Bio-additives Derived from Ricinoleic Acid and Choline with Improved Tribological Properties in Lithium Base Grease

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Abstract: In this study, bio-based ionic liquid prepared from ricinoleic acid and choline was firstly used as additive in lithium base grease. The characterization and tribological performance of the prepared ionic liquid ([cho][ricinoleic]) as additive in grease were studied compared with the traditional ionic liquid such as L-P104. All the concentrations showed promising friction-reducing and anti-wear properties, though a 3% concentration has superior lubricating properties than others. Furthermore, [cho][ricinoleic]) can greatly enhance the lubrication capability of lithium base grease under different conditions and load at room temperature. Although L-P104 showed good lubricating performance than [cho][ricinoleic] at 150°C, the chosen formulation (1.5% [cho][ricinoleic] + 1.5% L-P104) could have better synergism at high and room temperature, which could be a good supplement to ionic liquid as additive grease. Thin films formed according to the results of SEM and XPS were attributed to be the main account for the preferable tribological properties of [cho][ricinoleic] in lithium base grease.

Key words: bio-based additive, IL, grease, tribological properties

1 Introduction

With people’s attention to environmental pollution, more and more strict environmental laws and regulations, and non-renewable oil resources, renewable bio-based lubricants have become the most ideal substitute for petroleum-based lubricants because of their good environmental friendliness, non-toxicity and renewable degradability¹, ². Bio based vegetable oil, such as soybean oil and rapeseed oil, can be directly used as base oil in formula, or as precursor for manufacturing chemically modified base oils and effective additives³-⁵. Although bio-based base oils have been already used in some equipment lubrication, its poor oxidation resistance, low temperature performance and low working viscosity still limit its wide application in the field of lubrication⁶, ⁷. At the same time, although some chemical modifications for bio-based base oils have improved these shortcomings to a certain extent, there is still a certain gap compared with petroleum based base oils⁸-₁₀. Therefore, compared with the utilization as base oils, the bio-additive achieved by chemical modification has a certain practical application value at present. A series of papers have already investigated the bio-additives from renewable sources to obtain interesting formulation for lubricants₁¹-₂₁.

Since 2001, Ionic liquids (coded as ILs in the follows) has been widely studied in the field of tribology because they have excellent antifriction and anti-wear properties as lubricating base oils and additives under different environmental conditions²₂-₂₄. However, the synthesis process of ILs lubricant is complex and expensive. At the same time, ILs contains corrosive and low degradability elements such as chlorine, sulfur and phosphorus, which limits its practical application in environmentally friendly fields. To solve this problem, the recent study of a new family[PILs or ILs] based on proton ammonium cations and carboxylate anions have opened the way for a new class of ILs²₅-₃₆. This class of ILs not only embodies the advantages of traditional ionic liquid in terms of tribological properties, but also does not contain corrosive elements that affect the environment. Therefore, bio-based materials can use the preparation methods of ILs form carboxylic acid anion and ammonium ion to obtain green, environmentally friendly and high-performance lubricating additives.

As additives for lubricating grease, the advantage of
using ILs is that solubility problems can be avoided. As reported\(^{37}\), the extreme pressure capacity of the high temperature grease could be dramatically increased by the addition of ILs additives. When the traditional ILs was used in polyurea grease at a concentration of 1 wt\%, it showed better tribological properties for steel/steel contact at high temperature than at room temperature. In addition, the addition of 3 wt\% PILs without fluorine element dramatically enhanced the lubricity properties of the base lithium complex grease\(^{38}\). Compared with conventional additives, its advantages in some aspects were proved. However, a more comprehensive evaluation for bio-based additives in grease should be performed for specific appoint.

Recinoleic acid is the main component of castor oil, which is used to produce sebacic acid and undecanoic acid. In addition, choline is a strong organic base and a component of lecithin. ILs were synthesized from the above materials and used as corrosion inhibition and friction improvement additives in glycerol aqueous solution for the first time in our present work\(^{39}\). Then, the relatively ionic liquid was further investigated as base fluids for containing MoS\(_2\) quantum dots\(^{40}\). In addition, the synergism tribological properties were also studied in water in previous work\(^{32-34}\). The ionic liquid behaved superior lubricating properties under harsh conditions from the above results. However, most of these papers dedicated on tribological abilities of ILs as lubricants itself and additives in water. Seldom research studied on ILs as functional additives in grease. Therefore, ILs was synthesized from bio-based materials and considered as additive for lithium base grease in this paper. In additional, tribological properties compared with traditional L-P104 were also investigated.

### 2 Materials and Methods

#### 2.1 Materials

Ricinoleic acid (purity >97.0\%) and Choline hydroxide aqueous solution (46 wt\% in H\(_2\)O) was obtained from Macklin Biochemical and Sigma. By the previous literature\(^{40}\), Ionic liquid (coded as [cho][ricinoleic]) can be acquired from the simple neutralization method of choline hydroxide with ricinoleic acid. In addition, traditional L-P104 ILs was purchased from Qingdao Aolike New Material Technology Co., Ltd. Their chemical structure, properties, and the digital photo were depicted in Fig. 1. Lithium base grease was provided from Qingdao Lubemater Lubricating Material Technology Co., Ltd. The typical properties of lithium grease are listed in Table 1. For studying the influence of the additives on the tribological behavior of lithium base grease, the [cho][ricinoleic] additive and L-P104 were added into lithium grease at the 1-4\% concentrations.

#### 2.2 Analysis methods

The dropping point of grease with different additives was determined according to ASTM D566. The details are following. Fill the grease cup with the grease sample, remove the excess grease with a scraper, put the grease cup and thermometer into the test tube, and hang the test tube into the oil bath. Raise the temperature of the oil bath at 4\(^{\circ}\)C\ per minute until the temperature of the oil bath is about 17\(^{\circ}\)C lower than the dropping point of the lubricating grease, and reduce the heating temperature to 1-1.5\(^{\circ}\)C per minute. Then the temperature continues to rise. When the first drop drops from the fat cup, immediately record the temperature of the thermometer. The average of the two results is the drop point of the grease. The cone penetration (0.1 mm) of grease with different additives was determined following ASTM D217. Thermal stabilities of

<table>
<thead>
<tr>
<th>Code</th>
<th>Structure</th>
<th>Decomposition temperatures, °C (onset)</th>
<th>Viscosity index</th>
<th>Kinematic viscosity (mm(^2)/s)</th>
<th>Digital photo</th>
</tr>
</thead>
<tbody>
<tr>
<td>[cho][ricinoleic]</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>186.0</td>
<td>142</td>
<td>479.0</td>
<td>43.3</td>
</tr>
<tr>
<td>L-P104</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>380.8</td>
<td>123</td>
<td>72.7</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Fig. 1 The chemical structure and the digital photo of [cho][ricinoleic] ionic liquid and L-P104.
greases with different concentrations of additives were tested by using an NETZSCH STA 449F3 thermal analysis system from room temperature to 400°C under a nitrogen environment. The anticorrosion behavior of [cho] [ricinoleic] compounds with different concentrations and L-P104 with 3% concentration in grease to steel plate was tested at 100°C for 24 h. The surface details of steel parts were analyzed by Olympus BX41 optical microscope at 10 times.

2.3 Tribology analysis

The tribology behavior of the grease was tested and recorded by an Optimol SRV-V tester. The detailed experimental parameters of the SRV are shown in Table 2. The SRV friction and wear test under every applied load and each concentration with different additives was repeated for three times. The wear volumes of the lower disks were obtained by a noncontact 3D surface profiler. The morphology of the wear scars was accessed using SEM (JSM-5600LV). The worn surfaces were investigated by XPS.

<table>
<thead>
<tr>
<th>Grease property</th>
<th>Test standard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thicker Lithium Base oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dropping point (˚C)</td>
<td>ASTM D 566</td>
<td>210</td>
</tr>
<tr>
<td>Cone penetration (0.1 mm)</td>
<td>ASTM D 217</td>
<td>220</td>
</tr>
<tr>
<td>Copper corrosion (T2 copper, 100°C, 24 h)</td>
<td>GB/T 7326</td>
<td>Up to standard</td>
</tr>
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</table>

3 Results and Discussion

3.1 Characterization

The onset of decomposition temperature by the TGA curves presented in Fig. 2 of the lithium base grease and the greases with different concentrations of additives were all above 210°C. Although the tested 4% [cho] [ricinoleic] additive in grease showed relative-low thermal stability than others concentrations, they all showed good oxidation stability compared with base grease. In additional, the TGA curves of 3% [cho] [ricinoleic] additive and 3% L-P104 in grease are also shown in Fig. 2. The results showed 3% [cho] [ricinoleic] additive in grease have relatively good thermal stability than 3% L-P104 in grease. The positive and negative pairs of [cho] [ricinoleic] additive seemed to have little influence than L-P104 ionic liquid on the decomposition temperature of grease.

The cone penetration, the dropping point and the anticorrosion properties of [cho] [ricinoleic] compounds and L-P104 with different concentration in grease are shown in Fig. 3. With the increase of [cho] [ricinoleic] additive concentration from 1% to 4%, the dropping point of grease gradually decreased from 209.3°C to 198.8°C, as well as the cone penetration (0.1 mm) of grease gradually increase from 220 to 252. Although additives have a certain influ-
Fig. 2  The TGA curves of [cho][ricinoleic] compounds and L-P104 with different concentration in lithium base grease.

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Dropping point(°C)</th>
<th>Cone penetration (0.1mm)</th>
<th>Iron surface</th>
<th>SEM (50μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base grease</td>
<td>209.3</td>
<td>220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% [cho][ricinoleic]</td>
<td>206.4</td>
<td>228</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% [cho][ricinoleic]</td>
<td>203.1</td>
<td>236</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% [cho][ricinoleic]</td>
<td>200.0</td>
<td>244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4% [cho][ricinoleic]</td>
<td>198.8</td>
<td>252</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% L-P104</td>
<td>206.7</td>
<td>229</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3  The cone penetration, the dropping point and the anti-corrosion properties of [cho][ricinoleic] compounds and L-P104 with different concentration in lithium base grease.
ence on the stability of lithium base grease, the grease still maintains the characteristics of lithium grease and had not changed greatly. In the meanwhile, the grease with 3% L-P104 additive had only a small impact on its own. In additional, the results of the steel block test of [cho][ricinoleic] with different concentration and L-P104 with 3% in grease are also shown in Fig. 3. After the test, there was no corrosion on the surface of the steel block, indicating that the [cho][ricinoleic] additive and L-P104, as an additive of lubricating grease, did not seriously corrode the surface of the tested friction pair.

3.2 Tribology properties

3.2.1 Effect of concentrations

As previous literature reported, the traditional ILs like L-P104 as additives in grease behaved good lubricity properties at high temperature than at room temperature. For the sake of solving the problem of insufficient performance of ionic liquid as additive at room temperature, the tribological performance of [cho][ricinoleic] ionic liquid as additives with different concentration in grease at room temperature was firstly selected and tested. Figure 4a shows the friction curves of the lithium base grease and the base grease containing 1-4% concentrations of [cho][ricinoleic] ionic liquid under load of 50 N within 30 min. The curve of the friction coefficient lubricated by pure base grease fluctuated greatly in the first 10 min. Although the friction coefficient of base grease tended to be stable at the later stage of friction, the friction coefficient was always above 0.15. However, the friction curves of grease containing [cho][ricinoleic] ionic liquid was more stable and smoother than base grease, and the friction coefficient was lower than base grease, indicating [cho][ricinoleic] ionic liquid could effectively form the stable films under this condition. The results showed that [cho][ricinoleic] ionic liquid with 3% additive in lithium base grease had better lubricity properties than other concentrations at room temperature. At the same time, the friction curves with time of chosen 3% concentration of [cho][ricinoleic] ionic liquid and L-P104 are also shown in Fig. 4a. The base grease containing L-P104 obvious behaved almost same friction coefficient compared with pure grease, which was consistent with previous results. The friction coefficient of grease containing 3% [cho][ricinoleic] was reduced to relative low level than L-P104. This results further verified that [cho][ricinoleic] as additive in grease behave good lubricity at room temperature.

The wear volumes by the lithium base grease and the base grease containing 1% ~ 4% [cho][ricinoleic] and 3% L-P104 at room temperature are also shown in Fig. 4b. The results show that the steel disc lubricated with base grease produced a large amount of wear volume on its surface, while the grease containing [cho][ricinoleic] additives was very small. In particularly, the wear volume by the base grease containing 3% concentration of [cho][ricinoleic] ionic liquid decreased significantly than other concentrations, indication 3% concentration of [cho][ricinoleic] ionic liquid was the best-chosen concentration in lithium grease. In additional, although L-P104 with 3% concentration in base grease also behaved good anti-wear ability than base grease, the wear volume of the steel disc still greatly decreased by the grease containing 3% [cho][ricinoleic] than 3% L-P104. The good competing adsorption of [cho][ricinoleic] than L-P104 at room temperature may be attributed to the reason for this phenomenon.

3.2.2 Effect of frequency

When the grease is sheared, the contact part between the individual soap fibers constituting the continuous skeleton begins to slide to disengage, making the grease system from deformation to flow, thus affecting its tribological be-

![Fig. 4](image-url)
same friction coefficient compared with pure grease at the L-P104 obvious behaved almost base grease containing 3 \(^{`}\) high shear at room temperature. At the same time, the additives in grease can play a role in reducing friction under ʦ ducing ability than base grease at the frequency of 30 Hz ʦ ch of the base grease tended to be stable and low at the later stage of friction. This phenomenon may be due to the fact that under low shear, the ionic liquid additives in the grease could not be well separated from the soap structure of the grease to the surface of the steel to reduce friction and decrease wear. However, the base grease containing the 3% [cho] [ricinoleic] additive behave good friction-reducing ability than base grease at the frequency of 30 Hz and 50 Hz. This result shows that the [cho] [ricinoleic] additives in grease can play a role in reducing friction under high shear at room temperature. At the same time, the base grease containing 3% L-P104 obvious behaved almost same friction coefficient compared with pure grease at the frequency of 30 Hz and 50 Hz, which was further consistent with previous results\(^{37}\).

The wear volumes of the lithium base grease, the base grease containing 3% [cho] [ricinoleic] additive and the base grease containing L-P104 are shown in Fig. 5b. As the application frequency increased from 10 Hz to 50 Hz, the wear volumes of the grease containing 3% [cho] [ricinoleic] obvious behaved good anti-wear ability than the lithium base grease and the base grease containing L-P104, respectively. The increasing frequency from 10 Hz to 50 Hz could remarkably lead to two- or three-times wear volume of the base grease than base grease containing 3% [cho] [ricinoleic]. The reasonable explanation was proposed as follows. The increasing frequency could better increase the contact between additives and iron surface so as to provide a more stable lubrication film. In additional, base grease containing 3% [cho] [ricinoleic] additive still had a good anti-wear performance than base grease containing 3% L-P104.

3.2.3 Effect of load

The friction coefficients (as shown in Fig. 6a) and wear volumes (as shown in Fig. 6b) of the lithium base grease and the base grease with 3% additives at 25 Hz and under various applied loads are shown in Fig. 6. When the applied load increasing from 50 N to 150 N, the friction coefficients of the base grease with 3% [cho] [ricinoleic] were all lower than base grease, indicating the good lubricity property of [cho] [ricinoleic] as additive in grease at room temperature. The same results are shown in wear volumes, too. In the meanwhile, L-P104 shows worse friction coefficient and bigger wear volume, which still further shows that the traditional ionic liquid did not have a good tribological performance as a grease additive at room temperature. Evidently, it is favorable for [cho] [ricinoleic] than L-P104 as additives in grease to form a good stable film to protect the surface at room temperature.

3.2.4 Effect of temperature

The friction coefficients (as shown in Fig. 7a) and wear volumes (as shown in Fig. 7b) of the lithium base grease and the base grease with 3% additives at different temperature are shown in Fig. 7. Since traditional ILs like L-P104 had good tribological properties at high temperature than room temperature, the chosen formulation (1.5% [cho] [ricinoleic] + 1.5% L-P104) was also investigated in order to expect that the mixed system can make up for the lack of tribological properties at high and low temperature, respectively. As previously confirmed, the friction coefficients of the base grease containing 3% L-P104 indeed behaved good friction-reducing capacity than the base grease containing 3% [cho] [ricinoleic] at 150°C. At the same time, the anti-wear of the base grease containing 3% L-P104 was also better than that of the lithium base grease and the base grease containing 3% [cho] [ricinoleic] at 150°C. In addition, the friction curves of the lithium base
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Grease and the base grease with 3% additives at 80°C could not show obvious difference. This phenomenon shows that both [cho][ricinoleic] with better tribological properties at room temperature and L-P104 with better tribological properties at high temperature did not show very special lubrication properties at 80°C. It can be explained that [cho][ricinoleic] can better dissociate to the friction interface at room temperature and play the role of friction reduction and anti-wear. However, it may be not easy to fight against soap fiber and reduce the friction at temperature like 80°C and 150°C without active elements. On the contrary, the results further confirmed that only at high temperature the L-P104 could easy behave good tribological properties due to better high temperature mobility and high active element under high temperature.

Interestingly, the chosen formulation of base grease containing 1.5% [cho][ricinoleic] + 1.5% L-P104 showed better lubricating ability under both low and high temperature conditions. As shown in Fig. 7a, the friction curves of the chosen formulation behaved relative smooth than others after 600 s at each temperature. This result might be due to the production of the powerful adsorbed ordered film by [cho][ricinoleic] at room temperature and by L-P104 at high temperature. Similarly, the wear volumes significantly decreased by the chosen formulation than others (As seen in Fig. 7b). This phenomenon is further illustrated [cho][ricinoleic] additive could enhance the anti-wear capacity of base grease through better synergy effect.

3.3 Surface analysis

SEM was employed to discuss the morphology of the worn surfaces for determining the reason and mechanism of wear. Figure 8 displays SEM image of the worn steel surfaces lubricated by the lithium base grease (a, a1) and
the base grease containing 3% L-P104 (b, b1, b2) and the base grease containing 3% [cho][ricinoleic] (c, c1) and chosen formulation (1.5% [cho][ricinoleic] + 1.5% L-P104) (d, d1, d2) under 50 N and 25 Hz at room temperature. Compared with the base grease, the worn surfaces by base grease containing additives showed relatively little plough groove. In particular, the worn surfaces by the lubricating grease containing 3% [cho][ricinoleic] and chosen formulation were quite smooth, and no large fatigue pitting could be found on the worn surface of steel disks. The above results further suggested that the boundary film containing 3% [cho][ricinoleic] could effectively protect the steel block surface from wear caused by come into contact themselves, while the films of the grease containing 3% L-P104 may be more vulnerable and more easily destroyed.

When it comes to 150°C in Fig. 9, the wear surface of grease containing additives was just the opposite. The worn surface by base grease containing 3% [cho][ricinoleic] was characterized by wide scar even than base grease, indicating that it could not form an effective protective film at high temperature alone. However, the worn surface lubricated with chosen formulation was quite smaller and narrower from the image, indicating the [cho][ricinoleic] additive could behave good synergy effect with L-P104 at 150°C.

Figures 8 and 9 also shows the 3D image of the worn steel surfaces lubricated by the lithium base grease (a2) and the base grease containing 3% L-P104 (b2), 3% [cho][ricinoleic] (c2) and chosen formulation (1.5% [cho][ricinoleic] + 1.5% L-P104) (d2) at room temperature and at 150°C, respectively. The results further confirmed the surveyed wear volumes and SEM morphology. Especially, the surface roughness of worn surface in each steel specimen were also shown in Figs. 8 and 9. Compared with the base grease and the base grease containing 3% L-P104, the surface roughness of worn surface by 3%[cho][ricinoleic] was smaller at room temperature. This results further illustrate the 3%[cho][ricinoleic] could effectively protect the steel block surface at room temperature. On the contrary, the surface roughness of worn surface by 3%[cho][ricinoleic] was bigger than others, indicating that it could not effectively protect the steel block surface at 150°C.

XPS exploration of the worn surfaces was employed to further discuss the reason and mechanism of friction and wear. As shown in Fig. 10, obviously, the Fe2p peak at 710.4 eV was on behalf of the formation of iron oxide. Interestingly, the N 1s peaks at 400.2 eV on behalf of organic amine only were observed in the presence of [cho][ricinoleic] as additive in grease, probably due to the adsorption film formed by [cho][ricinoleic] on the worn surface. Similarly, the peaks of P 1s and P 2p of the worn surfaces under lubrication of the grease with L-P104 was not obvious at room temperature, which may be the reason that L-P104 does not form reaction films at this lubrication conditions. However, the peaks of P 1s at 684.5–685.6 eV and the peaks of P 2p appeared at around 133.2 eV could be assigned FeP2 and the compound containing the P–O bonding. These complex compounds played a key lubricating role for the friction reduction and anti-wear properties of grease with L-P104 at 150°C, which was consistent
with the previous conclusion. These results suggested that excellence lubricity behaviors of the [cho] [ricinoleic] ILs as grease additive attributed to the formation stable adsorbed layers containing organic amine compounds at room temperature other than 150°C, and the chosen formulation could significantly improve the tribological performance of the grease at 150°C.

4 Conclusions

In summary, the bio-additives [cho] [ricinoleic] derived from Ricinoleic Acid and Choline in lithium base grease was first studied for steel/steel contact under chosen conditions. The results showed that the bio-additives [cho] [ricinoleic] could substantially decrease the friction coefficient and wear volume of base grease at room temperature, which could be a good supplement to ionic liquid as grease additive. Although L-P104 showed good lubricating performance than [cho] [ricinoleic] at 150°C, the chosen formulation (1.5% [cho] [ricinoleic] + 1.5% L-P104) could have
better synergism at room and high temperature. This might be due to from the results of SEM and XPS that a surface protective film composed of FeF$_2$, compound containing the P–O bonding by L-P104 and a stable adsorbed film by [cho] [ricinoleic] were produced by tribo-chemical reaction on the lubricated metal surface.

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References


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