in base oils (Lei, et al. (7); Amiril, et al. (8)).

Several studies have reported that 3D structures with long alkyl chains improve an IL's oil miscibility, and the IL's overall miscibility with base oil is heavily affected by the oil miscibility of both the cation and anion parts (Barnhill, et al. (10); Khemchandani, et al. (11); Qu, et al. (12)). Many studies have reported good miscibility of ammonium- and phosphonium-based ILs in polar-based oils (Fernández-González, et al. (13); Viesca, et al. (14); Yu, et al. (15)), mainly due to their molecular structures, which consist of quaternary structures with long hydrocarbon chains (Barnhill, et al. (16); Zhou, et al. (17); Qu, et al. (18); Zhu, et al. (19)). Therefore, these IL groups are favored for use as lubricant additives. An increase in the lubrication performance of base oils is crucial in the development of lubricants for a variety of applications. Phosphorous-containing ILs have been the subject of many research studies because they have been repeatedly exhibited good tribological characteristics in terms of reducing friction and wear.

To date, only a few tribological studies have involved ILs as friction modifier additives in bio-based lubricants (Khemchandani, et al. (11); Zhu, et al. (19); Grace, et al. (20); Jiang, et al. (21); Shanhua, et al. (22); Amiril, et al. (23)). The idea is to study the combined effect of bio-based lubricants and ILs, because both can effectively reduce friction when used alone. At the optimum concentration, the addition of ILs further improved the antifriction performance and reduced the friction coefficient of base oils, with some showing a nearly 50% reduction in wear scar diameter (WSD) and coefficient of friction (COF; Khemchandani, et al. (11); Grace, et al. (20); Shanhua, et al. (22); Amiril, et al. (23)). It is also worth mentioning that the performance of the lubricant only peaked when the ILs were added at optimum concentrations; thus, increasing concentration of ILs does not necessarily lead to better tribological performance (Zhou and Qu (9); Grace, et al. (20)).

Phosphonium- or imidazolium-containing ILs have been the common focus of research studies due to their superior tribological performance and good miscibility in polar base oils (Grace, et al. (20); Amiril, et al. (23)). A research study reported good miscibility and tribological improvement when a phosphonium-based IL was used as an additive in modified Jatropha oil (bio-based lubricant; Amiril, et al. (23)). Improvements in corrosion inhibition, friction reduction, surface finishing, and tapping torque efficiency were observed. For ILs containing halogen, a study reported that when 1-hexyl-3-methylimidazolium tetrafluoroborate, [HMIM][BF4], was used as an additive in castor oil, low friction and wear were observed at a low IL concentration (<1 wt%; Shanhua, et al. (22)). At higher concentrations, an increase in the overall amount of wear was apparent due to the production of corrosive hydrogen fluoride acid. Though past studies have concluded that phosphonium- and halogen-containing ILs can effectively reduce friction when used as additives, information is still rather limited.

Therefore, the aim of the study was to investigate the combined effect of a bio-based lubricant and ILs in terms of tribological characteristics. Two phosphorus-based ILs and a halogen-based IL, namely, [BMIM][BF4], were used in this study. Though past studies have reported the steel corrosion problems posed by ILs containing [BF4]−, this study further evaluates the capabilities and limitations of this IL in the boundary lubrication regime, especially when different base oils, contact geometries, and test conditions are used (Shanhua, et al. (22); Kondo, et al. (24)). A synthetic oil, namely, polyalphaolefin (PAO8), was included for comparative analysis. Part of this work has been previously reported (Syahir, et al. (25)). The present study focuses on the influence of IL concentration on the tribological performance of the base oils. The performance of ILs under boundary lubrication regimes have been investigated using four-ball and high-frequency reciprocating rig (HFRR) tribotesters. The findings of this study will help to further understand the lubrication capabilities of ILs, thus paving the way toward a greener future with the development of environmentally friendly and energy-efficient lubricants.

Methodology

Lubricant sample preparation

The base oils used in this study are trimethylolpropane trioleate (TMPTO) and PAO8, both of which are synthetic base oils (bio-based and mineral-based, respectively). High-purity-grade TMPTO (~100%) and PAO8 (≥99%) were obtained commercially and used directly without any purification. TMPTO is produced through an esterification reaction of trimethylolpropane (TMP) with oleic acid. Trioleate indicates that the lubricant molecule contains three identical fatty acid chain components (oleic acid), as seen in Fig. 1. TMPTO is reported to have improved oxidative stability and low-temperature properties, excellent lubricity, and a high viscosity index. Therefore, it is suitable for utilization as a green and sustainable lubricant for various applications (Rajendiran, et al. (26); Qiao, et al. (27)).

Three types of ILs will be used in this study, namely, IL1, IL2, and IL3, as presented in Table 1. The three ILs were chosen due to their good miscibility in polar base oils as well as their relatively lower price compared to other ILs (Grace, et al. (20); Amiril, et al. (23)). They are also considered biocompatible due to the following reasons. IL1 was reported to be sufficiently biocompatible because its low level of toxicity can allow the growth of different microorganisms, including human coronary artery endothelial cells and Escherichia coli (Zhang, et al. (28)). Because IL2 contains the same cation as IL1 and the anion was derived from organic-based fatty acids, it is also considered biocompatible. In the case of halogen-containing IL3, it was reported that [BMIM][BF4] can be broken down by soil and wastewater microorganisms, implying that the IL is biodegradable (Thuy Pham, et al. (29); Kumar, et al. (30); Jastorff, et al. (31)).
All ILs were obtained commercially and used directly upon receipt. The molecular structures (i.e., cations and anions) of all ILs are presented in Fig. 1. Prior to mixing, the base oil and IL were heated separately until they both reached 70 °C. Then, the ILs were added into TMPTO and PAO8 at three different concentrations (0.5, 1.0, and 1.5 wt%) for each type of IL. The mixtures were based on the weight–weight percentage between the ILs and base oils. The mixtures of base oil and IL were stirred using a magnetic stirrer for 30 min in order to obtain a homogenous mixture (Amiril, et al. (23); Fernandes, et al. (32)). The mixtures were then visually examined for precipitation or separation of the layers that formed. In terms of physical properties, the kinematic viscosity at 40 and 100 °C as well as the corresponding viscosity index of each prepared sample were measured in accordance with ASTM D445 and ASTM D2270, respectively, using an automatic-type viscosimeter. The density at 15 °C was also determined using ASTM D4052. The lubricant properties of each sample tested in this study are presented in Table 2.

Table 1. Ionic liquids used in this study.

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL1</td>
<td>Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate, [P14,6,6,6][TMPP]</td>
<td>≥90.0</td>
</tr>
<tr>
<td>IL2</td>
<td>Trihexyl(tetradecyl)phosphonium decanoate, [P14,6,6,6][Deca]</td>
<td>≥95.0</td>
</tr>
<tr>
<td>IL3</td>
<td>1-Butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF4]</td>
<td>≥97.0</td>
</tr>
</tbody>
</table>

*Provided by the manufacturer.

**Investigation of tribological behavior**

**Four-ball tribotest**

The capability of the lubricant samples to prevent wear under a boundary lubrication regime was evaluated using a four-ball machine according to ASTM D4172. Steel balls and the ball pots were thoroughly washed with toluene and wiped to avoid surface contamination prior to the test. The resulting COF was calculated and the resulting WSD on the stationary balls was examined using a calibrated optical microscope. The average COF was obtained by averaging the COFs from the start of the experiment until the last recorded COF (60th minute). The mechanical properties of the steel balls used are presented in Table 3. The reported mean WSD value was the average of three measurements of the resulting wear scars on the steel balls.

**High-frequency reciprocating rig tribology test**

The tribological performance of the lubricant samples under a boundary lubrication regime was further evaluated using a reciprocating friction and wear monitor, also commonly known as a high-frequency reciprocating rig. For the HFRR test setup, the cylindrical roller bearing slides in a reciprocating motion against a steel plate at a 5-mm stroke length under fully submerged oil conditions, as shown in Fig. 2. The mechanical properties of the cylindrical roller bearing and steel plate are presented in Table 3. For preparation of the steel plates, all samples were polished using four different grades of sandpaper and a 1-μm diamond suspension was used as the final polishing step. Prior to testing, all specimens were thoroughly cleaned using toluene to avoid contamination. To ensure a boundary lubrication regime throughout the test, the combination of a high normal load and moderate speed was utilized. Thus, a normal load of 100 N at a frequency of 10 Hz was set for 60 min. The oil bath temperature was kept constant at 75 °C. Upon completion, the COF was determined as the ratio of frictional force, F (N), and applied load, W (N). The frictional force value was determined by the load cell. Similar to the four-ball test, the average COF was reported as the mean COF from the start of the experiment until the last recorded COF (60th minute).
Surface analyses of the steel plates were carried out using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDX), and surface profilometry. SEM and EDX analyses were carried out to examine the surface morphology and the chemical composition of elements deposited on the worn steel surfaces. EDX confirmed the involvement of ILs during tribotesting. Because distinct elements originate from each IL, it provides evidence of the formation of a tribolayer by the ILs. The topography of the worn steel surfaces was then examined using a non-contact-type surface profilometer. This equipment utilizes the wave-like nature of light to accurately measure distances, providing accurate topographical information, including surface roughness parameters ($R_a$, $R_q$, and $R_z$). Prior to surface profilometry, all steel plates were thoroughly cleaned and wiped with toluene and a soft lint-free cloth to remove the tribolayer formed on the surface. Then, an ultrasonic bath was employed using acetone as an aqueous medium to remove the remaining oil residue and wear particles.

Estimation of film thickness and lubrication regime

During tribotesting, a thin lubricant film was formed between two interacting surfaces. The thickness of this film is highly dependent on various factors such as normal load, surface roughness of the sliding components, sliding speed, viscosity of the lubricant, etc. In the present study, the minimum film thickness for HFRR (line contact) and four-ball testing (point contact) was calculated using two different equations as proposed by Dowson (33) for line contact geometry (Eq. [1]) and Hamrock and Dowson (34) for point contact geometry (Eq. [2]):

\[ h = \frac{4F}{πD^3} \]

\[ h = \frac{4F}{πD^3} \cdot \frac{1}{(1 - \nu^2)} \cdot \frac{1}{(1 - \nu^2)} \]

Table 2. Physical properties of lubricant samples.a

<table>
<thead>
<tr>
<th>Sample name</th>
<th>KV at 40 °C</th>
<th>KV at 100 °C</th>
<th>VI</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO8</td>
<td>45.98</td>
<td>7.76</td>
<td>137.3</td>
<td>0.8316</td>
</tr>
<tr>
<td>TMPTO</td>
<td>48.75</td>
<td>9.57</td>
<td>185.0</td>
<td>0.9190</td>
</tr>
<tr>
<td>IL1</td>
<td>570.4</td>
<td>55.90</td>
<td>163.2</td>
<td>0.8885</td>
</tr>
<tr>
<td>IL2</td>
<td>83.68</td>
<td>10.98</td>
<td>118.0</td>
<td>1.3732</td>
</tr>
<tr>
<td>IL3</td>
<td>170.2</td>
<td>19.37</td>
<td>130.2</td>
<td>0.8867</td>
</tr>
</tbody>
</table>

Comparison with literature

- TMPTO<sup>b</sup> 51.36 10.11 189.0 —
- TMPTO<sup>c</sup> 50.95 10.01 187.9 0.9157
- TMPTO<sup>d</sup> 50.06 9.92 189.4 0.9199

Table 3. Mechanical properties of used steel ball, roller bearing, and plate.

<table>
<thead>
<tr>
<th>Name</th>
<th>Material</th>
<th>Modulus of elasticity, $E$ (GPa)</th>
<th>Poisson ratio, $\nu$</th>
<th>Surface roughness, $\sigma$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel balls</td>
<td>AISI 52100</td>
<td>210</td>
<td>0.3</td>
<td>0.02</td>
</tr>
<tr>
<td>Cylindrical roller bearing</td>
<td>AISI 52100</td>
<td>205</td>
<td>0.3</td>
<td>0.03</td>
</tr>
<tr>
<td>Steel plate</td>
<td>AISI 52100</td>
<td>195</td>
<td>0.29</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Figure 2. HFRR test setup and chemical composition of stainless steel plates.
where

$$h_{\text{min}} = \frac{G^{0.54} U^{0.7}}{W^{0.13}}$$

and

$$h_{\text{min}} = \frac{2.65}{R'}$$

$$\lambda = \frac{h_{\text{min}}}{(\sigma_1^2 + \sigma_2^2)^{0.5}}.$$ 

### Results and discussion

#### Physical properties and miscibility

Table 2 shows the physical properties of various blends. It can be observed that the addition of ILs did not alter the properties much in terms of viscosity and density in comparison to neat base oils (PAO8 and TMPTO). This is due to the small amount of ILs added to the base oils, thus resulting in a minimal effect on viscosity and density. Nevertheless, it can be observed in general that the kinematic viscosity of all blended base oils increased steadily with increasing concentrations of ILs due to the highly viscous nature of ILs. The highest viscosity of PAO8 and TMPTO blends (46.55 and 50.35 cSt, respectively) was observed when 1.5 wt% of IL1 was added. From Table 2, it can be observed that IL1 had the highest viscosity among the three tested ILs. The viscosity index (VI) of a lubricant indicates the effect of temperature deviation on viscosity. From Table 2, it can be observed that TMPTO and its blends exhibited higher VI compared to PAO8 blends. The higher VI of bio-based lubricants is due to the presence of fatty acid chain components, resulting in higher overall molecular weight (Salmon, et al. (37)).

In terms of miscibility, visual inspection revealed that no precipitation or formation of separation layers occurred for the blends with IL1 and IL2, thus indicating that both ILs have good solubility in polar and nonpolar base oils (Grace, et al. (20); Amiril, et al. (23)). This might be due to the long alkyl chains for both cations and anions of IL1 and IL2. ILs with long hydrocarbon chains are reported to be more
miscible in oils, because their structures are well matched with the base oil (Otero, et al. (38)). IL3 was less miscible in TMPTO and PAO8 because the blends appeared cloudy. Although the blends appeared to be homogenous after stirring, a separation layer started to form after 3 days. This might be due to the fact that the pair of 2D-structured imidazolium cations and small inorganic tetrafluoroborate anion, [BF4]−/C0−, is well known to be less miscible in oils (Zhou and Qu (9)).

Estimation of lubrication regime

The calculated minimum film thickness, \( h_{\text{min}} \), and the lambda factor, \( \lambda \), of each sample are presented in Table 4. For all samples, a \( \lambda \) value less than 1 implies that all samples experienced a boundary lubrication regime in both HFRR and four-ball tests. Based on Eqs. [1] and [2], if the geometry and material properties of the contacting surfaces as well as the speed and load for the tribotest are fixed, the film thickness is highly dependent on the pressure–viscosity coefficient (\( \alpha \)) and dynamic viscosity (\( \eta \)). As previously mentioned, the addition of ILs in small amounts did not alter the viscosity much in comparison to the neat base oils. It also can be observed in Table 4 that for samples of the same base oil, the dynamic viscosity and pressure–viscosity coefficient are in proximity to one another, thus producing an overall similar film thickness for PAO8 and TMPTO blends. PAO8 blends showed on average slightly thicker film thicknesses compared to those of TMPTO blends due to higher pressure–viscosity coefficient of PAO8 blends. It is posited that lubricants with a higher pressure–viscosity coefficient produce thicker tribofilms under high loading conditions (Sharma and Stipanovic (39)).

Four-ball tribology test

Figures 3 and 4 show the variation in the COF over time for PAO8 and TMPTO samples, respectively, during wear tests using the four-ball tribometer. The mean WSD on the steel ball surfaces and average COF are presented in Figs. 5 and 6, respectively. Comparing the two base oils, TMPTO as a neat lubricant showed superior lubrication performance when compared to PAO8 in terms of lower average COF (0.084 vs. 0.101) and mean WSD (495.50 vs. 562.69 \( \mu \m \)). This was due to the presence of fatty acid molecules in bio-based oils that can react with metal surfaces to form a low-shear-strength metallic soap layer, therefore reducing friction between surfaces (Syahir, et al. (3)). For PAO8 base oil, the addition of ILs at various concentrations reduced the COF and WSD compared to neat PAO8, except for PAO8 with 1.5 wt% of IL3, which had an increase in the COF of about 5%. This corresponds to the good lubrication ability of ILs with the ability to form a strong lubrication layer on the steel surface during operation. IL2 at 1 wt% concentration in PAO8 exhibited the best performance, with a roughly 25% reduction in average COF and 17% reduction in mean WSD. This was because the anion of IL2 is composed of fatty acid chains, therefore improving the lubricity due to the formation of a tribolayer. High COF peaks were observed for PAO8 with IL1 at various concentrations. The same phenomenon was reported by Amiril, et al. (23), who used the same IL, [P14,6,6,6][TMPP], for a steel–steel contact condition. Such peaks could be the result of abrasive wear and are therefore indicate an increase in the overall worn surface area of the steel surface.

In the case of TMPTO, the addition of ILs further improved their lubrication performance. In general, the addition of ILs at various concentrations resulted in a lower
average COF and mean WSD when compared to neat TMPTO. At 1 wt% concentration in TMPTO, IL1 and IL2 exhibited superior performance, with 28 and 18% reductions, respectively, in the average COF and 13 and 18% reductions, respectively, in average WSD. The effectiveness of ILs in reducing the COF and WSD in both base oils is due to their polar in nature, which enables them to readily adsorb on metal surfaces, forming low-shear-rate layers that can facilitate the relative movement of tribotesting interfaces (Syahir, et al. (3)).

For all IL3 concentrations, only a 4% reduction was recorded for both COF and WSD. This might be because IL3 is incompatible with TMPTO. As seen in Fig. 3, the variation in COF over time for PAO8 samples during four-ball tribotesting and the COF curves for all TMPTO samples with the addition of IL3 fluctuated more throughout the test when compared to others, indicating that the lubricant samples could not form strong and stable tribolayers to effectively aid in friction and wear reduction.

From the COF curves, it can be clearly seen that PAO8 blends experienced less fluctuations compared to TMPTO blends. Most of the PAO8 blends achieved a steady-state condition in roughly 20 min except for PAO8 + IL1-0.5 (30 min). For TMPTO blends, it took roughly 25 min to reach a steady-state condition, followed by minor fluctuations.
fluctuations until the end of testing period. This indicated that at high normal load (400 N) and elevated temperature (75 °C), the tribofilm formed by fatty acids in the bio-based lubricant was broken down and re-formed repeatedly throughout testing period. Nevertheless, these fatty acid chains are surface-active materials that are able to cover the surface asperities, resulting in a low COF and WSD compared to PAO8 base oil (Zulkifli, et al. (40)).

High-frequency reciprocating rig tribology test

Determination of coefficient of friction

The effectiveness of IL blends in reducing the friction of reciprocating interfaces under a boundary lubrication regime was further evaluated using HFRR tests. Figures 7 and 8 show the variation in COF over time for PAO8 and TMPTO, respectively. Similar to four-ball test results, TMPTO as a neat lubricant showed a lower average COF than PAO8 due to fatty acid chain molecules, as discussed earlier. In general, results obtained from both HFRR and four-ball testing showed almost similar trends but differed in terms of average COF magnitude. A higher COF magnitude recorded in four-ball testing might be due to higher normal loading condition (400 vs. 100 N), thus generating a higher frictional force between interacting surfaces.

The addition of IL1 and IL2 in both PAO8 and TMPTO base oils caused a significant reduction in the magnitude of the average COF. At 1 wt% concentration, both IL1 and IL2 exhibited a 20% reduction in the average COF when compared to neat TMPTO. Such a reduction was due to their high polarity, enabling them to form strong and effective adsorption films and tribochemical reactions on the steel surfaces. In the case of lubricant samples containing IL3, the friction-reducing capability of the IL was only observed only at 0.5 wt% concentration. As seen in Figs. 7 and 8, a further increase in IL3 concentration caused heavy fluctuations in the COF, indicating that the lubricant samples could not form a tribolayer. The sudden increased in COF might also be due to wear debris that formed as a result of corrosive wear, which will be explained later.

From both tribotests, it can be observed that for both base oils, increasing the IL concentration from 0.5 to 1 wt% resulted in improvements in the COF and WSD. However, a further increment to 1.5 wt% IL concentration caused the COF to increase. Therefore, it can be deduced that increasing IL concentration does not necessarily translate to better friction and wear reduction, and the addition of ILS at 1 wt% concentration produced the most satisfactory results in terms of low COF and WSD compared to those of neat base oils.

SEM micrographs of worn surface

As mentioned earlier, the main reason for the use of an HFRR tribotester is due to its reciprocating sliding motion and line contact geometry. Wear generation as a result of line contact geometry is a more appropriate representation of wear that occurs in most machines, because a line contact geometry of interacting interfaces is more commonly found than a point contact geometry. Thus, information regarding the wear mechanism and surface morphology can be clearly obtained and analyzed with this testing method.

Figures 9 and 10 show SEM images of the worn surfaces using PAO8 and TMPTO base oils, respectively, labeled according to each type of lubricant sample. Micrographs at high magnification (1,500×) and ultrahigh magnification...
(5,000×) are provided in order to observe the wear mechanism at a micro level. In the absence of ILs, the surface tested with neat base oils exhibited a loss of material from the worn surface, with additive-free PAO8 showing an amount of wear similar to that of additive-free TMPTO, although with a different in wear mechanism. The high-magnification SEM micrograph shows material removal due to corrosive wear and abrasive wear when using additive-free TMPTO as lubricant, whereas additive-free PAO8 resulted in plastic deformation due to adhesive wear.

Such wear losses by TMPTO can be related to accelerated abrasive wear throughout the sliding test duration as well as the presence of free fatty acid, which promotes corrosive wear on the steel surface. Though the polar nature of

Figure 7. Variation in COF over time for PAO8 samples during HFRR tribotesting.

Figure 8. Variation in COF over time for TMPTO samples during HFRR tribotesting.
TMPTO helped to reduce the COF when compared to PAO8, the base oil itself had limited wear protection capability. Thus, suitable additives need to be added in order to further improve the wear-reducing behavior of TMPTO. Such additives are essential because they usually have much stronger surface affinity than base oils, enabling a stronger and more stable tribofilm to form.

From Figs. 9 and 10, it can be observed that the addition of IL1 and IL2 resulted in a decrease in overall wear for both TMPTO and PAO8 base oils at all concentrations. This

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**Figure 9.** SEM images at 1,500× (left) and 5,000× (right) magnification: (a, a') PAO8, (b, b') PAO8 + IL1-0.5, (c, c') PAO8 + IL1-1.0, (d, d') PAO8 + IL1-1.5, (e, e') PAO8 + IL2-0.5, (f, f') PAO8 + IL2-1.0, (g, g') PAO8 + IL3-0.5, (i, i') PAO8 + IL3-1.0, and (j, j') PAO8 + IL3-1.5.
proves that phosphate-containing ILs can improve the tribological properties of both synthetic and bio-based lubricants. This is in line with findings reported by Jiang, et al. (21). The smoother surface finish obtained when using TMP ester base oil can also be due to their polishing effect, as reported in previous research (Syahir, et al. (3); Zulkifli, et al. (40, 41)). However, for TMPTO with IL1 and IL2, detrimental wear such as delamination and cracking occurred, in
addition to corrosive wear, as previously discussed. This indicates that at high loading condition, the tribofilms formed by IL1 and IL2 were not able to withstand the load, eventually breaking down and being polished away together with the fatty acid metallic soap layer.

Looking at the effect of IL concentration, IL1 and IL2 at 1 wt% concentrations in both TMPTO and PAO8 base oils produced an overall smoother surface finish, as seen in the SEM micrographs at 1,000× magnification. Such low wear correlates with the low COF obtained at 1 wt% concentration for both IL1 and IL2. At 0.5 wt% concentration, a slight reduction in wear was observed for IL1 and IL2 when compared to neat base oils. However, detrimental wear including dense micropits and cracks was detected. This is undesirable because over an extended period of operation time, these micropits and cracks can propagate, causing severe material loss at the surface and eventually component failure. For TMPTO, the addition of ILs at 0.5 wt% was not enough to mitigate the corrosive effect of the base oil.

As observed in the high-magnification SEM micrographs, a further increase in IL1 and IL2 concentrations to 1.5 wt% resulted in severe wear for both base oils. In the case of PAO8, plastic deformations and material removal due to adhesive wear were more apparent when ILs were added at 1.5 wt% concentration compared to lower concentrations. The same was observed for TMPTO, where the presence of cracks and deep grooves was observed for 1.5 wt% IL concentration. Therefore, the SEM micrographs indicated that IL1 and IL2 could perform as an effective antiwear additive in small quantities at a concentration of approximately 1 wt%. This was consistent with COF analysis and thus it was concluded that an increase in IL concentration does not translate into better wear reduction performance.

For TMPTO and PAO8 with IL3, only 0.5 wt% concentration produced satisfactory results in terms of wear. An increase in IL3 concentration to 1 and 1.5 wt% resulted in severe wear on the steel surfaces, dominated by corrosive attacks and adhesive wear. Such a phenomenon is due to the hygroscopic nature of IL3 and the presence of halogen compounds in the anion structure of IL3, in this case, fluorine. Halogen-containing ILs are known to cause corrosion at steel interfaces, as reported by previous research (Ueringen, et al. (42); Zhao, et al. (43)). Due to the hygroscopic nature of IL, water from the atmosphere is drawn into the lubricant, eventually leading to decomposition of the IL. Fluorine can react on friction surfaces to form metal fluoride, which is believed to further react with water by tribochemical reactions, producing hydrogen fluoride, which is highly corrosive (Kondo, et al. (24)).

Such an occurrence might explain the sudden heavy fluctuation in the COF observed for TMPTO and PAO8 IL3 at 1 and 1.5 wt% concentrations. The formation of wear debris as a result of accelerated corrosive and adhesive wear can interrupt stable tribofilm formation during operation, which results in more metal–metal contact and eventually causes spikes in the COF. Compared to PAO8, such heavy fluctuations in the COF were less apparent for TMPTO with IL3. This was due to the good lubrication properties of TMPTO as a base oil.

**EDX analysis of worn surface**

EDX analysis provides elemental details for the same surface regions examined by SEM. This analysis assessed the involvement of ILs on the contacting surfaces during operation. Table 5 shows the atomic percentage of the elements found on the steel plates for lubricant samples with the addition of 1 wt% IL after 1 h of HFRR tribotesting.

In general, iron, carbon, and chromium are the main elements of the stainless steel plate. The presence of oxygen can be attributed to the formation of iron oxides as a result of oxidation, commonly referred to as an oxide layer. It is well known that the formation of an oxide layer on metal surfaces can reduce the transfer of material caused by adhesive wear mechanisms, preventing metal-to-metal contact and, thus, reducing the COF. However, if the oxide layer exceeds a critical thickness, it will break up and form debris, eventually causing an increase in abrasive wear (Merz, et al. (44)). When TMPTO-based lubricants were used, a higher atomic percentage of oxygen was observed in EDX results compared to PAO8-based lubricants. This was because the fatty acid chains of TMP esters contain oxygen molecule in the hydroxyl group. The presence of oxygen within TMP accelerates the formation of oxides, in contrast to PAO8, which only relies on atmospheric oxygen.

The presence of phosphorus on the worn surface when lubricated with lubricants containing IL1 and IL2 confirmed the formation of an IL-derived tribofilm during operation. It can be clearly seen from the SEM micrographs that the worn surfaces lubricated with IL1 and IL2 at 1 wt% produced an overall smoother surface finish, with some wear regions that are only visible under high magnification (Figures 9(d,d′) and 10(d,d′)). It was reported that for phosphonium-based ILs, both cation (phosphonium) and anion parts (phosphate) play an important role by adsorbing onto the surface to form a protective multilayered structure, reducing metal contacts (Totolin, et al. (45); Yu, et al. (46)). In this case, phosphonium cations (IL1 and IL2) and phosphate anions (IL1) increase the wear-reducing properties of both base oils at an optimum concentration (1 wt%).

In the case of IL3, the detection of a high atomic percentage of boron, nitrogen, and fluorine, as presented in Table 5, confirmed the formation of an IL3-derived tribofilm during operation. The presence of fluorine on the worn surface indicates the formation of metal fluoride as a result of

<table>
<thead>
<tr>
<th>Lubricant samples</th>
<th>Fe</th>
<th>O</th>
<th>Cr</th>
<th>C</th>
<th>P</th>
<th>B</th>
<th>N</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO8</td>
<td>48.8</td>
<td>21.3</td>
<td>6.1</td>
<td>23.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO8 + IL1-1%</td>
<td>46.5</td>
<td>21.6</td>
<td>5.9</td>
<td>24.1</td>
<td>1.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO8 + IL2-1%</td>
<td>34.6</td>
<td>24.9</td>
<td>5.5</td>
<td>33.9</td>
<td>1.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAO8 + IL3-1%</td>
<td>28.1</td>
<td>23.3</td>
<td>4.1</td>
<td>19.8</td>
<td>10.2</td>
<td>6.2</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>TMPTO</td>
<td>40.2</td>
<td>32.2</td>
<td>7.0</td>
<td>20.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + IL1-1%</td>
<td>36.4</td>
<td>34.2</td>
<td>6.6</td>
<td>21.1</td>
<td>1.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + IL2-1%</td>
<td>41.4</td>
<td>31.5</td>
<td>6.6</td>
<td>19.3</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TMP + IL3-1%</td>
<td>20.7</td>
<td>30.4</td>
<td>2.7</td>
<td>22.7</td>
<td>10.9</td>
<td>7.2</td>
<td>5.4</td>
<td></td>
</tr>
</tbody>
</table>
surface reactions. This metal fluoride layer will later react with water to produce hydrogen fluoride, which is highly corrosive (Kondo, et al. (24)). Such chemical reactions can be further analyzed and understood through in-depth analysis techniques such as X-ray photoelectron spectroscopy and auger electron microscopy. Another point worth mentioning is the reduction in chromium percentage on the worn surface lubricated with base oils with the addition of IL3. The reduction in chromium indicates that the passive chromium oxide (Cr₂O₃) layer of stainless steel was

Figure 11. 3D surface profile of the worn steel plate after 1 h of tribotesting.
damaged due to severe wear, as seen in Figs. 9j and 10j. Thinning of this layer is detrimental because the surface will be less protected from corrosion due to atmospheric humidity.

**Surface topography analysis**

Three-dimensional topographic features of the worn steel surface texture are presented in Fig. 11. It is posited that at high loading conditions, ILs can readily adsorb and react with the exposed metal surface to form a protective tribofilm due to their ionic form in nature. The tribofilm formed by ILs had rather low shear strength, resulting in lower friction and better overall surface finish, which could be validated quantitatively through the reduction of overall surface roughness.

Comparing the two base oils, it can be observed from Fig. 11 that TMPTO produced an overall smoother surface finish than PAO8 ($R_a = 0.014 \, \mu m$, $R_q = 0.017 \, \mu m$, $R_z = 0.056 \, \mu m$ vs. $R_a = 0.018 \, \mu m$, $R_q = 0.022 \, \mu m$, $R_z = 0.079 \, \mu m$, respectively). This was due to the surface polishing effect of bio-based lubricants due to the surface reactions of fatty acid chains with the metal surface (Syahir et al. (3); Zulkifli et al. (40)). Such a result is also in line with the COF results, where TMPTO exhibited a lower COF than PAO8 in both four-ball and HFRR tribotesting.

The addition of IL1 and IL2 in both PAO8 and TMPTO base oils caused a notable reduction in overall surface roughness, as shown in Fig. 11. In terms of $R_a$, $R_q$, and $R_z$, PAO8 with the addition of IL1 and IL2 produced surface roughness that was 25 and 23% lower, respectively, on average, than that of neat PAO8. For TMPTO, the addition of IL1 and IL2 at 1 wt% resulted in lower $R_a$, $R_q$, and $R_z$ by 26 and 28%, respectively, compared to neat TMPTO. As discussed previously, phosphorus-containing IL1 and IL2 help to further reduce the COF through the adsorption of a tribofilm on the interacting surfaces and the formation of phosphoric acid (friction modifier) during surface interaction (Totolin, et al. (45); Johnson (47)).

The best polishing effect in terms of low roughness parameter values was presented by both TMP-IL1-1% and TMP-IL2-1%. The corresponding values of surface roughness parameters were rather similar for both lubricant samples: $R_a = 0.010 \, \mu m$, $R_q = 0.013 \, \mu m$, $R_z = 0.042 \, \mu m$ for TMP-IL1-1% and $R_a = 0.009 \, \mu m$, $R_q = 0.012 \, \mu m$, $R_z = 0.045 \, \mu m$ for TMP-IL2-1%. From this surface texture analysis, a biolubricant and an IL-derived tribofilm can synergistically work together in reducing the COF and producing an overall better surface finish.

The addition of IL3 to both base oils resulted in a significant increase in the surface roughness parameters $R_a$ and $R_q$. Such an increase was caused by severe wear on the steel surfaces after HFRR tribotesting. As mentioned in the preceding section, IL3 promotes additional corrosive and adhesive wear due to the formation of halogen compounds during surface interaction. In this regard, the highest values of roughness parameters ($R_a = 0.073 \, \mu m$ and $R_q = 0.090$) were recorded for the steel surface tested with TMPTO-IL3-1%. Therefore, it can be concluded that the addition of IL3 interrupted the polishing effect provided by the biolubricant-derived tribofilm, producing a rougher worn surface compared to that of neat TMPTO.

**Conclusion**

The compatibility and tribological performance of ILs as additives in synthetic and bio-based lubricants were studied and analyzed. From the results obtained in this research study, the following conclusions can be drawn:

- IL1 and IL2 showed excellent miscibility, whereas IL3 was less miscible with both synthetic and bio-based oils. The optimum amounts of IL as an additive was 1 wt% for IL1 and IL2 and 0.5 wt% for IL3. At optimum concentrations, excellent tribological performance was observed in terms of friction and wear reduction, in addition to an improved overall surface finish when compared to neat base oil. The presence of phosphorus in IL1 and IL2 resulted in better surface finishing in terms of lower surface roughness parameter values.
- The addition of IL3 at concentrations higher than 0.5 wt% caused a spike in the average COF and overall wear due to the formation of halogen compounds. IL3 added to TMP resulted in severe surface damage compared to IL3 added to PAO8 base oil.

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