

Tribo-chemistry of Boundary Film Studied by Stable Isotopic Tracers

Ichiro Minami, Tomoo Kubo, Hidetaka Nanao and Shigeyuki Mori
Iwate University

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ABSTRACT

Stable isotopic tracer in combination with TOF-SIMS (time-of-flight secondary ion mass spectroscopy) is proposed as a versatile tool for investigation of tribo-chemistry. This unique technique is based on tracing 2H (deuterium, D)-labeled and/or ^{13}C -labeled hydrocarbon moiety that exist on rubbed surface. Two examples are given in this article: 1) A monomolecular film of perdeuterio-octadecanoic acid was deposited on Si(100) flat specimen. The tribological properties of the monomolecular film were evaluated by a ball-on-flat type tribo-test. Lifetime for low friction is influenced by the ball material. The transfer of the carboxylic acid from the flat specimen onto the ball surface was found to be beneficial for prolong the lifetime. 2) GMO (glycerol mono-oleate) in synthetic hydrocarbon provides extremely low friction at steel-DLC (diamond like carbon) contact. ^{13}C -labeled GMOs were employed to investigate the state of the additive on the DLC surface. Direct interaction of the additive on the DLC surface was suggested by TOF-SIMS analysis.

INTRODUCTION

Surface analysis is a useful method to study tribo-chemistry. For example, boundary film that is generated by the tribo-chemical reaction of anti-wear additives has been studied using EPMA and XPS [1]. These techniques mainly focus on hetero atoms such as phosphorus, sulfur, zinc, or molybdenum that exists on rubbed surface. On the other hand, the major components in lubricants are hydrocarbons and their derivatives. Unfortunately, hydrocarbon moieties on a surface are difficult to identify by the usual surface analysis, mainly for the following two reasons: 1) Chemical resolution is unsatisfactory to identify a variety of organic compounds. 2) Organic contaminants that exist everywhere make detection of the target molecule difficult.

Isotopes are defined as atoms having the same atomic number but a different mass number. They exhibit different physical properties but the same chemical ones. Both radio-active isotopes and inactive ones (namely, stable isotopes) are found in natural resources [2]. Some of them are applied as tracers to study metabolism or terrestrial ecosystem [3]. In the field of tribology, applications of radio isotopes of hetero-atoms have been reported to trace boundary film formation [4] and wear measurements [5,6]. While radio isotopes are easy to detect at low concentrations, the possibility of radiation damage has limited their usage by legislation.

Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) is one of the surface sensitive analytical methods [7]. The outline of the analysis is based on mass spectrum of compounds that exist on the surfaces. Advantages of this method in tribo-chemistry are high sensitivity, high spatial resolutions, and excellent chemical resolutions if fragmentation of the target molecule was well studied. Both organic and inorganic compounds on the surfaces are detectable by TOF-SIMS. Applications of TOF-SIMS in tribo-chemistry have been reported [8-17]. In addition, isotopes can be identified by the high-mass-resolution technique of TOF-SIMS [18].

This article deals with our work on the role of hydrocarbon moiety in tribo-chemistry. The target molecules were labeled by stable isotopes such as D (deuterium, ^2H) or ^{13}C . A monomolecular film, one of the well-studied models of boundary lubrication, was chosen in this fundamental study. Applicability of the stable isotopic tracers in studying additive mechanism is also shown herein.

Nomenclature

Abbreviation	Details
GMO	Glycerol monooleate (see also Figure 1)
^{13}C -ODA	^{13}C -Octadecanoic acid (see also Figure 1)
2d -ODA	2,2-Dideuteriooctadecanoic acid (see also Figure 1)
35d -ODA	Perdeuteriooctadecanoic acid (see also Figure 1)
GMO	Glycerol monooleate (see also Figure 1)
c-GMO	Carbonyl-labeled glycerol monooleate (see also Figure 1)
g-GMO	Glycerol-labeled glycerol monooleate (see also Figure 1)
D	Deuterium, ^2H
DLC	Diamond like carbon
EPMA	Electron probe microscope
M	Formular weight
m/z	Mass-to-charge ratio
PAO	Poly(alpha-olefin)
TOF-SIMS	Time-of-flight secondary ion mass spectroscopy
XPS	X-ray photoelectron spectroscopy

EXPERIMENTAL

2.1 Chemicals

2,2-Dideuteriooctadecanoic acid (2d-ODA), octadecanoic acid- ^{13}C (^{13}C -ODA), pentatriacontadeuteriooctadecanoic acid (35d-ODA) were selected as stable isotopic tracers for the preliminary work. Two labeled GMOs, namely ^{13}C -labeled at the glycerol moiety (g-GMO) and ^{13}C -labeled at the carboxylic acid moiety (c-GMO) were examined. Octadecanoic acid (ODA) and glycerol mono-oleate (GMO) were references for the labeled compounds. All chemicals are reagent grade. Structures of these compounds are given in Figure 1.

2.2 Preparation of monomolecular film

A monomolecular film of the labeled carboxylic acid for tribo-test was deposited on Si(100) flat surface using a computer-controlled Langmuir trough under air. The conditions of the film preparation are listed in Table 1.

2.3 Tribo-test

The tribological properties of monomolecular film were acquired by a ball-on-flat type tribo-tester under reciprocating motion. Balls made of steel, sapphire and glass were rubbed against a silicon-flat covered with the monomolecular film. Friction force was monitored throughout the test. The lifetime of the monomolecular film was defined as duration of steady state friction provided by the monomolecular film before friction force rose, as shown in Figure 2. The test conditions and properties of specimen are listed in Table 2 and Table 3, respectively.

A cylinder-on-plate reciprocating type tribo-tester was also employed to evaluate the tribological properties of GMO in synthetic hydrocarbon. The test conditions are described in Table 4. DLC on the flat specimen was deposited by the published procedure [19].

2.4 Surface analysis

AFM and TOF-SIMS of the rubbed surfaces were conducted to study the mechanism of lubrication. The conditions are listed in Table 5 and Table 6, respectively. The specimen rubbed with GMOs in PAO was rinsed with hexane prior to TOF-SIMS analysis. It should be noted that ultrasonic cleaning of the specimen sometimes results in removal of the boundary film composed of GMOs.

Table 1 Conditions for monomolecular film preparation

Concentration of sample, $\text{mmol} \cdot \text{dm}^{-3}$	2.0
Solvent	CHCl_3
Contents of water bath	$0.03 \text{ mmol} \cdot \text{dm}^{-3}$ aqueous BaCl_2
Temperature of water bath, C	20 ± 0.2
pH buffer	$0.4 \text{ mmol} \cdot \text{dm}^{-3}$ aqueous KHCO_3
Rate of film compression, $\text{mm} \cdot \text{s}^{-1}$	0.1
Rate of film built-up, $\text{mm} \cdot \text{minute}^{-1}$	1
Pressure of built-up, $\text{mN} \cdot \text{m}^{-1}$	30

Table 2 Conditions of ball-on-flat type tribo-test

Operation parameters	Applied load, mN	40		
	Frequency, Hz	20.0		
	Amplitude, mm	1.5		
	Temperature, C	20-25		
	Humidity, %	20-60		
Test specimen	Ball	Material	steel, sapphire, glass	
		Diameter, mm	1.0	
	Flat	Material	Si(100)	
		size, mm	10×10	
state of contact	Ball material	steel	sapphire	glass
	Hertzian contact diameter, μm	11	10	13
	Hertzian maximum stress, GPa	0.62	0.71	0.47

	Major component	Young's modulus, GPa	Poisson's ratio	Surface roughness Ra, nm	surface free energy, mJ·m ⁻²
Silicon (flat)	Si	130	0.28	0.12	73.1
Steel (ball)	Fe	210	0.30	3.1	60.7
Sapphire (ball)	Al ₂ O ₃	420	0.32	1.0	73.2
Glass (ball)	SiO ₂	90.9	0.26	3.4	73.0

Instrument	Seiko Instruments, SPI3800N
Measurement mode	tapping
Area of analysis, $\mu\text{ m}$	10×10
Cantilever	SI-DF20
Elastic module of cantilever, N/m	15.1

Operation parameters		Applied load, N	4.0E+ 02
		Stroke, mm	3.0
		Frequency, Hz	50
		Oil volume, μL	1.0E+ 02
		Oil temperature, $^{\circ}\text{C}$	80
		Test duration, minutes	30
Test specimen	cylinder	Material	SUJ2 (JIS)
		Contents: C (0.95-1.10%), Si (0.15-0.35%), Mn (< 0.5%), P (< 0.025%), S (0.025%), Cr (1.30-1.60%) and Fe (balance)	
		size, mm	ϕ 15 $\times$ 22mm
	flat	Material PVD arc-ion plated, hydrogen-free type DLC deposited on SUJ2 at thickness of 0.5 μm	

Instrument	Physical Electronics TFS-2100 (TRIFT-II)
Resolution at m/z 26.98 (Al)	M/ΔM > 5000
Primary ion	bunched Ga ⁺
Impact energy, keV	15
Ion current for one pulse, nA	2
Pulsewidth, ns	7
Bunching intervals, ps	960
Pulse frequency, kHz	11
The measured mass range, m/z	1–3000
Total ion doses in measurements, ions ·cm ⁻²	< 1 × 10 ¹²
Detected secondary ions	positive and negative
Area of analysis for chemical mapping, μm ²	60 × 60 or 120 × 120

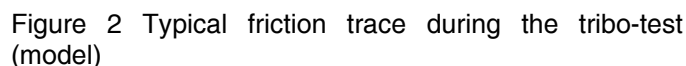
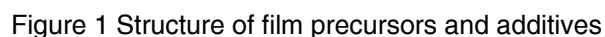


Figure 3 shows the diagram of molecular area and surface pressure while preparing monomolecular film from ODA or 35d-ODA on silicon-flat surface. The limiting area for these acids was in the range of 0.22-0.23 nm², which are slightly density-packed in comparison with the data in the literature, 0.24 nm² [20]. A semi-empirical molecular orbital simulation gives the conformation of 35d-ODA as a cylinder of 2 nm in length and 0.4 nm in diameter [21]. From these results, surface coverage by the acid was calculated in the range of 55-57%.