Analysis of the ultralow friction behavior of a mesogenic fluid in a reciprocating contact

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Received Date Line (to be inserted by Production) (8 pt)

Abstract

Frictional contacts that are lubricated by a mesogenic fluid exhibit ultralow friction coefficients. It is assumed that these specific mesogenic fluid forms a liquid crystalline-like structure in the sliding contact that induces hydrodynamic lubrication. This effect has been reproducibly observed in a reciprocating friction system after a certain running-in period.

The aim of the present work was to study the tribological behavior of a specific mesogenic fluid in detail in contrast to standard lubricants. Tribological experiments were performed using a reciprocating cylinder-on-disc test machine. The obtained results show that ultralow friction coefficients can reproducibly be realized. Special attention was given to the chemical transformation of the mesogenic fluid during the tribological test. It is assumed that chemical and physical interactions of the mesogenic fluid with the surface of the test specimens induce a change in the rheological parameters of the mesogenic fluid and therefore, the tribological behavior is strongly affected.

A better understanding of the tribological behavior is essential for the development of efficient production routes and for the qualification of mesogenic lubricants for possible future applications.

Keywords: Mesogenic-like fluids, stick-slip, steel slide bearings, ultralow friction, wear, friction mechanisms

Nomenclature

MF mesogenic fluid
LC Liquid crystal
COF coefficient of friction µ
RCD reciprocating cylinder-on-disc sliding geometry
XPS X-ray photoelectron spectroscopy

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1. Introduction

Given the current demand to increase the energy efficiency and reliability of technical systems, there is a significant need to minimize friction and wear between moving parts in tribological applications. Since their discovery in 1888 by F. Reinitzer, liquid crystals were subject of countless investigations [1]. The basis for the specific physical behavior of liquid crystals is their anisotropic molecular structure. Specific orientations of the liquid crystalline phases can be achieved with different surface treatments [2], by applying an electrical voltage [3] and by inducing mechanical shear and pressure [4-7].

In previously published work on the tribological behavior of mesogenic fluids (MFs), predominantly commercially available liquid crystals were used, which were in fact developed for display applications. The idea to use mesogenic fluids in tribological applications has been discussed for almost 30 years. The outcome of the growing interest in the theory and applications of MFs as lubricants was the celebration of the *Tribology and liquid crystalline state* symposium at the 198th American Chemical Society Meeting in 1990 [8]. A review of the latest developments of liquid crystalline lubricants is summarized by Carrión et al [9]. It is noticeable that the possibility to use MFs for tribological applications is not an exceptional way to reduce friction and wear because Kupchinov et al. [10] demonstrated that the low friction of joints in living organisms results from liquid crystalline substances in the synovial fluid.

By using MFs as pure lubricants [11-15] or as additives in base oils [16-18] a reduction of friction and wear was observed. As already mentioned, these tribological studies were performed using liquid crystals, which were optimized for optical applications and did not show ultralow coefficients of friction (COF). In contrast to these findings, it has been reported that sliding contacts, which were lubricated with specific MFs can reach ultralow friction values (μ<0.005) [19-22]. The first MFs which showed ultralow COF were synthesized by R. Eidenschink (Nematel GmbH, Mainz, Germany). The effect of ultralow friction was then also detected in a real engineering application [23]. The mechanisms that induce ultralow friction coefficients are not clear but the findings of Noiretz et al. [24] and Idziak et al. [4] showed that external pressure and shear stress induce a molecular ordering of the molecules. The rheological properties of MFs strongly depend on the orientation of the anisotropic shaped molecules [2]. As the tribological behavior is affected by the viscosity of the lubricant [25, 26] it is clear that molecular orientation effects influence the friction and wear values.

So far, one economic aspect of using MFs has been the production costs. Pure MFs that have been commercialized for LC-Displays are just too expensive for tribological applications. Therefore, this paper focuses
on the research of one specific molecular class which can be much more practicable to synthesize on an industrial scale. For further optimization for possible practicability it is necessary to understand the mechanisms, which lead to ultralow friction on the molecular scale.

In this paper further tribological studies on one MF are performed to understand the mechanisms which occur during the friction test. Therefore, surface analysis, rheological and chemical analyses of the reaction products are carried out. Based on presented findings, a model is proposed on how these mechanisms lead to ultralow friction.

2. Experimental

Reagents and Materials

A calamitic rod-shaped mesogenic fluid was used for the tribological tests (Fig. 1). The phenyl substituted 1,3-Diketone is called 07/10 (trade name Nematel™). 07/10 was already part of different tribological studies [19-22] which illustrated the special tribological behavior of 07/10 in pure form and in mixtures over a broad range of tribological parameters.

![Chemical structure of the mesogenic fluid 07/10](image)

The used test specimens are standardized for this tribological configuration (Optimol Instruments, Germany). Characteristics of the test specimens are given in Table 1. The XPS-analysis shows that there is an oxide layer on the surface and only low content of chromium is detected. 100Cr6 steel is used for rolling-element bearings, which is not a stainless steel because of the low content of chromium (1.5%).

Additionally, the tribological characteristics of three standard-lubricants were tested to get comparative results. Therefore, two commercially available lubricants were used: motor oil SAE 10W-40 (Valvoline) and gear oil Optigear 32 (Castrol). Both oils are enriched with several additives such as EP-additives, sulphated ash, zinc / phosphor and calcium because they are used in specific technical applications. The third oil is an additive-free paraffin oil, which only consists of alkane hydrocarbons (Merck GmbH, Germany).

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>Disc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diketone form 10%</td>
<td>Keto-Enol form 90%</td>
</tr>
</tbody>
</table>

![Table 1 Characteristics of the test specimens](image)
Material | Steel 100Cr6 | Steel 100Cr6
---|---|---
Diameter | 15.0 mm | 24.0 mm
Length, Height | 22.0 mm | 7.9 mm
Elastic modulus | 226.1 GPa | 226.1 GPa
Hardness | 62.3 HRC | 60.0 HRC
Surface roughness:
$R_a$ | 0.06 µm | 0.07 µm
$R_z$ | 0.46 µm | 0.60 µm

*Tribological experiments*

A practical tribological setup for testing lubricants is the reciprocating cylinder-on-disc test [28] (RCD, Fig. 2). This test can be used as a model test for the comparative investigation of friction and wear properties of lubricants. The typical test parameters used for the test are given in Table 2. The temperature of the testing specimen is applied by heating the disc from the seat area. Under this heating block there is a piezoelectric sensor which measures the coefficient of friction. The cylinder is inclined by $10^\circ$ to the sliding direction (Fig. 2). After cleaning the samples with ethanol and acetone the lubricant was applied on the cylinder before starting the friction test. Due to the constant applied load and growing contact surface area (caused by wear) the contact pressure decreases throughout the test from initially 130 MPa.

![Fig. 2. Sketch of loading geometry of reciprocating cylinder on disc (RCD)](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Testing temperature</td>
<td>90 °C</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>25 °C – 30 °C</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>20% – 30%</td>
</tr>
<tr>
<td>Normal load</td>
<td>50 N</td>
</tr>
<tr>
<td>Frequency</td>
<td>50 Hz</td>
</tr>
</tbody>
</table>
3. Results

The results of the RCD-tests with three standard lubricants and the MF 07/10 are shown in Fig. 3. The standard lubricants show a constant and nearly similar COF of approximately 0.15 during the whole testing period. In contrast, the MF shows an ultralow COF (<0.005) after a running-in period of 7 hours. During the running-in phase mixed lubrication is dominant. In this regime, wear is relatively high because of solid-solid contacts of the testing specimens [21]. This solid contact leads to stick-slip effects during the first two hours. It must be pointed out that at the testing temperature of 90 °C the mesogenic fluid is in the isotropic phase.

![Fig. 3. Comparison of the coefficient of friction of the MF and standard lubricants](image)

After the tribological tests, wear of the cylinder and disc was analyzed. Fig. 4 shows the wear profile of the disc which was measured using a stylus profilometry. The diagram in Fig. 5 illustrates the worn volume of the cylinder and the calculated mean contact pressure after the tribological test. It can be clearly seen, that the two reference lubricants show the lowest wear on the disc (Fig. 4) and on the cylinder (Fig. 5 b). The MF leads to a lower contact pressure (approximately 5 MPa) after the test because of the higher wear, which is generated during the running-in period.
The conclusion that nearly all wear is generated during the running-in period is verified in Fig. 5 a+b. To get a better understanding of the wear rates and the reproducibility of the COF, the tribological test were performed with different testing periods (Fig. 5 a). Fig. 5 b shows the measured worn area of the cylinder in dependency of the testing time. There is an explicit correlation between the ultralow COF and wear, according to equation (1). As the COF decreases, nearly no more wear is generated. At the period of ultralow friction the contact pressure in in the range of approximately 5 MPa.

\[ W_C = 8.847 - 6.13 \cdot e^{(-0.22 \cdot t)} \quad (R^2 = 0.94) \]  

Fig. 4. a) Wear profiles on the disc after friction test (20 h) b) Diagram of the worn volume on the cylinder and the resulting contact pressure after the friction test (20 h)

Fig. 5. a) Friction diagram of the MF 07/10 with different testing times. b) Wear analysis in dependency of the testing time
Through the tribological test shown in Fig. 6, we tried to analyze the influence of the contact pressure and the chemical change of the MF. Therefore a RCD-test with unused specimens and new MF was performed for 14 hours (V.1, Fig. 6). After the test, the specimens were separated from each other and were cleaned with acetone. The specimens were not removed from the fixture of the SRV-machine because the second tribological test (V.2, Fig. 6) was performed on the same surface, thus; at low surface pressure (approximately 5 MPa instead of 130 MPa with new specimens) and with new MF. After this test, the specimens were separated again. The third test (V.3, Fig. 6) was performed with the used MF from test V.2 at the same worn surface. V.3 was performed because it was observed that the color of MF 07/10 changed from yellow to red after the tribological test. Therefore, it was assumed that the chemical characteristics of the MF had changed. Fig. 6 clearly shows that the contact pressure (V.2) and the chemical change of 07/10 lead to a lower running-in period.

Fig. 6. Comparison of the COF of used and unused MF at high and low contact pressure

Based on these findings it is assumed that the MF reacts with the nascent Fe$^{3+}$-ions to a chelate-complex compound with three 07/10 molecules as ligand. Fig. 7 a shows the possible structure of the resulting iron tris-$\beta$-diketonate complex of 07/10 analogous to the description of Giroud-Godquin [29, 30]. This compound was synthesized by Nematel and is called 09/10. As wear increases during the tribological test till ultralow friction is reached, it was assumed that the content of this Fe-complex increases continuously. Fig. 7 b shows the results of photometric measurements of the MF to analyze the content of this compound after the tribological tests from Fig. 5. The content of the complex increases exponentially analogous to the gradient of wear (Fig. 5 b). In the range between 20 and 100 hours the content of complex is nearly constant at approximately 28%.
Fig. 7. a) 09/10: Iron tris-β-diketonate complex of 07/10 b) Photometric analysis of the Fe-complex content in the MF 07/10 after the tribological tests

Fig. 8 a shows the friction diagram of the MF 07/10 and the pure compound 09/10. It is noticeable that 09/10 exhibits a much worse tribological behavior than 07/10. 09/10 shows in the first four hours a constant COF of 0.2 but after this period the COF increases to values of 0.25 after 15 hours. The reason for this can be found by rheological analysis as shown in Fig. 8 b. 09/10 has a very high dynamic viscosity of 500 mPa·s at 40 °C in contrast to 07/10, which has a viscosity of only 7 mPa·s.

Fig. 8. a) Comparison of the COF of the MF 07/10 and the metal-complex 09/10 b) Diagram of the shear dependent viscosity of 07/10 and 09/10

The significant difference in the viscosity values of 07/10 and 09/10 leads to a further effect which affects the tribological behavior of the MF. As the content of the complex during the tribological test increases, the viscosity value of the MF increases, too. The tribological tests were performed with only small amount of MF as lubricant and therefore, the viscosity can not be measured directly after the test. However, the viscosity can be quantified...
indirectly via a calibration curve of the viscosity in dependency of the content of the synthesized compound 09/10 in 07/10. Fig. 9 a shows the measured exponential increase of the viscosity of different mixtures of 09/10 and 07/10. Using equation (2), which results from the calibration curve, the viscosity of the MF can be calculated after the tribological test by additional photometric measurement of the content of complex.

\[ \eta_{MF} = 3.619 + 2.78 \cdot e^{(0.052 \cdot x)} \quad (R^2 = 0.99) \quad (2) \]

where \( \eta_{MF} \) is the calculated viscosity of the MF after the tribological test and \( x \) the measured content of complex. Fig. 9 b shows the increase of the viscosity in dependence of the testing time. There is also a exponentially relationship between the viscosity and the testing time, according to equation (3). Therefore, one can calculate that the viscosity increases from initially 7 mPa·s to 13.9 ± 1.9 mPa·s after 100 hours. Thus, the viscosity already doubles after 20 hours testing time and therefore, it is clear that the tribological behavior also strongly changes.

\[ \eta_{MF} = 12.905 - 9.683 \cdot e^{(-0.068 \cdot t)} \quad (R^2 = 0.94) \quad (3) \]

where \( \eta_{MF} \) is the calculated viscosity of the MF after the tribological testing time \( t \).

![Diagram showing the increase of viscosity in dependence of the content of 09/10 in 07/10 and testing time.](image)

**Fig. 9.** a) Calibration curve: Diagram showing the increase of viscosity in dependence of the content of 09/10 in 07/10 b) Calculated viscosity after tribological test based on the photometric measured increase of the complex content

4. **Discussion**

Published papers on mesogenic fluids showed that ultralow friction can be obtained over a broad stress collective [20-23]. The present tribological results describe the effect of ultralow friction of one specific mesogenic fluid in more detail. It was shown that the ultralow COF, with the applied testing parameters (Table 2),
can only be realized at low contact pressure (Fig. 6). Additionally, it was observed that the color of the MF changes during the tribological test from yellow to (dark-) red. Chemical reactions of metal ions with 1,3-Diketones to different chelate-complexes were described in several publications [29-32]. Furthermore, possible reactions and interactions on a metallic surface with 1,3-Diketones were analyzed in the past [33-35]. Therefore, it is assumed that this possible chemical reaction of the MF in the fluid or at the boundary layer (iron/fluid) with nascent iron ions causes the change of color. This change of chemical composition of the MF will thus, lead to a change in the rheological and frictional characteristics.

V.1 in Fig. 6 shows the same tribological behavior of the MF as described in Fig. 3 and Fig. 5 a. The running-in period till ultralow COF was reached was approximately 6 hours. V.2 in Fig. 6 shows that the COF strongly depends on the predominant surface pressure, because ultralow COF is already reached after 2.5 hours at initially lower contact pressure. The assumption that chemical changes of the MF during the tribological test lead to a change of the rheological and frictional characteristics is presented in V.3 in Fig. 6. With the used MF the COF decreases after only 0.5 hour to values lower than 0.005. Therefore, this test gives a clear indication to the assumption that the physical and chemical characteristics of the MF has changed during the tribological test.

The presented results describe some friction mechanisms, which may lead to the observed ultralow friction values. In Fig. 10 an attempt was made to specify a model by combining the demonstrated effects. Mixed lubrication dominates during the first phase of the tribological test, thus, the asperities of the two testing specimens are in contact and wear is relatively high. During the tribological test, the COF decreases and the content of the iron tris-β-diketonate complex of 07/10 increases after the oxide layer and the surface layer is removed because of wear. Now it is assumed that the higher viscous complex adsorbs on the metallic surface, thus, forms a gel like fluid. The higher viscous fluid separates the asperities from each other. As the asperities have no longer contact and the contact pressure has reduced to values of approximately 5 MPa it is assumed that the low viscous 07/10 forms a lubrication film in the middle of the friction gap. As already mentioned, Idziak et al. [4-7] showed that under shear strain, higher ordered liquid crystalline phases can be induced at a constant temperature. Furthermore, it was demonstrated that shear strain increases the degree of orientation whereas in contrast, the pressure disturbs the orientation. Therefore, it is assumed that the mesogenic fluid forms a higher ordered structure under these moderate pressure conditions in which shear strain effects prevail. This assumption relates to the findings of Ruths et al. [36], who showed that highly ordered phases result in lower friction coefficients.

To confirm this model, it is necessary to investigate the friction gap during a tribological test. Therefore, an in-situ micro-tribo testing machine was developed to analyze the friction gap with optical or photometric instruments. Additionally, rheological measurements under pressure and with an In-situ analysis of the birefringence under shear will be performed.
5. Conclusions

It was shown that ultralow friction coefficients can be realized with a good reproducibility using the mesogenic fluid 07/10 with the sliding contact geometry cylinder-on-disc. The coefficient of friction decreases to values lower than 0.005 after a specific running-in period. During the running in time, in which mixed lubrication is dominant, wear is generated. In contrast, nearly no more wear is generated at the ultralow friction level.

The friction behavior strongly depends on the predominant contact pressure because ultralow friction coefficients were only reached at low contact pressures. Additionally, it seems that the mesogenic fluid chemically reacts with nascent iron ions, which leads to the formation of a chelate-complex with different rheological and tribological characteristics.

Acknowledgements

We gratefully acknowledge the assistance of Dr. Rudolf Eidenschink (Nematel GmbH, Mainz) with helpful discussions and supplying of the mesogenic fluid 07/10 and 09/10.

References

[27] Patent: Schmiermittel. DE 102007055554, Nematel GmbH Co. KG, Mainz, Germany
[28] DIN 51834- 1 bis 8; ASTM 5706; ASTM 5707
List of Figures:
Fig. 1. Chemical structure of the mesogenic fluid 07/10 [27] ................................................................................................. 3
Fig. 2. Sketch of loading geometry of reciprocating cylinder on disc (RCD) ................................................................. 4
Fig. 3. Comparison of the coefficient of friction of the MF and standard lubricants ......................................................... 5
Fig. 4. a) Wear profiles on the disc after friction test (20 h) b) Diagram of the worn volume on the cylinder and the resulting contact pressure after the friction test (20 h) ....................................................................................... 6
Fig. 5. a) Friction diagram of the MF 07/10 with different testing times. b) Wear analysis in dependency of the testing time ......................................................................................................................................................... 6
Fig. 6. Comparison of the COF of used and unused MF at high and low contact pressure ............................................... 7
Fig. 7. a) 09/10: Iron tris-β-diketonate complex of 07/10 b) Photometric analysis of the Fe-complex content in the MF 07/10 after the tribological tests ......................................................................................................................... 8
Fig. 8. a) Comparison of the COF of the MF 07/10 and the metal-complex 09/10 b) Diagram of the shear dependent viscosity of 07/10 and 09/10 ........................................................................................................................................ 8
Fig. 9. a) Calibration curve: Diagram showing the increase of viscosity in dependence of the content of 09/10 in 07/10 b) Calculated viscosity after tribological test based on the photometric measured increase of the complex content ........................................................................................................................................... 9
Fig. 10. Model conception of the friction mechanism in the friction gap ........................................................................... 11

List of Tables:
Table 1 Characteristics of the test specimens ........................................................................................................................ 3
Table 2 Test parameters of tribological experiments ........................................................................................................ 4