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Tribological research of leaf-surface wax derived from plants of Pinaceae

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Abstract

Two kinds of leaf-surface waxes are extracted from the leaves of Picea wilsonii Mast (PM) and Pinussylvestris (PS) and used as additive in synthetic ester base oil. The tribological properties were investigated using an MFT-R4000 tribology tester at room temperature. Gas chromatography-mass spectrometry analysis was performed to identify the composition of the PM and PS leaf-surface wax, and scanning electron microscopy and time of flight secondary ion mass spectrometry were used to investigate friction mechanisms. The results suggest that the leaf-surface wax of PM and PS could successfully reduce the friction and wear of steel-aluminium and steel-steel sliding pairs as compared with synthetic ester containing Terpineol additives. The excellent tribological properties were attributed to the protective film generated on the worn surfaces by leaf-surface wax during the friction process.

KEYWORDS
friction and wear, leaf-surface wax, tribology

1 | INTRODUCTION

Lubricating oils and greases are common ways in most mechanism to prevent components being damaged from friction. In order to make oils and greases suitable for variety of working condition, additives are added. In the past, Spermaceti oil from sperm whales, which is mainly composed of wax esters, was widely used in high performance lubricants as additives or even as base oil. After the global ban of sperm whale hunting, synthetical alternatives based on fossil oil have to be developed.[1] However, most frequently used fossil oils and their derivatives are difficult to degrade in a natural environment. Moreover, many additives contain the elements such as P, S, or halogen, which are not only difficult to degrade but also toxic to living creatures, although they are effective in lubrication. So far, the three most widely acknowledged processes of biodegradation are hydrolysis of esters, β-oxidation of long chain hydrocarbons, and hydrogen peroxide of aromatic hydrocarbons.[2] Therefore, synthetic esters (Ses) are considered to be base lubricating oils with the best degradation property.

Plants of Pinaceae have a wide distribution in China and all over the world. They are very common in temperate region. Meanwhile, Pinaceae has a very long historical standing, which indicates its ability of baring extreme temperature, especially extremely cold or drought weather. Pinussylvestris (PS) is a perennial herbaceous plant in the north of China. Some literatures reported its detailed structure of the leaf and suggested some chemicals from the leaves of PS could be used as medicine.[3-6] Picea wilsonii Mast is another species of Pinaceae plants, which can be found mainly in North China, especially in Inner Mongolia and Heilongjiang Provinces.[7] It is discovered that over-expression of some gene transcription factor in Picea wilsonii Mast improved significantly tolerance to salinity and drought resistance by generating transgenic arabidopsis gene segment.[8] These two species were all draught and low temperature tolerant; therefore, these leaves were of interests for practical applications.

As a significant part of plant leaves, a layer of wax can be found on leaves of most plants on this planet, which keeps from damages of outside radiation, chemical pollutions, and physical damages, etc. The literature suggests that leaf-surface waxes, covering the cuticle of leaves, are composed of very-long-chain fatty acids, alcohols, alkanes, aldehydes, ketones, and esters with the chain length ranging from 24 and 34.[9] Wax esters are formed by enzymes catalysing esterification of a fatty alcohol with a fatty acid, both of which can be found in the leaf body and the surface wax layer as well. This reaction can be performed by different enzymes that have acyl transferase activity.[10,11] Different wax components can exist as up to six kinds of crystal structures,[12] and different combinations of wax compositions can form different structures of outer layer on the leaf surface.[13] According to different function, the wax constituents of different sublayer may be different as well.[14] A research on wax coatings on *Phyllostachys aurea* leaves verified different weight densities on epi-and intracuticular layers. Esters, alkanes, alcohols, and fatty acids were found on these leaves, each with one or two primary carbon chain length.[15] Esters, alcohols, and acids in these constituents are proved to be efficient in many applications. Sanches found that some of the wax constituents are protective because of its ability to decline the influence of high temperature.[16] Montgomery[17,18] and St Pierre[19] discovered that long chain compounds can reduce the metal wear in the case of boundary lubrication. Xu extracted the leaf-surface waxes of *Hoya carnosa*, eggplant, and green Chinese onions, and tested them in polyalphaolefin base oil and found that these waxes performed excellent friction reducing and anti-wear properties as compared to molybdenum dialkyl dithiocarbamate.[20] Partly similar to the environment of Pineceae plants, desert is another environment where leaves need strong protection from dry air and sunshine. Xia discovered waxes derived from three kinds of desert plants and found relatively good performance in tribological test.[21] Xia also collected three kinds of plants that are familiar in North China and found better tribological performances than glycerol, a common lubricant additive.[22] Another study from the same research group showed that waxes covering wheat leaf surface can reduce the friction coefficient and wear volume on a friction pair of steel/bronze.[23] In the present study, PS and Picea wilsonii Mast (PM) as shown in Figure 1 were collected to derive waxes. Terpineol was chosen in this research as control group because it is a kind of chemicals derived from Pinaceae tree oil.[24] The tribological properties were investigated in detail, and the lubrication mechanisms were proposed based on the analysis of the worn surfaces.

2 | EXPERIMENTAL PROCEDURES

2.1 | Materials

Synthetic ester (Se) was purchased from Changsha Zhongcheng Co Ltd. Pinussylvestris (PS) and PM leaves were picked up at Heilongjiang (latitude: 52.09°; longitude: 116.31°). The terpineol, chloroform, and petroleum ether were purchased from Sinopharm Chemical Reagent Co., Ltd, and they were of analytical grade and without any further purification.

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. Then, clean leaves are brought out of direct sunshine and dried in the shade to remove any residual water to minimise the error in the measurement. Leaves are immersed in chloroform liquid for 20 seconds and took out in order to not to extract chlorophyll. Finally, the beaker was placed at a 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 was obtained via mixing 0.5, 1, and 2 wt% cuticular wax of PS leaves or PM leaves in Se, respectively. At the same time, the Se containing 0.5, 1, or 2 wt% of terpineol served as a contrast to explore the properties of the external surface wax.

2.2.3 | Cuticular wax content analysis

To analyse the primary component of the cuticular wax, gas chromatography-mass spectrometry (Agilent Technologies Inc., America) was adopted. The sample was injected on-column into a constant flow of He of 1.2 mL/min. The gas chromatography oven was initially set 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 minutes. A 5973 N Mass Selective Detector

FIGURE 1 Images of the two kinds of leaves (up: Picea wilsonii Mast; down: Pinussylvestris) [Colour figure can be viewed at wileyonlinelibrary.com]

(EI 70 eV; ionisation source temperature 230°C) was used to identify constituents of the cuticular wax.

2.2.4 | Tribological test

The tribological tests at ambient were conducted at an MFT-R4000 reciprocating friction and wear tester with a ball-on-disk configuration composed of upper ball and lower disk, which was designed by State Key State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). During this study, the balls were made of AISI 52100 steel (hardness 710 Hv) with a diameter of 5 mm. The disks were made of AISI 52100 steel (hardness 610 Hv) and Al2024 aluminium (hardness 170 Hv), respectively, with a diameter of 24 mm and a thickness of 7.9 mm. The samples were polished with different grades of diamond paste to obtain a surface roughness of approximately 0.05 um. The upper ball was driven to be in contact with the lower disk under the applied loads and then slides reciprocally against the lower disk at a stroke of 5 mm and a frequency of 5 Hz for 30 minutes at room temperature. The applied loads for the steel-steel friction pairs were 50, 100, and 125 N independently while the ones for steel-aluminium friction pairs were 20, 30, and 40 N. Before and after each test, all the balls and disks were cleaned ultrasonically in petroleum ether for 10 minutes. Prior to test, approximately 0.5-g lubricant was introduced into the friction region. The friction coefficient (COF) was recorded by a computer which was connected to the friction and wear tester. Repeated tests were performed for three times. As a result, the average values accompanied by an error bar were provided in the results. After friction test, the disks were cleaned ultrasonically in petroleum ether for 10 minutes, and the wear widths of the wear scars were determined using an optical microscopy with a micrometre. The morphologies of the worn surfaces were obtained using an EVO-18 scanning electron microscopy (SEM, Zeiss, Germany). The chemical compositions of the worn surfaces were characterised using a time-of-flight secondary ion mass spectroscopy (TOF-SIMS, Iontof, Germany).

3 | RESULTS

3.1 | The composition of cuticular wax analysis

The content of each component in different leaves has been depicted in Table 1. It can be seen that the most abundant components are alkanes and alcohols while the acids and esters contents in all the waxes are low. Hence, it is 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

Figure 2A depicts the evolution of the coefficients of friction for the testing lubricating oils with addition of different content of additives under the load of 20 N for steel/aluminium contact. It can be seen that under the condition of steel-aluminium friction pair, all the lubricating oils with addition of cuticular wax have low and stable COF, and the values of COF are in the sequence of Se + terpineol> Se + PS > Se + PM. The COF of the cuticular wax decreases first and then increases; however, it is always lower than that of terpineol. When the content of PS or PM in lubricating oil is 1.0%, the COF is the lowest. Figure 2B indicates the severity of attrition for different additives under tested conditions. The wear scar width also presents a trend of decreasing first and then rising whereas the width reaches the minimum value at 1.0%. The values of wear scar width for different cuticular wax are generally smaller than that of terpineol.

Figure 3A depicts the evolution of the coefficient of friction for the tested lubricating oils with addition of different concentrations of additives under the applied load of 100 N for the steel/steel friction pair. The overall situation is slightly similar to the condition of steel/aluminium contact. The values of COF presented by cuticular wax are lower than that of Se in the absence and presence of terpineol; meanwhile, the PM has the lowest level as well. Figure 3B exhibits the wear scar widths of different lubricants. It can be found that the PM always exhibits lower wear scar width than terpineol under the lubrication of Se with addition of different additive concentrations.

TABLE 1 The composition of cuticular

Constituents	PS	PM
Alkanes	49.69%	21.08%
Acids	0.65%	2.11%
Alcohols	11.43%	51.47%
Esters	4.02%	1.35%

3.2.2 | Influences of load

The COF variations which have been tested under various loads are unfolded in Figure 4A. The content value is 2%, and the friction pair is steel-aluminium. It can be seen that Se + PM and Se + PS all exhibit lower COFs than Se + terpineol under different loads. In particular, the COF is reduced by more than 50% under the load of 40 N. As shown in Figure 4B, all the wear scar widths display an upward trend with the increasing load. Under the

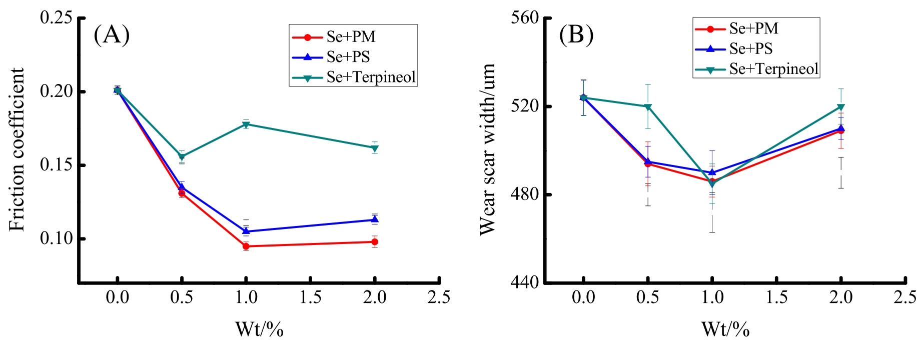

FIGURE 2 A, Average COFs and B, wear widths for the lubricating oil with additive content variation under steel/aluminium contact [Colour figure can be viewed at wileyonlinelibrary.com]

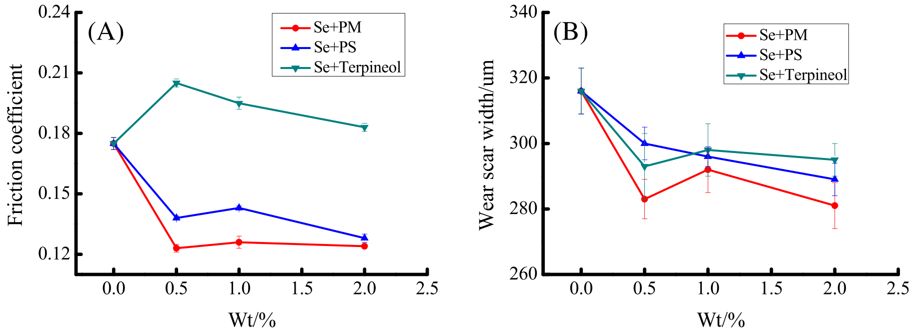

FIGURE 3 A, Average COFs and B, wear widths for the lubricating oil with additive content variation under steel/steel contact [Colour figure can be viewed at wileyonlinelibrary.com]

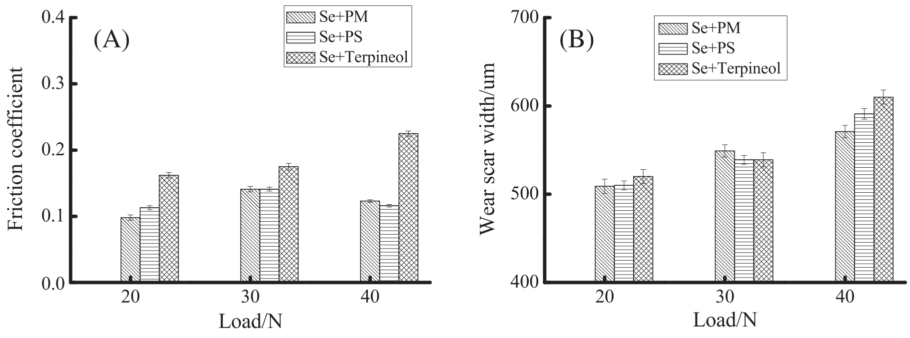

FIGURE 4 A, Average COFs and B, wear widths for the lubricating oil with different loads applied under steel/aluminium contact

loads of 20 and 40 N, the Se with addition of cuticular wax all has lower wear scar widths than Se + terpineol. Under the load of 30 N, Se + PS and Se + terpineol have close wear scar widths. These results indicate that the cuticular wax have some certain anti-wear ability for steel-aluminium friction pairs.

Figure 5, respectively, shows the COF and wear scar widths of different lubricants under various loads for steel-steel friction pair. As shown in Figure 5A, the COF values of the Se in the presence of cuticular wax are obviously lower than that of Se + terpineol under different loads. However, the wear scar widths of the Se + cuticular wax and Se + terpineol are close. These results suggest that cuticular wax exhibits better friction reduction ability under different loads for steel-steel friction pairs.

3.3 | Wear surface analysis

Figure 6 shows the high magnification SEM morphologies of the worn surfaces on the aluminium disks lubricated by different lubricants under 40 N. Figure 6A,B shows that the worn surfaces lubricated by Se + PM and Se + terpineol are smoother than others. There are

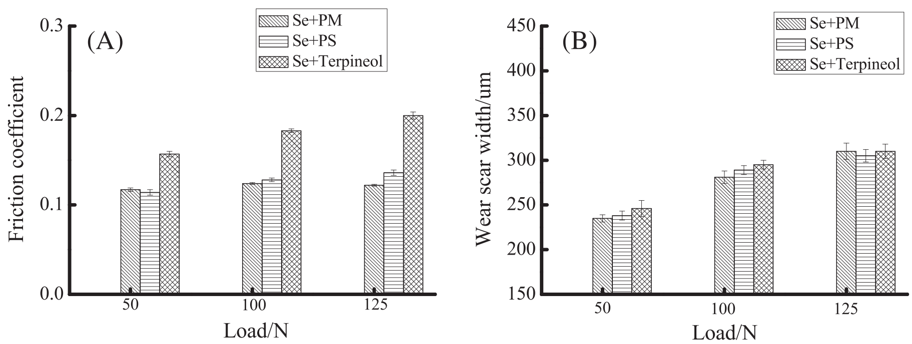

FIGURE 5 A, Average COFs and B, wear widths for the lubricating oil with different loads applied under steel/steel contact

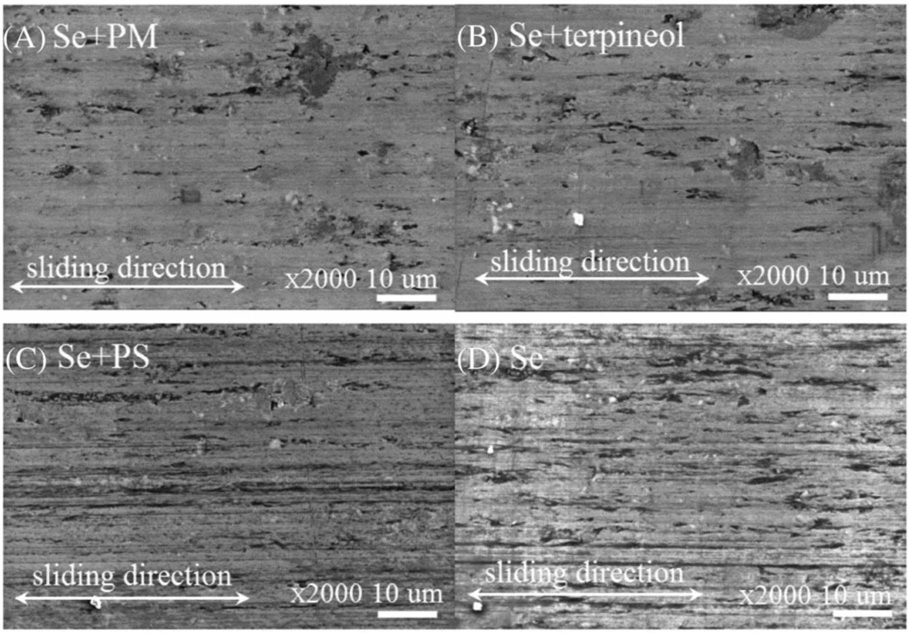

FIGURE 6 SEM images of worn surfaces on the aluminium disks with 40 N load

just few and shallow furrows and small amount of pits. Compared with Figure 6C,D, it can be inferred that PM and terpineol all can improve the anti-wear ability of the base oil. Figure 6C,D shows that the worn surfaces lubricated by Se + PS and Se all acquire large amount of deep and obvious grooves and some corrosion pits, indicating that severe abrasive wear and tribocorrosion taken place during the friction test. Additionally, it also can be seen that some spalling and plastics deformation occurred in the occasion. Stress change is the fundamental cause of pitting corrosion, and the occurrence and expansion of aluminium pitting need acid environment. Pitting corrosion is more likely to occur in the presence of acidic materials under friction. At the same time, drawback of aluminium alloys is their poor resistance to seizure and galling will lead to deep abrasive grooves, severe pitting, and scoring.

Figure 7 shows the high magnification SEM morphologies of the worn surfaces on the steel disks lubricated by different lubricants under 125 N. It can be seen that the worn surfaces lubricated by Se + PM and Se + terpineol acquire some shallow grooves. However, the worn

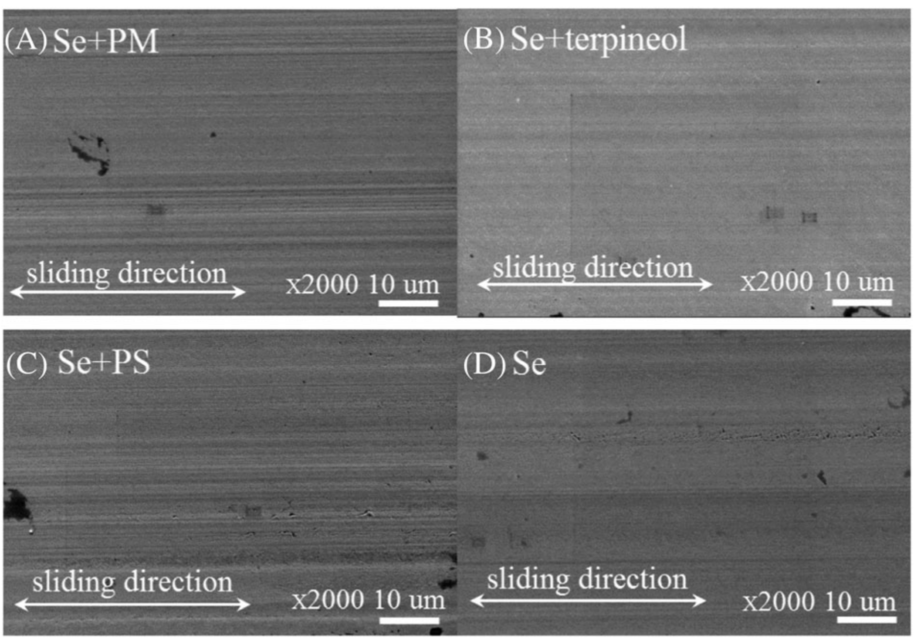

FIGURE 7 SEM images of worn surfaces on the steel disks with 125 N load

surfaces lubricated by Se + PS and Se not only have some grooves but also some micro pits. These results indicate that PM as additive in Se has some certain anti-wear ability during the friction process. In short, based on these two groups of images of the different friction pairs, it can be inferred that PM can form a protective film on the worn surfaces to reduce the direct metal contact to improve the anti-wear ability.

3.4 | TOF-SIMS analysis

Figure 8 gives the TOF-SIMS spectra of the positive and negative ions on the worn surfaces of lower aluminium disk lubricated by different lubricants after friction test. Compared with Figure 8A, Figure 8C,E shows that the intensity of Al^+ on the worn surfaces lubricated by Se + PM or Se + PS is reduced by approximately 25% whereas the intensity of the $C_3H_7^+$ obviously increases, indicating that a protective lubricating film was indeed generated on the worn surface to reduce the exposure of the fresh aluminium for enhanced tribological properties. Figure 8B,D shows that the worn surface lubricated by Se and Se + PM have similar spectra of positive ions. However, being different from Figure 8B,D, more medium-chain and long-chain ions including $C_{14}H_{29}O_8^-$ and $C_{22}H_{43}O_2^-$ appears on the worn surface lubricated by Se + PS. Figure 9 gives the TOF-SIMS positive and negative ions images recorded in the same area of the samples. The brightness shows the amount of the ions on the surfaces, which can give a direct evidence for the amount of the negative and positive ions on the worn surfaces. According to these images, aluminium positive ions are reduced on the surface lubricated with Se + PM and Se + PS as compared with pure Se, and on the top layer of the metal, ions containing C, H, and O increased, which is consistent with the results shown in Figure 8. The TOF-SIMS results show that the enhanced tribological properties of the Se containing leaf-surface wax depended on the protective film generated by leaf-surface wax during the friction process.

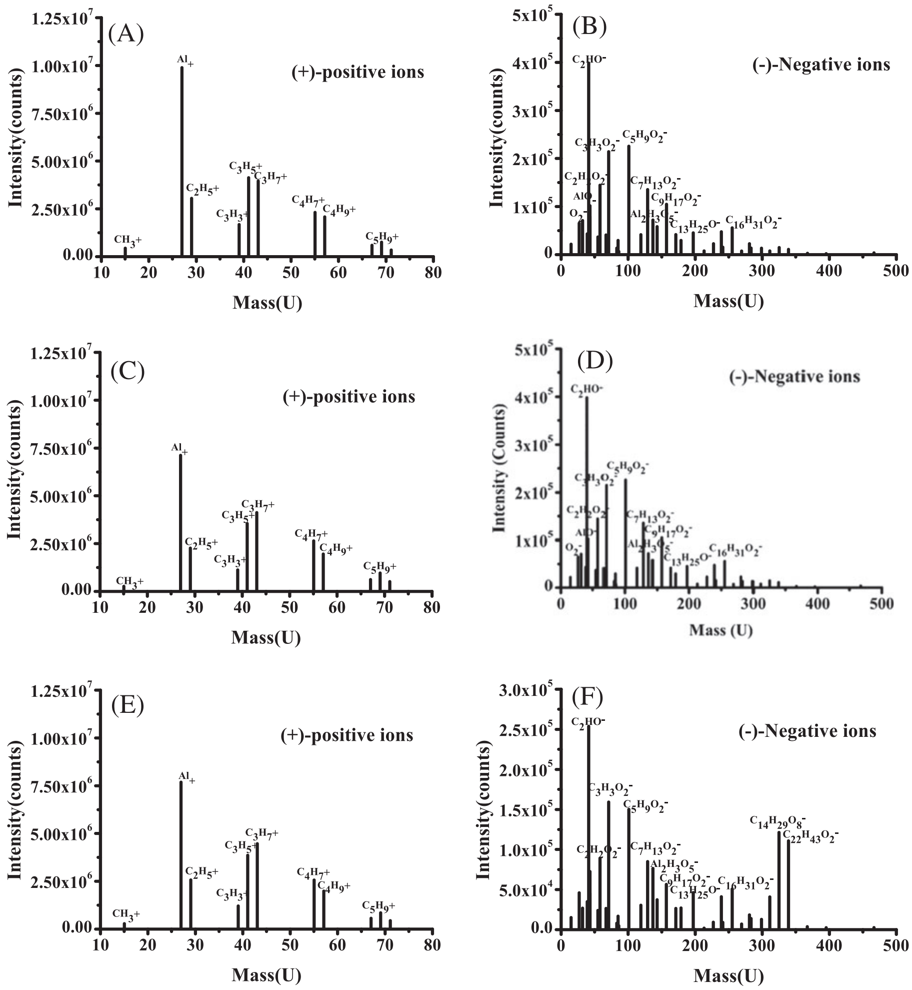

FIGURE 8 Positive and negative ions TOF-SIMS spectra obtained on the surface of aluminium after friction test (A) and (B) SE, (C) and (D) PM; (E) and (F) PS

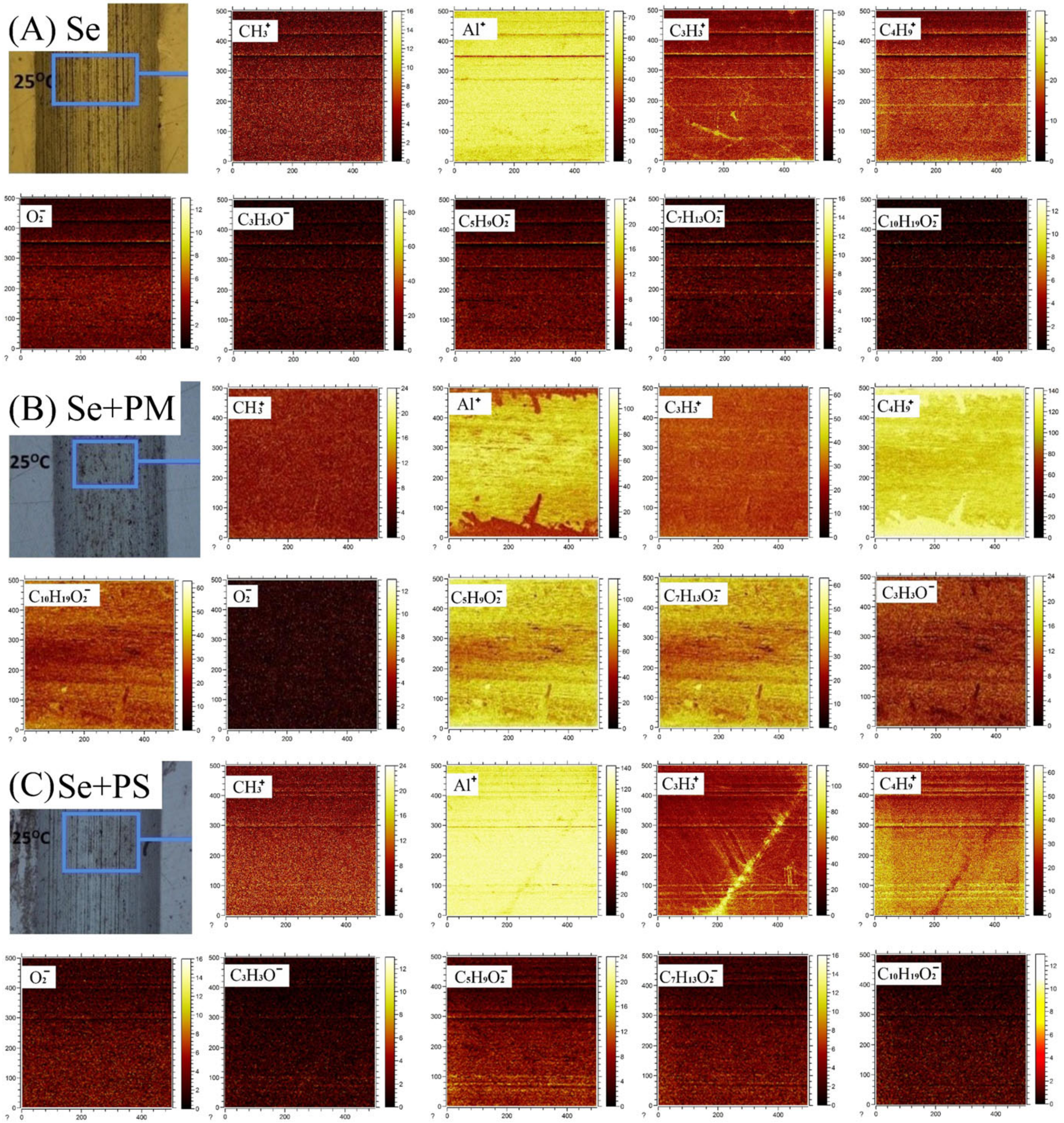

FIGURE 9 TOF-SIMS positive and negative ions images [Colour figure can be viewed at wileyonlinelibrary.com]

4 | DISCUSSION

The tribological tests demonstrate that the leaf-surface wax (PS and PM) have some certain friction reduction and anti-wear abilities for steel/aluminium and steel/steel friction pairs. Based on the SEM and TOF-SIMS analysis, the lubrication can be explained by following aspects. It is well known that the worn surface may carry a positive charge because the low-energy electrons could emit from the worn surface during friction process.[15,25] Meanwhile, under the action of the high temperature and loads, the long-chain alcohols etc. could break into short chains carrying negative charge, which could adsorb on the worn surface and react with the metal surface to form a protective film. This possible lubrication mechanisms could be supported by Figures 8 and 9.

Observing the SEM images shown in Figures 6 and 7, the worn surfaces on the lower aluminium disk are rougher than that on the lower steel disk. In general, higher hardness means better wear resistance.[26] Due to the relatively low hardness of aluminium, abrasive wear and plastics deformation could occur easily on the worn surfaces of aluminium disk, leading to that much grooves and spalling appear on the worn surfaces shown in Figure 6. Meanwhile, due to the exposure and the higher reactivity of the fresh aluminium during the friction process, there are also some corrosion pits appearing on the worn surfaces. However, comparing Figure 6A-B and Figure 6C-D, although fewer shallow grooves and corrosion pits still appear on the worn surfaces lubricated by Se + PM and Se + terpineol, the worn surfaces are improved to some extent, indicating some certain anti-wear ability. Comparing Figure 6A and C, PM exhibits better tribological properties than PS. The reason may be attributed to the different composition of the leaf-surface wax. As shown in Table 1, PS has a large amount of alkanes whereas PM has a large amount of alcohols. Meanwhile, combining Figure 8F, more medium-chain and long-chain ions appears on the worn surface lubricated by Se + PS than others. This may be a reason for the better tribological properties of PM than those of PS. In a word, based on the tribological data, SEM, and TOF-SIMS analysis of the worn surfaces, it suggests that leaf-surface wax as additives in Se could form a protective lubricating film to improve the friction reduction and anti-wear abilities for steel/aluminium and steel/steel friction pairs during the friction process.

5 | CONCLUSION

Two kinds of leaf-surface wax including PM and PS were extracted and evaluated as lubricant additives in Se. The typical chemical composition of the leaf-surface wax was composed of alkanes, esters, and acids etc. Tribological results show these leaf-surface wax as additives in Se not only reduce the friction coefficient, but also improve the wear resistance for the steel-aluminium pairs as well as steel-steel pairs under different loads. The SEM micrographs and TOF-SIMS analysis of the worn surfaces suggest the good tribological properties are attributed to protective lubricating film generated by leaf-surface wax throughout the sliding process. Because of the good tribological properties, leaf-surface wax as a green lubricant additive holds a great promise for a range of applications.

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