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Leaf-surface wax extracted from different pines as green additives exhibiting excellent tribological properties

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Abstract: Given the increasing attention on the topic of the "Green chemical", it is imperative to explore new environmental friendly and biodegradable lubricants to meet the tribological performances and environmental needs. In this work, three types of leaf-surface wax were extracted from different pines as green lubricant additives and their chemical compositions, friction reduction and anti-wear abilities were investigated in detail. The results show that the leaf-surface wax extracted from different pines as additives in synthetic ester exhibit superior friction reduction and anti-wear abilities for steel/steel and steel/aluminum pairs. Based on the scanning electron microscopy and time-of-flight secondary ion mass spectroscopy analysis, the preferable tribological performances are ascribed to the physical adsorption film and tribo-chemical reaction film generated by the leaf-surface wax on the worn surfaces during the sliding process.

Keyword: leaf-surface wax, tribology, green additive, friction and wear

1. Introduction

Under the action of force, relative motion or relative motion trend brings about friction between two close bodies, and the wear is the consequence of friction. Friction and wear result in a lot of mechanical failures and consumption of energy [1]. In consequence, a variety of lubricants are widely used to control the friction and wear of most machines or machine systems for saving energy and extending service life.

Lubricants usually need to perform various functions normally depending on the presence of different additives for a huge range of applications. Friction reduction and anti-wear additive is one of

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the foremost additives, which is mainly employed to improve the load-carrying capacities, friction reduction and anti-wear abilities under conditions of boundary lubrication [2-3]. In the past decades, a lot of lubricant additives have been throughout studied to decrease the friction and wear, and they have been successfully applied in the different friction pairs, thereby saving energy and creating a huge economic benefits [4-6]. However, parallel to the development of lubricant additives, the topic of "green additives" has been emphasized and receives an intensified attention because petroleum-based lubricants and the additives contained sulfur, phosphorus and zinc tec. are severe due to their inherent toxicity and non-biodegradable nature [7-11]. Therefore, it is imperative to explore environmental friendly and biodegradable lubricants to meet the both tribological performances and environmental needs. Zhang et al reported the tribological behaviors of $CaCO_3$ nanoparticle as a green additive in poly-alpha-olefin and the results showed it exhibited superior high load-carrying capacity, friction reduction and anti-wear abilities under different experimental conditions [2]. Chen et al 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 [12]. Adhvaryu et al employed the vegetable oil as environmental friendly lubricants and the results showed the vegetable oil had a positive impact on the wear resistance and extreme-pressure lubrication [13]. 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. We extracted two types of leaf-surface wax from the desert plants as lubricant additives and the experimental results showed leaf-surface wax as green additives could remarkably improve the friction reduction and anti-wear abilities [14]. This results inspire us to further investigate the tribological performances of leaf-surface wax as a green additive.

In this paper, because pine is highly adaptable to terrestrial environment including high/low temperature and drought and the leaf has developed stratum corneum, therefore, three types of pine leaves were picked up to extract the leaf-surface wax as lubricant additives. Meanwhile, the synthetic ester was used as base oil because of its excellent bio-degradability and non-toxicity [15]. 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 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. Experimental details

2.1 Materials

Synthetic ester (SE) obtained from Zhongcheng Petrochemical Co., Ltd. was used as the base oil. The Korean pine (KP) and larch (LA) were picked up at Heilongjiang Province, and Qinghai Spruce was picked up at Helan mountain area of Inner Mongolia. The terpionl and chloroform (analytically pure) were purchased from Sinopharm Chemical Reagent Co., Ltd. Figure 1 presents the plant leaf samples.

Figure 1 leaf samples: (a) KP, (b) LA and (c) QS

2.2 Extraction and content analysis of leaf wax

In a simple extraction method, the collected leaves were washed with clean water and then were natural withering. The desiccated leaves were immerged in chloroform solution for 10-30 seconds at room temperature. In a subsequent step, the mixed solution was placed in fuming cupboard to remove the chloroform. Finally, the precipitated substance would be the target product. The chemical composition of the leaf-surface wax was detected using a gas chromatography-mass spectrometry (GC-MS, Agilent Technologies Inc.).

2.3 Preparation and measurement of lubricating oil

The as-prepared leaf-surface wax was added into the base oil of Synthetic ester (SE) and the content of leaf-surface wax in SE was adjusted as 0.5%, 1.0% and 2.0% (mass fraction, the same hereafter). The terpinol was also added into SE as the contrastive lubricant to illustrate the tribological performances of leaf-surface wax. The tribological properties of lubricating oils for steel/steel and steel/aluminum pairs were evaluated on a ball-on-disk MFT-R4000 reciprocating friction and wear apparatus at room temperature. The upper ball (AISI 52100 steel ball, diameter 5 mm, hardness 710 Hv) was driven to reciprocally slide against the lower block (Φ24mm, 7.9 mm, steel block: AISI 52100 steel and hardness 590-610 Hv, aluminum block: 2024 aluminum and hardness 160-170 Hv, surface roughness 0.05 um) at the amplitude of 5 mm, frequency of 5 Hz and room temperature for 30 min. Before and after each sliding test, the upper ball and lower block were ultrasonically washed in petroleum ether for 10 min. Approximate 0.5 g of to-be-tested lubricating oil was dropped into the contact zone of the friction pair. The normal loads range from 50 N to 125 N for steel/steel pair and from 20 N to 40 N for steel/aluminum pair, respectively. Each friction test was repeated thrice to get a more responsible data and the mean values of the coefficient friction (COF) and wear widths with error bars were provided as well. After friction test, a scanning electron microscopy (SEM, Zeiss) was employed to take the images of the worn surfaces on lower blocks. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) was carried out on a ION-TOF-SIMS IN instrument to characterize the chemical composition, which used a Bi^+ plused ion beam of 30 keV energy.

3. Results

3.1 Typical composition of leaf-surface wax

GC-MS is an analytical method that combines the features of gas chromatograph and mass spectrometry to identify different substances within a test sample. Gas chromatograph is an effective method for the quantitative analysis and mass spectrometry is much preferable for qualitative analysis. These two components, used together, allow a much finer degree of substance identification than either unit used separately. It has been widely used to separate and identify complex compounds. Table 1 lists the typical composition of the leaf-surface wax by GC-MS analysis. It is obviously seen that the most abundant components of different leaf-surface wax were alcohols and alkanes, while small amount of olefins, esters and acids were also existent. These typical compositions of leaf-surface wax have an important influence on the tribological properties.

Table 1 typical composition of various leaf-surface wax

Constituents	Korean Pine	Larch	Qinghai Spruce
Olefins	2%	1%	10%
Alkanes	16%	18%	12%
Esters	-	2%	4%
Alcohols	62%	55%	43%
Acids	4%	1%	3%

3.2 Tribological behavior for steel/steel pair

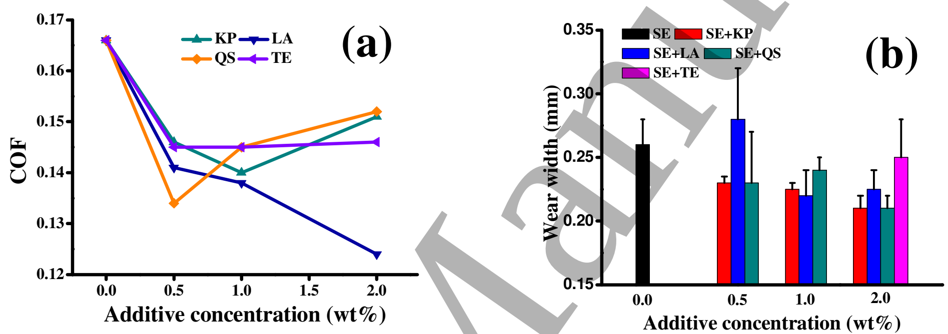


Figure 2 Average COFs (a) and wear widths (b) for the lubricating oils for steel/steel pair at different additive concentration at 50 N, 5 Hz and RT

Figure 2 reveals the evolution of COFs and wear widths of the steel/steel pairs at a constant load of 50 N and the frequency of 5 Hz for different lubricating oils. It can been seen that three types of leaf-surface wax (KP, LA and QS) all can remarkably improve the tribological performances in synthetic ester. Keeping eyes on the Figure 2(a), the COFs of KP and QS decrease first and then increase, while the COFs of LA follows a trend of decline and the COFs of TE are close in the range of the tested additive concentrations. The biggest reduction in COF for different leaf-surface wax were obtained by the synthetic ester containing 1.0% KP (COF: 0.140), 2.0% LA (COF: 0.124), 0.5% QS (COF: 0.134) and 2.0% TE (COF: 0.146), respectively. Figure 2(b) also indicates the leaf-surface wax could enhance the anti-wear ability as compared to base oil. The lubricating oils containing 2.0% leaf-surface wax all have relatively low wear widths. And among them, 2.0% QS exhibits the lowest wear width (0.21 mm), which is reduced by 19% as compared to base oil. These experimental data indicates the leaf-surface wax as additives can effectively improve the friction reduction and anti-wear abilities of base oil. Considering friction reduction and anti-wear abilities, the optimum concentrations of KP, LA, QS and TE in base oil are determined as 2.0 %.

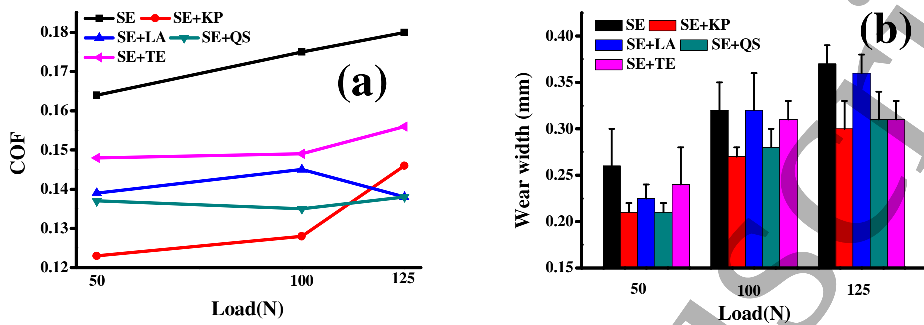


Figure 3 Average COFs (a) and wear widths (b) for the lubricating oils for steel/steel pair at different loads, 5 Hz and RT (additive content: 2.0%)

Figure 3 shows the mean values of COFs and wear widths of the steel block at 50 N, 100 N and 125 N and the frequency of 5 Hz at RT for different lubricating oils. As shown in Figure 3(a), the lubricating oils containing leaf-surface wax have lower COFs than SE and SE+TE at all the tested loads. When the applied loads are 50 N and 100 N, KP has the lowest COFs. However, when the applied load is 125 N, KP exhibits a higher COF than QS and LA, indicating QS and LA may have a better friction reduction ability than KP under high load. Figure 3(b) reveals the anti-wear ability of different lubricating oils by wear widths. It can be seen that all the leaf-surface wax and TE can improve the anti-wear ability at the load of 50 N. When the load are 100 N and 125 N, all the additives except LA show lower wear widths as well. This experimental tests indicate that SE containing leaf-surface wax exhibit preferable friction reduction and anti-wear abilities for steel/steel pair.

3.3 Tribological behavior for steel/aluminum pair

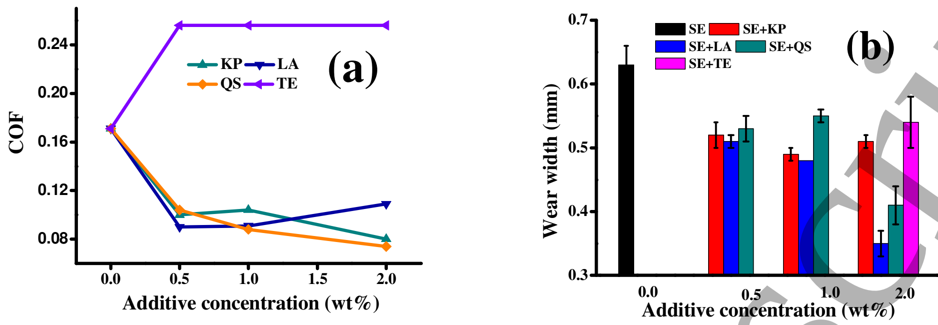


Figure 4 Average COFs (a) and wear widths (b) for the lubricating oils for steel/aluminum pair at different additive concentration at 50 N, 5 Hz and RT

The above experiments shown in Figure 2 and 3 reveal that KP, LA and QS as lubricant additives can decrease the friction and wear of synthetic ester for steel/steel pair. Therefore, we continue to investigate the effect of leaf-surface wax on tribological performances for steel/aluminum pair. As shown in Figure 4(a), all the leaf-surface wax greatly lower the COFs at different additive concentrations, whereas the COFs of TE is higher than synthetic ester. When the concentrations are 0.5% and 1.0%, three types of leaf-surface wax have close COFs. With the concentration increasing to 2.0%, the COFs of KP and QS further decrease and the values are still close whereas the 2.0% LA exhibits a higher COF than before. Observing the Figure 4(b), compared with SE and SE+TE, all the wear widths of the leaf-surface wax are lower, especially under the lubrication of SE+2.0% LA and SE+2.0% QS. The biggest reduction in wear width is 44%, which is obtained by SE+2% LA. These experimental results indicate that leaf-surface wax as additives also can greatly improve the friction reduction and anti-wear abilities of synthetic ester for steel/aluminum pair.

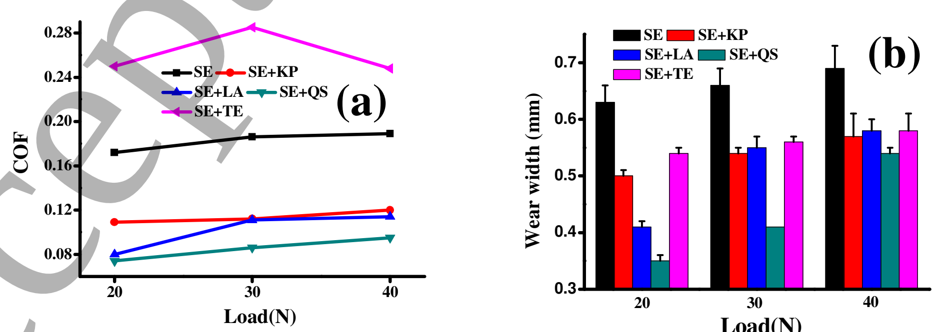
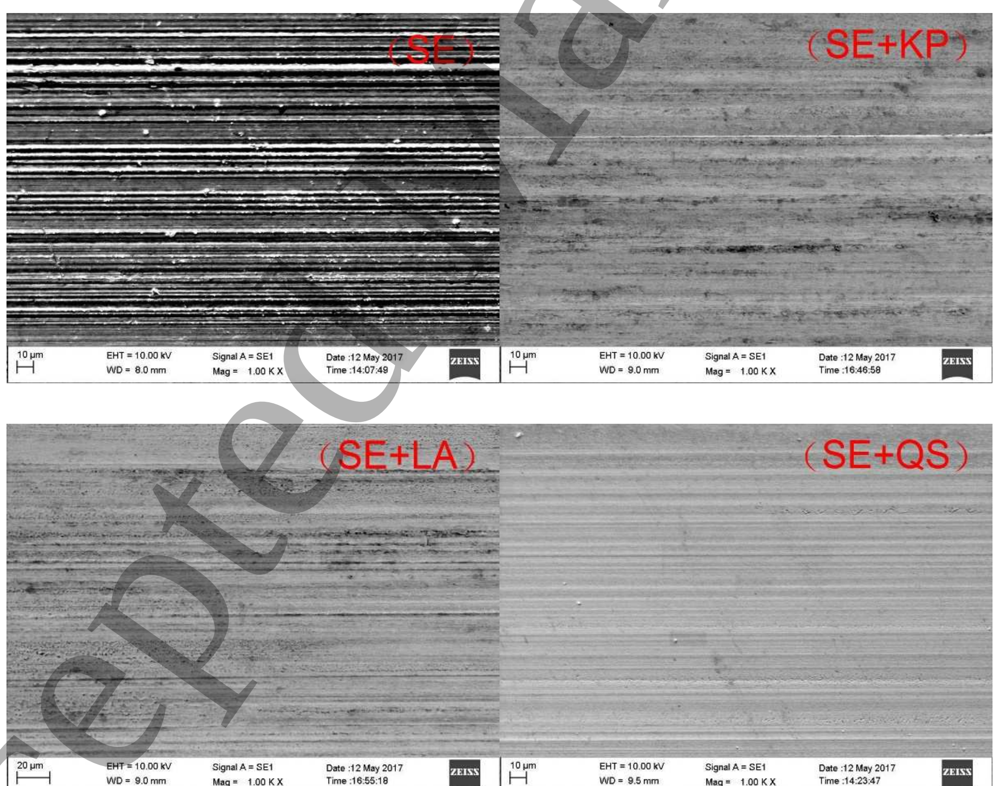


Figure 5 Average COFs (a) and wear widths (b) for the lubricating oil for steel/aluminum pair at

different loads, 5 Hz and RT (additive content: 2.0%)

Figure 5 presents the average COFs and wear widths of steel/aluminum pair at different loads, 5 Hz and RT. It is visible that three types of leaf-surface wax exhibit lower COFs than SE and SE+TE at different loads. KP and LA have close COFs at 30 N and 40 N, and QS always have the lowest COF at different loads. The friction reduction ability of synthetic ester is greatly enhanced by leaf-surface wax. Observing the Figure 5 (b), with the loads increasing, the wear widths gradually increase, while all the wear widths of leaf-surface wax and TE are still lower than those of synthetic ester at different loads for steel/aluminum pair. The results indicate that leaf-surface wax as additives can greatly improve the friction reduction and anti-wear abilities of synthetic ester for steel/aluminum pair at different loads.

4 Surface analysis and discussion



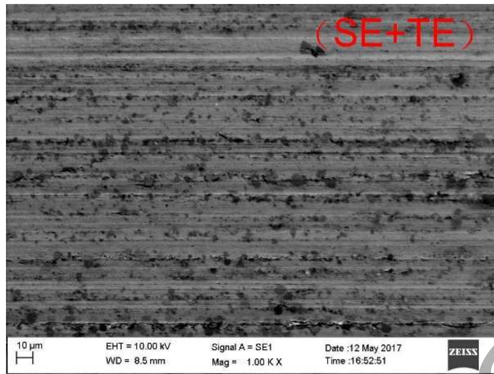
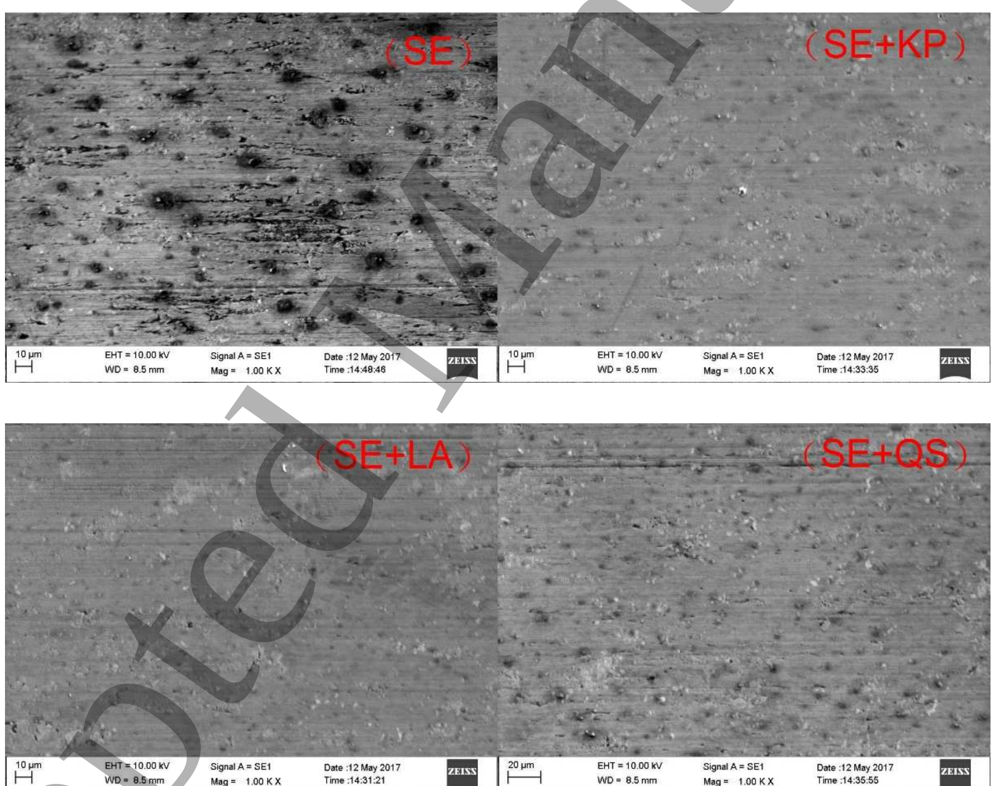


Figure 6 SEM morphologies of the worn surface on steel blocks lubricated by various lubricants at 125 N, 5 Hz and RT.



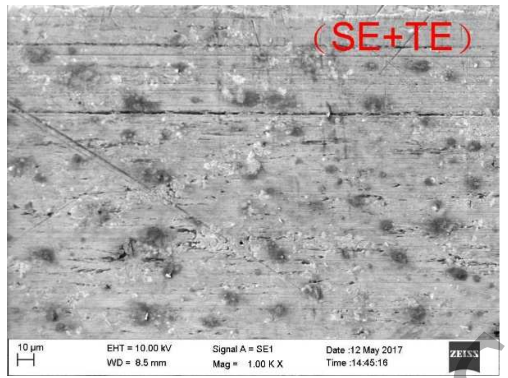
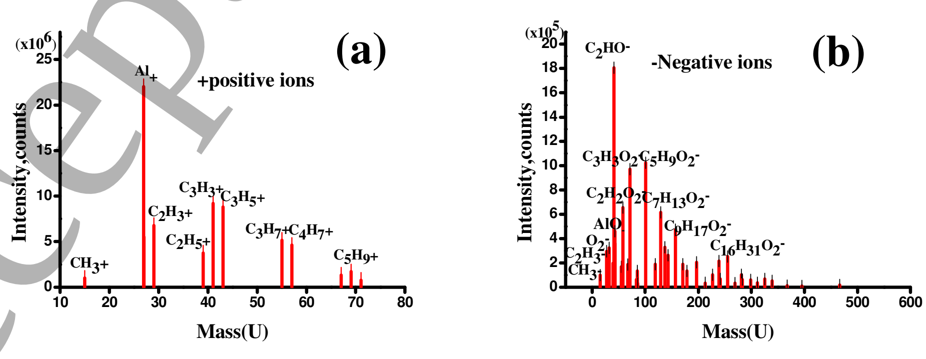


Figure 7 SEM morphologies of the worn surface on aluminum blocks lubricated by various lubricants at 40 N, 5 Hz and RT.

Figure 6 shows the SEM morphologies of the worn surfaces on the steel blocks lubricated by different lubricant oils at 125 N, 5 Hz and RT. Observing the Figure 6, the morphologies of the worn surfaces lubricated by SE+KP, SE+LA and SE+QS just have some shallow and slim grooves, whereas the wear scars lubricated by SE and SE+TE acquire deep furrows and pits, indicating leaf-surface wax as additives can significantly improve the friction reduction and anti-wear abilities of synthetic ester for steel/steel pairs.

Figure 7 presents the morphologies of the worn surfaces on the aluminum blocks lubricated by different lubricating oils at 40 N, 5 Hz, and RT. Similarly, the worn surfaces lubricated with SE containing leaf-surface wax are smoother, with slim grooves and little corrosive pits. The worn surfaces lubricated by SE and SE+TE are relatively rough, implying SE and SE+TE are not lubricous enough for steel/steel pairs. This results demonstrate that the preferable lubricity for steel/aluminum pairs can be obtained by employing leaf-surface wax including KP, LA and TE as additives.



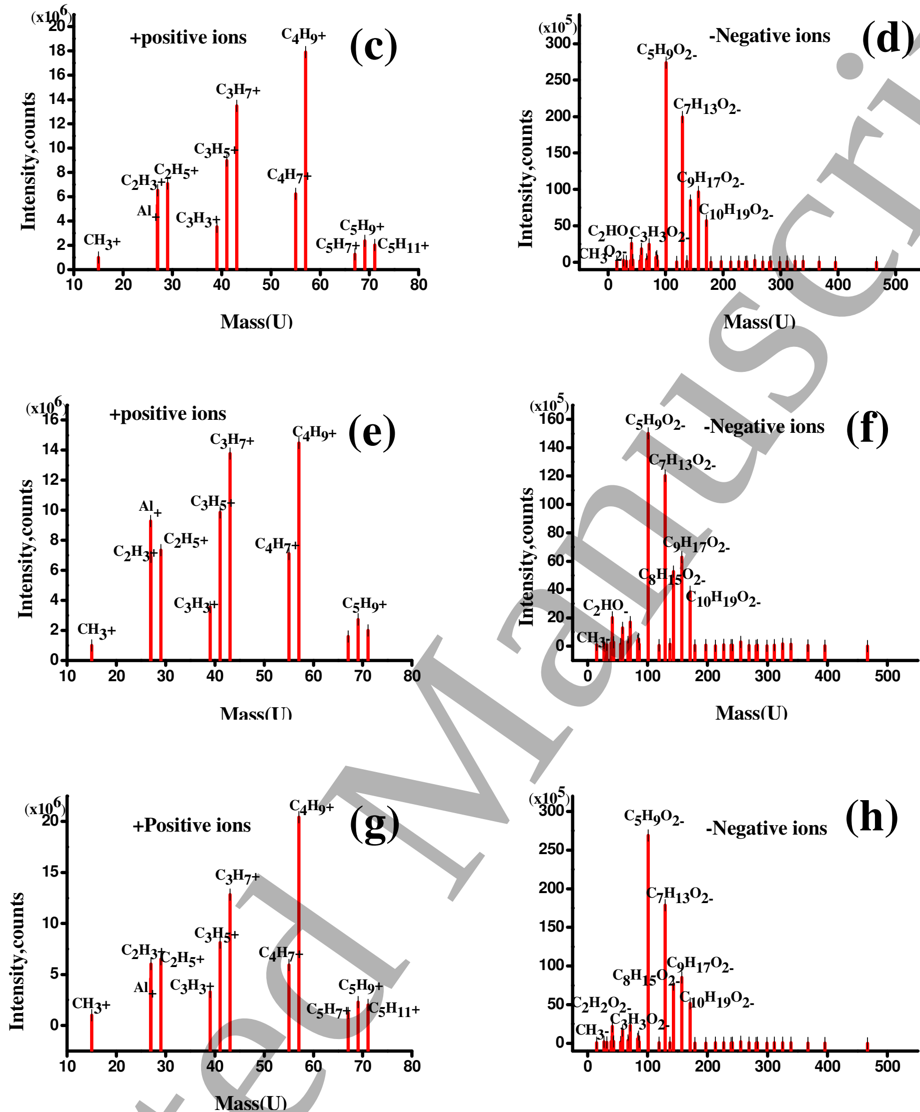


Figure 8 Positive and negative ions TOF-SIMS spectra of the worn surfaces on aluminum blocks after friction, (a) and (b) SE, (c) and (d) SE+KP, (e) and (f) SE+LA, (g) and (h) SE+QS.

In order to explore the lubrication mechanism of the leaf-surface wax, the TOF-SIMS was employed to characterize the chemical composition on the worn surfaces after friction test because it is more sensitive for a range of species than XPS [16-17]. Figure 8 gives the negative and positive ions TOF-SIMS spectra of the worn surfaces on the aluminum blocks lubricated by different lubricating oils. Compared with the TOF-SIMS spectra of the worn surface lubricated by SE, the TOF-SIMS spectra lubricated by leaf-surface wax all have a weak peak of Al^+ and strong peaks of $C_xH_y^+$ ions and $C_xH_yO_z^-$ ions. Meanwhile, the contents of multiple negative ions including $C_5H_9O_2^-$

$C_7H_{13}O_2^-$ and $C_9H_{17}O_2^-$ on worn surfaces lubricated by leaf-surface wax are several times of those on the worn surface lubricated by SE, indicating a great amount of medium and long chain ions residue on the rubbing surfaces throughout the sliding process.

The tribological data and SEM morphologies imply that the tested leaf-surface wax including KP, LA and QS could significantly enhance the friction reduction and anti-wear abilities for steel/steel and steel/aluminum pairs. This results inspire us to explore the possible lubrication mechanism of leaf-surface wax as additives. As shown in Figure 9, physical adsorption film and tribo-chemical reaction film may be involved in the friction and wear tests. It is well known that during the sliding process, the low-energy electrons could emit from the metal surface of the friction zone, leading metal surfaces carries a positive charge. [18-19]. Meanwhile, as shown in table 1, the tested leaf-surface wax have a large amount of alkanes and alcohols and some acids. In the process of friction, the alkanes, alcohols and acids with long chains could break into a lot of short chains which may carry negative charges. These short chains could adsorb on the rubbing surfaces to form a physical adsorption tribofilm to enhance the friction reduction. The strong peaks of $C_xH_yO_z^-$ ions on the TOF-SIMS spectra of the worn surfaces shown in Figure 8 also proves this conceivable lubrication mechanism. In addition to the physical adsorption tribofilm, the temperature of the contact region increases and fresh metal constantly exposes as the friction goes on, the leaf-surface wax also could react with the fresh metal to generate a tribochemical reaction film to improve the tribological properties. This analysis of lubrication mechanism also has been presented in our previous work [14]. In a word, based on the tribological data, SEM and TOF-SIMS analysis, the superior friction reduction and anti-wear abilities of leaf-surface wax as lubricant additives are attributed to the physical adsorption and tribochemical reaction film throughout the sliding process.

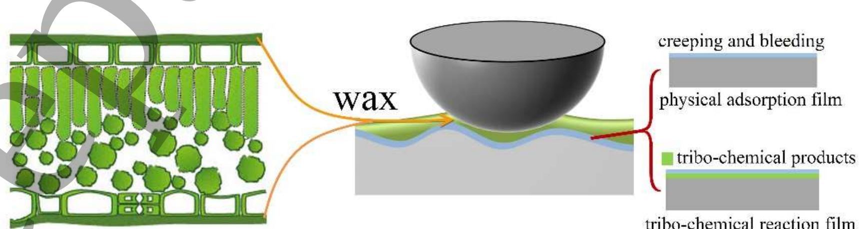


Figure 9 Schematic of friction mechanism of the leaf-surface wax as additive

5 Conclusions

Based on the results given above, the conclusions can be summarized as following. The typical chemical composition of the leaf-surface wax extracted from Korean pine (KP), larch (LA) and Qinghai Spruce (QS) are alkanes, alcohols and acids etc. The extracted leaf-surface wax used as green lubricant additives could not only remarkably lower the friction coefficient, but also greatly reduce the wear widths, indicating leaf-surface wax have excellent friction reduction and anti-wear abilities for steel/steel and steel/aluminum pairs. Based on the SEM and TOF-SIMS analysis, the excellent tribologcial properties are attributed to the physical adsorption and tribochemical reaction film generated by leaf-surface wax throughout the sliding process. Because of the excellent tribological properties, leaf-surface wax as a green lubricant additive holds a great promise for a range of applications.

Acknowledgments

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