Effect of thermorheological properties on tribological behaviors of lubricating grease

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Abstract
Lubricating grease has increased thermorheological properties during heating, which may affect the lubrication of the friction pair. And a friction pair usually heats up in the working process. This study explored the effect of surface temperature of the friction pair on the lubrication performance under lubrication conditions. The thermorheological properties of lubricating grease were analyzed using a rotational rheometer, and the variations and mechanisms of the thermo-rheological properties were explored. The friction-wear test on lubrication was conducted at different temperatures to examine the effects of thermorheological properties on the tribological behaviors of lubricating grease. Wear scar morphology, composition change, and friction-lubrication mechanisms at different temperatures were probed through SEM and X-ray spectrometer analysis. The results showed that lubricating grease has significant thermorheological properties. Moreover, its soap fiber entanglement decreases with rising temperature, and the entanglement properties are slowly lost at high temperature. The soap fiber structure of lubricating grease plays a vital role in lubrication. As temperature rises, the soap fiber entanglement of lubricating grease decreases and the base oil is more easily released under shear, exhibiting a trend of friction coefficient decreasing with the rising temperature. High temperatures weaken the soap fiber entanglement of lubricating grease, the film-forming property, and the surface friction-abrasion resistance of the friction pair and even cause oxidative wear.

1. Introduction

By virtue of its rheological properties, lubricating grease has a unique lubrication effect that results in its prevalent use in anti-friction bearings. It simultaneously exerts the dual effects of lubrication and sealing in the process of lubrication. The operations of anti-friction bearings are accompanied by heating, but rapid heating is often associated with the lubrication failures of bearings. Bearings used in large equipment are closely monitored for excessive increases in temperature. Many factors affect excessive increases in bearing temperature, including poor lubrication, heavy load, and ambient temperature changes. Once the bearing temperature changes, the thermal effect will be transmitted to the lubricating medium in the clearance of the friction pair. Lubricating grease exhibits considerable thermorheological properties, and its rheological properties change with temperature [1]. This outcome suggests that the change in bearing temperature will have an impact on the lubrication effect of lubricating grease.

Current studies on the effects of temperature on the performance of lubricating grease have mainly focused on the changing regularities of the rheological properties of lubricating grease and on how to modify the high-temperature behaviors of lubricating grease. Sánchez et al [2] found that as temperature increases, the soap fiber structure of lubricating grease becomes significantly thinner and the base oil is separated from the soap fiber structure, leading to reduced viscosity and better flowability of the lubricating grease. As observed by Paszkowski et al [3], the effects of temperature on the thixotropy of lubricating grease are closely related to the microscopic...
soap fiber structure. Pan et al [4] deduced the equations based on the grease flow along pipelines and analyzed the effects of temperature on the grease flow along pipelines. Owing to its rheological properties, lubricating grease has significant influences on the lubrication of lubricating grease at low and high temperatures. Under low-temperature conditions, lubricating grease is more viscous, has poorer flowability, and produces an additional torque because its viscosity-temperature characteristics must be overcome when starting up a device [5, 6]. Specifically, any change in temperature may cause the starting torque of such device to increase or decrease several times [7]. Therefore, a low-viscosity base oil and an appropriate thickener are usually used to prepare the lubricating grease at low temperature, resulting in lubricating grease that has better flowability at low temperatures [8, 9]. Researchers have mainly focused on how to improve the anti-friction and anti-wear properties of lubricating grease at high temperatures. Adding different types of anti-wear additives helps improve the preparation method of lubricating grease [10–13] Martin-Alfonso et al [14] used recycled low-density polyethylene (LDPE) as an additive to prepare lubricating grease and found through an analysis of the thermorheological properties of lubricating grease that the recycled LDPE could significantly improve the thermostability and mechanical stability of lubricating grease. Li et al [15] found that adding ultra-fine organobentonite to the base oil under a strict control of technological parameters elevates the dropping point of the prepared lubricating grease after being homogenized by high-speed shear to more than 200 °C. Moreover, at high temperatures, lubricating grease exhibits enhanced rheological properties and high-temperature behaviors. Du et al [16] found in their studies on the variations of the rheological properties of SiO2 grease that different kinds of base oil may affect the shear stability and high-temperature behaviors of lubricating grease. However, the majority of current studies focused on the changing regularities of the thermorheological properties of heated lubricating grease as well as the changing regularities of the structural performance of lubricating grease at high temperatures. The effects of the thermorheological properties of heated lubricating grease on lubrication have seldom been studied, though they are essential for revealing the failure analysis of friction pairs for grease lubricated bearings.

On the basis of the above findings, in this study, the tribological behaviors of grease at different temperatures were examined and the effects of temperature on the rheological properties of grease were revealed. An experimental platform was built for tribological testing. The tribological behaviors of grease at different temperatures and under different loads were analyzed. In addition, the correlation between lubrication and the thermorheological properties was probed. In combination with the surface wear morphology and energy spectrum analysis of the friction pair, the effects of the thermorheological properties of grease on the friction and lubrication mechanisms were examined. The findings of this study can provide experimental support for the analysis on bearing failure arising from rapid temperature rise.

2. Experimental

2.1. Experimental material

A NLGI 1 lithium grease was selected as the sample, which was manufactured by Lubricant Tianjin Company, Sinopec Lubricating Oil Co., LTD (China). The main components and technical parameters of experimental sample were listed in table 1.

2.2. Experimental methods

2.2.1. Thermorheological properties

Rheological measurements were performed in a controlled-shear and controlled-strain rheometer (Physica MCR302 from Anton Paar, Germany) at different temperatures by using a serrated plate-plate geometry (PP25/P2, 25 mm diameter, 1 mm gap), as shown in figure 1.

The flow curves were obtained by applying an increasing shear rate range of $10^{-2}$ s$^{-1}$ to $10^{2}$ s$^{-1}$. In order to further explore its flow performance, an apparent viscosity tests were carried out in a constant shear rate (100 s$^{-1}$) for 360 s.

Small amplitude oscillatory shear tests, at the strain of 0.01%, were carried out in a frequency range comprised between $10^{-1}$ s$^{-1}$ to $10^{2}$ s$^{-1}$. The storage and loss moduli, which were used to describe the entanglement of grease soap fibers, were obtained at different frequencies. The two-step-shear-stress tests were applied on the lubricating grease sample following the step of 10 Pa–400 Pa, and the evolutions of the complex modulus were recorded in the test.

2.2.2. Microstructural characterisation

Microstructural characterisation of lubricating greases was carried out by means of FESEM (Supera 55 from Zeiss, Germany) at 15 kV. Grease samples were prepared by extracting the oil with n-heptane in several batches. Afterwards, the sample was dried at room temperature. Finally, the samples were coated with gold.
Table 1. Main components and technical data for the lubricating greases studied.

| Thickener type                  | Thickener % (w/w) | Base Fluid | Lubricating Oil Viscosity at 40 °C ASTM D-445 (mm²·s⁻¹) | Dropping point ASTM D-566 (°C) | Consistency NLGI Grade | Worked penetration ASTM D-217 (dmm) |
|---------------------------------|-------------------|------------|----------------------------------------------------------|-------------------------------|------------------------|-------------------------------|
| Lithium 12-hydroxystearate     | 9.3               | Mineral    | 100                                                      | 178                           | 1                      | 325                           |
2.2.3. Tribological test

In this paper, the tribological properties of lubricating grease at different temperatures were investigated and figure 2(a) showed a schematic diagram of the apparatus. The tribological performance of lubricating grease was performed using a reciprocating sliding tribometer (Sinto Scientific, Japan). It consisted of a stationary holder where a 304 stainless steel ball with a diameter of 10 mm was placed and a reciprocating table where the substrate with heating block was mounted. The hardness and the surface roughness of the 304 stainless steel ball are 26 HRC and Ra 0.012 μm. A substrate of 304 stainless steel was used with the dimensions of 100 mm × 30 mm × 0.5 mm. The hardness of 304 stainless steel substrate is 150 ~ 160 HB. The substrate surface was successively polished by metallographic abrasive papers with the grit size of 320, 600 and 1200, respectively. Before conducting every tribological test, the 304 stainless steel ball and substrate were dipped into absolute ethanol and cleaned with ultrasonic washer for 30 min.
Figure 2(b) shows the temperature of the substrate surface. As can be seen, the temperature of the substrate surface fluctuates within a certain temperature range. The average temperatures are 60.67 °C, 93.26 °C and 139.11 °C, respectively.

The friction tests were conducted with a sliding frequency of 0.83 Hz and stroke of 10 mm. The test time was 1800s. The test load was 0.5 N, 2 N and 5 N. The corresponding Hertzian contact pressures were 353 MPa, 560 MPa and 760 MPa, respectively. All 3D surface parameters of worn surfaces were measured by a 3D optical microscopy (Bruker, USA). The chemical composition on the worn surfaces was carried out by means of scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

3.1. Flow properties

Figure 3 shows the effects of temperature on the apparent viscosity of grease. ‘Room temperature’ refers to the laboratory temperature on the experiment day (23 °C). Other temperature settings are set by getting the average of actual measured temperatures on the surface of the friction pair, as shown in figure 2(b) (60.67 °C, 93.26 °C, and 139.11 °C). Figure 3(a) shows the changing regularities of the apparent viscosity of grease with the shear rate at different temperatures. The figure reveals that the apparent viscosity of grease gradually decreases with the increasingly higher shear rate at different experimental temperatures, exhibiting a pronounced shear thinning. The shear thinning of grease is especially evident at low shear rates. The higher the temperature, the less pronounced the shear thinning of grease. To further analyze the effects of temperature on the apparent viscosity of grease, figure 3(b) shows the changing regularities of the apparent viscosity of grease with the shearing time at a constant shear rate (10 s⁻¹). As the figure shows, the apparent viscosity of grease gradually decreases with rising temperature and, at the same temperature, the apparent viscosity of grease gradually decreases with increase in shearing time. However, the thinning effect increases with the increase in shearing time. In particular, below 139.11 °C, the apparent viscosity of grease is extremely low and the shear thinning is very subtle.

Shear thinning and thermorheological properties are actually closely related to the structural colloidal dispersion system of grease. The structural colloidal dispersion system also enables grease to exert its unique dual effects of lubrication and sealing simultaneously during the lubrication process. To this end, the effects of temperature on the soap fiber structure of grease are further studied.

3.2. Structural properties

Figure 4 shows the morphological characteristics of grease soap fiber. The figure indicates that grease is a mesh structure of highly tangled soap fibers and has a shear thinning that is closely related to its soap fiber structure. Soap fibers constitute the structural skeleton of grease, and the base oil is dispersed in the clearance of the structural skeleton. In the process of shearing and squeezing grease, the base oil is released and acts as a lubricant. Grease that is squeezed onto the edge can act as a seal, effectively preventing any lubricant loss from the surface of the friction pair. Therefore, grease can maintain its soap fiber entanglement in the lubrication process, a capability that is of vital importance to its lubricating property. The soap fiber entanglement of grease shows dynamic changes because of external factors. At different temperatures and shear rates, the soap fiber entanglement of grease shows different changing regularities. Sánchez et al [2] used AFM to observe the soap
fiber structure of grease. However, for grease with low viscosity at high temperature, the tap mode of AFM failed to complete the test because of sticky needles.

The rheological properties of grease actually correspond closely to the soap fiber entanglement. The static and dynamic entanglement properties of grease can be characterized using a rotational rheometer in the oscillatory shear mode. Figure 5 shows the changing regularities of the viscoelastic behaviors of grease at different temperatures. Grease is a structural colloidal dispersion system, which exhibits both viscosity and elasticity during the shearing process. The storage and loss moduli reflect the elastic solid and viscous liquid behaviors of grease, respectively. When the storage modulus is higher than the loss modulus, grease is mainly characterized by solid properties; on the contrary, when storage modulus is lower than the loss modulus, it is mainly characterized by viscosity, thus exhibiting viscous flow behaviors. Figure 5 illustrates that the storage modulus of grease is generally higher than the loss modulus. This finding suggests that during heating, grease is mainly characterized by solid properties but still exhibits semi-solid properties. The reason grease exhibits this phenomenon is because its structural skeleton is a highly entangled soap fiber structure. In the heating process, the soap fiber entanglement changes and, in turn, exhibits semi-solid properties. However, the corresponding storage and loss moduli are no longer in accordance with the original changing regularities at 139.11 °C, indicating that the structural properties of grease have been lost at that temperature. During the experiment, grease was also found to show a liquid form at this approximate temperature.

Figure 6 shows the changing regularities of the complex modulus of grease under two-step shearing (10 Pa, 400 Pa) and at different temperatures. When the shear stress of the grease is 10 Pa, the soap fiber entanglement of...
grease is not seriously damaged at 23 °C, 60.67 °C, or 93.26 °C because the shear stress is less than the yield shear stress of grease. Furthermore, the complex modulus does not change significantly with the shearing time. When grease is under the shear stress at 400 Pa, the three sets of complex moduli significantly decrease because the grease is already in a flowing state. The experiment clearly revealed that when the rheometer rotor is undergoing the reciprocating oscillatory shearing, the storage modulus of grease under shear thinning will reduce rapidly. However, at 139.11 °C, the entanglement properties of the soap fiber structure are basically lost, and when the shear stress is 10 Pa or 400 Pa, grease under the oscillatory shear is in a viscous flow state because the complex modulus is basically unchanged at the two phases.

The soap fiber structure of grease in the lubrication of the friction pair is damaged under shear. To further reveal the damage of temperature to the soap fiber structure of grease under shear, the calculation formula of the structural damage rate of grease is given below, according to the methods presented by Sánchez et al [2].

\[
\%\text{Rheo-destruction} = \left( \frac{G_{0}^* - G_{1}^*}{G_{0}^*} \right) \times 100, \tag{1}
\]

where \( G_{0}^* \) is the complex modulus in the linear viscoelastic range for the first shear stress program (\( \tau = 10 \) Pa); \( G_{1}^* \) is the complex modulus in the non-linear viscoelastic range for the second shear stress program (\( \tau = 400 \) Pa).

Table 2 gives the structural damage rate of grease at different temperatures, wherein the higher the temperature, the greater the structural damage rate of grease. This result suggests that, at a certain shear rate, the higher the temperature, the more vulnerable the structure of grease to damage and the more likely the release of the lube base oil. Grease has special lubrication and sealing effects, which are closely related to its rheological properties. When the rheological properties of grease vary with temperature, the lubrication effect of grease is affected.

3.3. Tribological behaviors

Figure 7 gives the friction coefficient of the grease-lubricated friction pair under different load-temperature conditions. In general, at the same load, the friction coefficient decreases with temperature rising and, at the same temperature, the friction coefficient increases with the load. In particular, when the load is 5 N at 150 °C, the friction coefficient under lubrication rises sharply and is close to the dry friction coefficient of the material.
These variations are mainly caused by the rheological properties of grease varying with temperature, and under load, the thermorheological properties of grease has an impact on the surface lubrication of the friction pair. The variations in viscosity of grease have significant effects on its film-forming property and carrying capacity. The higher the temperature, the lower the apparent viscosity of grease, the thinner the film of grease, the weaker the entanglement properties of thickener, the more easily the base oil will be released from the soap fiber structure of grease, and the more likely the film will be formed. Thus, the effect of reducing friction appears. The higher the load, the thinner the film will be. Therefore, the friction coefficient increases accordingly. Especially at high temperature, the apparent viscosity of grease is low and the film is thin. Meanwhile, at high load, the friction pair cannot form an effective film, ultimately resulting in a direct contact with the friction pair surface and the friction coefficient approaching the dry friction.

3.4. Lubrication mechanism
To further reveal the lubrication mechanism under different temperature–lubrication conditions, the surface wear morphology of the friction pair at different temperatures and under the load of 2 N is investigated. The mechanism of actions of the thermorheological properties of grease on the lubrication effect is likewise discussed.

Figure 8 shows the 3D topography of the surface wear of the friction pair (steel sheet) under different experimental conditions. The figure reveals that at room temperature, 60 °C, and 100 °C, the surface wear morphology of the friction pair has few noticeable changes. The widths of corresponding wear tracks are 138 μm, 157 μm and 176μm. This result shows that within the temperature range, even if grease exhibits significant thermorheological properties, it will still maintain good anti-friction performance. However, the width of the wear track is 301 μm when temperature rises to 150 °C, and the value of surface wear width is significantly increased compared to that at any other temperature. Combined with the results of the abovementioned friction coefficient under lubrication, under the load of 2 N, no lubrication failure occurs on the surface, and as temperature rises, the friction coefficient remains at approximately 0.10. This finding suggests that, at the temperature (150 °C), the anti-friction property of grease does not change significantly, but the anti-wear property is reduced significantly.

Figure 9 shows the wear pattern of lubrication at different temperatures. In the figure, at room temperature, 60 °C, and 100 °C, the morphology of the wear scar surface remains almost unchanged. Additionally, the energy spectrum analysis on the wear surface indicates that the oxygen content is basically the same. This outcome shows that, within this temperature range, the lubrication mechanism of grease is similar. However, at 150 °C, the wear scar of grease is clear. The energy spectrum analysis on the wear scar surface also reveals that the oxygen content is higher than in the other sets of lubrication. This result shows that, at the temperature (150 °C) and under the lubrication condition, a certain degree of oxidative wear occurs. It can also be speculated that, at room temperature, 60 °C, and 100 °C, grease can still effectively lubricate even if it has significant thermorheological properties. However, because the structure of grease is basically destroyed, the lubrication effect on the friction surface becomes poorer at too high temperatures. As a result, partial oxidative wear occurs under light and medium loads. The lubricating film can also play an effective supporting role so that the friction coefficient has little change. Under heavy load, as temperature rises, the apparent viscosity of grease drops. The film-forming
The property of grease is decreased [17], which finally causes the film to fail in providing an effective support for the surface of the friction pair and worsens the direct surface contact and wear. With regard to the grease-lubricated friction pair for heavy-duty transmission, the temperature rise effect must be noted to ensure the film forms an effective support and avoids any dry friction phenomenon.
4. Conclusions

The soap fiber entanglement of grease gradually decreases with temperature rising, which causes grease to exhibit significant thermorheological properties during heating. Shear thinning caused by the structural properties of grease gradually weakens as temperature rises, and the structural recovery deteriorates with temperature rising. At high temperature, the structural characteristics of grease appear very weak.

The thermorheological properties of grease are closely related to its tribological behaviors. The soap fiber entanglement of grease gradually decreases with temperature rising, which causes grease to exhibit significant thermorheological properties during heating. The higher the temperature, the poorer the soap fiber entanglement, and the more likely the release of the base oil from the colloidal dispersion system. The base oil is better for lubricating the surface of the friction pair. At high temperature, the carrying capacity of the film decreases, and as the load increases, the friction coefficient becomes larger. When the load exceeds the carrying capacity of the film, it is very likely to cause lubrication failure.

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