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ORIGINAL PAPER

Preparation of High-Temperature Lubricants by Blending Castor Oil with Lithium Bis(trifluoromethylsulfonyl)imide

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Abstract The public awareness in environmental issues has been constantly growing. Lubricants are applied in many diverse areas; therefore, their environmental acceptability has become increasingly important. In this paper, a kind of eco-friendly high-temperature lubricant was prepared by mixing castor oil with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in molar ratios of 1:0.5, 1:1, and 1:1.5. Thermal and rheological analysis indicates that the in situ formed ILs, [Li(castor oil)]TFSI, with various molar ratios, are more resistant to high temperatures and substantially stronger than the pure castor oil. Tribological test results shown that the ILs have excellent friction reduction and antiwear properties for lubrication of steel/steel contacts at 200 °C. Moreover, the tribological performances of these lubricants were also better than those of epoxidized soybean oil fluid, which is an environment-friendly lubricant and has high oxidative stability. XPS analytical results indicated that a boundary lubrication film composed of Fe_2O_3, Fe_3O_4, FeOOH, $FeSO_4$ or $Fe_2(SO_4)_3$, FeF_2, FeF_3, and C–O bonding was formed on the worn steel surface, and the film is believed to be responsible for the excellent tribological properties of [Li(castor oil)]TFSI using at elevated temperature.

Keywords In situ formed ionic liquids (ILs) · Castor oil · High-temperature lubricants · Friction reduction and antiwear

1 Introduction

At one time, all lubricants used by humankind were entirely environmentally friendly and biodegradable. Natural lubricants such as water, vegetable oils, and animal fats were used to allow higher quality work to be done more efficiently. However, during the late 1800 s, the development of the petrochemical industry put aside the application of natural lubricants for reasons including its stability and economics [1–3]. Ten years ago, with the growing awareness of environment protection and rapidly depletion of crude petroleum-based resources, industry and its customers have again paid attention to natural lubricants [4–6]. Vegetable oils are the potential candidates for eco-friendly lubricants [4]. They generally have many advantages over mineral oils, including lower volatility, better inherent lubricity, higher viscosity index, higher bulk modulus, better fire resistance, and better solvency [2]. Castor oil (CO) is a non-edible and relatively inexpensive plant oil obtained from the seed of Ricinus communis. The oil is a viscous, pale yellow, nonvolatile and nondrying oil with a bland taste. CO exhibits more effective lubricity than other vegetable oils make it suitable for using as the base oil of biodegradable lubricants (such as aircraft engine, gear, and greases), which have drawn considerable interest in recent times [4, 7–11]. Additionally, castor oil, a natural triglyceride, has high content of ricinoleic acid (C18:1-OH) and low content of linoleic acid (C18:2) and linolenic acid (C18:3), which make CO appear to be more stable oxidatively than other vegetable oils [12]. So CO

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might be used as a potential base stock for environmentally friendly lubricant at high temperature.

With rapid development in aircrafts, turbines, automobiles, trucks, farm equipment, railroad equipment, industrial machinery, and so forth, the demand for lubricants to operate at high load, high speed and high-temperature conditions is increasing [9, 10]. Therefore, it is increasingly significant that the lubricants can provide adequate lubrication at elevated temperatures, that is, 149–232 °C or higher [13–15]. Although various high-performance base fluids such as polyalpha-olefins (PAO), synthetic esters, polyalkylene glycol (PAG), and epoxidized soybean oil (ESBO) [16–18] were developed to meet the demand of high-temperature lubricants, little has been done to explore CO in high-temperature lubrication, despite much effort in the area of CO for the earliest piston engine application [7]. Moreover, China is the third producer of castor seed in the world (behind India and Brazil), with the capacity to produce 20 tons of castor seed a year, so it might be significant to modify the structure of CO and use it as high-temperature lubricant.

We all know that the major component of CO is triacylglycerides (TAGs), so the ester groups give ample routes for modification. In recent years, Fan et al. put forward a novel concept called in situ preparation of ionic liquids (ILs) as lubricant additives in synthetic esters, polyethylene glycol and multiply-alkylated cyclopentanes [19–22]. The easy preparation, extremely good solubility and excellent tribological properties of the in situ formed ILs make them great advantages as compared with conventional ILs that can hardly be used as lubricant additives in synthetic esters due to their low solubility [23–26]. Wu et al. presented in situ formed ILs in polyol esters as high-performance lubricants [15]. They claimed that the Li^+ of Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) could coordinate with the O atom of C=O group in polyol ester and form the ILs, [Li(polyol ester)]TFSI, which possessed excellent friction reduction and antiwear (AW) performance for steel/steel contact at 300 °C. Considering the results mentioned above, we attempted at preparation of high-temperature lubricants by blending castor oil with LiTFSI for steel/steel contact at elevated temperature. The tribological behavior of this type of lubricant was also compared with epoxidized soybean oil (ESBO) fluids, which is an environment-friendly lubricant and has high oxidative stability [18].

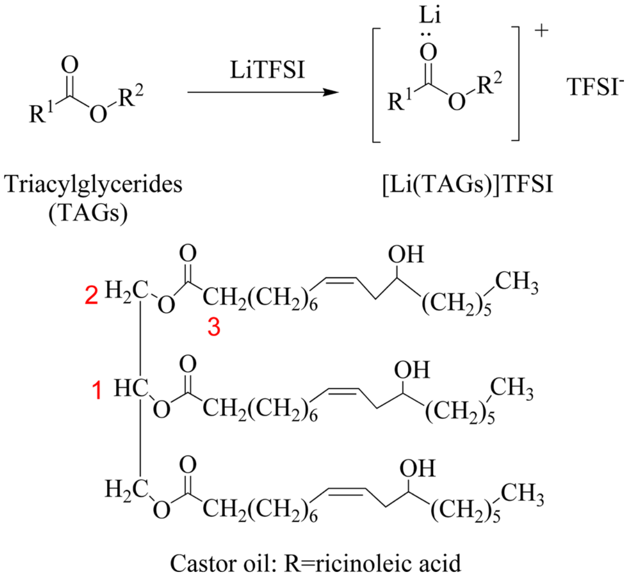
2 Experimental Section

2.1 Materials

Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and epoxidized soybean oil (ESBO) were purchased from J&K Chemical. Castor oil (CO) was supplied by Xilong Chemical Co., Ltd. Scheme 1 shows the proposed in situ formation of [Li(TAGs)]TFSI and the chemical structures of CO. The IL lubricants were prepared by mixing CO with LiTFSI in molar ratios of 1:0.5, 1:1 and 1:1.5 and stirring at 25–60 °C until it was totally dissolved, respectively. The kinematic viscosity of these lubricants was measured at 40 and 100 °C, and the results are shown in Table 1. In addition, the in situ ILs with higher fluorine content will not change the corrosion grade of pure CO according to the copper strip (Table 1).

2.2 Characterization

^1H NMR and ^{13}C NMR measurements for CO-LiTFSI with different molar ratios were performed on an INOVA-400M spectrometer and $CDCl_3$ as an external standard. Fourier transformation infrared (FTIR) spectra were recorded on an IFS120HR FTIR spectrometer. Thermogravimetric analysis (TGA) was studied on a STA 449 F3 Jupiter simultaneous TG-DSC instrument. The temperature was programmed to increase from 25 °C to approximately 800 °C at a heat rate of 10 °C min^{-1} in air. The antioxidant performance of the lubricants was assessed by pressurized differential scanning calorimetry (PDSC), which was performed using NETZSCH DSC 204 HP instrument (Bavarian, Germany). PDSC experiments were carried out in temperature-programmed mode. The oxygen flow rate was 40 mL min^{-1}, and the pressure of high-purity nitrogen is 3.5 MPa. The initial oxidative temperature (IOT) could be obtained through temperature-programmed experiment. Rheological analysis was carried out on an Anton Paar



Scheme 1 Formation of [Li(TAGs)]TFSI and the chemical structures of castor oil

Table 1 Physical properties of castor oil (CO), ESBO, and CO-LiTFSI at molar ratios of 1:0.5, 1:1, and 1:1.5

Samples	Kinematic viscosity (mm^2/s)		Viscosity index[a]	Copper strip test/corrosion grade[b]
	40 °C	100 °C		
Castor oil	241.5	18.24	81	1a
CO/LiTFSI = 1:0.5	930.5	46.7	93	1a
CO/LiTFSI = 1:1	3156.5	108.3	100	1a
CO/LiTFSI = 1:1.5	7455.8	197.6	111	1a
ESBO	211.2	26.1	157	1a

[a] The viscosity index was determined according to ASTM D2270-93 method

[b] The copper strip corrosion test was performed according to ASTM D130 83 method (temperature, 120 °C; time, 3 h)

instrument (model MCR 302) in oscillation mode. The measurements of storage modulus (G') and loss modulus (G'') 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.

The friction and wear tests were carried out on an Optimol SRV-IV oscillating reciprocating friction and wear test with a ball-on-disk configuration. The contact between the frictional pair was achieved by pressing the upper running ball (10 mm in diameter, AISI 52100 steel, hardness of ~58–60 HRC) against the lower stationary disk (Ø 24 mm × 7.9 mm, AISI 52100 steel, hardness of ~59–61 HRC) which was driven to reciprocate at a given frequency and displacement. The base oil or in situ formed ILs was added dropwise to the lower disk with amount of 0.1–0.2 g (ASTM Method D-5707-98). The wear volume of the lower disk was measured by a MicroXAM 3D noncontact surface mapping profiler. The morphology of the worn surfaces was analyzed by JSM-5600LV scanning electron microscopy (SEM). The chemical composition of the worn surfaces was also measured by a PHI-5702 multifunctional X-ray photoelectron spectrometry (XPS) using Al Kα radiation as the excitation source. The binding energy of contaminated carbon (C1s = 284.8 eV) was used as the reference. Three repetitive measurements were performed for each disk.

3 Results and Discussion

3.1 Spectroscopic Characterization

Characterization of castor oil and the in situ formed ILs, [Li(castor oil)]TFSI were carried out by ^{1}H NMR and ^{13}C NMR. The partial ^{1}H NMR and ^{13}C NMR spectrums of CO and CO-LiTFSI complex systems in molar ratios of 1:0.5, 1:1 and 1:1.5 are shown in Fig. 1. The chemical shifts appearing at 4.12–4.32 ppm are associated with the methylene/methine protons of CH_2CHCH_2-(triglyceride) backbone, and the signals at 2.29–2.34 ppm are the α-methylene protons of CH_2– adjacent to the carboxyl group (COO–) of oleic acid (Scheme 1, Fig. 1). By dissolving LiTFSI into CO, the signals became broad and shift to lower magnetic field. The broadening of signal is due to the increase in the viscosity of CO-LiTFSI complex system as increasing the concentration of LiTFSI [27], and the signals

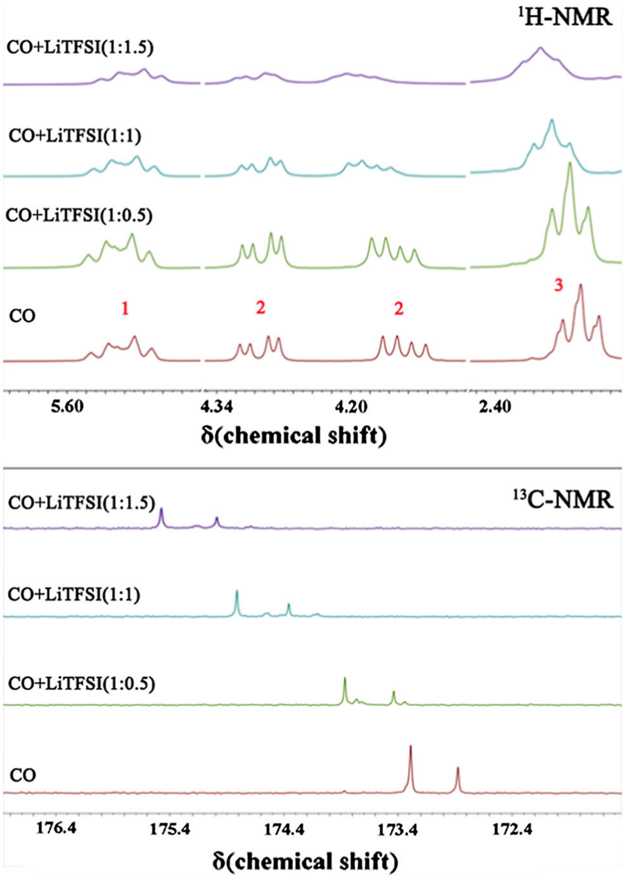


Fig. 1 Partial ^{1}H NMR and ^{13}C NMR spectra of castor oil (CO) and the in situ formed [Li(castor oil)]TFSI with different molar ratios

shift is caused by the coordination of Li^+ cation and C=O group that the lone pairs of electrons on oxygen atom tend to transfer from O to Li^+ cation resulting in lack of electrons on C=O carbons. Figure 1 also shows the partial ^{13}C NMR spectra of CO, and the peak at 172.87–173.29 ppm is due to the C=O carbons of triglyceride [28]. It can be seen that the peaks of C=O carbons shift significantly to lower magnetic field with the increase in LiTFSI content, which change from 172.87–173.29 to 173.43–173.87, 174.35–174.81 and 174.99–175.47 ppm for the CO-LiTFSI systems with molar ratios of 1:0.5, 1:1, and 1:1.5, respectively. Although the peaks shift of C=O carbons is caused by dissolving LiTFSI, the free C=O groups and the C=O groups bound to the Li^+ cation in the [Li(castor oil)]TFSI solution cannot be distinguished by ^{13}C NMR, which can be explained by the fact that the exchange rate of a free C=O group and a C=O group coordination with a Li^+ cation in the [Li(castor oil)]TFSI solution is sufficiently fast. Similar behavior has also been observed and demonstrated by Yoshida et al. [27]. Furthermore, the FTIR spectroscopy shows that the C=O stretching band of CO is broadened and shifts to lower frequency with increasing LiTFSI concentration, which is in agreement with the result reported by Fan et al. (data not shown) [19]. Consequently, both NMR and FTIR spectrums demonstrate that the Li^+ coordinates with the O atom of the C=O group in castor oil and forms the ILs, [Li(castor oil)]TFSI.

3.2 Thermal Stability

Thermogravimetric analysis (TGA) results of CO, LiTFSI, ESBO and CO-LiTFSI complex systems in different molar ratios are shown in Fig. 2 and Table 2. Although the decomposition temperature (T_d) of in situ formed ILs decreases with increasing the content of LiTFSI in CO, the temperature for 5, 10, and 50 wt% weight loss of these lubricants is increasing. Specifically, the temperature for 50 wt% weight loss of CO increases dramatically from 361 to 413 °C for 50 wt% CO-LiTFSI complex system in molar ration of 1:1.5, which is also higher than the temperature for 50 wt% weight loss of ESBO (Table 2). In order to further confirm the enhancement of the thermal stability of CO, Fig. 3 presents the initial oxidative temperature (IOT) results obtained from PDSC programmed temperature experiments for pure CO, ESBO, LiTFSI and LO-LiTFSI complex systems in different molar ratios. Figure 3a shows that CO has one broad exothermic peak at 194 °C. After the addition of LiTFSI, the exothermic peaks shift to lower temperature from 194 °C in CO to ~179 °C in CO-LiTFSI complex systems and some new peaks appear at 425, 415 and 403 °C for the in situ formed ILs with molar ratios of 1:0.5, 1:1, and 1:1.5, respectively. The new peaks are not the exothermic peak for pure LiTFSI (which has an exothermic peak at 348 °C) and may be associated with the ILs that CO/LiTFSI with different molar ratios. Simultaneously, with increasing content of LiTFSI in CO, the areas of the exothermic peaks at ~179 °C significantly decrease, corresponding to the areas at higher temperature increasing (Fig. 3b). For instance, the CO-LiTFSI complex system with molar ratio of 1:1.5 exhibits a sharp exothermic peak at 403 °C and a tiny peak at ~179 °C. The results indicated the composition of the in situ formed ILs in CO could increase with the increasing LiTFSI content, and the addition of LiTFSI could prominently improve the oxidation stability of pure CO.

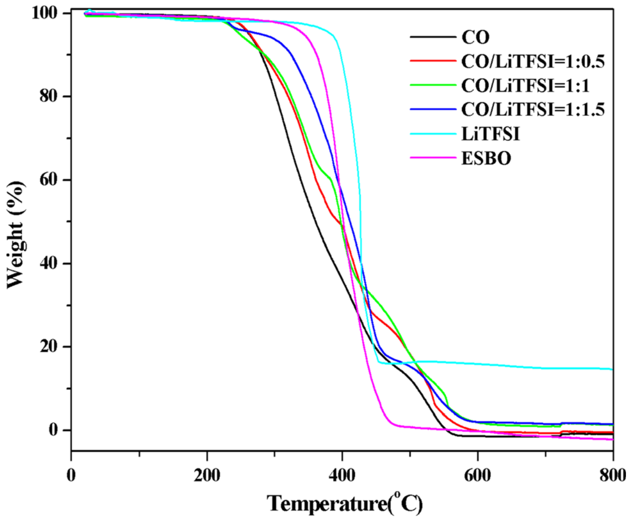


Fig. 2 TGA thermograms of castor oil (CO), LiTFSI, ESBO, and CO-LiTFSI in molar ratios of 1:0.5, 1:1, and 1:1.5

Table 2 TG temperature of CO and CO-LiTFSI complex systems at molar ratios of 1/0.5, 1/1, and 1/1.5

Samples	TG temperature/°C per weight loss			
	T_d (°C)	10%	20%	50%
Castor oil	254	280	302	361
CO/LiTFSI = 1/0.5	246	284	320	394
CO/LiTFSI = 1/1	232	285	325	397
CO/LiTFSI = 1/1.5	228	325	354	413
ESBO	348	362	378	401
LiTFSI	386	397	408	425

3.3 Physical Characterization

The kinematic viscosity and viscosity index of CO, ESBO and CO-LiTFSI complex systems with various molar ratios are shown in Table 1. The viscosity of CO increases

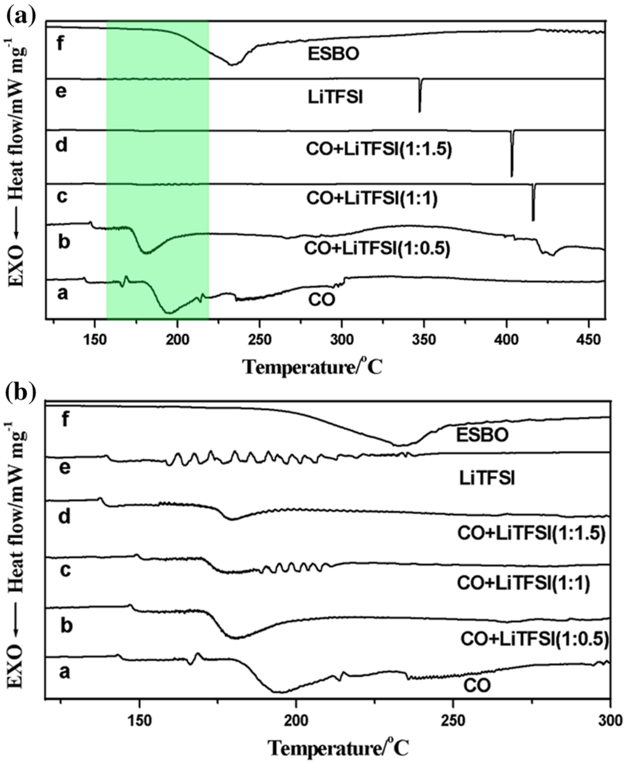


Fig. 3 **a** Programmed temperature PDSC results of CO, LiTFSI, ESBO, and LO-LiTFSI complex systems at various concentrations, and **b** the enlarged images for 100–300 °C positions

significantly with the addition of LiTFSI at both 40 and 100 °C, and the increase in viscosity index indicates the enhancement of the viscosity–temperature characteristics of the base oil. Further characterization of the different lubricants was carried out by means of rheological analysis. Oscillatory shear experiments were performed at a steady angular frequency (ω) = 10 rad s^{-1} and at shear strains increased from 0.01 to 100. The variation of storage (G') and loss (G'') moduli of CO, and CO-LiTFSI complex systems in different molar ratios are depicted in Fig. 4a. It can be seen that G'' is always larger than G' over the entire range of shear strains, which is a typical rheological feature of viscous liquid behavior [29, 30]. Moreover, G' and G'' for CO-LiTFSI in various molar ratios are much higher than for pure CO as the shear strains increase from 0.01 to 100. Figure 4b also shows the observation of the shear stress, which manifests a visible change of slope at shear strains. In comparison with pure CO, the shear stress of CO-LiTFSI complex systems is increased dramatically with the increment of the shear strains. Consequently, these results indicated that CO-LiTFSI complex systems are both substantially stronger and much thicker (more viscous) than pure CO [31], which are consistent with the kinematic viscosity result.

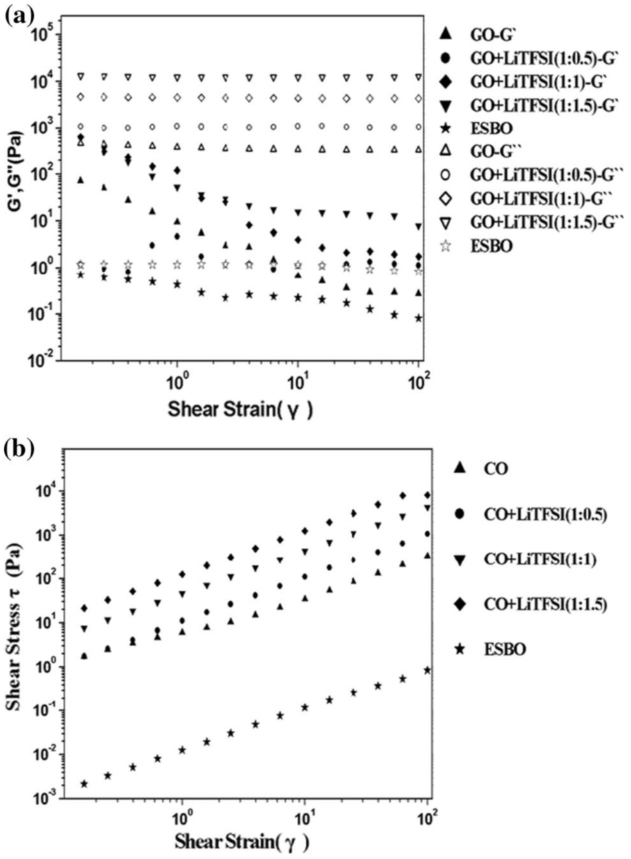


Fig. 4 **a** Storage modulus (G') and loss modulus (G'') versus strain (γ) and **b** shear stress (τ) versus strain (γ) of CO, ESBO, and CO-LiTFSI complex systems in molar ratios of 1:0.5, 1:1, and 1:1.5, respectively

3.4 Tribological Properties

The tribological performances of CO and CO-LiTFSI complex systems in various molar ratios at 200 °C were first investigated, and ESBO was used for comparison. Figure 5 shows the evolution of friction coefficient with the time at a constant load of 100 N and the frequency of 25 Hz for all of the lubricants and the wear volume of the disks after the tests. It is clearly seen that CO and ESBO produced relatively large friction coefficient between 0.18 and 0.20 throughout the entire test (Fig. 5a). In contrast, the friction coefficient of CO-LiTFSI complex system in molar ratio of 1:0.5 increased from about 0.119 to about 0.145 at the initial sliding stage, followed by a decrease to about 0.11 at 150–630 s, afterward stabilized at the value of about 0.108–0.11. As the molar ratio of CO/LiTFSI was 1:1 and 1:1.5, both of them experienced running-in time with smaller friction coefficients and shorter duration than the CO-LiTFSI complex system in molar ratio of 1:0.5 and then exhibited similar friction coefficient with the value between 0.100 and 0.108. Meanwhile, CO-LiTFSI complex system in molar ratios of 1:0.5, 1:1 and 1:1.5 can improve

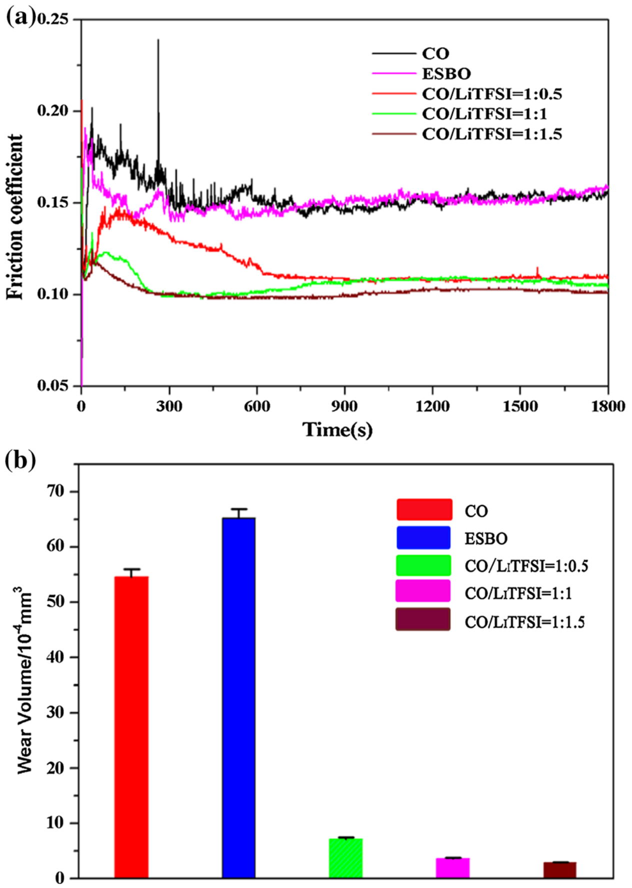


Fig. 5 **a** Friction coefficient and **b** wear volumes of the disks lubricated by CO, ESBO, and CO-LiTFSI with molar ratios of 1:0.5, 1:1, and 1:1.5 at 200 °C (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz)

the AW properties of CO by 7.6, 15, and 19 times, respectively (Fig. 5b). The result indicates that the complex system with molar ratio of 1:1 and 1:1.5 has excellent friction reduction and AW property at 200 °C and can be used as a potential candidate for eco-friendly high-temperature lubricant. Besides, taking into account the similar tribological performances of CO-LiTFSI complex system in molar ratio of 1:1 and 1:1.5, we will no longer consider the complex systems with higher concentrations of LiTFSI.

The friction reduction and AW properties of these lubricants were further tested by varying temperature. The temperatures were increased from 25 to 300 °C, with 5-min test duration for each temperature. As shown in Fig. 6a, CO-LiTFSI complex system could not significantly improve the friction coefficient of CO as the temperature below 100 °C, which is consistent with the result reported by Fan et al. [19]. When the molar ratio of CO/LiTFSI was 1:0.5, the friction coefficient decreased to a comparatively low level with temperature between 100 and 200 °C, then the friction coefficient increased with the increment of temperature from 200 to 300 °C. In marked contrast, it is seen that the CO-LiTFSI complex systems in molar ratio of 1:1 and 1:1.5 behaved similarly, and they had a much lower friction coefficient with the increase in temperature from 100 to 300 °C. Figure 6b displays that the wear volume of the steel disk increased in the order of: CO/LiTFSI (1:1.5) < CO/LiTFSI (1:1) < CO/LiTFSI (1:0.5) < CO < ESBO. These results indicated that the tribological property of CO-LiTFSI complex systems in molar ratio of 1:1 and 1:1.5 is much better than pure CO and ESBO when the temperature increased from 100 to 300 °C, and they also behaved better than CO-LiTFSI complex system in molar ratio of 1:0.5 at temperature of 200–300 °C. This may be due to the high thermal stability of ILs with high content of LiTFSI, and the effective boundary films formed on the worn surface of steel/steel contacts [32, 33]. Moreover, the friction reduction and AW property of CO-LiTFSI complex systems in molar ratio of 1:1 and 1:1.5 are quite similar to each other. These are consistent with the results shown in Fig. 5.

Figure 7 displays a load ramp test from 100 up to 500 N stepped by 100 N intervals for CO, ESBO, and CO-LiTFSI complex systems at 200 °C. The test duration for each load was 5 min. It is evident that CO and ESBO had similar

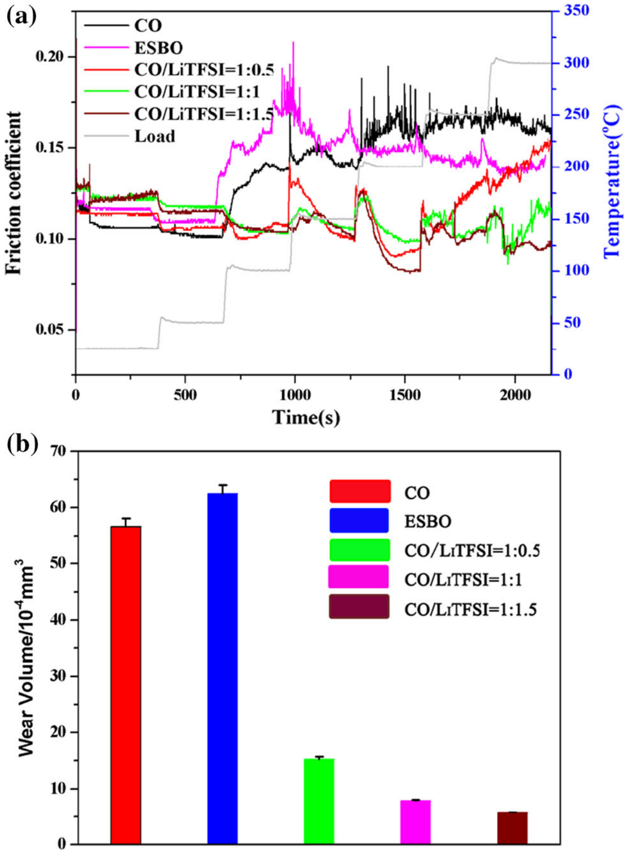


Fig. 6 **a** Friction coefficient and **b** wear volumes of the disks lubricated by CO, ESBO, and CO-LiTFSI with molar ratios of 1:0.5, 1:1, and 1:1.5 under a load of 100 N (temperature, 25–300 °C; stroke, 1 mm; frequency, 25 Hz)

friction coefficient with the value between 0.14 and 0.18 (Fig. 7a), and the AW property of CO was even better than ESBO under the harsh conditions (Fig. 7b). After the addition of LiTFSI in CO, the CO-LiTFSI complex system in molar ratio of 1:0.5 presented lower and relatively stable friction coefficient between 100 and 400 N and then the friction coefficient fluctuated with much high value (>0.25) when the load increased to 500 N, so the test had to be stopped after a few min. When the molar ratio of CO/LiTFSI was 1:1 and 1:1.5, both of them could dramatically improve the friction reduction and AW property of CO on the load ramp test from 100 to 500 N at elevated temperature. This result indicated that the ILs with higher content of LiTFSI exhibited much higher load-carrying capacity than pure CO.

3.5 Surface Analysis

Figure 8 gives the morphologies of worn steel surfaces lubricated by CO, ESBO, and CO-LiTFSI complex systems after the constant load tests at 100 N and a temperature of 200 °C. It can be seen that the worn surfaces of the steels lubricated by CO (Fig. 8a, a′) and ESBO (Fig. 8b, b′) show much wider wear scar, and severe scuffing occurred in this case, indicating severe wear. However, the width of the wear scar obviously becomes smaller in size and the friction scratches also become more shallow for the steel lubricated by CO-LiTFSI complex systems in molar ratio of 1:0.5 (Fig. 8c, c′), 1:1 (Fig. 8d, d′) and 1:1.5 (Fig. 8e, e′), respectively, which shows their excellent AW properties. The difference of wear surfaces shown in Fig. 8c, c′, d, d′ and e, e′ is that the wear scar in Fig. 8c, c′ is relatively deeper than in Fig. 8d, d′ and e, e′. This is consistent with previously measured wear volume in Fig. 5.

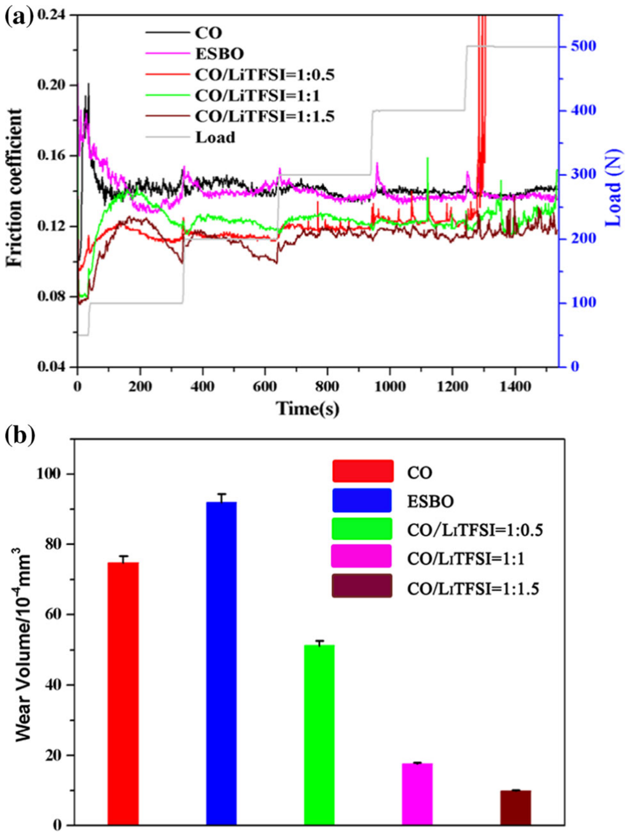


Fig. 7 **a** Friction coefficient and **b** wear volumes of the disks lubricated by CO, ESBO, and CO-LiTFSI with molar ratios of 1:0.5, 1:1, and 1:1.5 at 200 °C (Load, 100–500 N; stroke, 1 mm; frequency, 25 Hz)

Finally, in order to explore the friction reduction and AW mechanism of LiTFSI in CO, Fig. 9 presents the XPS spectra of worn surfaces lubricated by pure CO (a) and CO-LiTFSI complex system in molar ratio of 1:1.5 (b). It is seen that the peaks of Fe 2p are similar to each other (Fig. 9A), appearing at ~711.0 and 724.5 eV, which corresponds to FeOOH and Fe_3O_4 [34, 35]. Almost no difference is observed in XPS spectra of O 1 s for worn steel surface lubricated by the two lubricants (Fig. 9B), and the O 1 s signal for the worn steel surfaces lubricated with [Li(castor oil)]TFSI can be deconvoluted into five peaks at the binding energy of 530.1, 531.7, 532.0, and 533.3 eV, respectively (inset in Fig. 9B), which is identifiable as Fe_2O_3, Fe_3O_4, FeOOH, $FeSO_4$ or $Fe_2(SO_4)_3$ and the C–O binding [34, 35]. The $FeSO_4$ or $Fe_2(SO_4)_3$ component on the worn steel disks surfaces was further confirmed by XPS spectra of S 2p. As shown in Fig. 9C, no characteristic peak was detected on the worn surface lubricated by pure CO, while an obvious peak appears at 168.6 eV for worn surface lubricated by the ILs, and it may be ascribed to $FeSO_4$ or $Fe_2(SO_4)_3$ [35, 36]. Similarly, the F 1 s peak of the worn surface lubricated with the ILs appears at 685.1 eV (Fig. 9D), which can be assigned to the formation of FeF_2 and FeF_3 [35, 37]. XPS analysis revealed that complicated tribochemical reactions occurred during the friction process [19, 20, 38]. Active elements S and F of the ILs reacted with substrate irons, generating Fe_2O_3, Fe_3O_4, FeOOH, $FeSO_4$ or $Fe_2(SO_4)_3$, FeF_2 or FeF_3 and compounds containing the C-O, which acted as the protective film to reduce friction of fresh metal and to alleviate wear. Additionally, during friction of sliding pairs, polarity-induced physical adsorption films of CO-LiTFSI complex system on the surfaces also formed [19, 20]. Thus, both the physical adsorption layers and tribochemical reaction films benefit the friction reduction and antiwear.

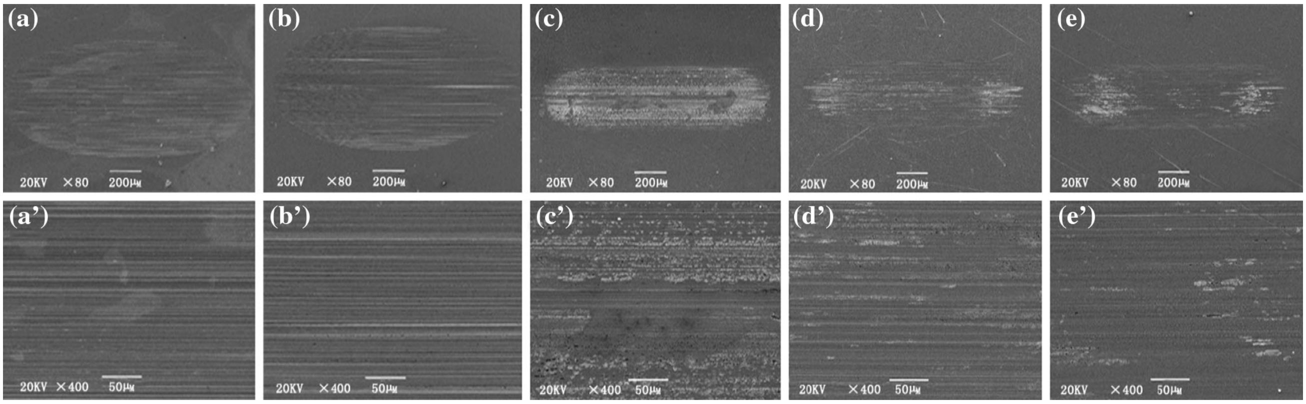


Fig. 8 Scanning electron microscopy images of the worn surfaces lubricated by different lubricants: (**a**, **a**′) CO, (**b**, **b**′) ESBO, and CO-LiTFSI at molar ratio of (**c**, **c**′)1:0.5, (**d**, **d**′) 1:1 and (**e**, **e**′) 1:1.5 (the magnification of the top is ×80 and that of the bottom is ×400; load, 100 N; temperature, 200 °C; stroke, 1 mm; frequency, 20 Hz; duration, 30 min)

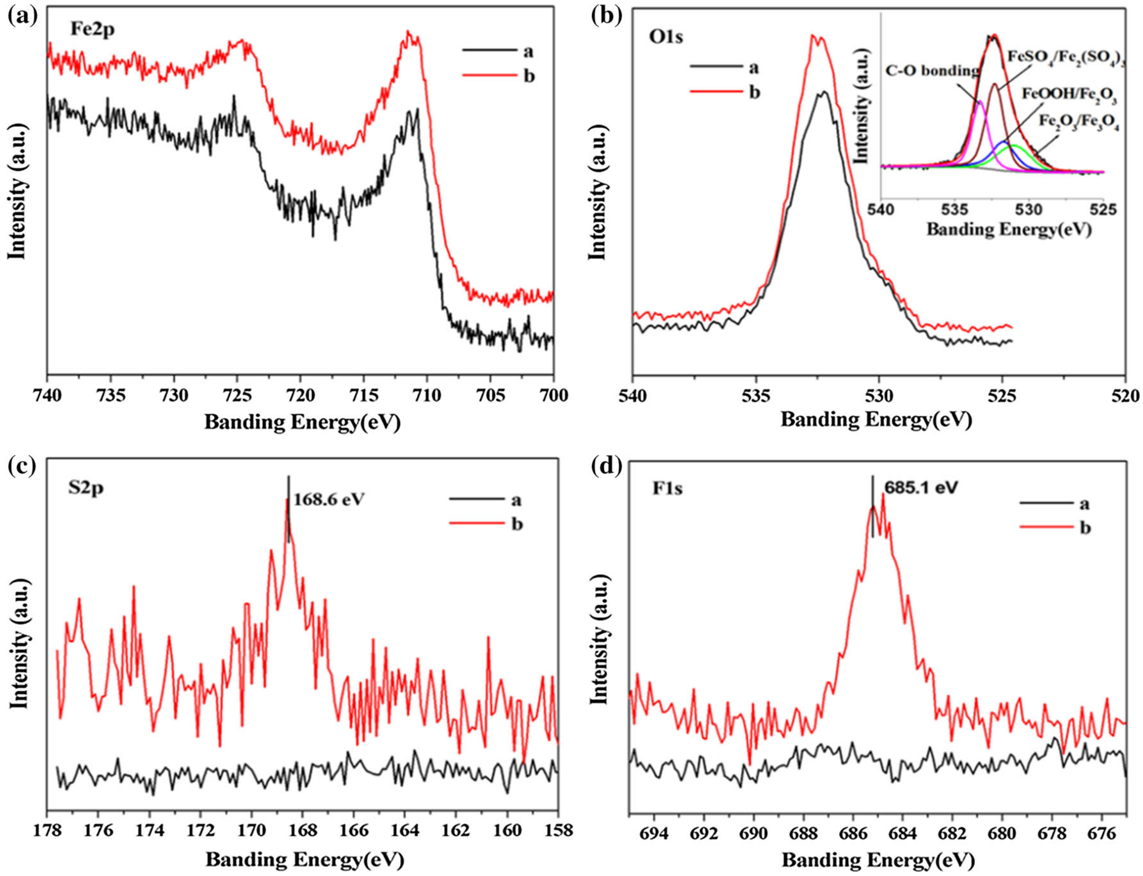


Fig. 9 XPS spectra of **a** Fe 2p, **b** O 1 s, **c** S 2p and **d** F 1 s of the worn surfaces lubricated by the neat CO (*a*) and CO-LiTFSI with molar ratios of 1:1.5 (*b*) at 200 °C (SRV load = 100 N; frequency = 25 Hz; stroke = 1 mm; duration = 30 min). *Inset* in **b** shows the deconvolution of O 1 s spectra for the worn surfaces lubricated by CO-LiTFSI in molar ratios of 1:1.5

4 Conclusions

From the above discussion, it is clear that the in situ formed ILs, [Li(castor oil)]TFSI, which were prepared by simply blending castor oil (CO) with LiTFSI, exhibited better thermal stability and mechanical properties than the pure base oil. The friction and wear test results indicated that the ILs with various molar ratios of CO/LiTFSI have excellent friction reduction and AW property for lubrication of steel/steel contacts at 200 °C, specifically the ILs in molar ratios of 1:1 and 1:1.5. Moreover, both of them can also dramatically improve the tribological property of CO under harsh conditions, for instance, at a temperature ramp test from 100 to 300 °C, and a load ramp test from 100 to 500 N. The excellent tribological performance of the ILs is attributed to the formation of effective physical adsorption films and further tribochemical reaction products on the worn surface at elevated temperature. XPS analytical results indicated that the tribochemical films are composed of Fe_2O_3, Fe_3O_4, FeOOH, $FeSO_4$ or $Fe_2(SO_4)_3$, FeF_2, FeF_3, and C–O bonding.

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Compliance with Ethical Standards

Conflict of interest The authors declare no competing financial interest.

References

1. Nagendramma, P., Kaul, S.: Development of ecofriendly/biodegradable lubricants: an overview. Renew. Sustain. Energy Rev. **16**, 764–774 (2012)
2. Wilson, B.: Lubricants and functional fluids from renewable sources. Ind. Lubr. Tribol. **50**, 6–15 (1998)
3. Gryglewicz, S., Piechocki, W., Gryglewicz, G.: Preparation of polyol esters based on vegetable and animal fats. Bioresour. Technol. **87**, 35–39 (2003)
4. SathwikChatra, K.R., Jayadas, N.H., Satish, V.K.: Natural oil-based lubricants. In: Nosonovsky, M., Bhushan, B. (eds.) Green tribology-biomimetics, energy conservation and sustainability, p. 287. Springer, Heidelberg (2012)
5. Karmakar, G., Ghosh, P.: Soybean oil as a biocompatible multifunctional additive for lubricating oil. ACS Sustainable Chem. Eng. **3**, 19–25 (2015)
6. Karmakar, G., Ghosh, P.: Green additives for lubricating oil. ACS Sustainable Chem. Eng. **1**, 1364–1370 (2013)
7. Mortier, R.M., Fox, M.F., Orszulik, S.T.: Aviation lubricants. In: Lansdown, A.R., Lee, S. (eds.) Chemistry and Technology of Lubricants, pp. 345–352. Springer, New York (2010)
8. Asadauskas, S., Perez, J.M., Duda, J.L.: Lubrication properties of castor oil-potential basestock for biodegradable lubricants. Lubr. Eng. **53**, 35–40 (1997)
9. Kar, P., Asthana, P., Liang, H.: Formation and characterization of tribofilm. J. Tribol. **130**, 4201–4206 (2008)
10. Chadha, B.R., Gupta, M., Gupta, L.R.: Some experimental studies of lubricants in a two-stroke methanol engine. J. Synth. Lubr. **8**, 295–306 (1992)
11. Ye, B., Yu, W.L., Wang, B., Tao, D.H.: Rheological and tribological characteristics of chemically modified castor oil. Lubr. Eng. **1**, 37–38 (2005)
12. John, W.G., Daniel, P.G.: Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. Bioresour. Technol. **96**, 851–855 (2005)
13. Stevens, C.: Practical pointers for grease and antiseize selection. Plant Eng. **52**, 67–69 (1998)
14. Loomis, W.R., Fusaro, R.L.: Overview of liquid lubricants for advanced aircraft engines. NASA Tech. Memo. 83529 (1982)
15. Wu, X.H., Liu, J.M., Zhao, Q., Zhang, M., Zhao, G.Q., Wang, X.B.: In situ formed ionic liquids in polyol esters as high performance lubricants for steel/steel contacts at 300 °C. ACS Sustain. Chem. Eng. **3**, 2281–2290 (2015)
16. Rudnick, L.R., Shubkin, R.L.: Synthetic lubricants and high-performance functional fluids, revised and expanded. Taylor & Franci, New York (1999)
17. Cavdar, B.: Effect of temperature, substrate type, additive and humidity on the boundary lubrication in a linear perfluoropolyalkylether fluid. Wear **206**, 15–23 (1997)
18. Adhvaryu, A., Erhan, S.Z.: Epoxidized soybean oil as a potential source of high-temperature lubricants. Ind. Crops Prod. **15**, 247–254 (2002)
19. Fan, M.J., Song, Z.H., Liang, Y.M., Zhou, F., Liu, W.M.: In situ formed ionic liquids in synthetic esters for significantly improved lubrication. ACS Appl. Mater. Interfaces **4**, 6683–6689 (2012)
20. Fan, M.J., Liang, Y.M., Zhou, F., Liu, W.M.: Dramatically improved friction reduction and wear resistance by in situ formed ionic liquids. RSC Adv. **2**, 6824–6830 (2012)
21. Song, Z.H., Cai, M.R., Liang, Y.M., Fan, M.J., Zhou, F., Liu, W.M.: In situ preparation of anti-corrosion ionic liquids as the lubricant additives in multiply-alkylated cyclopentanes. RSC Adv. **3**, 21715–21721 (2013)
22. Song, Z.H., Fan, M.J., Liang, Y.M., Zhou, F., Liu, W.M.: Lithium-based ionic liquids: in situ-formed lubricant additive only by blending. Tribol. Lett. **49**, 127–133 (2013)
23. Shah, F.U., Glavatskih, S., Antzutkin, O.N.: Boron in tribology: from borates to ionic liquids. Tribol. Lett. **51**, 281–301 (2013)
24. Palacio, M., Bhushan, B.: A review of ionic liquids for green molecular lubrication in nanotechnology. Tribol. Lett. **40**, 247–268 (2010)
25. Zhou, F., Liang, Y.M., Liu, W.M.: Ionic liquid lubricants: designed chemistry for engineering applications. Chem. Soc. Rev. **38**, 2590–2599 (2009)
26. Qu, J., Truhan, J.J., Dai, S., Luo, H., Blau, P.J.: Ionic liquids with ammonium cations as lubricants or additives. Tribol. Lett. **22**, 207–214 (2006)
27. Yoshida, K., Nakamura, M., Kazue, Y., Tachikawa, N., Tsuzuki, S., Seki, S., Dokko, K., Watanabe, M.: Oxidative-stability enhancement and charge transport mechanism in glyme–lithium salt equimolar complexes. J. Am. Chem. Soc. **133**, 13121–13129 (2011)
28. Allauddin, S., Narayan, R., Raju, K.V.S.N.: Synthesis and properties of alkoxysilane castor oil and their polyurethane/urea–silica hybrid coating films. ACS Sustain. Chem. Eng. **1**, 910–918 (2013)
29. Wang, B.G., Wang, X.B., Lou, W.J., Hao, J.C.: Rheological and tribological properties of ionic liquid-based nanofluids containing functionalized multi-walled carbon nanotubes. J. Phys. Chem. C **114**, 8749–8754 (2010)
30. Ferry, J.D.: In Viscoelastic Properties of Polymers. Wiley, New York (1980)
31. Kim, D., Archer, L.A.: Nanoscale organic–inorganic hybrid lubricants. Langmuir **27**, 3083–3094 (2011)
32. Wu, X.H., Wang, X.B., Liu, W.M.: Tribological properties of naphthyl phenyl diphosphates as antiwear additive in polyalkylene glycol and polyurea grease for steel/steel contacts at elevated temperature. RSC Adv. **4**, 6074–6082 (2014)
33. Shah, F.U., Glavatskih, S., Höglund, E., Lindberg, M., Antzutkin, O.N.: Interfacial antiwear and physicochemical properties of alkylborate-dithiophosphates. ACS Appl. Mater. Interfaces **3**, 956–968 (2011)
34. Qu, J., Bansal, D.G., Yu, B., Howe, J.Y., Luo, H.M., Dai, S., Li, H.Q., Blau, P.J., Bunting, B.G., Mordukhovich, G., Smolenski, D.J.: Antiwear performance and mechanism of an oil-miscible ionic liquid as a lubricant additive. ACS Appl. Mater. Interfaces **4**, 997–1002 (2012)

35. Naumkin, A.V., Kraut-Vass, A., Gaarenstroom, S.W., Powell, C.J.: NIST X-ray Photoelectron Spectroscopy Database. https://srdata.nist.gov/xps/Default.aspx
36. Sun, Y.B., Hu, L.T., Xue, Q.J.: Tribological properties and action mechanism of N, N-dialkyl dithiocarbamate-derived S-hydroxyethyl borate esters as additives in rapeseed oil. Wear **266**, 917–924 (2009)
37. Zhao, G.Q., Wu, X.H., Li, W.M., Wang, X.B.: Hydroquinone bis(diphenyl phosphate) as an antiwear/extreme pressure additive in polyalkylene glycol for steel/steel contacts at elevated temperature. Ind. Eng. Chem. Res. **52**, 7419–7424 (2013)
38. Cai, M.R., Liang, Y.M., Zhou, F., Liu, W.M.: Tribological properties of novel imidazolium ionic liquids bearing benzotriazole group as the antiwear/anticorrosion additive in poly(ethylene glycol) and polyurea grease for steel/steel contacts. ACS Appl. Mater. Interfaces **3**, 4580–4592 (2011)