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In Situ Formed Ionic Liquids in Polyol Esters as High Performance Lubricants for Steel/Steel Contacts at 300 °C

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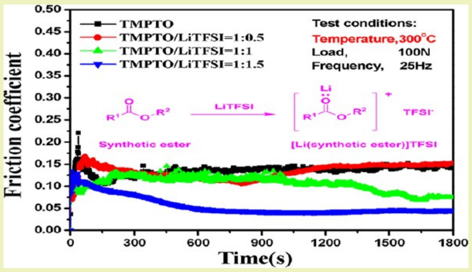
ABSTRACT: In situ formed ionic liquids (ILs) as high temperature lubricants can be obtained by mixing polyol esters (pentaerythritol oleate or trihydroxymethylpropyl trioleate) with lithium bis(trifluoromethylsulfonyl)-imide (LiTFSI) in molar ratios of 1/0.5, 1/1 and 1/1.5. Thermal and rheological analysis indicate that the in situ formed ILs, [Li(polyol ester)]TFSI, with various molar ratios are more resistant to high temperatures and substantially stronger than the polyol ester base oils. Tribological results revealed that these in situ forming ILs with molar ratios of 1/1 and 1/1.5 possessed excellent friction reduction and antiwear performance for steel/steel contact at 300 °C. Moreover, their tribological properties were significantly better than the pure polyol ester base oils and perfluoroalkyl polyether (PFPE, as a reference lubricant) under the same conditions. The results of SEM-EDS show that tribo-films formed on the worn steel discs surface lubricated by [Li(polyol ester)]TFSI. The XPS analytical results further proved the formation of a boundary lubrication films which composed of Fe_2O_3, Fe_3O_4, Fe(OH)O, FeF_2, $FeSO_4$ or $Fe_2(SO_4)_3$ and C−O bonding. This surface-protective film is believed to be responsible for the excellent tribological performances of in situ forming ILs using at elevated temperature.



KEYWORDS: *Biocomponent, Ionic liquids, Polyol esters, Steel/steel contacts*

INTRODUCTION

Rapid development of the gas turbine engine and the quest for greater power require lubricants that function reliably under harsh conditions,[1] such as high temperature and strenuous vibration, and trends indicate that these conditions will continue to grow much more severe, especially in temperature. At the beginning of the 1980s, tentative general requirements for ideal liquid lubricants to operate satisfactorily in future engines were put forward by the U.S. Air Force according to the development and trend of aircraft engines. One of the requirements is that modern engine bulk lubricant temperatures can range between 260 and 427 °C.[2] The usage temperatures have exceeded the limits of ester-based lubricants. To meet the demands of future high performance turbine engine, new high temperature lubricants must be prepared.

Although a number of candidate fluids, including perfluoroalkyl polyether (PFPE), polyphenyl ether and phosphazene, etc. were synthesized and studied with the objective of meeting the high temperature lubricant requirements, these synthetic lubricants possess the deficiency of themselves.[3] For example, traditional lubricating additives do not dissolve in PFPE due to the PFPE's extreme inertness and insolubility in chemicals. Titanium alloys that contain aluminum can catalyze the decomposition of PFPE oils above 136 °C, this deficiency has restricted their use as high temperature lubricant fluids. The extremely poor low temperature operational capability is a main deficiency of the polyphenyl ether lubricants. In addition, the relatively poor lubricity characteristics and high cost of polyphenyl ether, have restricted their applications in which no other lubricating oils would function. The major factor that has limited extensive development of phosphazene lubricants is the high cost relative to commercial lubricants. Thus, it is essential to explore new lubricant fluids to meet the demands of high temperature lubrication.

Previous studies have shown potential for ionic liquids (ILs) as a new generation of synthetic lubricants.[1,4−6] It was found that the tribological performances of ILs are superior to those of traditional lubricants, such as synthetic hydrocarbons, synthetic esters, and synthetic fluorinated ethers.[7] Some ILs also exhibit excellent tribological properties even at 300 °C, which suggests use as high temperature lubricants.[1,8] Unfortunately, the costly and lengthy procedure for preparation of ILs are major problems to put them into industrialization after a dozen years of extensive development. Furthermore, the poor solubility of ILs severely limits their application as most lubricating oil additives.[9,10]

In recent years, Fan and co-workers reported a novel concept for in situ preparing IL additives in synthetic esters and polyethylene glycol.[10−13] This method significantly simplifies the process of producing ILs and lowers the cost. However, much less is known with respect to using the in situ formed ILs as high temperature lubricants, especially for studying their tribological properties at elevated temperature of 300 °C. Furthermore, polyol esters have certain inherent properties

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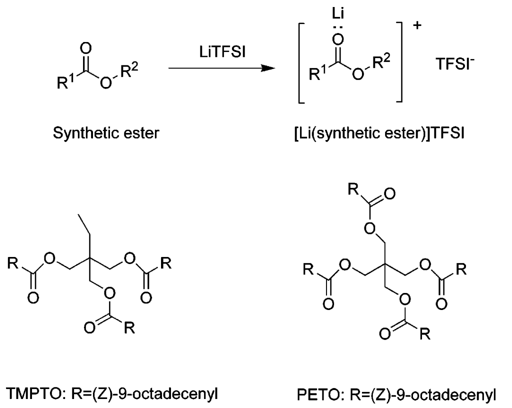
such as good viscosity index, additive solubility, an affinity for metal surfaces, and are more biodegradable than mineral oils. They are commonly used in aviation lubricants, although diesters are used, as well. Market drivers are improved thermal stability and reduced volatility.[14] Trihydroxymethylpropyl trioleate (TMPTO) and pentaerythritol oleate (PETO) are very important biocomponent of polyol ester compositions. In this work, a series of high content of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in TMPTO and PETO to form a homogeneous liquid phase ([Li(polyol ester)]TFSI) were prepared and their tribological performances using as high temperature lubricants for steel/steel contacts were evaluated on an Optimal SRV-IV oscillating friction and wear tester at 300 °C. The morphology and chemical composition of wear scar surface were studied by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) in order to explore the lubrication mechanism of [Li(polyol ester)]TFSI under high temperature, and the chemical composition of the wear scar surfaces were also measured by X-ray photoelectron spectrometry (XPS).

EXPERIMENTAL SECTION

Materials. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was purchased from J&K Chemical. Trihydroxymethylpropyl trioleate (TMPTO) and pentaerythritol oleate (PETO) were synthesized by our laboratory. Fomblin YL VAC 25/6 perfluoroalkyl polyether (PFPE) was obtained from Solvay Solexis. The in situ formed IL lubricants were prepared (Scheme 1) by stirring 10.7, 19 and 26 wt % LiTFSI in PETO and 12.3, 21.8 and 29 wt % LiTFSI in TMPTO at 40−60 °C until it was totally dissolved, respectively. The molar ratios of polyol ester/LiTFSI are 1/0.5, 1/1 and 1/1.5. The kinematic viscosity of these compounds were measured at 40 and 100 °C, and the results are shown in Table 1. Moreover, the results of copper strip corrosion tests indicated that higher fluorine content of the in situ ILs shows no apparent corrosion difference from that with the pure TMPTO and PETO (Table 1).

Scheme 1. Formation of [Li(Synthetic Ester)]TFSI and the Chemical Structures of TMPTO and PETO



Spectroscopic Analysis. ^{1}H NMR and ^{13}C NMR measurements for polyol ester−LiTFSI with various molar ratios were performed on an INOVA-400 M spectrometer and $CDCl_3$ as an external standard. Fourier transformation infrared (FT-IR) spectra were recorded on an IFS120HR FT-IR spectrometer.

Thermal Analysis. Thermogravimetric analysis (TGA) was studied on a STA 449 F3 Jupiter simultaneous TG-DSC instrument. A total of 5 mg of sample was placed in the TGA sample holder. The temperature was programmed to increase from 25 °C to approximately 800 °C at a heat rate of 10 °C/min in air.

Table 1. Physical Properties of Polyol Esters and Polyol Ester−LiTFSI at Molar Ratios of 1/0.5, 1/1 and 1/1.5

samples	kinematic viscosity (mm^2/s) 40 °C	kinematic viscosity (mm^2/s) 100 °C	viscosity index[a]	copper strip test/corrosion grade[b]
TMPTO	48.0	9.50	187	1a
TMPTO/LiTFSI = 1:0.5	176	21.9	149	1a
TMPTO/LiTFSI = 1:1	818	54.5	123	1a
TMPTO/LiTFSI = 1:1.5	5044	187	132	1a
PETO	67.0	12.5	188	1a
PETO/LiTFSI = 1:0.5	230	27.1	151	1a
PETO/LiTFSI = 1:1	1107	68.9	127	1a
PETO/LiTFSI = 1:1.5	5442	188	127	1a
PFPE	68.0	11.3	160	2b

[a] The viscosity index was determined according to the ASTM D2270-93 method. [b] The copper strip corrosion test was performed according to the ASTM D130-83 method (temperature, 120 °C; time, 3 h).

Rheological Analysis. Rheological analysis was carried out on an Anton Paar instrument (model MCR 302) in oscillation mode. The values of storage modulus, G', and loss modulus, G'', as a function of a variety of variables: shear strain, γ, oscillation frequency, ω, and temperature, T were recorded for each fluid. Moduli measurements were performed at fixed oscillation frequency and temperature but variable shear strain in order to establish quickly the universal class (e.g., Newtonian liquids, linearly elastic, nonlinear viscoelastic, gel) to which our ILs belong.

Tribology Test. The Optimol SRV-IV oscillating reciprocating friction and wear test was performed with a ball-on-disk conguration. The upper ball was a ø 10 mm GCr15 bearing steel (AISI-52100) ball, and the lower stationary disc was a ø 24.00 × 7.88 mm GCr15 bearing steel (AISI-52100) flat disc. The friction and wear tests in this work were conducted at frequency of 25 Hz and amplitude of 1 mm. The relative humidity was 50−60%. The wear volume of the lower disc was measured by a MicroXAM 3D noncontact surface mapping profiler. The morphology and chemical composition (elemental distribution) of the worn surfaces were analyzed by JSM-5600LV scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). The chemical composition of the worn surfaces were also measured by a PHI-5702 multifunctional X-ray photoelectron spectrometry (XPS) using Al Kα radiation as the excitation source. The wear scars of the upper steel ball were measured by a JSM-5600LV scanning electron microscopy (SEM) instrument.

RESULTS AND DISCUSSION

Spectroscopic Characterization. To prove the formation of the in situ formed ILs, [Li(polyol ester)]TFSI, the states of the polyol esters and these ILs were explored by ^{1}H NMR and ^{13}C NMR (Figure 1). The partial ^{1}H NMR and ^{13}C NMR spectra of TMPTO, TMPTO−LiTFSI complex system at molar ratios of 1/0.5, 1/1 and 1/1.5 are shown in Figure 1a,b as examples. The peak at 4.01 ppm corresponds to the methylene protons of $CH_3CH_2C(CH_2-)_3$ (trimethylolpropane) backbone, and the signals at 2.28−2.32 ppm are the α-methylene protons of CH_2- adjacent to the carboxyl group (COO−) of oleic acid (Figure 1a). By dissolving LiTFSI into TMPTO, the signals became broad and shift to a lower magnetic field (Figure 1a). This common feature is caused by the coordination of Li^+ and C═O group that the lone pairs of electrons on oxygen atom tend to transfer from O to Li^+ resulting in lack of electrons on C═O carbons. Figure 1b shows the partial ^{13}C NMR spectra of TMPTO, and the peak at 173.56 ppm is due to the **C**═O carbons of oleic acid. Similarly, the peak of **C**═O

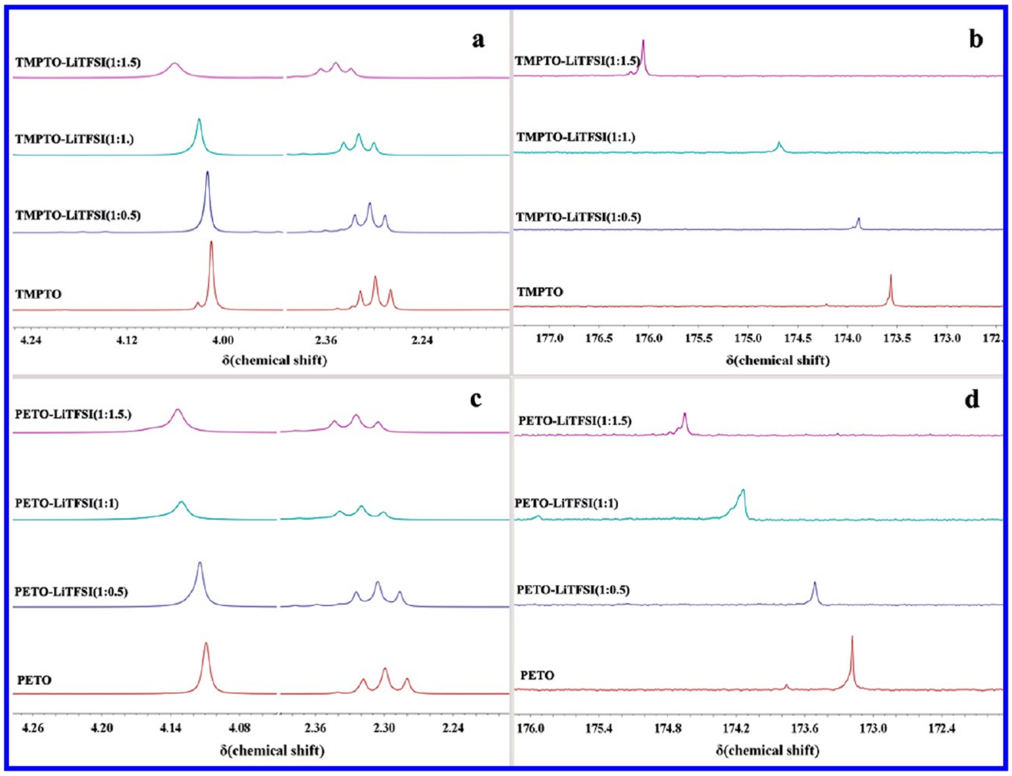


Figure 1. Partial ^{1}H NMR and ^{13}C NMR spectra of poly ester and the in situ formed [Li(polyol ester)]TFSI.

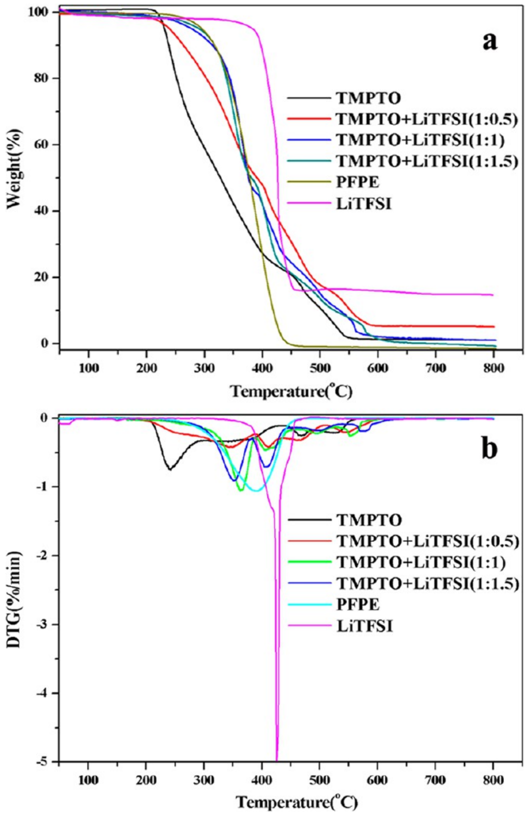


Figure 2. TGA and DTG curves of TMPTO, PFPE, LiTFSI and polyol ester−LiTFSI at molar ratios of 1/0.5, 1/1 and 1/1.5.

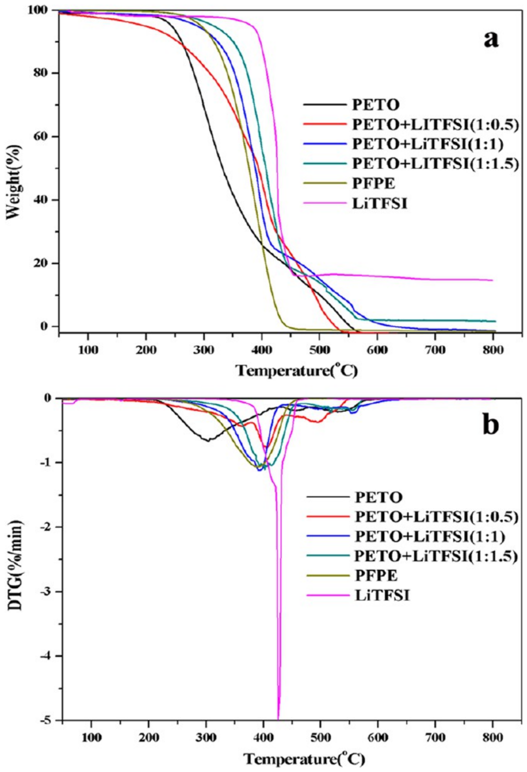


Figure 3. TGA and DTG curves of PETO, PFPE, LiTFSI and polyol ester−LiTFSI at molar ratios of 1/0.5, 1/1 and 1/1.5.

carbons shifts to lower magnetic field with the increase of LiTFSI content. The peak of the C═O carbon shifts from 173.56 ppm to 173.88, 174.69 and 176.04 ppm for the TMPTO−LiTFSI systems with molar ratios of 1:0.5, 1:1 and 1:1.5, respectively. Figure 1c,d shows partial ^{1}H NMR and ^{13}C NMR spectra of PETO, PETO−LiTFSI at different molar ratios. These are in agreement with the results shown in Figure

Table 2. TG Temperature and Evaporation Loss of Polyol Esters and Polyol Ester−LiTFSI at Molar Ratios of 1/0.5, 1/1 and 1/1.5

	TG temperature/°C per weight loss			
samples	T_d (°C)	10%	20%	50%
TMPTO	225	238	251	327
TMPTO/LiTFSI = 1/0.5	240	263	327	390
TMPTO/LiTFSI = 1/1	316	313	343	376
TMPTO/LiTFSI = 1/1.5	324	317	337	380
PETO	247	261	282	332
PETO/LiTFSI = 1/0.5	273	255	310	394
PETO/LiTFSI = 1/1	330	323	353	389
PETO/LiTFSI = 1/1.5	350	350	375	407
PFPE	318	317	340	378
LiTFSI	386	397	408	425

1a,b. Additionally, the FT-IR spectroscopy results of these in situ formed IL lubricants are similar to the result reported by Fan et al. (data not shown).[10] Consequently, both NMR and FT-IR spectra demonstate that the Li^+ coordinate with the O atom of the C═O group in polyol ester and form the [Li(polyol ester)]TFSI.

Thermal Stability. Figures 2 and 3 show the TGA and derivative thermogravimetric (DTG) curves of TMPTO, PETO, PFPE, LiTFSI, TMPTO−LiTFSI and PETO−LiTFSI at different molar ratios. It is clearly seen that the decomposition temperature (T_d) of the in situ formed IL increases with increasing the content of LiTFSI in the complex system (Figures 2a and 3a). For example, the decomposition temperature (T_d) of pure TMPTO is 225 °C, and TMPTO−LiTFSI complex systems at molar ratios of 1/0.5, 1/1 and 1/1.5 are 240, 316 and 324 °C, respectively. PFPE, a good candidate liquid lubricant for use in advanced turbine engines, has a decomposition temperature of 318 °C. The result is comparable to TMPTO−LiTFSI at molar ratios of 1/1 and 1/1.5. In addition, the temperature for 10%, 20% and 50% weight losses of polyol−LiTFSI at various molar ratios are shown in Table 2. The DTG curves show a weight loss per minute with an increase in temperature (Figures 2b and 3b). The temperature at which the highest rate of weight loss for polyol ester−LiTFSI complex system increases with increasing molar ratios of polyol ester/LiTFSI. These results are consistent with the decomposition temperature of polyol ester−LiTFSI complex systems and indicate undoubtedly the enhancement of the thermal stability of TMPTO and PETO.

Rheological Characterization. Oscillatory shear experiments were performed at a steady angular frequency (ω) = 10 rad/s and at shear strains increased from 0.01 to 100. The variation of storage (G') and loss (G'') moduli derived from these experiments are shown in Figure 4a for pure TMPTO and TMPTO−LiTFSI complex at different molar ratios and

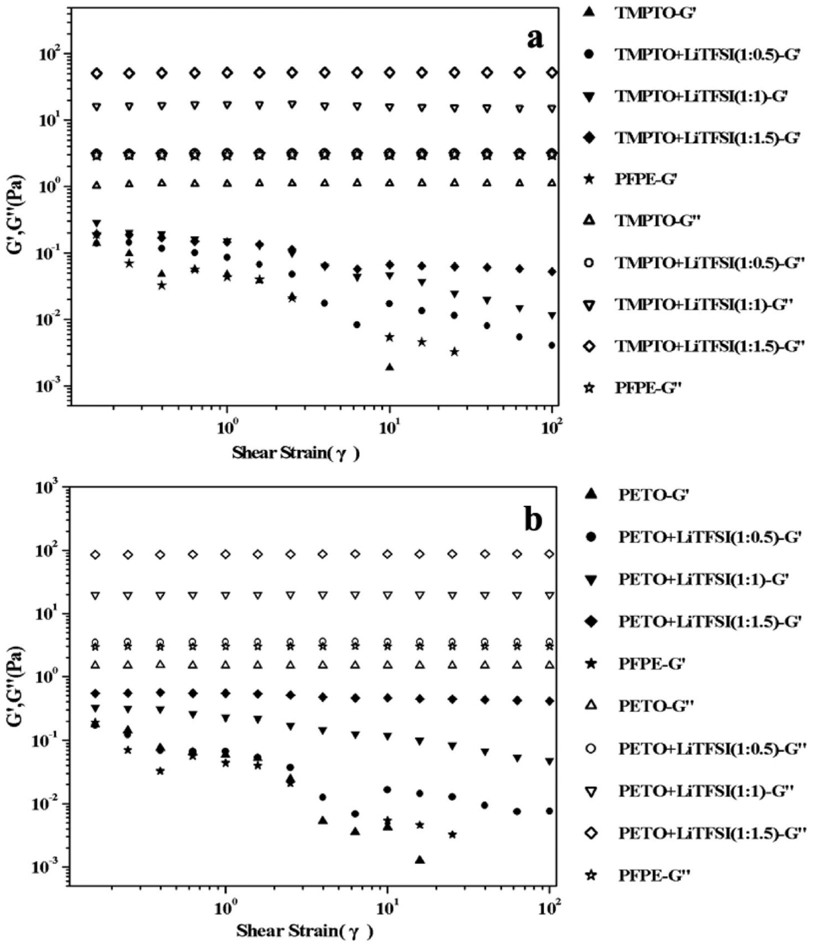


Figure 4. Storage modulus (G') and loss modulus (G'') versus strain (γ) of (a) TMPTO and TMPTO−LiTFSI (molar ratios of 1/0.5, 1/1 and 1/1.5) and (b) PETO and PETO−LiTFSI (molar ratios of 1/0.5, 1/1 and 1/1.5).

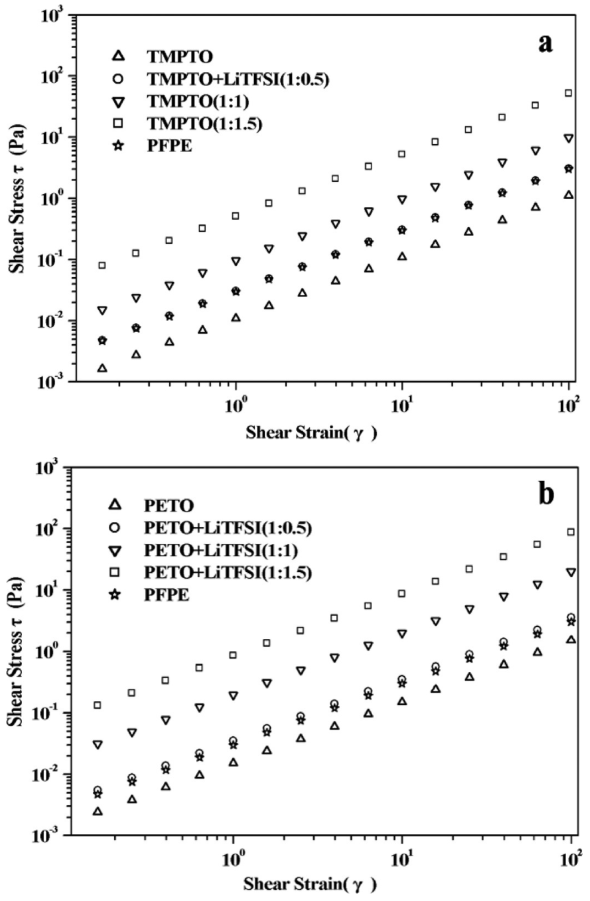


Figure 5. Shear stress (τ) versus strain (γ) of (a) TMPTO and TMPTO−LiTFSI (molar ratios of 1/0.5, 1/1 and 1/1.5) and (b) PETO and PETO−LiTFSI (molar ratios of 1/0.5, 1/1 and 1/1.5).

Figure 4b for pure PETO and PETO−LiTFSI complex with varying LiTFSI content. Meanwhile, PFPE was used for comparison and the date was incorporated in Figure 4. It is apparent from the Figure that G'' is always larger than G' over the entire range of shear strains, which is a typical rheological feature of viscous liquid behavior.[15,16] Additionally, at all shear strains, G' and G'' for TMPTO−LiTFSI and PETO−LiTFSI at different molar ratios are substantially higher than for pure TMPTO and PETO. The result is also similar to the observation of the shear stress, which manifests a visible change of slope at shear strains (Figure 5). In comparison with those of the pure TMPTO and PETO, the shear stress of polyol ester−LiTFSI complex systems are increased to some extent with the increment of the shear strains. Together, these results mean that TMPTO−LiTFSI and PETO−LiTFSI complex systems are both substantially stronger and much thicker (more viscous) than pure TMPTO and PETO.[17]

Friction and Wear Behavior. In recent years, many studies have used SRV tests as the main method to evaluate the tribological performance of lubricating oils,[1,10,11,18−20] because it is a convenient and economical means for aiding researchers in their measurement and analysis needs. In this study, the tribological performance of TMPTO−LiTFSI and PETO−LiTFSI at different molar ratios were benchmarked against that of TMPTO and PETO synthetic ester oils, and PFPE was used for comparison. The friction coefficient of pure LiTFSI was also measured at the same conditions. The SRV test conditions were as follows: load 100 N, frequency 25 Hz, test duration time 30 min and temperature 300 °C. The friction curves and wear volume of sliding discs are presented in Figure 6.

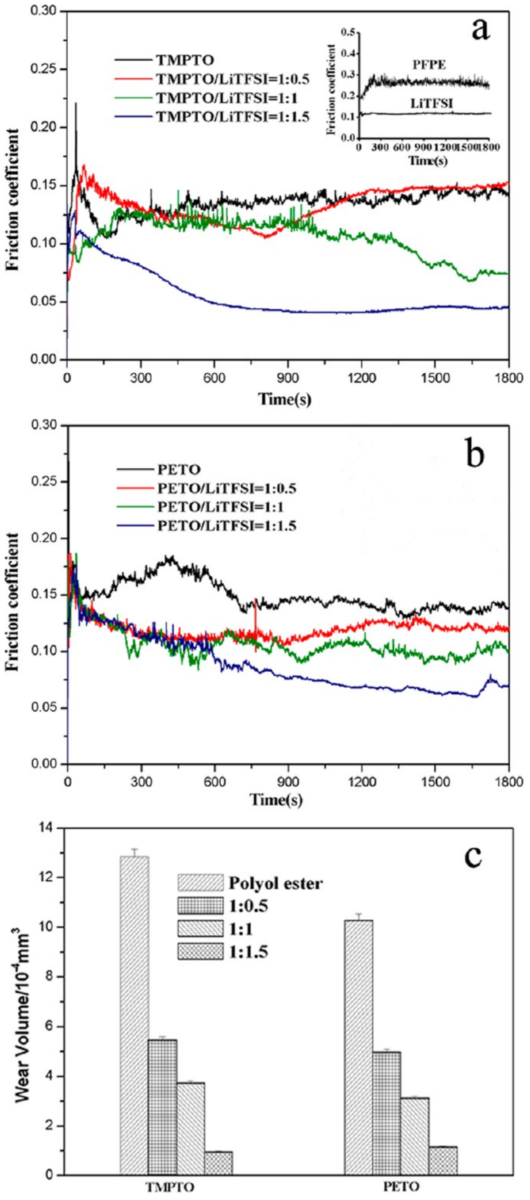


Figure 6. (a,b) Friction coefficient and (c) wear volumes of the discs lubricated by TMPTO, PETO and polyol ester-LiTFSI with molar ratios of 1/0.5, 1/1 and 1/1.5 at 300 °C. The figure inserted in Figure 5a shows the friction curve of the disc lubricated by PFPE and pure LiTFSI under the same conditions (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz).

The friction coefficient for PFPE oil started around 0.2, but transitioned to above 0.25 after 3 min later and then fluctuated between 0.25 and 0.3 (inset in Figure 6a), which are obviously larger compared with those TMPTO and PETO base oils. In fact, both TMPTO and PETO produced relatively small friction coefficient below 0.18 throughout the entire test. In contrast, LiTFSI was added into polyol esters to form TMPTO−LiTFSI and PETO−LiTFSI complex system with a molar ratio of 1/0.5. Although little change were observed in friction behavior, the wear volume was decreased by ∼50% for the sliding disc under lubrication of polyol ester−LiTFSI complex systems. As the molar ratio of TMPTO/LiTFSI or PETO/LiTFSI was 1/1, the friction coefficient of the complex

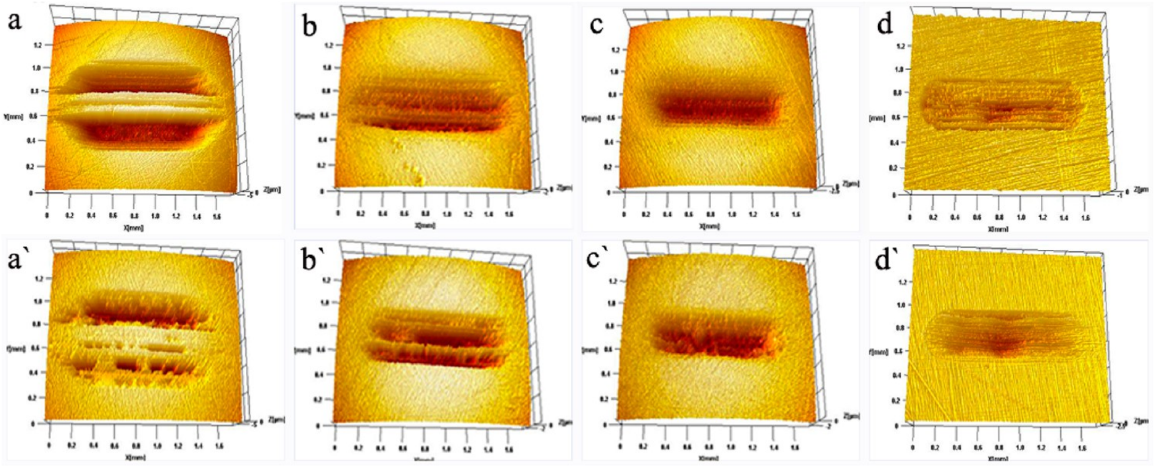


Figure 7. 3D optical microscopic images of the wear scar surfaces lubricated by TMPTO (a), PETO (a′), TMPTO−LiTFSI (b−d) and PETO−LiTFSI (b′−d′) with molar ratios of 1/0.5, 1/1 and 1/1.5 at 300 °C (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz).

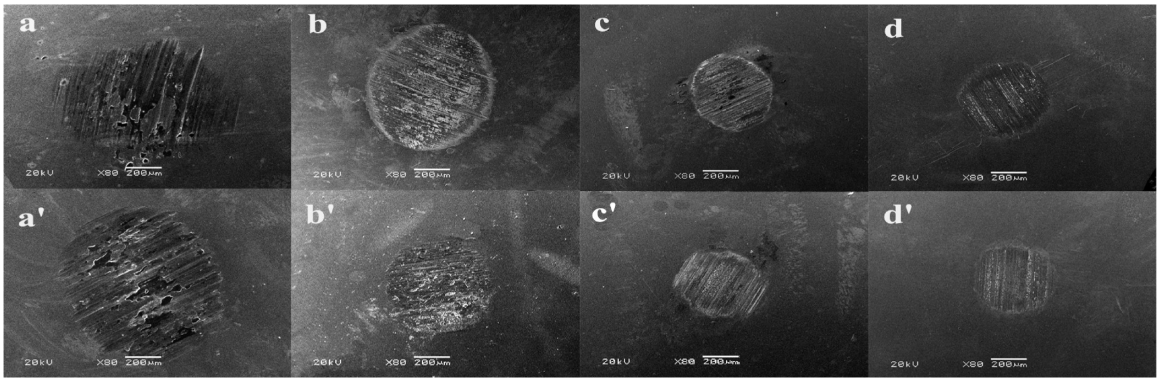


Figure 8. SEM morphologies of wear scars on the upper steel ball lubricated by TMPTO, TMPTO−LiTFSI at molar ratios of 1:0.5, 1:1 and 1/1.5 (a,b); PETO, PETO−LiTFSI at molar ratios of 1:0.5, 1:1 and 1/1.5 (a′−d′).

system changed dramatically and wear volume of the system reduced significantly. In marked contrast, when the molar ratio of TMPTO/LiTFSI or PETO/LiTFSI was 1/1.5, the complex system has very low and relatively stable friction coefficient. Meanwhile, TMPTO−LiTFSI and PETO−LiTFSI complex system also can improve the AW properties of TMPTO and PETO base oils by 3.9 times and 2.7 times as compared with the complex systems with molar ratio of 1/1, respectively. This indicates that the complex system with molar ratio of 1/1.5 is the optimum proportion to provide excellent friction reduction and antiwear property at high temperature. Moreover, take into account the solubility of LiTFSI in TMPTO and PETO,[10] we will no longer consider the complex systems with higher concentrations of LiTFSI.

Figure 7 shows the three-dimensional optical microscopic images of wear surfaces lubricated by polyol esters and polyol ester−LiTFSI complex systems. Wear scars lubricated with pure base oils clearly shows wide and deep grooves, indicating serious wear (Figure 7a,a′). Figures 7b−d and 7b′−d′ show worn surfaces lubricated by TMPTO−LiTFSI and PETO−LiTFSI with different molar ratios, respectively. These images suggest that the wear scenario becomes relatively narrow and shallow with the increase of LiTFSI content in polyol ester, especially for the molar ratio of 1/1.5 (Figure 7d,d′). Figure 8 displays the SEM morphologies of wear scars on the upper steel ball lubricated by polyol esters and polyol ester−LiTFSI with molar ratio of 1:0.5, 1:1 and 1/1.5. These are consistent with the wear volume results in Figure 6.

Polyol ester−LiTFSI at molar ratios of 1/1 and 1/1.5 were used as candidates for tribological tests with a temperature ramp test from 300 °C up to 420 °C stepped by 20 °C intervals. The test duration for each temperature was 5 min. At 300 °C, the friction trace of both TMPTO and PETO base oils show breakdown occurring and eventually failure after a few minutes of efficient lubrication occurring (Figure 9a,b). TMPTO−LiTFSI complex at molar ratio of 1/1 shows a relatively stable friction curve around 0.12 at 300−360 °C (Figure 9a). When the temperature was increased to 380 °C, signs of the lubrication failure occurs within a few minutes. TMPTO−LiTFSI complex system at molar ratio of 1/1.5 is the only lubricant that displays stable and low friction coefficient (below 0.1) up to a temperature of 400 °C (Figure 9a). The date from PETO−LiTFSI at molar ratios of 1/1 and 1/1.5 are very similar to relatively stable friction values at 300−360 °C, then the former presents friction curve fluctuating between 0.1 and 0.25 at 380−420 °C, whereas the latter still shows stability friction curve until the lubricant tested failed immediately at 400 °C (Figure 9b). Figure 9c demonstrates that the AW properties of polyol esters improved with increasing LiTFSI content under the testing conditions. These results indicate that TMPTO−LiTFSI and PETO−LiTFSI at 1/1.5 molar ratio have higher temperature lubricant property than the complex systems at 1/1 molar ratio, which can be explained that the

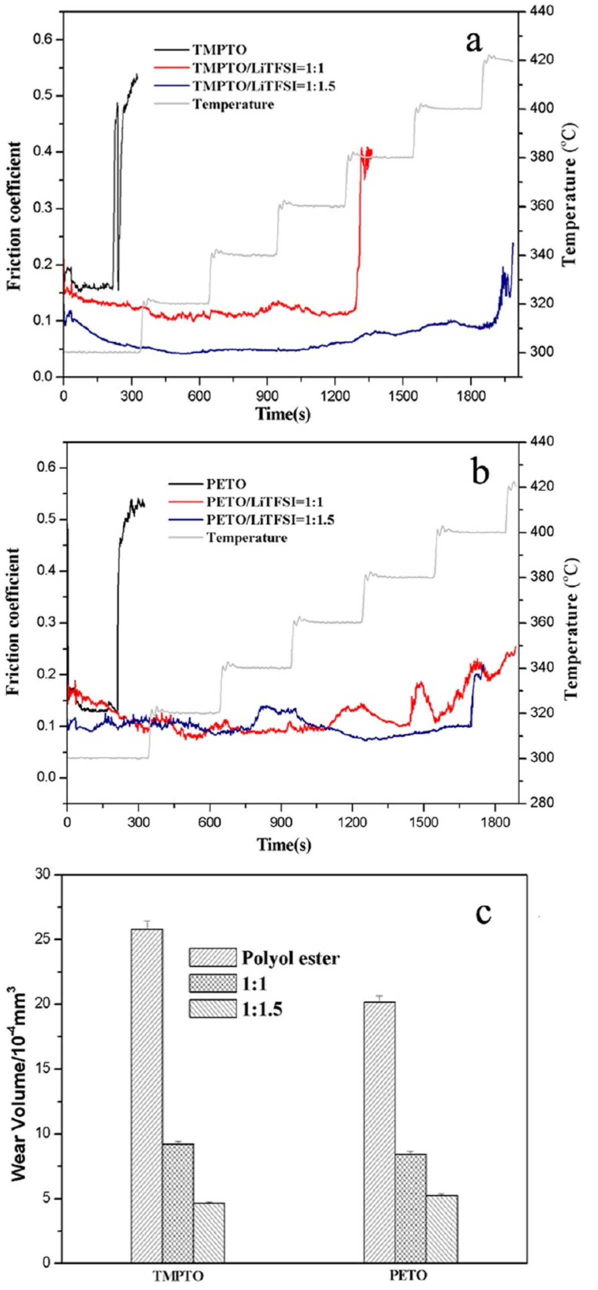


Figure 9. (a, b) Friction coefficient and (c) wear volumes of the discs lubricated by TMPTO, PETO and polyol−LiTFSI with molar ratios of 1/1 and 1/1.5 under a load of 100 N (temperature, 300−420 °C; stroke, 1 mm; frequency, 25 Hz).

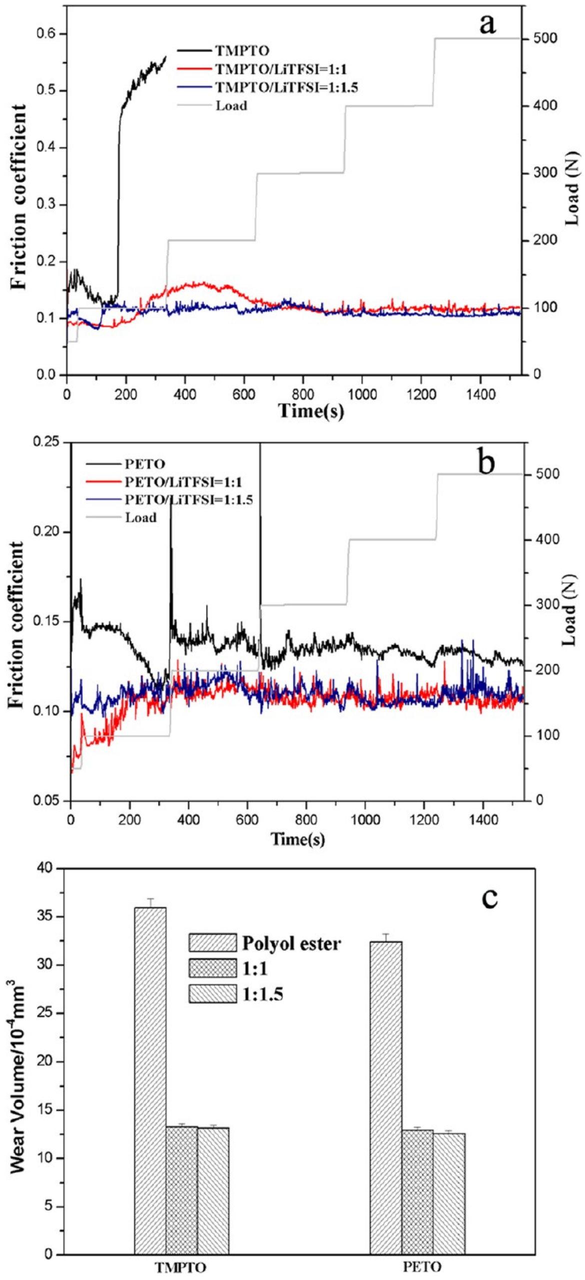


Figure 10. (a, b) Friction coefficient and (c) wear volumes of the discs lubricated by TMPTO, PETO and polyol−LiTFSI with molar ratios of 1/1 and 1/1.5 at 300 °C (load, 100−500 N; stroke, 1 mm; frequency, 25 Hz).

existence of higher fluorine content favorably boosts the high temperature lubricant property.[8]

The friction reduction and AW properties of polyol ester−LiTFSI at molar ratios of 1/1 and 1/1.5 were further tested by varying applied loads at 300 °C. The loads were increased from 100 to 500 N stepped by 100 N intervals, with a 5 min test duration for each load. From the test, it can be seen that the TMPTO−LiTFSI complex at the two molar ratios both present lower and stable friction coefficients (Figure 10a). Meanwhile, all the polyol ester−LiTFSI complex systems can improve the AW properties by about 2.5 times compared with the pure base oil (Figure 10c). This result further proves the friction-reducing and AW proprieties of TMPTO and PETO with high content of LiTFSI under the harsh conditions.

Surface Analysis. After friction tests, the worn surfaces of steel discs lubricated by the fluids at 100 N and 300 °C were analyzed using SEM-EDS techniques (Figures 11 and 12). The SEM micrograph of steel disc lubricated by TMPTO base oil clearly shows wide and deep grooves, indicating severe wear (Figure 11a). The micrograph of steel disc lubricated by PETO is very similar to TMPTO (data not shown). Figure 11b,c shows worn surfaces of steel discs lubricated with TMPTO−LiTFSI (Figure 11b) and PETO−LiTFSI (Figure 11c) complex at molar ratio of 1/1.5. These spectra indicate that tribo-films formed on the worn surfaces lubricated by TMPTO−LiTFSI and PETO−LiTFSI complex systems.[21,22] A corresponding EDS analysis shows changes in surface composition (elemental distribution) (Figure 12). Figure 12b,c clearly demonstrates the

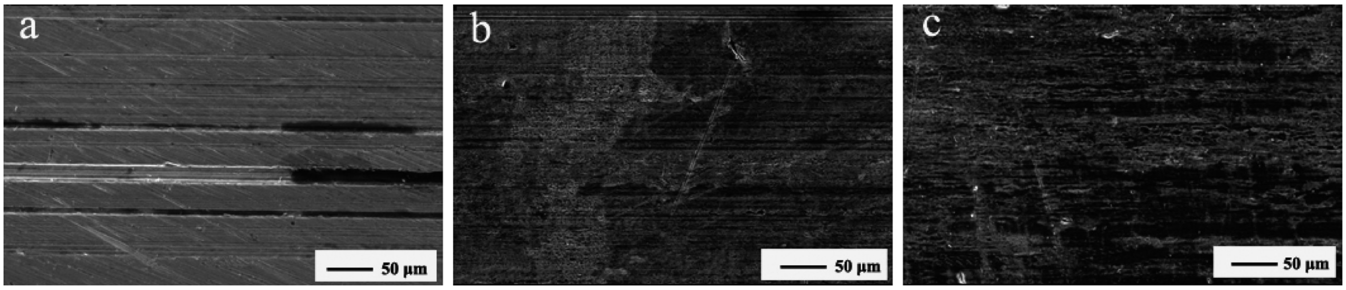


Figure 11. SEM micrograph of worn surfaces lubricated by (a)TMPTO, (b) TMPTO−LiTFSI and (c) PETO−LiTFSI with molar ratios of 1/1.5 at 300 °C (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz).

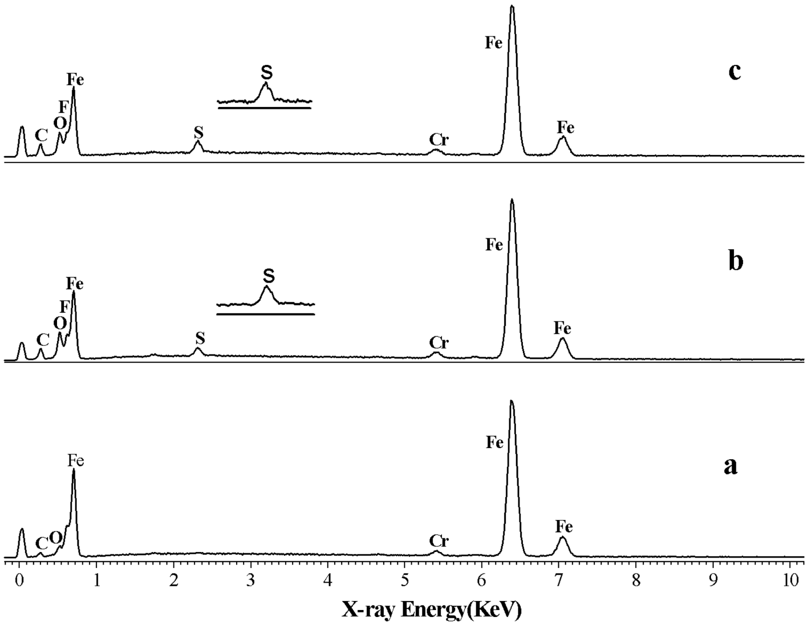


Figure 12. EDS element mapping of tribofilms formed on worn surfaces lubricated by (a) TMPTO, (b) TMPTO−LiTFSI and (c) PETO−LiTFSI with molar ratios of 1/1.5.

presence of sulfur and fluorine on the tribo-film as a result of interactions between polyol ester−LiTFSI complex system and metal surface.[22] No nitrogen was detected on the wear scars lubricated either by TMPTO−LiTFSI or PETO−LiTFSI complex system, because the EDS test sensitivity was low for light elements.[21]

To explore further the lubrication mechanism of these in situ formed ILs at high temperature, the XPS spectra of worn surfaces lubricated by TMPTO−LiTFSI and PETO−LiTFSI at 1:1.5 molar ratio are provided in Figure 13. It can be seen that the figure shows XPS peaks of Fe 2p at approximately 711.5 and 725.1 eV, which corresponds to Fe(OH)O and Fe_3O_4.[18,23] The peaks of O 1s appear at the binding energies of 531.0, 531.7, 532.2 and 533.3 eV, which are respectively identifiable as Fe_2O_3, Fe_3O_4, Fe(OH)O, $FeSO_4$ or $Fe_2(SO_4)_3$ and C−O bonding.[23,24] Figure 13 displays that the XPS spectra of F 1s appear at 685.2 eV, which may be ascribed to FeF_2.[18,23] The S 2p peaks of the worn surface lubricated by TMPTO−LiTFSI or PETO−LiTFSI complex system appear at around 168.9 eV, which can be assign to $FeSO_4$, $Fe_2(SO_4)_3$, or organic sulfides.[23] The above XPS analysis reveals that a stable protection film has been formed on the rubbed surface lubricated by the in situ formed ILs. The protection film composed of Fe_2O_3, Fe_3O_4, Fe(OH)O, $FeSO_4$ or $Fe_2(SO_4)_3$, FeF_2 and C−O bonding, which contributes to the excellent friction-reducing and AW performance of in situ formed ILs at 300 °C.

CONCLUSIONS

A series of in situ forming ionic liquids with different molar ratios of TMPTO or PETO to LiTFSI were prepared. Thermal and rheological measurements revealed that high content of LiTFSI in TMPTO and PETO were benefit to enhancing the thermal stability and mechanical properties of the two polyol esters. The tribological properties of [Li(TMPTO or PETO)]-TFSI have been studied as high performance lubricants for steel/steel contacts at 300 °C. The friction and wear test results indicate that polyol ester−LiTFSI with molar ratios of 1/1 and 1/1.5 have excellent friction reduction and antiwear behaviors. This may be attributed to their high thermal stability, and the capability to form effective boundary lubrication films. SEM-EDS analysis indicated that a boundary tribo-film formed on the worn surface lubricated by TMPTO−LiTFSI or PETO−LiTFSI complex. The film was formed on the worn surface, leading to good friction reduction and antiwear performance at high temperature. XPS analysis indicated that the effective lubrication of [Li(polyol ester)]TFSI for steel/steel contacts is attributed to the formation of a boundary lubrication film composed of Fe_2O_3, Fe_3O_4, Fe(OH)O, $FeSO_4$ or $Fe_2(SO_4)_3$, FeF_2 and C−O bonding.

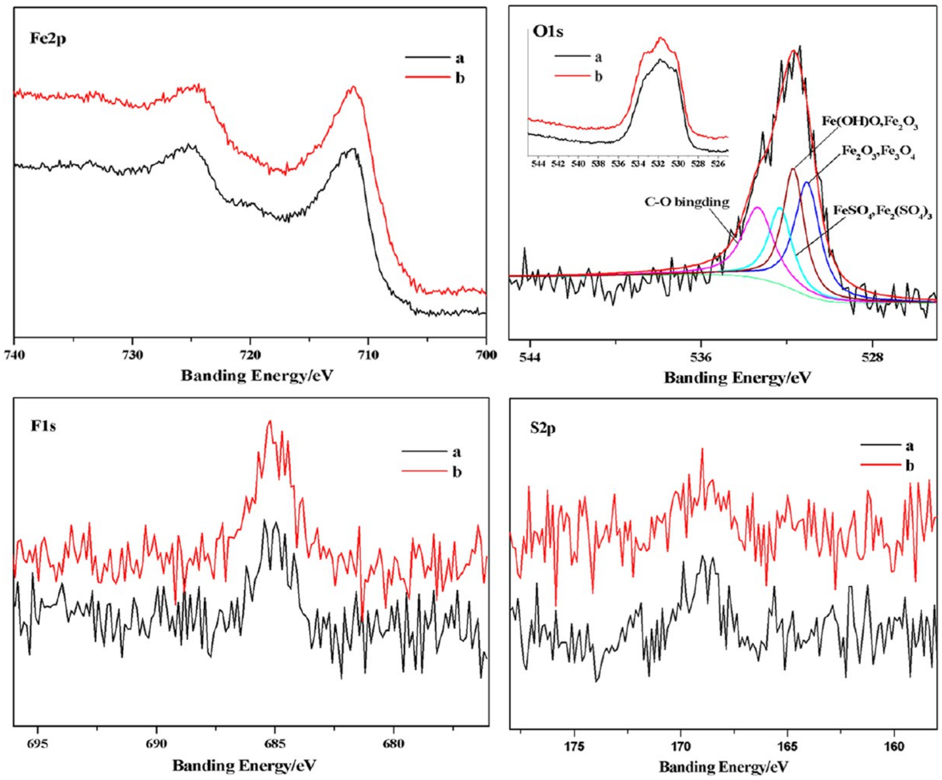


Figure 13. XPS spectra of Fe 2p, O 1s, S 2p and F 1s of the worn surfaces lubricated by (a) TMPTO−LiTFSI with molar ratios of 1/1.5, (b) PETO−LiTFSI with molar ratios of 1/1.5 at 300 °C (SRV load = 100 N; frequency = 25 Hz; stroke = 1 mm; duration = 30 min).

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Notes

The authors declare no competing financial interest.

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