Origin of the tribofilm from MoS₂ nanoparticle oil additives: Dependence of oil film thickness on particle aggregation in rolling point contact

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Abstract: The lubrication effectiveness of MoS₂ nanoparticles as an oil additive remains unclear, restricting its application in industry to reduce friction. The goal of this work was to explore the lubrication mechanism of MoS₂ nanoparticles as an oil additive. In this study, the oil film thickness behaviors of MoS₂ nanoparticles in poly-alpha olefin (PAO4) base oil, PAO4 with 3 wt% dispersant (polyisobutyleneamine succinimide, PIBS), and 0W20 engine oil were investigated using an elastohydrodynamic lubrication (EHL) testing machine. Following the EHL tests, the flow patterns around the contact area and the tribofilm covering rate on contact area were studied using optical microscopy to understand the lubrication mechanism. The results indicate that both the dispersant and nanoparticle aggregation significantly affected the oil film thickness. The expected oil film thickness increase in the case of 0.1 wt% MoS₂ in PAO4 base oil was obtained, with an increase from 30 to 60 nm over 15 min at a velocity of 50 mm/s. Flow pattern analysis revealed the formation of particle aggregation on the rolling path when lubricated with 0.1 wt% MoS₂, which is associated with a tribofilm coverage rate of 41.5% on the contact area. However, an oil film thickness increase and particle aggregation were not observed during the tests with 0.1 wt% MoS₂ blended with 3 wt% PIBS as the dispersant in PAO4 base oil, and for 0.75 wt% MoS₂ in 0W20 engine oil. The results suggest that nanoparticles responsible for tribofilm formation originated from aggregates, but not the well-dispersed nanoparticles in point contact. This understanding should aid the advancement of novel lubricant additive design.

Keywords: nanoparticle lubrication; oil film thickness; flow pattern; particle aggregation

1 Introduction

Low viscosity engine oil is required to reduce friction and to enhance fuel efficiency in response to global warming [1, 2]. Lubricant material design for modern engines must consider low oil viscosity, which results in low oil-film thickness and reduced

energy consumption in the hydrodynamic lubrication regime. However, this is associated with direct asperity contact in both boundary lubrication and mixed lubrication [3, 4].

Nanoparticles as an anti-friction additive have been considered as a promising candidate to reduce friction and wear in boundary lubrication and mixed

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Nomenclature

H_c	Non-dimensional central film thickness	k	Ellipticity ratio
U	Non-dimensional entrainment velocity	R^*	Combined radius of curvature of the two surfaces in the direction of lubricant entrainment
G	Non-dimensional material parameter	h_c	Central film thickness
Q	Non-dimensional load		

lubrication regimes [5–8]. MoS₂ nanoparticles show remarkable anti-friction and anti-wear properties in point contact with base oil [9–12]. However, few studies have reported the tribological behavior of nanoparticles blended with engine oil [13, 14]. The influence of nanoparticles on the anti-friction and anti-wear properties of engine oil remains unclear. It is challenging to reach conclusions as a result of the unclear lubrication mechanisms of nanoparticles as oil additives. Lubrication mechanisms, such as micro-rolling bearings [15], deposition films [16], self-repair effect [17], and competitive adsorption [18, 19] have been proposed to understand the lubrication behavior of nanoparticles. These mechanisms worked well in certain cases. We noted that these lubrication mechanisms focus on particle behavior in the contact area, and thus how particles behaved after entering the contact area. However, it remains a challenge to determine the driving force for particles entering the contact area.

An earlier study found that nanoparticles as an oil additive did not work as expected. Rabaso et al. revealed that the dispersant reduced the friction-

reduction ability of MoS₂ nanoparticles [19], and the oil had to be stirred during testing to obtain the expected low friction and low wear rate [20]. In an earlier study [21, 22], MoS₂ particles of approximately 250 nm revealed remarkable lubrication performance in point contact, despite a contact gap of approximately 15 nm between the ball and disk (theoretical oil film thickness) in boundary lubrication. The energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) results show the formation of a MoS₂ tribofilm on the wear scar, indicating that large MoS₂ particles entered the contact area. We are intrigued by how a large particle (250 nm) can pass through a small contact gap (15 nm), as shown in Fig. 1(a). The presence of side flow around the contact area presents a further challenge [23, 24], as shown in Fig. 1(b). Well-dispersed particles would move with the side flow, and not enter the contact area [14, 25, 26].

Usually, it is difficult to observe a single MoS₂ nanoparticle (such as that of size 200 nm) using an optical microscope. However, earlier results [19, 22] showed large particle aggregation (~50 μm) around the contact area, which makes it possible to study

Fig. 1 Nanoparticle lubrication challenges. (a) Large particle (250 nm) entering small gap (15 nm), (b) side flow around contact area: particle may move with side flow, but not enter contact area.

the flow pattern behavior of nanoparticles using an optical microscope. Furthermore, we note that a transparent glass disk can be used to measure the oil film thickness and to understand the lubrication mechanism [27–29], which inspired us to further explore the influence of flow pattern on the lubrication behavior of MoS₂ nanoparticles. This facilitates matching of the oil film thickness behavior of oil containing nanoparticles with the tribofilm distribution and particle aggregation during tests.

In this study, an *in-situ* observation device with a microscope was applied to investigate the flow pattern and tribofilm distribution on the contact area after elastohydrodynamic lubrication (EHL) tests. First, the oil film thickness behaviors of 0.1 wt% MoS₂ nanoparticles in PAO4 (without polyisobutyleneamine succinimide (PIBS)) and 0.1 wt% MoS₂ nanoparticles +3 wt% PIBS+PAO4 were studied at various rolling speeds. After the tests, the tribofilm cover rates on the contact area were investigated by analyzing their flow patterns. Finally, the oil film thickness of 0W20 base lubricant and 0.75 wt% MoS₂+0W20 were explored to understand the tribofilm source of nanoparticles as oil additives in point contact.

2 Material and experimental process

2.1 Material

A well-distributed MoS₂ nanoparticle suspension with a particle size of 250 nm was provided by Shaanxi Hande Axle Co., Ltd., China. The PIBS as a dispersant was obtained from Jinzhou BETT Chemical Co., Ltd., China, it has a kinematic viscosity of approximately 205 mm²/s at 100 °C, and a specific gravity of 912 g/cm³ with a molecular weight of approximately 3,000. PAO4 base oil with viscosity $\eta = 0.024$ Pa·s at 30 °C and 0W20 engine oil were provided by Valvoline Inc. The 0W20 engine oil was selected for its two advantages: (1) low viscosity, which is similar to that of PAO4 base oil at room temperature; (2) it contains numerous polar additives, such as dispersants, detergents, and anti-friction and anti-wear additives, which act as dispersants to graft on the particle surface [30] and prevent particle aggregation.

The particle size distribution of the MoS₂ nanoparticles

was measured using a laser scattering particle size analyzer (Delsa Nano C). The size and shape of the particles were imaged using a transmission electron microscope (TEM, JEOL JEM 2100).

Oil samples containing MoS₂ nanoparticles were prepared by mixing them in an ultrasonic bath for 15 min. PIBS of 3 wt% was added to poly-alpha olefin (PAO4) oil to evaluate the influence of the dispersant (PIBS) on the oil film thickness of the lubricant containing nanoparticles. In the present study, three oil samples in PAO4 were tested: PAO4 (base oil), PAO4+0.1 wt% nano-MoS₂, and PAO4+0.1 wt% nano-MoS₂+3 wt% PIBS; a further two oil samples in 0W20 engine oil were prepared: 0W20 engine oil (base lubricant) and 0W20 engine oil+0.75 wt% nano-MoS₂.

2.2 Film thickness measurement

The elastohydrodynamic lubricant film thickness was measured with a PCS thin-film tribometer [31, 32]. A polished AISI 52100 steel ball of 19.050-mm diameter was pressed against an optically transparent glass disk under a 20-N load. The Young's modulus of the glass disk is 75 GPa and that of the steel ball is 210 GPa, resulting in a maximum Hertzian pressure of 0.54 GPa under the test conditions. The disk has a 500-nm-thick silica spacer, allowing measurement of the lubricant film thicknesses with a precision within 5% for film thicknesses > 30 nm and to within 1 nm for films < 30 nm. The root mean square (r.m.s.) roughness values of the glass disk and steel ball are 5 and 14 nm, respectively, resulting in a composite roughness of 15 nm. The film thickness was measured under nominally pure rolling conditions with the ball completely driven by the disk as the disk velocity was varied between 10, 15, 30, 50, 100, and 200 mm/s.

For the particle flow pattern observation after the elastohydrodynamic lubrication (EHL) tests, a system with a CCD camera (Basler scA1390-17fc, Germany) was used to focus on the contact area on the ball surface and record the relevant images on a personal computer, as shown in Fig. 2. The disk speed was 2 mm/s during the observation. This velocity was different to those chosen for the oil film thickness testing in order to ensure adequate resolution for the exploitable images. The flow pattern after the EHL tests was

Fig. 2 Schematic of nanoparticle flow pattern observation device.

observed immediately, which is helpful to correlate the oil film thickness at high speeds with the flow pattern behavior.

2.3 Calculation of tribofilm covering rate on contact area

After observation, the images were processed using image binarization to obtain clear images. The threshold was processed based on RGB color: for green values larger than 125, the threshold was set to white (RGB = 256, 256, 256), which means a negligible tribofilm formed on the contact area, such as on the contact area of pure PAO4 base oil; for green values from 120 to 125, the threshold was set to medium black, which indicates poor particle tribofilm distribution on the contact area; for green values smaller than 120, the threshold was set to black (RGB = 0, 0, 0), which suggests a well-distributed tribofilm. This aids understanding of the influence of the particle tribofilm on the contact area on the oil film thickness, which depends on the particle distribution state or the dispersant.

2.4 Central oil film thickness calculation

The Hamrock–Dowson equation [33, 34] applied for the theoretical estimation of the central oil film thickness of the base lubricant in the test is as follows:

$$H_c = 2.69U^{0.67}G^{0.53}Q^{-0.067}(1 - 0.61e^{-0.73k}) \quad (1)$$

$$h_c = H_c R^* \quad (2)$$

where H_c is the non-dimensional central film thickness; h_c is the central film thickness; R^* is the combined radius of curvature of the two surfaces in the direction of lubricant entrainment; $1/R^* = 1/R_1 + 1/R_2$, where R_1 and R_2 are the radius of the ball and disk,

respectively (in this research, $R_2 = \infty$). $U = \eta u / (E^* R^*)$ is the non-dimensional entrainment velocity, where E^* is the effective elastic modulus of the composite;

$$1/E^* = \frac{1}{2} \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right); u = (u_1 + u_2)/2 \text{ is the average}$$

speed; E and ν are the elastic modulus and Poisson's ratio of the ball and disk, respectively; subscripts 1 and 2 refer to the two bodies 1 and 2, respectively; η is the dynamic viscosity of the lubricant under the ambient condition; $G = \alpha E^*$ is the non-dimensional material parameter; α is the pressure–viscosity coefficient of the lubricant; $Q = F / (E^* R^{*2})$ is the non-dimensional load; F is the normal load; and k is the ellipticity ratio, which equals one for the current cases.

3 Oil film thickness behavior in PAO4

3.1 Characterization of MoS₂ nanoparticles

Figure 3 (a) shows a TEM image of the MoS₂ nanoparticles, which indicates they have an average size of approximately 250 nm and are well-dispersed. Figure 3 (b) shows the particle size distribution of the MoS₂ nanoparticles, measured using a dynamic light scattering method. The average diameter of the MoS₂ nanoparticles was 265.4 nm, and the d50 diameter of the particle was approximately 247.8 nm, which is consistent with the TEM results. These MoS₂ nanoparticles can be well-dispersed in 0W20 oil for one month without obvious sedimentation, as shown in Fig. 3 (c).

3.2 Effect of dispersant on oil film thickness

Figure 4 reveals the influence of MoS₂ nanoparticles on the oil film thickness in PAO4 base oil at velocities from 50 to 10 mm/s. Figure 4(a) shows that the oil film thickness of PAO4 base oil was constant throughout the test, and it was close to the theoretical value predicted by Eq. (1). As expected, the oil film thickness improved for the 0.1 wt% MoS₂ nanoparticles, as shown in Fig. 4(b). Its oil film thickness increased from 30 to approximately 60 nm over 15 min, which is much larger than the PAO4 theoretical value (28 nm), and it was immeasurable at 30 mm/s after 30 min.

Fig. 3 Well-distributed MoS₂ nanoparticles in static state. (a) TEM map, (b) particle size distribution, and (c) stable dispersion of MoS₂ nanoparticles in 0W20 engine oil for one month.

However, such oil film thickness improvement was not found for the 0.1 wt% MoS₂ nanoparticles after the addition of 3 wt% PIBS, as shown in Fig. 4(b). Its oil film thickness was stable during testing, which is in contrast to the oil film thickness behavior of 0.1 wt% MoS₂ (without PIBS). This indicates that PIBS as a dispersant significantly influenced the oil film thickness of PAO4 with 0.1 wt% MoS₂ nanoparticles. These results suggest that MoS₂ nanoparticles without PIBS could be entrained into the contact area to form a tribofilm and increase the oil film thickness. However, in the case of 3 wt% PIBS, the MoS₂ nanoparticles could not enter the contact area, preventing tribofilm formation.

Further EHL tests of 0.1 wt% MoS₂ nanoparticles without PIBS were carried out to examine the oil film improvement, as shown in Fig. 5. The oil film thickness increased from 22 nm to approximately

40 nm over 10 min at 30 mm/s, which is substantially larger than the PAO4 theoretical value (19 nm). Further oil film improvement was observed at 17 min when the speed increased to 50 mm/s. This confirms that the oil film thickness can be enhanced by the addition of MoS₂ nanoparticles.

It should be noted that the average size of MoS₂ in this study was approximately 250 nm, which is much larger than the oil film thickness (68 nm). This suggests that MoS₂ nanoparticles were present to form a tribofilm on the contact area. However, the method by which these larger particles entering the small gap remains unclear. Moreover, we are

Fig. 4 Influence of MoS₂ nanoparticles on oil film thickness in PAO4 base oil. (a) PAO4 base oil and (b) MoS₂ nanoparticles as additive with and without PIBS.

Fig. 5 Oil film thickness with speed increase from 30 to 50 mm/s.

intrigued as to why PIBS (dispersant) significantly affected the oil film thickness of the MoS₂ nanoparticles. The nanoparticle flow pattern after the EHL tests was observed *in-situ* to determine the tribofilm formation mechanism on the contact area.

3.3 Flow pattern analysis: Matching tribofilm covering rate with particle aggregations

After the EHL tests, the flow pattern images around

contact area were recorded using a CCD camera, as shown in Fig. 6. Figure 6(a) shows that the contact area was green for PAO4 base oil. Particle aggregations on the rolling path and tribofilm on the contact area were observed for the 0.1 wt% MoS₂ nanoparticles, as shown in Figs. 6(b) and 6(c), respectively. Particle aggregations on rolling path were clearly observed and captured at a rolling speed of 2 mm/s, and the contact area was unclear

Fig. 6 Flow patterns of PAO4 base oil, 0.1 wt% MoS₂ nanoparticles, and 0.1 wt% MoS₂ nanoparticles with 3 wt% PIBS after EHL tests. (a1) PAO4 base oil, (a2) grayscale map of (a1), (b1) observation during moving (2 mm/s) for 0.1 wt% MoS₂, (b2) grayscale map of (b1), (c1) static observation for 0.1 wt% MoS₂, (c2) grayscale map of (c1), (d1) static observation for 0.1 wt% MoS₂ with 3 wt% PIBS, and (d2) grayscale map of (d1).

during observation. In the static state, the color in the inner contact area was yellow, but not green, which is different to that of PAO4 base oil in Fig. 6(a). This suggests that the inner contact area was covered by a MoS₂ nanoparticle tribofilm. These results are in agreement with the oil film thickness increase in Figs. 4 and 5 for the 0.1 wt% MoS₂ nanoparticles.

However, these particle aggregations and tribofilms were not observed under the microscope for 0.1 wt% MoS₂ with 3 wt% PIBS, as shown in Fig. 6(d). Its flow pattern was similar to that of PAO4 base oil, and no particles were observed. This suggests well-distributed MoS₂ nanoparticles in PAO4 with PIBS in the dynamic state, and thus a single MoS₂ nanoparticle (approximately 250 nm) was unobservable under the microscope.

It is noted that the oil film increase is associated with particle aggregation. Aggregations on the rolling path and the tribofilm on the contact area were formed for 0.1 wt% MoS₂ nanoparticles without PIBS during the EHL tests; however, no tribofilm was found in the case of 0.1 wt% MoS₂ with PIBS, which had a flow pattern identical to that of pure PAO4 base oil.

These contact areas in Figs. 6(a), 6(c), and 6(d) were processed using image binarization to clearly show the tribofilm distribution, as shown in Fig. 7. The contact area of PAO4 base oil was set to white, which means no tribofilm coverage, as shown in Fig. 7(a). The case of 0.1 wt% MoS₂ nanoparticles without PIBS clearly reveals the tribofilm covering the contact area, as shown in Fig. 7(b), which resulted in the oil film increase. The tribofilm coverage rate was approximately 41.5%, concentrated on the inner contact area. However, the tribofilm coverage rate for 0.1 wt% MoS₂ nanoparticles with 3 wt% PIBS was similar to that of PAO4 base oil, i.e., almost zero, as shown in Fig. 7(c). This suggests that it is difficult for MoS₂ nanoparticles to form well-distributed tribofilms in the presence of a dispersant.

3.4 Critical velocity for oil film thickness increase

Figure 8 presents the oil film thickness of 0.1 wt% MoS₂ nanoparticles in PAO4 (without PIBS) at a

velocity of 200 mm/s. However, we observed no oil film thickness increase. The film thickness of 0.1 wt% MoS₂ nanoparticles was approximately 78 nm and was stable during the tests (over 10 min), approaching the PAO4 theoretical value. This is contrast to the results in Figs. 4 and 5, which reveals that the addition of 0.1 wt% MoS₂ nanoparticles in PAO4 significantly improved the oil film thickness

Fig. 7 Image binarization of contact areas in flow pattern maps. (a) PAO4 base oil (cover rate, 0.5%), (b) PAO4+0.1 wt%-MoS₂, and (c) PAO4+0.1 wt%-MoS₂+3 wt% PIBS.

Fig. 8 Oil film thickness of 0.1 wt% MoS₂ nanoparticles in PAO4 at 200 mm/s.

at speeds of 30 and 50 mm/s. The results in Figs. 4 and 8 suggest that the operating velocity also influences the increase in oil film thickness, even for the same oil sample (0.1 wt% MoS₂ nanoparticles). An appropriate velocity should be applied to achieve the increase in oil film thickness.

Figure 9 depicts the oil film thickness of 0.1 wt% MoS₂ nanoparticles for the case of the velocity decrease from 100 to 10 mm/s. The oil film thickness was stable at 100 and 50 mm/s, similar to that of PAO base oil. However, the oil film thickness increased again at speeds of 30 and 10 mm/s, which were larger than the PAO4 base oil theoretical value.

Figures 4(b) and 5 show that the oil film thickness increased at 50 mm/s by the addition of 0.1 wt% MoS₂ nanoparticles; however, such an oil film increase was not observed at 50 mm/s in Fig. 9. This indicates that the oil film thickness increase was affected by the initial speed as well. A possible reason for the stable oil film thickness at 50 mm/s in Fig. 9 is that the particles were thrown to the outer disk by the centrifugal force at high velocity.

Together with Figs. 4(b), 5, and 9, it was found that the initial speed significantly influenced the oil film thickness at 50 mm/s, as shown in Fig. 10. Various oil film thicknesses were obtained at 50 mm/s with different initial speeds. These results suggest that the oil film thickness increase induced by MoS₂ nanoparticles was also influenced by the operating condition. In the present study, MoS₂ nanoparticles as an oil additives worked at low operating velocity (≤ 50 mm/s).

Fig. 9 Oil film thickness in the case of velocity decrease from 100 to 10 mm/s.

Fig. 10 Oil film thickness of MoS₂ nanoparticles at 50 mm/s with different initial speeds.

Figure 11 shows the flow pattern of 0.1 wt% MoS₂ after EHL tests from 100 to 10 mm/s. Again, particle aggregations on the rolling path were clearly observed and captured during movement (2 mm/s) and static observation, as shown in Figs. 11(a, b). Figure 11(c) shows that part of the contact area was covered by the tribofilm, which is consistent with the results in Fig. 7. These results further suggest that the particles for tribofilm formation originated from the aggregates.

4 Missing oil film thickness improvement in 0W20 engine oil

4.1 Oil film thickness and flow pattern

Figure 12 shows the oil film thickness of 0W20 engine oil with and without 0.75 wt% MoS₂ nanoparticles. It reveals that the oil film thickness of 0W20 with 0.75 wt% MoS₂ nanoparticles at 50 mm/s was approximately 36 nm, which is similar to that of 0W20 base lubricant (35 nm). No obvious oil film thickness increase was observed for 0W20 with MoS₂ nanoparticles at the tested speeds, similar to that of 0.1 wt% MoS₂ nanoparticles in PAO4 with PIBS (Fig. 4(b)). This suggests absent or negligible tribofilm formation in the contact area.

Figure 13 reveals the flow pattern of 0W20 with and without 0.75 wt% MoS₂ nanoparticles at a load of 4 N and speed of 2 mm/s. The flow pattern of 0.75 wt% MoS₂ nanoparticles after running for 16 min (Fig. 13(b)) was the same to that of the 0W20

Fig. 11 Flow pattern of 0.1 wt% MoS₂ after EHL tests (100 to 10 mm/s). (a1) Observation during moving (2 mm/s), (a2) grayscale map of (a1), (b1) static observation, (b2) grayscale map of (b1), and (c) image binarization of contact areas in flow pattern maps.

Fig. 12 Oil film thickness of 0W20 engine oil with 0.75 wt% MoS₂ nanoparticles.

base lubricant in Fig. 13(a). No particles or particle aggregation was observed in Fig. 13(b), indicating well-dispersed MoS₂ nanoparticles in the 0W20 engine oil.

4.2 Discussion

We note that MoS₂ nanoparticles had little influence on the oil film thickness of 0W20 engine oil, without particle aggregation. Together with the results of MoS₂ nanoparticles with 3 wt% PIBS (dispersant) in this study, this suggests that the dispersant significantly affects the tribofilm formation. Moreover, it indicates that these well-dispersed particles cannot form the expected tribofilm for MoS₂ nanoparticles.

The dispersant influence on the tribofilm formation may be due to: (i) Competitive adsorption between the particle and dispersant [18, 19]; (ii) no or few particles entering the contact area in the case of 3 wt% PIBS and engine oil, and therefore no tribofilm or immeasurable tribofilm forming on the contact area. It should be noted that the MoS₂ nanoparticle size (approximately 250 nm) is much larger than the

Fig. 13 Influence of MoS₂ on the flow pattern of 0W20 engine oil (4 N, 2 mm/s). (a1) 0W20 original oil, (a2) grayscale map of (a1), (b1) 0W20+0.75 wt% MoS₂ after running for 16 min, and (b2) grayscale map of (b1).

gap (approximately 30 nm at 50 mm/s for PAO4 base oil) between the ball and disk; if a MoS₂ nanoparticle enters the contact area, it should collapse from being squeezed between the ball and disk. This collapsed particle exposes its fresh surface with high surface energy, forming visible particle aggregation under the microscope and bonding with the friction surface to form a tribofilm. Furthermore, the particle aggregation associated with the oil film thickness increase may suggest that a group of particles were required to form the measurable or well-distributed tribofilm on the contact area. This supports the second proposal that no or few particles entered the contact area in the case of well-dispersed nanoparticles in the dynamic state.

In this study, we show that the tribofilm is attributed to MoS₂ particle aggregation in point contact, and not well-dispersed nanoparticles, as shown in Table 1. If the particles in the tribofilm are well-dispersed nanoparticles, we should observe an oil film thickness increase in 0W20 engine oil and PAO4 with PIBS. This further confirms that tribofilm formation significantly depended on the particle aggregation in nanoparticle lubrication in point contact in the case of MoS₂ nanoparticles.

Table 1 Summary of oil film thickness increase as a function of particle aggregation.

Oil sample	Oil film thickness behavior	Particle aggregation	
PAO4 + 0.1 wt% MoS ₂	Increased with time below 50 mm/s	Visible particle aggregation	MoS ₂ nanoparticle worked well as expected
PAO4+0.1 wt% MoS ₂ + 3 wt% PIBS	No oil film thickness increase	No particle aggregation	Particle dispersed well, but worked poorly
0W20 engine oil + 0.75 wt% MoS ₂	No oil film thickness increase	No particle aggregation	Particle dispersed well, but worked poorly

Based on the aforementioned results and discussion, a lubrication mechanism for understanding the influence of dispersants on the oil film thickness was proposed, as shown in Fig. 14. In PAO4 base oil, the particles tended to aggregate while moving owing to the absence of proper dispersants, even though these particles dispersed well in the static state. This agrees with the observation results in Fig. 6(b). These aggregates with poor flowability were entrained into the contact area to form a tribofilm under the contact extrusion, which increased the oil film thickness, as shown in Fig. 14(a). However, the particles dispersed relatively well without obvious aggregations with the presence of dispersants (Fig.

6(d)). These well-dispersed nanoparticles moved with the side flow without entering the contact area [26], leading to the absence of a tribofilm. Therefore, an oil film thickness increase was not observed, as shown in Fig. 14(b).

5 Conclusions

In this study, we explored the tribofilm source of MoS_2 nanoparticles as an oil additive, by investigating the influence of MoS_2 nanoparticles on the oil film thickness of PAO4 and 0W20 engine oil, together

with particle flow pattern observation. The results show that the tribofilm of MoS_2 nanoparticle is attributed to its particle aggregation, but not well-dispersed particles in point contact. The following conclusions can be drawn:

1) In this study, MoS_2 nanoparticles without PIBS increased the oil film thickness at low speeds, and the critical velocity for oil film thickness increase was approximately 50 mm/s. At a velocity of 50 mm/s, the oil film thickness increased from 30 to 58 nm over 15 min. Above 50 mm/s, the oil film thickness was stable and was similar to that of PAO4 base oil.

Fig. 14 Proposed lubrication mechanism for influence of dispersants on oil film thickness. (a) In PAO4 base oil without proper dispersants and (b) in the presence of rich dispersants.

2) The dispersant significantly influenced the oil film thickness for lubricants containing MoS₂ nanoparticles. An oil film thickness increase was not observed for 0.1 wt% MoS₂ nanoparticles with 3 wt% PIBS and 0.75 wt% MoS₂ nanoparticles in 0W20 engine oil.

3) The oil film thickness increase was due to the formation of a tribofilm on the contact area. Nanoparticle aggregation and the tribofilm on the contact area formed during EHL tests for 0.1 wt% MoS₂ nanoparticles at low speeds, with no PIBS. The tribofilm coverage rate on the contact area was approximately 42.1%, resulting in the expected oil film thickness increase. The particle dispersed well in the case of 3 wt% PIBS and in 0W20 engine oil, leading to the absence of aggregation and tribofilm on the contact area.

In conclusion, our results reveal that particle aggregation was the source of the tribofilm in the case of point contact with MoS₂ nanoparticles.

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