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# Tribological study of leaf-surface wax extracted from sorghum leaves as a lubricant additive

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# Tribological study of leaf-surface wax extracted from sorghum leaves as a lubricant additive

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**ABSTRACT**

The leaf-surface wax was extracted from the sorghum bicolor (L.) Moench (abbreviated as sorghum) leaves and evaluated as a kind of new lubricant additive in poly-alpha-olefin (PAO) for steel/steel, steel/aluminum and steel/copper contacts using a MFT-R4000 friction and wear tester at room temperature. A gas chromatography-mass spectrometry (GC-MS) analysis system was used to analyze the compositions of sorghum leaf-surface wax (SLW). Scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (SIMS) were employed to characterize the worn surfaces to explore the lubrication mechanisms. The results show that the SLW could effectively reduce the friction and wear for steel/steel and steel/copper friction pairs. The analysis of the worn surfaces suggest the good tribological properties were attributed to the protective films including physical adsorption film and tribochemical reaction film generated during the friction process.

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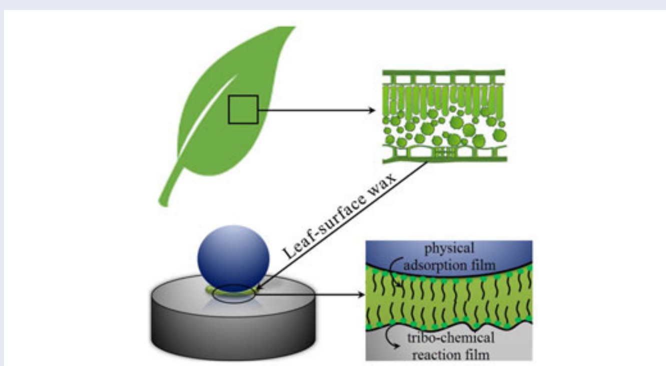
Leaf-surface wax; sorghum; lubricant additive; friction and wear

**GRAPHICAL ABSTRACT**




## Introduction

Lubricant has been widely utilized as an engineering material to perform various functions including minimizing the friction and wear, removing heat, providing a liquid seal and corrosion prevention, etc., thereby improving the mechanical efficiency and prolonging the service life.[1–3] Over the past decades, the global demand for lubricant has increased at a rate of 2% per year.[4] Liquid lubricant is one of the most common form of lubricants, which is composed of base oil and dedicated chemical named additives. In general, base oil devotes the basic performances whereas the additives impart the final lubricants extra properties. In the most of industrial applications, petroleum-based lubricants have been applied for 100 years.[5] According to the assessment, due to the improper disposal, spills, volatility etc., more than 50% of the lubricants enter the environment every year.[5] The most of the lubricants enter the environment are petroleum-based and they could generate a bad influence on the soil, air, water and human and plant life.[2,6–9] Given the increasing attention on the detrimental impact of petroleum-based lubricants and traditional additives containing sulfur, phosphorus and zinc on environment, it is imperative to explore environmental friendly and biodegradable lubricants to meet the tribological performances and environmental needs.

The leaves of the most plants have a lot of leaf-surface wax, which could work as a protective screen to reduce the damages of outside radiation, damages and pollutions, etc. It has been reported that leaf-surface waxes are mainly composed of alcohols, esters, long-chain fatty acids, alkanes and

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Figure 1. (a) sorghum plants and (b) abaxial side of a sorghum leaf.

so forth.[10,11] These single ingredients all have been evaluated as lubricants and the results show that they all have some certain friction reduction and anti-wear abilities.[5,12–14] Therefore, the leaf-surface wax as a mixture composed of these compounds may also be employed as environmentally friendly additives to improve the tribological properties. Recently, a research extracted different leaf-surface waxes as additives and found that the leaf-surface waxes promoted the friction reduction and anti-wear properties.[15,16]

Sorghum bicolor (L.) Moench (abbreviated as sorghum) is a grass species cultivated for its grain, which is used for food, both for animals and humans, and for ethanol production. Sorghum could grow in a wide range of temperature, high altitudes, toxic soils and drought. The leaf surface of sorghum has developed a thick cuticle where contains cuticular wax. Herein, the leaf-surface wax was extracted from the sorghum leaves and the chemical composition of the sorghum leaf-surface wax (SLW) was analyzed by a gas chromatography-mass spectrometry (GC-MS). Sorghum leaf-surface wax was used as an additive in poly-alpha-olefin (PAO) to explore its tribological properties for steel/steel, steel/aluminum and steel/copper friction pairs. After friction test, the worn surfaces were characterized to analyze the possible lubrication mechanisms by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (SIMS).

## Experimental

### Materials

Sorghum leaves were picked up in Hengshui (North China, near 37° 40′ 14.00″ north latitude, 115° 50′ 34.38″ east longitude) and Figure 1 presents the samples. PAO was purchased from Exxon Mobile Corp. (Irving, TX, USA) and used as the base oil. The chloroform and acetone (analytically pure) were all purchased from Sinopharm Chemical Reagent Co., Ltd. The commercial additive molybdenum-dithiocarbamate (MoDTC) was obtained from Adahi Denka Co., Ltd.

### Extraction and analysis of leaf-surface wax

The sorghum leaf-surface wax (SLW) was extracted as the following steps. First, the picked leaves were washed with clean water and allowed to dry at room temperature (RT). Then, the rinsed leaves were immersed in chloroform solution for about 15 seconds at RT. In a subsequent step, the mixed solution was placed in fuming cupboard to remove the chloroform. Finally, the gelatinous precipitate would be the substance initially planning to get.

The chemical composition of the leaf-surface wax was explored using a GC-MS. The as-prepared leaf-surface wax was injected into an on-column under a constant flow of He of 1.2 ml/min. The GC oven was initially conducted at a temperature of 80 °C, followed by a 4 °C/min ramp to 290 °C, and then the temperature was maintained at 290 °C for 20 min. A 5973 N Mass Selective Detector (EI 70 eV; ionization source temperature 230 °C) was used to identify the chemical compositions of the leaf-surface wax.

### Preparation and tribological measurement of lubricants

The lubricants were obtained by dispersing ultrasonically SLW in PAO and the content of SLW in PAO was adjusted as 0.5, 1.0 and 2.0% (mass fraction). According to our previous research, the maximum solubility of MoDTC in PAO was about 1.0% and the PAO containing 0.5% MoDTC exhibited better tribological properties than PAO containing other concentrations of MoDTC. Therefore, MoDTC was used as a contrastive additive and its concentration was determined as 0.5%.[15]

The friction reduction and anti-wear abilities of lubricants for steel/steel, steel/aluminum and steel/copper pairs were evaluated on a ball-on-disk MFT-R4000 reciprocating friction and wear apparatus at RT. The upper ball (AISI 52100 steel ball, diameter 5 mm, hardness 710 Hv) was driven to be in contact with the lower discs (steel disc: $\Phi 24 \times 7.9$ mm, AISI 52100 steel, hardness 600 Hv; aluminum disc: $\Phi 24 \times 7.9$ mm, 2024 aluminum, hardness 160 Hv; copper disc: $\Phi 24 \times 7.9$ mm, bronze copper, hardness 210 Hv) and reciprocally slided at an amplitude of 5 mm and RT for 30 min. All the discs were polished with different

Table 1. Chemical composition of SLW.

| Samples | Alcohols | Alkanes | Olefins | Acids | Esters | Others |
|---|---|---|---|---|---|---|
| SLW | 58% | 17% | 9% | 5% | 3% | 8% |

grades of diamond pastes to achieve a surface roughness (Ra) of about 0.05 um. During the test, it was found that when the loads for steel, aluminum and copper were higher than 50 N, 20 N and 40 N, respectively, extremely sever wear and plastic deformation would occur on the lower discs. All the tested lubricants would fail under these conditions. Therefore, to compare the tribologcial properties, the loads for steel/steel, steel/aluminum and steel/copper friction pairs were 50 N, 20 N and 40 N, respectively. As for the frequency, due to the property of the friction and wear tester, the frequency could only be set as 5 Hz. Before and after each sliding test, the upper ball and lower disc were ultrasonically washed in acetone for 10 min. About 0.5 g of to-be-tested lubricant was dropped into the contact zone of the friction pair. Each friction test was repeated thrice to get a more responsible data.

### Surface characterization

After friction test, a Micro-XAM 3D surface mapping microscopy profile meter was employed to determine the wear volumes on the lower discs and a scanning electron microscopy (SEM, Zeiss) was employed to take the images of the worn surfaces on lower discs. The chemical state of the characteristics elements on worn surfaces was detected by a PHI-5702 multifunctional X-ray photoelectron spectroscopy (XPS, American Institute of Physics Electronics Company) with K-alpha irradiation as the excitation source. The carbon binding energy of 284.6 eV was used as the reference and the pass energy was 29.3 eV. The positive and negative ions on the rubbing surfaces were detected by a time-of-flight secondary ion mass spectroscopy (SIMS) with a Bi + plused ion beam of 30 keV energy.

## Results and discussion

### Chemical compositions of SLW

GC-MS has been widely used to identify complex compounds because it is an effective approach to quantitatively analyze different substances. Table 1 gives the chemical compositions of the SLW. It is visible that the main compositions of the SLW were alcohols and alkanes and some small amounts of olefins, acids and esters. These characteristics compositions have an important influence on the friction reduction and anti-wear abilities of the lubricants.

### Tribological behaviors of lubricants for different friction pairs

Figure 2 gives the friction coefficient curves and wear volumes of the different lubricants for steel/steel pair under 50 N, 5 Hz and RT. As shown in Figure 2a, the addition of different concentrations of SLW all could remarkably lower the friction coefficients as compared with pure PAO. The lowest friction coefficient of about 0.06 was obtained by PAO + 0.5%SLW, indicating that SLW exhibited a preferable friction reduction ability. Figure 2b gives the wear volumes to compare the anti-wear ability of the lubricants. MoDTC showed the lowest wear volume among all the lubricants. Compared with pure PAO, PAO containing different concentrations of SLW all reduced the wear volumes by about 62%, indicating an outstanding anti-wear ability. This results suggest that SLW as an additive in PAO could significantly improve the tribological properties of steel/steel friction pair.

Figure 3a presents the friction coefficients of different lubricants for steel/aluminum pair under 20 N, 5 Hz and RT. It was visible that pure PAO exhibited much high and unstable friction coefficients. Combining the result shown in Figure 5d, it was inferred that sever adhesive wear taken place under this condition. In a sharp contrast, PAO containing SLW performed lower and more stable friction coefficients, indicating three concentrations of SLW in PAO exhibited good friction reduction ability. However, as for the wear volumes, the results shown in Figure 3b suggested that the addition of SLW and MoDTC in PAO all increased the wear volumes as compared with pure PAO, indicating a negative influence on the anti-wear ability.

Figure 4 compares the friction reduction and anti-wear abilities of the lubricants for steel/copper pair under 40 N, 5 Hz and RT. As shown in Figure 4a, all the lubricants exhibited the obvious running-in periods at the beginning of the friction test. Then, MoDTC exhibited the lowest friction coefficient whereas it was much unstable. After the running-in period, all the PAO containing SLW exhibited lower friction coefficients than pure PAO. Figure 4b gives the wear volumes of the different lubricants. PAO containing SLW showed much lower and close wear volumes, indicating a good anti-wear ability for steel/copper friction pair.

### Analysis of the worn surfaces

Figure 5a–c give the SEM images of worn surfaces on the steel discs lubricated by different lubricants. As shown in Figure 5a and c, the worn surfaces lubricated by pure PAO and PAO + MoDTC acquired many wear cracks and corrosion points, respectively. However, Figure 5b shows an improved worn surfaces lubricated by PAO + SLW in which there were just some shallow furrows, indicating SLW had some certain anti-wear ability under steel/steel lubrication. Figure 5d–f show the worn morphologies on the aluminum discs lubricated by different lubricants. Observing the Figure 5d–f, it was found that the worn surface lubricated by pure PAO was much rougher than the worn surfaces lubricated by PAO containing SLW or MoDTC, indicating that sever adhesive wear taken place under this condition. This may be the reason why pure PAO exhibited a much higher friction coefficient than other lubricants shown in Figure 3a. Combining the results as shown in Figure 3b where PAO containing different additives all exhibited higher wear volumes than pure PAO, it was inferred that although Figure

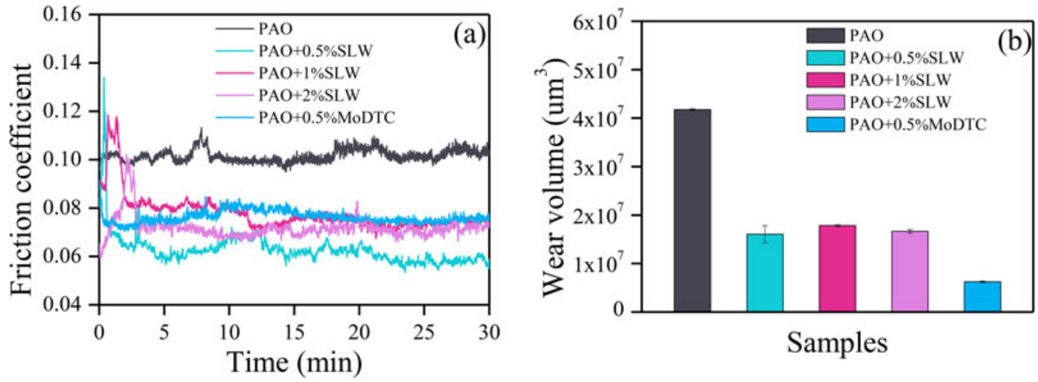


**Figure 2.** (a) friction coefficients and (b) wear volumes of the lubricants for steel/steel pair under 50 N, 5 Hz and RT.

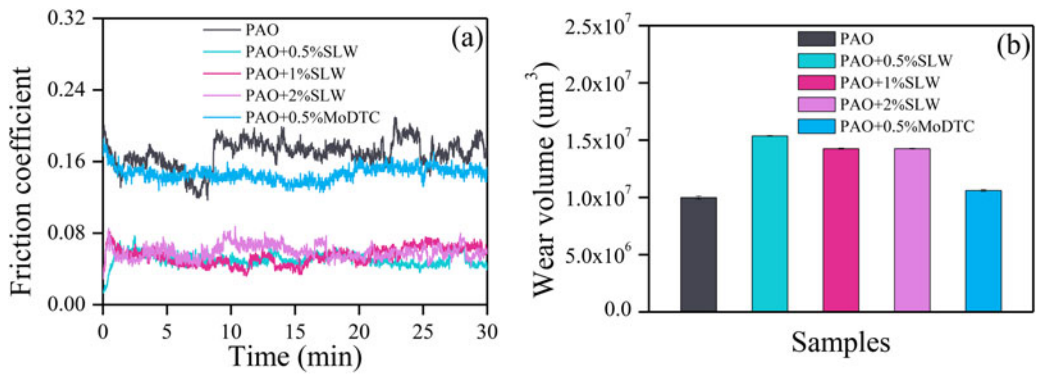


**Figure 3.** (a) friction coefficients and (b) wear volumes of the lubricants for steel/aluminum pair under 20 N, 5 Hz and RT.

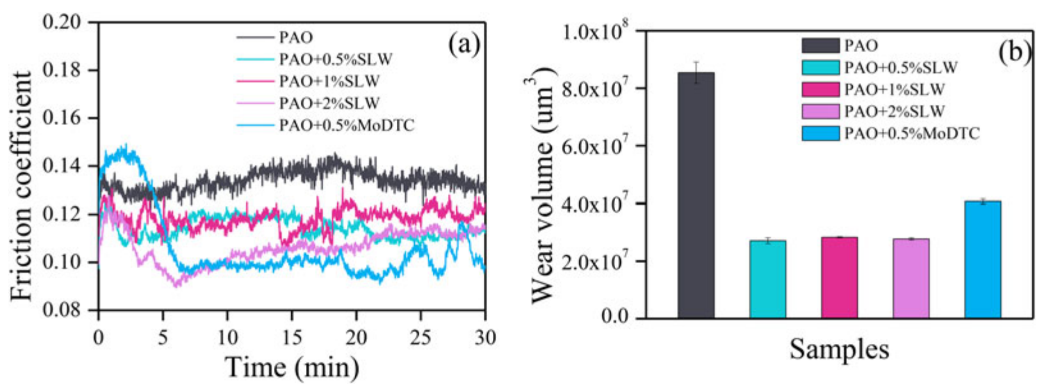


**Figure 4.** (a) friction coefficients and (b) wear volumes of the lubricants for steel/copper pair under 40 N, 5 Hz and RT.

5d–f suggested that SLW and MoDTC made the worn surfaces smoother, these additives may also make the wear scar much wider, resulting in a large wear volume. The results show that SLW and MoDTC all had a negative influence on the anti-wear ability of PAO for steel/aluminum friction pairs. Figure 5g–i show the worn surfaces on copper discs lubricated by different lubricants. The worn surfaces lubricated by PAO and PAO + MoDTC had more furrows than that lubricated by PAO + SLW, indicating SLW exhibited a better anti-wear ability.

Tribological tests suggest that SLW as an additive can improve the tribological properties of PAO, therein the biggest improvement was achieved under the steel/steel friction pair. Therefore, the worn surfaces on the steel discs were further characterized by XPS and SIMS to analyze the possible lubrication mechanisms. Figure 6 gives the XPS spectra of typical elements including C1s, O1s and Fe2p on the steel worn surface lubricated by PAO + SLW. C1s has the peak at 284.6 eV which is used as the reference. The peaks of O1s at 530.0–531.5 eV indicate some complex oxides species were generated on the worn surface.[17,18] Fe2p has the peaks at 724.4 eV and 710.7 eV belonging to FeO, $Fe_2O_3$ and $Fe_3O_4$, indicating a lubricating film composed of oxides species was generated on the worn surface to improve the tribological properties.[17,18] SIMS is a very sensitive equipment to detect a range of species, therefore it was employed to investigate the characteristics positive and negative ions on the worn surface to explore the lubrication mechanisms.[19,20] Figure 7 gives the images of the characteristics negative and positive ions on the worn surface lubricated by PAO + 0.5%SLW. A brighter area means a higher concentration of the objective ions. It was visible that all the images of the positive ions

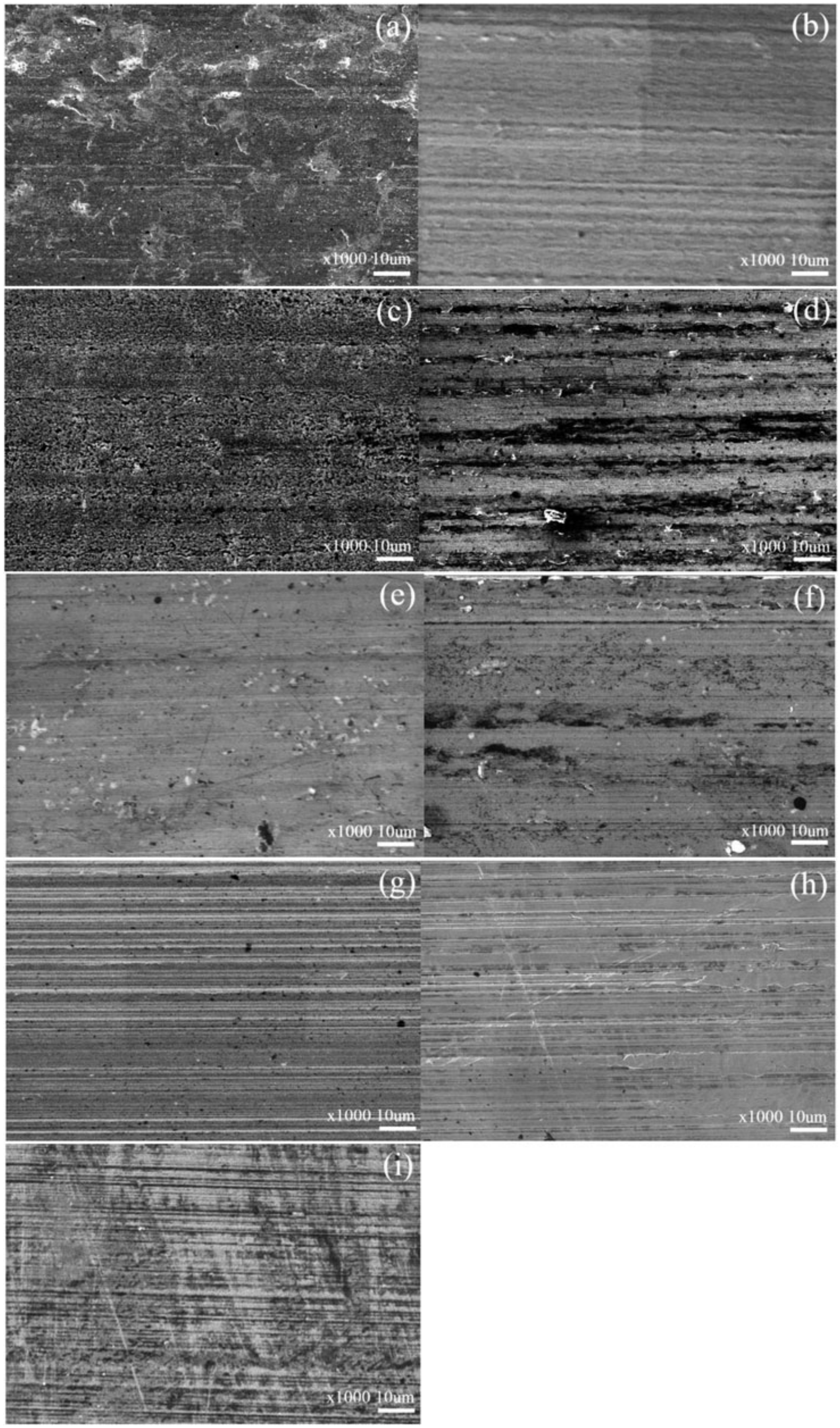


**Figure 5.** SEM images of the worn surface on steel discs (a–c), aluminum discs (d–f) and copper discs (g–i) lubricated by PAO (a, d and g), PAO + 0.5%SLW (b, e and h) and PAO + 0.5%MoDTC (c, f and i).

were much brighter than those of the negative ions, indicating positive ions played a more important role in forming the lubricating film during the friction process. It was also found that the ions with relatively short carbon chain were brighter, suggesting the protective film was mainly composed of short-chain ions. SIMS images give a direct evidence for the formation of protective film generated by the negative and positive ions on the worn surfaces.

A series of tribological tests suggest that sorghum leaf-surface wax as an additive in PAO exhibited some certain

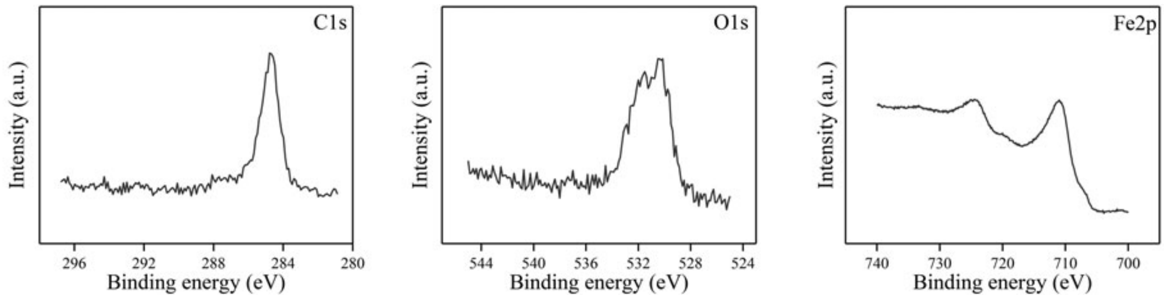

Figure 6. XPS spectra of typical elements on the steel worn surface lubricated by PAO + SLW.

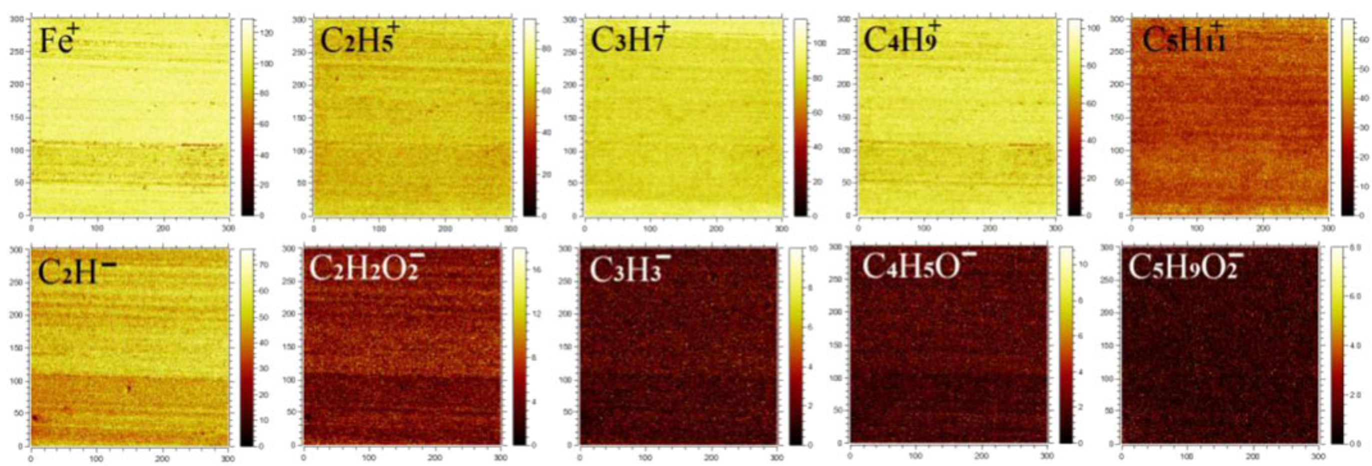

Figure 7. SIMS images of typical positive and negative ions on the steel worn surface lubricated by PAO + SLW.

friction reduction and anti-wear abilities under different friction pairs. The XPS and SIMS analysis show that such good tribological properties of the SLW were dependent on the complex physical adsorption and chemical reaction film generated on the worn surfaces. Based on the characterization and analysis, the detailed lubrication mechanisms can be explained as follow. As shown in Table 1, SLW was mainly composed of alcohols and alkanes. Under the action of applied normal load, these long-chain compounds could break into short chains carrying negative charge.[9,21] Meanwhile, it is well known that the worn surface may carry positive charge during the friction process.[22] Therefore, these broken short chains could adsorb on the worn surfaces to form a physical adsorption film to protect the rubbing surface from damage. This possible lubrication mechanisms could be supported by the SIMS images (Figure 7) of the worn surfaces. Besides the physical adsorption film, the tribochemical reaction also taken place. In general, as the friction continues, fresh metal constantly exposes and the temperature rises. Then, a tribochemical reaction film can be formed by the chemical interactions between sorghum leaf-surface wax and the fresh metal to enhance the friction reduction and anti-wear abilities. XPS (Figure 6) suggests the tribochemcial reaction film was mainly composed of FeO, $Fe_2O_3$ and $Fe_3O_4$, which significantly improves the tribological properties. In a word, based on the tribological data, SEM, XPS and SIMS analysis of the worn surfaces, it suggests that sorghum leaf-surface wax as an additive in PAO could form a protective lubricating film to improve the friction reduction and anti-wear abilities during the friction process.

## Conclusion

Sorghum leaf-surface wax was successfully extracted from the sorghum leaves and used as an additive in PAO to evaluate the tribological properties for steel/steel, steel/aluminum and steel/copper friction pairs. The content analysis shows that SLW was mainly composed of alcohols and alkanes and some small amount of olefins, acids and esters. Tribological tests suggest that SLW in PAO exhibited good friction reduction and anti-wear abilities for steel/steel and steel/copper friction pairs. However, SLW was not suitable for steel/aluminum friction pairs because it could increase the wear volume. XPS and SIMS analysis show that the good tribological properties of SLW were mainly attributed to the protective films generated by complex physical adsorption and tribochemcial reaction on the worn surface. Given the simple preparation and effective friction reduction and anti-wear abilities, SLW as an additive holds a great potential for a range applications.

## Funding

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## References

[1] Lugt, P. M. Modern Advancements in Lubricating Grease Technology. *Tribol. Int.* **2016**, *97*, 467–477. DOI: 10.1016/j.triboint.2016.01.045.

[2] Chen, B. S.; Gao, L. Y.; Fang, J. H.; Zhang, N.; Wu, J.; Wang, J. Lubricant Biodegradation Enhancers: Designed Chemistry and

Engineered Technology. *China Pet. Process. Petrochem. Technol.* **2015**, *17*, 102–110.

[3] Ge, X.; Li, J.; Zhang, C.; Luo, J. Liquid Superlubricity of Polyethylene Glycol Aqueous Solution Achieved with Boric Acid Additive. *Langmuir* **2018**, *34*, 3578–3587. DOI: 10.1021/acs.langmuir.7b04113.

[4] Rudnick, L. R. *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*; CRC Press, Taylor & Francis Group: New York, **2006**.

[5] Mannekote, J. K.; Kailas, S. V.; Venkatesh, K.; Kathyayini, N. Environmentally Friendly Functional Fluids from Renewable and Sustainable Sources – A Review. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1787–1801. DOI: 10.1016/j.rser.2017.05.274.

[6] Ding, J. H.; Fang, J. H.; Chen, B. S.; Zhang, N.; Fan, X.Y.; Zheng, Z. Effect of Oleic Acid Tris-(2-Hydroxyethyl) Isocyanurate Phosphate Ester on Biodegradability and Tribological Performance of Mineral Lubricating Oil. *China Pet. Process. Petrochem. Technol.* **2018**, *20*, 97–103.

[7] You, J.; Li, F.; Chen, B. Tribological Performance of Two Potential Environmentally Friendly Ashless Vegetable Oil Additives. *China Pet. Process. Petrochem. Technol.* **2010**, *12*, 43–48.

[8] Adhvaryu, A.; Erhan, S. Z.; Perez, J. M. Tribological Studies of Thermally and Chemically Modified Vegetable Oils for Use as Environmentally Friendly Lubricants. *Wear* **2004**, *257*, 359–367. DOI: 10.1016/j.wear.2004.01.005.

[9] Chen, B.; Wang, J.; Fang, J.; Huang, W.J.; Sun, X.; Yu, Y. Tribological Performances of Fatty Acyl Amino Acids Used as Green Additives in Lubricating Oil. *China Pet. Process. Petrochem. Technol.* **2010**, *12*, 49–53.

[10] Kunst, L.; Samuels, A. L. Biosynthesis and Secretion of Plant Cuticular Wax. *Prog. Lipid Res.* **2003**, *42*, 51–80. DOI: 10.1016/S0163-7827(02)00045-0.

[11] Tassone, E. E.; Lipka, A. E.; Tomasi, P.; Lohrey, G. T.; Qian, W.; Dyer, J. M.; Gore, M. A.; Jenks, M. A. Chemical Variation for Leaf Cuticular Waxes and Their Levels Revealed in a Diverse Panel of Brassica Napus L. *Indus. Crops Prod.* **2016**, *79*, 77–83. DOI: 10.1016/j.indcrop.2015.10.047.

[12] Cao, Y. P.; Yu, L. G.; Liu, W. M. Study of the Tribological Behavior of Sulfurized Fatty Acids as Additives in Rapeseed Oil. *Wear* **2000**, *244*, 126–131. DOI: 10.1016/S0043-1648(00)00445-2.

[13] Hu, Y. H.; Liu, W. M. Tribological Properties of Alcohols as Lubricating Additives for Aluminum-on-Steel Contact. *Wear* **1998**, *218*, 244–249.

[14] Ukonsaari, J. Wear and Friction of Synthetic Esters in a Boundary Lubricated Journal Bearing. *Tribol. Int.* **2003**, *36*, 821–826. DOI: 10.1016/S0301-679X(03)00099-9.

[15] Xia, Y.; Xu, X.; Feng, X.; Chen, G. Leaf-Surface Wax of Desert Plants as a Potential Lubricant Additive. *Friction* **2015**, *3*, 208–213. DOI: 10.1007/s40544-015-0081-7.

[16] Xia, Y.; Hu, Y.; Feng, X.; Ma, T. Study of Tribological Properties of Ecofriendly Lubricant Additives Derived from Leaf-Surface Waxes. *Sci. China Technol. Sci.* **2018**, *61*, 408–416. DOI: 10.1007/s11431-017-9076-0.

[17] Cao, Z. F.; Xia, Y. Q. Synthesis and Tribological Properties of Polyaniline Functionalized by Ionic Liquids. *J. Mater. Sci.* **2018**, *53*, 7060–7071. DOI: 10.1007/s10853-018-2028-7.

[18] Battez, A. H.; González, R.; Viesca, J. L.; Blanco, D.; Asedegbega, E.; Osorio, A. Tribological Behaviour of Two Imidazolium Ionic Liquids as Lubricant Additives for Steel/Steel Contacts. *Wear* **2009**, *266*, 1224–1228. DOI: 10.1016/j.wear.2009.03.043.

[19] Sodhi, R. N. S. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS):-Versatility in Chemical and Imaging Surface Analysis. *Analyst* **2004**, *129*, 483–487. DOI: 10.1039/b402607c.

[20] Fan, X.; Wang, L.; Li, W.; Wan, S. Improving Tribological Properties of Multialkylated Cyclopentanes under Simulated Space Environment: Two Feasible Approaches. *ACS Appl. Mater. Interfaces* **2015**, *7*, 14359–14368. DOI: 10.1021/acsami.5b03088.

[21] Zhong, X. W.; Xia, Y. Q.; Feng, X. Tribological Application and Mechanism of Epicuticular Wax. *Friction* **2018**, *1*, 1–15.

[22] Antusch, S.; Dienwiebel, M.; Nold, E.; Albers, P.; Spicher, U.; Scherge, M. On the Tribochemical Action of Engine Soot. *Wear* **2010**, *269*, 1–12. DOI: 10.1016/j.wear.2010.02.028.