

Article

The Enhancement of Friction Reduction and Anti-Wear Properties of Polyurea Greases Mediated by a Lithium Salt at Elevated Temperatures

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Abstract

Polyurea grease (PU) is widely used in the lubrication of heavy machinery, but it can still suffer from structural or performance degradation under extreme conditions such as high temperatures and heavy loads. This study successfully synthesized a hybrid polyurea grease (LiTFSI-PU) by incorporating lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) into polyurea matrix. LiTFSI coordinates with the carbonyl groups (C=O) in the thickener molecules to form weakly Lewis acidic complex, thereby reinforcing the soap fiber network structure. As a result, LiTFSI-PU exhibits increased apparent viscosity under shear. The tribological properties of LiTFSI-PU were evaluated under both ambient and elevated temperature conditions. At a load of 200 N and 150 °C, the average coefficient of friction for the 3 wt% LiTFSI-PU formulation was 0.094, which is 32.3% lower than that of the baseline polyurea grease (PU), while the wear volume was reduced by 77.5%. XPS and FIB-STEM/EDS analyses confirmed that LiTFSI-PU forms a multicomponent protective film in situ during friction, which simultaneously shields the substrate and provides lubrication. The additive strategy proposed in this work offers novel insights for the development of high-performance lubricants suitable for extreme thermomechanical conditions.

Keywords: polyurea grease; lithium bis(trifluoromethanesulfonyl)imide; rheological; friction-reducing; anti-wear



Received: 20 August 2025
Revised: 11 September 2025
Accepted: 3 October 2025
Published: 17 October 2025

Citation: Nan, S.; Wu, X.; Zhou, Q.; Wang, X.; Li, B.; Liu, J.; Zhao, Q.; Wang, X.; Wang, B.; Gong, K. The Enhancement of Friction Reduction and Anti-Wear Properties of Polyurea Greases Mediated by a Lithium Salt at Elevated Temperatures. *Lubricants* **2025**, *13*, 452. <https://doi.org/10.3390/lubricants13100452>

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1. Introduction

While operating heavy equipment, it is unavoidable that friction loss and critical wear and tear failures under extreme conditions will be encountered [1,2]. Being a stable colloidal dispersion system, lubricating grease possesses superior stability, sealing performance, and load-bearing capacity compared to liquid lubricants [3]. Consequently, grease is particularly well-suited for large-scale equipment drive system lubrication, accounting for up to 90% of the bearings in these systems [4,5]. Notwithstanding, the primary disadvantage associated with grease is its limited service life [6]. The mechanical action between the bearings

results in alterations to the grease structure, particularly at elevated temperatures, which leads to thermal ageing and degradation [7–9]. Advancing high-temperature lubricant performance remains a critical research imperative, particularly for mitigating frictional energy dissipation and preventing catastrophic wear in extreme operating environments.

Polyurea grease (PU), invented in the 1980s, is regarded as a lubricant grease with considerable development potential in the 21st century [10]. In comparison with the most widely used lithium grease, it possesses a wide temperature range, excellent mechanical and chemical stability, a long service life and environmental friendliness [11]. Its primary function is the lubrication of various equipment under high-temperature working conditions [12,13]. To enhance the high-temperature resistance of polyurea greases, a commonly adopted measure is the incorporation of additives. Wang et al. selected molybdenum dialkyl dithiophosphate (MoDDP) and potassium borate (PB) as additives for polyurea grease (PU). The PB/MoDDP combination demonstrated synergistic effects that improved friction reduction and anti-wear properties at room temperature. Nevertheless, under elevated temperature and load conditions, the content of metal phosphates and molybdenum disulfide decreased while metal oxide content increased. This phenomenon resulted in increased instability of the friction film, accompanied by elevated friction and wear on metal surfaces [14]. However, the synthesis of ionic liquids is a cumbersome and costly process, which makes it difficult to prepare them in large quantities. Zhu et al. developed a Bisphenol S bis(diphenyl phosphate) (BSDP) anti-wear agent and evaluated its tribological behavior in PU under steel/steel contact using an Optimol SRV-IV oscillating reciprocating friction and wear tester at 200 °C. The results demonstrated that BSDP could significantly reduce frictional wear in polyurea-based grease systems, exhibiting superior tribological performance compared to conventional molybdenum disulfide (MoS₂)-based additive packages [15]. Beyond these studies, limited research has been conducted on PU additives specifically designed for high-temperature applications. Therefore, continued development of high-temperature additives for PU remains essential to further improve its friction reduction and anti-wear capabilities.

Currently, mechanical mixing is commonly used to incorporate solid additives into greases to enhance their relevant properties [16,17]. However, this method not only readily disrupts stable colloidal structures but also often results in uneven dispersion of additives [18]. Composite materials are increasingly being studied as lubricants to avoid disrupting grease structure and to improve additive dispersibility [19]. In this study, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was incorporated into polyurethane (PU), leading to the successful synthesis of composite (LiTFSI-PU). LiTFSI couples with the carbonyl groups (C=O) in the thickener molecules to form Lewis acid-base complexes [20]. The interaction mechanism between LiTFSI and PU was confirmed through Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The tribological properties of LiTFSI-PU at elevated temperatures were assessed with an Optimal SRV-IV oscillating friction and wear tester. To elucidate the anti-friction and anti-wear mechanisms of LiTFSI-PU, the lubricating film formed during friction tests on steel discs was characterized using XPS and focused ion beam-assisted scanning transmission electron microscopy coupled with energy-dispersive spectroscopy (FIB-STEM/EDS).

2. Experimental Details

2.1. Chemicals and Materials

The reactants (octadecylamine, 4,4-methylenedianiline, toluene diisocyanate) were purchased from Shanghai McLean Biochemical Science and Technology Co., Ltd. (Shanghai, China); Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, purity $\geq 98\%$, was purchased from J&K Chemical Co., Beijing, China); and polyalphaolefin (PAO) base oil was supplied by

Qingdao Lubemater Lubrication Material Technology Co., Ltd. (Qingdao, China). The three-roller grinder (EXAKT80E PLUS, EXAKT Advanced Technologies GmbH, Gelsenkirchen, Germany) with finely adjustable shaft spacing was used to grind the grease.

2.2. Synthesis and Processing of LiTFSI-PU

PU is synthesized via an in situ addition reaction within a base oil. The flow chart illustrating the preparation of LiTFSI-PU is shown in Figure 1. For this study, PAO was selected as the base oil, with a tetraurea thickener formed by reacting octadecylamine, 4,4'-methylenedianiline, and toluene diisocyanate. In the synthesis process, the organic thickener and 6.8 g of PAO base oil were charged into a stainless-steel reactor, homogenized, and heated to 140 °C. Subsequently, 5.1 g of PAO was introduced to dilute the mixture. Upon raising the temperature to 220 °C, the reaction proceeded under isothermal conditions for 20 min before heating cessation. When cooled to 180 °C, an additional 5.1 g of PAO was added to reduce viscosity, followed by the incorporation of LiTFSI. After cooling to ambient temperature, the mixture underwent triple grinding in a three-roller mill, yielding five LiTFSI-PU variants with LiTFSI concentrations of 1 wt%, 3 wt%, 5 wt%, 10 wt% and 15 wt%, respectively.

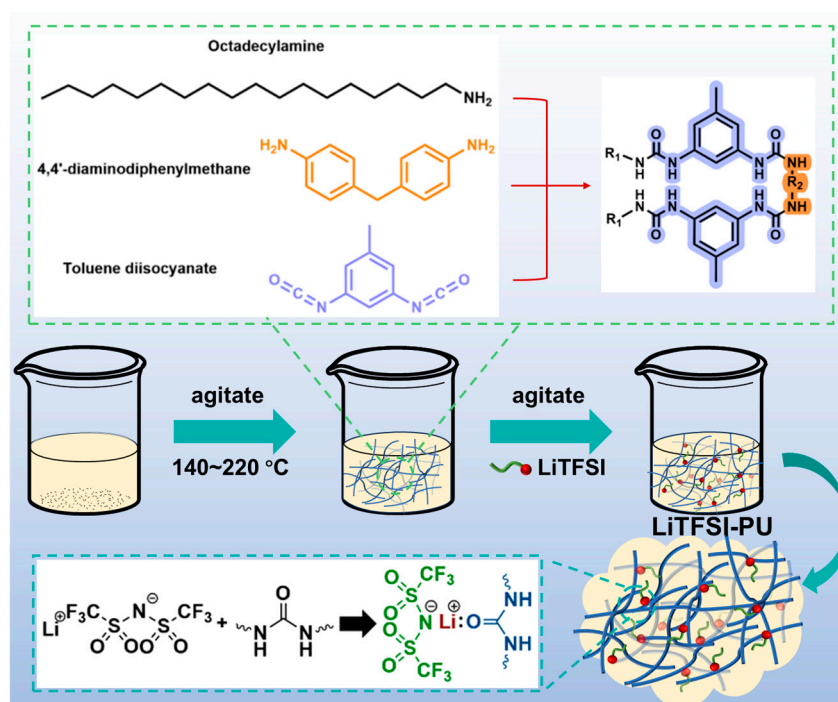


Figure 1. Schematic preparation of LiTFSI-PU.

Thickener fibers in the greases could be obtained by the following method: 10 g of LiTFSI-PU was subjected to repeated hexane washes to eliminate residual PAO base oil, followed by anhydrous ethanol rinses to remove unbound LiTFSI. The purified fibers were then oven-dried at 60 °C overnight.

2.3. Structural and Performance Characterization of LiTFSI-PU

The grease sample was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) using the potassium bromide (KBr) pellet method with a Nicolet iS 10 spectrometer. X-ray photoelectron spectroscopy (XPS) characterization of soap fibers was performed on a Thermo Fisher Scientific K-Alpha spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) operating at 100 W. Microstructural characterization was conducted

using a transmission electron microscope (TEM, JEM-2100PLUS, JEOL, Japan) operating at 200 kV, with images acquired in both conventional TEM mode and annular dark field (ADF) mode.

Steady-state rheological testing of the grease was performed using a rotational rheometer (Anton Paar GmbH, MCR-92, Graz, Austria) equipped with 20 mm parallel plates and a 1 mm gap. Shear measurements were conducted at constant shear rate (100 s^{-1}) and different temperatures (25 and 150°C) to investigate the evolution of grease viscosity over time. The thermal stability of the grease was evaluated using a thermogravimetric analyzer (TGA; STA 449 F5, Netzsch, Selb, Germany) under a nitrogen (N_2) atmosphere with a flow rate of 25 mL/min and a heating rate of 10°C/min over a temperature range of $40\text{--}800^\circ\text{C}$.

To investigate the tribological properties of LiTFSI as a polyurea grease additive, a high-contact-stress ball-on-disc reciprocating oscillation test was conducted by an oscillating reciprocating tribometer (Optimol Instruments Prüftechnik GmbH, Munich, Germany). Figure S1 shows a schematic of the Standard SRV-IV test instrument. An AISI 52100 steel ball (Dong'e County Huaxin Steel Ball Co., Ltd., Dong'e, China. 10 mm diameter, hardness $\sim 626 \text{ HV}$) and a stationary AISI 52100 steel disc (Dongguan Tianqiang Special Steel Co., Ltd., Dongguan, China. 24.00 mm diameter $\times$ 7.88 mm thickness, hardness $\sim 700 \text{ HV}$) were reciprocated against each other with a 1 mm stroke at 25 Hz oscillation frequency. The friction coefficient was automatically recorded via a computer-connected data acquisition system integrated with the SRV micro-tribometer (SRV-V, Optimol Grease Co., Munich, Germany). Following each tribological test, the wear volume of steel discs was quantified using a non-contact optical 3D surface profiler (MicroXAM-800, KLA-Tencor, Milpitas, CA, USA). Simultaneously, 3D optical microscopic images of the wear tracks were acquired to characterize morphology evolution under different LiTFSI grease concentrations. Morphological analysis of the soap fibers before and after treatment with 3 wt% LiTFSI-PU was performed using a scanning electron microscope (SEM; model Sigma 560, ZEISS, Oberkochen, Germany). Surface composition analysis of the worn discs was performed by X-ray photoelectron spectroscopy (XPS). The binding energies of the target elements were determined at a passing energy of 29.35 eV with a resolution of approximately $\pm 0.3 \text{ eV}$, with the binding energy of contaminated carbon ($\text{C } 1s = 284.8 \text{ eV}$) being used as a reference. The Focused Ion Beam (FIB) was utilized to obtain a cross-section of the worn surface; this surface was subsequently observed by Transmission Electron Microscopy (TEM), after which the elemental composition of the surface was analyzed. Prior to the FIB process, a Pt protective film was deposited on the surface.

3. Results and Discussion

3.1. Spectroscopic Characterization

To verify the interaction between LiTFSI and soap fibers, LiTFSI-PU was first analyzed via FTIR. Figure 2a presents the FTIR spectra of LiTFSI and LiTFSI-PU in the range of $800\text{--}2000 \text{ cm}^{-1}$. In the spectrum of the lithium salt-free sample, the peak at 1739 cm^{-1} corresponds to the stretching vibration of the carbonyl group (C=O) in polyurea molecules. Upon incremental introduction of LiTFSI into the polyurea grease, no significant changes in the C=O stretching-vibration peaks were observed at concentrations of 1 wt% and 3 wt%. However, when the lithium salt concentration reached 5 wt%, a distinct absorption peak emerged at 1710 cm^{-1} . This shift is attributed to the lone electron pairs on the carbonyl oxygen undergoing charge transfer to Li^+ ions, which weakens the double-bond character of the C=O group [20]. The IR spectra further revealed that increasing LiTFSI content in the grease resulted in broadening of the C=O stretching band and a redshift to lower frequencies. These studies indicate that the oxygen atom of the C=O group donates its

lone pair of electrons to Li^+ , leading to coordination and the formation of a Lewis acid–base complex.

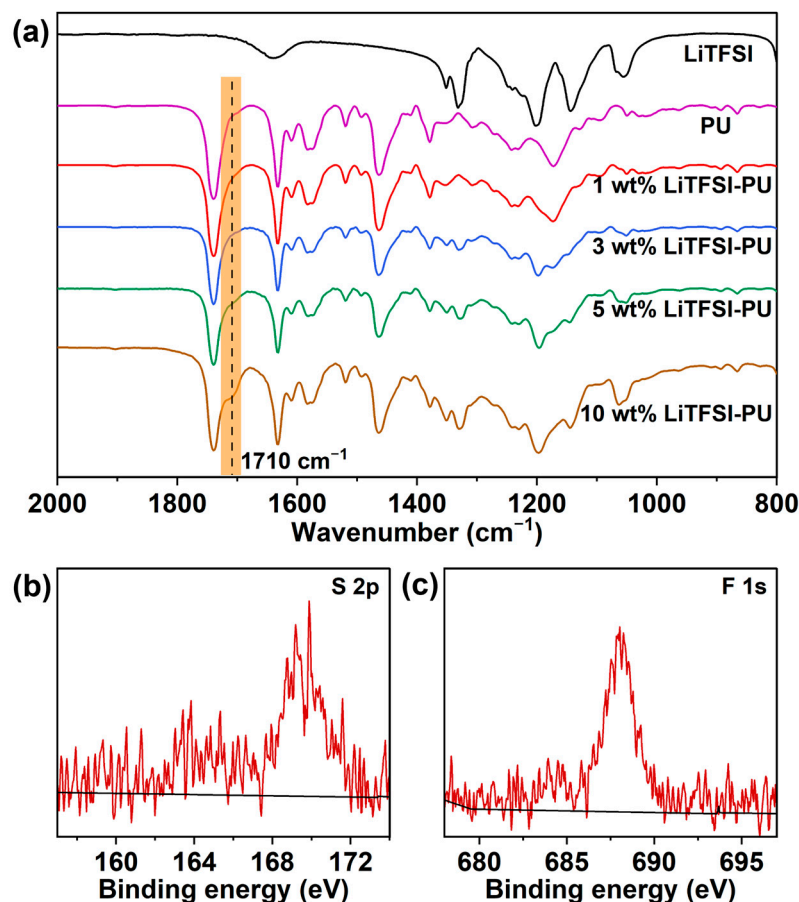


Figure 2. (a) FTIR spectra of LiTFSI, PU, and LiTFSI-PU; X-ray photoelectron spectroscopy (XPS) analysis of the soap fiber obtained from 5 wt% LiTFSI-PU, showing (b) the S 2p and (c) F 1s spectra.

The 5 wt% LiTFSI-PU was washed sequentially with hexane and anhydrous ethanol to isolate thickener fibers. The resulting soap fibers were analyzed via XPS. High-resolution XPS spectra of the soap powder (Figure 3a,b) revealed distinct peaks for S2p at 168.89 eV and F1s at 688.05 eV. Quantitative elemental analysis confirmed the presence of sulfur (0.42 atomic%) and fluorine (1.17 atomic%) in the soap fibers, both characteristic elements of LiTFSI (Table 1). This finding indicates that LiTFSI persists on the soap fibers after grease removal, demonstrating interaction between LiTFSI and the soap fiber structure.

Table 1. Quantitative XPS elemental analysis of soap fibers.

Name	Start BE	Peak BE	End BE	Atomic %
Li1s	59.81	56.57	49.46	2.37
S2p	173.31	169.89	156.46	0.42
C1s	292.66	284.81	278.46	79.95
N1s	409.36	399.36	391.46	10.35
O1s	538.86	530.77	524.46	5.73
F1s	693.66	688.05	677.46	1.17

To validate LiTFSI retention in the soap powder, the morphology and elemental distribution of the base oil and soap fibers were characterized using transmission electron microscopy (TEM) (Figure 3). Figure 3b demonstrates that LiTFSI addition alters the fiber

structure compared to pristine PU. As anticipated, the elemental distribution maps of carbon (C), sulfur (S), and fluorine (F) in the 5 wt% LiTFSI-polyurea sample (Figure 3b) confirm the presence of sulfur and fluorine—elements absent in pure polyurea—within the soap powder even after ethanol washing, while also demonstrating their uniform distribution. The detection of S 2p and F 1s peaks in the XPS spectrum, together with the TEM-EDS elemental images, collectively indicates that LiTFSI is stably bound to the thickener molecules and uniformly dispersed within the structure.

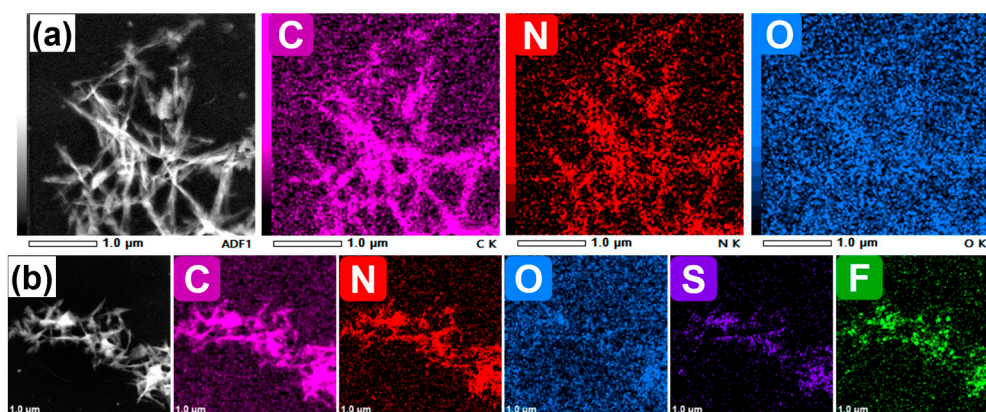


Figure 3. (a) TEM image and corresponding elemental maps of soap fibers from polyurea (PU), showing the distribution of carbon (C), nitrogen (N), and oxygen (O); (b) TEM image and corresponding elemental maps of soap fibers from 5 wt% LiTFSI-PU, showing the distribution of carbon (C), nitrogen (N), oxygen (O), sulfur (S), and fluorine (F).

3.2. Characterization of LiTFSI-PU

Polyurea greases maintain their structural integrity by generating numerous short fibers under shear and establishing new cross-linking points. This compensates for their reduced base oil binding capacity. This mechanism enables the thickener network to continuously release base oil to the friction surface at test temperatures, promoting lubricant film formation even during continuous operation [21]. To investigate the additive's effect on grease shear viscosity, LiTFSI-PU grease was analyzed via steady-state rheometry using an Anton Paar rotational rheometer (20 mm parallel plates, 1 mm gap). Figure 4 shows the viscosity evolution of LiTFSI-PU over time at a shear rate of 100 s^{-1} for 25°C and 150°C . As a colloidal dispersion system stabilized by a thickener-derived 3D network, the grease exhibits distinct rheological behavior. At 25°C (Figure 4a), shear-induced deformation of its colloidal structure manifests as shear thinning. All formulations displayed similar shear-thinning behavior. However, increasing LiTFSI concentrations led to a progressive rise in viscosity. This demonstrates that LiTFSI enhances the grease's structural integrity and shear resistance. The resultant high viscosity improves high-temperature tribological performance. Critically, accelerated disintegration of the thickener fiber network under combined thermal (150°C) and shear stress degrades rheological properties, compromising lubrication effectiveness. At 150°C , both LiTFSI-PU formulations exhibited fluid-like behavior (Figure 4b), indicating structural collapse. Notably, at 15 wt% LiTFSI, this shear-thinning trend diminished, and the grease demonstrated enhanced shear stability, indicating the formation of a more robust soap fiber structure at this concentration. These results suggest that LiTFSI strengthens the thickener network, thereby increasing grease viscosity. This phenomenon is attributed to the lithium salts' complexation with carbonyl groups in the thickener. This complexation introduces additional cross-linking points and intermolecular interactions, thereby improving mechanical strength and shear resistance. In particular, the formation of fiber cross-linking points in LiTFSI-PU under shear resulted in the material

exhibiting a high apparent viscosity in the test. This gives LiTFSI-PU superior structural integrity and minimal oil separation, enabling consistent base oil release to the friction surface and thereby enhancing friction reduction performance. The thermal stability of the grease was evaluated by performing thermogravimetric (TG) analysis under a nitrogen (N_2) atmosphere. As shown in Figure S2, the initial decomposition temperature increased from 231.1 °C to 258.6 °C after the incorporation of LiTFSI. In contrast, the sample containing 3 wt% ZDDP-PU exhibited a lower initial decomposition temperature of 212.5 °C. These results indicate that LiTFSI not only reinforces the fiber network of the thickener but also significantly enhances the thermal stability of the polyurea grease.

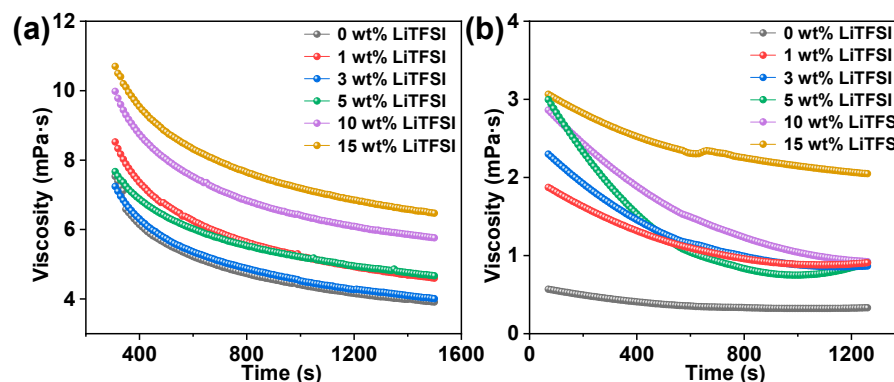


Figure 4. The changes in shear viscosity of LiTFSI-PU over time at a shear rate of 100 s^{-1} , measured at (a) 25 °C and (b) 150 °C.

3.3. Tribological Properties of the LiTFSI-PU

The tribological performance of LiTFSI-PU under high-temperature, high-load, and high-frequency conditions was evaluated using an Optimal SRV-IV oscillating friction and wear tester and compared with that of zinc dialkyldithiophosphate (ZDDP), a conventional anti-wear additive. Figure 5 presents the time-varying friction coefficient (CoF) curves and corresponding wear volume measurements for different concentrations of LiTFSI-PU under various operating conditions. Since most mechanical equipment operates at or near ambient temperature during initial run-in, ambient temperature testing offers fundamental insight into the stability of polyurea grease under shear stress and its ability to sustain lubricating properties. Accordingly, the tribological behavior of LiTFSI-PU was first assessed at 25 °C under a 200 N load. The addition of LiTFSI significantly reduced both the CoF and wear loss (Figure 5a,b). The CoF curve for unmodified PU exhibited considerable fluctuation, with an initial peak of 0.120 during run-in and an average CoF of 0.112 throughout the test. This frictional behavior resulted from inadequate lubrication under high contact pressure in the absence of additives, leading to accelerated wear. In contrast, the incorporation of 1%, 3%, 5%, and 10% (by weight) LiTFSI into PU markedly reduced both the CoF and wear volume. It is worth noting that when the LiTFSI content exceeded 3%, the wear volume increased slightly despite a continued decline in the CoF. This may be attributed to the higher viscosity of the enhanced formulation, which could impede the formation of a continuous lubricating film under friction. Among all tested concentrations, the 1 wt% LiTFSI-PU formulation demonstrated the most effective anti-friction and anti-wear performance, achieving an 8.9% reduction in average CoF (0.102) and a 78.7% decrease in wear volume compared to pure PU. Therefore, 1 wt% LiTFSI is identified as the optimal concentration for minimizing friction and wear at 25 °C under a 200 N load. For comparative purposes, the tribological properties of PU containing 3 wt% ZDDP were evaluated under the same conditions. The results demonstrate that 3 wt%

LiTFSI-PU exhibits a lower coefficient of friction than 3 wt% ZDDP (0.106) at 25 °C under a 200 N load, although the difference in wear resistance between the two is negligible.

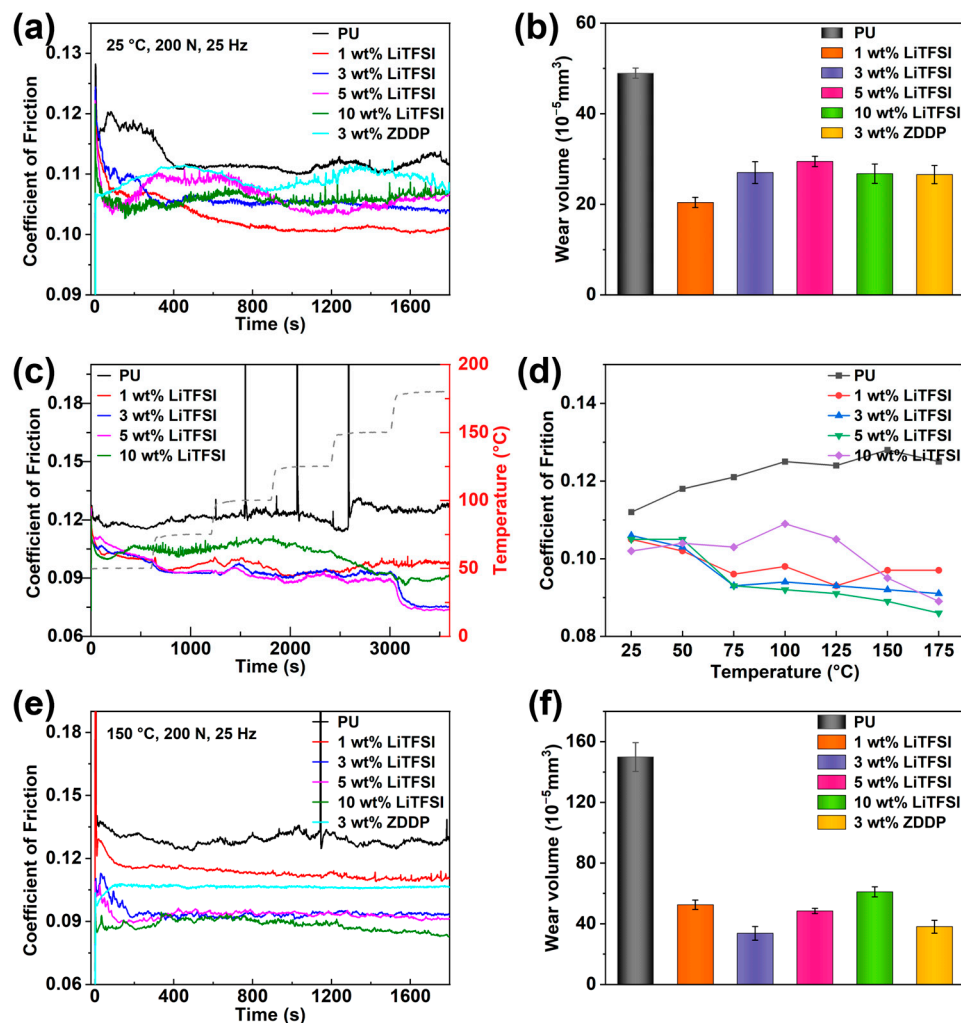


Figure 5. (a) Coefficient of friction (CoF) of PU and LiTFSI-PU under 25 °C and 200 N; (b) corresponding wear volume; (c) CoF curves of PU and LiTFSI-PU at different concentrations over time under varying temperatures (The dashed line in the figure illustrates the evolution of temperature over time. SRV test parameters: 200 N, 25 Hz); (d) average CoF of PU and LiTFSI-PU at different concentrations and temperatures; (e) CoF of PU and LiTFSI-PU under 150 °C and 200 N; (f) corresponding wear volume. SRV test parameters: load: 200 N; frequency: 25 Hz; stroke: 1 mm; temperatures: 25 °C and 150 °C; duration: 30 min.

To investigate the temperature-dependent friction behavior of LiTFSI-PU, friction coefficient measurements were conducted under variable temperature conditions. Figure 5c displays the friction curves for different concentrations of LiTFSI-PU at 200 N over a temperature range of 50–180 °C. As temperature increased progressively, the grease softened, facilitating the formation of a continuous oil film during friction. Further temperature rise reduced the base oil viscosity, necessitating reinforcement from the thickener network to maintain film strength. Notably, the PU exhibited significant friction coefficient fluctuations and experienced lubrication failure. This film rupture led to direct asperity contact and loss of film continuity, potentially accelerating wear, indicating diminished grease viscosity and structural stability at elevated temperatures. The addition of LiTFSI to PU substantially reduced the friction coefficient, eliminating severe fluctuations and lubrication failures. This demonstrates that LiTFSI enhances the thickener's structural integrity,

thereby ensuring lubrication stability across a broad temperature range. However, when temperature reached 150 °C, the friction coefficients of higher-concentration LiTFSI-PU samples decreased abruptly. Based on these variable-temperature friction tests, LiTFSI-PU was selected for additional testing at 150 °C and 200 N.

As shown in Figure 5d, the fluctuation amplitude of the friction coefficient for all LiTFSI-PU concentrations at 150 °C was smaller than that observed at 25 °C, indicating better performance at elevated temperatures. This improvement may be attributed to the thermal sensitivity of LiTFSI, which promotes the formation of a protective film on the friction pair surface under high-temperature conditions, thereby enhancing lubrication and wear resistance. At 150 °C, the friction coefficient of unmodified PU showed significant fluctuations with sharp peaks throughout the test, eventually stabilizing around 0.130 after the run-in period. In contrast, the lubrication performance improved consistently with increasing LiTFSI content, reflected by a gradual reduction in the friction coefficient. The 10 wt% LiTFSI-PU formulation achieved the most substantial friction reduction under these conditions, with the average coefficient decreasing to 0.088—a reduction of 32.3% compared to pure PU. Figure 5e shows the corresponding wear volumes of the friction tracks after testing. Without additives, PU experienced severe wear following the high-temperature test. The incorporation of LiTFSI provided effective protection to the friction pair at high temperature, resulting in significantly reduced wear volume. The 3 wt% LiTFSI-PU formulation demonstrated the best anti-wear performance at 150 °C, reducing wear by 77.5% compared to the base PU. For comparison, the tribological properties of PU containing 3 wt% ZDDP were evaluated under the same conditions. The results confirm that LiTFSI outperformed ZDDP in both the friction coefficient and wear volume at elevated temperatures.

Figure 6 shows the morphology and depth of wear scars on the lower steel disc lubricated with PU, 3 wt% LiTFSI-PU, and 3 wt% ZDDP-PU at different temperatures. The morphology and depth of the wear scars are consistent with the wear volume results shown in Figure 5. The color of the Fe substrate is set to pink, transitioning to dark blue with increasing wear depth. The wear depth profile is obtained by scanning along the dashed line in the 3D morphology image. When pure PU was used as the lubricant, severe wear was observed on the steel disc surface. At 25 °C (Figure 6a,b), the wear width reached 0.4 mm with a depth of 1.5 µm, accompanied by pronounced abrasive grooving. In contrast, the wear scars became significantly smoother and shallower with the addition of either LiTFSI or ZDDP. The wear depth was reduced to approximately 1.0 µm (Figure 6c–f). Notably, the wear scars formed with ZDDP were shallower, correlating with the lower wear volume shown in Figure 5. At the elevated temperature of 150 °C, the anti-wear effects of both additives became more evident. Under PU lubrication (Figure 6g,h), the wear width and depth increased to 0.6 mm and 3.0 µm, respectively, with visible deep grooves and extended scar morphology due to inadequate lubrication. The addition of LiTFSI or ZDDP substantially improved wear resistance, reducing both the wear width (to 0.5 mm) and depth (to 1.5 µm). As shown in Figure 6i–l, at 150 °C, LiTFSI-PU resulted in shallower wear scars compared to ZDDP-PU. This improvement can be attributed to the formation of a complex tribo-film by LiTFSI during friction, which reduces direct contact between sliding surfaces and thereby enhances anti-wear performance. As a result, the wear scars became shallower and narrower, leading to significantly reduced wear loss.

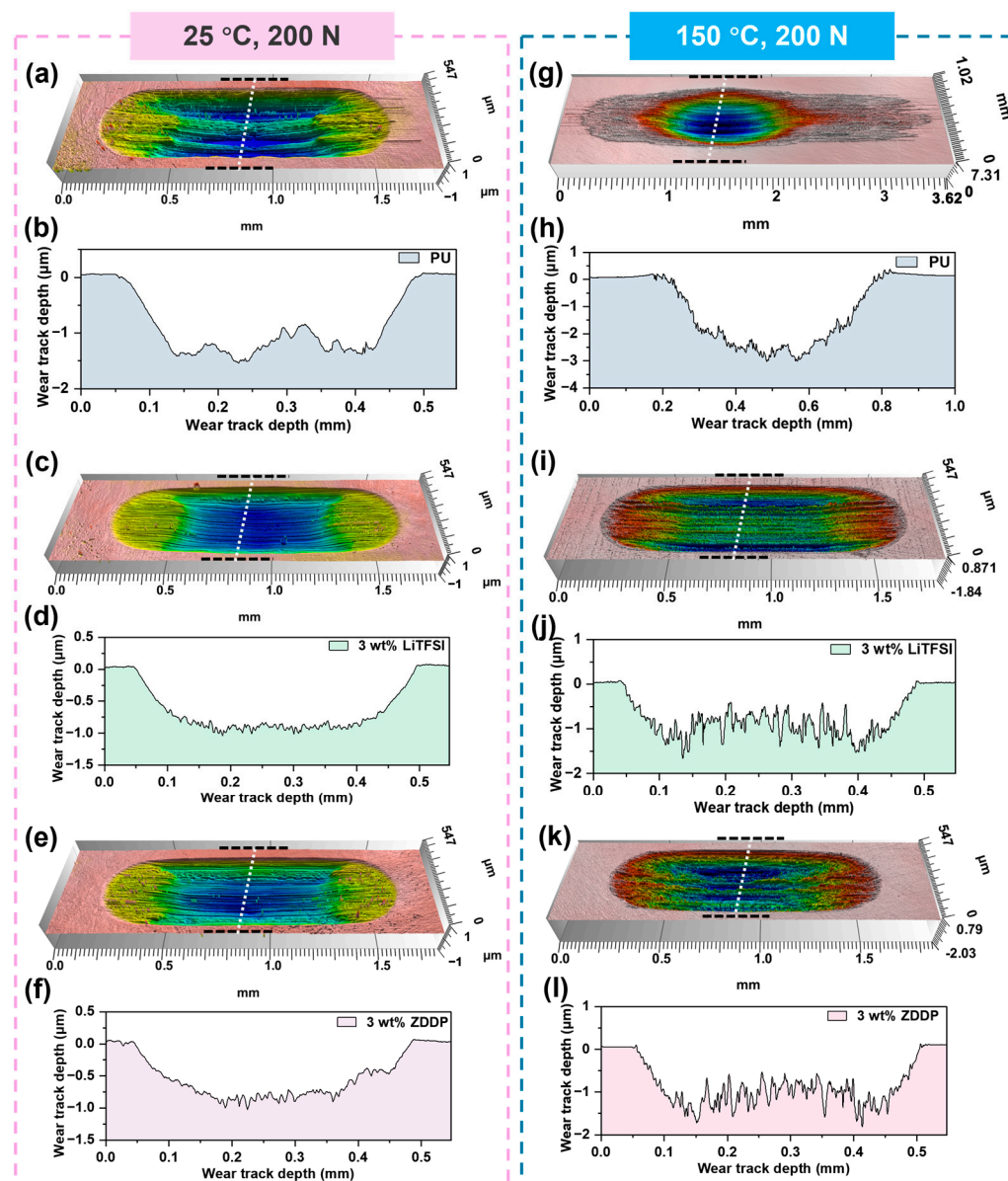


Figure 6. Under conditions of (a–f) 25 °C and (g–l) 150 °C, wear scar morphology and depth profiles were characterized on the lower steel discs lubricated with: pure PU (a,b,g,h), 3 wt% LiTFSI-PU (c,d,i,j), and 3 wt% ZDDP-PU (e,f,k,l). The SRV tests were performed under the following parameters: load: 200 N; frequency: 25 Hz; stroke: 1 mm; temperatures: 25 °C and 150 °C; duration: 30 min.

3.4. The Mechanism of Lubrication of the LiTFSI-PU

XPS analysis was performed on wear scars following lubrication with 3 wt% LiTFSI-PU to characterize the friction film properties and elucidate the lubricating enhancement mechanism. This analysis was performed under both ambient (25 °C) and elevated temperature (150 °C) conditions. Figure 7a–f present C 1s, N 1s, O 1s, F 1s, S 2p, and Fe 2p spectra, respectively. Notably, the C, N, F, and Fe elemental spectra exhibited nearly identical peak profiles and binding energies across both temperature conditions (Figure 7a–d,f). This similarity suggests comparable tribo-chemical reactions occurring within the lubricant system. Deconvolution of the C 1s spectrum at 25 °C, 200 N revealed four distinct components: O=C-O (283.0 eV), C-C/C-H (284.8 eV), C-N (286.2 eV), and C=O (288.4 eV), consistent with polyurea structural characteristics [22]. However, the O=C-O peak at 283.0 eV was notably absent in the 150 °C spectrum, implying thermal decomposition or participation of this functional group in high-temperature interfacial reactions. The N 1s spectra displayed

a prominent peak at 399.6 eV corresponding to C-N bonding [23], corroborated by the C 1s spectral features. This combined evidence strongly indicates polyurea molecular adsorption on the steel surface with subsequent tribo-film formation. O 1s analysis revealed temperature-dependent chemical states: At 25 °C, four components were identified corresponding to Fe_2O_3 (529.6 eV), FeO (529.8 eV), Fe_3O_4 (530.2 eV), and $\text{Fe}(\text{OH})_3$ (531.3 eV), along with a $\text{C}=\text{O}/\text{FeSO}_4$ contribution at 532.2 eV [22]. The high-temperature condition (150 °C) simplified the oxygen speciation, showing only two predominant peaks associated with iron oxides.

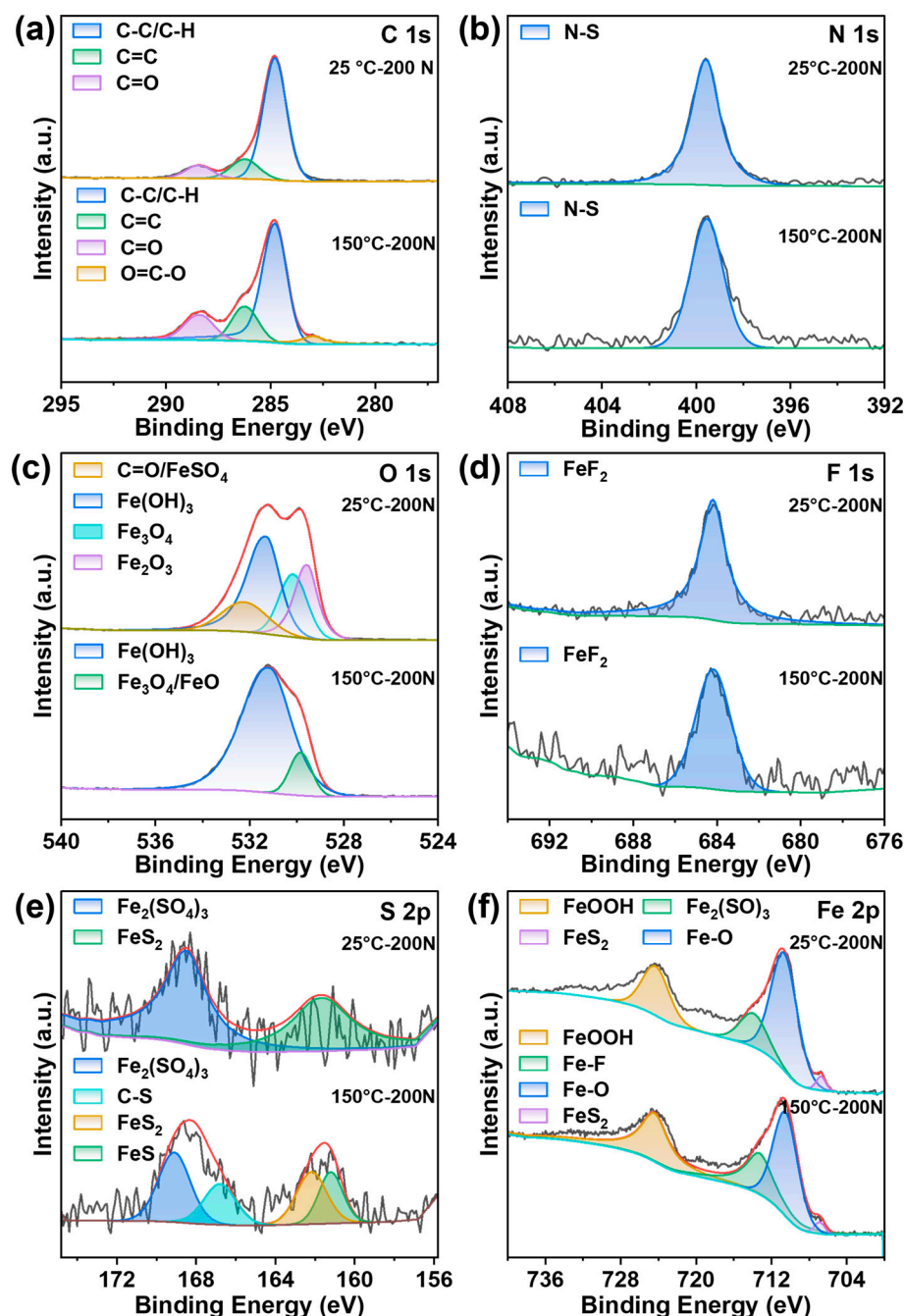


Figure 7. (a–f) The high-resolution XPS spectra of a C 1s, N 1s, O 1s, S 2p, F 1s, and Fe 2p of the wear scars after lubrication with 3 wt% LiTFSI-PU at 25 °C and 150 °C (load: 200 N; frequency: 25 Hz; stroke: 1 mm; temperatures: 25 °C and 150 °C; duration: 30 min).

Notable variations emerged in the S 2p spectra of lubricated wear scars between 25 °C and 150 °C conditions (Figure 7d). At 25 °C, 200 N, the S 2p spectrum exhibited

two characteristic peaks at 168.6 eV ($\text{Fe}_2(\text{SO}_4)_3$) and 161.7 eV (FeS_2), indicative of basic sulfur-containing compounds [24]. Elevating the temperature to 150 °C induced significant spectral modifications, revealing five distinct components: $\text{Fe}_2(\text{SO}_4)_3$ (169.1 eV), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (168.0 eV), C-S bonding (166.8 eV), FeS_2 (162.2 eV), and FeS (161.1 eV) [25]. This chemical complexity correlates with the lower friction coefficient observed at 150 °C compared to 25 °C, demonstrating enhanced tribo-film stability through multi-component protective layer formation. The F 1s spectrum displayed a persistent peak at 684.2 eV (Figure 7e), characteristic of FeF_2 formation [26]. Iron chemical state analysis through Fe 2p spectra showed structural consistency across temperatures: Both conditions yielded four resolved peaks at 706.7 eV (FeS_2), 710.6 eV (Fe oxides), 713.3/714.2 eV (Fe^{3+}), and 724.3 eV (FeOOH) [27]. The 0.9 eV positive shift in Fe^{3+} -associated peaks at 150 °C suggests modified oxide layer properties [28]. Cross-referencing with O 1s data confirms iron oxide speciation, including $\text{Fe}(\text{OH})_3$, Fe_2O_3 , and Fe_3O_4 . Spectral evidence from S 2p and F 1s analyses collectively indicates synergistic interfacial reactions involving S, O, and F elements, generating $\text{Fe}_2(\text{SO}_4)_3$, FeS_2 , and FeF_2 phases [14]. These findings corroborate our hypothesis that two mechanisms—physical adsorption and tribo-chemical reaction—are involved in the lubrication process. Physical adsorption of LiTFSI-PU onto the friction surfaces clearly occurred under both test conditions. However, elevated temperature (150 °C) promoted a tribo-chemical reaction, as evidenced by the more complex composition of the protective tribo-film. The synergistic effect of these mechanisms significantly contributed to low friction and reduced wear. To investigate the structural degradation behavior of LiTFSI-PU during friction, the 3 wt% LiTFSI-PU formulation was selected. Scanning electron microscopy (SEM) images of the soap fibers were obtained before and after testing under different conditions (25 °C, 200 N and 150 °C, 200 N) for comparative analysis. As shown in Figure S3a, the thickener network of the untreated 3 wt% LiTFSI-PU exhibits a dense morphology with well-defined fibers. After 30 min of friction testing at 25 °C under a 200 N load, the fiber structure showed signs of disruption (Figure S3b). This effect became more pronounced at 150 °C, where the thickener network no longer remained aggregated and the fibrous architecture appeared noticeably sparse (Figure S3c). Consistent with these observations, Kuhn Et Al. reported similar degradation of thickener fibers due to shear-induced stress during grease friction, using optical measurement techniques [29].

To gain deeper insight into the friction film and explore potential mechanisms of lubrication enhancement, focused ion beam (FIB) technology was used to prepare thin cross-sections from the wear tracks on steel surfaces lubricated with 3 wt% LiTFSI-PU at 150 °C under a 200 N load. Prior to FIB processing, the friction film was protected with a platinum (Pt) coating. Figure 8a shows a scanning electron microscopy (SEM) image of the cross-section, revealing a friction film layer on the steel substrate. The complex interfacial interactions during friction led to a non-uniform thickness distribution of this film [30]. Figure 8b–f present transmission electron microscopy (TEM) images of the FIB-prepared cross-section. Figure 8c provides a high-resolution view of the region marked in Figure 8a, where the film thickness ranges from approximately 80 to 140 nm (Figure 8b). High-resolution TEM (HRTEM) images of the areas annotated in Figure 8d–f were obtained to further characterize the chemical nature of the friction film. The XPS results presented above suggest that the friction film likely consists of a multi-component protective layer containing iron oxide, iron fluoride, iron sulfide, and carbon-based oxides. However, higher-magnification imaging reveals that the friction film in both the central region (Figure 8e) and near the steel substrate (Figure 8f) exhibits an amorphous structure. This amorphous structure likely results from the decomposition and reorganization of molecular fragments of LiTFSI-PU under high contact pressure and friction-induced reactions with the substrate [31]. High-angle annular dark-field (HAADF) imaging (Figure 8d)

and energy-dispersive X-ray spectroscopy (EDS) mapping of the cross-section (Figure 8g) reveal a stratified composition. Line-scan profiles across the region indicated in Figure 8d show significant enrichment of oxygen (O) and iron (Fe) within the friction film. Additionally, trace amounts of sulfur (S), fluorine (F), carbon (C), and nitrogen (N) are present. The detection of S and F suggests that TFSI[−] anions from LiTFSI-PU may adsorb electrostatically onto the substrate and participate preferentially in tribo-chemical reactions, contributing to the formation of a lubricating film. These results support a synergistic mechanism involving both physical adsorption and tribo-chemical reactions, leading to the formation of an amorphous friction film containing O, Fe, S, F, C, and N on the substrate surface. This layer effectively prevented direct metal-to-metal contact while providing enhanced friction reduction and anti-wear performance.

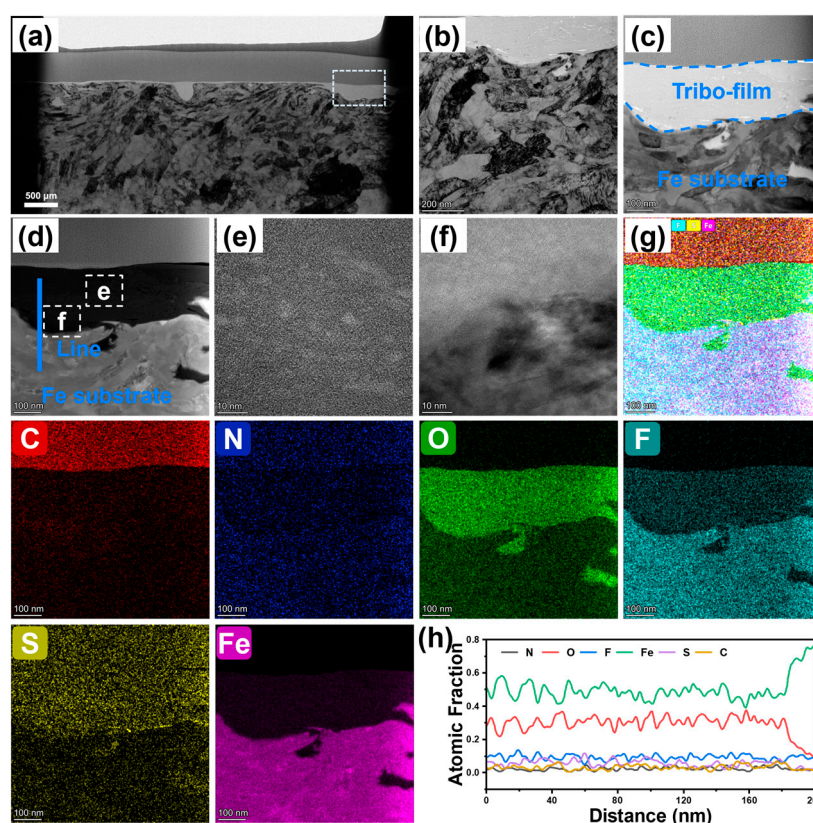


Figure 8. Cross-sectional TEM and EDS characterization of the friction film formed on the worn surface lubricated with 3 wt% LiTFSI-PU at 150 °C under a 200 N load. (a) Transmission electron microscopy (TEM) image of the sample topography after focused ion beam (FIB) milling. (b–d) TEM image of the region boxed in (a). (e,f) HRTEM images acquired from the designated positions e and f on the friction film. (g) Element distribution map of the boxed area in (a). (h) Elemental distribution profile across the friction film along the line marked in (d).

The lubrication mechanism of LiTFSI-PU is schematically illustrated in Figure 9. During ball-on-disc sliding friction, shear forces gradually release the base oil from the grease to participate in lubrication (Figure 9b). Under high load and elevated temperature conditions, coupled with the interaction of the counter-faces, the steel ball surface develops a positive charge. This charge preferentially adsorbs the anion TFSI[−] in LiTFSI-PU. Subsequently, residual LiTFSI-PU components adsorb via electrostatic interactions, forming a physical adsorption film (Figure 9c). Finally, as demonstrated in Figure 9d, under the combined influence of temperature and pressure, the adsorbed TFSI[−] undergoes a tribo-chemical reaction with the counter-face. This reaction forms a boundary film composed of compounds

such as Fe_2O_3 , Fe_3O_4 , FeS_2 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}(\text{OH})_3$, FeF_2 , etc. [32]. This synergistic formation of adsorption and tribo-chemical reaction films underpins the excellent tribological properties of LiTFSI-PU.

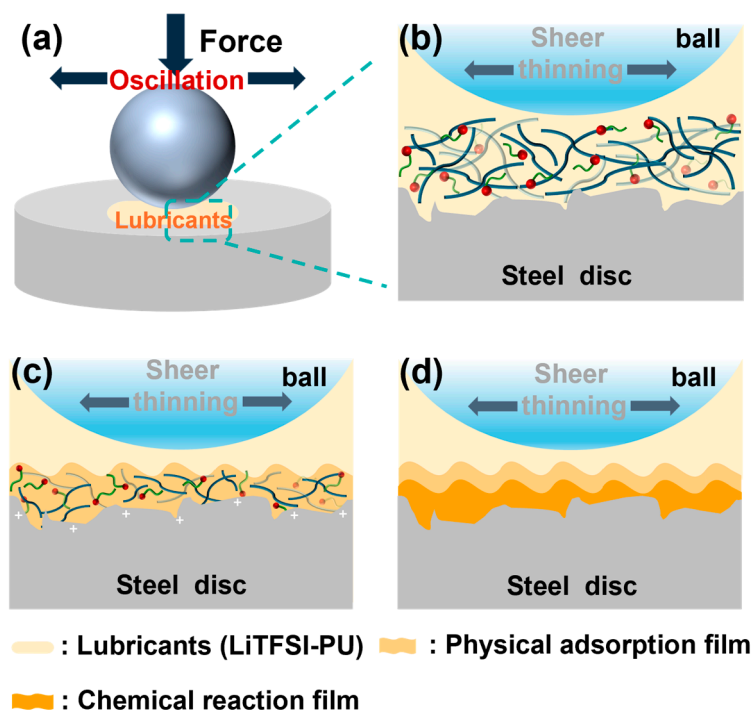


Figure 9. Schematic of the lubrication mechanism of LiTFSI as a PU additive. (a) Schematic diagram of Ball-Disc reciprocating friction test apparatus under high contact stress. (b) The initial state of the friction process. (c) The running-in period. (The white plus sign in the figure symbolizes the positive charge that the friction pair acquires during friction.) (d) The steady lubricated period.

4. Conclusions

This study was designed to enhance the tribological performance of polyurea (PU) grease under high-temperature conditions by modifying the thickener molecules with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), with comparative evaluation against the conventional lubricant additive zinc dialkyldithiophosphate (ZDDP). LiTFSI was successfully incorporated into the PU matrix through coordination with the $\text{C}=\text{O}$ groups in the thickener molecules. The viscosity–temperature behavior and tribological properties of LiTFSI-PU at various concentrations were systematically investigated, and the underlying friction mechanism was thoroughly examined. The main conclusions are as follows: (i) Chemical characterization confirmed the coordination between Li^+ ions (from LiTFSI) and carbonyl groups ($\text{C}=\text{O}$) within the thickener molecules in the LiTFSI-PU system. (ii) The incorporation of LiTFSI introduced additional molecular cross-linking sites, reinforcing the thickener network structure. LiTFSI-PU exhibits not only improved viscosity–temperature performance at $150\text{ }^\circ\text{C}$ but also enhanced thermal stability, with the initial decomposition temperature of the 3 wt% formulation increasing to $258.6\text{ }^\circ\text{C}$. (iii) As an enhancing additive, LiTFSI demonstrated significant anti-friction and anti-wear performance at elevated temperatures ($150\text{ }^\circ\text{C}$). Compared with pure PU, LiTFSI-PU achieved a 32.3% reduction in the coefficient of friction (CoF) and a 77.5% decrease in wear volume. Surface analysis of the wear tracks revealed that the enhancement mechanism originates from a synergy between grease adsorption and thermally activated tribo-chemistry, leading to the formation of a composite protective film on the worn surface, containing iron, fluorine, sulfur, oxygen, and other elements. This film contributes to exceptional anti-friction and anti-wear

properties under high-temperature conditions. The developed coating effectively alleviates accelerated wear in transmission components at high temperatures, providing valuable insights for the design and development of novel high-temperature resistant additives.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants13100452/s1>, Figure S1: Schematic diagram of the Optimal SRV-IV device; Figure S2: TG curves of various grease samples measured in a nitrogen atmosphere over a temperature range of 40–800 °C; Figure S3: SEM images of soap fibers containing 3 wt% LiTFSI-PU: (a) untreated; (b) tested at 25 °C under 200 N; (c) tested at 150 °C under 200 N.

Author Contributions: Conceptualization, S.N. and K.G.; methodology, X.W. (Xinhu Wu) and K.G.; validation, X.W. (Xiaozhen Wang), B.L. and J.L.; formal analysis, S.N. and J.L.; investigation, Q.Z. (Quan Zhou); resources, X.W. (Xinhu Wu) and X.W. (Xiaobo Wang); data curation, S.N. and K.G.; writing—original draft preparation, S.N.; writing—review and editing, X.W. (Xinhu Wu), J.L. and K.G.; visualization, S.N.; supervision, B.W., Q.Z. (Qin Zhao) and K.G.; project administration, B.W. and K.G.; funding acquisition, B.L. and K.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB047030102), Qingdao Natural Science Foundation (25-1-1-218-zyyd-jch), Key Research and Development Program of Shandong Province (2022CXGC020309), and National Natural Science Foundation of China (51975560).

Data Availability Statement: The authors declare that all the relevant data are available within the paper or from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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