要約

- **論文題目：**

  Tribological and Morphological Properties of Novel TEMPO-based Organic Friction Modifiers

  （新規 TEMPO 系有機摩擦調整剤のトライボロジーおよびモルフォロジー特性に関する研究）

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Approximately 23% of the world's energy consumption is lost due to friction and wear. This leads to not only substantial economic losses but also a significant amount of carbon emissions, exacerbating the greenhouse effect. The use of low-viscosity lubricating oils can significantly reduce shear resistance and thus friction. However, it can also render load withstanding challenging, especially at low sliding speeds. An undesirable consequence is that hydrodynamic lubrication may transit to boundary lubrication, resulting in more direct solid–solid contacts, leading to higher friction and wear and even catastrophic failures of machines. Therefore, to foster the use of low-viscosity lubricating oils, the performance of boundary lubrication must be improved by adding friction modifiers. Particularly, organic friction modifiers (OFMs) containing only carbon, hydrogen, oxygen, and nitrogen have a promising application prospect owing to the urgent need for environmental protection. However, as existing OFMs are not as good at reducing friction and wear as commonly used organo-molybdenum compounds, the development of higher-performance OFMs is critical.

Tsukamoto lab and our lab have proposed some novel TEMPO-based OFMs, which are characterized by a rigid six-membered ring with free oxygen radical. The experimental results in our previous study showed that the friction and wear reduction performance of one TEMPO-based OFM, which is referred to as C_{12}Amide-TEMPO, is much better than traditional OFMs, such as stearic acid. However, the lubrication mechanism of C_{12}Amide-TEMPO remained unknown. A comprehensive understanding of the lubrication mechanisms behind the high-performance C_{12}Amide-TEMPO is of great significance in designing improved OFMs.

Therefore, the aim of this dissertation is to investigate the lubrication mechanism of C_{12}Amide-TEMPO by studying the tribological and morphological properties. The tribological properties refer to the characteristics related to friction and wear, while the morphological properties refer to the relevant features of the adsorption films, including the distribution, surface coverage, and thickness. The dissertation consists of five

chapters, as outlined below.

In Chapter 1, fundamental knowledge about friction, wear, and lubrication was introduced, and relevant researches on organic friction modifiers and the remaining challenges were summarized. The objectives and outline of the dissertation were presented.

In Chapter 2, the tribological characteristics of C_{12}Amide-TEMPO at the macroscale were measured, and the lubrication mechanism was elucidated through a comparison with conventional OFMs, glyceryl monooleate (GMO) and stearic acid, and TEMPO-based OFMs, C_{12}Amino-TEMPO, and C_{12}Ester-TEMPO. Among all the OFMs, C_{12}Amide-TEMPO exhibited the lowest friction coefficient and highest load capacity. Particularly, C_{12}Amide-TEMPO demonstrated excellent anti-wear properties, with a reduction of specific wear rate and surface roughness of wear tracks by more than 60% as compared with the other OFMs. The superior performance of C_{12}Amide-TEMPO compared to C_{12}Ester-TEMPO and C_{12}Amino-TEMPO suggests that the amide group plays a crucial role in its effectiveness. The quantum mechanical calculation results suggest that the boundary films formed by C_{12}Amide-TEMPO have a unique double-layer structure. A strong surface adsorption layer is developed by the chemical interactions, and an upper layer is formed by the interlayer hydrogen-bonding. The strong adsorption and interlayer and intralayer hydrogen-bonding enhance the strength of the boundary films to withstand long-time and heavily-loaded sliding, thereby leading to the high tribological performance of C_{12}Amide-TEMPO. The findings in this study are expected to provide new hints for future research on the molecular design of OFMs.

In Chapter 3, the nanoscale tribological properties of TEMPO-based and conventional OFMs on stainless steel surfaces were examined using lateral force microscope (LFM) and analyzed using the Eyring activation energy model. The parameters in this model provide insights into the molecular-level properties of OFMs during loaded sliding. Specifically, a larger pressure activation energy $P\Omega$ represents thicker boundary films and higher load-carrying capacity. The trend of $P\Omega$ with sliding velocity reflects the adsorption speeds of OFMs, where an increase in $P\Omega$ represents a high adsorption speed. A larger shear activation energy $\tau\varphi$ indicats a thicker lubrication film. A larger Q represents a higher potential energy barrier due to the neighboring molecules and can be used to determine the location where shear motion may occur. From the analysis, the TEMPO-based OFMs exhibit low adsorption speeds but high load-carrying capacities and that the shear motion occur between base oil molecules or base oil molecules and the adsorption films, both of which require less energy to be initiated. The analysis using the Eyring activation energy model effectively complements the LFM measurements and provides a new perspective for evaluating the boundary lubrication characteristics of OFMs beneficial for the development of high-performance OFMs.

In Chapter 4, adsorption films of OFMs on mica surfaces were prepared, and the morphological properties of these films were directly measured using atomic force microscope (AFM). The results showed that as the adsorption and growth time of C_{12}Amide-TEMPO on the mica surface increases, double-layer films, monolayer films,

and multilayer films are formed. After cleaning with ethanol, a decrease in surface coverage and an increase in the thickness of the adsorption film were observed. The ranking of the thickness of adsorption films for different OFMs was found to be consistent with the ranking presented in Chapter 3. This further supports the conclusion in Chapter 3 that the thickness of the adsorption film reflects the value of $P\Omega$, which represents the thickness of boundary films.

In chapter 5 the principal conclusions of the conducted research were presented and the focus of further investigation was proposed.

To sum up, this dissertation investigated the tribological and morphological characteristics of C_{12}Amide-TEMPO and other TEMPO-based OFMs, leading to a better understanding of their lubrication mechanisms. The findings from this dissertation are expected to contribute to the development of OFMs with better performance.