Tribological Properties of Wax on Different Trees Leaf Surface Containing Different Chemical Components

Yanqiu Xia (✉ xiayq@ncepu.edu.cn)
North China Electric Power University School of Energy Power and Mechanical Engineering

Xin Feng
NCEPU: North China Electric Power University

Wenyi Zhang
NCEPU: North China Electric Power University

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Abstract

Three kinds of leaf-surface waxes were extracted from different trees, and their chemical compositions were analyzed by Gas Chromatography-Mass Spectrometer (GC-MS). A MFT-R4000 tester was employed to investigate the tribological performances of samples, and the Scanning Electron Microscope (SEM) and Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) were used to characterize the morphologies and chemical compositions on the worn surfaces, respectively. The result showed that waxes can effectively improve the friction reduction and anti-wear abilities of base oil, and different composition of waxes have different improve degree. This can be attributed to the chemical compositions and degree of chemical action.

1. Introduction

In the mechanical transmission system, almost all friction pairs are in relative motion. Such as bearings, gears and screw pair, etc. In such cases, friction always exists between the two sliding surfaces. Not only energy loss and wear, but also seizure may take place. In order to prevent this phenomenon, almost all equipment needs lubrication. Proper lubricant can reduce friction and wear, and improve the reliability and life of machinery and equipment. However, many of the mineral and synthetic based-oil in use today are highly toxic to the environment and are not easily biodegradable. With more than 50% of all lubricants consumed worldwide ending up in the environment through leak, evaporation, improper dumping and improper use. It has been estimated that nearly 95% of the lubricants which enter the environment are non-bio-based oils, and they are harmful to numerous organic ecosystems [1]. Recently, bio-based lubricants have been widely studied and applied. The bio-based lubricants include vegetable oils, animal fats and any other environmentally benign hydrocarbons. Vegetable oils such as sunflower, canola, Peanut, Castor bean and Olive oil have also been adopted for industrial cutting fluid applications [2–3]. The performance of lubricating oil is determined by lubricating oil additives. The key to the performance of lubricant is its wear resistance, friction reduction, load-carrying capacity and oxidation resistance. Commercial lubricant additive formulation includes the chlorine, phosphorus, sulfur, and metals elements [4–5]. These additives have been used less and less because of their toxicity and environmental limitations. This helps to mitigate environmental impact, as it is well known that the toxic and not readily degradable additives may accumulate in the environment and harm the ecosystem [6]. To meet increasingly stringent environmental requirements, the research of lubricants and additives has gradually turned to environmentally friendly and degradable formulations [7]. Chen [8] found the fatty acyl amino acids as a green additive could effectively improve the anti-wear and friction reduction abilities of the HVI 350 mineral oil. Vermeer [9] found that surface of castor leaves contain mixture comprised alkanes (C(26)-C(29)), primary alcohols (C(22)-C(38)), aldehydes (C(26) and C(28)) and fatty acids (C(20)-C(34)) etc. Ji [10] also found the constituents of leaf-surface waxes of several plants species, and demonstrated again that alkanes, alcohols, and fatty acids are main ingredient in waxes. Recently, the leaf-surface wax as a green additive has attracted our group’s great attention because it shows excellent friction reduction and anti-wear abilities in lubricating oil. More than 20 kinds of leaf-
surface wax were extracted, include desert plants [11], hardy plants [12], pines [13] and Pinaceae [14] etc. could remarkably improve the friction reduction and anti-wear abilities.

In this paper, we investigated tribological properties of wax on leaf surface containing different chemical components as lubricant additives in order to explore the difference in tribological performances among different leaf waxes. The chemical composition of leaf-surface wax was characterized by a gas chromatography-mass spectrometry (GC-MS). The friction reduction and anti-wear abilities of leaf-surface wax as green additives in synthetic ester (SE) for steel/steel and steel/aluminum pairs were investigated in detail and the lubrication mechanisms were analyzed by scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS).

2 Experiments

2.1 Materials

There are three kinds of leaf-surface waxes, Syringa oblata Lindl. wax (SOL), Euonymus japonicus Thunb. wax (EJT) and Fraxinus pennsylvanica Marsh wax (FPM). Therein, SOL came from (40.6792 degrees north latitude and 122.1586 degrees east longitude), EJT came from (40.6650 degrees north latitude and 122.1661 degrees east longitude) and FPM came from (40.0892 degrees north latitude and 116.3003 degrees east longitude). These leaves are shown as Fig. 1, and the waxes were extracted using chloroform.

The chemical components of leaf-surface waxes were measured by employing a gas chromatography-mass spectrometry. The SE was used as base oil and waxes were added into it. The mass fraction of wax were 0.4%, 0.8%, 1.2%, 1.6% and 2.0%, respectively.

2.2 Friction and wear test

The MFT-R4000 is a reciprocating ball-on-disk sliding friction tester, and the diameter and hardness of experimental AISI52100 steel balls are 5 mm and 710 Hv, respectively. The aluminum disks are diameter 24 mm and thickness 7.78 mm with the hardness 132 Hv, and the steel disks are diameter 24 mm and thickness 7.9 mm with the hardness 450 Hv.

The test temperatures are 25°C, and the humidities are from 26–36%. The reciprocating amplitude is 5 mm and the frequency is 5 Hz with the test time is 30 min for each test. The loads are 20 N, 30 N and 40 N of steel-aluminum friction pairs and 50 N, 100 N and 150N of steel-steel friction pairs. The average of three tests is used as the coefficient of friction (COF).

2.3 Characterization of wear scar

The wear scar widths (WSW) were obtained by an optical microscope, and the WSW also is the average of three tests. A scanning electron microscope (SEM) was employed to show the high magnification surface morphologies of wear scar.
3 Results And Discussion

3.1 Leaf-surface wax chemical components

The chemical compositions of Leaf-surface wax were analyzed using GC-MS. The result showed in Table 1. The major components of SOL are hydrocarbons, the major components of EJT are hydrocarbons and alcohols, and for FPM the major components are esters and hydrocarbons. The other components listed in table are a bit less.

|                | SOL   | EJT   | FPM   |
|----------------|-------|-------|-------|
| Hydrocarbons   | 87.59%| 36.53%| 17.12%|
| Alcohols       | 0.56% | 29.25%| -     |
| Esters         | 3.39% | -     | 25.17%|
| Ketones        | 0.31% | 13.92%| 1.66% |
| Ethers         | 0.69% | 0.51% | 4.26% |
| Carboxylic acids| 0.48% | -     | -     |
| Others         | 6.98% | 19.79%| 51.79%|

Because alcohol, acid and ester are good antifriction and anti-wear additives in lubricating oils, and the content of alcohol and ester in the SOL, EJT, FPM waxes is different, what is the difference of their lubricating performance?

3.2 Friction reduction and anti-wear properties

Figure 2 shows the COF and WSW of steel-aluminum contact at 20 N. It can be seen that when the mass fraction of EJT and FPM is 1.6%, the COFs of them are the lowest ones, and the COF is the lowest one when the mass fraction of SOL is 1.2%. The situations of WSW for EJT and FPM are similar: the 1.6% additives have the lowest WSW, while the WSW is the lowest one when the mass fraction of SOL is 2.0%.

Figure 3 shows the COF and WSW of steel-aluminum contact at different loads when the additives are 1.2% SOL, 1.6% EJT and 1.6% FPM, respectively. It can be seen that the COF of all the lubricants increase with the loads increase, and the WSW of all the lubricants increase with the loads increase.

The results show that the lubrication performance of alcohol is better than that of wax containing ester and other components for steel-aluminium friction pairs.

Figure 4 shows the COF and WSW of steel-steel contact at 50 N. It can be seen that when the mass fraction of EJT and FPM is 1.6%, the COFs of them are the lowest ones. The effect of additives for reducing WSW is not very obvious.
Figure 5 shows the COF and WSW of steel-steel contact at different loads when the additives are 2.0% SOL, 1.6% EJT and 1.6% FPM, respectively. It can be seen that the COF and WSW of all the lubricants increase with the loads increase.

The results show that the lubrication properties of alcohol and ester are similar for steel and steel friction pairs.

### 3.3 Wear scar morphology

Figure 6 suggests the wear scar surface morphologies on the aluminum discs at 40 N. It can be seen that the surface lubricated by SE has very serious damage, both abrasive wear and adhesive wear. In terms of the other four surfaces, SE lubricating surface is the roughest one and EJT lubricating surface is the smoothest one.

Figure 7 displays the wear scar surface morphologies of the steel discs. As steel has a higher hardness than aluminum, the surfaces are smoother. The surface lubricated by SE is the roughest and the other four surfaces are not much different, therein EJT lubricating surface is smoothest.

### 3.4 Wear scar composition analysis

To investigate the chemical component on the surface of wear scar, the TOF-SIMS analysis was employed to analyze the ions on the surface of aluminum disc. For ease of analysis processing, the data were normalized by Al. The highest ion intensity of Al+ was chosen as the normalized intensity of positive ion mass spectrum while the highest ion intensity of AlO- as the normalized intensity of negative ion mass spectrum. As shown in Fig. 1 and Fig. 2, in terms of the measured positive ions, there are many kinds of hydrocarbon ions (such as C2H5+) and common positive ions such as H+. With respect to the measured negative ions, there are some carboxylic acid ions (such as C5H9O2-), several alcohol ions and some other common negative ions such as OH-.

Table 2 shows the data that ion normalized intensity area data for the wear scar surface. As can be seen, there are most and least positive ion content on the surface lubricated by EJT and FPM, respectively. The short carbon chain (C1 ~ 3) content is less and long carbon chain (C4 ~ 9) content is more on the surface lubricated by SOL. In terms of total negative ion content, there is FPM > SOL > EJT. In terms of the short carbon chain (C < 7) positive ion intensities, in general, EJT > SOL > FPM.

Table 2 The ion normalized intensity area on the wear scar surface
|                  | SOL     | EJT     | FPM     |
|------------------|---------|---------|---------|
| **Positive ion intensity** |         |         |         |
| CH$_3^+$         | 0.10464 | 0.11582 | 0.09796 |
| Al$^+$           | 1       | 1       | 1       |
| C$_2$H$_3^+$     | 0.66228 | 0.76411 | 0.61342 |
| C$_2$H$_5^+$     | 0.68668 | 0.76617 | 0.59548 |
| C$_3$H$_3^+$     | 0.36714 | 0.39667 | 0.31499 |
| C$_3$H$_5^+$     | 0.94943 | 1.01830 | 0.80190 |
| C$_3$H$_7^+$     | 0.87671 | 0.94258 | 0.70426 |
| C$_4$H$_9^+$     | 0.32020 | 0.32395 | 0.23890 |
| C$_5$H$_8^+$     | 0.03131 | 0.03101 | 0.02516 |
| C$_6$H$_9^+$     | 0.05882 | 0.06071 | 0.05071 |
| C$_7$H$_{10}^+$  | 0.00352 | 0.00345 | 0.00316 |
| C$_8$H$_{12}^+$  | 0.00131 | 0.00130 | 0.00119 |
| C$_9$H$_{12}^+$  | 0.00139 | 0.00136 | 0.00116 |
| **Negative ion intensity** |         |         |         |
| CH$_3^-$         | 1.53690 | 1.29460 | 1.83630 |
| O$_2^-$          | 0.98106 | 0.87963 | 0.82999 |
| C$_2$H$_2$O$_2^-$| 7.63280 | 7.11460 | 8.89660 |
| AlO$^-$          | 1       | 1       | 1       |
| C$_2$H$_2$O$_2^-$| 2.88580 | 2.58670 | 3.45730 |
| C$_3$H$_3$O$_2^-$| 6.53470 | 5.81060 | 7.08570 |
| C$_5$H$_9$O$_2^-$| 1.22700 | 0.70320 | 1.17790 |
3.5 Discussion

It could be inferred from above results that the improvement of the friction surface for two kinds of friction pairs lubricated by waxes are better than those of the pure SE. The leaf-surface waxes lubricating surfaces are smoother because the wax lubricants form a lubricating film and reduce the contact between friction pairs [15–16].

It can be seen from the above analysis that in terms of the optimal wax additive concentration at 40N load of steel-aluminum friction pair, there are less hydrocarbons and more polar negative ions on the worn surface lubricated by FPM, so that FPM lubricants have lower COF and WSW in this condition. It can be inferred that the polar negative ions have better friction reduction and anti-wear abilities than hydrocarbon ions because of their polarity which can makes the lubricating film firmer.

4 Conclusions

In this study, three kinds of leaf-surface waxes were investigated and results showed that all of them have excellent friction reduction and anti-wear abilities. It can be indicated from analysis that the species of plant affect the chemical compositions of leaf-surface wax, and produce different compositions on the worn surfaces and then constructing different lubricating films.

Declarations

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Not applicable.

Authors’ contributions

Yanqiu Xia was responsible for the design and theoretical analysis of the experimental scheme and the manuscript. Xin Feng was responsible for the theoretical analysis of the analysis. Zhang Wenyi in charge of part of the experimental work. All authors read and approved the final manuscript.

Authors’ Information

Yanqiu Xia, born in 1964, is currently a professor and a PhD candidate supervisor at School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing, China. His main research interests include the tribology of mechanical and electrical equipment, oil monitoring.
Xin Feng, born in 1965, is currently an associate professor at School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing, China. Her main research areas cover tribology and artificial intelligence.

Wenyi Zhang born in 1994, was a master candidate at School of Energy Power and Mechanical Engineering, North China Electric Power University, China. His main research interests is tribology.

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**Competing Interests**

The authors declare no competing financial interests.

**References**

1. A. Siddaiah, A. K. Kasar, A. Mano and P. L. Menezes, Influence of environmental friendly multiphase lubricants on the friction and transfer layer formation during sliding against textured surfaces, Journal of Cleaner Production, 209(2019)1245–1251.

2. A. Z. Syahir, N. W. M. Zulkifli, H. H. Masjuki, M. A. Kalam, A. Alabdulkarem, M. Gulzar, L. S. Khuong and M. H. Harith, A review on bio-based lubricants and their applications, Journal of Cleaner Production, 168(2017)997–1016.

3. N. A. Zainal, N. W. M. Zulkifli, M. Gulzar and H.H. Masjuki, A review on the chemistry, production, and technological potential of bio-based lubricants, Renewable and Sustainable Energy Reviews, 82(2018)80–102.

4. A. M. Barnes, K. D. Bartle and V. R. A, A review of zinc dialkyldithiophosphates (ZDDPS): characterisation and role in the lubricating oil, Tribology International, 34(2001)389–395.

5. X. Feng, Y.Q. Xia, S. Shinya, M. Takashi, Tribological properties of gray cast iron lubricated using organic compounds containing Mo and ZnDTP additives, Lubrication Sciences, 24(2012)153–164. (DOI: 10.1002/ls.1167)

6. R. K. Hewstone, Environmental health aspects of lubricant additives, Science of the Total Environment, 156(1994)243–254.

7. C. H. Chan, S. W. Tang, N. K. Mohd, W. H. Lim, S.K. Yeong and Z. Idris, Tribological behavior of biolubricant base stocks and additives, Renewable and Sustainable Energy Reviews, 93(2018)145–157.

8. B.S. Chen, J. Wang, J.H. Fang, W.J. Huang, X. Sun and Y. Yu, Tribological performances of fatty acyl amino acids used as green additives in lubricating oil. China Petroleum Processing and Petrochemical Technology, 12(2010)49–53.
9. C. P. Vermeer, P. Nastold and R. Jetter, Homologous very-long-chain 1,3-alkanediols and 3-hydroxyaldehydes in leaf cuticular waxes of Ricinus communis L., Phytochemistry, 62(2003)433–438.

10. X.F. Ji and R. Jetter, Very long chain alkylresorcinols accumulate in the intracuticular wax of rye (Secale cereale L.) leaves near the tissue surface. Phytochemistry 2008;69:1197–1207.

11. Y.-Q. Xia, X.-C. Xu, X. Feng and G.-X. Chen, Leaf-surface wax of desert plants as a potential lubricant additive. Friction 2015;3:208–213.

12. Y.Q. Xia, Y.C. Hu, X. Feng and T. Ma, Study of tribological properties of ecofriendly lubricant additives derived from leaf-surface waxes, Science China Technological Sciences, 61(2018)408–416.

13. X. Feng, Z.F. Cao and Y.Q. Xia, Leaf-surface wax extracted from different pines as green additives exhibiting excellent tribological properties, Materials Research Express, 4(2017)115505.

14. X. Feng, Y.C. Hu, Y.Q. Xia, Tribological research of leaf-surface wax derived from plants of Pinaceae, Lubrication Science, 31(2019)1–10.

15. C. Pritchard, Role of the lubricant in three-body abrasion, Nature,226(1970)446–447.

16. F.Mamoun, A. Linda, A.S. Mohammed, I. Alain, M.Z.Touhami, M.Alex, N. Corinne, Effect of replacing vanadium by niobium and iron on the tribological behavior of HIPed titanium alloys, Acta Metall Sin-Engl, 30(2017)1089–1099.

**Figures**

![Leaves](image1)

**Figure 1**

Leaves of (a) SOL, (b) EJT and (c) FPM.
Figure 2

The (a) COF and (b) WSW of steel-aluminum friction pair at 20N.

Figure 3

The (a) COF and (b) WSW of steel-aluminum friction pair at different loads.
Figure 4

The (a) COF and (b) WSW of steel-steel friction pair at 50N.

Figure 5

The (a) COF and (b) WSW of steel-steel friction pair at different loads.
Figure 6

The wear scar surface morphologies lubricated by (a) SE, (b) SE+1.2% SOL, (c) SE+1.6% EJT and (d) SE+1.6% FPM.
Figure 7

The wear scar surface morphologies lubricated by (a) SE, (b) SE+2.0% SOL, (c) SE+1.6% EJT and (d) SE+1.6% FPM.
Figure 8

The positive ion intensity on the wear scar surface lubricated by (a) SE+1.2% SOL, (b) SE+1.6% EJT and (c) SE+1.6% FPM
Figure 9

The negative ion intensity on the wear scar surface lubricated by (a) SE+1.2% SOL, (b) SE+1.6% EJT and (c) SE+1.6% FPM.