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Study of tribological properties of ecofriendly lubricant additives derived from leaf-surface waxes

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Three kinds of leaf-surface waxes are extracted from the leaves of *Euonymus japonicas* (EJ), *Sabina chinensis* (SC) and *Sabina procumbens* (SP) to be tested for their tribological properties. Lubricating oils containing these 3 waxes respectively were analyzed via gas chromatography-mass spectrometer (GC-MS) for their chemical constituents and tested with friction and wear testing machine and time of flight secondary ion mass spectrometry (TOF-SIMS) for the tribological mechanism. It was found that all the tested cuticular wax can reduce the coefficient of friction, and the waxes of SC and EJ can reduce the wear width. The contents of acid and esters in the wax can improve the friction reducing property by forming tribochemical films on the metal, but result in the increase of wear due to corrosion. The increase of ions containing C, H, O and the decline of aluminum positive ions on the worn surface, demonstrate that the tribofilms derived from long chain compounds play a role of protecting the metal surfaces.

leaf-surface wax, friction, wear, lubricant additives, ecofriendly lubricant

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1 Introduction

Machinery is necessary in industrial manufacturing and human's daily life. But predictable friction and wear in machines not only consume excessive energy, but also shorter the service lives [1]. Lubricating oils are used in machines to reduce the friction and wear between two relatively moving surfaces. And besides, we can also expect more advantages to the machine components from lubricating oil, such as cleaning, sealing, cooling, anti-corrosion and anti-rust. Among all lubricating oils, mineral oil-based lubricants are used the most [2]. These common oil materials might be hard to degradation, or degradation-resistant in the environment. Moreover, many additives containing the elements of P, S or halogen, are not only degradation-resistant, but also noxious to nature and living creatures, although they are effective in lubrication [3,4]. It becomes more and more significant to discover environment friendly lubricating oils to reduce these disadvantages mentioned above. Synthetic esters are considered to be base lubricating oils with the best degradation property [5]. And vegetable oils, such as the colleseed oil and caster oil, are also potential materials after modification process, due to their biological origin [6–8]. Compared to the base oil, more works have been done to develop environmental friendly additives. Fang et al. [9] modified chemically methyl oleate to obtain a kind of "green" additive, and evaluated its tribological properties as added in vegetable-oils on steel/steel and steel/aluminum friction pairs. Zhang et al. [10] investigated the mechanism of tribological behavior of basil seed gel.

Leaf-surface wax, also known as cuticular wax, is the outermost layer of most leaves of plant kingdom generated by the leaves themselves. These waxes keep leaves from damages of UV violets, chemical pollutions and physical damages, etc.

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According to Kunst and Samuels [11], leaf-surface waxes, covering the cuticle of leaves, are composed of very-long-chain fatty acid (VLCFAs), alcohols, alkanes, aldehydes, ketones and esters with the chain length ranging from C24–C34. And another previous research extracted hydrophobic waxes from eucalyptus, and figured out the components included fatty acids (C16 to C36), alkanes, alcohols, and esters [12]. Cornelia et al. [13] and Ji et al. [14] also investigated the constituents of leaf-surface waxes of several plants species, and demonstrated again that alkanes, alcohols, and fatty acids are main ingredient in waxes. Xu et al. [15] extracted the leaf-surface waxes of hoya carnosa, eggplant and green Chinese onions, and tested them in PAO base oil compared to MoDTC, and found that these waxes performed excellently as additives in friction reducing and anti-wear. The study of Shi et al. [16] showed that waxes covering wheat leaf surface can reduce the friction coefficient and wear volume on a friction pair of Steel/Bronze. Desert plants can survive in cold and extremely dry environment, mostly thanks to their protection on their leaves or rootstocks. Focusing on the protection mechanism of these plants, researchers are getting down to study the constituents that are common on these leaves. Xu et al. [17] studied a type of desert moss, *Syntrichia caninervis*, and found similar constituents in its wax, which are fatty acids, alcohols, and alkanes. A research of Xia et al. [18] about two kinds of desert plants, *Ammopiptanthus mongolicus* and *Reaumuria soongorica*, found that effective constituents in their leaf-surface waxes promote the friction reducing and anti-wear properties of lubricating oil. There are many other plants that can survive in cold or dry environment. Euonymus japonicus plants have dense foliage, remain green throughout the year and have bright green leaves even in cold areas. They are typically used as an urban greening tree species and are planted commonly throughout many provinces all over China, often used for ornamental plants because of their resistance to pruning and also commonly used as hedgerow plants [19]. The experimental results reported by the Jiangsu Institute of Botany showed that the *E. japonicus* tree species has strong resistance to sulfur dioxide [20]. *Sabina chinensis* is an evergreen woody plant, mainly growing at altitudes ranging from 500 m to 1900 m on Plains of China, and is important virescence tree species in northwest area [21,22]. *Sabina procumbens*, mainly growing in North China, is proved to be drought and low temperature tolerant. The later two plants are typical drought-enduring plant, because of which, they are important in northwest China. However, few studies have been done on waxes of these three sorts of plants. In this research, waxes of these plants are extracted and added into synthetic esters, to investigate there tribological properties on steel/steel and steel/aluminum contacts. Figure 1 shows the images of the 3 kinds of leaves.

2 Experiment

2.1 Materials

Synthetic ester (Se) was purchased from Changsha zhongcheng Company (China), and its essential parameters are listed in Table 1. *Euonymus japonica* (EJ), *Sabina chinensis* (SC) and *Sabina procumbens* (SP) leaves were picked up at Beijing, China (latitude: 40.09°; longitude: 116.31°). The other reagents were at analyticle level or higher.

Figure 1 (Color online) Images of the 3 kinds of leaves. (a) *Euonymus japonicu*; (b) *Sabina chinensis*; (c) *Sabina procumbens*.

Table 1 The essential parameters of the synthetic ester

Item	Synthetic ester
Appearance	Faint yellow, transparent liquid
Kinematic viscosity	25 cSt (40°C)
	2 cSt (100°C)
Viscosity index	136
Condensation point	<60°C
Open cup flash point	252°C

2.2 Methods

2.2.1 Cuticular wax extraction

Before the test, the collected leaves need to be washed in clean water with a brush to remove the dust and impurities away from the surface of the leaves. Then bring the clean leaves out of direct sunshine and dry them in the shade to remove any residual water to minimize the error in the measurement. Leaves are immersed in chloroform liquid for 30 s and took out in order to not to extract chlorophyll. Finally put the beaker at ventilated place. As the solvent evaporated, the gelatinous precipitate would be the substance initially planning to get.

2.2.2 Lubricating oil preparation

Ahead of the test, all containers were rinsed thoroughly in acetone reagent under ultrasonic circumstance. The specimen were obtained via mixing 0.5 wt%, 1 wt%, 2 wt% cuticular wax of ginkgo leaves, ammopiptanthus mongolicus leaves and cinnamomuim camphora leaves with synthetic ester respectively. At the same time, mixture that 0.5 wt%, 1 wt%, 2 wt% glycerol as additive in lubricating oil sample served as a contrast to explore the properties of the external surface wax.

2.2.3 Cuticular wax contents analysis

To analyze the primary component of the cuticular wax, GC-MS (7890A GC, Agilent, USA) was adopted. Comparison between the strongest peak which was determined as the metric and the rest peaks, then content of each peak could be inferred.

2.2.4 Tribological test

The tribological tests at ambient were conducted at an MFT-R4000 (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China) reciprocating friction and wear tester to characterize the tribological properties of the synthetic lubricating oil. During this study, the balls were made from AISI 52100 steel (hardness 710 Hv) having a dimension of 5 mm in diameter. The disks were made from AISI 52100 steel and Al2024 aluminum respectively with finish sizes of 24 mm in diameter and 7.9 mm in thickness. Running through the test, the ball above was attached tightly to the disk below under different loading conditions. The round trip of the upper ball was 5 mm at a lasting time of 30 min with the frequency of 5 Hz at room temperature. The external loads applied to the steel-steel friction pair were 50, 100 and 125 N independently while the ones for steel-aluminum friction pair were 20, 30, 40 N. All of the ball and disk test-pieces would have a soak clearing using an ultrasonic cleaner with petroleum solution whether before or after each tribological test. Prior to every experiment, oil drop method was put to use to lubricate the friction coupling. The friction coefficient (COF) was recorded by a self-operated measuring unit which was connected to the frictional tester. The wear width was measured when the worn surfaces were observed with a scanning electron microscope (SEM, EVO-18, ZEISS, Germany). Data were automatically read out via a basic function of the ZEISS software as both edges of a scar were selected. An example of the measurement is shown in Figure 2. Repeated tests were performed for three times, as a result, the average values accompanied by an error bar were produced in the results.

2.2.5 Surface analysis

The morphologies of the worn surfaces were analyzed using ZEISS scanning electron microscope (Germany). Meanwhile, the elements in the surface were explored using energy dispersive X-ray spectrometer (EDS, XFlash® 6|30, Bruker, Germany), installed on the SEM device. Furthermore, more specific chemical components in the material surfaces before and after friction test were probed by means of time of flight secondary ion mass spectrometry (TOF-SIMS IV, CAMECA, France). All specimens were cleaned with petroleum ether in ultrasonic cleaning machine before observation and measurement, to remove the residual organic matter and other pollution.

3 Results and discussion

3.1 Composition of cuticular wax analysis

The content of each component in different leaves has been depicted in Table 2. It can be seen that the most abundant

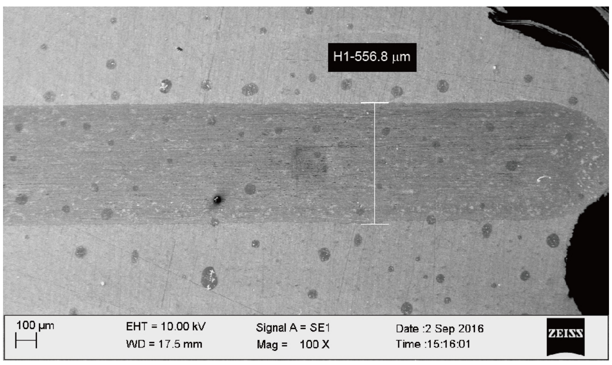

Figure 2 An example of the measurement of wear width (Worn aluminum surface of SE+SC, 40 N).

Table 2 The composition of cuticular waxes

Constituents	Plant species		
	Euonymus japonica	*Sabina chinensis*	*Sabina procumbens*
Alkanes	54.22%	23.86%	3.62%
Acids	0.06%	5.42%	21.16%
Alcohols	28.90%	33.83%	25.96%
Esters	0.24%	1.28%	5.3%
Ketone	12.82%	0.86%	2.51%

components are alkanes and alcohols while the acids and esters contents in all the waxes are low. Hence, it's important to investigate the tribological performance of different cuticular wax via friction test, to verify the influence to the friction process from different constituents.

3.2 Tribological tests

3.2.1 Influences of additive concentration

The Figure 3(a) depicts the fluctuations of the coefficient of friction for the testing lubricating oil with different content of additive added into it under the load of 20 N on steel/aluminum contact. It can be seen that under the condition of steel-aluminum friction pair, the lubricating oil with cuticular wax as additive has low and stable COF, values of COF are in the sequence of SE+Glycerol>Se+SP>Se+SC>Se+EJ. Compared with glycerol, the cuticular wax could greatly reduce the COF as for SC, the COF first decrease and then increase. COFs of SP and EJ all decrease as the content increases to 2.0%, where the EJ shows the lowest COF value among all additives. The Figure 3(b) indicates the severity of attrition for different additives under ambient conditions. Similar to SE+SC, the wear scar width of all 3 additives presents a down and up trend whereas the width reaches the minimum value at 0.5% or 1.0%. The values of wear scar width for SC and EJ wax are generally smaller than that of glycerol and the width of EJ is the smallest one. On contrary, the wear width of SP increased significantly, and even more than SE+Glycerol, as the content rises above 1%.

The Figure 4(a) depicts the fluctuations of the coefficient of friction for the testing lubricating oil with different concentration of additive added into it when the load is 100 N under the condition of steel/steel friction pair. The overall situation is slightly similar to the condition of steel/aluminum contact. The values of COF presented by plant additives are lower than that of neat SE and glycerol, meanwhile the SP has generally the lowest level and other waxes also kept low levels. The Figure 4(b) exhibits the wear scar width of different additives. It is can be found that compared with glycerol, SC and EJ performed for most cases, and especially when the concentration is 0.5%, the wear rate were the lowest with SC and 2% with EJ. However, the SE+SP has a really high level, even higher than glycerol. It is interesting considering its low COF, and it will be discussed in the next section.

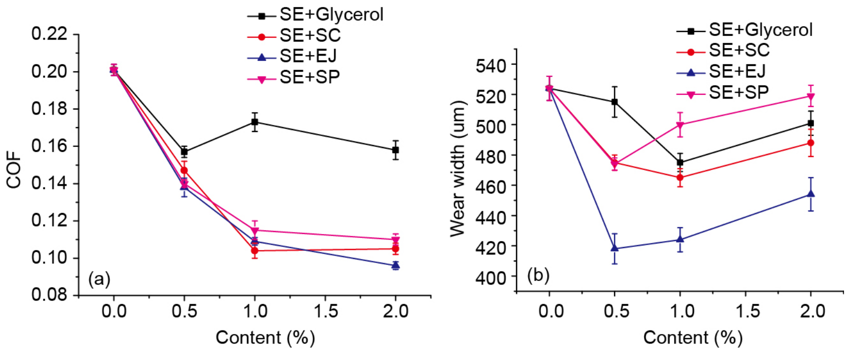

Figure 3 (Color online) Average (a) COFs and (b) wear widths for the lubricating oil with additive content variation under steel/aluminum contact.

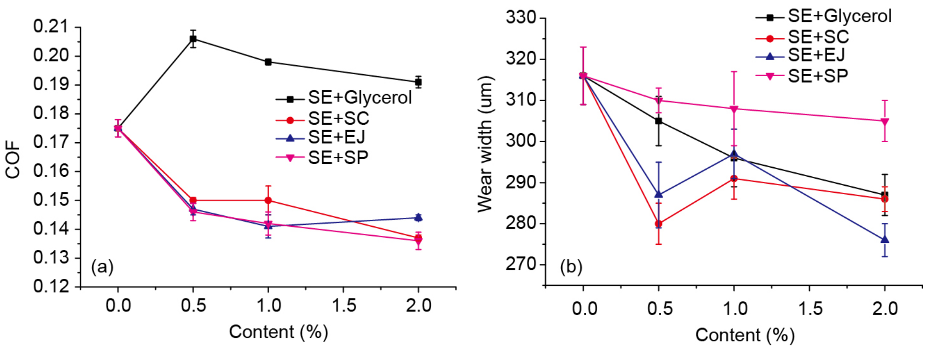

Figure 4 (Color online) Average (a) COFs and (b) wear widths for the lubricating oil with additive content variation under steel/steel contact.

3.2.2 Influences of load

The COF variations which have been tested under various load conditions are unfolded in Figure 5(a). The content value is 2% and the friction pair is steel-aluminum. For the additives of SC and EJ waxes, the COF values display an upward trend as more load is applied. Differently, the COFs of SE+Glycerol and SE+SP remain stable as the load increases. But for most cases of wax additives, the COFs are lower than glycerol, especially for the SP, whose COFs are far lower than glycerol at each load. The Figure 5(b) represents wear scar width of different additives under various loading conditions and the width values rise along with the load increasing. In the cases of SE+SC and SE+EJ, the wear widths are obviously smaller than the one of SE+Glycerol, showing good anti-wear properties. But for the additive of SP wax, the wear widths are greater than glycerol. The results of wear width showed different trend as the additives changes.

The Figure 6 respectively shows the COFs and wear widths of different additives with various load condition and the additive concentration is 2% in steel-steel friction pair case. Under this friction pair condition, the COFs of lear-surface waxes are almost stable, among which the COF of SE+SC remains the lowest. In comparison, the SE+Glycerol shows much higher COF than the others. Similar to the friction pair of steel/aluminum, the results of wear widths indicate better anti-wear properties of SE+EJ and SE+SC, than that of SE+Glycerol. Meanwhile, the SP wax possesses the weakest anti-wear protection all the same.

3.3 Surface analysis

Figure 7 shows the surface morphology of the aluminum disk, after friction test lubricated with different plant waxes. According to the images, the surface of EJ and SC are relatively smooth, compared to the SP and neat Se. In the case of EJ and SC, fewer furrows can be found, and the small amount of dark holes indicates the existence of adhesion and plastic forming. In the case of SP wax, furrows increase and bigger holes with bigger area of deforming indicate more contacts between the steel ball and aluminum disc. But in this case, only thin and shallow furrows can be found instead of thick ones, unlike the neat Se, indicating the good lubricity with not so good anti-wear properties. SC wax brings the smoothest surface under the friction pair of steel-aluminum.

Figure 8 shows the surface morphology of the steel disk, after friction test lubricated with different plant waxes. In these cases, it can be still seen that the surfaces of all three waxes are smoother than Se, while on the surface of Se, a row of micro holes appear, indicating the direct and furious contact in this area. Based on these two groups of images, it can be inferred that leaf-surface waxes can protect the metal

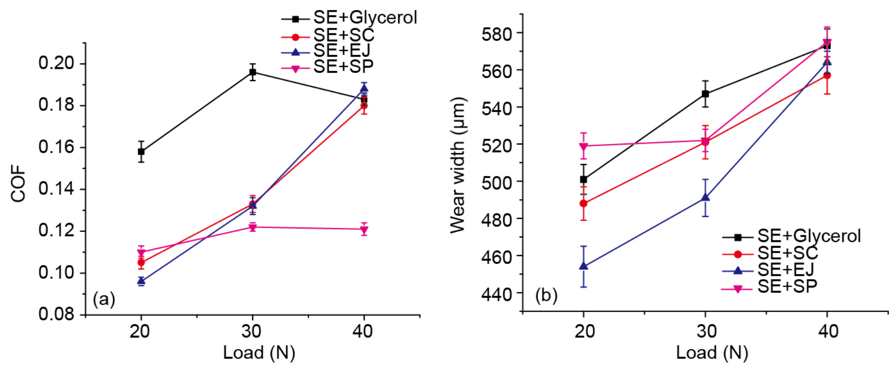

Figure 5 (Color online) Average (a) COFs and (b) wear widths for the lubricating oil with different loads applied under steel/aluminum contact.

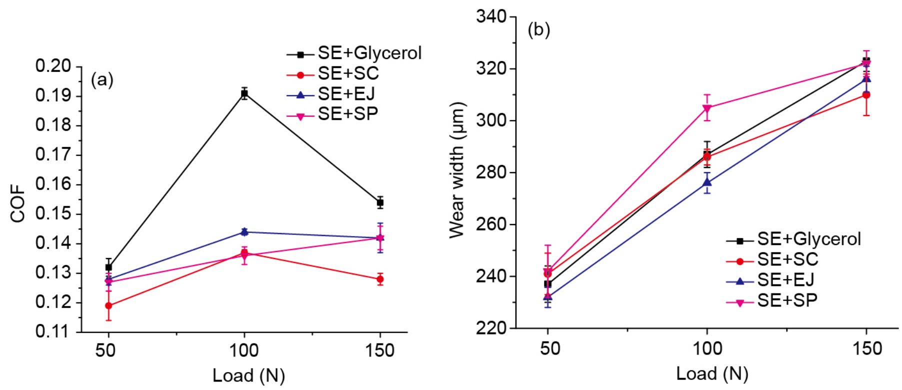

Figure 6 (Color online) Average (a) COFs and (b) wear widths for the lubricating oil with different loads applied under steel/steel contact.

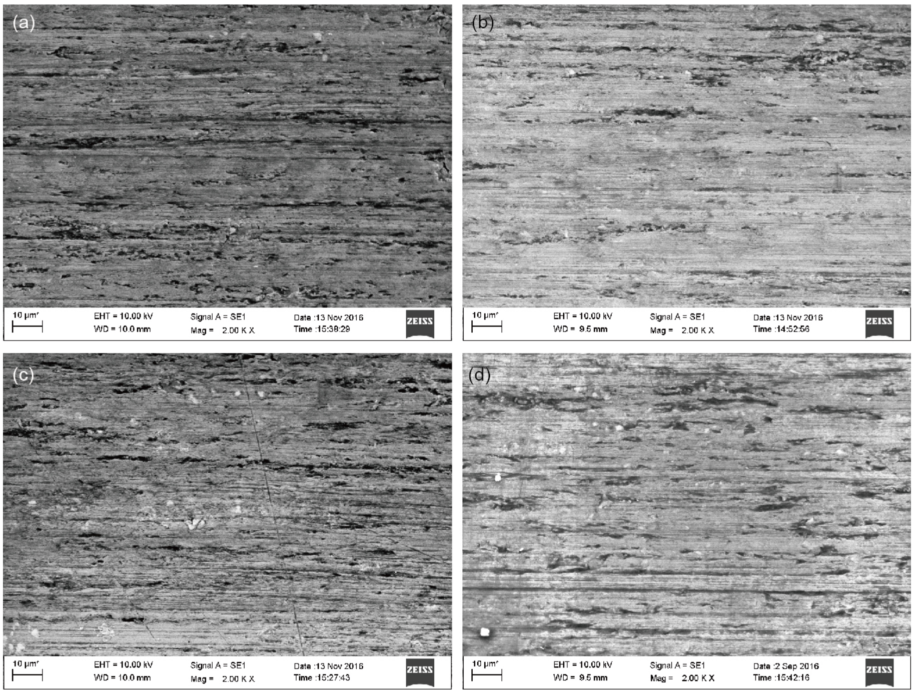

Figure 7 SEM images of worn surfaces lubricated with (a) Se+EJ, (b) Se+SC, (c) Se+SP, (d) Se+Glycerol under the steel-aluminum friction pair condition with 40 N load.

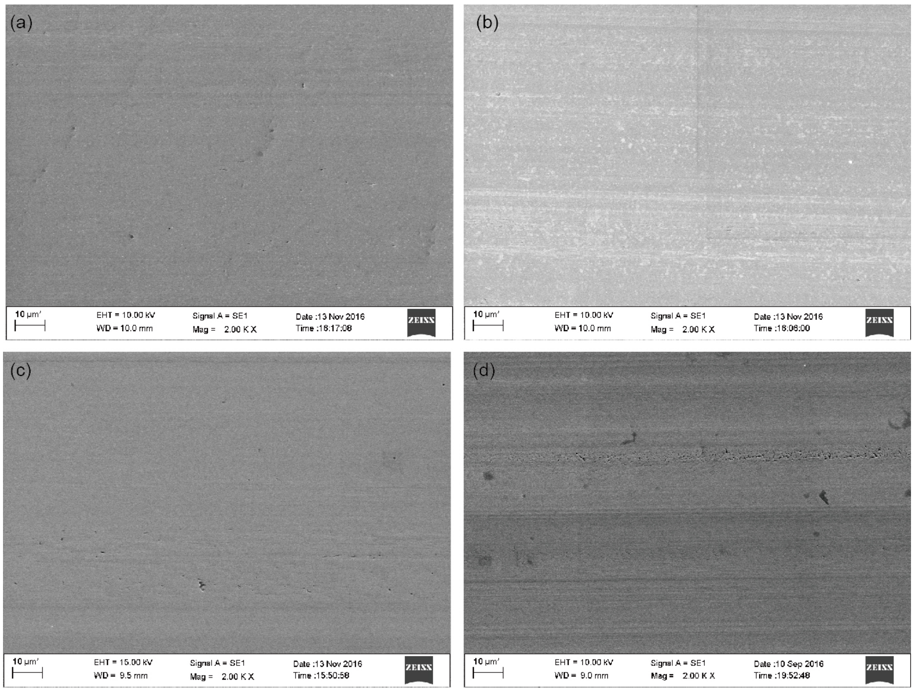

Figure 8 SEM images of worn surfaces lubricated with (a) Se+EJ, (b) Se+SC, (c) Se+SP, (d) Se+Glycerol under steel/steel friction pair condition with 150 N load.

surface from getting damaged seriously, such as being scratched.

3.4 TOF-SIMS analysis

Positive and negative ions TOF-SIMS spectra obtained on the surface of aluminum after friction test lubricated with Se, SP and SC are shown in Figure 9. The plots of positive ions show a decrease of about 25% of Al^+ ions after adding SP or SC leaf-surface waxes into the Se. And meanwhile, the amount of $C_3H_7^+$ and $C_4H_7^+$ increased, indicating that more positive ions containing C and H formed the protective film on the metal surface. In the case of negative ions, it is obvious that

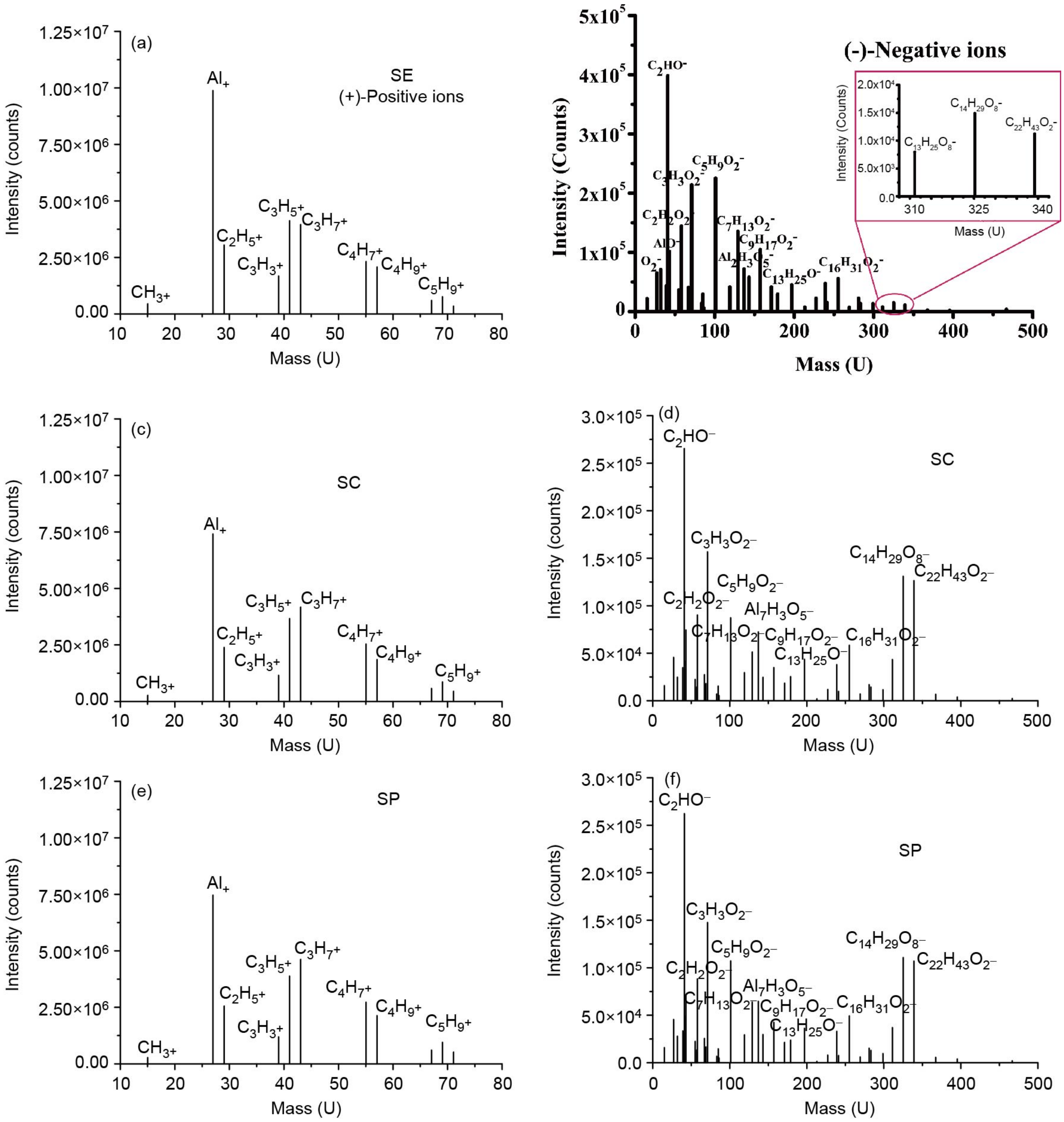

Figure 9 (Color online) Positive (a, c, e) and negative (b, d, f) ions SSIMS spectra obtained on the surface of aluminum after friction test.

in both cases of SP and SC, a great amount of medium- and long-chain ions (containing C, H, O) residue on the rubbed surface.

3.5 Discussion

Figure 5(a) shows great increases of COFs of Se+SC and Se+EJ, when the load increased to 40 N. This gap indicates sudden aggrandizing of direct contact between the steel ball and the aluminum block surface. Tribofilms and lubricating fluid between the pairs can protect the surface till the load of 30 N. After that, tribofilms are broken and fluid are squeezed out the contacting area. In the case of Se+Glycerol, poor protections cannot keep the surface from excessive contacting even at 30 N. By contrast, the leaf-surface of SP in the Se can keep the COFs stable as the load increases, indicating that the direct contacts between the substrate metal of the ball and the block does not change much as the load increases. Combining with the results shown in Figure 5(b) and Table 2, it can be inferred that a protecting tribochemical film is generated on the surface of the substrate metal in the case of SP wax, due to the large content of acid, which can react with active metal, such as aluminum and iron. The generated aluminum salt or ferrous/ferric salt adheres to the metal surface, forming a firm film protecting the substrate metal. In the case of SC, less content of acid or ester (which can also form metallic salts because of its property of decomposing to acid and alcohol [23–25]) can only form a thin or rare film on the metal. These films cannot protect the metal at great loads. Corresponding with the EDS results, the SSIMS analysis displayed in Figure 9 shows the residue of long chain negative ions and

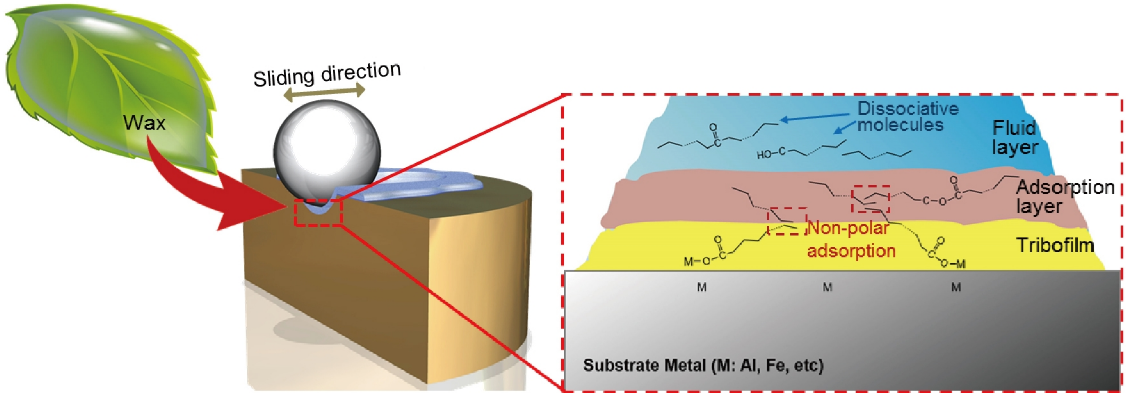

Figure 10 (Color online) Structure of part of the leaf-surface and the mechanism of the wax lubricating.

relatively low contents of short chain negative ions on the worn surfaces of SP and SC, supporting the tribochemical mechanism mentioned above.

However, the tribofilm generated from acids and metal substrate will be expended as the friction process goes on, the substrate metal will then expose continuously. Since the contents of acid and ester in the SP wax are sufficient, new films will be generated then, resulting in more corrosion of the substrate metal. Therefore, the wear width of Se+SP was even greater than Se+Glycerol, although the COF was much lower.

Beside the tribochemical reaction between the acid or ester decomposed acid and the metal, other long chain alkanes, alcohols and ketones can also protect the surface to some extent. For these three sorts of compounds, non-polar adsorption to the non-polar ends of the salts would be a dominating mechanism of reducing friction and wear. Otherwise, these long chain compounds would be dissociative in the fluids between the metals, which can also improve the lubricity of the lubricant. The results of steel-steel friction pair may provide evidence for these two mechanisms. Figure 10 displays a schematic diagram for the friction reducing mechanism of leaf-surface wax.

4 Conclusion

The cuticular wax performs well as lubricant additives and shows anti-wear properties. And among the three kinds of waxes tested, SC and SP waxes performed better than EJ on friction reducing, probably because of the large amount of acids. SC and SP waxes can reduce the aluminum positive ions on the worn surface, and increase the amount of other ions containing C, H and O, indicating protective effect to the metal surface.

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