



Article Synergistic Effect of Acrylate of Dialkyl Dithiophosphoric Acid Combined with Molybdenum Dialkyl Dithiocarbamate as Additives in Gear Oil

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Abstract: With the aim of improving the tribological properties of low-viscosity gear oil for automobiles, an acrylate of dialkyl dithiophosphoric acid (ADDP) with strong polar groups was synthesized. The tribological behavior of ADDP combined with molybdenum dialkyl dithiocarbamate (MoDTC) in gear oil was systematically studied. Tribological performances of gear oil containing different additives were assessed using a four-ball friction and wear tester. The obtained tribological characteristics reveal that ADDP and MoDTC can significantly improve the antiwear and antifriction performance of low-viscosity gear oil. Moreover, compared with using MoDTC or ADDP alone, the average friction coefficient and wear scar diameter of ADDP combined with MoDTC further decreased by 2.41–19.15% and 5.00–18.19%, respectively. Analysis of the worn surface showed that the structural characteristics and physical synergistic lubricating actions of the ADDP with MoDTC additives during the friction process can contribute to the exceptional tribological properties of the hybrid additives.

Keywords: acrylate of dialkyl dithiophosphoric acid; MoDTC; gear oil; tribological performance



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1. Introduction

Reducing friction power loss is one of the important topics in the development of modern automobiles [1]. Low-viscosity gear oil can reduce the running resistance of the gear [2], thereby reducing the power loss of the gear during churning and squeezing [3]. However, the decrease in the viscosity of gear oil will aggravate gear tooth surface wear, scraping, micro-pitting, and pitting [4]. Moreover, when the automotive gear box works under harsh conditions such as high speed and heavy load, the gears are also vulnerable to friction damage, resulting in failures such as surface failure [5]. In order to reduce frictional power loss and prevent gear failure, gear oil with excellent antifriction, antiwear, and extreme pressure properties is needed to improve the efficiency and durability of gears working under extremely severe working conditions [5]. It is necessary to meet the current high performance requirements of gear oils by using antiwear additives and friction modifiers that can work in conjunction with each other.

Antiwear agents are the core additive of heavy-duty gear oil and their main function is to prevent gear scuffing, seizure, and welding [6]. Lubricating oil additives composed of organophosphates have excellent tribological properties [7–9]. Phosphate ester additives can form a strong antiwear film under friction contact or high temperature conditions and can adhere to the surface of the friction pair, even under extreme load and high temperature conditions [10–12]. Zinc dialkyl dithiophosphate (ZDDP), as a phosphate antiwear additive containing zinc and sulfur, has been widely used in the automotive industry [13]. Under relatively high temperature and contact pressure conditions, ZDDP can form a film of tens to hundreds of nanometers on the sliding surface, providing excellent antiwear properties [14]. However, ZDDP is harmful to the environment [15] and its usage is limited. Therefore, it is

necessary to develop ash-free antiwear additives. Dialkyl dithiophosphate acrylate ashless antiwear agent has excellent antiwear properties and can effectively improve the FZG failure level of gear oil with a low dosage. In addition, it also has good thermal oxidation stability, hydrolytic stability, and anti-emulsification ability [16], which has research value as an antiwear additive for low-viscosity gear oil.

The application of friction modifiers in gear oil can effectively reduce friction and wear [17], enabling the smooth operation of gear transmission systems. Molybdenum dithiocarbamate (MoDTC) is a typical friction modifier. It can decompose to form a tribochemical film containing MoS_2 on the worn surface, which can effectively reduce friction and wear between friction pairs [18–21]. However, with the development trend of low-viscosity gear oil, the range of hybrid lubrication and boundary lubrication is constantly expanding in the operation of mechanical systems [22,23], making it increasingly difficult to use MoDTC alone, to meet the needs of high-performance gear oil. In order to solve this problem, friction modifiers and antiwear additives are mixed into low-viscosity gear oil to obtain improved tribological properties. By monitoring the growth and friction coefficient distribution of the friction film formed by ZDDP and/or MoDTC, Renguo Lu et al. [24] found that when ZDDP and MoDTC are used at the same time, a synergistic effect can be obtained [25,26], i.e., the ZDDP/MoDTC friction film has low friction and high antiwear properties. Dawit Zenebe Segu and Chang-Lae Kim [27] obtained the optimal mixing ratio and concentration of ZrO₂ nanoparticles and MoDTC at 1:2 and 0.25–0.75 wt%, respectively, by using a pin-disk tribometry with a steel-steel contact pair. This excellent tribological performance can be attributed to the physical and chemical advantages and synergistic lubrication of nanoparticles and MoDTC additives during friction [28,29]. Langi Zhang and Nan Li [30] found that the graphene–MoDTC combination has good lubrication synergies in the PAO base oil at the steel-steel interface, which can enhance the antiwear properties of the dual system.

However, there are few studies on phosphorothioate acrylate derivatives, which can be used as antiwear additives of gear oil, so an acrylate of dialkyl dithiophosphoric acid (ADDP) was synthesized in this paper, to study its extreme pressure and antiwear properties. In addition, in order to obtain a gear oil with more excellent antifriction and antiwear properties, it is necessary to study the tribological behavior of ADDP combined with MoDTC in gear oil. Therefore, in this paper, MoDTC and ADDP are used to prepare three kinds of gear oil. The tribological behavior of MoDTC, ADDP, and their compositions as gear oil additives on the surface of GCr15 is studied, while the antifriction and antiwear mechanism of the ADDP and MoDTC compounds is discussed. It provides theoretical and experimental support for the design and preparation of low-viscosity gear oil with excellent antifriction and antiwear properties.

2. Materials and Methods

2.1. Preparation of ADDP

Add quantitative n-butanol (or isooctanol) into a four-necked flask, immerse the flask in a thermostatic oil bath, heat up to 40 °C, stir with a precision force-enhancing electric stirrer. Slowly add quantitative phosphorus pentasulfide, in batches, under stirring and vacuum and then heat up to about 80 °C, after all of the phosphorus pentasulfide is added, reacting for 1 h. Stand and cool to obtain the intermediate product sulfur phosphoric acid (reaction Equation (1)). Then, the sulfur phosphoric acid produced using Reaction (1) is heated to 70 °C under stirring, adding an appropriate amount of methacrylic acid (or methyl acrylate) in batches, while continuously increasing the temperature to 85 °C, reacting for 3 h, to obtain ADDP crude products (reaction Equation (2)). The crude product is refined and distilled and the ADDP additive is obtained after the solvent is removed. The raw materials used are all CP grade reagents.

$$R_1OH + P_2S_5 \to (R_1O)_2PS_2H + H_2S$$
 (1)

$$(R_1O)_2 PS_2 H + C_4 H_6 O_2 \to (R_1O)_2 PS_2 C_4 H_7 O_2 \tag{2}$$

2.2. Preparation of Test Oil

In this tribological test, the base oil from a low-viscosity gear oil (SINOPEC Lubricant Co., Ltd., Beijing, China) of 75 W grade was selected. A functional additive package consisting of detergent dispersant and viscosity index improver was added to the base oil to increase the solubility of MoDTC and to adjust the viscosity of the base oil. Three different additive combinations were blended with the gear oil, namely 1.0 wt% MoDTC (Luoyang Pacific United Petrochemical Co., Ltd., Luoyang, Henan, China), 1.0 wt% ADDP, and a combination of 1.0 wt% MoDTC and 1.0 wt% ADDP. The mixing process is as follows: the additive and gear oil are stirred with a magnetic stirrer for 2 h at 60 °C, followed by ultrasonic stirring for 0.5 h until the mixture is homogeneous. The specific technical formula of the sample lubricants is shown in Table 1 and the optical image is shown in Figure 1.

Table 1. Technical formulation of lubricating oils.

Property	Additive Content	Viscosity at 40 °C/(mm²/s)	Viscosity at 100 °C/(mm²/s)	Test Method
BO	Base oil + Compound functional additive package	26.96	5.67	
BM	BO + MoDTC (1.0 wt%)	29.24	6.13	100 2104 [21]
BA	BO + ADDP (1.0 wt%)	27.43	5.95	150 3104 [31]
BMA	BO + MoDTC (1.0 wt%) + ADDP (1.0 wt%)	28.12	6.04	



Figure 1. Optical image of the prepared lubricants.

2.3. Tribological Test

Use the MRS-1J (Jinan, China) four-ball friction and wear testing machine for the tribological test of the gear oils. The friction element of the four-ball friction and wear testing machine is composed of four steel balls—the upper steel ball rotates under the drive of the spindle, the other three steel balls are fixed in the oil tank, and the contact points of the upper and lower steel balls are immersed in the gear oil. The working principle of the four-ball wear tester is shown in Figure 2. The steel balls used in this paper are all GCr15 steel balls with a diameter of 12.7 mm and a hardness of 65 HRC (Rockwell hardness). The extreme pressure performance of the gear oil was evaluated according to the ASTM D2783 standard [32]. The load continuously increases at 1760 rpm for a series of tests lasting 10 s, until welding occurs. The influence of different additives on the extreme pressure performance of gear oil was reflected by measuring the maximum nonseizure load, P_B, and sintering load, P_D, of different gear oils. The antifriction and antiwear properties of the gear oils were evaluated according to the ASTM D4172 standard [33]. The friction coefficient and wear scar diameter of the steel balls were measured at 75 °C, 1200 rpm, and 392 N constant load. Each test was carried out for 60 min. Three rounds of friction test were performed for each sample lubricant and the average value was taken as the test result.



Figure 2. Schematic view of the four-ball wear tester.

2.4. Surface Analysis and Characterization

A Fourier transform infrared spectrometer (FT-IR, IRTracer 100, Kyoto, Japan) was used to characterize the molecular structure of the synthesized ADDP, scanning 32 times with a resolution of 4 cm⁻¹. After the tribological tests, scanning electron microscopy (SEM, TESCAN MIRA4, Brno, Czech Republic) and energy-dispersive X-ray spectroscopy (EDS, OXFORD XPLORE30, Oxford, UK) were used to observe the surface morphology and elemental composition of the wear marks. Tribochemical analysis was carried out using an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, Waltham, MA, USA). Al-K α was used as the excitation source, the test energy was 20.0 eV, the resolution was ± 0.3 eV, and the carbon binding energy (C 1s: 284.8 eV) was used as the reference calibration. The roughness of worn surfaces was measured using a three-dimensional laser profilometer (Bruker ContourX-200, Tucson, AZ, USA). The middle position of the worn surfaces on the lower ball was selected as the measurement position, the surface roughness of each sample was recorded 10 times, and the average value was taken as the test result.

3. Results

3.1. Molecular Structure of ADDP

Figure 3 shows the infrared spectrum of the acrylate of dialkyl dithiophosphoric acid product, synthesized in Section 2.1. In Figure 3, 545 cm⁻¹ is the P-S absorption peak, 575 cm^{-1} is the S-C absorption peak, 676 cm^{-1} is the P=S absorption peak, 854 cm^{-1} is the O-P-O absorption peak, 996 cm^{-1} is the C-O-P-O-P absorption peak, 1369 cm^{-1} is the alkyl absorption peak in sulfur phosphoric acid, and 1469 cm^{-1} is the -CH₃ absorption peak. Since the synthetic material is n-butanol, the area of the -CH₃ absorption peak is relatively obvious The C=O absorption peak in -COOR is at 1710 cm^{-1} and the frequencydoubled absorption peak of -CH₃ and -CH₂ is at 2963 cm^{-1} . Shoulder peaks containing -COOH groups can be found in the range of 2500 cm^{-1} to 3100 cm^{-1} , indicating that the structure contains carboxylic acid groups. Accordingly, the molecular structure of the ADDP synthesized in Section 2.1 can be verified, as shown in Figure 4.



Figure 3. FTIR spectra of ADDP.

$$i - C_4H_9 - O P S CH_3$$

 $i - C_4H_9 - O S - H_2C - CH - COOH$

Figure 4. Molecular structure of ADDP: 3-(O, O-Di-n-butyl dithiophosphoryl group)-Methyl propionate.

3.2. Tribological Properties of the Sample

The maximum nonseizure load, P_B , represents the oil film strength of the given gear oil, while the sintering load, P_D , represents the ultimate working capacity of the given gear oil. It is shown from the P_B and P_D results in Table 2 that, compared with BO and BM, the P_B and P_D values of BA and BMA are significantly elevated, which reflects that the addition of ADDP can promote the gear oil to form a stable continuous film with higher strength and can improve the extreme pressure performance. Moreover, in the case where MoDTC cannot effectively improve the extreme pressure performance of gear oil, the P_B and P_D values of BMA are further increased by 26.98% and 25.00%, respectively, compared with BA. This reflects that when MoDTC and ADDP coexist in a lubrication system, a synergistic effect, which can further improve the oil film strength of gear oil, may be formed between them.

Table 2. Extreme pressure property of prepared lubricants.

Specimen	P _B /kg	P _D /kg
ВО	80	100
BM	80	100
BA	126	160
BMA	160	200

The wear scar diameter (WSD) can reflect the antiwear performance of the prepared gear oil; the WSD of the three lower steel balls was calculated using an optical microscope, as shown in Figure 5. Each steel ball was tested three times and its average value was calculated; the calculation results are displayed in Table 3. Compared with BO, the WSD of BM and BA decreases by 14.55% and 27.27%, respectively, and the gear oil containing ADDP shows excellent antiwear properties. BMA shows the most superior antiwear performance and WSD decreases by 29.09% compared with BO. As can be seen from Figure 4, the synthesized ADDP has a strong polar group carboxyl group at the molecular end, which will not only form a chemical reaction film to protect the surface of the friction pair, but also bring certain corrosion and wear, while the MoS₂ tribochemical film [18–21] formed by the decomposition of MoDTC on the surface of the friction pair. Thus, the corrosion of ADDP on the worn surface is alleviated, the WSD of BMA decreases by 5.00% compared with BA, and the antiwear performance of the gear oil is further slightly improved.

All the sample oils (BO, BM, BA, and BMA) were subjected to a four-ball friction and wear test at 392 N, 1200 rpm, and 75 °C for a duration of 60 min. After three tests of each gear oil, the mean value was taken, to generate the dynamic friction coefficient curve, as shown in Figure 6a. According to the trend of the curve, the friction coefficient of BO increases slowly to 0.109 at first, then rapidly to 0.121 (about 1000 s), and, finally, slowly to 0.139. This may be because the micro interval between the friction pairs decreases with the increase in time, the amount of gear oil flowing into the friction pair decreases, and the direct contact between the surface bumps increases, due to the failure of the friction film. The overall friction coefficient of BM is much lower than that of BO, indicating that MoDTC has an excellent antifriction performance. The friction coefficient of BM was lower than BO at the initial stage of the test, which fluctuates around 0.085 at first, then slowly decreases to 0.079, but gradually increases to 0.095 after 2400 s. This may be because, in the late period of the test, the friction film formed by the decomposition of MoDTC is destroyed under the severe friction conditions and the remaining MoDTC in the gear oil is

not enough to continue to form a sufficient lubricating film, resulting in an increase in the friction coefficient. The friction coefficient of BMA increases rapidly to 0.125, at first, and then gradually decreases to 0.099 and remains stable. This may be because the lubricating film formed by ADDP grows slowly in the initial period of the test and the corrosion of ADDP on the worn surface is more serious at this time, so the friction coefficient is larger. The lubricating film gradually grows and improves over time, the antiwear effect of ADDP begins to manifest itself, and the friction coefficient shows a decline and tends to be stable. Similarly, the friction coefficient of BMA with ADDP also shows a rapid rising trend at the initial stage of the test, but, at this time, MoDTC is also present in the gear oil system and MoDTC can quickly decompose and form a friction film at the initial stage of the test [18], producing a friction reduction effect. It is also possible that the existence of this friction film makes the corrosion of BMA on the worn surface less serious than that of BA. The maximum friction coefficient of BMA is lower than that of BA. The friction coefficient of BMA is lower than that of BA. The friction coefficient of BMA is lower than that of BA. The friction coefficient of BMA shows a faster declining trend, with the decline amplitude being larger than that of BA, and can finally stabilize at about 0.081.



Figure 5. Wear scar diameter of wear balls formulated with different prepared lubricants after friction and wear test.

Specimen	Wear Scar Diameter/mm	Average Friction Coefficient	Frictional Torque/N·m
BO	0.55	0.121	0.19
BM	0.47	0.083	0.16
BA	0.40	0.099	0.17
BMA	0.38	0.081	0.16

Table 3. Friction and wear test results of different prepared lubricants.

According to Figure 6b, the average and standard deviation of the friction coefficient of different gear oils during the stable stage can be calculated. The confidence interval, in the case of standard deviation is, 95%. BO has the highest average friction coefficient of 0.121. Compared with BO, the mean friction coefficient of BM, BA, and BMA decrease by 31.40%, 18.18%, and 33.06%, respectively. Due to the presence of ADDP, the average friction coefficient of BMA is 2.41% lower than that of BM using MoDTC alone. In terms of the standard deviation of the friction coefficient, the standard deviation of BM is 36.14% smaller than that of BO, while the standard deviation of BA is the smallest at 0.17×10^{-2} . Due to the presence of ADDP, the standard deviation of BMA is 50.94% smaller than that of BM using MoDTC alone, i.e., the friction coefficient is more stable. It can be seen that using ADDP combined with MoDTC can obtain a longer and more stable low friction coefficient than using MoDTC alone, achieving a better antifriction effect.



Figure 6. Tribological properties of the lubricating specimens from four-ball wear tester: (**a**) dynamic curve of friction coefficient; (**b**) the average and standard deviation of the friction coefficient during the stable stage.

3.3. Microstructure Characteristics

As shown in Figure 7, with the aim of studying the friction and wear of four sample oils on the surface of GCr15 steel, SEM was used to observe the wear morphology, while a three-dimensional laser profilometer was used to characterize the surface roughness (Ra) of the worn surface. As can be seen from Figure 7a, the worn surface of BO is heavily scuffed and covered with grooves. During the friction process, the metal material cracks and separates from the surface of the base material, forming wear debris and presenting a layered surface topography. In contrast, the worn surfaces of BM and BA are smoother and have less wear debris, but there are still micro-cracks and grooves caused by plowing wear on the surface of both. Moreover, due to the lack of friction film, the worn surface is peeled off and the infiltration of gear oil promotes the development of cracks to form peeling pits. The worn surface of BMA only has obvious abrasive wear marks, with minimal surface damage.



Figure 7. SEM images at low magnification and optical profilometry surface roughness profile: (**a**) BO; (**b**) BM; (**c**) BA; (**d**) BMA.

The roughness of the worn surface is measured in the direction perpendicular to the sliding direction of the steel ball. BMA has the smallest surface roughness (Ra = 0.32μ m) and the smoothest wear marks, followed by BM (Ra = 0.34μ m) and BA (Ra = 0.42μ m). BO has the roughest surface (Ra = 0.51μ m) and there are deep valleys in its roughness curve, indicating deep surface damage. This difference in surface roughness can also explain the difference in the friction coefficient curves in Figure 6a. The antiwear layer of ADDP protects the worn surface, while the low-shear layer of MoDTC provides low friction. The difference in their working mechanism results in different patterns of wear scars. The presence of ADDP makes the wear scar smaller and the presence of MoDTC makes the worn surface smoother. The synergistic effect of ADDP and MoDTC provides BMA with the best antiwear properties.

As shown in Figure 8, the representative feature region within the worn surface (Figure 7) is further zoomed in. It can be clearly observed that the worn surface of BO is covered with plow grooves and discontinuous irregular deep peeling pits with severe delamination. The plow grooves are mainly produced by the micro-cutting action of spalling wear debris along the sliding direction, while the wear debris are mainly the products of oxidative wear on the worn surface. In the uninterrupted sliding process, they will fall off from the surface of the friction pair, forming secondary damage. It can be inferred that the low-viscosity gear oil has a low lubricant film carrying capacity, leading to serious direct contact between the steel surface. MoDTC can smooth the worn surface and inhibit delamination, but plow grooves and flaky shallow peeling pits can still be observed on the worn surface of BM, which corresponds to the upward trend of the friction coefficient curve of BM in the late test period (Figure 6a). Moreover, the existence of obvious peeling pits on the worn surfaces of BO and BM can also be the reason for the relatively large fluctuation of their friction coefficients. ADDP shows excellent antiwear effects, BA's worn surface has fewer grooves and a few small and shallow peeling pits. However, there is a large amount of tiny long strip pitting, which reflects that ADDP relies on high activity to constantly react on the surface of the friction pair to form a chemical film, which not only provides antiwear effects, but also corrodes the surface of the steel ball. The worn surface peeling pits of BMA disappear, the number and scope of plow grooves and pitting decrease, and the rest are slightly uneven, left by abrasive wear. This reflects that the lubrication film formed by the decomposition of MoDTC can alleviate the corrosion of ADDP on the steel surface, while ADDP combined with MoDTC can effectively prevent the wear of the steel surface by reducing the peeling pits and plow grooving, thus maintaining a low friction coefficient. It can be seen that the combination of these two additives has a positive lubricating synergistic effect on the steel-steel interface.

3.4. Worn Surface Element Analysis

As shown in Figure 9, the friction film formation on the worn surface was further studied using EDS. As can be seen from Figure 9b, there are a small amount of Mo and S elements on the worn surface of BM, which can correspond to the formation of the MoS₂ lubrication film [18–21]. This layer of lubrication film can inhibit the oxidation of iron on the worn surface, leading to a significant reduction in O content, compared with Figure 9a. In Figure 9c,d, the content of O increases significantly, which indicates that ADDP reacts violently with the surface of the friction pair, causing corrosion, while forming a chemical film composed of iron-containing oxides and/or salt to protect the worn surface. Although both MoDTC and ADDP contain S element, the content of O and P in Figure 9d decreases relative to that in Figure 9c, i.e., a decrease in the amount of iron oxides and/or phosphates, which indicates that the lubricating film formed by the decomposition of MoDTC can not only inhibit oxidation, but also alleviate the corrosion of iron by ADDP. Compared with Figure 9b, the Mo content in Figure 9d increases. This suggests that more Mo element remain on the worn surface after the friction test, which reflects that ADDP can extend the life of the MoS₂ lubrication film and achieve a longer period of low friction, corresponding



to the friction coefficient curve of BMA being continuously lower than that of BM after 2400 s in Figure 6a.

Figure 8. SEM images of wear marks: (a) BO; (b) BM; (c) BA; (d) BMA.

To study the antifriction and antiwear mechanism of combined ADDP with MoDTC as gear oil additives, XPS was used to further characterize the worn surface of BMA. As shown in Figure 10, detailed energy absorption spectra of Mo 3d, S 2p, P 2p, C 1s, Fe 2p, and O 1s validate the chemical state and composition of BMA's lubricated worn surface. The peaks of Mo 3d in Figure 10a are divided into two sub-peaks at 229.8 eV and 232.4 eV, representing Mo in the form of MoS_2 and MoO_3 (related to the O 1s peak at 530.2 eV), respectively. The electron binding energy of 226.3 eV corresponds to S 2s, which, in combination with the peak of S 2p at 161.9 eV in Figure 10b, confirms the presence of MoS_2 on the worn surface. The electron binding energy of S 2p at 168.0 eV corresponds to sulfate, while the electron binding energy of P 2p at 133.4 eV in Figure 10c corresponds to phosphate (both correlated with O 1s at 532.1 eV). It can be found that MoDTC decomposes to form a MoS_2 friction film with low shear strength, while ADDP reacts with the steel surface of the friction pair to form an inorganic extreme pressure antiwear film composed of phosphate and sulfate of iron. The combination of the ADDP and MoDTC forms a low-friction lubrication film with extreme strength. The electron binding energy of Fe 2p at 723.4 eV and 710.5 eV in Figure 10d indicates that there may be Fe_3O_4 , Fe_2O_3 , and FeO on the surface of the substrate, which indicates that the oxidation reaction of Fe has always existed. The electron



binding energy of C 1s is 285.1 eV and 288.9 eV, relevant to the C-C single bond and the C=O double bond, respectively.

Figure 9. Worn surface EDS spectra of wear balls after friction and wear test: (**a**) BO; (**b**) BM; (**c**) BA; (**d**) BMA.

3.5. The Interaction Mechanism of ADDP and MoDTC

According to the above results and analysis, the lubrication mechanism of ADDP combined with MoDTC as an antiwear and antifriction additive of low-viscosity gear oil on the surface of GCr15 can be determined. As shown in Figure 11c, under the action of load, F_{N_r} and friction force, f_X , the upper steel ball rotates at the relative speed, ω . During friction, a composite lubrication system is formed between the friction pairs under the synergistic action of ADDP and MoDTC. The chemical friction film formed by BMA has a layered mat structure (Figure 11d), whereby the bottom layer near the substrate is composed of iron oxides, the central area is composed of iron sulfate and phosphate inorganic extreme pressure antiwear lubrication film, while there are some iron sulfides. As can be seen from the molecular structure of ADDP, the S atom is easier to separate from ADDP than the P atom. The element S is more reactive than the element P and there is more element S than element P in the whole system. This may make it easier for sulfates to take the lead to form than phosphates. The outermost layer is the MoS₂ friction film decomposed by MoDTC. The low shear stability MoS₂ layer is favorable to reduce the friction between the contact surfaces, acting as a friction reducer. High-strength sulphate and phosphate layers are favorable to reduce adhesion and scuffing between contact surfaces, providing an antiwear effect.



Figure 10. Worn surface XPS spectra of BMA. (a) Mo 3d; (b) S 2p; (c) P 2p; (d) Fe 1s; (e) C 2p; (f) O 1s.

At the initial stage of friction, compared with the slow-growing sulfate and phosphate, MoDTC rapidly decomposes to form MoS₂, covering the worn surface under the effect of temperature and shear stress, which reduces the corrosion of ADDP on the steel surface to a certain extent, while bringing low friction. MoS₂ with low shear resistance is easy to be eliminated, while ADDP relies on the strong polar group -COOH at the molecular end to adsorb effectively on the metal surface and form an antiwear film composed of iron sulfate and phosphate, through a chemical reaction. Moreover, under the influence of the strong polar group, the thickness and strength of the antiwear film are increased, effectively protecting the worn surface. At this time, the MoS₂ friction film will be formed on the surface of this solid antiwear film, which can alleviate the corrosion of ADDP on the worn surface, by hindering the entry of oxygen elements; it will also be oxidized itself, to form MoO₃. During the removal and formation of MoS₂, the flaky solid lubricant FeS, with a hexagonal structure, will also be produced. The soft FeS layer is porous and can be used as a lubricant reservoir to promote the oil film retention between the worn surfaces.

Although FeS is easy to remove, the S atoms remaining on the substrate continue to react with Fe atoms to generate new FeS [34]. Similarly, Mo atoms also remain on the lubricated surface, under the influence of the strong polarity of ADDP, and continue to form MoS₂. It can be seen that MoDTC can alleviate the corrosion of the metal, while giving full play to the antiwear performance of ADDP, while ADDP can extend the life of MoDTC and form continuous long-term low friction. When the two are mixed, the chemical reaction film is easier to form, improving the adsorption strength and carrying capacity, thus increasing the maximum nonseizure load and sintering load. Therefore, the synergistic effect between ADDP and MoDTC can sufficiently improve the extreme pressure performance, antiwear performance, and antifriction performance of low-viscosity gear oil, but the optimal ratio of the two needs to be further studied.



Figure 11. Tribological behavior and lubrication mechanism of ADDP combined with MoDTC in gear oil. (a) Tribological properties; (b) profile characteristics; (c) schematic diagram of friction test; (d) composite lubrication system; (e) wear marks; (f) worn surface elements; (g) tribochemistry.

4. Conclusions

In this paper, a kind of acrylate of dialkyl dithiophosphoric acid with strong polar groups was synthesized and the tribological behavior of its blended MoDTC in gear oil was studied. Based on the four-ball tests and surface analysis, the following conclusions can be drawn:

(1) Compared with BO, the P_B and P_D values of BM do not change, the P_B and P_D values of BA and BMA significantly increase, and the P_B and P_D values of BMA increase by 26.98% and 25.00% compared with BA, respectively. ADDP combined with MoDTC possesses the best extreme pressure performance.

- (2) Compared with BO, the WSD of BM, BA, and BMA decrease by 14.55%, 27.27%, and 29.09%, respectively. The worn surface of BMA is smooth, with the least number of defects; ADDP combined with MoDTC has the best antiwear performance.
- (3) Compared with BO, the average friction coefficients of BM, BA, and BMA decrease by 31.40%, 18.18%, and 33.06%, respectively. Although the addition of ADDP will increase the friction coefficient at the initial stage of friction, ADDP can extend the life of MoDTC. The combined use of the two can achieve a longer period of low friction.
- (4) MoDTC can alleviate the corrosion of metal on the worn surface by ADDP. ADDP can not only effectively adsorb on the metal surface by relying on strong polar groups, but can also help the MoS₂ friction film with low shear performance stay on the worn surface for a longer time. This synergistic effect makes it easier to form a chemically reactive film with high load-bearing capacity, when the two are blended, obtaining excellent tribological properties.

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