

Comparative study on corrosion resistance and lubrication function of lithium complex grease and polyurea grease

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Received: 02 July 2019 / Revised: 06 August 2019 / Accepted: 03 September 2019

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Abstract: In this study, lithium complex grease (LCG) and polyurea grease (PUG) were synthesized using mineral oil (500SN) and polyalphaolefin (PAO40) as base oil, adsorbed onto lithium complex soap and polyurea as thickeners, respectively. The effects of grease formulation (thickener and base oil with different amounts (80, 85, and 90 wt%) on the corrosion resistance and lubrication function were investigated in detail. The results have verified that the as-prepared greases have good anti-corrosion ability, ascribed to good salt-spray resistance and sealing function. Furthermore, the increase in the amount of base oil reduces the friction of the contact interface to some extent, whereas the wear resistance of these greases is not consistent with the friction reduction, because the thickener has a significant influence on the tribological property of greases, especially load-carrying capacity. PUG displays better physicochemical performance and lubrication function than LCG under the same conditions, mainly depending on the component/structure of polyurea thickener. The polyurea grease with 90 wt% PAO displays the best wear resistance owing to the synergistic lubrication of grease-film and tribochemical film, composed of Fe_2O_3 , $\text{FeO}(\text{OH})$, and nitrogen oxide.

Keywords: lithium complex grease; polyurea grease; salt-spray resistance; tribological property

1 Introduction

In recent years, increasing attention has been paid to offshore engineering equipments, because their operating conditions remain hot and humid air, seawater splashing, and salt-spray corrosion, causing serious corrosion and wear to metal components [1–3]. These causes of damage are the main threats to the performance and service life of marine engineering equipments [4]. Salt-spray corrosion causes serious damage, even failure, to mechanical parts in the ocean atmosphere [5, 6]. Therefore, it is of great significance to take effective protection to ensure the reliability and security of offshore engineering equipments.

Lubricating grease could serve as corrosion resistant material owing to its inherent sealing function [7]. The higher consistency differed from liquid lubricant, preventing contaminants from entering the contact surface, possibly displaying good corrosion protection [8]. Nevertheless, the corrosion resistance of grease has been rarely investigated up to now. Therefore, it is imperative to exploit the salt-spray resistance of grease.

As a semi-solid colloidal dispersion system, lubricating grease has been widely applied to many fields owing to its excellent friction-reducing and anti-wear properties. Grease contains two main components: base oil as a fluid lubricant and thickener for thickening the base oil to a certain consistency [9]. The properties

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of base oil and thickener mainly determine the physicochemical property and usability of grease. The previous study suggested that the solvency of the base oil strongly impacts the pumpability and rheological properties of grease, and is in a close relation with the thickener [10]. The base oil could bleed from the thickener; then, the grease softens under compression and shearing [11]. The type of base oil, structure of thickener, and their interaction strongly determine the operating conditions (load-bearing ability, running speed) and environment (e.g., high/low temperature, humid, dust) [12]. Meanwhile, the lubricating function of grease strongly depends on the base oil and thickener. It has been ensured that the thickener could deposit on the worn surface during the friction process and form a boundary protective film [13]. For greases with the same formulation, higher thickener concentration and higher viscosity of base oil can form a thicker film [14], which is closely correlated to the anti-wear and extreme pressure performance. The base oil, thickener, and their concentration play an important role in the performance of lubricating grease. However, only a few reports have methodically pointed out the effect of grease components.

Generally, lubricating grease can be divided into two categories: soap grease and non-soap grease [15]. Lithium complex grease and polyurea grease as the most prominent representatives of soap-base grease and non-soap base grease, respectively, have been applied in many fields. The ever-increasing production of the two greases accounts for more than half of the high-performance grease market. Lithium complex grease (LCG), as a type of high-performance soap grease, assumes the major share of the worldwide industrial grease market. It differs from traditional soap-based grease because of the thickener with diverse lithium soaps [16]. Lithium complex soap is prepared by the saponification reaction of stearic acid and organic acid with LiOH [17]. The development of LCG began in the 1960s, because of its higher dropping point. It has quickly replaced many traditional greases, such as calcium-based grease and sodium-based grease in various fields. In recent years, the relationship between the components and properties of LCG has been a popular research topic. A previous study reported that formulated LCG has excellent rheology and anti-wear

properties via the saponification reaction (12-OH stearic acid, nonanedioic acid, and lithium hydroxide) [18]. Antioxidant additives with different chemical structures were selected to improve the oxidation stability of LCG [19]. ZDDP and MoDTC as LCG additives could strongly enhance anti-wear performances [20]. In the development of LCG thus far, it has possessed the advantages of high dropping point, wide temperature range, excellent colloidal stability, shear stability, and long service life [21]. Polyurea grease (PUG), as a type of non-soap grease, has become a new multipurpose grease after complex soap grease and bentonite grease [22]. Since its invention in 1954, PUG has been the subject of many research efforts, owing to its excellent performance characteristics. As of 2013, the total production of polyurea grease was 66.1 kt, accounting for 5.62% of the global grease production. Its thickener from reacting organic amine with isocyanate avoided the oxidation of metallic soap to base oils [23]. The long working life over a wide temperature range is mainly ascribed to the oxidation stability of the thickener. PUG has a series of excellent comprehensive properties, such as high dropping point, oxidation stability, thermal and mechanical shearing stability, rust resistance, and water resistance [24]. Ref. [25] has investigated the relationship between the PUG formulation and performance, and the tribological performance via adding ionic liquid. The rheology and anti-wear properties of PUG were also investigated via using sebacic acid ester and esters of polyols as a base oil [26]. The effect of thickener structure on the performance of PUG was also evaluated [27]. Above all, although a large amount of literature reported the relationship between performance characteristics and ingredients/structure of the two greases, the salt-spray resistance of grease has never been investigated thus far [28].

Here, the effects of base oil, thickener, and their concentrations on the performance characteristics of grease were investigated, especially corrosion resistance. Lithium complex soap and polyurea were used to thicken two types of base oil, with the different concentrations of 20, 15, and 10 wt%. The selected base oils were mineral oil (500SN, MO) and PAO40 (poly- α -olefin, PAO). The physicochemical properties, salt-spray resistance, and tribological performance of the as-prepared greases were evaluated in detail. The

friction mechanism was analyzed by surface/interface technology.

2 Experimental details

2.1 Materials

Sebacic acid, 12-OH stearic acid, LiOH, diphenylmethane diisocyanate, octadecylamine, octadecyl alcohol, and ethanol and petroleum ether used in this study were purchased from Kelong Chemical Reagent Company. Base oil (500SN, PAO40) was commercially obtained from Lanzhou Refinery Company (Lanzhou, China). All chemicals in this work were employed without further purification.

2.2 Preparation of salt-spray resistant greases

2.2.1 Lithium complex grease

First, 60 wt% base oil was heated to 80 °C, following the complete dissolution of 12-OH stearic acid in base oil under uniform stirring. Then, the temperature of the mixture was raised to approximately 125 °C, and sebacic acid was added into the mixture. After forming the homogeneous solution, the temperature was decreased to 100 °C, and heat was preserved. Second, LiOH was dissolved in warm water (water is more than 3 times of the LiOH mass), and the LiOH aqueous solution was slowly added to the solution for approximately a half-hour. After the saponification at 115 °C for 1 h, the rest of the base oil was added. The blend was heated to 205 °C and kept warm for 10 min, then cooled to 180 °C for a half-hour. Finally, the initial grease was naturally cooled to 15–25 °C, after being grounded/homogenized on a three-roll mill three times, and high-end LCG was obtained. In this experiment, the base oils are MO and PAO, and the thickener concentrations are 80, 85, and 90 wt%; thus, six LCGs were obtained.

2.2.2 Polyurea grease

First, the base oil was heated to 120 °C and kept warm for 5–10 min to remove moisture. Second, 50 and 30 wt% base oils were offloaded into two beakers and kept warm with vigorous stirring; then, diphenylmethane diisocyanate (MDI) and octadecylamine were

completely dissolved into them, respectively. Third, the mixture with octadecylamine was blended quickly into the 50 wt% mixture with MDI under constant stirring. Fourth, the remaining mixture in the beaker was cleaned with the remaining base oil, with the reaction temperature maintained between 105 and 125 °C for 60 min. Finally, stearyl alcohol was added into the stirred vessel and reacted for 10–15 min. The temperature was heated to 170–180 °C for 20 min for high-temperature refining. The initial grease was naturally cooled to ~25 °C, after being grounded/homogenized on a three-roll mill three times, the high-end PUG was obtained. In this experiment, the base oils are MO and PAO, and their viscosities are listed in Table 1. The thickener concentrations are 80, 85, and 90 wt%; thus, six PUGs were generated. Figure 1 shows the photos of as-prepared LCG and PUG.

2.3 Physicochemical properties of as-prepared greases

The dropping points of as-prepared greases were measured by the SYD-3498-I drop point tester (Shanghai JingXi Instrument Manufacturing Co., Ltd.) following

Table 1 Viscosity of MO (500SN) and PAO (PAO40).

Project	Kinematic viscosity (mm ² /s)		Viscosity index
	40 °C	100 °C	
MO (500SN)	97	11	88
PAO (PAO40)	386	40.03	154

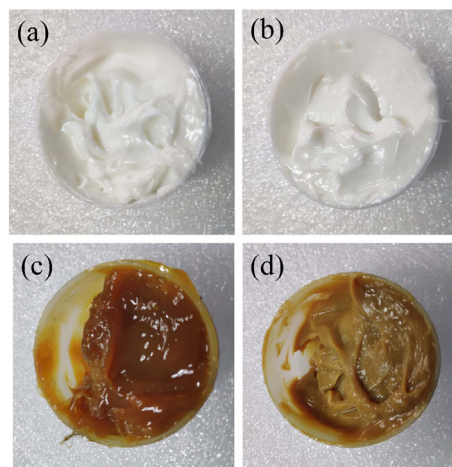


Fig. 1 Representative photos of as-prepared LCG and PUG: (a) LCG (85% PAO), (b) PUG (85% PAO), (c) LCG (85% MO), and (d) PUG (85% MO).

ASTM-D566. The cone penetrations of the salt-spray resistant grease were measured by SYD-2801C lubricating grease cone penetrometer (Shanghai Changji Geological Instrument Co., Ltd.) according to GB/T 269 (ASTM D1403). The copper strip test was evaluated by national standards GB/T 7326-87 (ASTM D4048-81). The colloidal stability was tested by the National Petrochemical Industry standards SH/T 0324-92. Thermogravimetric analysis was performed in depth by NETZSCH SAT 449 F3 (NETZSCH Instrument Manufacturing Co., Ltd.), and the functional groups were analyzed by Fourier transform infrared analysis (FTIR, Nicolet-5700).

2.4 Salt-spray test

Salt-spray test is an accelerated corrosion method via simulating an ocean atmosphere [29]. The salt solution is sprayed into an airtight case at constant temperature, which atomizes a certain concentration of salt water. The salt concentrations are several or dozens of times higher than their natural concentrations. Therefore, the corrosion rate is greatly accelerated, and the corrosion time is considerably shortened. The salt-spray resistance was evaluated by observing the changes in the specimens before and after the test. LCG, containing 85 wt% MO and PAO (LCG (85% MO) and LCG (85 wt% PAO)), and PUG, containing 85 wt% MO and 85% PAO (PUG (85 wt% MO) and PUG (85 wt% PAO)), were sorted out to investigate the salt-spray resistance. The tested titanium alloy sheets were polished before coating the grease. The neutral salt-spray test was employed in this experiment following GB/T 1771-2007. The temperature in the salt-spray test chamber is 35 °C, and the concentration of NaCl solution is 5%. Each grease was daubed uniformly on the surfaces of titanium alloy sheet and blank titanium alloy sheet as a reference. All the specimens are hung in the salt-spray test box with a rope. The salt-spray test was performed for two weeks, and the corrosion phenomenon was observed at intervals. After the salt-spray test, the grease was slightly scraped off the surface of titanium alloy with a scraper and ultrasonically cleaned in alcohol several times until cleaned completely. To evaluate the corrosion degree of the titanium alloy sheet, the changes in surface morphology were observed by scanning electron microscopy (SEM), using the JMS-6610 (SEM, JEOL, Japan), and the elemental composition and chemical

state of the surface of titanium alloy were analyzed by Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). Considering that titanium alloy exhibits low-temperature performance, high chemical activity, thermal conductivity, and small modulus of elasticity, titanium alloy was applied to explore the corrosion resistance of grease. In this case, the protection effect of grease can be highlighted. The coated grease on the titanium alloy sheet plays a sealing function role and prevents corrosive media from entering.

2.5 Tribological properties of as-prepared greases

The tribological performance of as-prepared greases was evaluated via UMT-3 reciprocating friction and wear tribometer (Center For Tribology Company, America) with the applied loads of 20 N (Hertzian contact pressure (HCP): 1.20 GPa), 40 N (HCP: 1.59 GPa), and 60 N (HCP: 1.82 GPa) at ~25 °C for 1 h. The UMT-3 reciprocating friction and wear tribometer was designed with ball-on-disk contact configuration. The fixed upper specimen is made up of an AISI 52100 steel ball with a diameter of 10 mm and hardness of 710 HV, whereas the stationary lower specimen is also composed of AISI 52100 steel disks with $\Phi 24$ mm \times 7.9 mm and a hardness of approximately 630 HV. The friction coefficients were measured by the computer linked to the UMT-3 reciprocating friction and wear tribometer. All the friction tests under the same condition were repeatedly performed three times. The friction pairs were ultrasonically cleaned several times in acetone before characterization.

2.6 Surface analysis

To investigate the tribological mechanism lubricated by the as-prepared greases, the morphology of the worn surfaces was analyzed by SEM, and the chemical state of elements on the surfaces was analyzed by XPS. Before the test, the specimens were cleaned ultrasonically several times in baths of petroleum ether and dried with pure nitrogen.

3 Results and discussion

3.1 Physicochemical properties

Table 2 shows the physicochemical properties of the

Table 2 Physicochemical properties of salt-spray resistant greases.

Project		Dropping point (°C)	Penetration (0.5 mm)	Copper corrosion (100 °C, 24 h)	Oil separation (w/w%)	
National standard		ASTM-D566	ASTM-D217	ASTM-D4048-81	SH/T 0324-92	
LCG	MO	80 wt%	315.33	21.03	1a	1.65
		85 wt%	302.00	23.40	1a	1.87
		90 wt%	234.33	28.64	1a	3.09
	PAO	80 wt%	314.67	15.49	1a	1.06
		85 wt%	307.33	34.33	1a	1.32
		90 wt%	256.67	44.59	1a	2.00
PUG	MO	80 wt%	303.00	22.16	1a	1.51
		85 wt%	218.33	25.51	1a	7.59
		90 wt%	331.33	29.12	1a	12.61
	PAO	80 wt%	345.00	15.24	1a	4.95
		85 wt%	336.00	33.77	1a	3.80
		90 wt%	259.67	42.64	1a	3.68

as-prepared salt-spray resistant greases. It can be found that the dropping point of LCG was reduced as the concentration of thickener decreases, whereas the penetration of LCG shows the opposite trend. The LCG (80 wt% MO) has the highest dropping point, reaching 315.3 °C, followed by LCG (80 wt% PAO) and LCG (85 wt% PAO). The majority of the dropping points of the as-prepared salt-spray greases are above 300 °C, indicating that the thermal stability of the as-prepared greases is outstanding. The penetration of the as-prepared greases increases as the concentration of the thickener decreases, suggesting that the thickening capacity is improved by the increase in the thickener concentration. The oil separation of LCG was no greater than 5%, indicating good colloidal stability of LCG. The oil separation of PUG (85 wt% MO) and PUG (90 wt% MO) is higher than that of the PUG prepared by PAO. The oil separation test of LCG illustrates that the colloidal stability was improved in the following sequence: LCG (90 wt% MO) > LCG (90 wt% PAO) > LCG (85 wt% MO) > LCG (80 wt% MO) > LCG (85 wt% PAO) > LCG (80 wt% PAO), and the colloidal stability of PUG was improved in the following sequence: PUG (90 wt% MO) > PUG (85 wt% MO) > PUG (80 wt% PAO) > PUG (85 wt% PAO) > PUG (90 wt% PAO) > PUG (80 wt% MO). Thus, lithium complex soap and polyurea display a

better thickening effect to MO. The copper corrosion test shows that grease-coated copper strips have nearly no change compared with polished copper ones, whereas coating-free copper strips appear to exhibit severe oxidation corrosion. These greases allow degrees of copper corrosion to be located at 1a, indicating the good corrosion resistance of the as-prepared greases.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves of as-prepared greases (85 wt% base oil) are shown in Fig. 2. The temperature was increased gradually from ambient temperature to 600 °C at a heating rate of 10 °C·min⁻¹ in nitrogen. The thermal decomposition temperature of the greases synthesized by PAO is higher than the greases synthesized by MO. The decomposition of LCG (85 wt% PAO) and PUG (85 wt% PAO) appeared at approximately 380 °C, whereas the decomposition of the other greases appeared at 320 °C, indicating that the as-prepared greases have outstanding thermal stability.

The FTIR spectra of the as-prepared greases are shown in Fig. 3. The peak of the N–H bond for PUG is located at 1,560 cm⁻¹, and the stretching vibration peak of C=O bond appears at 1,630 cm⁻¹, inferring the carbamido of polyurea thickener [30]. The stretching vibration peak of C=O bond for LCG appears at 1,370 cm⁻¹, which corresponds to the carboxylate-

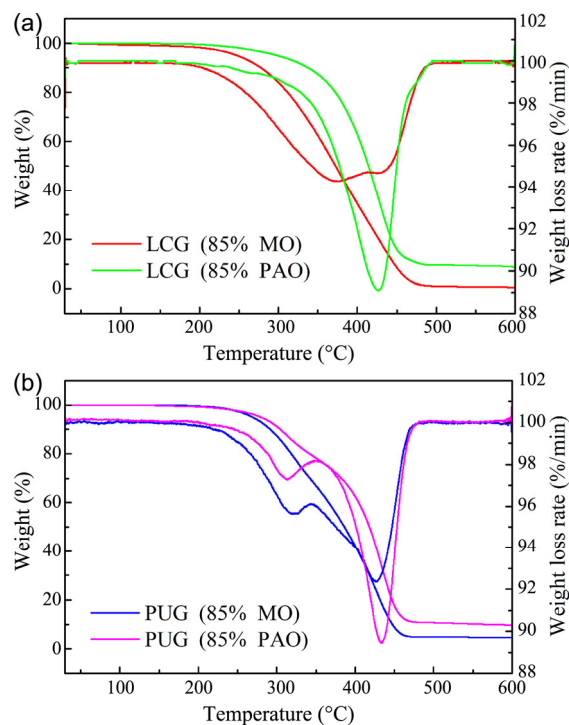


Fig. 2 Thermo-gravimetric analysis curves of as-prepared greases: (a) LCG and (b) PUG.

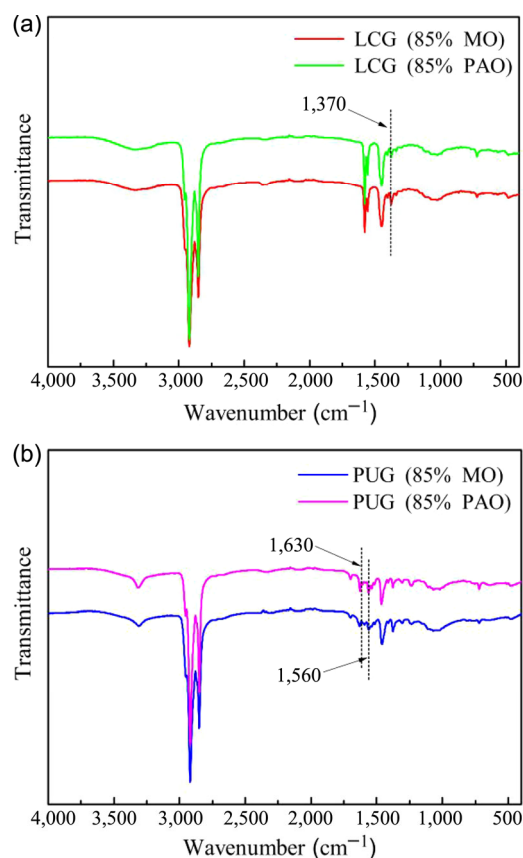


Fig. 3 Fourier transform infrared analysis spectra of as-prepared salt-spray resistant grease.

containing groups from lithium complex soap [31]. The diversity of the physicochemical characteristics for the as-prepared greases could be attributed to the sensitivity of the base oil and thickener, chemical component, and structure of thickener.

3.2 Surface analysis of salt-spray test

SEM is an effective and universal tool for analyzing surface topography. Thus, SEM was employed to observe the morphology of titanium alloy coated by the greases after the salt-spray test. Figure 4 displays severe corrosion with an obvious rusty spot on the surface of the coating-free titanium alloy. In contrast, the surface of the grease-coated titanium alloy is nearly identical to that of the new polished titanium alloy. The grease protected the titanium alloy from the external environment owing to the sealing function; thus, it prevented the corrosive medium from reaching the titanium alloys. Thus, as-prepared greases can effectively prevent the metal from corrosive damage, which can prolong the service life of machinery equipment and reduce waste of resources.

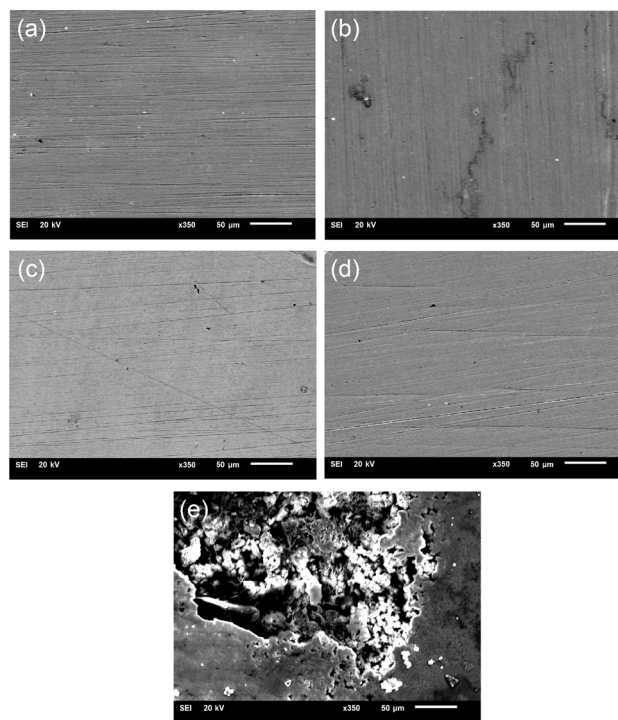


Fig. 4 SEM morphologies of the titanium alloy after the salt-spray tests: (a) LCG (85 wt% MO), (b) LCG (85 wt% PAO), (c) PUG (85 wt% MO), (d) PUG (85 wt% PAO), and (e) blank titanium alloy.

3.3 XPS analysis of salt-spray test

XPS spectra of corrosion surfaces on titanium alloys are displayed in Fig. 5, with the peak of C1s at 284.8 eV corresponding to C in the air. The peaks of O1s on the grease-coated surfaces at 532.3 eV are attributed to the appearance of TiO_2 . The O1s peak on the coating-free titanium alloy appears at 531.3 eV, which was inferred as the appearance of oxidative products, such

as Al_2O_3 and TiO_2 . The Cl2p peak on the coating-free titanium alloy is at 198.4 eV, whereas weaker peaks appear on the grease-coated surfaces, indicating the appearance of chloride (e.g., LiCl , NaCl , and VCl_2) on the coating-free surface. In addition, the V2p peak of the coating-free surface is located at 531.2 eV, whereas the V2p peaks of the grease-coated surfaces appear at 530 and 532.1 eV, possibly ascribed to the appearance of V_2O_5 . Although there was slight oxidation on the

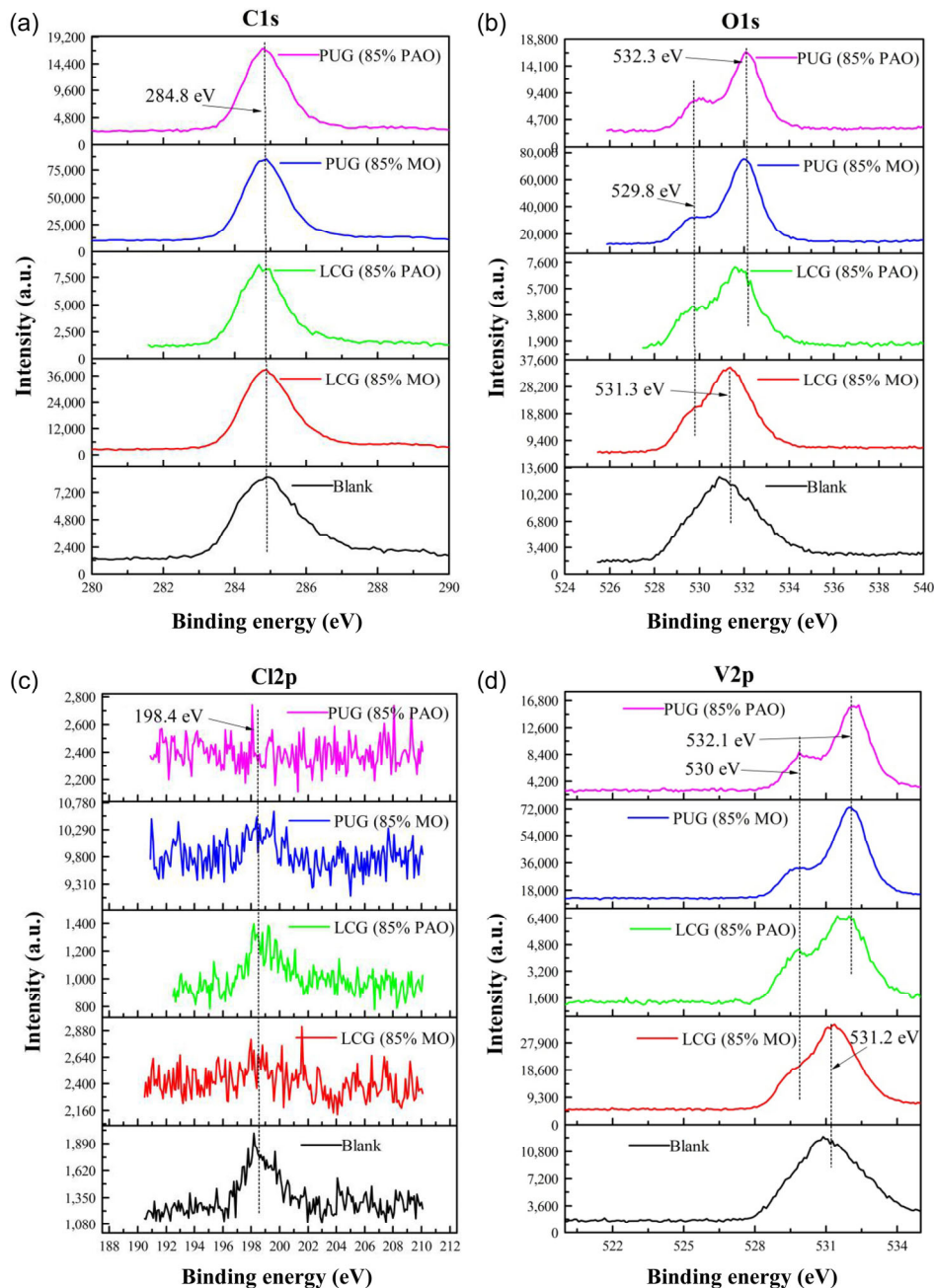


Fig. 5 X-ray photoelectron spectra of the elements on the surface of titanium alloys after salt-spray test.

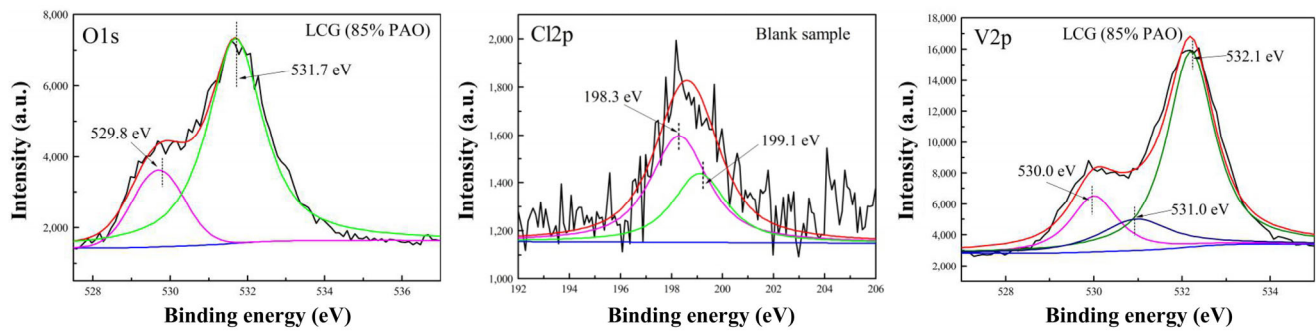


Fig. 5 (Continued)

surface of the grease-coated titanium alloy, few obvious examples of corrosion occurred on the worn surface compared with that of the coating-free surface. Consequently, it is concluded that the grease displays good corrosion protection effect, preventing the metal parts from corroding.

3.4 Tribological properties

The tribological properties of lubricating greases were evaluated on a reciprocating ball-on-disk UMT-3 sliding tester at $\sim 25^\circ\text{C}$. Figure 6 shows the friction curves and average friction coefficients of steel/steel contact

under grease lubrication at 20, 40, and 60 N. Under the applied load of 20 and 40 N, the friction curves lubricated by LCG (80 wt% MO), LCG (80 wt% PAO), and LCG (85 wt% PAO) fluctuate vigorously, showing a tendency of first increase then level off, possibly because the high consistency has an adverse effect on the liquidity of grease (highly-thickened grease is of replenishing base oil to form new lubricating film). The friction reduction of LCG decreases with thickener concentration, namely, the thinner consistency of grease is good for the formation of lubricating film. The LCG (except for LCG with 90 wt% PAO) provides roughly

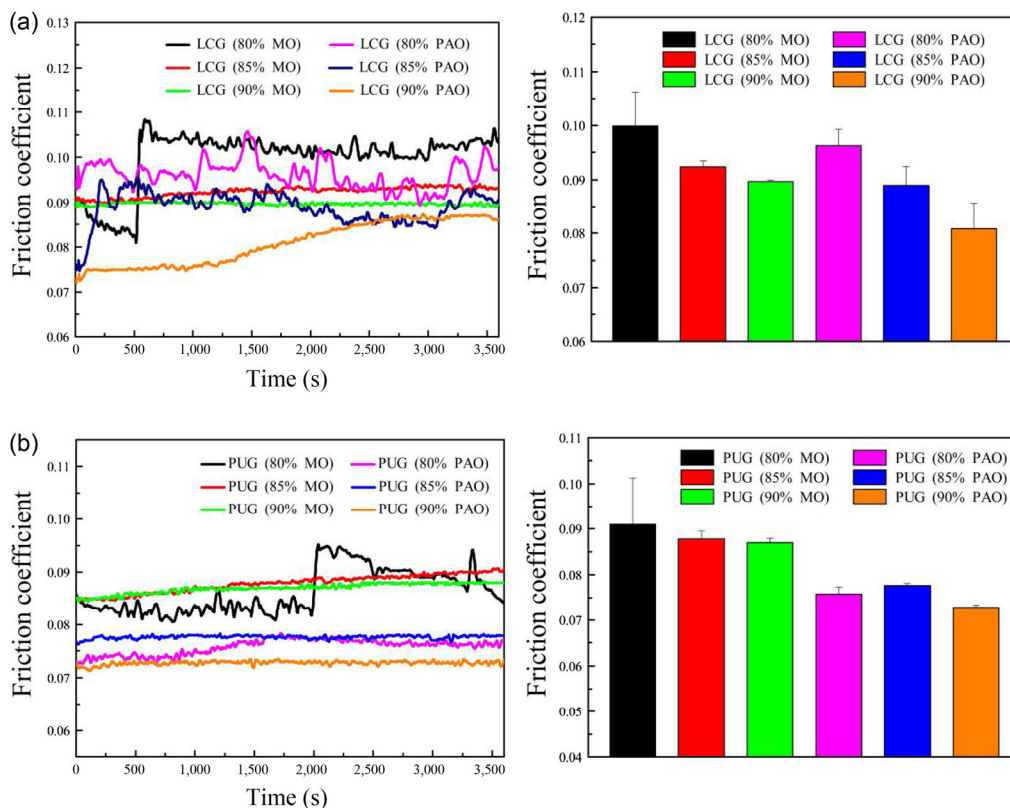


Fig. 6 Evolution of the friction coefficient with time under the applied load of (a, b) 20, (c, d) 40, and (e, f) 60 N.

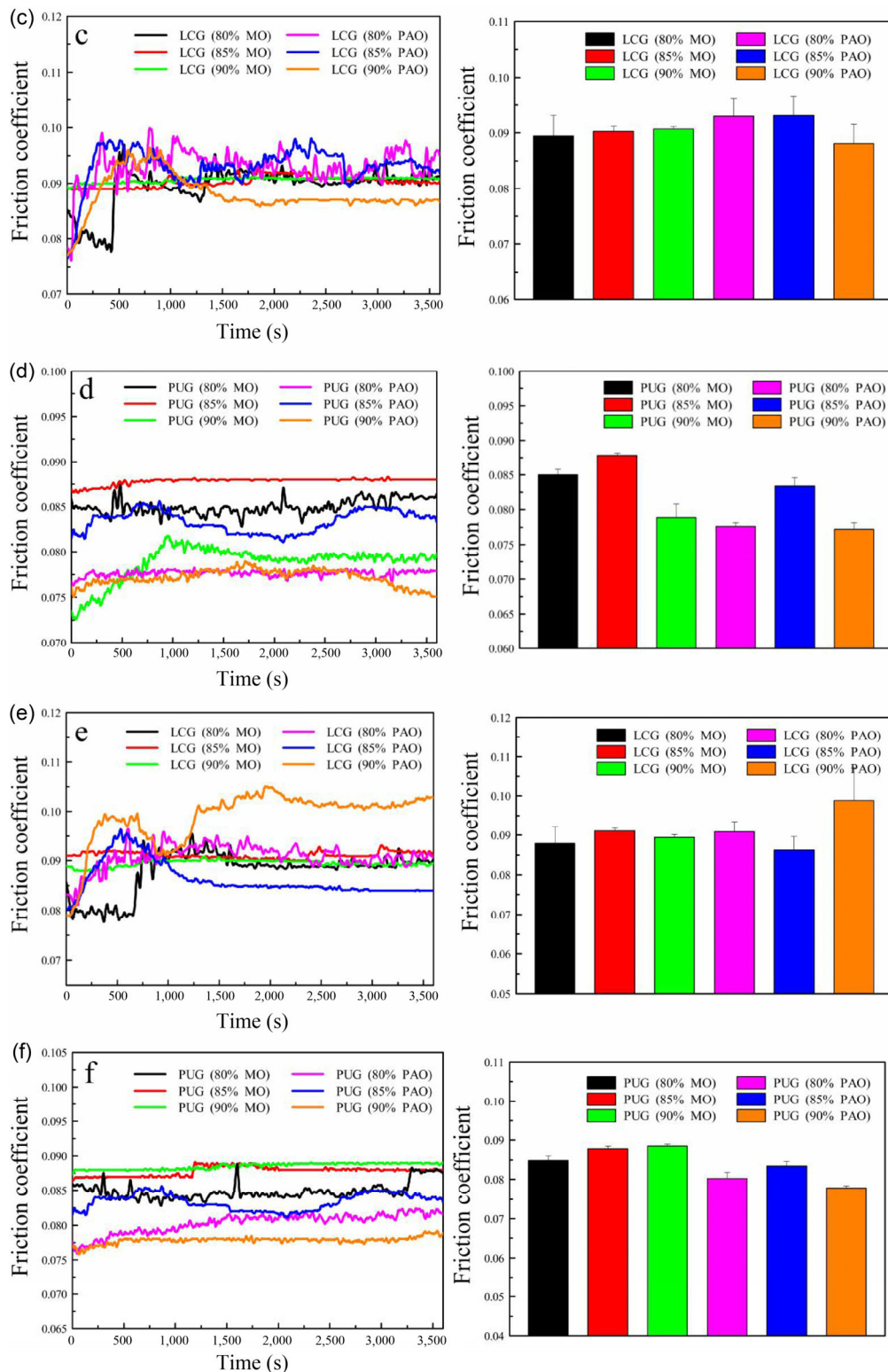


Fig. 6 (Continued)

uniform friction coefficients at the applied load of 60 N, whereas the friction coefficient of PUG with PAO is lower than that of PUG with MO, indicating that PUG

with PAO exhibits better friction-reducing ability. Above all, the LCG formulated by the same base oil gives low friction coefficients values with the decrease

in the content of thickener, indicating that LCG with low thickener content provides better friction-reducing and anti-wear abilities. From what has been discussed above, the friction coefficients of the as-prepared grease are less than 0.1, and the friction coefficient under LCG lubrication increases as follows: LCG (90 wt% PAO) < LCG (85 wt% PAO) < LCG (90 wt% MO) < LCG (85 wt% MO) < LCG (80 wt% MO) < LCG (80 wt% PAO). Under PUG lubrication, the friction coefficient increases as the following: PUG (90 wt% PAO) < PUG (80 wt% PAO) < PUG (85 wt% PAO) < PUG (90 wt% MO) < PUG (80 wt% MO) < PUG (85 wt% MO).

Figure 7 displays the wear volume of the lower specimen under as-prepared grease lubrication. Under the applied load of 20 N, the grease containing 80 wt% base oil provides a higher wear volume than that of other greases, possibly owing to the poor bleeding oil ability of high-consistency grease, resulting from the starved conditions of grease lubrication. Under the applied load of 40 N, the LCG containing 80 wt% and 85 wt% PAO shows higher wear volume than do others. All the greases with 90 wt% base oil appear to exhibit lower wear volume, indicating the excellent anti-wear ability of the as-prepared grease with high-content base oil. The PUG exhibits a lower wear volume than does LCG. The LCG with 80 wt% and 90 wt% PAO at 60 N gives a higher wear volume as well, indicating that the LCG prepared by PAO possesses weaker anti-wear ability. As-prepared greases with MO possess superior wear resistance to those prepared by PAO as a comparison. The wear volumes lubricated by PUG are lower than those lubricated by LCG, indicating that the anti-wear property of PUG is superior to that of LCG, especially PUG containing 90 wt% MO with the best anti-wear property. Thus, good interaction of polyurea and MO allows the as-prepared greases to have excellent physicochemical and tribological properties. The good interaction is mainly derived from the chemical composition and structure of the thickener, and its sensitivity to base oil.

3.5 Morphology analysis of worn surface

Figure 8 displays the SEM images and corresponding three-dimensional morphologies of wear tracks under LCG lubrication at the applied load of 40 N. From

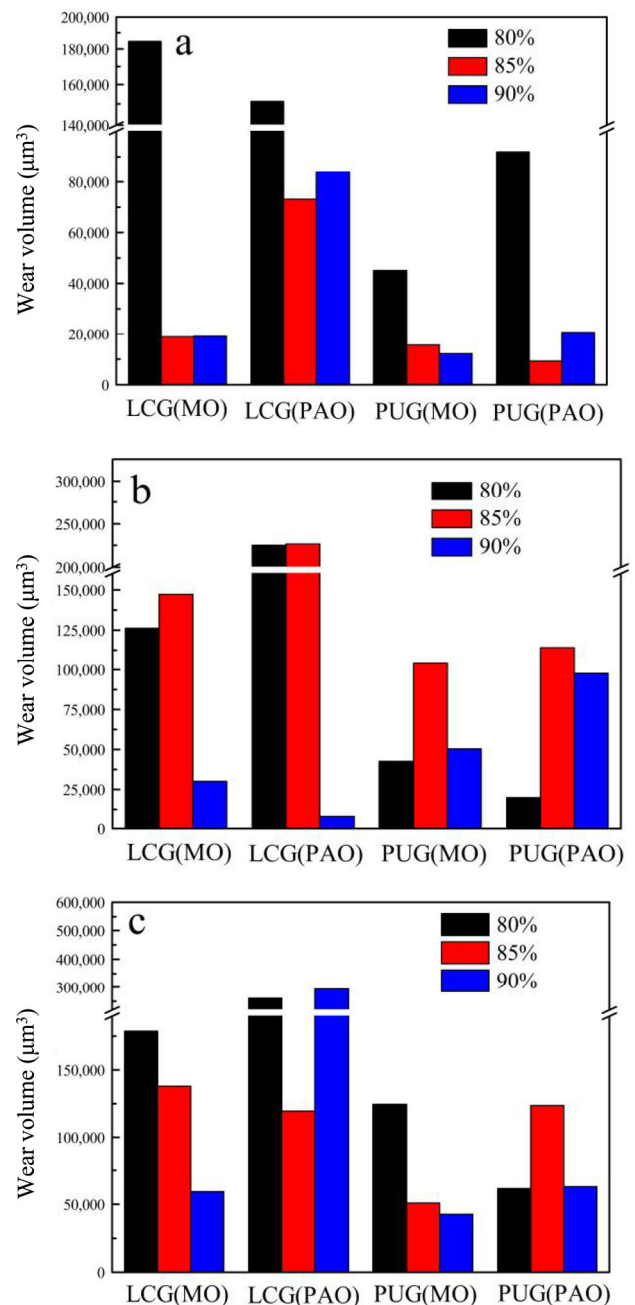


Fig. 7 Wear volumes of the lower specimen lubricated by the as-prepared salt-spray resistant greases: (a) 20 N, (b) 40 N, and (c) 60 N.

Fig. 8, the rubbing surfaces lubricated by LCG with 80 wt% and 85 wt% MO appear with some wide and deep furrows, whereas the LCG containing 90 wt% MO shows a flat and shallow wear scar. Meanwhile, the rubbing surface lubricated by PAO-based LCG appears to exhibit the same phenomenon, suggesting that the LCG with 90% base oil has a superior lubrication function to LCG with other concentrations

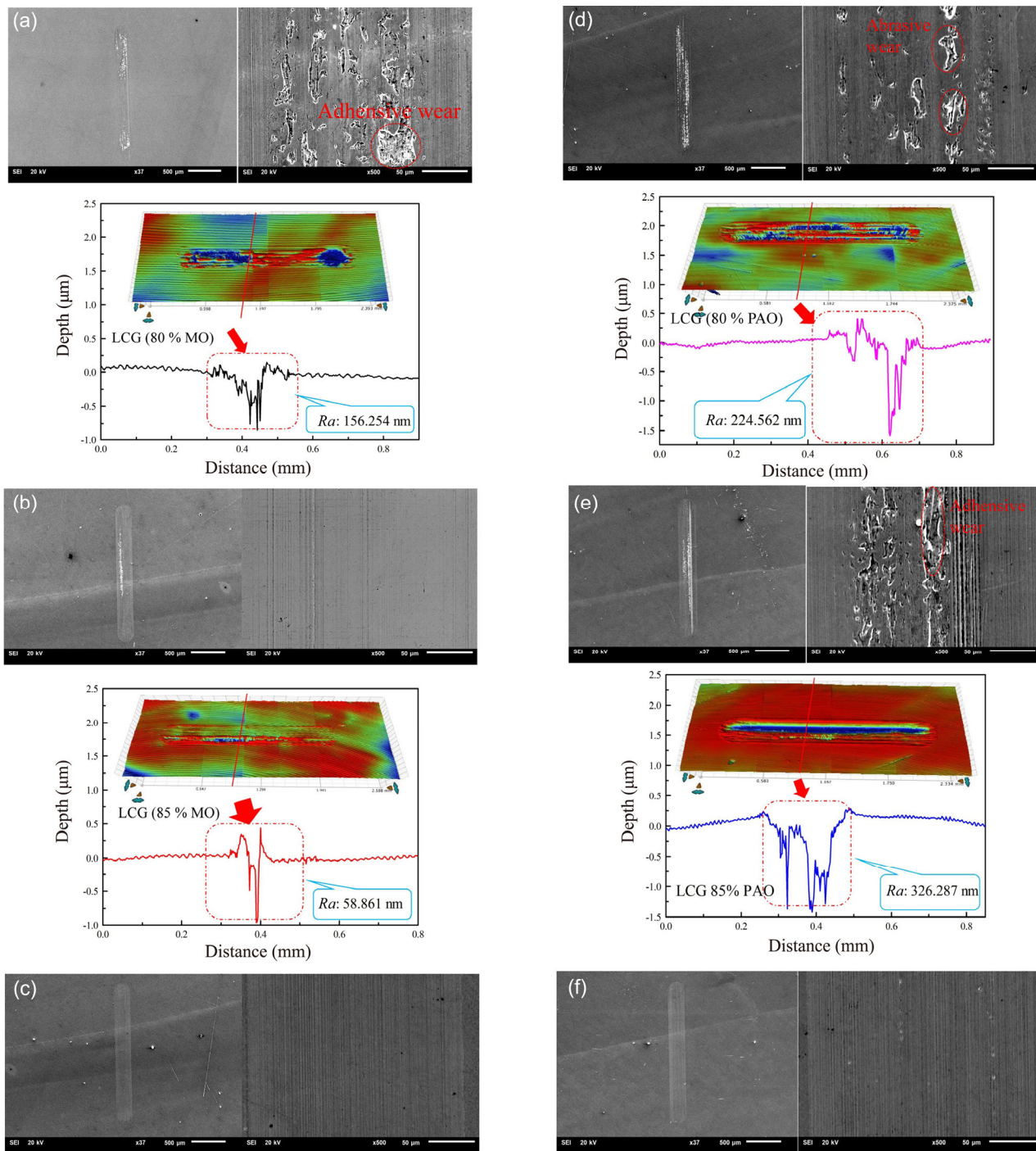


Fig. 8 SEM morphologies and particle of three-dimensional morphologies of the worn surfaces of lower specimen lubricated by LCG with the applied load of 40 N. (a) LCG 80% MO, (b) LCG 85% MO, (c) LCG 90% MO, (d) LCG 80% PAO, (e) LCG 85% PAO, and (f) LCG 90% PAO.

of base oil. In addition, the PAO-based LCG with concentrations of 80% and 85% appear to exhibit severe wear compared with the PUG with 80% and 85% MO, indicating the MO-based PUG has a better lubrication function.

Compared with the LCG, Fig. 9 gives the surface morphologies under PUG lubrication at the applied load of 40 N. The wear tracks lubricated by the PUG with all formulations show narrow and shallow wear tracks with shallow furrows, indicating that the PUG

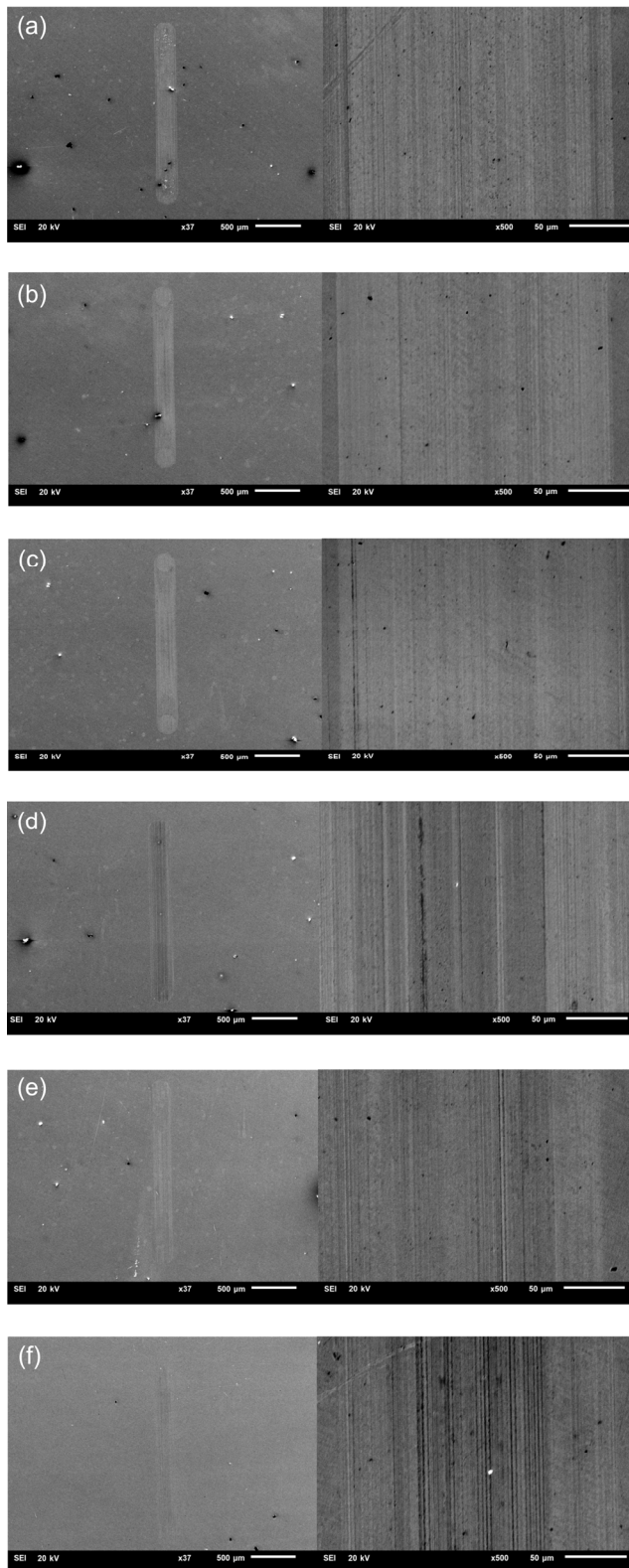


Fig. 9 SEM morphologies of the worn surfaces of the lower specimen lubricated by PUG with the applied load of 40 N. (a) PUG 80% MO, (b) PUG 85% MO, (c) PUG 90% MO, (d) PUG 80% PAO, (e) PUG 85% PAO, and (f) PUG 90% PAO.

has better anti-wear ability than does the LCG. It can be inferred that under LCG and PUG lubrication, abrasive wear plays the dominant role and little adhesive wear is exhibited. As-prepared grease with different contents of base oil shows varying consistency, resulting from the different oil-bleeding ability. Therefore, the consistency of grease determines the lubrication conditions. The LCG (80% MO), LCG (85% MO), and LCG (80% PAO) operate under starved lubrication conditions, showing higher wear volume. The PUG and other LCG operate under fully flooded conditions, providing lower wear volume.

The roughness of the worn surface is displayed in Table 2. The roughness of the worn surface under LCG with 80 wt% and 85 wt% base oil lubrication shows a larger value than that under LCG with 90 wt% base oil, further indicating that the LCG with higher concentration of base oil shows better anti-wear ability. The wear tracks lubricated by the PAO-based PUG are rougher than those of the MO-based PUG, and the roughness of wear tracks lubricated by LCG appears with the same regularity, indicating that as-prepared MO grease has better anti-wear ability. It is of great significance for the grease with good physicochemical properties, anti-corrosion, and friction-reducing and anti-wear performance to improve the durability and reliability of mechanical systems.

3.6 XPS analysis of the worn surface

To further explore the tribology mechanism of grease lubrication, the elemental composition and chemical state on the worn surfaces were analyzed by XPS. Figure 10 shows the XPS spectra of typical elements on the worn surfaces. The peak of C1s at 284.8 eV

Table 3 Roughness of the worn surface lubricated by as-prepared grease (unit: nm).

	Grease roughness (R_a)	R_a (grease with MO)	R_a (grease with PAO)
LCG	80 wt%	156.254	224.562
	85 wt%	58.861	326.287
	90 wt%	37.546	89.426
PUG	80 wt%	49.992	89.745
	85 wt%	49.027	54.386
	90 wt%	67.186	80.769

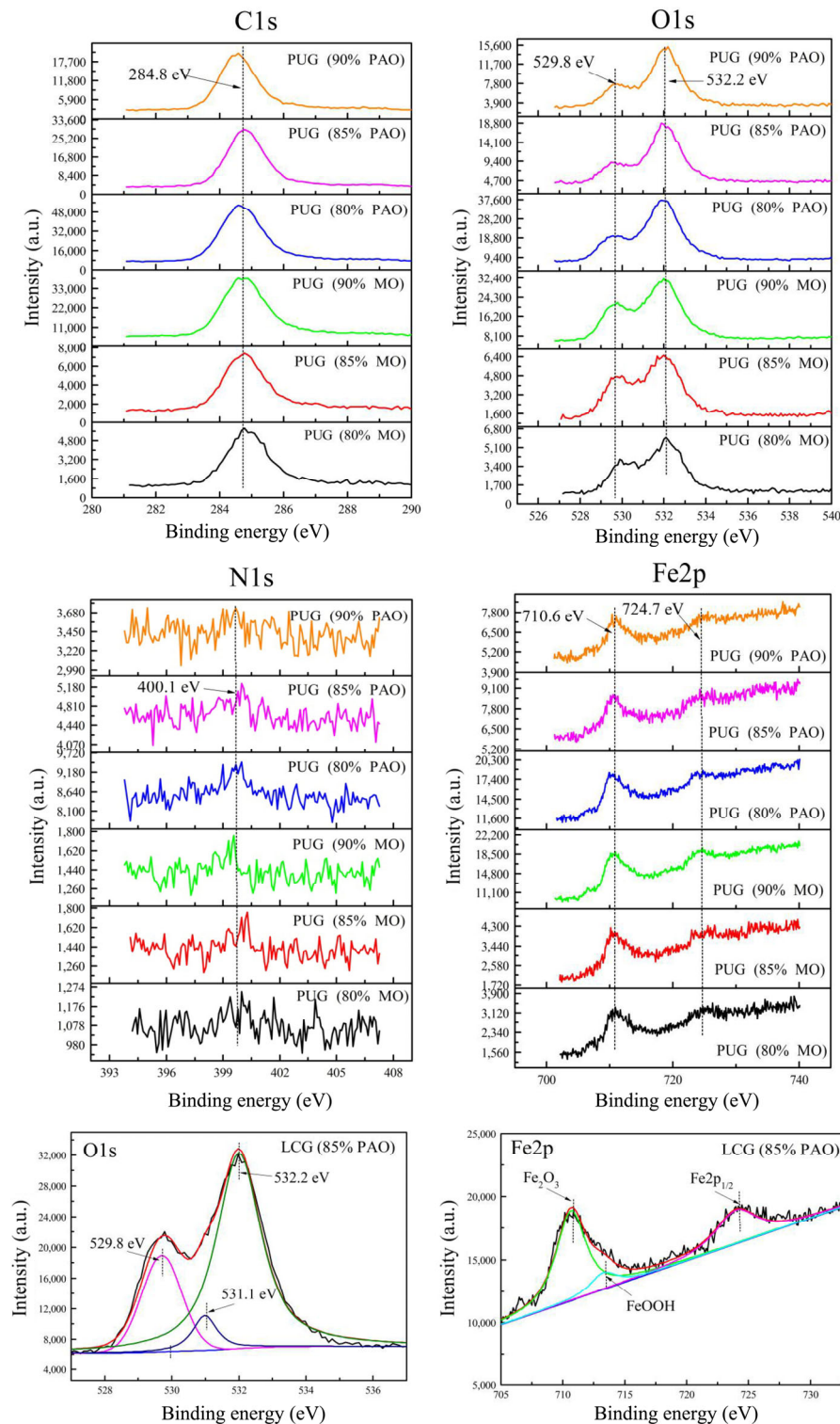


Fig. 10 X-ray photoelectron spectra of the elements on the worn surface lubricated by as-prepared salt-spray resistant greases.

is defined as the carbon in the atmosphere, as the reference. The peaks of O1s at 529.9 and 532.2 eV are attributed to the generation of iron oxide [32]. Fe2p spectra exhibit two peaks at 710.6 and 724.7 eV, further

demonstrating the appearance of Fe₂O₃ and FeO(OH). The peak of N1s at 400 eV indicates the appearance of C–N bonding and nitrogen transformation to amine or nitrogen oxide, possibly ascribed to thickener

components and tribochemical reaction products [33]. XPS analysis can powerfully support the formation of tribochemical reaction film on the worn surfaces. These new products (Fe_2O_3 , $\text{FeO}(\text{OH})$, nitrides) were formed by the reaction of active elements, such as Fe, O, and N, on the friction interface. The tribochemical reaction film and as-deposited thickener on the worn surface prevent the direct contact of the friction pair. Thus, the tribochemical reaction film and as-deposited thickener as the protective layer contribute to the enhancement of wear resistance and load-carrying capacity [34].

During the process of grease lubrication, the bulk of grease was pushed outside the contact area, promoting grease lubrication at the starved areas. When the residual grease was subjected to the shear and stress of friction pairs, the original structure of the thickener was destroyed and deformed. Thus, the base oil was released from the thickener structure and replenished the contact area [35]. The fluidity of grease determines the bleeding-oil capacity, further determining the lubrication conditions of grease. The base oil and thickener determines the bleeding-oil ability of grease [13]. A higher content of thickener results in grease with poor oil-bleeding ability. Therefore, grease with higher content of thickener operates under starved conditions. Once lacking the base oil, the thickener is deposited on the worn surface, preventing direct contact with the metallic substrate, and the deposited layer acts as a protective film, promoting the formation of tribochemical reaction film. As shown in Figure 8, the lubrication of LCG (80% MO), LCG (85% MO), and LCG (80% PAO) belongs to the starved condition. When the grease operates under fully flooded conditions, the oil film and thickener take part in the lubrication process, and the tribochemical reaction occurs on the contact surface, contributing to the enhancement of the lubrication function [36]. As shown in Figs. 8 and 9, the PUG and LCG (90% MO), LCG (85% MO), and LCG (90% MO) are under fully flooded lubrication conditions. In the process of friction, the tribochemical reaction film is continuously ground to form new film, accompanied by a gradually polished and smoothed surface. Thus, the furrows are reduced [37]. The grease could form a physical absorption film or chemical absorption film on the worn surface to provide a low-shear-resistance interface. The synergistic

effect of grease film, thickener-deposited film, and tribochemical reaction film plays a dominant role in lubrication function. The PUG containing 90% MO provides the best lubrication function, further demonstrating the tribological mechanism. The schematic diagram of the synergistic lubrication effect is shown in Fig. 11.

The acceleration effect of corrosion and wear on each other has become an important factor in the failure of mechanical equipment, with the resulting failure and damage to equipment having never been fully resolved. Grease, to some extent, can solve this difficult problem owing to two basic characteristics—sealing and lubrication. However, the corrosion resistance of grease has not yet been explored. Considering the multi-phase formulation of grease, each component could play a significant role in regulating performance characteristics.

In terms of the effect of the base oil, thickener, and its composition/structure on the performance of grease, experimental results demonstrate that regulation of

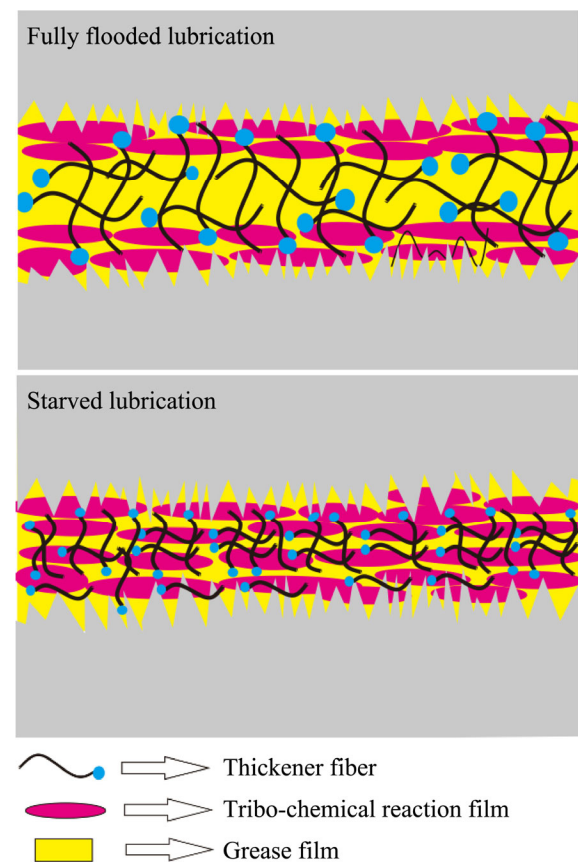


Fig. 11 The schematic diagram of tribological mechanism of as-prepared grease.

grease formulation can achieve good physicochemical properties, salt-spray resistance, and tribological performance. With the rapid development of modern industrial technology and equipment, regulating grease formulation is of significance in responding to complicated working conditions, especially regarding marine engineering/mechanical equipment.

4 Conclusions

Here, various greases were successfully synthesized via regulating base oil (mineral oil, poly- α -olefin) and thickener (lithium complex soap and polyurea), with their salt-spray resistant property and tribological performance evaluated in detail. The following conclusions can be drawn:

(1) Regulation of grease formulation obtains high-performance products with high dropping point, colloidal stability, corrosion resistance, and thermal stability. Good physicochemical properties of PUG and LCG with 80 wt% MO are mainly attributed to the interaction between the base oil and thickener.

(2) As-prepared greases have superior salt-spray resistance owing to a good sealing effect, thereby preventing the invasion of corrosive media, extending service life, and enhancing operation reliability.

(3) Friction reduction and wear resistance are regulated via grease formulation (friction coefficient at 0.07–0.10, wear volume reduced by orders of magnitude), especially PUG prepared by MO with a more pronounced effect.

(4) Although the damage under grease lubrication is mainly caused by abrasive wear, the synergy of grease film, thickener-deposited film, and tribochemical film (composed of Fe_2O_3 , $\text{FeO}(\text{OH})$, and nitrogen oxide) contributes to excellent friction-reducing and anti-wear abilities.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (No. 51705435), Fundamental Research Funds for the Central Universities (2018GF05), and Key Laboratory of Material Corrosion and Protection of Sichuan (2018CL14).

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