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Tribology and Rheology of Polypropylene Grease with MoS_2 and ZDDP Additives at Low Temperatures

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Abstract: Polypropylene (PP) grease is a type of lubricating grease with excellent low-temperature performance. The wear and friction performance of steel/steel couples lubricated with PP grease containing molybdenum disulfide (MoS_2), zinc dialkyldithophosphate (ZDDP) and MoS_2/ZDDP as additives at low temperatures was investigated using an Optimol SRV reciprocating tester. Compared with MoS_2 or ZDDP as single additives, the combination of MoS_2 and ZDDP resulted in outstanding tribological properties, especially for higher-load, longer-duration and low-temperature working conditions. The analysis of the wear surface indicated that MoS_2 not only adhered to the steel surfaces to form a solid film, but also combined with ZDDP to form a tribofilm. The active components of the additives reached the metal surfaces effectively, indicating that the polymer system did not interfere with the function of the additives. The rheological experiment results also showed that PP grease with additives can maintain stable viscoelasticity, viscosity recovery rates and ductility at low temperatures.

Keywords: PP grease; MoS_2; ZDDP; tribological and rheological properties; low temperature

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1. Introduction

Polypropylene grease has been acknowledged as a promising grease due to its outstanding oxidation and thermal stability and its long operating life, especially at low working temperatures [1]. The possible application of PP as a thickener for grease was first reported in the late 1950s [2–5]. SKF tested the lifetime of PP grease with an ROF testing machine and found that it can reach more than 5000 h [6]. Gonçalves et al. [7] also conducted a series of studies on PP grease, illustrating its long grease life and excellent oxidation stability. A United States patent [8] reported that PP grease had good oil bleeding characteristics at 0 °C. Muller et al. [9] found that PP grease has excellent start-up performance even at −65 °C. Thus, PP grease has good prospects for application in windmills, cooling units and other equipment [8].

With the complexity of modern mechanical systems and the severe demands of application conditions, additives have become important factors in endowing and improving the lubrication performance of greases under harsh working conditions [10–13]. ZDDP is a typical multifunctional lubricating additive, which can play the triple role of antioxidation, antiwear and corrosion inhibition [14]. Since the patent was reported in 1944 [15,16], ZDDP has been widely studied and applied. To date, it is still the best antiwear and antioxidant additive [17]. However, its tribofilm may also increase friction [6,18–21]. In addition, when bearings operate under harsh working conditions, such as high loads for long running times, rough bearing surfaces and low temperatures, PP grease with ZDDP alone is not sufficient, and other additives are required to obtain good tribological properties. Among the numerous additives, solid additives not only effectively enhance the antiwear and antifriction performance of the substrate, but also display a greater stability over a wide temperature range [22]. The most common example is in low-temperature environments such as aerospace/space applications, where the viscosity of liquid lubricants increases or even solidifies, leading to lubrication failure [23,24]. The traditional solid additive MoS_2 is frequently used for this purpose due to its reliable operating ability over a wide temperature range, especially at low temperatures. There are many reports about the combination of ZDDP and MoS_2, which can effectively improve the friction-reducing performance of grease [25,26]. ZDDP can slow down the oxidation of MoS_2 and hinder the formation of the high-friction product MoO_3 to prolong the service life of the solid additives [25]. Thus, the combination of solid additives and ZDDP can overcome the challenges faced by lubricants in low-temperature conditions.

There are only a few reports on the effect of additives on PP grease in the existing literature. Dixena et al. [27] investigated the tribological performance of PP grease containing ZDDP at 75 °C. The results of both four-ball and SRV tests showed that the addition of ZDDP was helpful in improving the extreme pressure properties of the base grease with minimal reduction in wear but no effect on friction reduction. Shu et al. [28] studied the synergistic performance of PP grease with ZDDP and MoDTC as additives. Compared with ZDDP alone, the friction reduction and antiwear properties of the base grease could be effectively improved by mixing the ZDDP and MoDTC as additives at different tested temperatures (40, 80 and 120 °C).

However, all the above tribological experiments on PP grease were carried out at conventional temperatures. It is well known that PP grease is a non-polar grease with excellent low-temperature performance [1,6,29]. Additives in non-polar greases can more easily reach the metal surface than in soap-based greases [1]. To date, the effect of MoS_2 and ZDDP on the tribological properties of PP grease has not been reported in low-temperature conditions. Therefore, it is particularly valuable to study whether MoS_2 and ZDDP have a synergistic lubrication effect on PP grease, especially under low-temperature, high-load and long-term working conditions.

In addition to the PP grease system, test conditions and related parameters, such as wear-testing apparatus, relative motion mode and applied load also play a significant role in controlling the wear behavior of materials. With the exception of the rolling element bearings of road wheel hubs, there are also many grease-lubricated bearings that undergo oscillating motion rather than continuous rotary motion, such as the vehicle chassis, steering swivels and the ball joints of steering linkages. Therefore, in this study, the tribological performance of PP grease with the addition of MoS_2 and ZDDP was examined using an SRV reciprocating tester at a temperature range from 25 to −15 °C. The effect of the additives on the viscoelasticity and thixotropy behaviors of PP grease at low temperatures was investigated using a rheometer. The wear morphology, elemental distribution and chemical state of the wear scars of the lower steel plate were analyzed using a three-dimensional (3D) optical surface profiler, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). This work enhances the present understanding of how PP grease with additives behaves at low temperatures, which is valuable for its practical applications under harsh working conditions.

2. Materials and Methods

2.1. Materials

Two PP samples, one (M_1) with M_w = 12,000 and M_w/M_n = 2.4 and one (M_2) with M_w = 340,000 and M_w/M_n = 3.5, were purchased from Sigma Aldrich, St. Louis, MO, USA. Poly-α-olefins (kinematic viscosity = 45.40 mm^2/s (40 °C) and viscosity index = 132) as the base oil were purchased from Mobil Corporation, Irving, TX, USA. MoS_2 (thin sheet, average particle size of 3.5 μm) was obtained from Daizo Corporation, Osaka, Japan. ZDDP (basic zinc salt of bisoctylthiophosphate, S content is 13.50–16.00 wt.%) was purchased from the Jinzhou Huifa Tianhe Chemical Co., Ltd., Jinzhou, China. Petroleum ether was acquired from Tianjin Kemiou Reagent Co., Ltd., Tianjin, China.

2.2. Preparation of Greases

The grease thickener content was 10 wt.% and the mixing ratio of PP was M_1:M_2 = 80:20 wt.%. First, the two PPs with different molecular weights were mixed with the base oil in a certain proportion. This mixture was placed into a steel reactor with a volume of 50 mL. And then, the reactor was tightened and put into an oven with a constant temperature of 240 °C. Two quench cycles were required throughout the whole synthesis process. The cooling process was about 0.5–1 min, and the PP grease dropped to room temperature or slightly below. The whole synthesis time was about 12 h.

After completing the preparation process of the pure PP grease, the additives (MoS_2, ZDDP and MoS_2/ZDDP) were added in a certain proportion. The amounts of MoS_2 used were 2.0, 3.0, 4.0, 5.0 and 6.0 wt.%. The amounts of ZDDP used were 1.0, 1.5, 2.0 and 2.5 wt.%. The additive amounts of MoS_2 and ZDDP in MoS_2/ZDDP grease were 5.0 wt.% and 1.5 wt.%, respectively. The order in which the additives were added was as follows: A single additive was directly mixed with the pure grease. For the MoS_2/ZDDP grease, ZDDP and the pure PP grease were firstly mixed together thoroughly, and then MoS_2 was added. Finally, each grease sample needed to pass through a mill three times to obtain homogenized grease. The dropping points of all the greases were within 143 ± 3 °C according to the national standard GB/T 3498.

2.3. Characterization of Tribology

The tribological properties of the grease samples were tested using a ball-on-plate tribometer (Optimol SRV-V Instruments, Munich, Germany). The friction pair consists of an upper steel ball (AISI52100 steel ball with a diameter of 10 mm, HRC59–64, Ra = 0.017 μm) and a lower steel plate (AISI52100 steel plate with dimensions of 24 mm × 7.85 mm, HRC59–61, Ra = 0.068 μm). Before the friction test, the steel plates and balls were ultrasonically cleaned with petroleum ether. According to the standard ASTM D5707, a small amount of the tested grease (about 0.15 g) was placed on the cleaned lower test plate by using a caliper. The cleaned test ball was placed on the top and in the middle of the grease specimen, so that the grease made a symmetrical circular pad between the ball and plate. In order to prevent water vapor from condensing on the steel plate, in addition to the grease that had been placed, the remaining portion of the steel plate also needed to be covered with the tested grease. The humidity sensor was also placed inside the SRV chamber during the entire tribological experiment to monitor the moisture content. The humidity was maintained at 20–30% during the entirety of the experiments.

The experimental conditions were test temperatures of 25, 0 or −15 °C, a stroke length of 1 mm, a frequency of 50 Hz, a running time of 30 or 360 min and an applied load ranging from 200 to 800 N (corresponding contact pressure from 2.74 to 4.35 GPa). Each test was repeated three times. The experimental device is shown in Figure 1 and the cooling oil circulates in the arrows' direction.

A 3D non-contact optical surface profiler (Zygo, Middlefield, CT, USA, ZeGage) was employed to measure the wear volume of the lower plates after each SRV test. The average wear volumes were measured three times. SEM (Hitachi, Tokyo, Japan, TM-3000) was used to observe the wear scars on the steel plates. Energy-dispersive spectroscopy (EDS, Bruker, Billerica, MA, USA, QUANTAX 70) was used to analyze the elemental composition on the rubbing surface. The chemical states of the elements of the wear surfaces were analyzed by XPS (Thermo Fisher Scientific, Waltham, MA, USA, ESCALAB 250Xi).

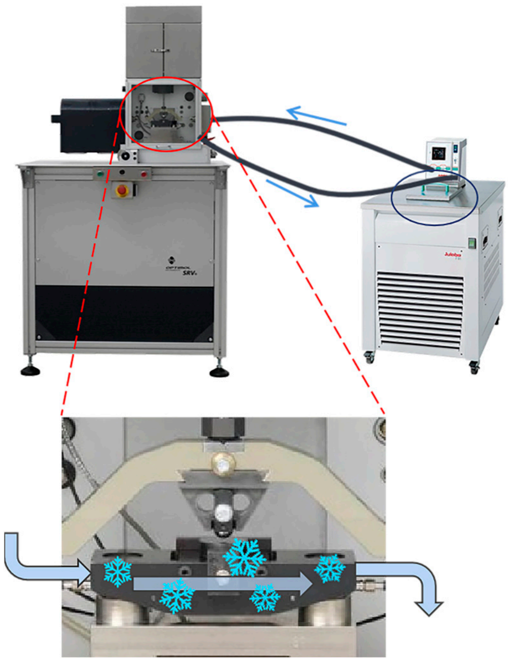

Figure 1. Low-temperature tribological device.

2.4. Characterization of Rheology

An Anton Paar MCR302 rheometer from Austria was used to test the rheological properties of the PP grease. The rough plate–plate geometry PS25 (diameter of 25 mm, roughness depth of 4–7 μm, and gap of 1 mm) was used in all rheological measurements. The grease sample was added between the two plates and any excess sample was removed after the upper plate was pressed down. The grease sample was left standing at the test temperature for 10 min. The rheological experiments were usually repeated two times. For each test, it was necessary to place a new grease sample. All the rheological experiments were conducted at three different tested temperatures (25, 0 and −15 °C). The Peltier temperature control system (H-PTD200) was fitted to the rheometer to maintain a stable temperature during the test, and we also continuously supplied dry air to prevent water from condensing on the plate.

Two sets of experiments for the viscoelastic characterization were conducted. The first group was amplitude sweep experiments with a frequency of 1 Hz, and the shear strain (γ) varied from 0.01% to 100%. The second group was frequency sweep experiments with a shear strain of 0.1%, and the frequency varied from 0.01 rad/s to 100 rad/s.

The thixotropy experiment was conducted using the following steps. The test was divided into three stages. The shear rate of the first stage was 0.1 s^{-1} for 100 s to simulate the static state of the grease. The second stage applied a high instantaneous shear rate (100, 500 and 1000 s^{-1}) for 1 s or applied a different shear time (1, 10, 100 s) with a shear rate of 100 s^{-1} to simulate the running process. The third stage had the same shear rate as the first stage, and was monitored for 180 s to evaluate the recoverability of the grease.

3. Results

3.1. Influence of Additive Concentrations on the Tribological Properties of PP Grease

ZDDP as an additive in PP grease has shown good friction reduction and antiwear performance [28]. Due to the components and thickener of the PP grease in this study being different from those in previous reports, the effect of ZDDP concentration on the tribological properties of the PP grease was carried out at 25 °C for 0.5 h; the results are shown in Figure 2.

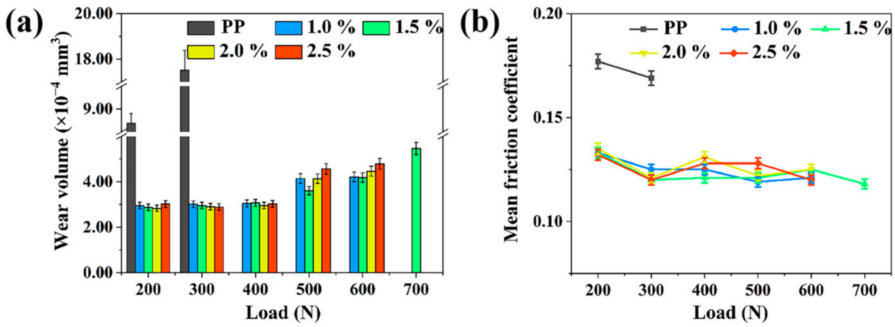

Figure 2. (**a**) Wear volumes and (**b**) mean friction coefficients of PP grease with different concentrations of ZDDP (frequency = 50 Hz, stroke = 1 mm, duration = 30 min and temperature = 25 °C).

As the applied loads increased from 200 to 700 N, the pure PP grease could only run at 300 N as there was a breakdown of the lubricating film with an applied load of 400 N. Only the PP grease with 1.5 wt.% ZDDP ran the whole process at 700 N, increasing the load of the pure PP grease by 133%. When the load was varied from 200 to 400 N, the wear volumes were ~3 × 10^{-4} mm^3 with different ZDDP contents, and all were significantly smaller than that of the pure PP grease. However, as the load increased up to 500 N, the wear volume began to increase. At an applied load of 700 N, the wear volume of 1.5 wt.% ZDDP was about 5.46 × 10^{-4} mm^3. The mean friction coefficient of ZDDP grease was much lower than that of pure grease and the friction coefficients showed some small fluctuations between 0.118 and 0.135 at the tested concentrations. At 1.5 wt.%, ZDDP had the highest carrying capacity and relatively lower friction and wear reduction properties. Therefore, 1.5 wt.% ZDDP was chosen for the subsequent experiments in this study.

Figure 3 shows the tribological properties of the PP grease with different concentrations of MoS_2. As the pure PP grease could only run at 300 N, the initial applied load of the test was 300 N for the MoS_2 grease. PP grease with different MoS_2 concentrations could only operate at 400 N. As the applied load increased to 500 N, the friction test failed. With MoS_2 concentrations ranging from 2.0 to 5.0 wt.%, the wear volume values exhibited minimal change at 300 N. With the applied load increased to 400 N, the wear volumes showed some relatively large fluctuations. The 5.0 wt.% MoS_2 grease displayed the best antiwear properties among all the concentrations. As shown in Figure 3b, the mean friction coefficient of the MoS_2 grease did not significantly change with different concentrations. Based on the results of the tribological experiments, 5.0 wt.% was considered to be the optimal concentration for MoS_2.

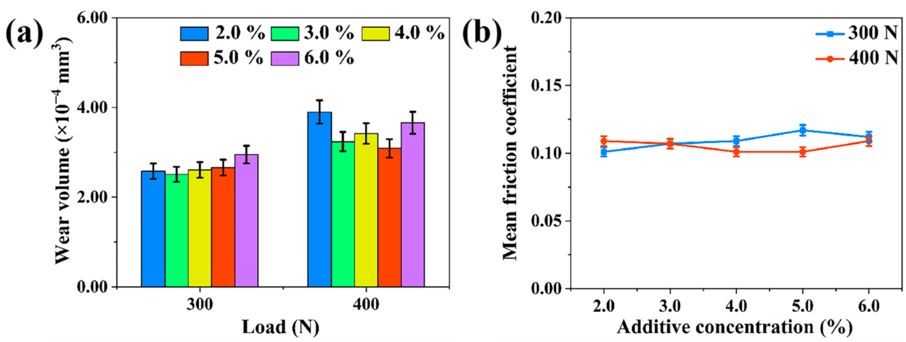

Figure 3. (**a**) Wear volumes and (**b**) mean friction coefficients of PP grease with different concentrations of MoS_2 (frequency = 50 Hz, stroke = 1 mm, duration = 30 min and temperature = 25 °C).

3.2. Influence of Combined Additives on the Tribological Properties of PP Grease at Different Temperatures

The tribological properties of the 5.0 wt.% MoS_2, 1.5 wt.% ZDDP and 5.0 wt.% MoS_2/1.5 wt.% ZDDP greases under applied loads from 200 to 800 N at 25 °C were first investigated, and the results are shown in Figure 4. The highest loads that could be applied to the MoS_2, ZDDP and MoS_2/ZDDP greases were 400, 700 and 800 N, respectively. Obviously, ZDDP acted synergistically with the MoS_2 in the PP grease. The highest load that could be applied for the MoS_2/ZDDP grease increased by 100% compared to that of the MoS_2 grease. The tribological tests also demonstrated that the highest loads that could be applied to the PP grease with both additives were not only improved (Figure 4a) but the friction coefficients were also reduced (Figure 4b).

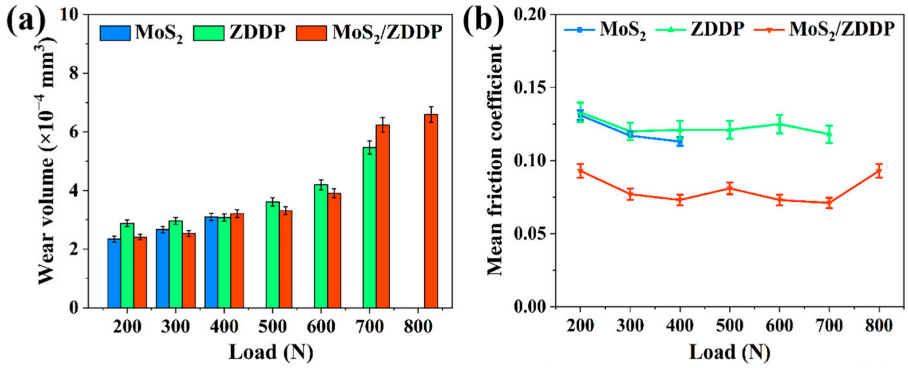

Figure 4. Comparison of (**a**) wear volumes and (**b**) mean friction coefficients among MoS_2 grease, ZDDP grease and MoS_2/ZDDP grease (frequency = 50 Hz, stroke = 1 mm, duration = 30 min, temperature = 25 °C).

According to previous reports on PP grease, it has excellent performance at low temperatures [8,9]. Therefore, the effect of temperature on the PP grease with the MoS_2/ZDDP additives was further studied at 0 and −15 °C.

As shown in Figure 5a, the highest load that could be applied to the MoS_2/ZDDP grease reached 800 N at the three temperatures. As the applied load increased from 200 to 500 N, the change in the wear volumes was not significant. When the applied load exceeded 500 N, the wear volumes tended to increase, but the amplitudes of the increase at 0 and −15 °C were obviously smaller than that at 25 °C. Under an applied load of 800 N, the wear volumes ($\times 10^{-4}$ mm^3) at 25, 0 and −15 °C were 6.59, 5.47 and 4.82, respectively. Clearly, under a higher load and lower temperature, the wear volumes of the MoS_2/ZDDP grease at 0 and −15 °C were lower than that at 25 °C.

Figure 5b shows the mean friction coefficients of the MoS_2/ZDDP grease at 25, 0 and −15 °C. The difference in mean friction coefficients was minimal under applied loads below 500 N. When the load was increased to 600 N, the values began to show some fluctuation. The mean friction coefficients of the MoS_2/ZDDP grease varied from 0.071 to 0.093. The dynamic friction coefficient curves under the highest applied load of 800 N are shown in Figure 5c. It can be observed that the friction coefficient first increased and then became stable in ~5 min after the start of the friction test. The fluctuation range of the friction coefficient at 25 °C was 0.079–0.168. In contrast, the range was 0.06–0.145 at 0 °C and 0.070–0.135 at −15 °C. Obviously, the friction coefficient at low temperatures fluctuated less.

3D images of the MoS_2/ZDDP grease under the highest applied load of 800 N at 25, 0 and −15 °C are shown in Figure 6 to give a visual representation of the wear situation. The wear scar at −15 °C was the smallest among the three tested temperatures, with only slight scratches on the wear surface. However, the wear area at 25 °C was obviously larger than that at 0 and −15 °C and the wear surface had more deeper furrows. These results were consistent with the experimental data.

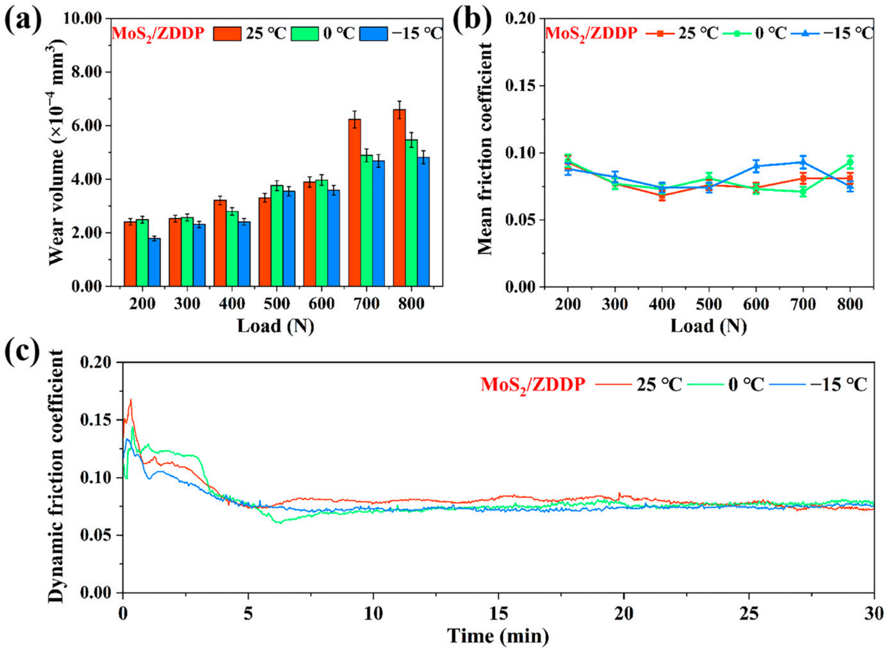

Figure 5. (**a**) Wear volumes and (**b**) mean friction coefficients of MoS_2/ZDDP grease at different temperatures (frequency = 50 Hz, stroke = 1 mm, duration = 30 min and temperature = 25 °C). (**c**) Dynamic friction coefficient curves under the highest applied load of 800 N.

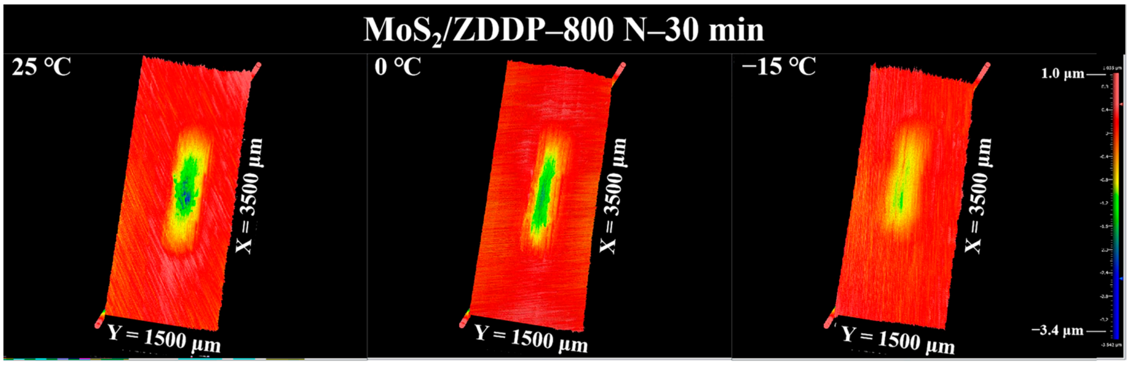

Figure 6. Microscopic 3D images of steel plates lubricated by MoS_2/ZDDP grease at the highest applied load (load = 800 N, frequency = 50 Hz, stroke = 1 mm and duration = 30 min).

The experimental results showed that the antiwear performances of the MoS_2/ZDDP grease at −15 and 0 °C were better than that at 25 °C.

3.3. Influence of Combined Additives on the Tribological Properties of PP Grease at Different Temperatures for Long-Time Tests

The 30 min lubrication tests showed that the tribological performances of the MoS_2/ZDDP grease at low temperatures were superior to that at room temperature. Therefore, the tribological performance was further studied under the three temperatures at a higher load (700 N) and greater friction test time (360 min).

As shown in Figure 7a, the wear volumes gradually decreased with decreasing temperature. The wear volumes ($\times 10^{-4}$ mm^3) of the MoS_2/ZDDP grease at 25, 0 and −15 °C were 13.24, 12.20 and 11.11, respectively. The corresponding mean friction coefficients were 0.067, 0.071 and 0.071, respectively. The mean friction coefficients were basically stable and only increased slightly at 0 and −15 °C. During the whole testing process, the dynamic friction coefficient curves at 0 and −15 °C were also steady but the curve at 25 °C displayed some fluctuations, indicating that MoS_2/ZDDP can be continuously adsorbed on the wear surface without delay and form a protective tribofilm (Figure 7b).

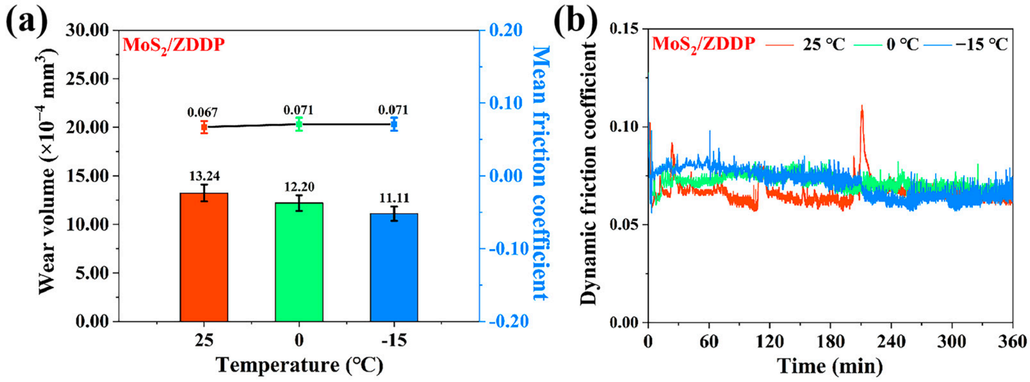

Figure 7. (**a**) Wear volumes and mean friction coefficients and (**b**) dynamic friction coefficient curves of MoS_2/ZDDP grease at different temperatures for long-time experiments (load = 700 N, frequency = 50 Hz, stroke = 1 mm and duration = 360 min).

The 3D images of the wear surface of the steel plate in Figure 8 show that the wear state at the three temperatures was nearly the same, with deeper wear depth and more furrows after a higher load and longer friction time. From this experiment, we can still see that the MoS_2/ZDDP grease showed stable friction reduction and antiwear performance at low temperatures.

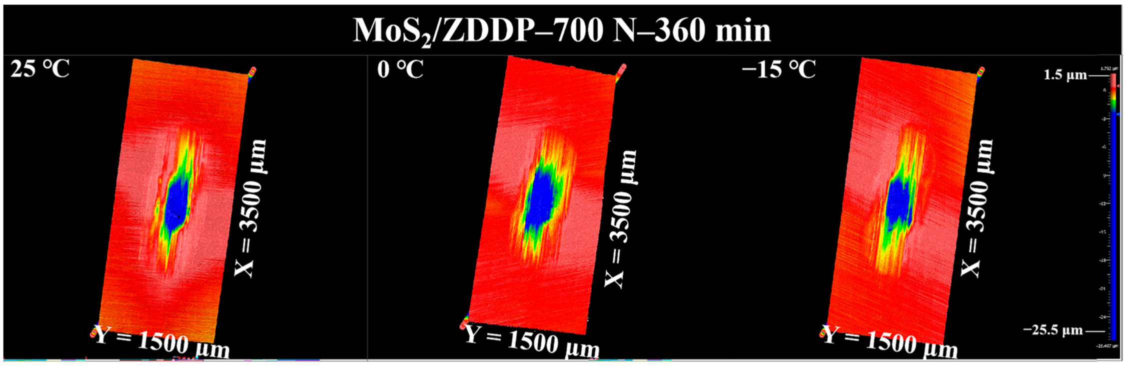

Figure 8. Microscopic 3D images of steel plates lubricated by MoS_2/ZDDP grease at different temperatures for long-time experiments.

3.4. Surface Morphologies and Elemental Analysis of Wear Scars

The wear surfaces and elemental distribution of the steel plates were analyzed by SEM and EDS. Figure 9a shows the SEM micrographs and EDS spectra of the wear surfaces lubricated by the pure PP, MoS_2 and ZDDP greases under their respective highest applied loads at 25 °C. The wear surface of the pure PP grease had large-scale irregular furrows and the wear state was the most serious. The wear surface of the MoS_2 grease was smooth and had no obvious furrows. For the ZDDP grease, there were two lines of small and big valleys aligned in the rubbing direction. Based on the EDS spectra, C, Fe and Cr steel plate elements were detected on the wear surface of the pure PP grease. For the ZDDP and MoS_2 greases, the characteristic elements of the additives were detected on the steel surface in addition to the steel plate elements, indicating that a protective film formed on the wear surface.

Figure 9b shows the SEM images and EDS spectra of the wear surfaces lubricated by the MoS_2/ZDDP grease at different temperatures under the highest applied load of 800 N. At 25 °C, the wear state was obviously better than for a single additive: the steel plate surface was smooth, with no obvious furrows on the wear surface, even at an applied load of 800 N. When the temperature dropped to 0 °C or −15 °C, the wear surface was still as flat as that at 25 °C. According to the EDS analysis, there was a large amount of

Mo, S, P and Zn elements distributed over the whole surfaces. Both MoS_2 and ZDDP together formed a tribofilm to achieve good antiwear properties. These results show that the compounding of additives had a good synergistic effect to protect the steel surfaces.

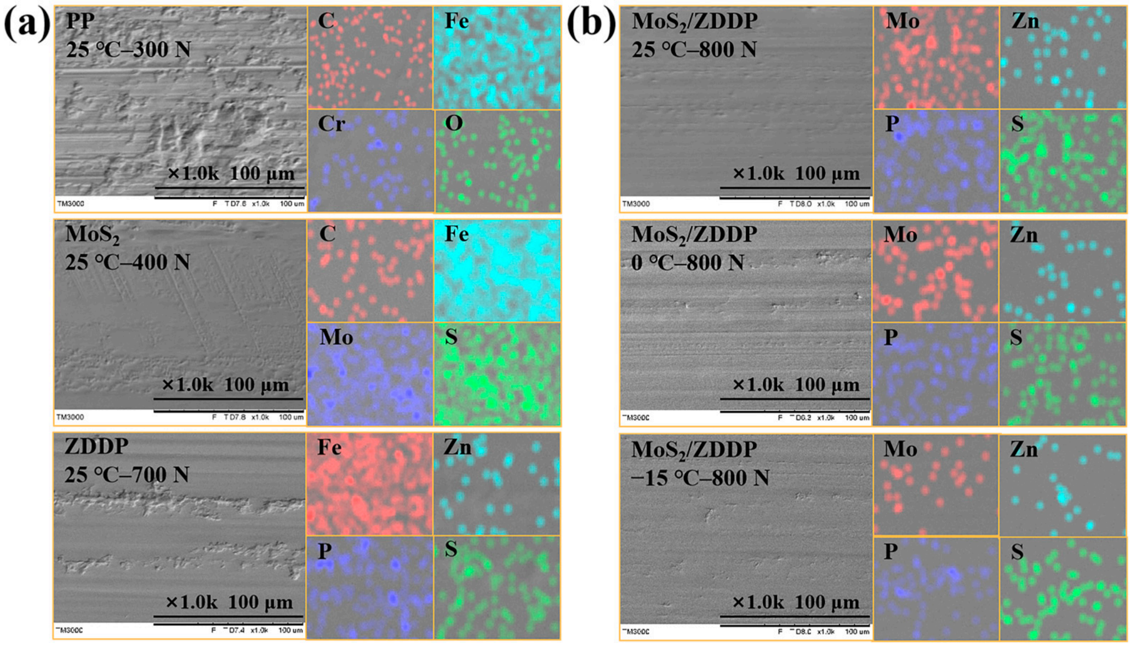

Figure 9. SEM images and EDS spectra of steel plates lubricated by (**a**) PP, MoS_2 and ZDDP greases under each highest applied load at 25 °C and (**b**) MoS_2/ZDDP grease at three different temperatures under the highest applied load (duration = 30 min).

The SEM images and EDS spectra of the MoS_2/ZDDP grease after the 360 min friction test under an applied load of 700 N are shown in Figure 10. The steel plates lubricated by the MoS_2/ZDDP grease had an obvious large-area pit at the center and the wear track was deep and wide in size, but the damaged area decreased with decreasing temperatures, indicating that wear reduction had occurred. The EDS analysis showed that there were still large quantities of Mo and S elements contained on the surface, indicating that the solid lubricant MoS_2 adhered to the rubbed surface after a long time period of running during the test. In contrast, the amount of Zn and P elements became smaller. Obviously, the ZDDP tribofilms were reduced, possibly due to mechanical removal after long-term friction [17]. This result illustrated that there was more protective tribofilm originating from the MoS_2 that remained on the sliding surface after long-term friction. Obviously, MoS_2 has a surprisingly beneficial effect under severe conditions.

Having completed the surface topography and element distribution analysis, an attempt was made to detect the chemical states of the characteristic elements on the wear scars. For this purpose, the wear scars of the steel plates lubricated by the MoS_2/ZDDP grease after the 360 min friction experiment at −15 °C were analyzed by XPS.

Figure 11a,b show the Mo3d and S2p characteristic peaks on the wear surface of the steel plate lubricated by the MoS_2/ZDDP grease. The characteristic peaks of Mo3d can be fitted to the three peaks of 235.5, 232.3 and 229.5 eV. The peaks at 232.3 and 229.5 eV belong to Mo^{4+}, which proves the existence of MoS_2. The peak at 235.5 eV represents Mo^{6+}, indicating the oxidation of Mo [30]. The characteristic peak of S2s near 225.5 eV in Figure 11a is consistent with the S2p characteristic peak in Figure 11b. The characteristic peak at 168.4 eV in Figure 11b represents S^{6+}, which represents the peak of the S-O bond of ZDDP. The peaks at 162.5 and 161.3 eV represent S^{2-}, which indicate the presence of the metal sulfides MoS_2 and FeS, respectively [31]. Figure 11c–e show the Zn2p, P2p and O1s characteristic peaks on the surface of the steel plates corresponding to the MoS_2/ZDDP grease. The characteristic peak at 1021.5 eV in Figure 11c represents Zn^{2+}, which indicates the presence of zinc phosphates and zinc sulfide. The characteristic peak of P2p in Figure 11d can be fitted to one peak at 133.0 eV, which indicates the existence of various phosphates [32]. The characteristic peak at 531.0 eV in Figure 11e is O1s, indicating the presence of the P-O bonds [32] and metal oxides, such as FeO [33].

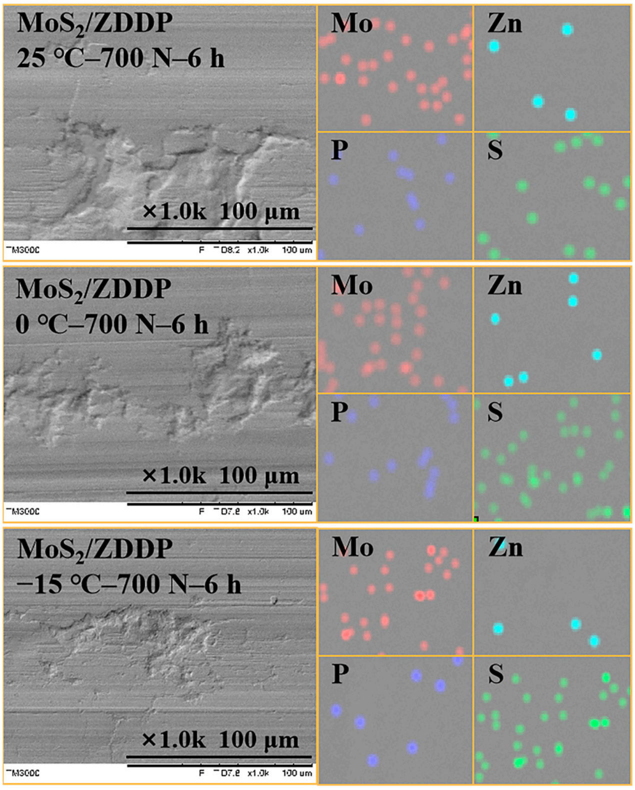

Figure 10. SEM images and EDS spectra of steel plates lubricated by MoS_2/ZDDP grease at three different temperatures for long-time experiments (load = 700 N, frequency = 50 Hz, stroke = 1 mm and duration = 360 min).

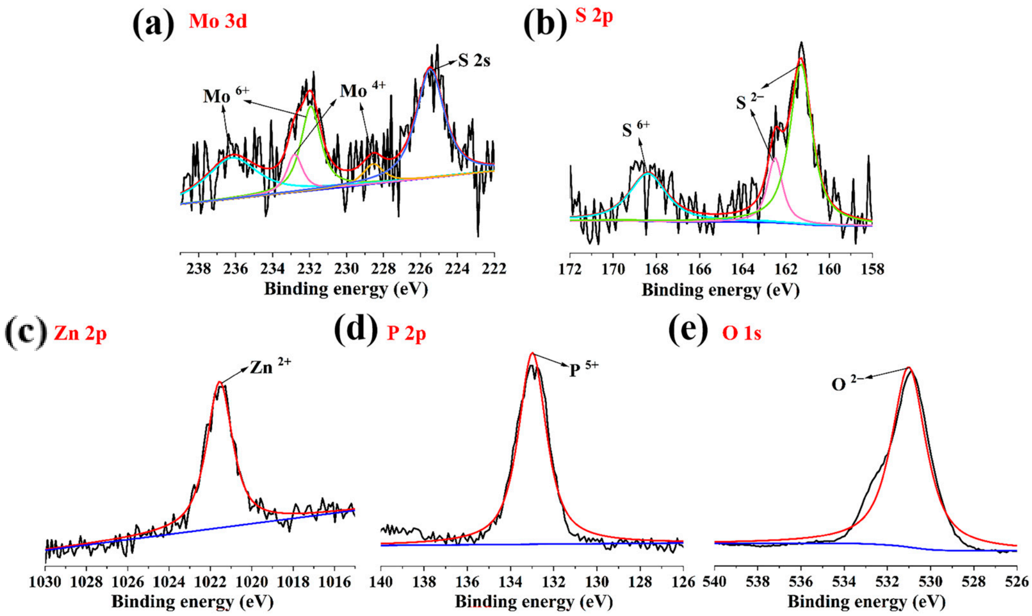

Figure 11. XPS spectra ((**a**) Mo 3d, (**b**) S2p, (**c**) Zn2p, (**d**) P2p and (**e**) O1s) of wear surface lubricated by MoS_2/ZDDP grease at −15 °C for long-time experiments.

According to the overall XPS analysis, the protective tribofilms were formed by absorption and chemical reactions. The solid additive MoS_2 not only penetrates into the steel surfaces to form a solid film, but it also undergoes a tribochemical reaction with Fe on the steel plate [31,34,35]. The organic additive ZDDP also chemically reacts with Fe to form an FeS protective film [36].

3.5. Rheological Properties of PP Grease with Additives at Different Temperatures

It is well known that lubricating grease exhibits a kind of elastic deformation that is characteristic of a semi-solid and its properties largely depend on temperature. Low temperatures will cause an increase in the grease stiffness, decreasing the flowability. This will result in high friction that can damage the bearings [37]. As PP grease also has a colloidal structure, its physical properties depend on the application conditions. A variation in additives and temperatures might have an impact on the rheological behavior of the grease. At present, there have been very few reports about the effect of additives on the rheological behavior of lubricants at low temperatures. The rheological behavior of the PP grease with additives was investigated from 25 to −15 °C. The viscoelastic and thixotropic properties of the 5.0 wt.% MoS_2, 1.5 wt.% ZDDP and 5.0 wt.% MoS_2/1.5 wt.% ZDDP grease samples were determined using rheological analysis.

Figure 12 shows the viscoelastic characterization of the grease samples through an amplitude sweep experiment. The linear viscoelastic region (LVE) corresponding to the strain values of all grease samples at the three different temperature conditions was greater than 0.1%. Therefore, the viscoelastic properties of the PP grease with additives under the LVE range (γ = 0.1%) were studied. The loss tangent (tan δ) is the quotient of the loss modulus (G'') and storage modulus (G'), i.e., tan $\delta = G''/G'$, which represents the relationship between the viscosity (G'') and elasticity (G') of the grease. When the strain value is greater than 0.1%, the grease gradually enters the non-linear regions. The value of G'' shows a trend of first increasing and then decreasing, which indicates a weak strain overshoot phenomenon. As G' and G'' are defined only in the linear viscoelastic regime, the moduli at large strains lose their mathematical underpinnings [38].

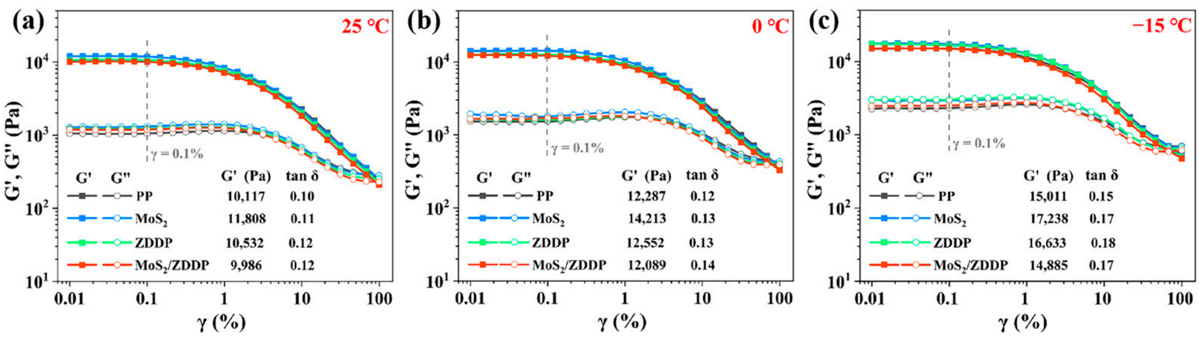

Figure 12. The moduli and tan δ (γ = 0.1%) of the PP grease with additives as function of shear strain at (**a**) 25 °C, (**b**) 0 °C and (**c**) −15 °C.

As shown in Figure 12a–c, all greases had plateau regions at different temperatures, indicating that PP grease is a typically viscoelastic semi-solid and the presence of additives did not destroy this state. The G' value of each grease gradually increased as the temperature decreased. G'' maintained the same trend as G'. The trends with temperature changes were consistent between the PP grease containing additives and pure PP grease. The addition of additives had a slight impact on the moduli of the grease, but there was no substantial change in the viscoelasticity of the grease.

Figure 12a–c also show that the tan δ curves for a grease with a single or compound additive were almost the same as that of the pure PP grease at the three tested temperatures. At 25 °C, the tan δ values of the pure PP, MoS_2, ZDDP and MoS_2/ZDDP greases were 0.10, 0.11, 0.12 and 0.12, respectively. When the test temperature decreased to −15 °C, the tan δ values were 0.15, 0.17, 0.18 and 0.17, respectively. The tan δ values increased with decreasing temperature, indicating that the viscosity (G″) also increased with decreasing temperature. The values of the PP grease with additives at 25 and −15 °C were nearly the same as that of the base grease. The results show that the additives had little effect on the viscoelastic properties of the base PP grease at the tested temperatures.

Based on the analysis of the amplitude sweep experiment results, we ruled out the possible impact of instrument inertia on the subsequent experiments. The selection of these experimental parameters, below, ensured that the whole frequency sweep process was not interfered with by the fluid inertia of the sample, and the accuracy of the experimental results was guaranteed. Frequency sweep tests were carried out in a frequency range from 0.01 to 100 rad/s within the LVE (γ = 0.1%). Figure 13 presents the mechanical spectra of the pure PP, MoS_2, ZDDP and MoS_2/ZDDP greases at the three temperatures. It can be observed that the viscoelasticity responses of all the grease samples were very similar at each tested temperature. The G′ value of all samples was higher than the G″ value over the whole frequency range. The G′ values exhibited an increase with increasing frequency at all tested temperatures. Meanwhile, G″ always showed a minimum value, which tended to become more pronounced as the temperature decreased. The tan δ values showed the same tendency as G″. These phenomena indicate that PP grease is a typical highly entangled system with a plateau region in the mechanical spectrum [39,40].

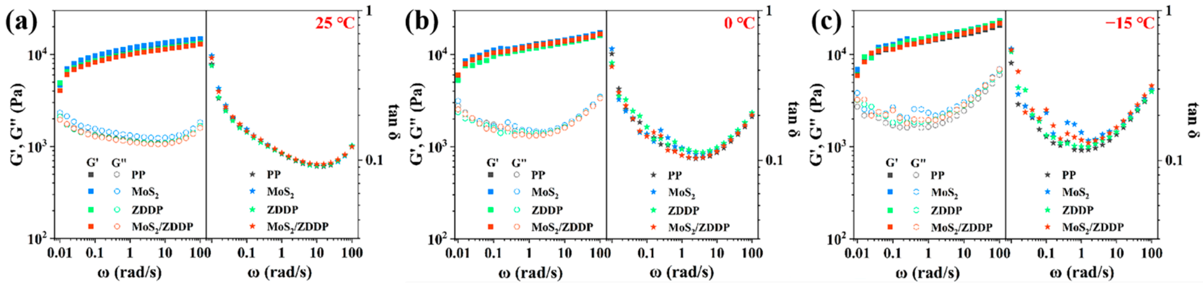

Figure 13. The moduli and tan δ of the PP grease with additives as function of frequency at (**a**) 25 °C, (**b**) 0 °C and (**c**) −15 °C.

Regarding the influence of temperatures on the linear viscoelastic functions, both G′ and G″ slightly increase as temperatures decrease, although this rise depends on the nature of the thickener and base oil. The γ value corresponding to the minimum G″ value showed a decreasing tendency as the temperatures decreased, indicating that the viscous properties gradually become prominent at low temperatures. The better adhesion of PP grease to the surface at low temperatures may also be one of the reasons for its better tribological performance.

Thixotropy is very important for lubricating greases. The grease should have good rheological performance and behave as a viscoelastic material at low shear. When the shear rate becomes large, the viscosity of the grease decreases and a shear thinning phenomenon occurs, thereby giving it excellent flow and lubrication properties. The thixotropy of a grease thickener largely depends on the recovery response speed of its microstructure [41]. Thus, the flow recovery behavior of the PP grease with additives at different temperatures was determined using shear rheological tests. This test can determine whether the shear regime used has a temporary or a permanent shear thinning effect on the microstructure of the PP grease with additives. The viscosity recovery rate was carefully observed in a time range from 10 to 120 s. The experimental results are shown in Figure 14a–c.

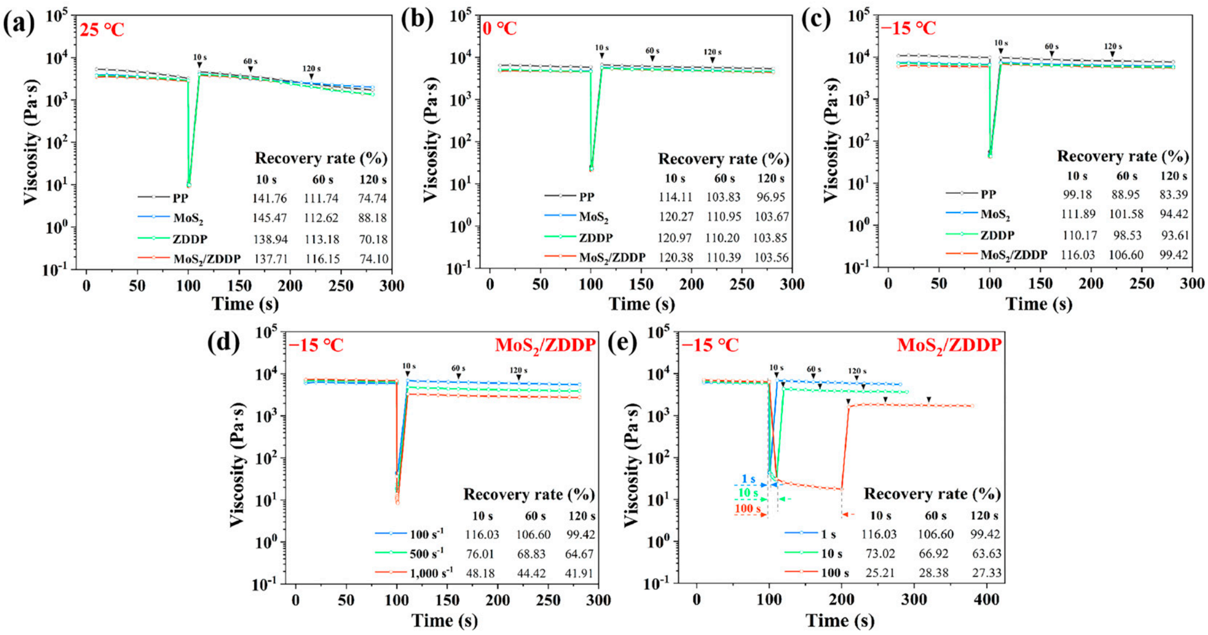

Figure 14. The thixotropic properties of the PP grease alone and with additives at (**a**) 25 °C, (**b**) 0 °C and (**c**) −15 °C, (**d**) MoS_2/ZDDP grease at a different shear rate at −15 °C and (**e**) MoS_2/ZDDP grease at a different shear time at −15 °C.

Figure 14a–c show a comparison of the thixotropic curves at an instantaneous shear rate of 100 s^{-1} of the PP grease alone and with a single or a combination of additives at the three tested temperatures. Although the inertia of the grease samples caused the recovery rate to be a little higher than 100% due to the sudden stop after the high-speed shear at the three test temperatures, the thixotropic curves of all grease samples were smooth and they could return to a steady state. At a test temperature of 25 °C, the viscosity recovery rates of all the grease samples gradually decreased with increasing time (Figure 14a). At 0 °C, the decline in the viscosity recovery rate slowed and the recovery rate values of the PP grease with additives were marginally higher than that of the pure grease (Figure 14b). When the test temperature continued cooling to −15 °C, the shear time lasted for 120 s and the viscosity recovery rates were marginally lower than those at 0 °C (Figure 14c), indicating a good mobility and relatively stable gel structure for the PP grease samples at this low temperature.

In order to further examine the thixotropic ability of the MoS_2/ZDDP grease at low temperatures, we used different shear rates (100, 500 and 1000 s^{-1} with a shear duration of 1 s) and shear durations (1, 10 and 100 s with a shear rate of 100 s^{-1}) in the second stage, and the results are shown in Figures 14d and 14e, respectively. Although the recovery curves were closer to the line, an obvious shear thinning phenomenon still occurred after the high-speed shearing, especially under higher shear rates or longer shear durations. It can be seen that when the recovery stage was carried out at 60 s, the viscosity recovery rates of the MoS_2/ZDDP grease under shear rates of 100, 500 and 1000 s^{-1} were 106.60%, 68.83% and 44.42%, respectively. The greater the instantaneous shear rate, the greater the degree of damage to the structure of the MoS_2/ZDDP grease. Therefore, the recovery rate of the grease decreased with the increase in the shear rate. When we extended the high-speed shear duration as shown in Figure 14e, we observed that a longer shear duration has a significant impact on the structural recoverability of the MoS_2/ZDDP grease, and the grease required a longer recovery response. However, the viscosity recovery rate exhibited little change with the prolonged recovery time. This result indicates that the MoS_2/ZDDP grease at −15 °C not only maintained good fluidity under a high shear rate but also retained its gel structure.

The above thixotropic and viscoelastic experimental results show that the addition of the additives did not change the colloidal structure and flow characteristics of the PP grease, especially at lower temperatures.

4. Discussion

Although several studies have reported an excellent low-temperature lubrication performance of PP grease [1,6,29], the effect of additives at low temperatures has been rarely reported. In this work, additive concentration, applied load, the lubrication film and rheological behaviors were evaluated by SRV reciprocating tests and rheological analysis under temperatures ranging from 25 °C to −15 °C.

The tribological performance of additives will change under different working conditions. In our research work, the friction test was carried out under reciprocating sliding in low-temperature conditions. The temperature, humidity, friction pairs, movement mode and grease system could all possibly influence the tribological behavior of PP grease with MoS_2/ZDDP additives. According to previous studies, the temperature and humidity may influence the tribological performance of MoS_2 [23], while the experimental results of the tribological properties of MoS_2 at a low temperature were inconsistent. Some studies demonstrated that the friction coefficient increased as the temperature decreased [42,43]. However, other research results found that when the temperature decreased below a certain level, the friction coefficient did not rise [44–47]. Barry et al. researched the friction properties of MoS_2 coatings under different atmosphere conditions, and the experimental results showed that the friction decreased with increasing applied load and running speed in a humid environment; they believe that the friction heat leads to a reduction in surface humidity, thereby affecting the friction behavior [48]. For ZDDP, there are a few studies on the effect of temperature and water on tribofilm formation [49–51]. H. Cen et al. reported that water may lead to the depolymerization of longer-chain phosphates, and the reaction layer thickness of ZDDP decreased with increasing humidity [49]. Although the effects of temperature and humidity in lubrication have been well recognized, the working conditions in this research work were different. In this study, we took some measures to avoid the humid environment affecting the experiment results, such as applying the tested PP grease sample over the whole steel plate, monitoring humidity throughout the friction experiment process and installing a temperature control system for the rheometer. A more detailed lubrication mechanism is discussed in Figures 15 and 16.

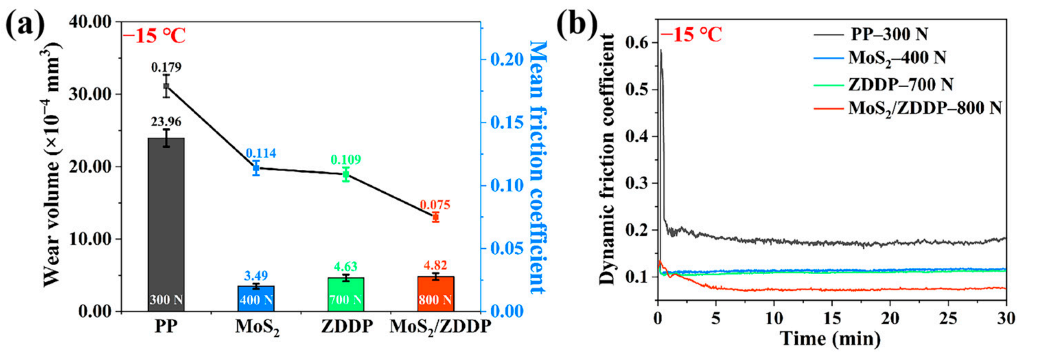

Figure 15. (**a**) Wear volumes and mean friction coefficients and (**b**) dynamic friction coefficient curves of PP grease alone and with additives at each highest applied load (frequency = 50 Hz, stroke = 1 mm and duration = 30 min).

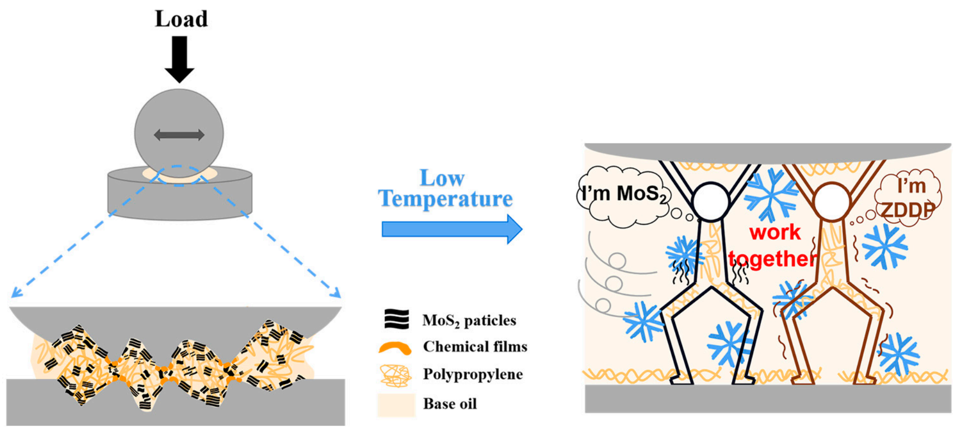

Figure 16. Schematic illustration of possible mechanism of lubrication by PP grease with MoS_2/ZDDP.

Figure 15 displays the antiwear and antifriction properties of the pure PP grease and the PP grease containing additives at −15 °C under their respective highest applied loads. It can be seen that the carrying load capacity of the pure PP grease was the smallest among the four grease samples. The values of the mean friction coefficient and wear volume of the pure PP grease were all the highest and the dynamic friction coefficient curve fluctuated considerably at the beginning. When MoS_2 or ZDDP was added to the pure grease, the lubrication performance of the base grease was markedly improved. Not only did the carrying load capacity increase but the values of the mean friction coefficient and wear volume all decreased. When MoS_2 and ZDDP were used as co-additives, there was a synergistic effect that was greater than that for the individual additives, especially regarding the antifriction properties. Compared with the pure grease, the operating load of the MoS_2/ZDDP grease increased to 800 N, the wear decreased to 4.82×10^{-4} mm^3 and the coefficient friction was reduced from 0.179 to 0.075. Similar test results were also found at 0 and −15 °C in the long-duration experiment: the friction coefficient only slightly increased, and the dynamic friction coefficient curves were steady during the whole friction test. The wear volume value decreased gradually with the temperature decrease (see Figure 7). These results indicated that MoS_2/ZDDP can continue to adsorb onto the wear surface to form a protective tribofilm. As shown in Figure 9, the steel surface lubricated by MoS_2/ZDDP grease was smooth, with no obvious furrows on the wear surface, even at an applied load of 800 N. Lubricity evaluation further demonstrated that the MoS_2/ZDDP additives can easily reach the metal surfaces on a non-polar PP thickener system. Obviously, a PP thickener system is a very good cryogenic carrier; its good low-temperature performance and excellent water resistance properties enable the additive to play a positive role in lubrication. The solid additive MoS_2 not only acted as a third body to overcome the pitfalls, but it also combined with ZDDP to form a friction-reducing tribofilm (see Figures 9–11). Therefore, the synergistic effects from layering MoS_2 and ZDDP resulted in an excellent lubricating performance under higher loads, longer durations and lower temperatures. For the additives, the addition of MoS_2 and ZDDP had little influence on the colloidal structure and flow characteristics of the pure PP grease at low temperatures. Therefore, PP grease and MoS_2/ZDDP additives achieved excellent lubricating performance together. The lubrication mechanism is illustrated in Figure 16.

5. Conclusions

The effects of MoS_2, ZDDP or MoS_2/ZDDP as additives on the tribological behaviors of PP grease with steel/steel contacts were investigated using a reciprocating sliding ball-on-plate tribometer at low-temperature working conditions. The effects of additive concentration, carrying load capacity, temperature and the lubrication film were evaluated. The viscoelastic and thixotropic rheological behaviors of PP grease with additives were also determined at different temperatures. The corresponding conclusions are as follows:

(1) Based on the results of the tribological experiments, the optimal concentration for MoS_2 was 5.0 wt.%, and 1.5 wt.% for ZDDP in the PP grease system.
(2) Compared with PP grease and PP grease with MoS_2 or ZDDP as an additive at a temperature of −15 °C, there was an outstanding synergistic effect for the MoS_2/ZDDP additives. The carrying load of the MoS_2/ZDDP grease reached 800 N, 3.67 times that of the pure PP grease. Under the highest applied load, the antiwear and friction reduction properties of the MoS_2/ZDDP grease were the best among the four grease samples. The dynamic friction coefficient of the MoS_2/ZDDP grease cloud maintained a stable state at an applied load of 800 N.
(3) The effect of temperature on the tribological performance of PP grease with MoS_2/ZDDP additives was realized at temperatures ranging from 25 °C to −15 °C. The wear volumes of the MoS_2/ZDDP grease at 0 and −15 °C were lower than that at 25 °C under the higher load. The temperatures and applied loads had little impact on the friction coefficient. The dynamic friction coefficient curves showed that the friction coefficient was stable at lower temperatures, especially with the higher load and longer friction time.
(4) Under the low-temperature and high-applied-load friction process, the active components of the additives reached the metal surfaces effectively in the polymer grease system: the polymer system did not interfere with the function of the additives. Protective tribofilms originating from the MoS_2 and ZDDP were formed by absorption and chemical reactions. The solid additive MoS_2 not only penetrated into the steel surfaces to form a solid film, but also adhered to the surface tribochemical layer formed by the organic additive ZDDP. MoS_2 and ZDDP played a synergistic role in severe working conditions.
(5) The viscoelastic and thixotropic rheological results showed that the additives of MoS_2, ZDDP and MoS_2/ZDDP did not affect the gel structure, viscoelasticity or flow characteristics of the base PP grease. The grease containing additives had a good viscosity recovery rate and ductility at low temperatures.

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