

The rheological and tribological properties of calcium sulfonate complex greases

Zeyun WANG^{1,2}, Yanqiu XIA^{3,*}, Zhilu LIU²

¹ School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, China

² State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

³ School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing, 210094, China

Received: 20 February 2014 / Revised: 28 May 2014 / Accepted: 22 August 2014

© The author(s) 2014. This article is published with open access at Springerlink.com

Abstract: In this study, we synthesized two types of calcium sulfonate complex greases (barium soap and calcium soap) and investigated their physical, rheological, and tribological properties in detail. The test results showed that the evolution of their linear viscoelasticity functions with frequency were quite similar to those of traditional lubricating greases. Moreover, these two calcium sulfonate complex greases had good friction-reducing and antiwear properties at room temperature and at 150 °C. In addition, by adding an organic molybdenum compound (MoDTC) to the base greases, we obtained a very low friction coefficient (0.065) for one of the greases (calcium soap) at 400 N and 500 N (maximum Hertzian pressures of 3.47 GPa and 3.74 GPa, respectively) at 150 °C. X-ray photoelectron spectroscopy (XPS) analysis showed that the tribofilm was composed of some complex oxide species and CaCO₃ that had formed on the worn surface.

Keywords: calcium sulfonate complex greases; tribological properties; rheology; viscoelasticity

1 Introduction

Lubricating greases generally consist of a thickener dispersed in a mineral or synthetic oil. The thickener forms an entanglement network, which traps the oil and confers the appropriate rheological and tribological properties to the grease. Fatty acid soaps made of lithium, calcium, sodium, aluminum, and barium are most commonly used as thickeners [1, 2]. In recent years, a multipurpose grease known as calcium sulfonate complex grease, has attracted much attention due to its good performances at high and low temperatures and its resistance to clipping and rubbing friction. Calcium sulfonate complex grease contains calcium tetraborate and calcium 12-hydroxystearate together with ultrabasic calcium sulfonate (T106D). Its structural formula is shown in Fig. 1. The fabrication process for calcium sulfonate complex grease can be

divided into two stages. In the first stage, Newtonian ultrabasic calcium sulfonate is changed to non-Newtonian ultrabasic calcium sulfonate. In the second stage, boric acid, 12-hydroxystearic acid, and calcium soap are added to the non-Newtonian ultrabasic calcium sulfonate, yielding the calcium sulfonate complex grease.

Recent studies of calcium sulfonate complex grease have for the most part focused on manufacturing techniques and the mechanism of its extreme pressure and antiwear properties. There have been few studies reporting on the rheological and tribological properties of calcium sulfonate complex grease at higher temperatures. In this paper, we used barium and calcium soaps to fabricate ultrabasic calcium sulfonate and studied the physical, rheological, and tribological properties of each. We also investigated the sensitivity

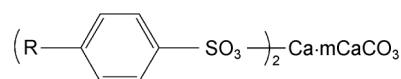


Fig. 1 The structural formula of ultrabasic calcium sulfonate.

* Corresponding author: Yanqiu XIA.
E-mail: xiayanqiu@yahoo.com

of a MoDTC friction modifier in the two calcium sulfonate complex greases at room temperature and at a high temperature (150 °C).

2 Experimental

2.1 Materials

T106D, 12-hydroxystearate, and synthetic PAO (poly-alpha-olefin) 40 were commercially obtained from the Lanzhou Refinery Company (Lanzhou, China). Calcium hydroxide was purchased from the Shanghai Chemical Regent Company. Barium hydroxide was obtained from the Laiyang Chemical Engineering Company. Acetic acid and boric acid were purchased from the Tianjin Chemical Regent Company. All chemical reagents were of analytical grade and were used without further purification.

2.2 Grease manufacture

We prepared the greases using the base oil synthetic PAO 40, which has a kinematic viscosity of 40 mm²·s⁻¹ at 100 °C. The calcium sulfonate complex greases were prepared following patent CN 1414076. First, a certain amount of T106D was added to a prescribed amount of base oil, and the mixture was then stirred and heated. We then added to the above mixture a certain amount of acetic acid, as a promoter, in batches. When the Newtonian ultrabasic calcium sulfonate was completely changed to non-Newtonian ultrabasic calcium sulfonate, a prescribed amount of 12-hydroxystearic acid was added to it. When the 12-hydroxystearic acid was completely dissolved, calcium hydroxide and boric acid aqueous solutions were added to the above mixed solution to allow the saponification process to proceed at 110–120 °C for 4 h. Then, the mixed solution was heated to 130–140 °C to evaporate the water present at the end of the saponification process. Subsequently, the solution was heated to 210 °C to thicken it. Finally, the solution was cooled to room temperature and then was ground on a three-roller mill three times to obtain calcium sulfonate complex grease (calcium soap) (abbreviated as “calcium soap base grease”). The barium soap calcium sulfonate complex grease (barium soap) (abbreviated as “barium soap base grease”) was

obtained following the same procedures described above, with the only difference being that barium hydroxide was used instead of calcium hydroxide.

To investigate the sensitivity of a MoDTC friction modifier, 3.0 wt% concentration MoDTC was added to the calcium sulfonate complex greases.

2.3 Characterization tests

The dropping points of the prepared greases were measured by the BF-22 dropping point of lubricating grease over wide temperature range tester according to the China national standards GB/T 3498, which are similar to the American society for testing and materials (ASTM) D2265 standard. The penetrations were measured using a SYP4100 lubricating grease cone penetrometer according to the China national standards GB/T 269, which are similar to the ASTM D217 standard. The copper strip tests of the prepared greases were conducted according to the China national standard GB/T7326-87. Steel mesh sub-oil tests were measured using a SYP4108 steel mesh sub-oil tester according to the China petrochemical industry standard SH/T 0324. Thermogravimetric analyses (TGA) were carried out on a ZRY-2P thermal analyzer at a heating rate of 10 °C·min⁻¹ in flowing air.

The rheological properties of the prepared base greases were measured using a controlled-stress rheometry rheoscope (ThermoHaake, Germany). Small-amplitude oscillatory shear (SAOS) tests were carried out inside the linear viscoelastic region, using plate-plate geometry (30 mm, 1 mm gap) in a frequency range of 10⁻²–10² rad/s at room temperature. Stress sweep tests, at a frequency of 1 Hz, were performed earlier on each sample to determine their linear viscoelasticity regions.

An Optimol SRV oscillating friction and wear tester (Optimol Instruments Prüftechnik GmbH, Munich, Germany) was used to evaluate the tribological properties of the lubricated greases, and the lubricated greases containing MoDTC, at room temperature and at 150 °C. Upper ball (diameter of 10 mm, AISI 52100 steel, hardness 710 HV) slides reciprocated at an amplitude of 1 mm against a stationary disk (AISI 52100 steel, hardness 800 HV). All tests were conducted in the reciprocating mode under a normal load of 200–800 N (corresponding to a maximum Hertzian

pressure in the range of 2.76–4.37 GPa) at a frequency of 25 Hz for a testing duration of 30 min. The friction coefficient was recorded automatically by a computer connected to the SRV tester. Prior to the friction and wear tests, about 1 g of grease was introduced to the ball-disk contact area. The wear volumes loss of the lower disk was measured using a MicroXAM-3D surface mapping microscope profilometer. The result reported here represents the average of duplicate tests.

The morphologies of the worn surfaces lubricated with the base greases and the greases containing MoDTC were observed using a JEM-5600LV scanning electron microscope (SEM). The binding energies of some typical elements in the worn surfaces were analyzed using a PHI-5702 multi-functional X-ray photoelectron spectroscope (XPS, America). Mg-K α radiation was used as the excitation source and the binding energy of carbon (C1s: 284.6 eV) was used as the reference.

3 Results and discussion

3.1 Physical properties of the prepared base greases

The physical properties of the prepared base greases are shown in Table 1. We can clearly see that the dropping point of the calcium soap base grease was higher than that of the barium soap base grease. For the barium soap base grease, the steel mesh sub-oil result was 0%, which was lower than that of the calcium soap base grease. This means that the colloidal stability of the barium soap base grease is better than that of the calcium soap base grease. Figure 2 shows weight loss with temperature, using air flux, for the prepared base greases. As shown in the figure, the two lubricated base greases both decomposed at about 300 °C.

Table 1 The physical properties of the prepared base greases.

	Barium soap base grease	Calcium soap base grease
Penetration (1/4 mm)	77	83
Dropping point (°C)	308	344
Copper corrosion (100 °C, 24 h)	1a	1a
Steel mesh sub-oil (100 °C, 24 h) (%)	0	1.03

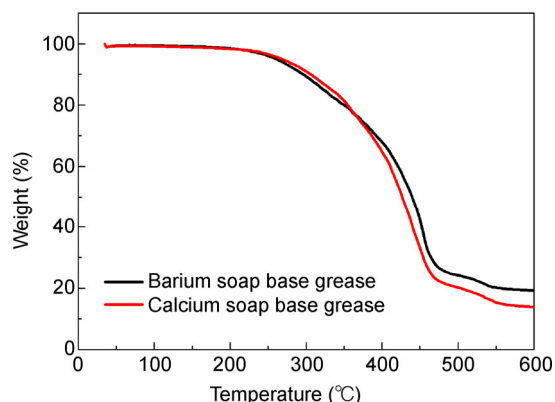


Fig. 2 TGA thermograms for the prepared base greases under air atmosphere.

3.2 Rheological properties

Figure 3(a) shows the stress sweep curves, with the change of the modulus as a function of stress at a frequency of 1 Hz. We can see that at low stress levels, the dominant modulus is the storage modulus (G') and before 100 Pa, the relationship between the storage modulus and the loss modulus (G'') is linear. This region is known as the linear viscoelastic region and 100 Pa is the critical stress. Beyond the critical stress, G' starts to decrease while G'' increases until a certain crossover point is reached where G' is equal to G'' , and hence $\tan\delta = 1$ ($\tan\delta = G''/G'$). From then on, the loss modulus is greater than the storage modulus, indicating that the prepared base greases start to flow [3].

Figure 4(a) shows the evolution of the SAOS functions with frequency for the prepared base greases at room temperature. As we can see, their linear viscoelasticity responses are qualitatively similar to other lubricating greases [2, 4]. Across the frequency range studied, the storage modulus (G') is always higher than the loss modulus (G''), which is characteristic of polymeric systems with physical entanglements [2]. This shows that the prepared base greases are highly structured systems. In this region, G' slightly evolves with frequency, while G'' maintains a minimum value. Also, from Fig. 3(a), we can see that the values of G' and G'' for the calcium soap base grease are higher than those of the barium soap base grease, which indicates that the microstructural network of the calcium soap base grease is stronger than that of the barium soap base grease.

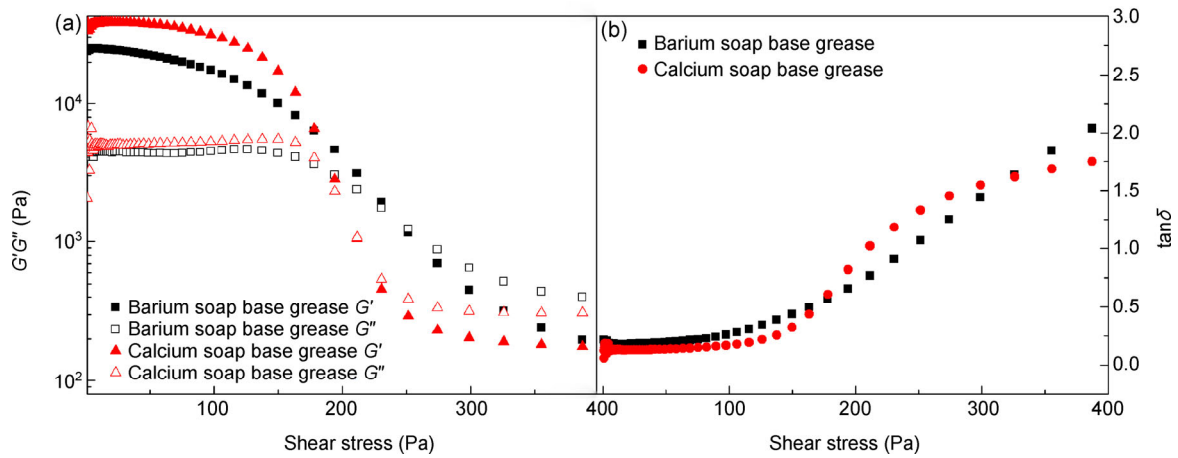


Fig. 3 Stress sweeps for the prepared base greases at room temperature.

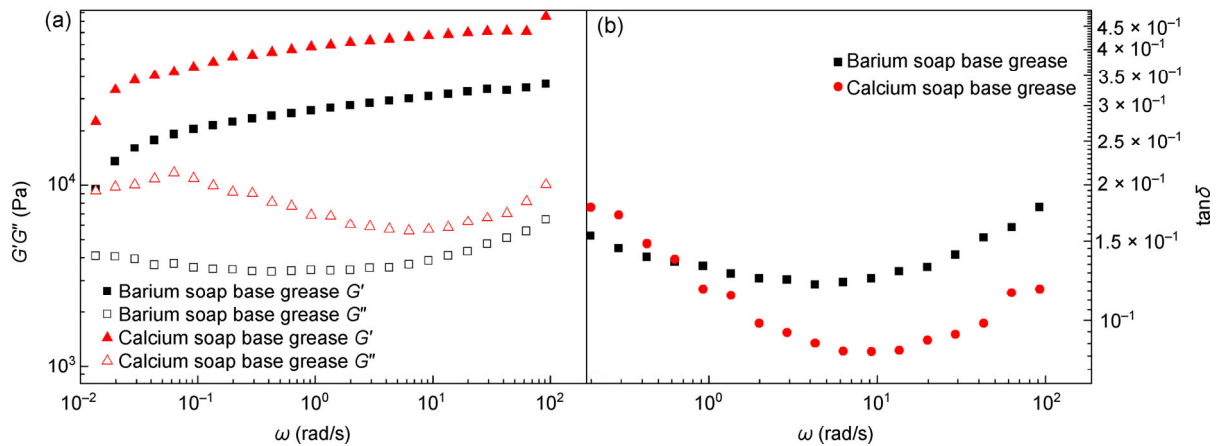


Fig. 4 Evolution of the SAOS functions with frequency for the prepared base grease at room temperature.

The values of the loss tangent ($\tan\delta = G''/G'$) versus frequency are plotted in Fig. 4(b). We can see that all greases show a minimum in $\tan\delta$ at intermediate frequencies, which is a phenomenon related to the appearance of the plateau region. A characteristic viscoelastic parameter of this region is the plateau modulus, G_N^0 . This parameter may be considered to be a measure of the aggregation number among dispersed units of sand, and is consequently related to the strength of the soap network. We used a short-cut method to estimate G_N^0 from the loss tangent [5]. Using this method, we determined that the G_N^0 value of calcium soap base grease is about 66,808 Pa, which was higher than the G_N^0 value of barium soap base grease (29,249 Pa). The higher G_N^0 value of the calcium soap base grease indicates that the calcium soap has more developed fibers than the barium soap.

$$G_N^0 = [G']_{\tan\delta \rightarrow \text{minimum}}$$

3.3 Tribological properties

3.3.1 Tribological results

Figure 5 shows the variations in the friction coefficient and wear volume under loads lubricated with the prepared base greases, with and without MoDTC, at room temperature. We can see that the friction coefficients and wear volumes of the barium and calcium soap base greases are quite similar under different loads at room temperature. However, after adding MoDTC to these two base greases, the friction coefficients significantly decrease at loads of 600 N and 800 N (maximum Hertzian pressure of 3.97 GPa and 4.37 GPa, respectively), and the wear volumes slightly decrease over the range of the loads studied.

Figure 6 shows the friction coefficient and wear volume versus load with lubrication of the prepared base greases, with and without MoDTC, at 150 °C.

Lower friction coefficients and larger wear volumes are observed at 150 °C than at room temperature. At 150 °C, when MoDTC was added to the base greases, the load-carrying capacity increased from 500 N to 600 N and the maximum Hertzian pressure increased from 3.74 GPa to 3.97 GPa, respectively. Meanwhile, the friction coefficients decreased.

From the figure, we can see that the friction coefficients and wear volumes of the two prepared base greases are quite similar at room temperature and at 150 °C. However, after adding MoDTC to the base greases, the friction coefficients of the calcium soap base grease are lower than those of the barium soap base grease. We may deduce that the calcium soap base grease is more sensitive to MoDTC than the barium soap base grease. The difference in sensitivity to the MoDTC may be attributed to the different structure of the thickener. In the calcium

soap base grease, the MoDTC easily makes contact and reacts with the metal surface to form a surface protective film that reduces friction and wear.

3.3.2 SEM analysis of the worn surface

Figure 7 shows SEM images of the worn surfaces lubricated with the different greases at 600 N (3.97 GPa), 25 Hz, and at room temperature. All the SEM images were obtained at the same magnification. As shown in the figure, the worn surfaces lubricated by the base greases were quite rough and showed obvious signs of severe adhesion (Figs. 7(b) and 7(f)). In contrast, only slight grooves are found on the worn surfaces lubricated by the base greases containing 3.0 wt% MoDTC (Figs. 7(d) and 7(h)).

Figure 8 shows SEM images of the worn surfaces lubricated with the different greases at 400 N (3.47 GPa), 25 Hz and at 150 °C. All the SEM images were obtained

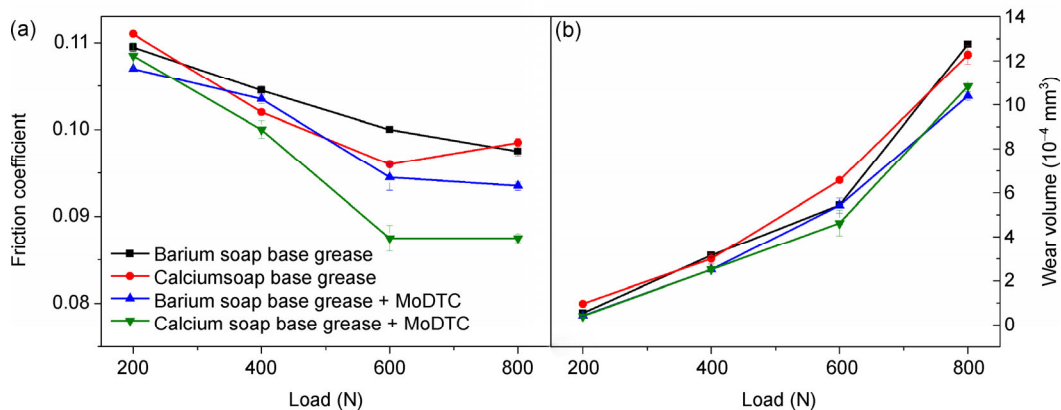


Fig. 5 Variations in the friction coefficient and wear volume with the loads under the lubrication of the prepared base greases and the base greases containing MoDTC at room temperature.

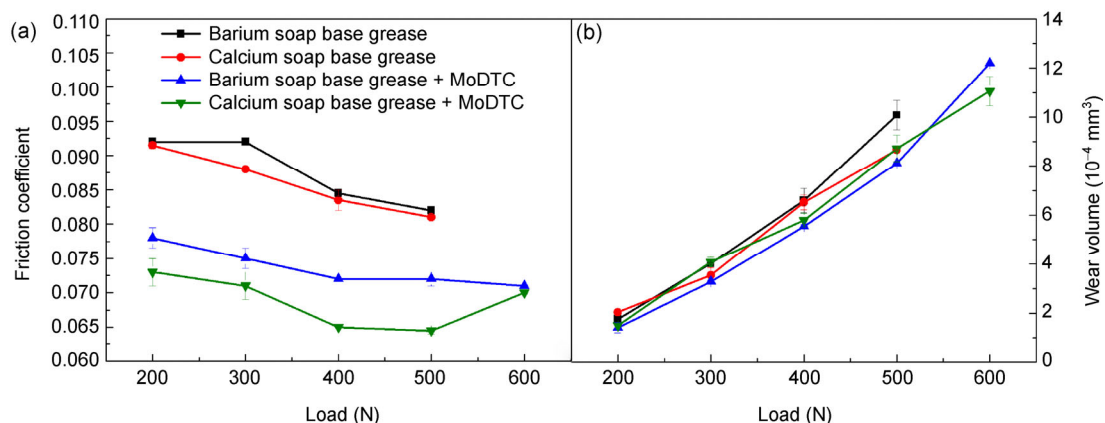


Fig. 6 Friction coefficient and wear volume versus the loads under the lubrication of the prepared base greases and the base greases containing MoDTC at 150 °C.

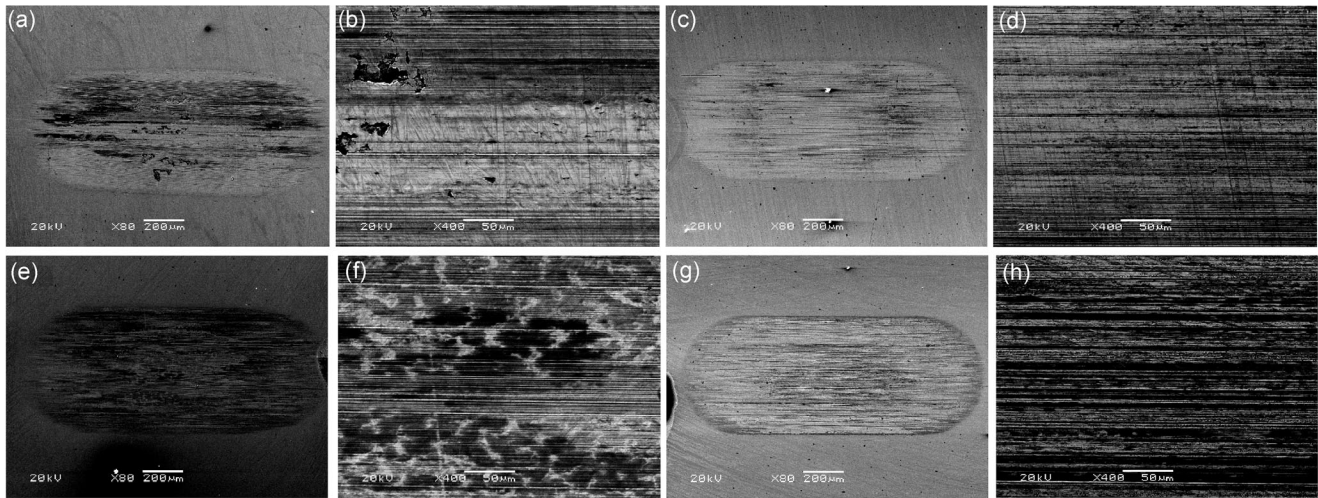


Fig. 7 SEM images of the worn surfaces lubricated with different lubrication at 600 N, 25 Hz and room temperature: (a, b) barium soap base grease; (c, d) barium soap base grease containing 3.0 wt% MoDTC; (e, f) calcium soap base grease; (g, h) calcium soap base grease containing 3.0 wt% MoDTC.

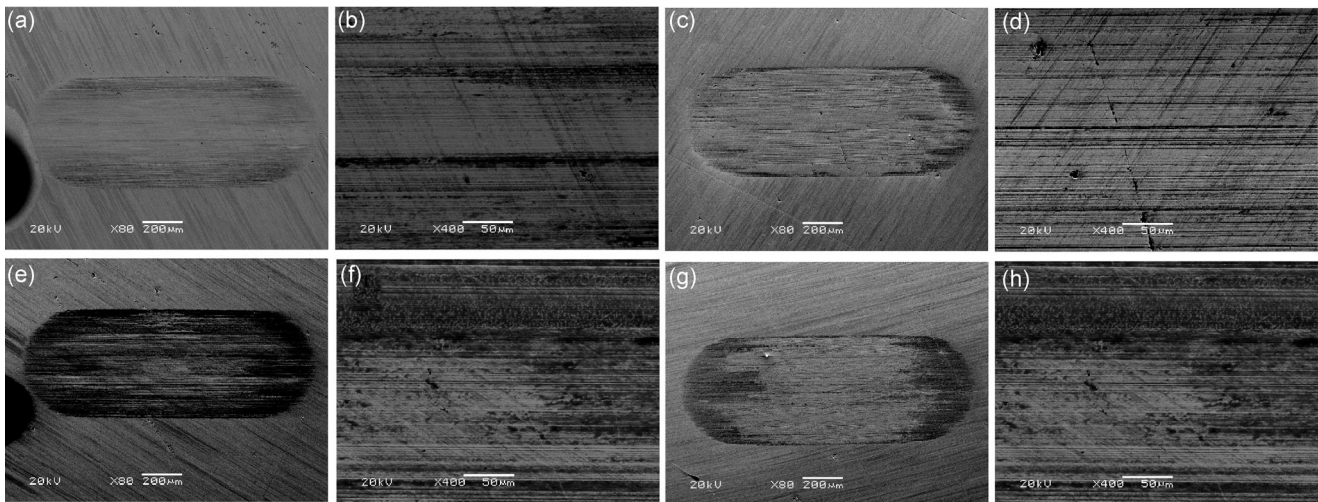


Fig. 8 SEM images of the worn surfaces lubricated with different lubrication at 400 N, 25 Hz and 150°C: (a, b) barium soap base grease; (c, d) barium soap base grease containing 3.0 wt% MoDTC; (e, f) calcium soap base grease; (g, h) calcium soap base grease containing 3.0 wt% MoDTC.

at the same magnification. As clearly shown, the worn surfaces lubricated by the base greases were quite rough (Figs. 8(b) and 8(f)). However, the worn surfaces lubricated with the base greases containing MoDTC showed only slight grooves and smooth surfaces (Figs. 8(d) and 8(h)), thereby demonstrating the antiwear properties of greases containing MoDTC.

3.3.3 XPS analysis of the worn surface

In recent years, much attention has been given to the mechanism of extreme pressure and the antiwear properties of calcium sulfonate complex grease. In this

paper, using barium soap base grease, we performed XPS analysis to investigate the mechanism of extreme pressure and the antiwear properties of calcium sulfonate complex grease. Figure 9 shows XPS spectra of typical elements on worn surfaces lubricated with barium soap base grease, with and without MoDTC, at room temperature and at 150 °C. As shown in the figure, these XPS spectra are almost identical, which indicates that similar chemical reactions occurred.

The binding energy of Ba3d at 780.00 eV corresponds to BaO [6]. The peak of Fe2p at about 709.64 eV is assigned to Fe₂O₃ [7]. The B1s peak at 191.40 eV is

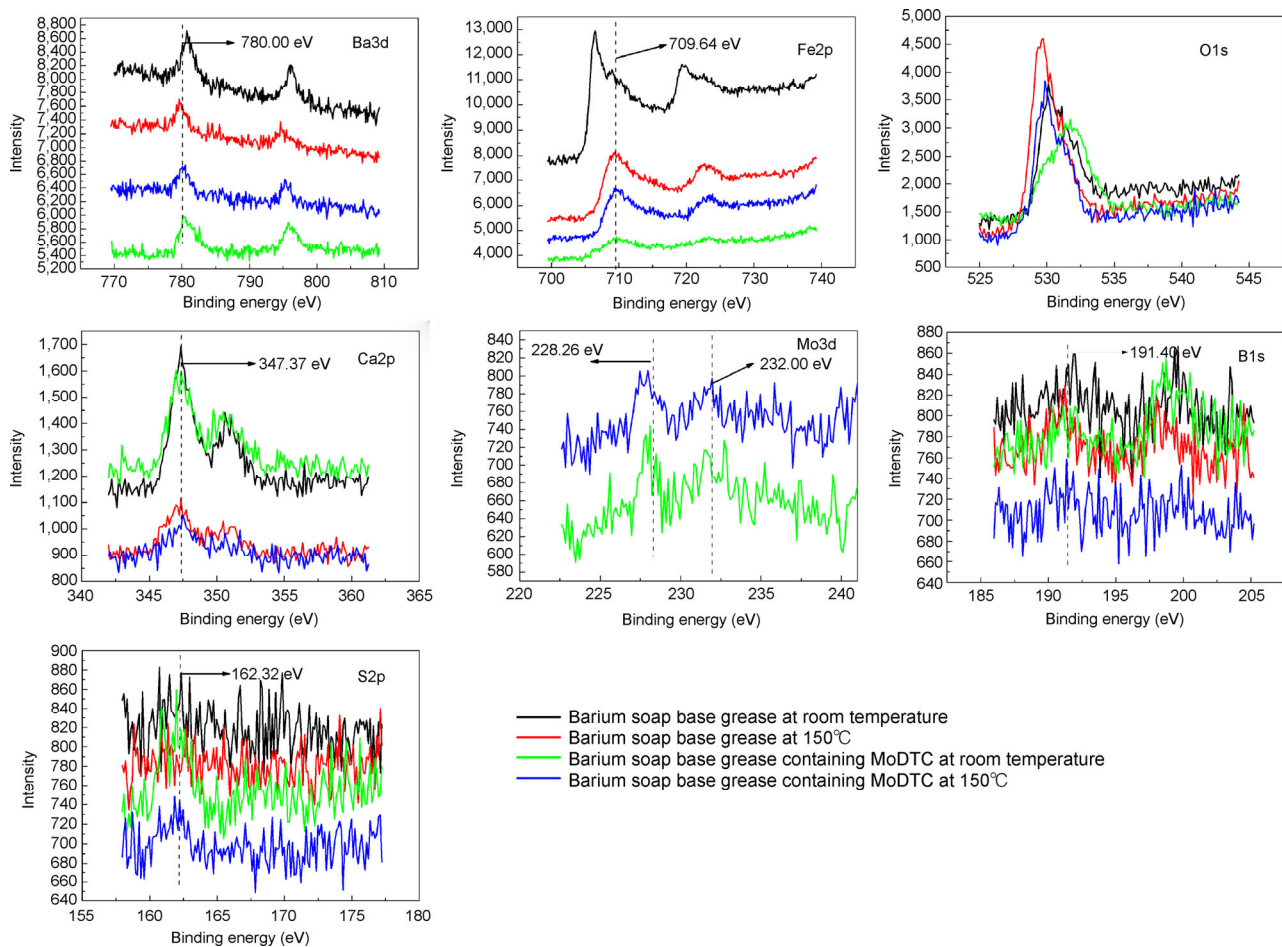


Fig. 9 The XPS spectra of typical elements on the worn surfaces lubricated with the barium soap base grease and the base grease containing MoDTC at room temperature and 150°C.

assigned to B_2O_3 [8, 9]. The wide peak of O1s, which appears in the range of 529.60–531.80 eV, verifies the existence of a complex oxide species on the worn surfaces. The Ca2p peak at 347.37 eV corresponds to the $CaCO_3$ [6] absorbed on the worn surfaces. Based on these data, we conclude that the barium soap base grease can reduce friction and wear due to the generation of a surface protective film composed of BaO , Fe_2O_3 , B_2O_3 , and $CaCO_3$. After adding MoDTC to the base grease, the Mo3d peaks at 228.26 eV and 232.00 eV correspond to MoS_2 and MoO_3 [8], respectively. The S2p peak at 162.32 eV verifies the existence of MoS_2 on the worn surface. From the above analysis, we can conclude that a tribochemical reaction occurs during the sliding process and a tribofilm consisting of MoS_2 and MoO_3 is formed. Therefore, the presence of MoDTC in the base grease can effectively reduce friction and wear.

4 Conclusions

In this study, we used barium and calcium soaps to form non-Newtonian ultrabasic calcium sulfonate complexes to obtain two kinds of calcium sulfonate complex grease. The physical properties of the greases show that the dropping point and the colloid stability values for the calcium soap base grease are respectively higher and poorer than those of the barium soap base grease. The evolution of the linear viscoelasticity functions with frequency is similar to that of other lubricating greases. The SAOS modulus values of the calcium soap base grease are slightly higher than those of the barium soap base grease. The tribological properties of the two prepared base greases are quite similar at room temperature and at 150 °C. However, the calcium soap base grease is more sensitive to the MoDTC than the barium base grease. XPS analysis

results show that the good extreme pressure, antiwear, and friction-reducing properties of barium soap base grease may be attributed to a tribofilm, consisting of BaO, Fe₂O₃, B₂O₃, and CaCO₃, that forms during the sliding process. Also, the good friction-reducing and antiwear properties of the barium soap base grease containing MoDTC may be attributed to a tribofilm consisting of MoS₂ and MoO₃.

Acknowledgements

This work is supported by the open project of State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (1211) and Natural Science foundation of Ningxia University (ZR1216).

Open Access: This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

[1] Mas R, Magnin A. Rheology of colloidal suspensions: Case of lubricating greases. *J Rheol* **38**: 889–908 (1994)



Yanqiu XIA. He received his Ph.D. degree in mechanical design and theory from Northeast University in China, in 1999. He continued his postdoctoral study at the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences and National Institute of Advanced Industrial Science and Technology (AIST) at Tsukuba, Japan, in



Zeyun WANG. She received her Ph.D. degree in physical chemistry in 2012 from the Lanzhou Institute of Chemical Physics, Chinese

- [2] Delgado M A, Valencia C, Sánchez M C, Franco J M, Gallegos C. Influence of soap concentration and oil viscosity on the rheology and microstructure of lubricating greases. *Ind Eng Chem Res* **45**: 1902–1910 (2006)
- [3] Yeong S K, Luckham P F, Tadros T F. Steady flow and viscoelastic properties of lubricating grease containing various thickener concentrations. *J Colloid Interf Sci* **274**: 285–293 (2004)
- [4] Madiedo J M, Franco J M, Valencia C, Gallegos C J. Modeling of the nonlinear rheological behavior of lubricating grease at low shear rates. *J Tribol* **122**: 590–596 (2000)
- [5] García Morales J A, Franco J M, Valencia C, Sánchez M C, Gallegos C. Influence of processing variables on the rheological properties of lubricating grease manufactured in a stirred tank. *J Ind Eng Chem* **10**: 368–378 (2004)
- [6] <http://www.srdata.nist.gov/xps/>, 2014.
- [7] Sun Y B, Hu LT, Xue Q J. Tribological properties and action mechanism of N, N-dialkyl dithiocarbamate-derived S-hydroxyethyl borate esters as additives in rapeseed oil. *Wear* **266**: 917–924 (2009)
- [8] Wang Z Y, Xia Y Q, Liu Z L. Study the sensitivity of solid lubricating additives to attapulgite clay base grease. *Tribol Lett* **42**: 141–148 (2011)
- [9] Jia Z F, Xia Y Q, Li J L, Pang X J, Shao X. Friction and wear behavior of diamond-like carbon coating on plasma nitrided mild steel under boundary lubrication. *Tribol Int* **43**: 474–482 (2009)

2002 and 2007 respectively. In 2005, he was offered a titled professorship, Hundreds Talent Program of Chinese Academy of Sciences. Currently he has moved to School of Energy Power and Mechanical Engineering, North China Electric Power University at Beijing. His research areas cover the lubricants, grease, additives, lubrication for power equipment, equipment fault diagnosis etc.

Academy of Sciences. Now she is a lecturer at Ningxia University. Her research interests include lubricating grease and additives.