

Interaction Between Rubber and Oil in Lubricated Sliding Contact

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<https://hdl.handle.net/2324/6787610>

出版情報 : Kyushu University, 2022, 博士 (工学), 課程博士
バージョン :
権利関係 :



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in Lubricated Sliding Contact

Ayako Aoyagi

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1 Introduction

1.1 Social requirements

1.1.1 Global trends in energy strategy

Since the industrial revolution in 18th century, human economic activities have increased the emission of carbon dioxide (CO₂). The Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) 2021[1] concluded clearly that

“It is unequivocal that human influence has warmed the atmosphere, ocean, and land. Widespread and rapid changes in the atmosphere, ocean, cryosphere, and biosphere have occurred.”

According to the report, average temperatures have increased by about 1 °C compared with pre-industrial times. In a report by NASA[2] shows changes in CO₂ levels over the past 800,000 years. The trend in this century shows that the rate of increase in CO₂ has been accelerating. The temperature rises of 1.5 °C can cause significant damage to ecosystems. To avoid this, we have the crucial and challenging task. We should achieve “zero CO₂ emissions” by 2050. Many developed countries express and support this vision and have pledged to make significant efforts to achieve carbon neutrality.

This requires the selection of appropriate energy sources. Options for carbon-neutral (CN) energy sources are nuclear power and renewable energy sources such as solar, wind, hydrogen, and biomass. Countries can also choose a combination of fossil fuels and CO₂ absorption and capture technologies. For instance, the European Union is taking the lead because of following reasons.

- A) The European Union has geographical connections with countries rich in natural resources, such as Russia and Middle eastern countries.
- B) Natural gas emits 30 percent less CO₂ than fossil fuels.
- C) Electricity can be shared among European Union countries through the international grid.
- D) Public awareness of the environment is high.

According to the Eurostat press release (1 / 19 / 2022), the EU-wide target of 22.1 per cent renewable energy was achieved in 2020. However, the situation in the European Union is also politically volatile.

1.1.2 Current status of Japanese carbon neutralization

On April 22, 2021, the Japanese Prime Minister announced at the meeting of Global Warming Prevention Headquarters that they aim to reduce their greenhouse gas emissions by 46 percent in fiscal year 2030 from the fiscal year 2013 levels. However, there are a lot of difficulties about carbon neutral particular to Japan.

Firstly, compared with major countries, the area where mega-solar power plants can be constructed is limited in Japan. This is because both ratio of the land area to the population and the ratio of the flatland are small. Also, sunshine hours and wind have no advantage over other countries. Secondary, it is impossible to develop an international electric transportation network like Europe because Japan is an island nation. The amount of power generated by renewable energy depends on the natural condition, such as weather. For this reason, it is necessary to adjust the amount of transmission. Finally, the vulnerability of nuclear power plants was exposed by the Great East Japan Earthquake in 2011.

In summary, the disadvantage of Japan in CN energy generation is following respects:

- A) Less area is suitable for mega-solar plant
- B) Being an island nation, it is difficult to set up an international transmission line network.
- C) Nuclear power is at great risk from earthquakes and tsunamis.

The only positive factor for Japanese CN strategy is the prospect of a declining population due to the decrease of birthrate and aging population. A declining population will reduce overall energy consumption. As a result, it is expected that the amount of fossil fuel usage for the power generation will decrease. Apparently, the decline in population is not delightful because it causes serious problems such as shortage of human resources and economic contraction. How can Japan realize a CN society? One of the important aspects is to acquire an international superiority by developing CN technology. The next section describes technological areas that contribute to Japan's CN society.

1.1.3 Future Technological Development

As discussed in the previous section, it is necessary to establish the strategy how Japan approach to CN society. Following technical areas are important for CN society.:

- A) Energy conservation technologies
- B) Electrification of mobility

- C) Power generation technologies taking advantage of Japanese climate: offshore power generation, geothermal power generation
- D) CO₂ recycling technologies
- E) Transmission technologies

These technological shifts will lead the change in the usage environment of the machines and their components such as electrification mobility and renewable energy source. In the view of prospects, they will require more durability for maintenance-free. For instance, when the machines are used in renewable energy power plants, they are used underground, under the sea, outdoors, etc. It should be difficult to repair them or replace the parts when failure occurs. In general, the components will be used in environments where they are exposed to high pressure, corrosion, ozone, heat, etc. which promote degradation. It is necessary to aim longer life than conventional ones against those harsh environments.

From the other perspective view, the raw materials of lubricant or the ingredients of materials will be limited because of requirement of environmental-friendly. For instance, EU REACH Substances of Very High Concern (SVHC) List includes 224 substances in 2022, while it started with 15 substances in 2009[3], as is shown in Fig. 1-1

In summary, there is a possibility that the machines and their components will be subject to various restrictions for the environment, but on the other hand more durability is required. It is necessary to have a fundamental understanding of the functions of them, in order to guarantee a reliability in a new environment and to solve problems quickly when a failure occurs.

1.2 Radial shaft seals

1.2.1 Outline of radial shaft seals

In the 1950s, the structure of modern synthetic rubber radial shaft seals was established. The cross-section of radial shaft seals is shown in Fig. 1-2. They are mainly composed of three components: the rubber lip, the metal ring and the spring that apply loads to the seal surface.

The roles of a radial shaft seals are as follows:

- 1) To prevent leakage of fluid and gas from the inside of the machines, such as fuel, lubricant, and coolant.
- 2) To prevent foreign substances from the outside.

As a matter of course, low torque is required in order not to hinder the rotation of the shaft. However, in principle, well-lubricated conditions and perfect sealing are contradictory. To clarify the sealing and lubrication mechanism, the research in the field of tribology was positively continued. The measurement of COF and oil film thickness and verification of theory by numerical analysis have played an important role in clarifying the mechanism of the lubrication and sealing.

1.2.2 The science of radial shaft seals

Radial shaft seals have been used since 1930s, but it took more than 50 year to achieve fundamental understanding on the lubrication and sealing mechanisms[4]. When sealing is attempted by ensuring boundary lubrication with necessary radial force to a radial shaft seal as in the case of a static seal, reliability to guarantee complete sealing is low, and further, the allowable viscosity range of the sealing liquid is extremely narrow. Additionally, significant direct contact occurs and the friction force and wear increase under higher pressure. Therefore, radial shaft seals have been designed to realize hydrodynamic lubrication and sealing simultaneously [5].

1.2.2.1 Lubrication mechanism

It was revealed in the 1970s that the lip of a radial shaft seal lubricated with the mechanism in which the fluid pressure generated at the lip top of the surface asperity[4]. COF could be described using the bearing characteristic number G as follows [6].

$$\mu = \phi G^n \quad (1-1)$$

where ϕ is the proportional constant and n is the constant (generally $1/4 \sim 1/2$). And G stands for

$$G = \eta u b / P_r \quad (1-2)$$

where η is the viscosity of lubricant, Pa·s, u is the sliding speed, m/s, b is the contact width, m, P_r is the tension force, N. P_r can be measured by a method using a split cylinder. The frictional force F between the shaft and the seal is defined as follows.

$$F = \frac{T_r}{D/2} \quad (1-3)$$

$$\mu = \frac{F}{P_r} \quad (1-4)$$

where F is the frictional force, N, T_r is the rotational torque, N·m, D is the radius of the shaft, m, μ is COF, -.

To confirm the existence of a fluid film, some studies attempted to measure an oil film thickness. In the 2000s, Sato et.al found that the oil film thickness of the actual radial shaft seal can be measured by means of the laser induced fluorescence method and its thickness was found to be 1 to 10 μm [7]. These investigations revealed that the lubrication mechanism of the radial shaft seal was elasto - hydrodynamic lubrication (EHL).

The other important study was about cavitation observed on the sliding surface of well-sealing radial shaft seals. There are two types of cavitation: gaseous cavitation and vapor cavitation. Cavitation on the sliding surface of the radial shaft seals can be mainly the gaseous cavitation[8]. The cavitation can suppress excessive negative pressure, and the sum of fluid pressure is positive over the entire sliding surface. Since the cavitation can decrease viscous resistance, it also contributes to achieve low friction of sliding surface.

On the other hand, a lots of facts peculiar to elastomer radial shaft seals has also been reported as listed below[9].

- 1) The G_c point, in which the friction starts to increase in the low G region and the lip and the shaft start contacting, does not appear clearly depending on the material. Depending on the material and the oil, COF does not start to increase at the low G region[10].
- 2) The slope of increase of COF decreases in the high G region.
- 3) COF is not uniquely determined by G but differs depending on the lubricant, material and surface treatment[11]
- 4) The shape of oil film becomes thinner from the oil tank side to the air side

These facts indicate that EHL is not sufficient to model the sliding surface of radial shaft seals. They suggest the contribution of the mixed to boundary lubrication and the significance of the understanding of boundary friction of the rubber lip.

1.2.2.2 Sealing mechanism

Some models have been proposed in which oil is actively transported from the air side to the oil side in order to prevent oil leakage. This effect is called a pumping action. The oil is sealed by balancing the pumping action with natural leakage. The pumping action is assumed to be caused by the micro-roughness of the lip. It is both experimentally and theoretically proposed that the micro-roughness of the lip affected the lubrication state of the radial shaft seal.

The three models are shown below.

- 1) Micro-undulations model
- 2) Micro-asperities model
- 3) Cascade model

In the micro-undulations model.[12] The shear stress of the lubricating film deformed the sliding surface in the circumferential direction, forming a vane-like pattern on the micro order. Oil was transported by the rotation of this vane, and a pumping action occurred.

However, vane-like wrinkles were not always observed at sealing condition. To explain this, a micro-asperities model was proposed. In this model, it was proposed that both of the inward and outward flow existed. This can be observed using a hollow glass shaft with a microscope.[13][14] Extending this mechanism, a cascade model was proposed in which the seal lip surface is designed to have micro-roughness beforehand to form a circulating flow.[15] The roughness is formed on the worn surface by the filler contained in the rubber material. The experimental results of gas moving in the same direction as oil also showed that the existence of circulation flow of oil[8]. These micro-order models were main sealing mechanism of radial shaft seals.

Oscillation or wiping edge hypothesis and normal stress hypotheses had also been proposed in macroscale. These are considered to be inadequate experimental proofs or additional effects.[16]

In practice, the installing errors causes poor sealing performance, such as an installation at wrong angle, the damaged shaft, or the inverted lip. In order to prevent the leakage, the pumping action is improved by imprint of twist ribs added to the air side or sliding surface of the lip. This structure was able to provide the pumping action supporting micro-roughness mechanisms. Its function has been proved experimentally and it is useful because it can be applied to both rotary shafts.[17]

As has been shown, different physical processes are involved in the sealing mechanism of radial shaft seals. Various and some of combinations of physical processes determine the sealing performance of actual sealing surfaces.

1.2.2.3 Numerical analysis

Attempts of numerical analysis began in the 1980s[18]. A theoretical and quantitative experimental analysis have been conducted in order to clarify the relationship between the state of the sliding surface and friction/lubrication. Compared with metal bearings, it is important to consider the deformation of the sliding surface and the cavitation between microasperities in the numerical calculation of the elastomer radial shaft seals.

Numerical calculations resulted in the consistent with the experimental results regarding factors that affected the amount of pumping and the occurrence of cavitation[19]. Under severe lubrication conditions, the contact between the shaft and the seal lip should be taken into account in the calculation model of mixed lubrication. For this purpose, the mechanical deformation model of the entire rubber and the surface was combined with the hydrodynamic model of the lubricating film.

It also required to model the sliding surface roughness because the micro-roughness of the lip and its deformation strongly effected on the lubrication and sealing mechanism[20].

According to numerical analysis results, Mizuta described that lubrication mechanism of radial shaft seal was partly mixed lubrication and boundary friction distributed to a total friction force[9]. When the load capacity of the seal lip did not generate enough, surface microasperities contact with shaft, which generates pressure and loads. Thus, it was concluded that the radial shaft seal rotated with mixed lubrication state in which partial contact (boundary lubrication) existed, in other words, not fully under hydrodynamic lubrication. Though it is necessary to consider boundary friction in order to quantitatively express the lubrication state on the lip surface, there are few studies which discussed the details of the boundary friction of rubber.

1.2.2.4 Summary

- Regarding the lubrication mechanism of radial shaft seals, elastic fluid lubrication (EHL) is dominant and is affected by the roughness of the sliding surface.
- The elastic lubrication mechanism has different characteristics from metal bearings, suggesting the contribution of boundary friction.
- The following models have been proposed as the main sealing mechanisms.
 - Micro-undulation model
 - Micro-asperities model

- Cascade model
- Spiral threads are provided on the air side and sliding surface of the lip to prevent seal leakage by increase pumping action (screw seal, helix-rib seal). It is applicable to both rotating shafts.
- Theoretical verifications by numerical calculation had greatly contributed to the elucidation of the lubrication and sealing mechanism.
- COF may differ depending on the rubber material and lubricant. The mechanism is unknown.
- The boundary lubrication should be taken into account to understand the lubrication of radial shaft seals, but few studies have been conducted in this respect.

1.2.3 Material of radial shaft seals

1.2.3.1 Rubber

The second voyage of Columbus brought rubber materials to Europe. The existence of rubber came to be known among western civilization at the end of the 15th century. Rubber was industrialized as the items such as rubber tubing, erasers, waterproof clothes, rubber shoes, etc.

In 1839, Goodyear accidentally discovered that sulfur and heat made rubber elastic. It is called as “vulcanization”. However, the chemical structure of vulcanized rubber had not been revealed until the 20th century.

The development of automobiles in the 19th century delivered the frontier of the industrial applications of rubber. For example, taking advantage of its ability to absorb shocks, Dunlop invented the hollow tire in 1888 and it have been widely used up to now.

As an academic study, Kekulé proposed the fundamental theory of organic chemistry in which he indicated that carbon atoms had tetravalence, and submitted the idea of carbon chains in 1857.[21] During the same period, a complex chemistry for colloids was just developing [22]. Thus, polymer material, which was not recognized as macromolecule at that time, was expected to be an aggregate of small molecules, like other colloidal materials. In 1904 Harries et al. proposed the theory that cyclic dimers of isoprene formed an aggregate and it was the isoprene rubber. It is shown in Fig. 1-3 The unit structure was modified by Pickles in 1914 as the macrocycle, which was pentamers or more.

In this historical context, Staudinger proved the existence of macromolecule measuring osmotic pressures as a means for the determination of the molecular weight. He firstly published the long-chain structural formula of rubber in 1920[23]. Because of the aforementioned background, his idea was refused by a lot of scientists, and he was forced to struggle alone in academia. However, he continued to publish experimental results that supported his theory. In addition, the technique of measuring crystal lattice by X-ray diffraction, which had been discovered by Max von Laue in 1912, was developed[24]. This measurement revealed the crystal lattice size of polymers and the number of molecular chains constituting them. As a result, physical chemists and physicists, who had been skeptical of the polymer theory, gradually started to recognize the existence of molecules with large molecular weights.

Finally, in 1928 at the Symposium Organische Chemie und Kolloidchemie; Symposium of organic chemistry and kolloid chemistry in Frankfurt, the macromolecular theory prevailed, though some issues remained. At the symposium, he estimated the molecular weight of the rubber to be 68,000. In 1932, he published “Die hochmolekularen organischen Verbindungen – Kautschuk und Cellulose”; The Macromolecule organic chemicals – Rubber and Cellulose). And then “Macromolecule” is widely recognized among the world. [25]. In 1953, he received the Nobel Prize in Chemistry, for his achievements in establishing the polymer theory.

The main representative types of rubber are listed in Table 1.1. They are divided into two types, the natural rubber and the others, the synthetic rubbers. The invention of synthetic rubber and the development of the rubber industry are closely related to the two world wars[26]. Around the World War I, the rubbers used were the natural rubber (NR), which is obtained from a natural latex of the tree *Hevea brasiliensis*. Shortly before the World War II, some synthesis rubbers were produced artificially such as chloroprene by US Calosas in 1931 and NBR and SBR by German consortium of companies called Interessen Gemeinschaft. In the US where the import of natural rubber was insufficient during World War II, the supply became urgent, and the development of synthetic rubber greatly advanced[27].

With the development of synthetic rubber, their application and capable environment to be used with was expanded. The raw material of rubber was mainly petrochemical products. The substances obtained from petroleum were bonded in a process called polymerization. The constituent units were called monomers. There were mainly two types of polymerization, emulsion polymerization and solution polymerization, and they were selected according to the monomer and the properties required for polymer product[28]. The synthetic rubber could be a copolymer introducing a second or a third monomer at the polymerization. Various functional groups composed of oxygen, nitrogen, fluorine, etc. were introduced. Through these techniques, the rubber acquired a variety of characteristics. It was especially important to have a resistance to the nonpolar

oil. The application of the rubber was expanded to the oil contact applications such as packings. Furthermore, since it was also possible to introduce reaction sites for cross-linking, the rubber products could be chemically more stable. Regarding the natural rubber, cross-linking network was formed by the reaction of sulfur with double bonds at the main chain. Because the double bond and the sulfur crosslinks were chemically reactive, it could be the starting point of degradation of rubber by heat, oxygen, and other chemical factors. Therefore, the ability to form a network structure without double bonds in the main chain was very effective to prevent degradation of rubber. The development of special cross-linking systems such as peroxide also contributed to improvement. It greatly contributed to the expansion of the operating temperature range improving heat resistance of the rubber. As above, the rubber could be designed to withstand a wide range of applications from low temperatures below - 70 °C to high temperatures above 200 °C and to resist various types of liquids.

1.2.3.2 Tribology of rubber

The first scientific study of friction was made by Leonardo da Vinci (1452 -1519). Later, G. Amontons (1663 -1706), Charles-Augustin de Coulomb (1736 -1806) and others systematized the Amontons-Coulomb friction law[29]. In the 19th century and the early 20th century, the friction of products, such as tires, power transmission belts, shoe soles, flooring, and water-lubricated bearings, were mainly investigated in the area of the tribology of the rubber[30].

In 1940s, Roth's basic friction test showed that there was a positive dependence on the sliding speed, and construction of a friction model of the rubber started[31]. In addition, Tabor et al. reported that the friction force of the rubber is non-linear in load dependence and strongly depends on the sliding speed and temperature. Regarding solid friction without lubricant, the idea that a friction between solids can be expressed in terms of deformation and adhesion was presented by Bowden and Tabor[32] .

$$F = F_{adh.} + F_{def.} \quad (1-5)$$

Grosch conducted friction tests in which the rubber slid on a rough substrate. Basic friction tests with varying temperature and sliding speed were conducted and it was shown that they could be represented by a single master curve using the WLF law [33][34]. The high frequency peak observed in this curve was considered to be the viscoelastic peak of rubber, while the low frequency peak is considered to be caused by adhesion.

Moore mentioned that other terms should be added to compute total friction force;

$$F = F'_{adh.} + F'_{def.} + F_{cohesion} + F_{viscous} \quad (1-6)$$

where $F_{cohesion}$ is a cohesive force term as the energy loss associated with wear in the bulk and $F_{viscous}$ is a viscosity term under conditions where the interface is wetting[35].

Where $F'_{def.}$ includes friction due to hysteresis loss ($F_{hys.}$) and ploughing component due to plastic deformation ($F_{plough.}$), where $F_{hys.}$ is dominant in the case of rubber. Therefore

$$F = F'_{adh.} + F_{hys.} + F_{cohesion} + F_{viscous} \quad (1-7)$$

Regarding the adhesive friction, Schallamach proposed the mechanism with molecular-bond model[36][37]. The mechanism consists of the adsorption steps of polymer chains to the counter surface, stretching with sliding, detaches caused by heat and elongation stress, relaxes, and reattaches.

This classical idea could be too ideal, but this mechanism delivered the frontier of the modern approach to the adhesive friction. Kummer proposed a schematic diagram of adhesion friction. In the diagram, the origin of adhesion force in various scales, macro-scale shape, micro-scale roughness, and nano-scale molecular chain were analogically depicted[38]. These ideal and simple models were extended to a more realistic model by Leonov, Persson, and others [39][40][41]. In the experimental results, the shear stress had a Gaussian distribution and takes a shape very similar to the Grosch measurement.

Momozono conducted the research on the kinetic properties of boundary friction in elastomers and discussed with a molecular-bond model. He showed the Stribeck curve of elastomers with lubrication compared to that of a metal [42]. This indicates that it is possible to decrease the friction of boundary lubrication by decreasing the adhesion friction at low G region. He also mentioned that a similar model could explain friction of polymer brushes.

The molecular-Bond model can be widely applied as a friction model for polymer materials, such as rubber, plastic, gel, and polymer brush. For instance, a gel friction can also be considered using this model. Gong et al. proposed a model for the friction mechanism of gels in which repulsive and attractive forces were exerted between the molecular chain and the countersurface [43]. When repulsive forces are applied, the molecular chains on the gel surface are less likely to be adsorbed on the countersurface. In other words, it was proposed that the adhesive friction was caused by the decrease in the adsorption ratio of the gel polymer chain to the countersurface. Its Stribeck curve at low G region was similar to the one shown by Momozono.

1.2.3.3 Rubber for radial shaft seals

Rubber has been chosen to main components of the radial shaft seals

- 1) to absorb a unilateral load caused by the eccentricity of shaft or housing
- 2) to produce a pumping action by deformation of a sliding surface which has microasperities

A rubber is chosen as the material for radial shaft seals because a flexibility and an elasticity are required for it. Rubber seals are used in the various environment and applications. For example, 15000 types of oil are commercially available in the market [44]. This means that the properties and chemical structures of sealing liquids are so diverse. Furthermore, the operating temperature, pressure, and frequency of starting and stopping differ depending on the part where the radial shaft seal is used.

Considering the lubrication mechanism, the rubber materials are required to have the following characteristic:

- A) Thermal stability: It should not harden after prolonged exposure to high temperatures.
- B) Cold resistance: It should not lose the rubber elasticity even at the lower temperature of the operating environment.
- C) Chemical stability: When immersed in the sealing liquid, it should not be hardened by extraction and chemical reactions such as reaction with additives.
- D) Swellability: It should maintain its shape and hardness without excessive swelling when immersed in sealing liquid.
- E) Wear resistance: It should not wear out excessively.
- F) Surface roughness: It should have a micro roughness on the sliding surface. The roughness should not disappear when the sliding surface is worn maintaining the roughness of the sliding surface

The industrial rubber materials are developed in order to achieve the above performance. There are also many chemicals or formulations for rubber materials. Rubber materials are made of base polymer blended with fillers, such as carbon and/or inorganic oxides, antiaging agents, and vulcanizing agents.

The type of polymer has the greatest influence on the properties of the rubber. The types of rubber materials are shown in Table 1-1. Synthetic polymers are used because radial shaft seals are required to be resistant against severe conditions.

Additionally various synthetic polymers are used depending on the application. For example, NBR and HNBR are generally used for radial shaft seals because of their oil resistance. ACM is used for the drive systems seal because heat resistance is required. FKM is used for engine seals that are required the resistance of extremely high temperatures and long life. Besides, EPDM, which is less polar and more resistant to water, is used around water such as water pumps.

Cross-linking systems is the second dominant factor for designing rubber materials formulation. Typically, it can categorize sulfur systems, peroxide systems, and the other specialized systems. When the backbone of a polymer has double bonds, it can be crosslinked by both sulfur and peroxide. The differences between the two systems are as follows.

The peroxide vulcanization can provide crosslinks which have the better heat resistance than that generated by the sulfur vulcanization. It is led by the difference between the binding energies of sulfur and carbon bonds. Each value of binding energy is shown in the Table 1-2 [45]. In the case of peroxide crosslinking, it is necessary that crosslinking is conducted in anoxic environment. This is because peroxide is highly reactive with oxygen. It reacts with oxygen and is deactivated before cross-linking occurs. Sulfur systems are also preferred for radial shaft seals with complex shapes because of better elongation and brittleness.

If the backbone of polymer has no double bonds, cross-linking is performed by the either of following methods.

- A) Crosslink by radical reaction started by peroxide
- B) Introduce certain chemical structure as a crosslinking point into the polymer chain and use the appropriate crosslink agent.

Both carbon black and inorganic oxides are used as fillers for the materials of radial shaft seals. Carbon black bonds with the polymer and reinforces it. Therefore, rubber containing carbon black has high mechanical properties. When inorganic oxides are used in radial shaft seals, heat resistance can be improved, and roughness of sliding surface can be controlled. As mentioned in the previous section, roughness of sliding surface is important for pumping action.

Antioxidants are used to prevent the rubber material from being cured by heat. Since the oxidation mechanism is a radical reaction, the role of antioxidants is to inhibit the reaction by trapping radicals.

1.2.3.4 Issues for rubber of radial shaft seal

As has been pointed out in Section 1.1, all machines and machine components are required to contribute to CN. The transition to a CN society is underway as a countermeasure to the rapid climate change. The minimization of energy loss due to friction is required not only for automobiles but also for all machinery. In order to overcome these big issues, it is necessary to investigate the boundary lubrication mechanism of a radial shaft seal for the following two points.

The first point is to decrease the rotational torque for the reduction of the energy loss. It was believed that the radial shaft seals were lubricated mainly with hydrodynamic fluid film, which however was found to be not the case. The contribution of boundary friction is too large to be ignored. Therefore, taking particular note of the further reduction of the torque, the boundary friction should be taken into account. Some experimental facts suggest that boundary lubrication contributes to the total friction force as forementioned in Section 1.2.2.

There are few studies on boundary lubrication of rubber, and many matters remain to be investigated. It is known that the types of rubber and a lubricant affect COF of rubber under boundary lubrication[46], but the detailed mechanism has not been clarified yet. In the interface of the rubber, the rubber and the lubricant could interact each other at the molecular level. This is because the rubber and the lubricant have similar chemical structures and hence have compatibility. Rubber friction is mainly caused by adhesion friction with repeated adsorption and desorption of surface molecular chains to the opposing surface, and hysteresis loss friction caused by deformation of the bulk. The existence of the lubricant could affect both of the adhesion friction and the hysteresis friction, and therefore there should be additional factors that affect friction.

The second point is that many seals are used in severe environment such as in power plants where longer life is required to achieve maintenance-free. The liquid used for the machinery tends to have low viscosity in order to reduce a rotational torque, and the low friction in low G region will be required. If used in a power plant, it will be required to have a long life by reduction of wear even under severe lubrication conditions such as a high load. The elucidation of the fundamental boundary lubrication mechanism will solve this issue and contribute to development of new design of radial shaft seals suitable for the new application which can be used in the severe environments.

1.3 Aims

It was widely accepted that the lip of a radial shaft seal was lubricated with the mechanism in which the fluid pressure was generated at the lip top of the surface asperity. Theoretical verifications

by numerical calculation greatly contributed to the elucidation of the lubrication and sealing mechanism.

However, it is known that boundary friction also contributes to the friction of radial shaft seals. Since its details are not clear, COF of oil seals in boundary lubrication regime has been assumed to be a constant value in the numerical analysis[47], although it is actually affected by the type of rubber and oil. It is necessary to understand the mechanism of boundary lubrication of rubber and establish a model for the boundary friction in order to estimate COF of the radial shaft seals in a wide range of the lubrication regimes.

The purpose of this study is to elucidate the boundary lubrication mechanism of rubbers by focusing on the combination of the rubber and the lubricant in order to achieve the following:

- 1) To reduce the rotational torque of radial shaft seals based on the understanding of their friction
- 2) To enable flexible response to new applications with an eye on CN society

This thesis starts from the current state surrounding Japanese industry and the positioning of this research in the approach to the sustainable society. Besides, the importance of investigating the boundary lubrication of rubber is described from the viewpoint of the scientific approach, and the review of the sealing and lubrication mechanism of the radial shaft seals and the fundamentals of rubber for radial shaft seals are described in Chapter 1.

Chapter 2 describes the experimental methods of this investigations. At first, sample preparation is described. The rubber samples were designed and molded for these investigations. And next, experimental methods for measurement of friction force, observation of the sliding surfaces and the chemical analysis of the sliding surfaces are described. The chemical analysis of rubber on the sliding surfaces using in-situ FT-IR microscopy and the idea on the treatment of the spectra has been developed during this thesis.

Chapter 3 contains the experimental results focusing on the combination of the rubbers and the lubricants. The pin-on-disc experiment was conducted for measurement of COF. Besides, observation and chemical analysis on the sliding surface are described.

In Chapter 4, the results are summarized and discussed. In addition, further experiments are conducted to clarify details of the mechanism, such as the observation by optical interferometry, measurement of contact angle and measurement of evaporation rate by TGA (Thermal gravimetric analysis). The hypothesis was proposed and the experiment with swollen rubber was conducted. Besides, the theoretical background of the swelling of the rubber and the intermolecular interaction were described.

Chapter 5 showed the conceptual model for the rubber interface of boundary lubrication. In addition, the numerical simulation with different combination of flow characteristics was conducted. The model was correlated with the flow of the lubricant into/outward sliding surface..

Chapter 6 contains the summary and final conclusion as well as proposal of further research to be conducted.

Table 1-1 Typical type of rubbers for sealing applications [45]

Group	Backbone	Rubber	Name
R	Un-saturated backbone	BR	Butadiene rubber
		NR	Natural rubber
		SBR	Styrene-butadiene rubber
		NBR	Nitrile-butadiene rubber
		HNBR	Hydrogenated NBR rubber
		CR	Chloroprene rubber
		IIR	Butyl rubber
M	Saturated backbone	EPDM	Ethylene-propylene rubber
		EPDM	Ethylene-propylene-terpolymer
		ACM	Alkyl acrylate rubber
		FKM	Fluoroelastomer
U	Urethane functional group	EU	Urethane rubber
Q	Silicone	VMQ	Silicone rubber

Table 1-2 Binding energy of chemical bonds[45]

Type of chemical bond	Chemical formula	Bonding energy, kJ/mol
Polysulfidic	- C - S _x - C -(x > 3)	<270
Disulfidic	- C - S ₂ - C -	270
Monosulfidic	- C - S - C -	272
Carbon-Carbon	- C - C -	346

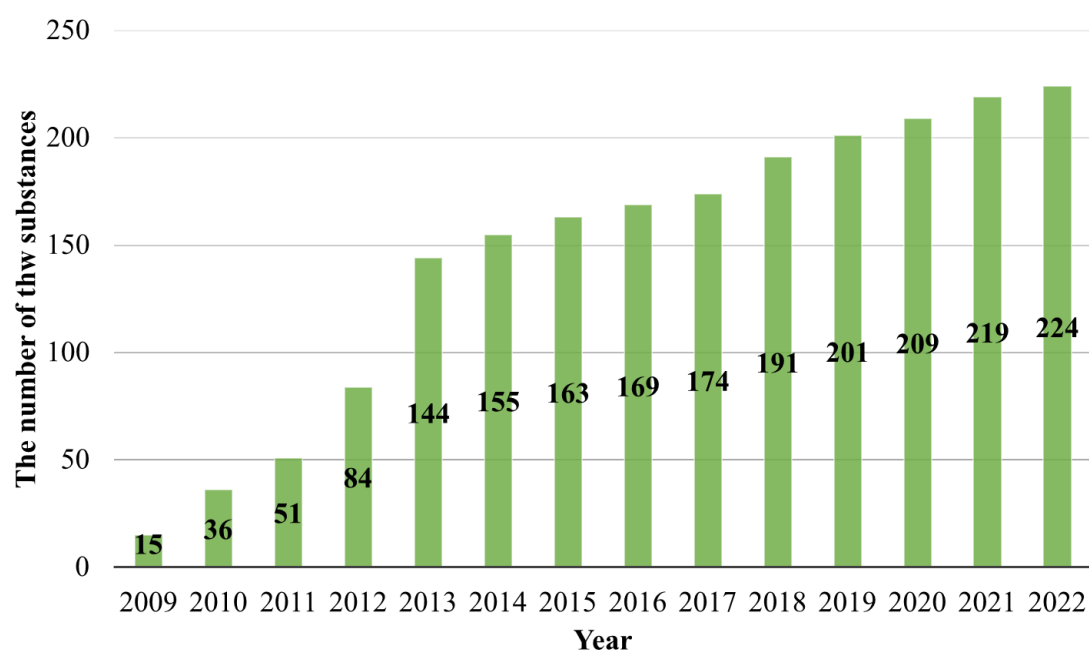


Fig. 1-1 The number of the substances included in the list of REACH (Substances of Very High Concern)

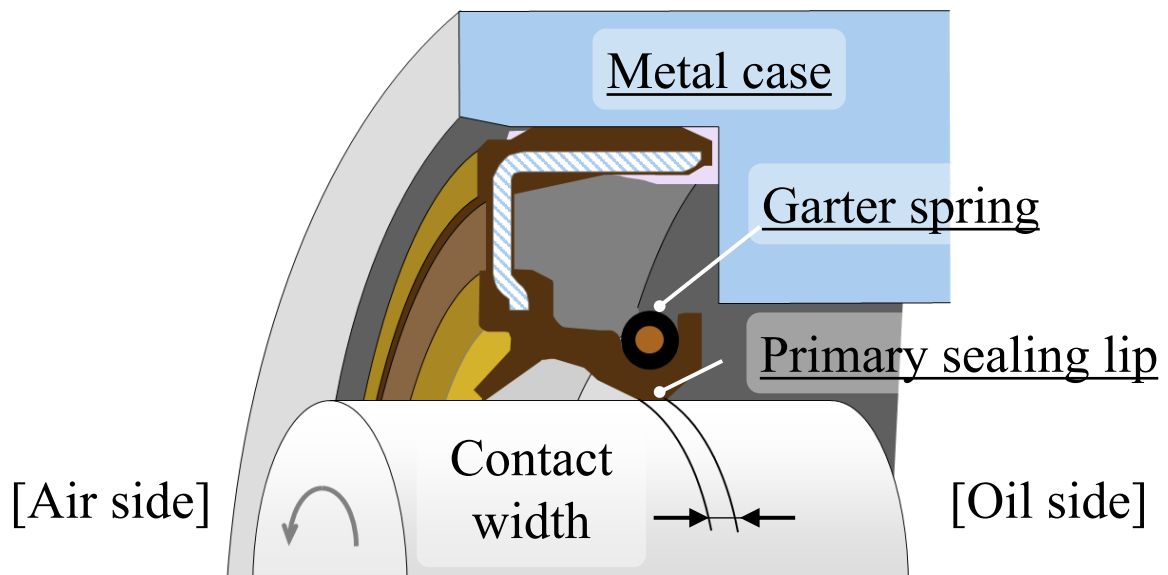


Fig. 1-2 Typical radial shaft seal

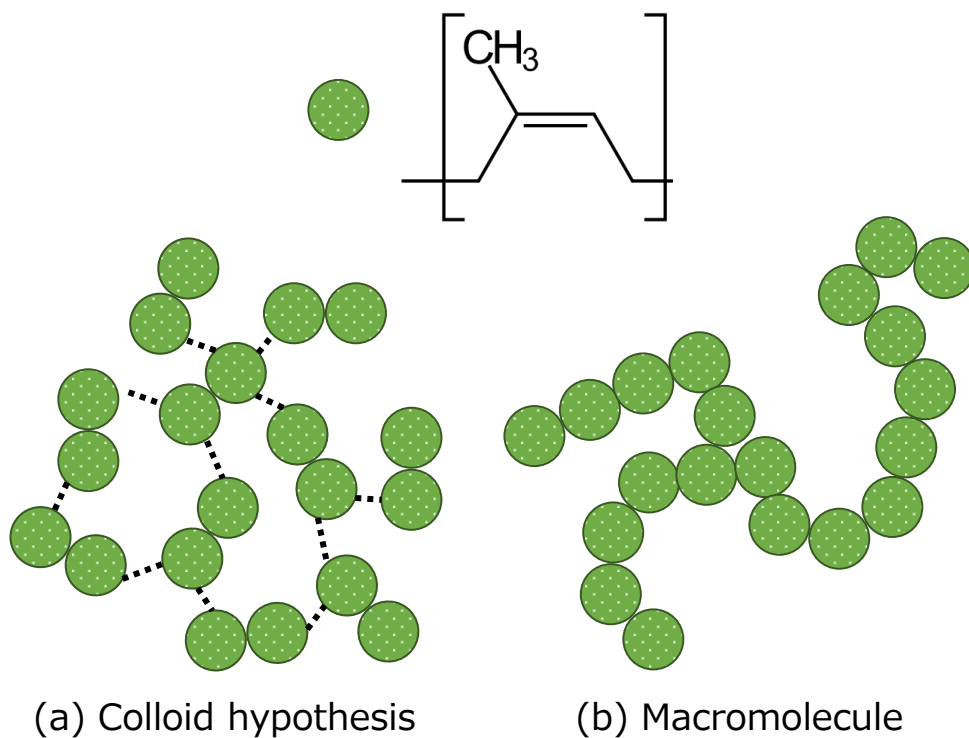


Fig. 1-3 Schematic views of isoprene rubber. (a) Image accepted in early 20th century. Rubber was thought to be aggregate like colloid. (b) Image of isoprene rubber which was first proposed by Staudinger. Polymer is thought to be composed of thousands of covalently bonded atoms.

2 Materials and methods

The aim of this study is to clarify the mechanism of rubber boundary lubrication. In particular, the compatibility between rubber and lubricants was focused. In the view of that, the different types of the rubber and the lubricant were chosen. The techniques for investigating the boundary lubrication of rubber are shown in

Fig. 2-1. In this thesis, the boundary friction was investigated, sliding surfaces was observed in microscopic scale, and the interaction between rubber and lubricant was carried out focusing on the molecular scale systems. The details are as follows.

- A) Friction test
 - (i) Pin-on-disc friction test
- B) Investigation of sliding surfaces
 - (i) Microscopic observation with total reflection method
 - (ii) Microscopic observation with light interferometry
 - (iii) Chemical analysis with in-situ FT-IR microscopy
- C) Evaluation on the interaction between rubber and lubricant and the polarity
 - (i) Measurement of contact angle
 - (ii) Liquid permeation test

2.1 Rubber specimen

2.1.1 Formulation of compounds

Model rubber formulation for samples is selected, considering following points:

- A) To be commonly used for radial shaft seals
- B) Good mechanical properties
- C) Good processability
- D) To be simple, especially not to involve low molecular substance like plasticizer

The formulations of the rubber compound are shown in Table 2-1.

2.1.2 Mixing and vulcanization molding

The rubber hemisphere of radius 2.5 mm was used as sliding pin. The form is shown in Fig. 2-2. The hemisphere was integrally molded with the base part. The base part was fixed to the testing machine using metal holders. The manufacturing procedure rubber specimen is as follows.

1. Compounding of the raw compound
2. Press cure: molding.
3. Post cure: oven heating.

The raw compound was placed in a mold, and pressure was applied for a predetermined time. The temperature and vulcanization time were appropriately determined depending on the materials, and the time at which the degree of vulcanization reached 80% plus at least one minute. Finally, the mixture was heated in an oven at 150 ° C. for 30 minutes. This is to remove low volatile matter, particularly peroxide, remaining in the rubber by heat. This process is called post cure.

2.1.1 Material characteristics

Material characteristics was measured with flat plates which have 2 mm thick.

The tensile strength, the elongation at break and the Young's modulus were measured according to JIS K6251 and the specific gravity was measured according to JIS K6268.

Swelling ratio was calculated by following equations:

$$\Delta V = \frac{V_t}{V_0} \quad (2-1)$$

ΔV is the swelling ratio in the volume, V_t is the volume after t hours of immersing in a liquid and V_0 is the volume before immersing in it.

$$\Delta W = \frac{W_t}{W_0} \quad (2-2)$$

ΔW is the swelling ratio in the weight, W_t is the weight after t hours of immersing and W_0 is the weight before immersing.

Viscoelastic properties were measured using Rheogel E4000 by UBM. The measurement frequencies were 1, 2, 4, 8, 16, 32 Hz. The measurement temperature continuously increased by step of 5 °C in a range of -70 to 100 °C. The displacement was 0.013 % in the tensile direction.

Contact angle was measured using Dropmaster by Kyowa Interface Science Co., Ltd. From contact angle measured using n-hexadecane, water, and diiodomethane as the probe liquids, the surface free energy was calculated with Kitazaki-Hata method[48] in three components, (d: dispersion, p: polar, and h: hydrogen bond).

The liquid permeation test was conducted by the cup method. The schematic diagram of the test apparatus and permeation curve are shown in Fig. 2-4. The cup was filled with the liquid and covered with a flat rubber plate. Turning the cup upside down so that the liquid contacted the rubber. The cup was left at room temperature and atmospheric pressure. Because the liquid permeates the rubber, the overall weight of the cup was reduced by the amount permeated. The lost weight was measured with a precision balance. The amount of decrease was plotted against time, which was called the permeation curve. The time which it takes for the liquid to penetrate the rubber and reach equilibrium was called time lag. Solubility S was calculated from the time lag. When equilibrium is reached, that is, when the permeation curve becomes straight, the permeation speed P was calculated from its slope [49]

2.2 Lubricants

Methyl oleate (MO) and n-hexadecane (HD) were used for the lubricants. Their chemical structures are shown in Fig. 2-3. Hereinafter, the combination of rubber and lubricant is described “rubber/lubricant”, like “NBR1/MO”.

2.3 Experimental method

Friction force was measured by pin-on-disc friction tester. The friction coefficient (COF) was calculated from the lateral force detected by the load cell, which held the rubber pin.

$$\mu = \frac{F_r}{W} \quad (2-3)$$

where μ is COF, F_r is the friction force, N and W is the Load, N.

2.3.1 Friction tester

The pin-on-disc friction tester is shown in Fig. 2-5. In an experiment, the rubber sample was loaded by the weight. The SPCC disc was mounted on the shaft. The disc was polished to $R_a < 0.06 \mu\text{m}$ and finished to a mirror surface so as to minimize the digging-up friction generated by the surface roughness of the SPCC disc. The shaft rotated by a DC brushless motor. The rotation speed was controlled by the voltage.

2.3.2 Observation and analysis method for the interpret of mechanism of boundary lubrication

The observation of the sliding surfaces is the key technology in tribology. Techniques for the observation and analysis of the sliding surfaces and the measurement of the film thickness are shown in Table 2-2[50]. In this study, total reflection method was used for visualizing the sliding surface because of its simplicity. Secondary, in-situ FT-IR was used for the analysis of the sliding surfaces. Besides, then white light interferometry was used for the measurement of the film thickness of the lubricant. In following sections, the details of the techniques are described.

2.3.2.1 Total reflection method

The sliding surfaces were observed by the total reflection method with the white visible light. The outline of the apparatus and the example of the measurement are shown in Fig. 2-6. In this apparatus, the contact surface was able to be directly observed by using the total internal reflection of the prism with the incident light which was obliquely to the sliding surfaces[51]. The light source was a daytime white fluorescent lamp, CMOS camera was applied, and the magnification of the lens was 1.2. The disk was made of high refractive index glass to widen the observation field. In the non-contact part, the incident light was totally reflected, and it is observed bright (white). When the gap became as long as the wavelength of the incident light, the reflectivity gradually decreases, and the contact part was observed dark (black) [52].

In this experiment, each material/lubricant was used under the specific conditions for photographing and image processing. Based on the images before sliding, the dark part was called black and was judged as the contact part. The bright part was called white and was judged as the non-contact part at intervals of μm or more. Some areas appeared gray. The gray part, which may have had nm-order to sub μm -order gap, were counted as contact area in the binarization described next.

The area of real contact was calculated with following schemes:

1. The images were binarized.
2. The number of black pixels was counted.
3. The area of one pixel was obtained from the calibration image.
4. The real contact was calculated by multiplying the number of black pixels by the area of one pixel.

The example of the binarized image is shown in Fig. 2-6 (d).

2.3.2.2 In-situ FT-IR microscopy

FT-IR stands for Fourier Transform Infrared, and it is a method using infrared spectroscopy. The spectrum represents the molecular absorption therefore the chemical structure of an object to be measured can be determined. Based on Beer-Lambert's law, the absorbance is proportional to the molar absorptivity, so that it is possible to quantify by appropriate processing of the sample and obtained data. Beer-Lambert's law is the law relating the absorption of electromagnetic waves to the concentration of the sample. It can be described as the following equation:

$$A(\lambda) = \varepsilon(\lambda)Cx \quad (2-4)$$

where $A(\lambda)$ is the absorbance spectrum, $\varepsilon(\lambda)$ is the molar absorptivity, C is the concentration of the molecule and x is the transmission distance of the light[53].

The two methods are mainly applied to investigate the film thickness of the sliding surface. One is a reflection-absorption method, and the other is Attenuated Reflectance Spectroscopy (ATR) method. In this study a reflection-absorption method was used because the same area of the rubber has to contact to the counterparts. In the case of the ATR FT-IR, the prism slides on the rubber, which is described in Fig. 2-7. As forementioned in 2.3.1, the rubber lip of the radial shaft seals is in constant contact with the shaft. The contact of the ATR FT-IR differs greatly from that of the radial shaft seals.

A schematic diagram of the reflection-absorption FT-IR microscopy is shown Fig. 2-8. The incident infrared light transmitted through the lubricant, reflected on the rubber surface. The lubricant film thickness during sliding can be calculated from the absorbance. An example of the measurement with NBR1/HD is shown in Fig. 2-9.

The calibration curve of the film thickness is shown in Fig. 2-10. It was obtained by the measurement without load and sliding with the rubber hemisphere sample. It was revealed that the film thickness and the peak area were correlated.

The IR light penetration depth is estimated about 1-3 μm from the following equation:

$$D_p = \frac{\lambda}{2\pi\sqrt{n_1 \sin^2 \theta - n_2^2}} \quad (2-5)$$

where D_p is the light penetration depth, λ is the wavelength of the infrared light, n_1 is the refractive index of the counterface, n_2 is the refractive index of the lubricant and θ is the incident angle [54]. For the reflected IR light, Kramers-Krönig transformation should be conducted.

The details of the data correction and procedure obtaining of calibration curves were discussed in Chapter 3 and 4.

2.3.2.3 White light interferometry

Light interferometry is a method for the visualization and the measurement of film thickness[55]. White light is irradiated on the sliding surface, when the sample and the disc are lubricated with the lubricant. The irradiated white light is divided into the light reflected at the disc-lubricant interface and the light reflected at the sample-lubricant interface. When these two waves are combined, a constructive interference occur in the case of that the film thickness was in phase and a destructive interference occur in the case of that the film thickness was out of phase. The distance is the function of the wavelength and the order.

In an experiment, the rubber sample loaded by the weight on the other side of the cantilever. The transparent glass disc was mounted on the shaft. The shaft rotated by a DC brushless motor.

The glass disc is a N-BK7 window, which is 75 mm thick and with Anti-reflecting (AR) coating. AR coating is necessary to decrease reflection on the disc surface opposite sliding surface because the reflection on the rubber surface was weak. The AR coating was multi-layer of metal oxide dielectric. For the purpose of measuring the film thickness less than 100 nm, the spacer method was used[50]. Only one side of the disc used for this method was coated with Cr and SiO_2 .

Methodology of the calibration procedure is shown in Fig. 2-12. The Newton rings were observed when the convex lens with the known radius of curvature contacted the glass disc. From the Hue of the image of the Newton rings the calibration curve was obtained. All of the digital image processing was performed using Open CV 4.5 on Python 3.9.

2.4 Summary

The different types of the rubber and the lubricant were chosen to investigate the influence of the compatibility between the rubber and the lubricant. The boundary friction was investigated with pin-on-disc friction tester, sliding surfaces was simultaneously observed in microscopic scale, and the interaction between rubber and lubricant was carried out focusing on the molecular scale systems.

Table 2-1 Formulation of rubber compounds and mechanical properties of material

	NBR1	NBR2
Formulation of material		
NBR ACN 20%	100	
NBR ACN 40%		100
FKM		
EPDM		
FEF Carbon black	55	55
Antioxidant RD	1	1
Hydrotalcite		
Taic		
Dicumyl Peroxide	3	3
Perhexa25B		
Mechanical properties		
Hardness, ShoreA	83	81
Tensile strength, MPa	15.8	25.0
Elongation at break, %	90	180
Young's modulus, MPa	12.4	11.3
Density, g/cm ³	1.15	1.19

Table 2-2 Techniques for the observation and analysis of the sliding surfaces and measurement of the film thickness

Methods	Strengths	Weaknesses
Optical total reflection method	Visualizing	Measurement of the film thickness
Chemical analysis (FT-IR) method	Determination of chemical composition	Complicated and high cost of the apparatus
Light interferometry	Visualizing and nanoscale measurement of film thickness	Low reflective index and high roughness
Laser induced fluorescence	Visualizing and measurement of the film thickness	Influence of the fluorescence substances
Electric resistance method	Measurement of the film thickness	Visualizing

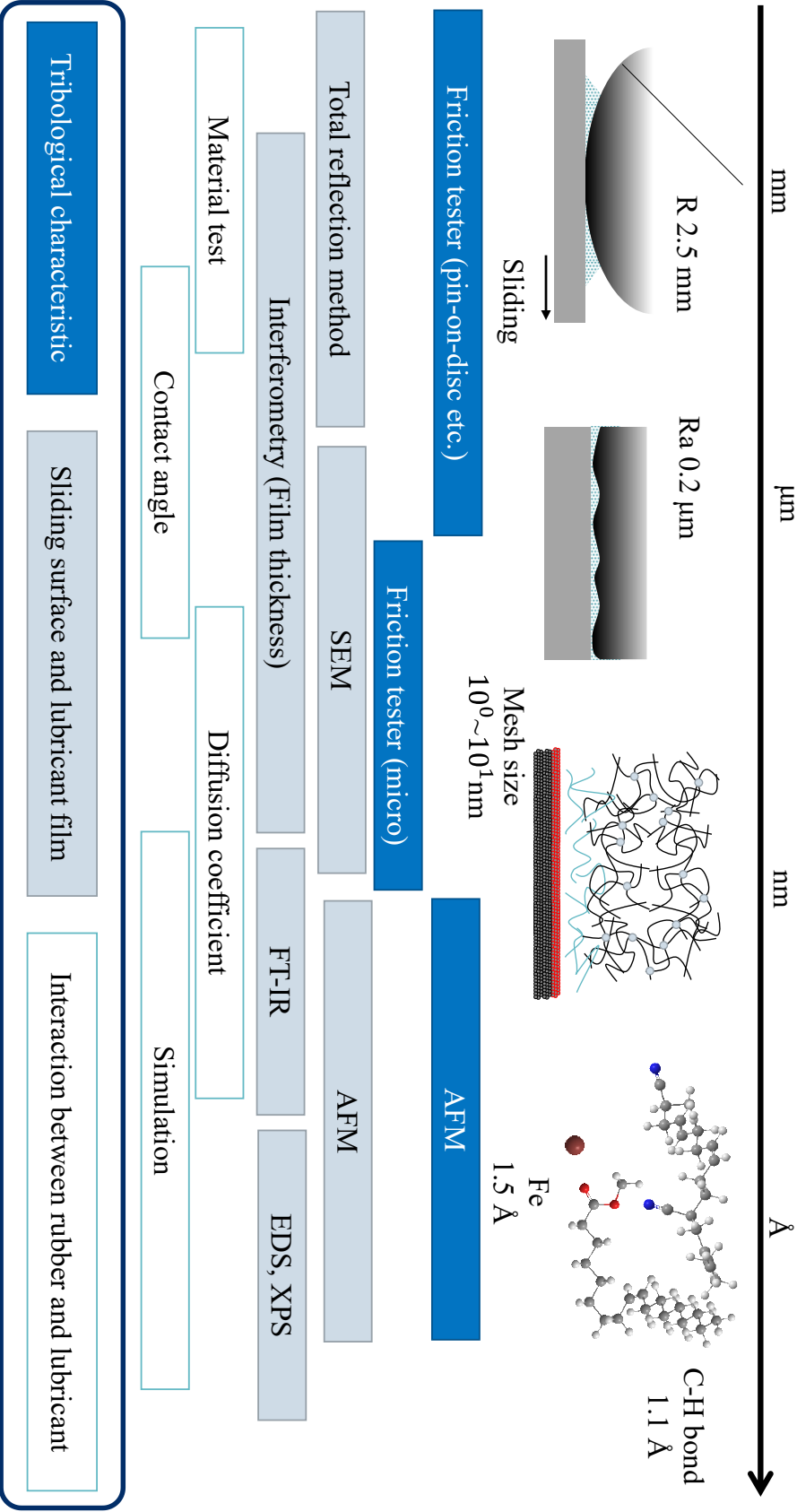
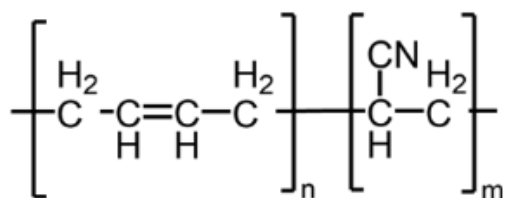


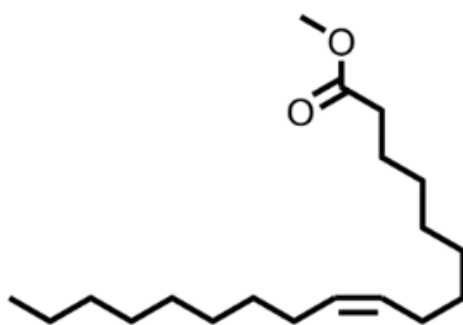
Fig. 2-1 Techniques for investigating the boundary lubrication of rubber



Fig. 2-2 Hemisphere pin made of rubber



(a) Nitrile-butadiene rubber (NBR)



(b) Methyl oleate (MO)



(c) n-Hexadecane (HD)

Fig. 2-3 Chemical structures

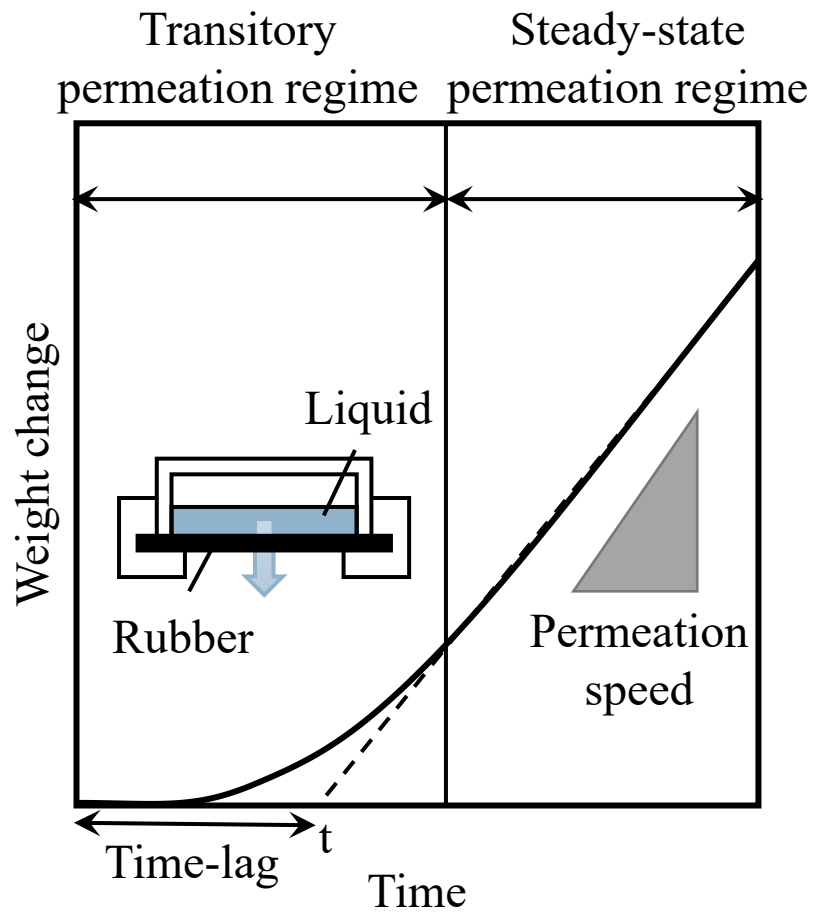
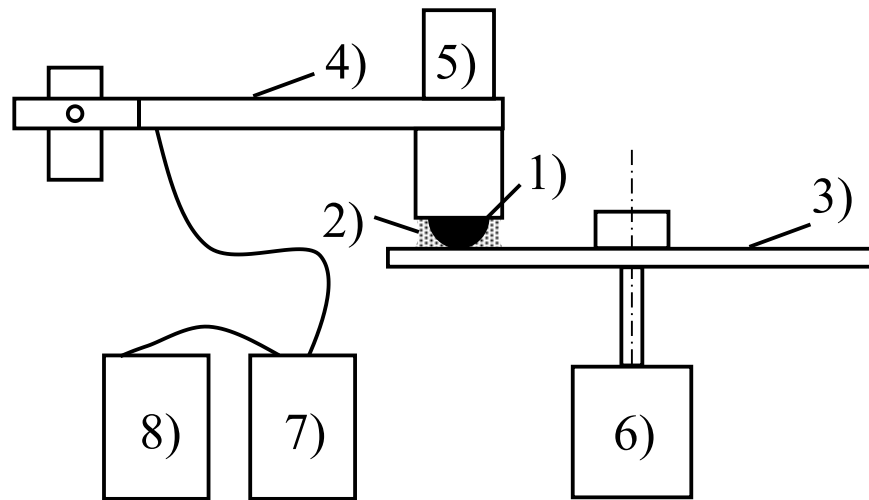


Fig. 2-4 Schematic diagram of the test apparatus and the permeation curve.

(a)



- | | |
|--------------------|----------------|
| 1) Rubber specimen | 5) Weight |
| 2) Lubricant | 6) Motor |
| 3) Disc | 7) Amplifier |
| 4) Load cell | 8) Data logger |

(b)

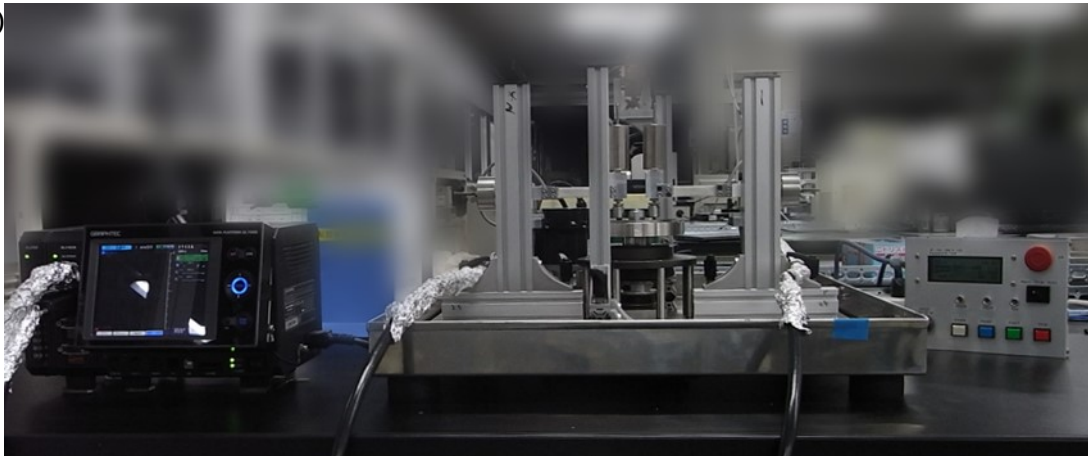
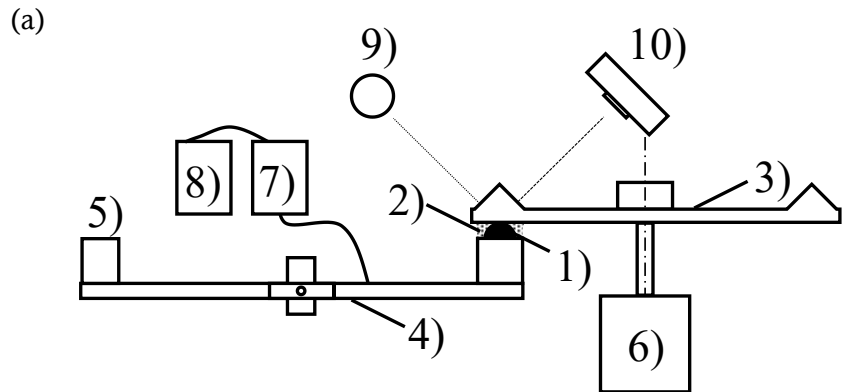


Fig. 2-5 (a) Schematic illustration of friction tester and (b) its photograph



- | | |
|--------------------|----------------|
| 1) Rubber specimen | 6) Motor |
| 2) Lubricant | 7) Amplifier |
| 3) Glass disc | 8) Data logger |
| 4) Load cell | 9) Light |
| 5) Weight | 10) Camera |

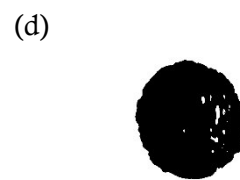
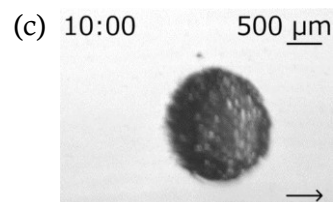


Fig. 2-6 (a) Schematic illustration of total reflection observation apparatus, (b) its photograph, and (c) the observation image of NBR1/HD. The number on upper left of images indicate the sliding time and the arrows on lower right of images indicate the sliding direction of the disc. (d) binrized image of the original image (c).

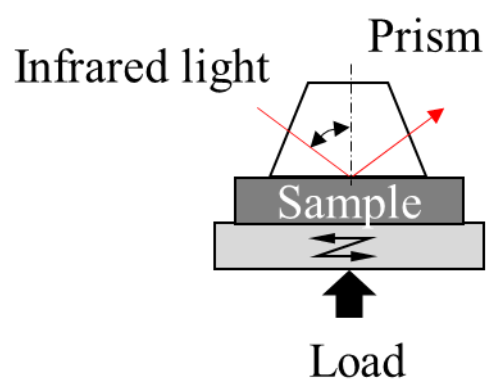


Fig. 2-7 Schematic of friction tester with ATR FT-IR.

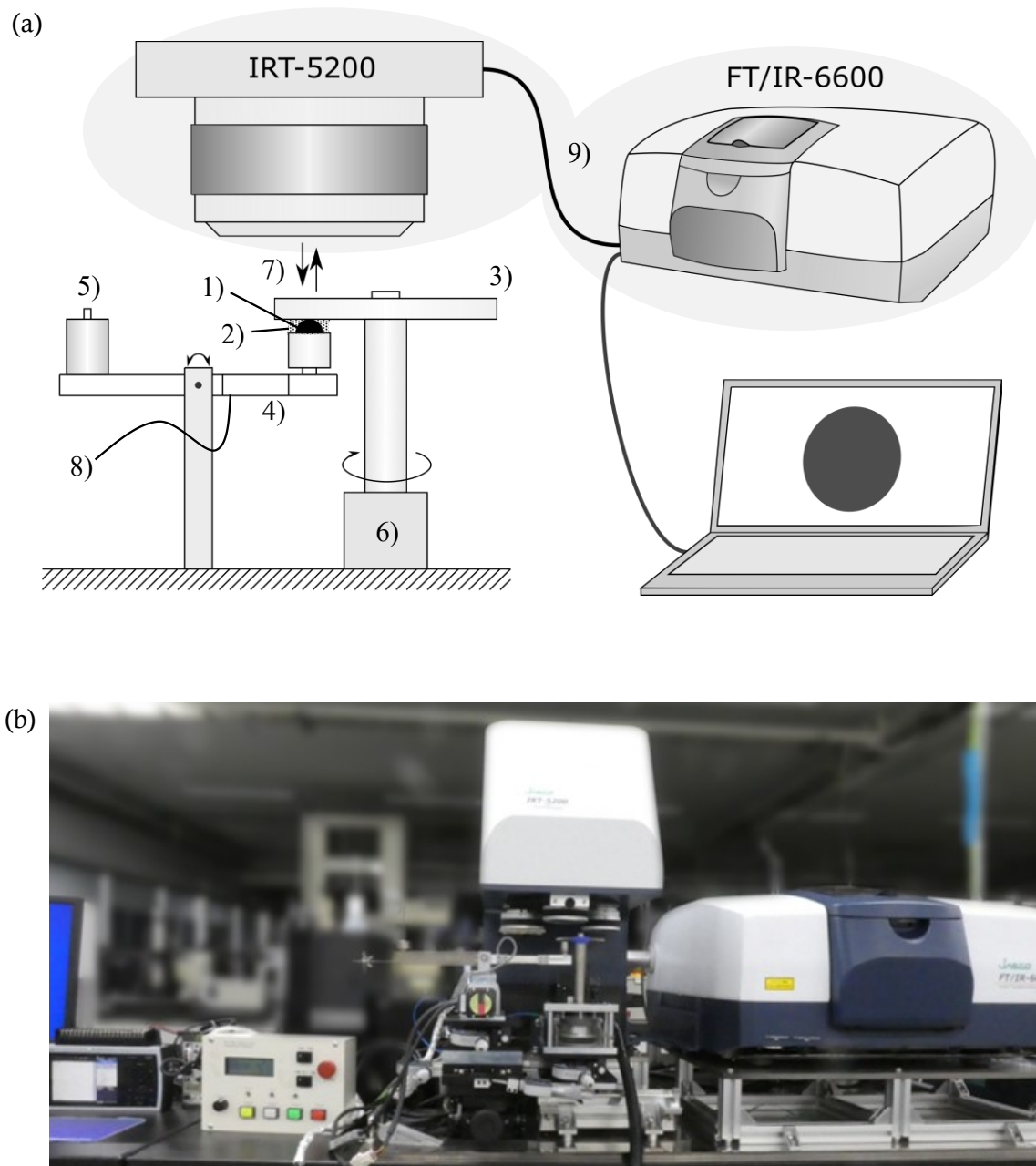


Fig. 2-8 (a) Schematic of FT-IR microscopy (reflection-absorption method) and (b) its photograph. (c) The relationship between the peak area and the film thickness of HD on the rubber.

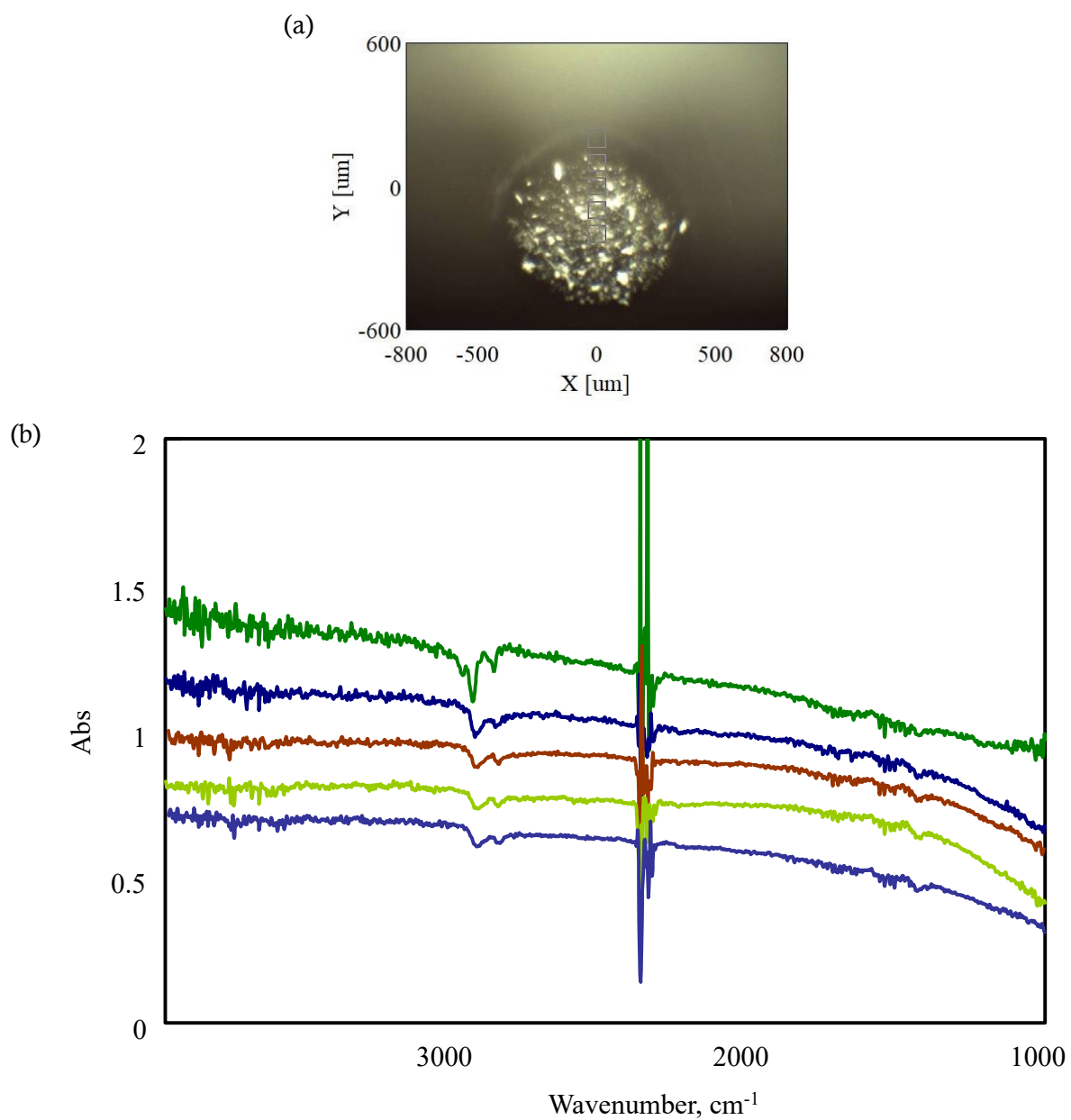


Fig. 2-9 (a) Microscopic image of the sliding surface, where the five squares at $Y = -200, -100, 0, +100, +200 \mu\text{m}$ represent measuring points. (b) the spectra measured at each point.

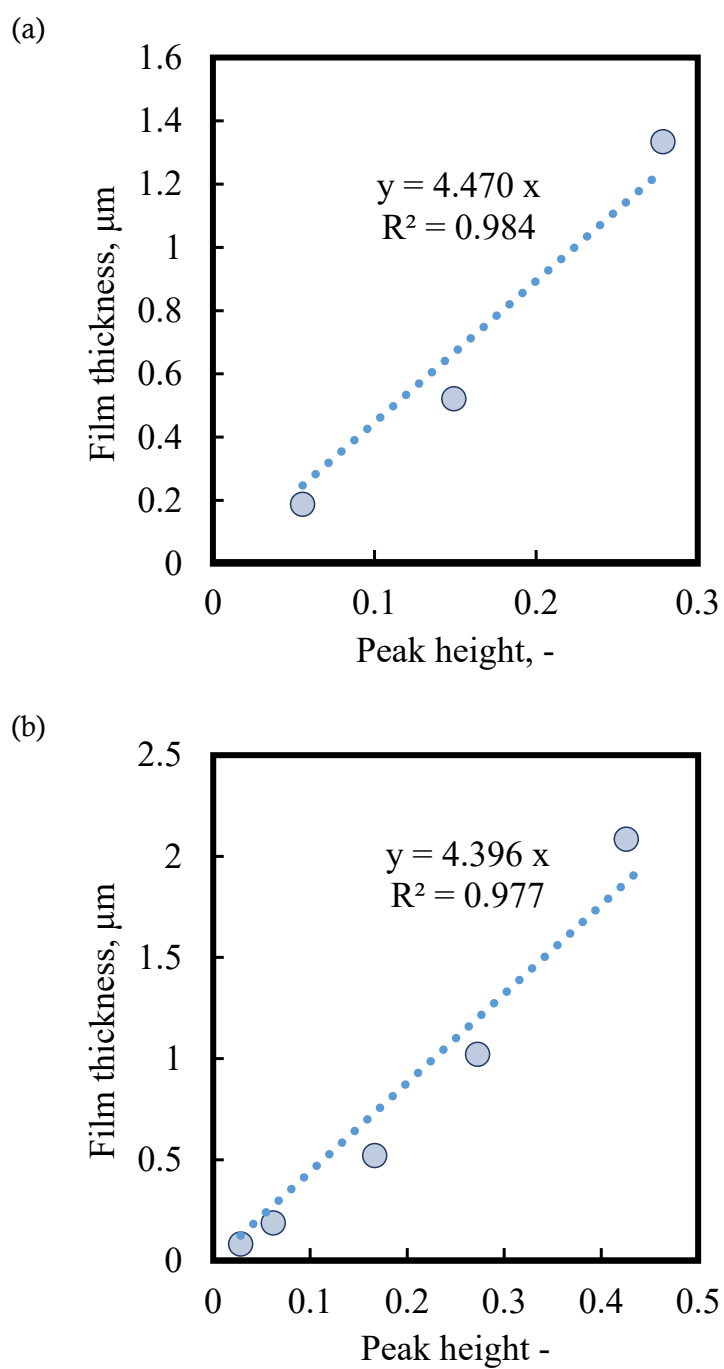
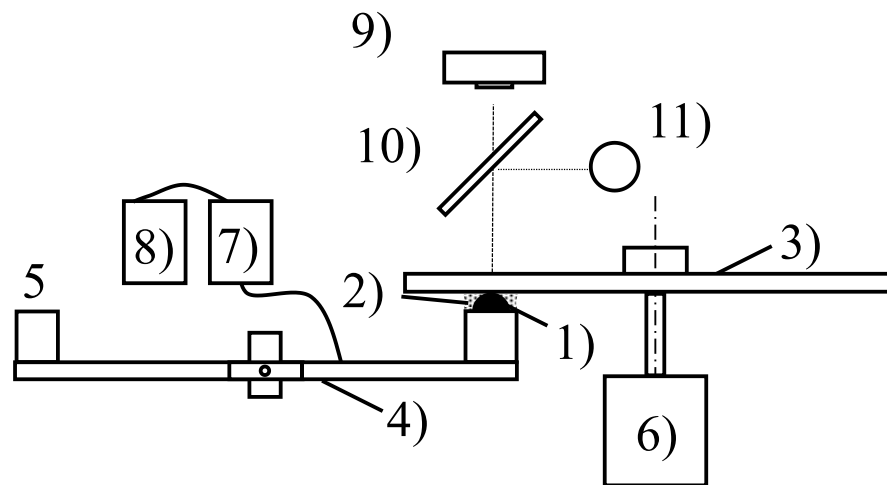


Fig. 2-10 Calibration curves of (a) NBR1/HD and (b) NBR2/HD

(a)



- | | |
|--------------------|-----------------|
| 1) Rubber specimen | 7) Amplifier |
| 2) Lubricant | 8) Data logger |
| 3) Glass disc | 9) CMOS Camera |
| 4) Load cell | 10) Half mirror |
| 5) Weight | 11) LED |
| 6) Motor | |

(b)



Fig. 2-11 Schematic illustration of optical interferometric and (b) its photograph.

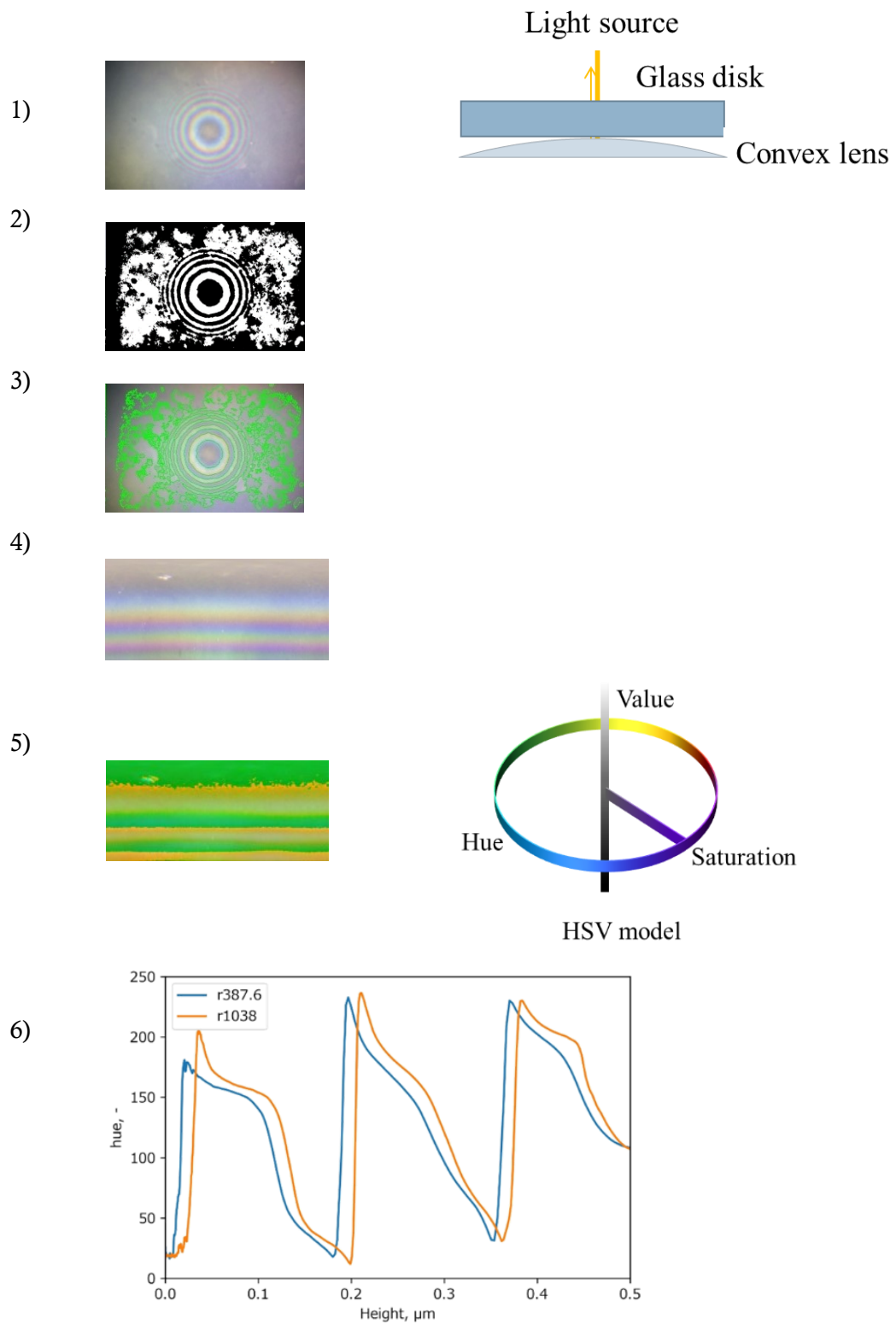


Fig. 2-12 Calibration procedure using Hue of HSV color space. 1) Obtaining image from the convex lens with known radius of curvature, 2) binarization, 3) determining the center of the Newton rings by the contour detection, 4) polar coordinate conversion, 5) conversion to HSL and mapping Hue and 6) plotting the Hue to the film thickness.

3 Experimental results

3.1 Effect of compatibility of rubber and lubricant on friction behavior

The objective of this section is to reveal the basic relationship between the frictional behavior and the compatibility of rubber and lubricants in order to understand the boundary lubrication mechanism of rubber. To achieve this, sliding experiments at low speed, where the fluid film was not thick enough to avoid direct contact were conducted, using NBR1 and NBR2 with the different polarity.

3.1.1 Lubricated sliding test

The friction force was measured by the pin-on-disc friction measurement. COF under lubricated condition is shown in Fig. 3-1. Each test was repeated twice independently.

While COF scattered in the two times of the tests at the early period, there was the common tendency depending on the combinations of rubber/lubricant. In terms of the latter period, from 10 to 15 hours, COF converged to certain values. COF of NBR1/MO increased to 1.5 for 6.7 h and then it decreased. COF of NBR1/HD increased to 1.2 at for 1.0 h and then decreased. COF of NBR2/MO increased to 0.4 for 0.7 h and that of NBR2/HD increased to 0.25 for 0.3h and then decreased.

The common tendency had three characteristics.

- A) COF of NBR1 was higher than that of NBR2 on average.
- B) NBR2 has spiky peaks. The friction curves of NBR1 were smoother than those of NBR2.
- C) COF of NBR1 increased for the first several hours and then decreased. NBR1/MO increased for longer time. COF of NBR2 also increased soon after starting of sliding, but it dropped immediately.

3.1.2 Dry sliding test

COF of NBR1 and NBR2 under dry condition was shown in Fig. 3-2 . COF of NBR1 was almost the same as that of NBR2. COF after one hour from the start of sliding reached at 1.84 for NBR1 and 1.80 for NBR2.

3.1.3 Speed dependency under lubricated condition

The speed dependency under the lubricated condition was shown in Fig. 3-3 and Fig. 3-4. As a tendency, COF decreased as sliding speed increased. It showed a stable COF, which was about 0.1, at the speed of 2.5 mm/s or more. In this speed region, the fluid lubrication was dominant. At the speed less than 0.83 or less, COF changed during sliding.

COF of NBR1/MO increased up to 1.2 at 0.42 mm/s or less. At 0.83 mm/s, COF initially increased and then decreased. COF of NBR1/HD initially increased and decreased after one or two hours at 0.42 mm/s or less. COF of NBR2 increased soon after starting of sliding but immediately decreased while the friction curves were spiky.

In this thesis, the regime where the fluid lubrication was lost referred as the boundary lubrication. The boundary friction differed among the combinations of the rubber/the lubricant.

In Fig. 3-5, the horizontal axis corresponds to the sliding distance. This graph shows that the sliding distance affected on the behavior of the friction coefficient under boundary lubrication. This implied that the lubricant carried away absorbing on the disc.

The results were briefly summarized below:

- A) COF decreased as sliding speed increased.
- B) At speeds higher than 0.83 mm/s, the frictional force curve was not spike-like but close to constant.
- C) At speeds of less than 2.5 mm/s, the friction force curve increased at first and then decreased. This speed region was referred as boundary lubrication regime. In boundary lubrication regime, the friction varied among the rubber/lubricant combinations.

3.2 Observation of the sliding surfaces by total reflection method

For the purpose of understanding the mechanism of the change in COF during long term sliding, the direct observation of sliding surface using a total reflection method was conducted under both lubricated and dry conditions.

3.2.1 Lubricated conditions

The observation of the sliding surfaces and the measurement of COF were conducted simultaneously. The results are shown in Fig. 3-6 and Fig. 3-7. The sliding surfaces and COF differed depending on the combination of rubber/lubricant. There appeared the characteristic

periodic fluctuation of COF. Its period varied based on the period of the rotation. This result implied that these noises were caused by neither the motor nor the disc rotation. The fluctuation of COF of NBR2/HD was larger than that of the other combinations. During the sliding test of this combination, it was observed that the rubber vibrated in parallel to the sliding direction. It was assumed that the stick-slip like vibration occurred.

In another point of view, COF of NBR1/MO, NBR1/HD, and NBR2/MO increased in the initial stage and then gradually decreased. This tendency was the same as the results of the friction test with SPCC disc, which was discussed in the previous section.

With the aim of clarifying the mechanism of the slope change in COF, the images of the sliding surfaces were obtained by the total reflection method. The images are shown in Fig. 3-7. At the condition that the rubber was loaded statically before the start of sliding (0 h), rubber surface contacted the glass without gap.

No sooner than sliding started, COF of NBR1/MO, NBR1/HD, and NBR2/MO increased, and white spot-like pattern appeared, which meant the gap generated in-between the rubber and the glass disc. Besides, when the spots were observed, COF was high.

After certain period of the sliding, COF of NBR1/MO, NBR1/HD, and NBR2/MO decreased. At this time, the white pattern gradually became indistinct, and from the left end of the sliding surface (the side of the lubricant introduction), a gray contact surface was formed gradually. The increase of the gray contact surface and the decrease of COF occurred simultaneously.

The change in the real area of contact is shown in Fig. 3-8, where the contact area was normalized by initial contact area. The real area of contact of NBR1 increased during sliding. That of NBR2 became larger than initial value, though it did not always keep increasing.

3.2.2 Dry conditions

The images of the sliding surface under dry condition are shown in Fig. 3-9. COF was 1.7, which was almost same as the pin-on disc sliding test mentioned in Section 3.1, where the SPCC disc was used. The contact surface was circular before sliding and it was deformed into an ellipse during sliding as to be deformed to the direction of the sliding. Besides it was observed that white spots and striped patterns are formed on the contact surface as if they were connected vertically. The undulations and the wrinkles insist non-uniform deformation of the contact surface.

The non-uniform deformation was caused by the heterogeneous structure of the rubber material at the micron sizes. Heterogeneity comes from several aspects. One of the aspects is the rubber material compounds, in other words, rubber was formulated by the mixture of several chemical

agents. The other aspect was the distribution of cross-linking density, which can also be related with the inhomogeneous rubber network structure [56][45].

3.3 Chemical analysis and observation by in-situ FT-IR microscopy

Using in-situ FT-IR microscopy, the sliding surfaces were investigated in the following points:

The changes of

- A) chemical components of the sliding surfaces during sliding
- B) the sliding surfaces in microscopic images of the sliding surfaces
- C) COF

3.3.1 FT-IR spectra of rubber and lubricant

The spectra of the lubricant are shown in Fig. 3-10 (1) and (2). In the spectrum of the HD, the vibrations of C-H bond of alkanes appeared in $2800 - 3100\text{ cm}^{-1}$ and 1300 to 1500 cm^{-1} . In addition to that, the peaks at 1200 and 3010 cm^{-1} corresponded to the double bonds of C=C, and the peak in the spectrum of MO at 1745 cm^{-1} corresponded to the C=O.

The spectra of the rubber are shown in Fig. 3-10 (3) and (4). They show an anomalous dispersion effect since they were reflectance spectra. This is well known as the spectra on the rubber surface filled with carbon black [54]. By the effect, the negative peaks appeared in the spectra. Those spectra can be approximately transformed to the normal waveform of the absorbance (k value) by Kramers-Krönig [54]. The spectra obtained through KK transformation are shown in Fig. 3-11. The CH₂ in the main chain was represented by $2800 - 3000\text{ cm}^{-1}$ and 1450 cm^{-1} . The nitrile group appeared at $2240 - 1745\text{ cm}^{-1}$.

3.3.2 Investigation of sliding surfaces with in-situ FT-IR microscopy

The spectra of NBR1/HD during sliding are shown in Fig. 3-12, where the sliding time is (1) 0 h, (2) 1 h, (3) 10 h, and (4) 20 h. (b) is the enlarged the view of part of the graph around 3000 cm^{-1} , which corresponded to the structure of hydrocarbon. The peak became larger during sliding. The other part of spectra did not show any evidence of creating new chemical components or chemical bonds in sliding surfaces. Only the peaks of the hydrocarbon were detected.

The changes in COF and the peak area from 2800 to 3100 (see Fig. 3-12 (b)) are calculated and shown in Fig. 3-13 (a) and (b). COF of NBR 1 increased at the earlier stage of sliding. However,

after a long period of sliding, COF decreased, when the absorbance of HD increased. The change in the friction and the absorbance of HD with NBR 2 was much smaller than that of NBR 1.

The images of the sliding surfaces are shown in Fig. 3-13 (c) and (d). The bright spots appeared on the sliding surfaces of NBR1, and the contours of the contact surface were difficult to discern. Regarding NBR2, the sliding surface was observed by microscopy brighter than NBR1 and it vibrated in a direction parallel to the sliding direction.

3.3.3 Calibration curves for calculating film thickness

With the aim of measuring the film thickness during sliding, the spectra for the calibration curves were obtained. The calibration curve for determining the film thickness is shown in Fig. 3-14, which were obtained as follows.

Firstly, the spectra of NBR1/HD were measured for calibration curve without sliding, where the gaps between the disc and sample were from zero to one μm . The original spectra are shown in Fig. 3-15 (a). The details of the method were mentioned in Chapter 2.

Secondary, the differential spectra were obtained by subtracting the background spectrum from each original spectrum. They are shown in Fig. 3-15 (b), where the background spectrum was the spectrum with zero μm gap without sliding. From this point forward, all references to background spectrum referred the spectrum with zero μm gap. The background spectrum was Fig. 3-15 (a)-(4) for NBR1/HD.

Then, the peak height at 2915 cm^{-1} was calculated. Finally, the peak height was plotted against the gap between rubber surface and disc. The calculation curves are shown in Fig. 3-18 (a). They had a linear relation. Using these curves, the film thickness could be calculated.

Regarding NBR2, the same data correction was conducted. The differential spectra of NBR2/HD for the calibration curve are shown in Fig. 3-17 (a).

3.3.4 Experiments on sliding speed dependence

The different spectrum in Fig. 3-16 corresponded to spectrum with varying sliding speed., where the sliding speed of (1) 620, (2) 520, (3) 260, (4) 130, (5) 52, (6) 5.2, (7) 0.52, (8) 0.05 and (9) 0 mm/s. The original spectra are shown in Fig. 3-16 (a), and the differential spectra are shown in Fig. 3-16 (b). The differential spectra were obtained by subtracting the background spectrum so as to reduce distortion of the baseline.

The same data correction was applied on the spectra of NBR2/HD. The differential spectra of NBR2/HD are shown in Fig. 3-17 (b). The background spectrum was the spectrum with 0 μm gap without sliding.

For the calculation of the film thickness, the peak height at 2915 cm^{-1} were calculated. The film thickness of HD was calculated from the calibration curve, which obtained in Section 3.3.3. However, it was not calculable in the spectra at 0-5.2 mm/s for NBR1/HD and at 0-52 mm/s for NBR2/HD because they had a negative peak around 3000 cm^{-1} . The film thickness and COF were plotted in Fig. 3-18 in sum.

3.4 Summary

The lubricated sliding test resulted that each combination of rubber/lubricant had differences in COF especially at mixed and boundary lubrication regime, while the results of dry sliding test delivered that there was no large difference.

Whereas COF did not change during sliding in the fluid lubrication regime, it changed during sliding in mixed and boundary lubrication regime. The time tendency of NBR1/MO, NBR1/HD and NBR2/MO can be described in follows:

During sliding,

- A) COF initially increased and then decreased.
- B) In the sliding surfaces, white pattern was appeared at the beginning of the sliding, the pattern gradually disappeared and gray contact area increased
- C) Real area of contact increased.
- D) With the in-situ FT-IR microscopy, following results were obtained:
- E) Bright spots observed on the sliding surface of NBR1/HD
- F) The peaks of only the rubber and the lubricant were detected in the spectra.
- G) The amount of hydrocarbon in the sliding surface of NBR1/HD increased.

The sliding surface was analyzed by in-situ FT-IR microscopy. The peaks of lubricant were detected, and it found that the shape of the peaks could differ film thickness. It was necessary to be applied the data correction such as subtracting background spectra or KK transformation.

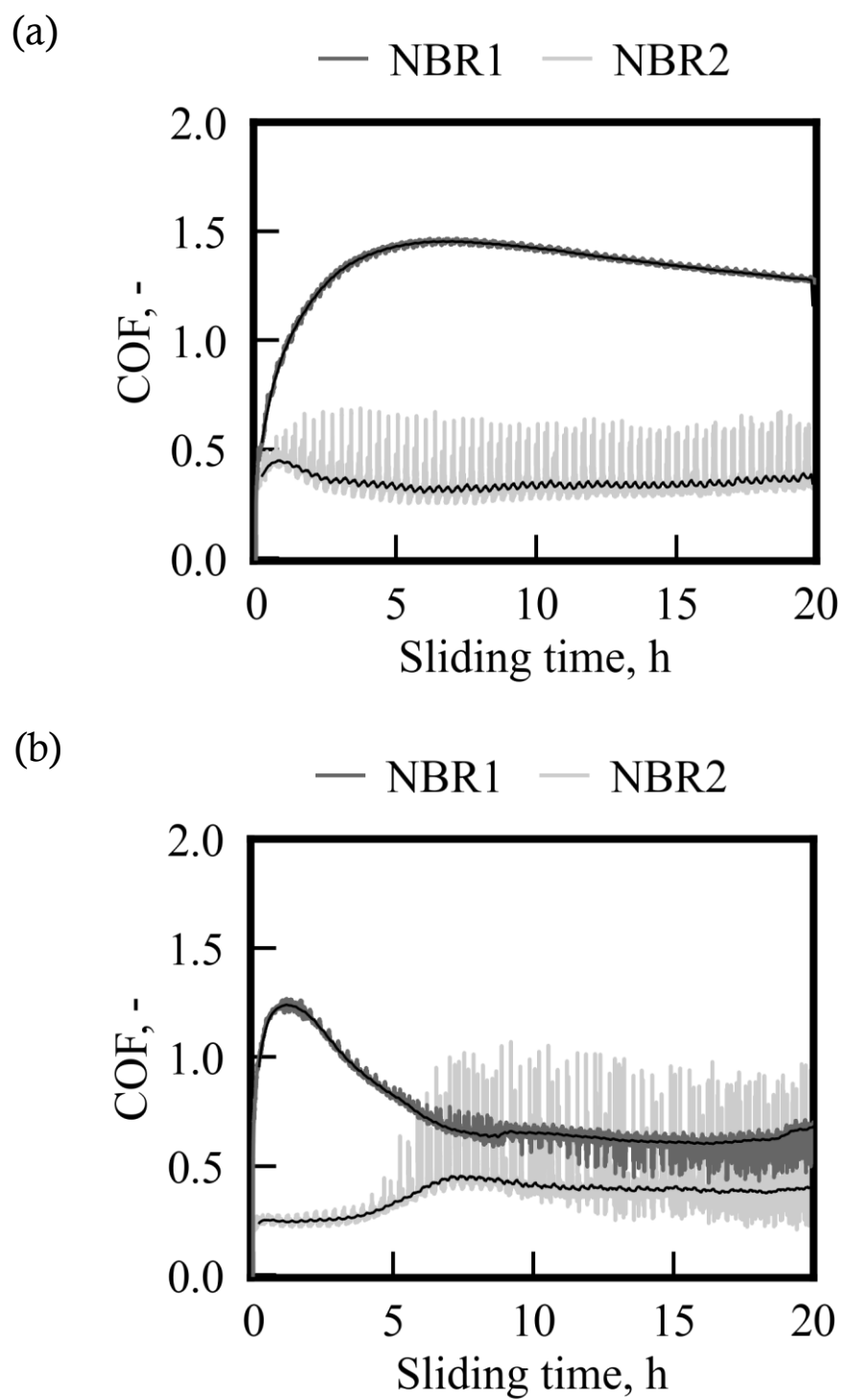


Fig. 3-1 Changes in COF lubricated with (a) MO and (b) HD at 0.1 mm/s

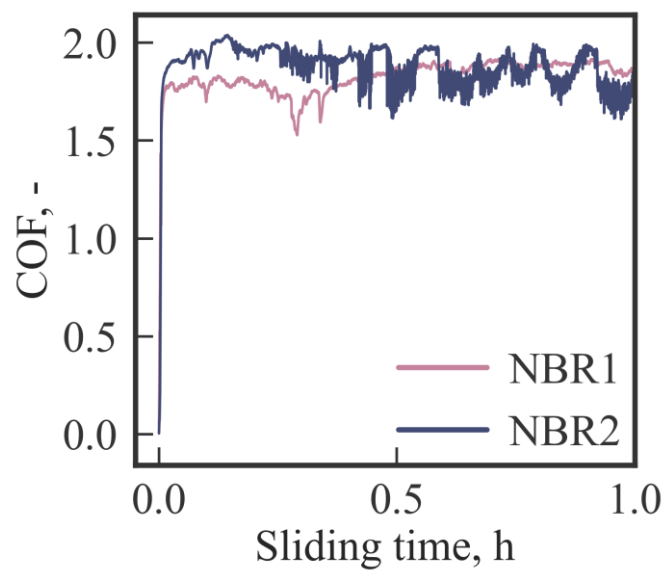


Fig. 3-2 COF of NBR1 and NBR2 without lubricant

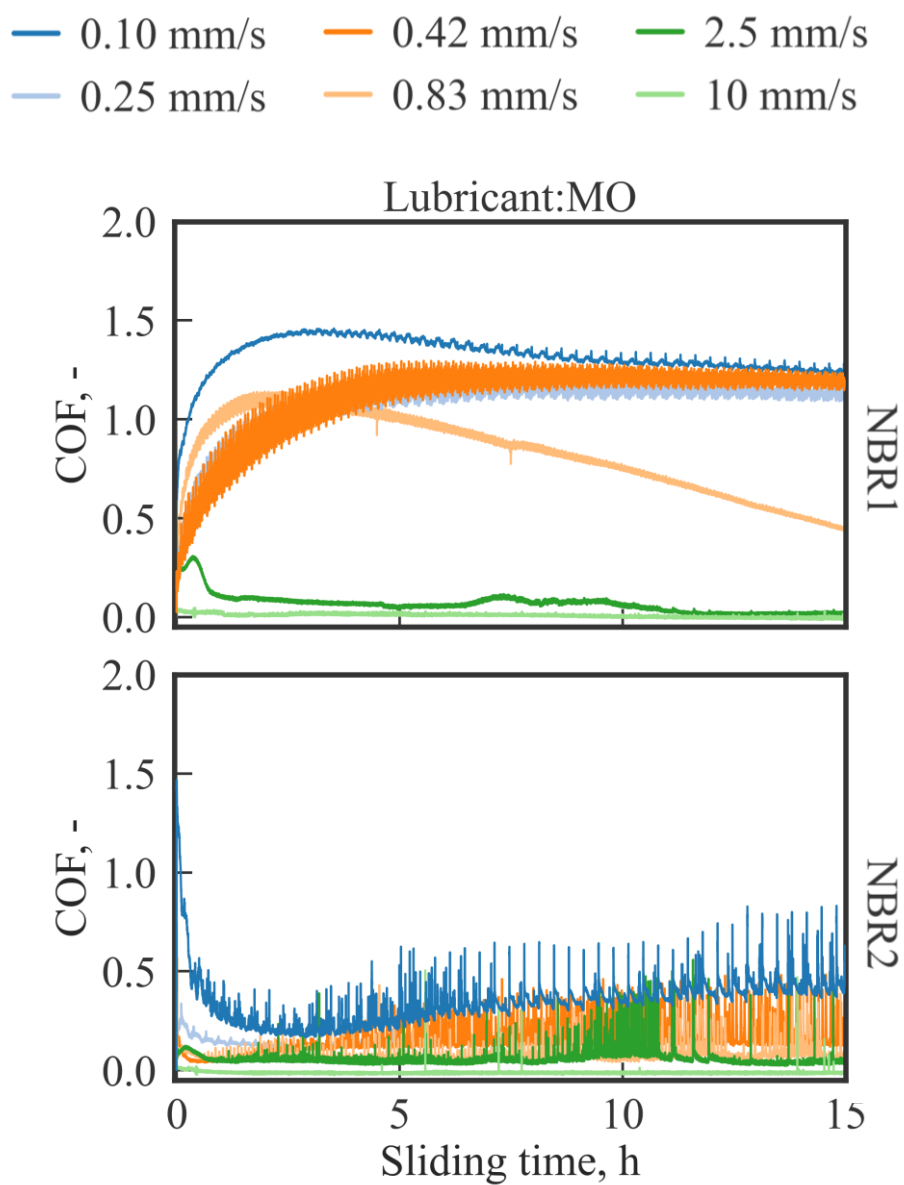


Fig. 3-3 COF of NBR1 and NBR2 lubricated with MO in difference sliding speed. The horizontal axis corresponds to the sliding time and the vertical axis corresponds to COF.

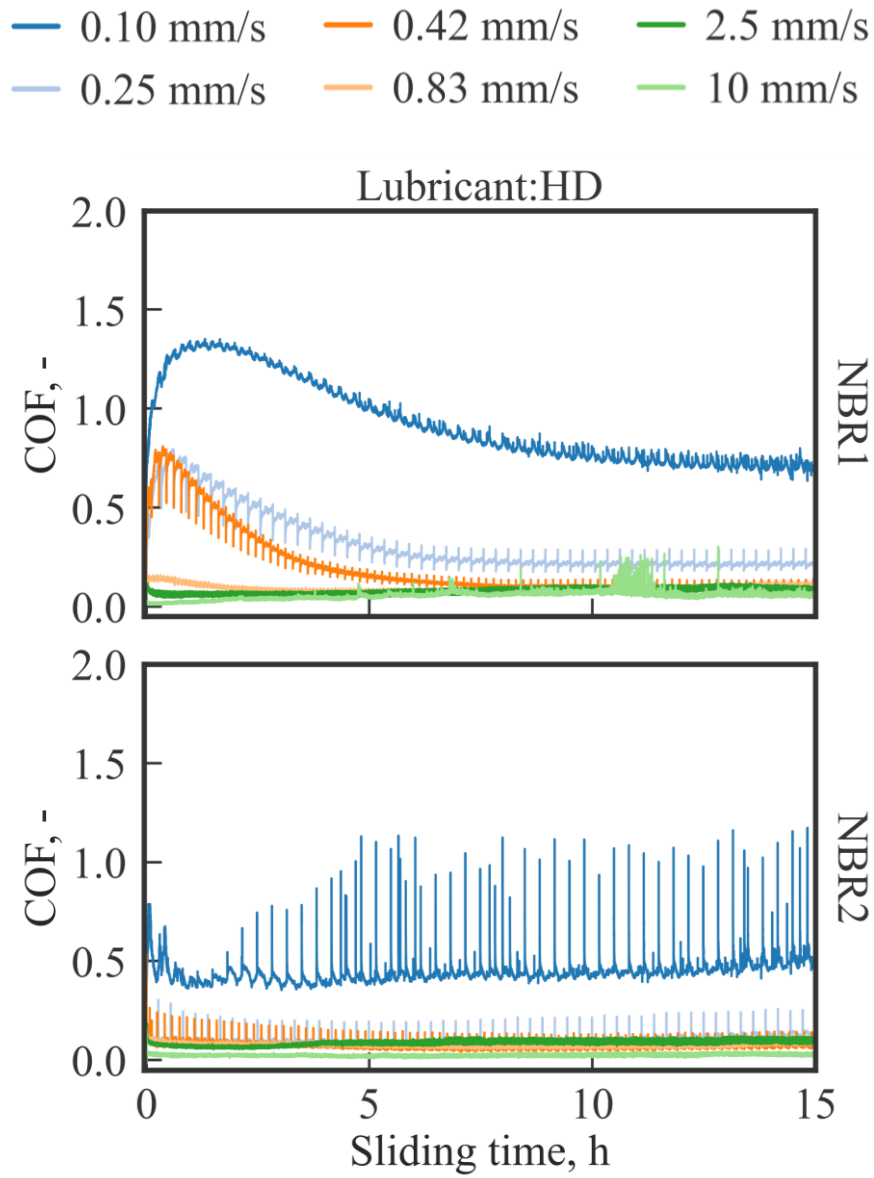


Fig. 3-4 COF of NBR1 and NBR2 lubricated with HD in difference sliding speed. The horizontal axis corresponds to the sliding time and the vertical axis corresponds to COF.

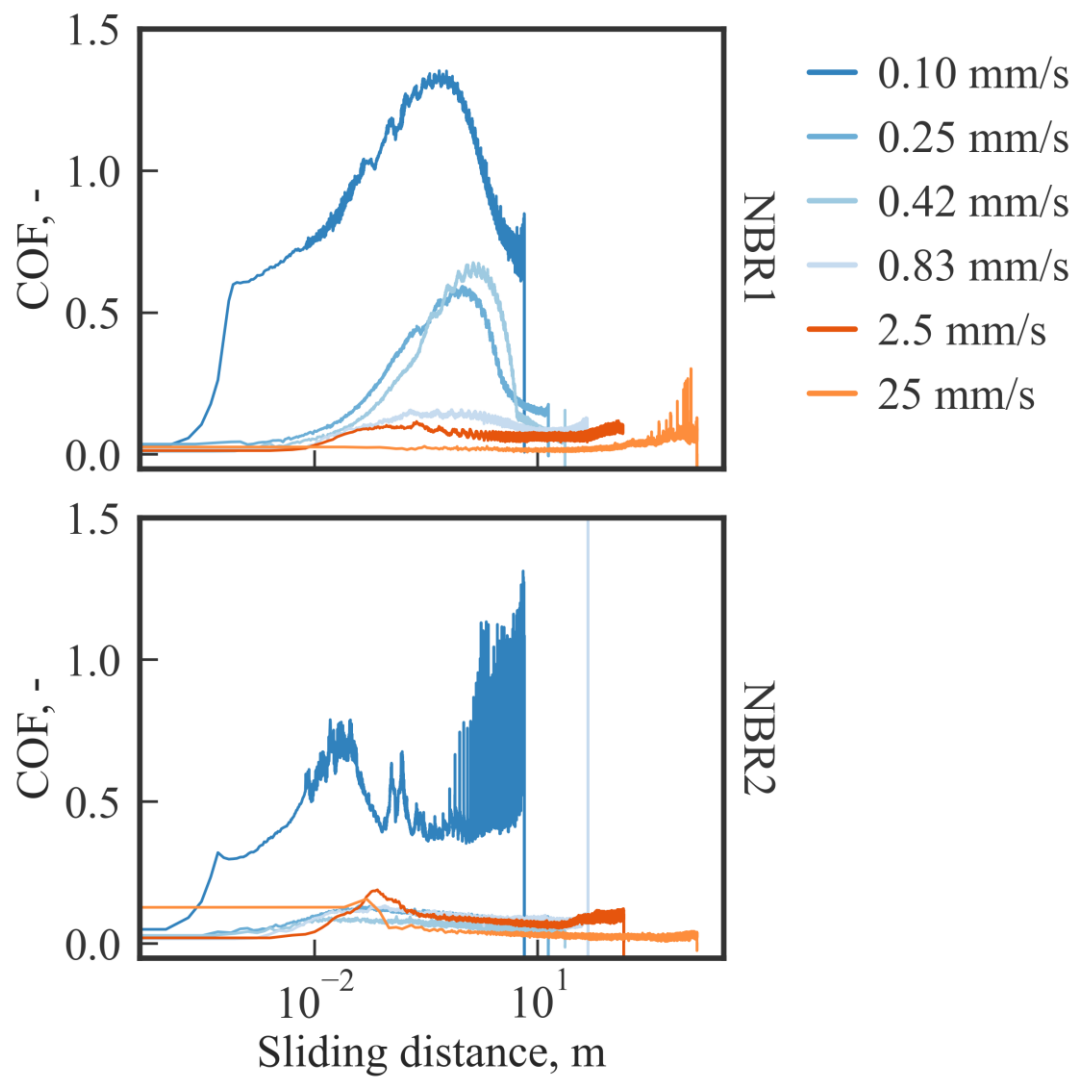
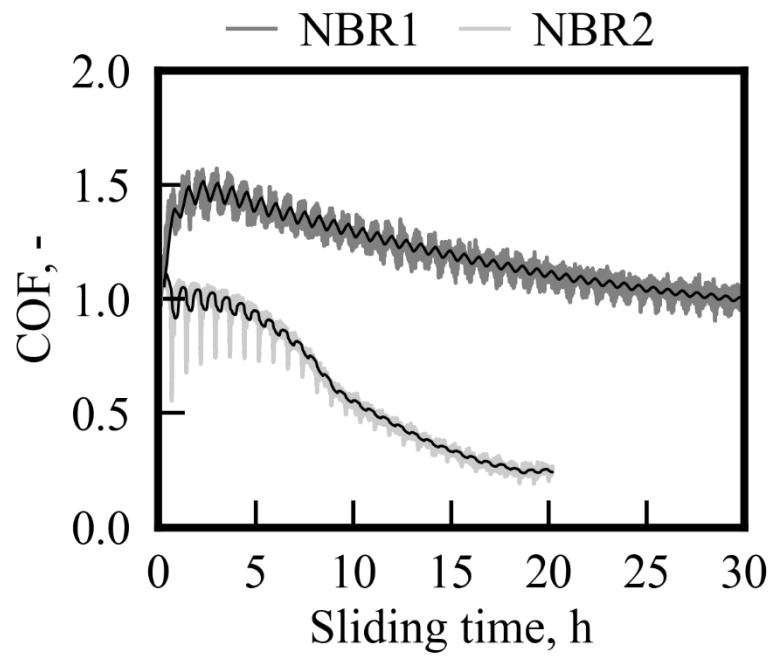


Fig. 3-5 Speed dependency of COF of NBR1/HD and NBR2/HD, the horizontal axis corresponds to the sliding distance.

(a) MO



(b) HD

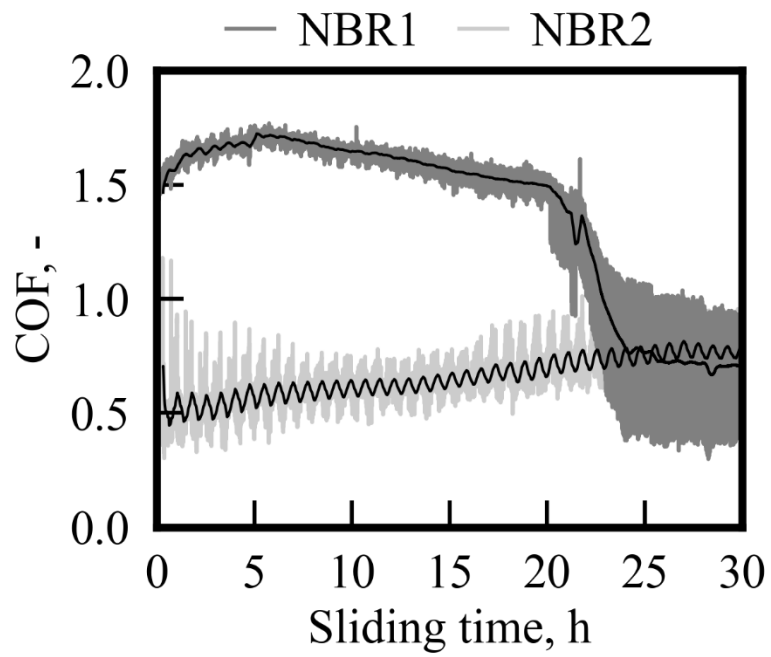


Fig. 3-6 COF of NBR1 and NBR2 lubricated with (a) MO and (b) HD measured under the observation of total reflection method.

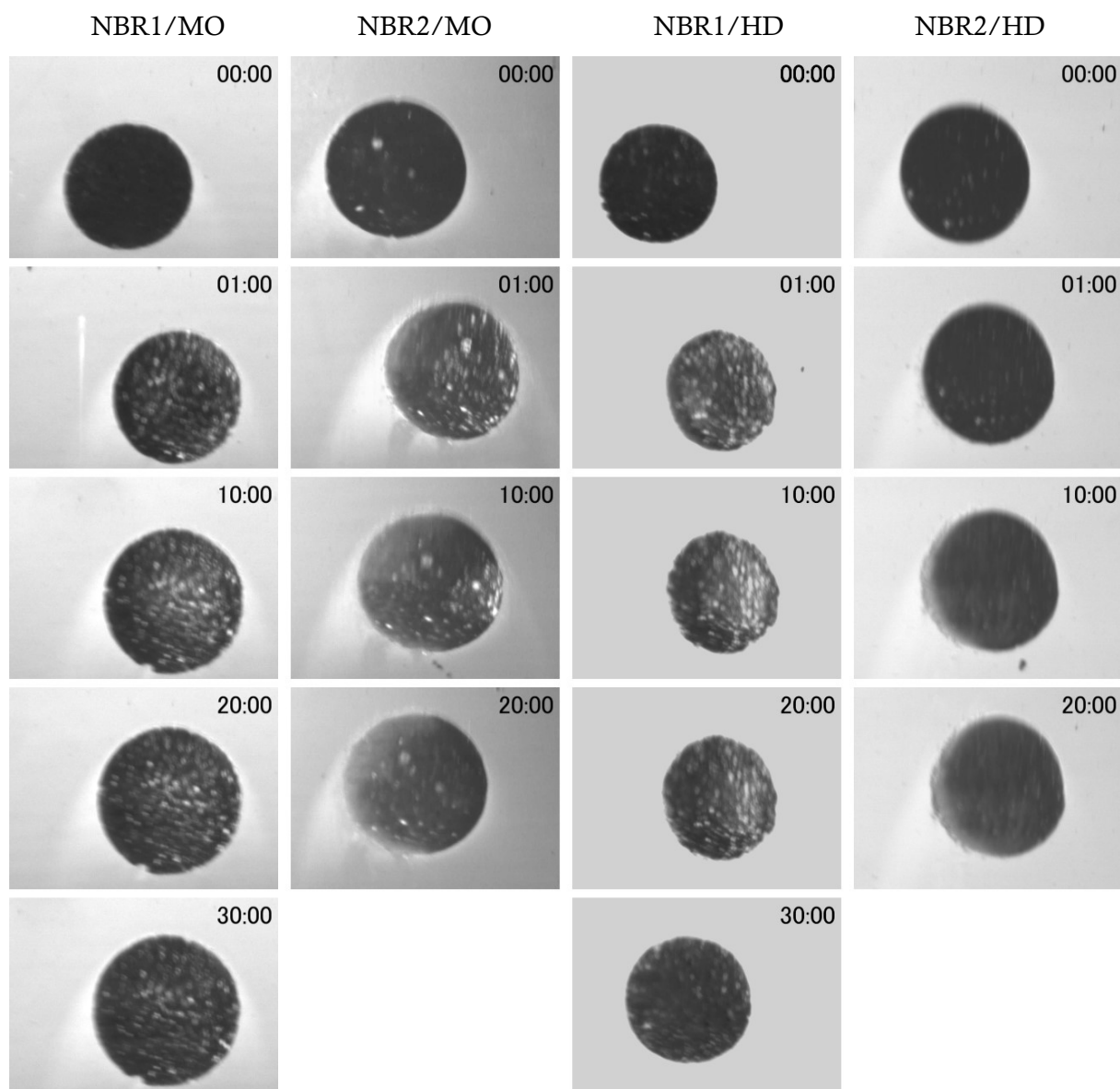


Fig. 3-7 Images obtained by the total reflection method. The numbers on upper left of images indicate the sliding time (hrs:min) and the arrows on lower right of images indicate the sliding direction of the disc.

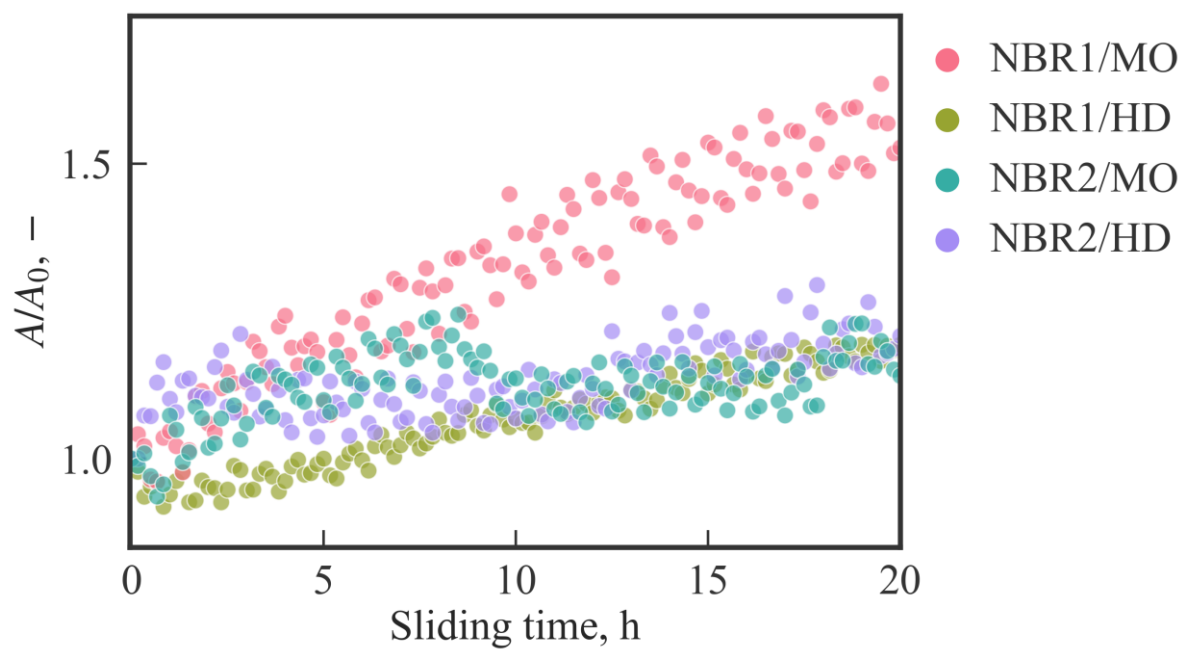


Fig. 3-8 Change of the real area of contact A . A_0 was the initial real area of contact without sliding.

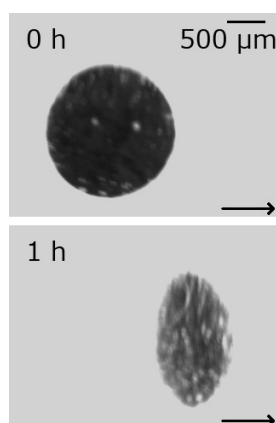


Fig. 3-9 Sliding surfaces of NBR1 without lubricant. The numbers on upper left of images indicate the sliding time and the arrows on lower right of images indicate the sliding direction of the disc.

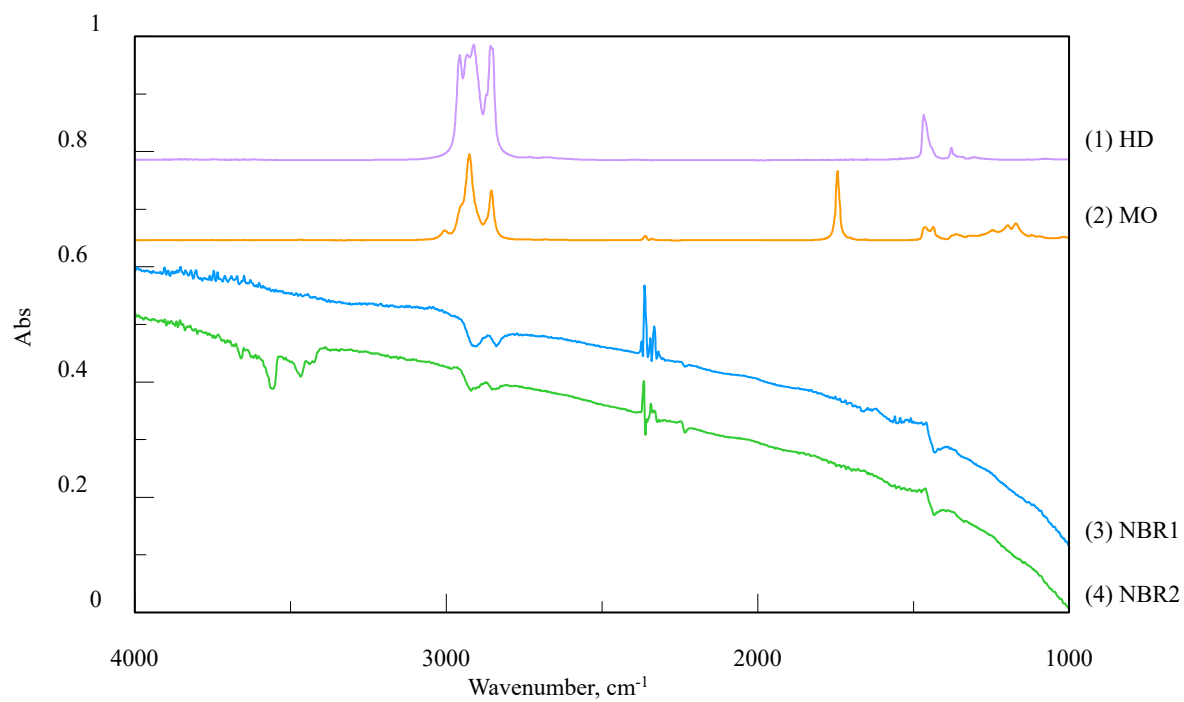


Fig. 3-10 FT-IR spectra of the lubricant and rubber.

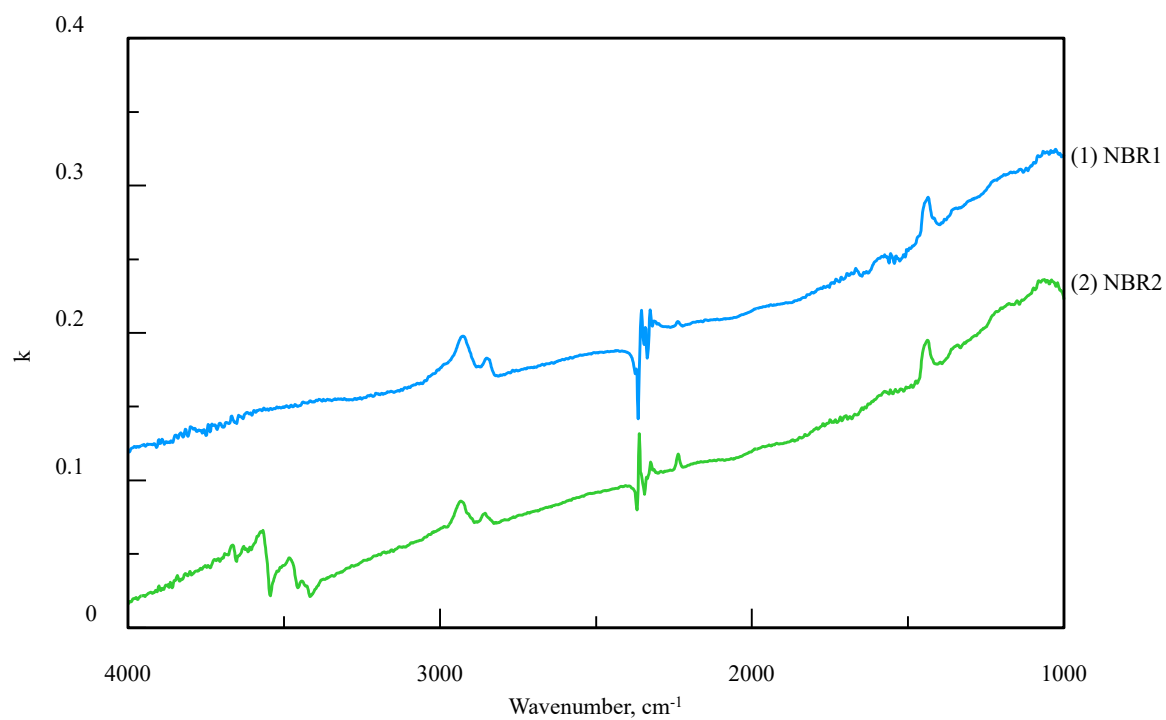


Fig. 3-11 Specular reflectance spectra of rubber obtained through Kramers-Krönig transformation.

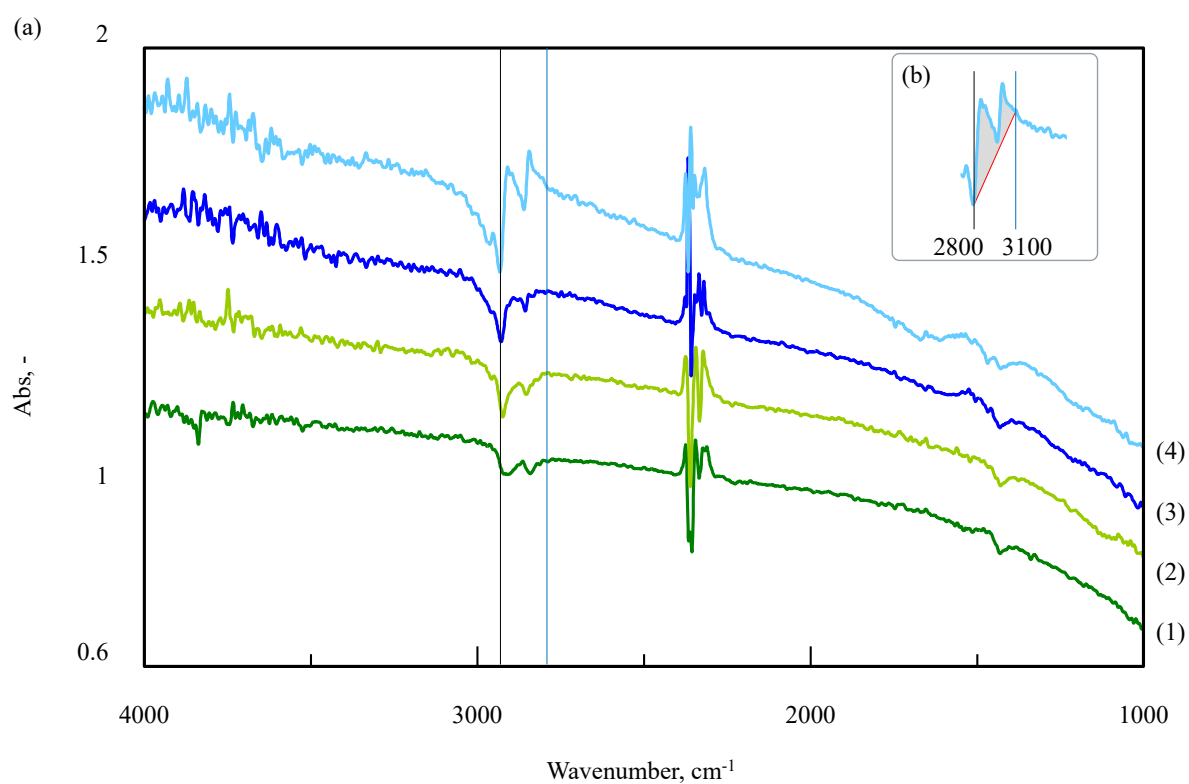


Fig. 3-12 Spectra of NBR1/HD during sliding at sliding time of (1) 0h, (2) 1h, (3) 10h and (4) 20h. (b) is an enlarged view of part of the graph around 3000 cm^{-1} , which corresponded to the structure of hydrocarbon.

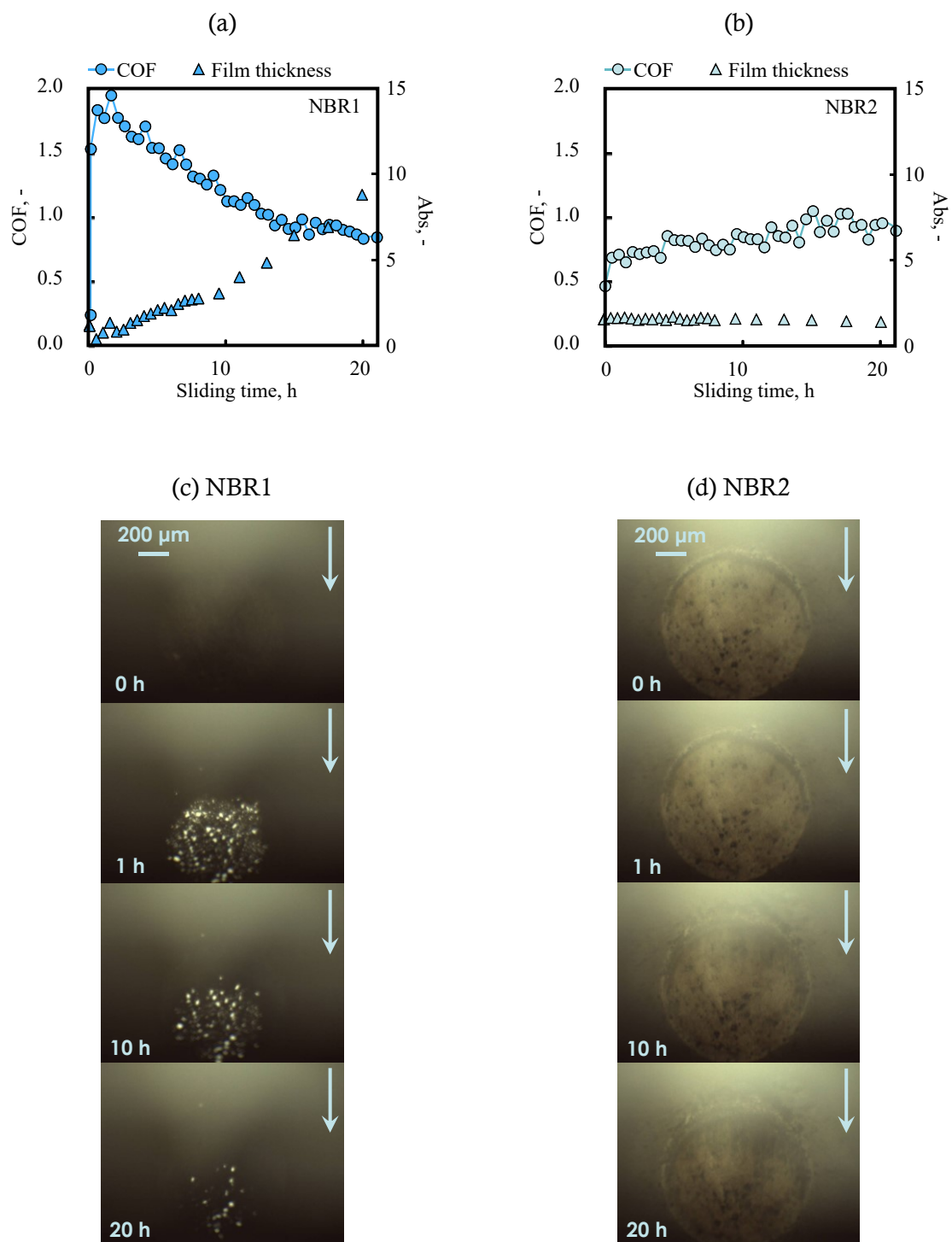


Fig. 3-13 COF and the peak area between 2800 and 3100 cm^{-1} in the FTIR spectra of (a) NBR1 and (b) NBR2. The sliding surfaces of (c) NBR1 and (d) NBR2. The arrows show sliding direction of the disc and values on the lower light of the images represent sliding time.

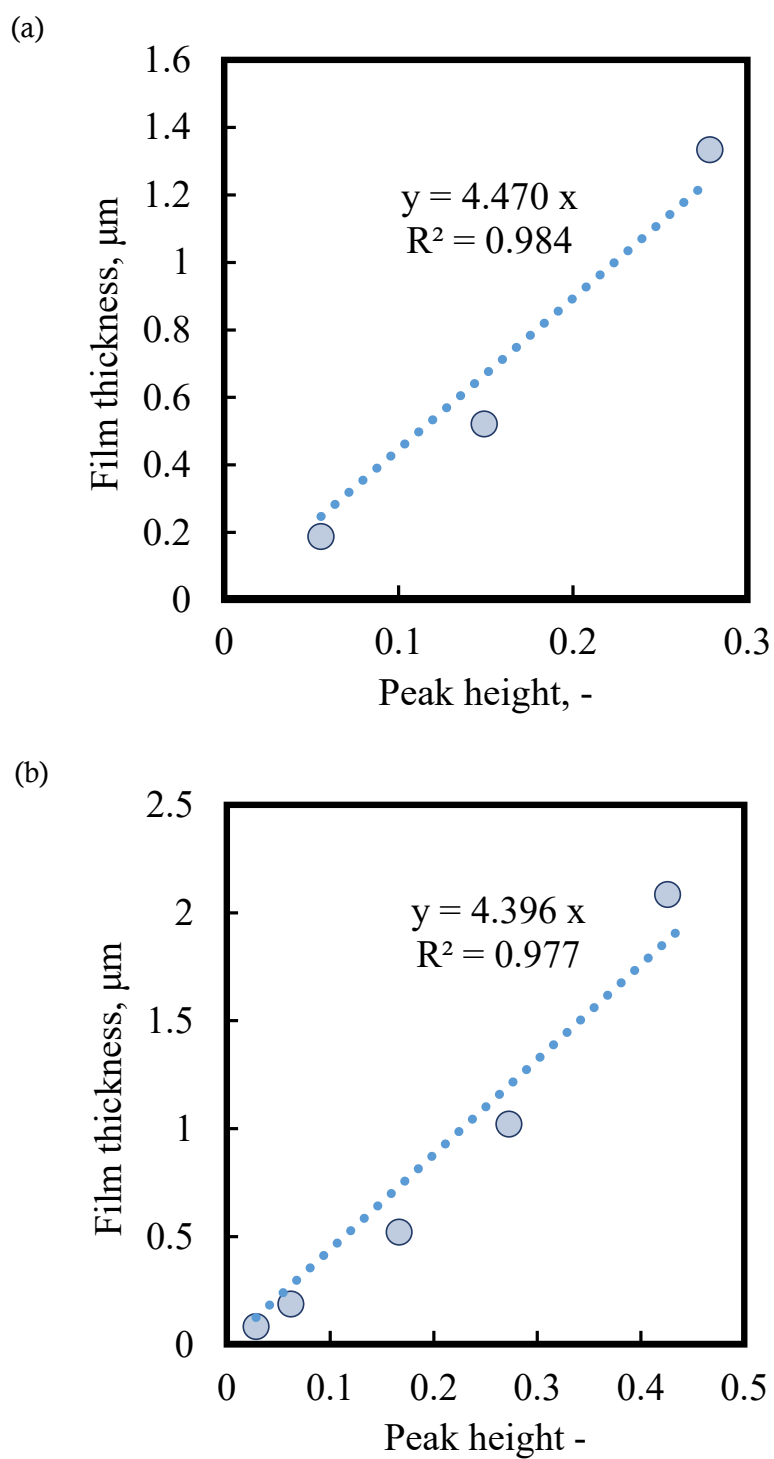


Fig. 3-14 The calibration curves of (a) NBR1/HD and (b) NBR2/HD calculated using peak height at 2915 cm^{-1} . The lines are linear trendlines, the equations are its linear equations and R is the residue.

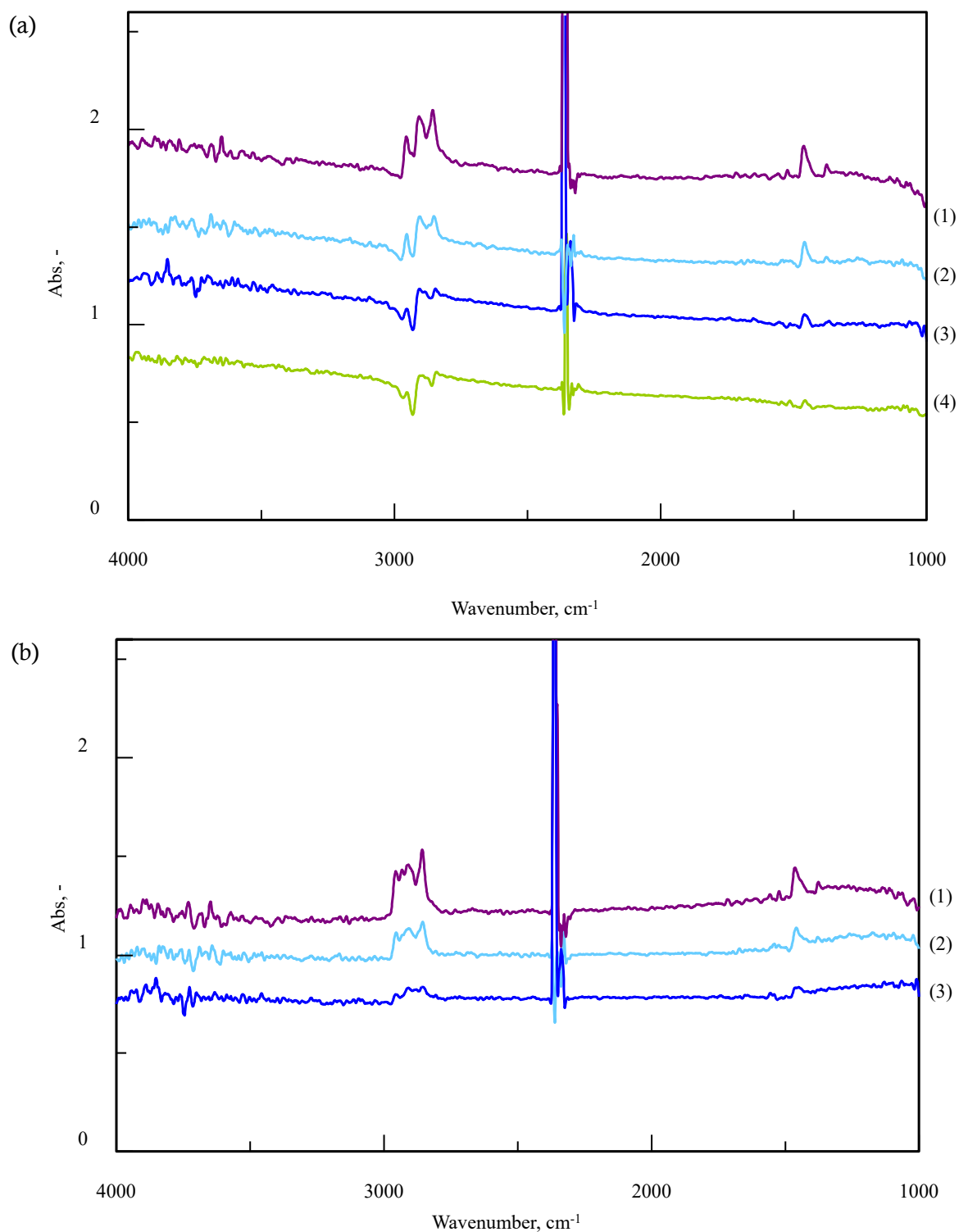


Fig. 3-15 The spectra of NBR1/HD for calibration curve of the gap between the disc and sample was (1) 10, (2) 2.7, (3) 2.3 and (4) 0 μm without sliding. (a) The original spectra and (b) the differential spectra which were obtained by subtracting the background spectrum from each original spectrum. The background spectrum was the spectrum with 0 μm gap without sliding ((a)-(6)).

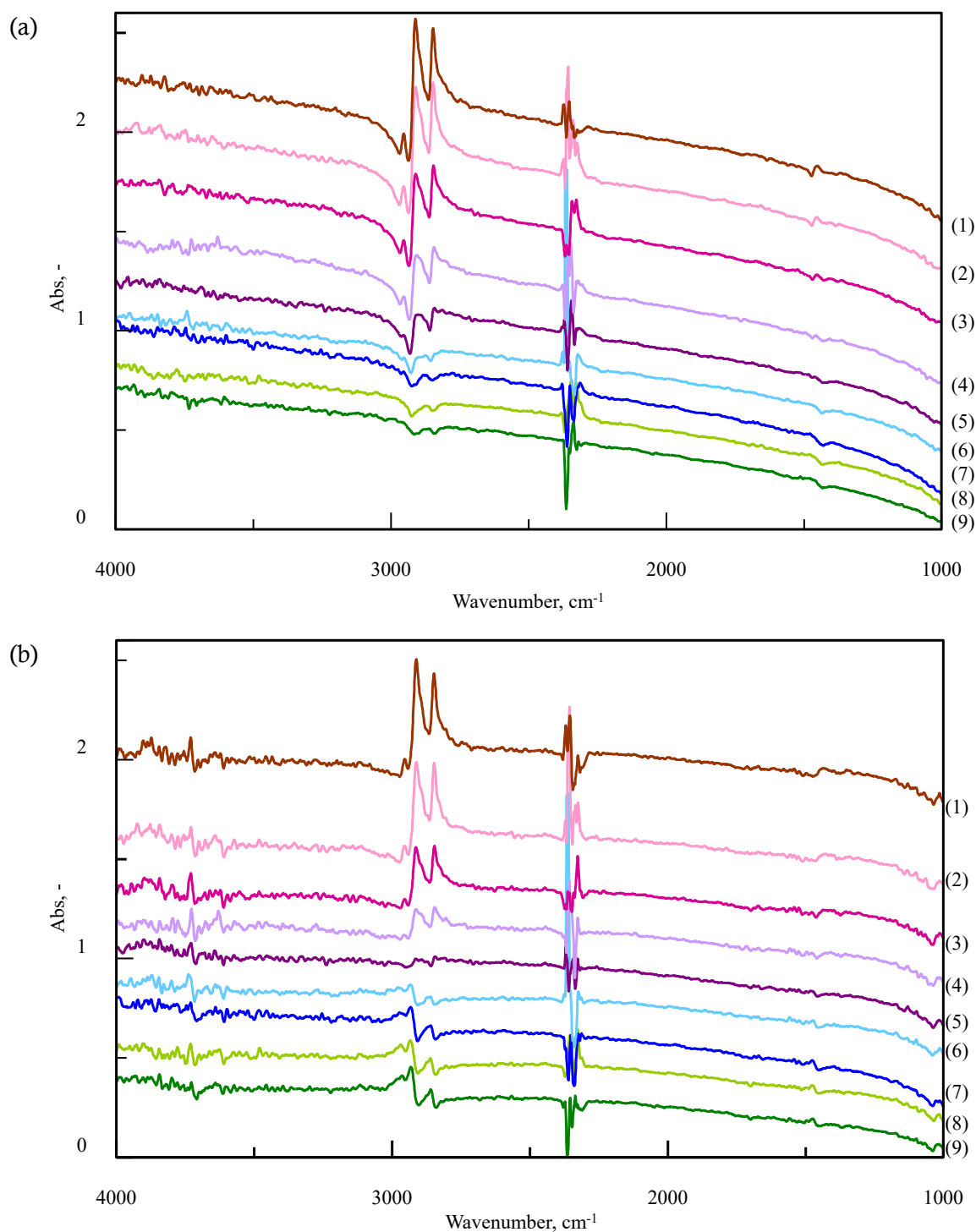


Fig. 3-16 The spectra of NBR1/HD detected during sliding at sliding speed of (1) 620, (2) 520, (3) 260, (4) 130, (5) 52, (6) 5.2, (7) 0.52, (8) 0.05 and (9) 0 mm/s, where the apercher size was 70 μm . (a) The original spectra and (b) the differential spectra which were obtained by subtracting the background spectrum from each original spectrum. The background spectrum was the spectrum with 0 μm gap without sliding (Fig. 3-15 (a)-(4)).

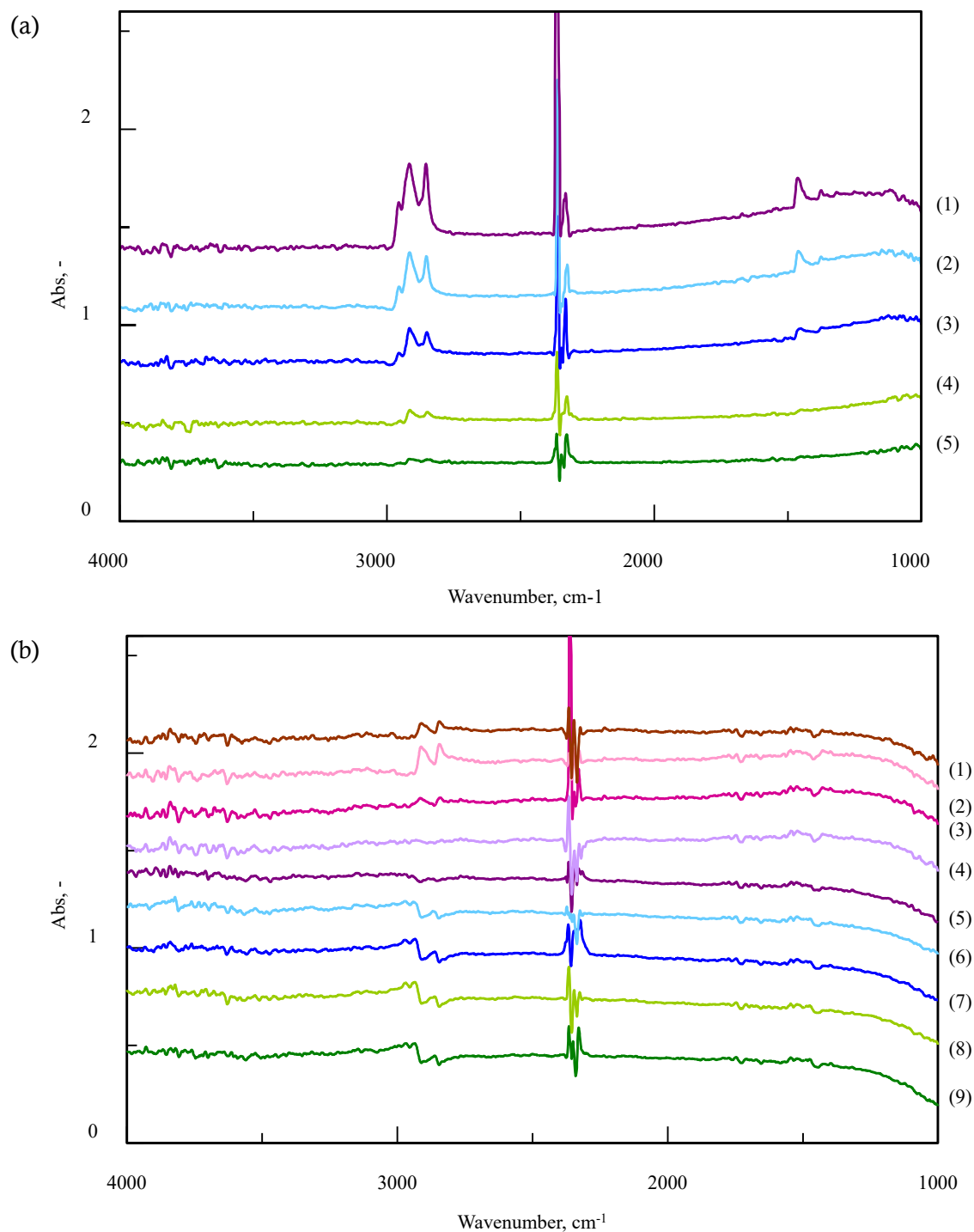


Fig. 3-17 (a) The differential spectra of NBR2/HD for calibration curve, which were obtained by subtracting the background spectrum from each original spectrum. The gap between the disc and sample was (1) 34, (2) 18, (3) 10, (4) 2.7, and (5) 2.3 μm . (b) The differential spectra of NBR2/HD detected during sliding at sliding speed of (1) 620, (2) 520, (3) 260, (4) 130, (5) 52, (6) 5.2, (7) 0.52, (8) 0.05 and (9) 0 mm/s, where the apercher size was 70 μm . The background spectrum was the spectrum with 0 μm gap without sliding.

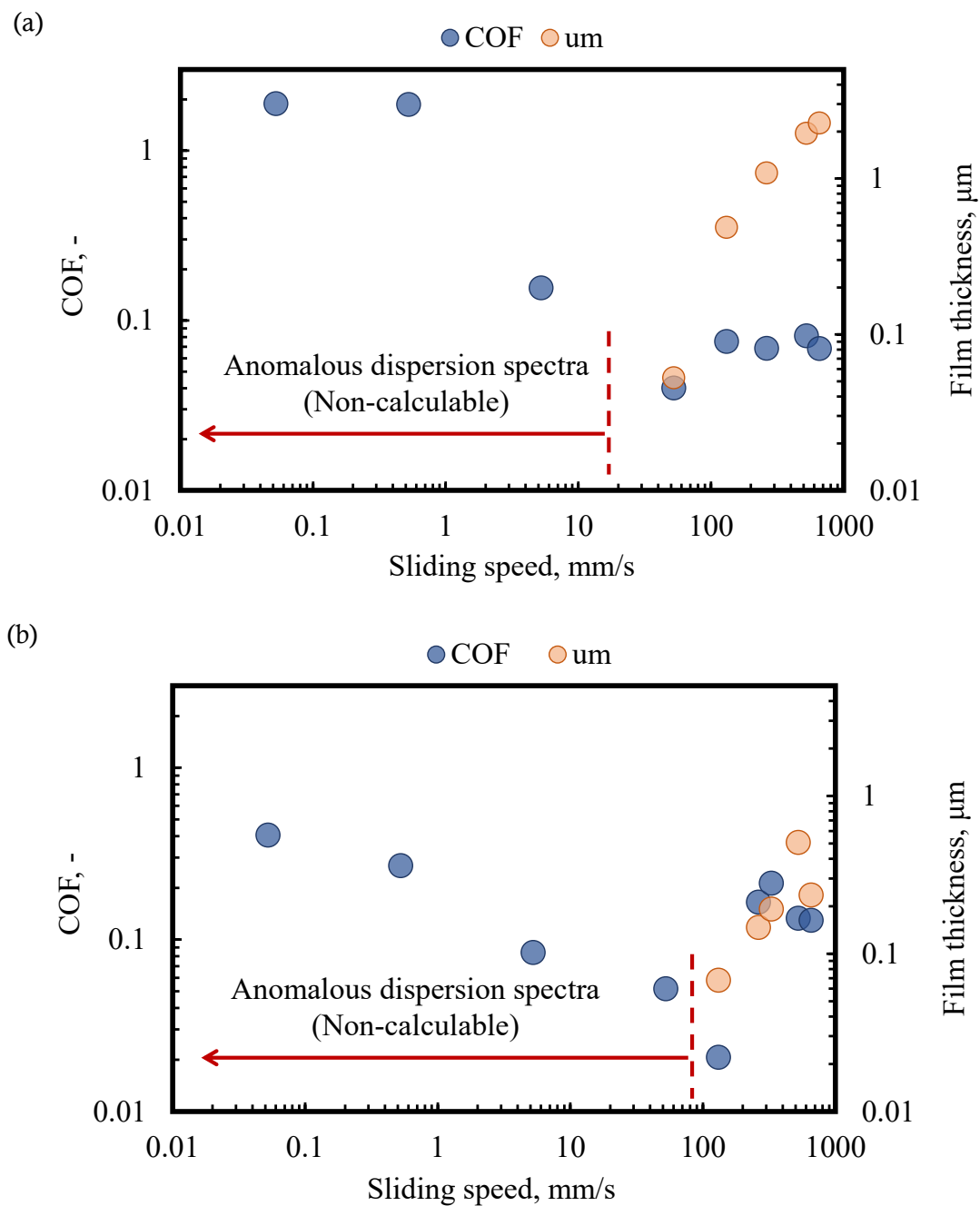


Fig. 3-18 Film thickness and COF of (a) NBR1/HD and (2) NBR2/HD

4 Discussion

4.1 Discussion

Under the fluid lubrication, the influencing factors were the sliding speed, the pressure, and the viscosity of the lubricant. Hence the friction force of each combination was similar because the viscosity of HD and MO was almost same.

However, COF varied among the combinations of rubber/lubricant at the boundary lubrication regime. The chemical structure of rubber and lubricant apparently influenced on the friction as seen above in Chapter 3. Hence, when the fluid film was not thick enough to avoid direct contact, other factors had to be considered.

The time dependency of NBR1/MO, NBR1/HD and NBR2/MO could be described as follows:

At early period of sliding:

- A) White (bright) spots were observed on the sliding surfaces
- B) COF increased

After long time of sliding:

- A) White (bright) spots disappeared, and gray area increased in the sliding surfaces
- B) COF decreased
- C) Real area of contact increased

The gray area should correspond to a lubrication film. From the results of the changes in COF, the friction force generated at the contact surface observed gray was smaller than that generated at the contact surface observed black. The gray contact surface meant that there was the gap of about nm thick, which should be a boundary lubricant film. In the friction test described in the previous chapter, the coefficient of friction increased in the initial stage and turned to decrease. It is also considered that the direct contact area was formed on the sliding surface first, and then the lubricant film was formed. The schematic diagram of this hypothesis is shown in Fig. 4-1.

In these experiments, the sliding surface of the rubber test piece was immersed in the lubricant during sliding. Therefore, it was considered that the rubber gradually swelled by the lubricant. The swelling is a phenomenon in which liquid the rubber according to the degree of compatibility with the rubber.

4.1.1 Cavity on sliding surfaces and increasing of COF at early stages of sliding

At first, what were the white (bright) spots which appeared on the sliding surfaces was discussed, which are shown in Fig. 3-7. The white spots meant there was a gap between rubber and disc as forementioned in Section 2.3. There were two possibilities for the composition of the gap. One is that the gap was filled with the lubricant, and the other was that it was cavity.

The bright spots were also observed by in-situ FT-IR microscopy in Fig. 3-13. This indicated that the gap was cavity consisted of air or vacuum. This was estimated by the Fresnel equation. From the Fresnel equation in the case of the normal incidence, the following relation is derived between refractive index and reflectivity:

$$R = \left| \frac{n_1 - n_2}{n_1 + n_2} \right|^2$$

where R is the reflectance and the n_1, n_2 are the reflective index of the media. From this equation it is derived that $R \approx 0$ when $n_1 \approx n_2$. In this case, the outside of the contact area observed darkly because the HD and the disc has the similar reflective index. To be observed brightly, the gap between n_1 and n_2 have to be large. Hence, it was estimated that there was a large gap between the reflective index of the glass and the component of the bright spots. The possibility of remaining was that bright spots consisted of the air and a vacuum.

From the discussion above, the white pattern was the cavity consisted of air or vacuum and the following hypothesis could be put forward. The amount of lubricant in the inlet region was limited so that the contact could suffer from the effects of lubricant starvation[57]. At the beginning of the sliding, the lubricant did not flow into the interface since the hydrodynamic lubrication action was insufficient. Simultaneously, the lubricant which remained in the interface was adsorbed on the disk and carried away from the interface and was also absorbed into the rubber. Therefore, the lubricant was gradually lost from the interface. The lack of lubricants caused the increasing of COF and generated low-pressure cavities which were observed as bright spots in microscopic images.

After certain period of sliding, COF of NBR1/MO, NBR1/HD NBR1/HD, and NBR2/MO decreased. At this time, the white pattern gradually became indistinct, and from the left end of the sliding surface (lubricant introduction side), a gray contact surface was formed gradually. The increase of the gray contact surface and the decrease of COF occurred simultaneously.

4.1.2 Spiky peaks in COF curves

Some of COF curve had spiky peaks. In the case of MO, the cycle of spiky peaks coincided with the rotation cycle of the disk. The large roughness peaks on the disk could break the oil film, and the friction coefficient increased by direct contact between the rubber and the disk.

In the case of NBR2/HD, there was a fluctuation of COF periodically, where its period was different from the rotation cycle. The observation by the total reflection method revealed that the sliding surface was vibrating parallel to the sliding direction. Therefore, a stick-slip-like vibration occurred at the test of NBR2/HD. This stick-slip was also observed by FT-IR microscopy with NBR2/HD. The details of the spiky peaks in COF curve will be discussed in Section 4.3.2.

4.1.3 The observation results of optical interferometry at early period of sliding and discussion

To confirm the decrease of the lubricant at the sliding surfaces, the observation results of optical interferometry was conducted. The images of the sliding surface of NBR1 lubricated with HD are shown in Fig. 4-2. The Cr-Si coating of the disc was used for the obtaining high contrast images of the lubricant film which had within 100 nm thick. The details of this method are mentioned in Section 2.3. The images were obtained at 50-minute intervals. The images on (a) are the original images and (b)-(c) are images obtained by digital processing. The original images were transformed to the HSV model and the obtained HSV images were combined to three components. Each component was drawn in each image.

In the original images (a), the yellow interference light was observed but the rest of that was obscure. In addition, with the sliding, the yellow area was observed at the beginning also gradually became obscure.

The change was more apparent in the Fig. 4-2(b) and (c) than the original images (a). Namely, the yellow had Hue value of about 30. It appeared on the sliding surface as soon as the sliding started. The area decreased during sliding and then disappeared after about 6 hours. The images of Newton's rings observed in the condition of the glass lens contacted to the glass disc in HD (2) and in the air (3) are shown in Fig. 4-3. The meaning of the (a), (b), (c) and (d) is as same as Fig. 4-2. The gap between the glass disk and the lens was calculated from the form of the lens at each part of the Newton's rings. The clearance at yellow area was calculated as 50 nm thick. Besides, the yellow area had larger saturation value compared with the surrounded area. The saturation value of Fig. 4-3-3 was larger than that of Fig. 4-3-2. That implies that the clearance between the glass disc and the glass lens was not filled with HD but the air like Fig. 4-3-3 or a vacuum.

The mechanism could be as follows. Before sliding test started, HD existed in the valley of the asperities on the rubber surface. However, it was absorbed into the rubber due to the swellability. As a results, the valleys of the asperities became vacuum. The dissolved air came out from the lubricant or rubber because of the gap in the pressure.

Why does the low-pressure air layer or vacuum layer show high friction? It can be modeled as a number of micro - or nano-sized suction cups lined up at the contact surface. This is called a micro suction cup array, and the smaller the size, the larger the force acting in the shear direction[58].

4.1.4 Change in real area of contact

In Fig. 3-8, it was shown that real area of contact increased during sliding. This implied that the shear force decreased during sliding. There were two possible causes of the increase of the real area of contact. One was swelling of rubber, and the other was stress relaxation. There was no significant difference in stress relaxation properties between the two materials. Therefore, it is considered that the change in the real area of the contact was largely affected by the swelling of rubber.

4.1.5 Change in sliding surfaces and its hypothetical mechanism

Besides, the swelling of rubber would influence on the changes in COF. From the observation images of the sliding surfaces in Fig. 4-1, not only the change of the real area of the contact but also the gradual change of the condition of the sliding surface during long sliding were found, as mentioned in Section 3.2.1. The cavities on the sliding surfaces disappeared, and from the left end of the sliding surface (the side of the lubricant introduction) the sliding surfaces became being observed gray gradually during sliding. The increase of the gray contact surface and the decrease of COF occurred simultaneously.

According to the images of the sliding surfaces, the gray contact area could be characterized as lubrication film. The gray contact surface meant that there was a gap of about nm thick. As the sliding time increased, a nm-thick lubricant film was formed between the disc and the rubber, and COF decreased.

A hypothesis on boundary lubrication of rubber for the swollen systems was proposed as following. The schematic images are shown in Fig. 4-1. At the start of sliding, the lubricant was absorbed in the rubber, and the lubricant on the sliding surface was lost. This was inferred from the existence of low-pressure gas cavities formed in the sliding surfaces and the fact that COF increased to the same level as that in dry sliding.

As the sliding time increased, the sliding surface was swollen by the lubricant. Therefore, the real area of contact increased. Furthermore, the lubricant became present on the sliding surfaces and worked as a lubricant film, reducing COF. The lubricant film was formed by the lubricant provided from swollen rubber.

The rest of the Section 4.1, the theory of swelling and interaction which related to the lubrication and COF is going to be discussed. After that, the evidence of this hypothesis is going to be shown in Section 4.2 and frictional behavior of the swelling rubber is going to be described in Section 4.3.

4.1.6 Theory of rubber swelling

The theory of rubber swelling was summarized here. The first step of rubber swelling was understood as the mixing of polymer and liquid. Flory and Huggins simplified it and modeled it using a dimensional lattice[59][60]. The free energy change due to mixing was expressed as follows:

$$f(\phi, T) = \frac{k_B T}{v} \left[\frac{1}{N} \phi \ln(\phi) + (1 - \phi) \ln(1 - \phi) + \chi(T) \phi(1 - \phi) \right] \quad (4-1)$$

where k_B is the Boltzmann constant, T is the temperature, v is the volume, N is the number of polymer chain and ϕ is the volume fraction of the solvent. The first and second terms of the equation represented the entropy term, and the third term represented the enthalpy. χ parameter represented interaction between the polymer and the solvent.

This equation led that the entropy increased, and the energy stabilized by the interaction between the polymer and the solvent to determine the solubility. As the interaction between polymer and solvent was stronger, the solubility of the polymer and the solvent became high.[61].

In terms of rubber and lubricant in the sliding, this was described as follows. The lubricant penetrated into rubber due to increasing entropy and stabilized energy. The higher the interaction between the rubber and the lubricant was, the more the lubricant was absorbed into rubber. Besides, the rubber network expanded due to absorbing lubricant and stored energy due to rubber elasticity. Where the expansion due to the dissolving force and the contraction due to rubber elasticity are balanced, the swelling of rubber reached an equilibrium state[61]. The interaction between the rubber and the lubricant was important for the stabilized energy. In Section 4.1.7, details of the interaction were described.

4.1.7 Interaction between rubber and lubricant

4.1.7.1 Kinds of intermolecular interactions

As mentioned in the previous section, the interaction between rubber and lubricant affected on the penetration of lubricant into rubber. There were some kinds of interaction force which acted between molecules. The type of the interaction were followings:

- A) Electrostatic interaction
 - i. Coulomb interaction (ion-ion)
 - ii. Dipolar interaction (ion-dipole, dipole-dipole)
- B) Van der Waals interaction
- C) Hydrogen bond
- D) Hydrophobic interaction

Between rubber and lubricant, dipolar interactions and van der Waals interaction act. A polar molecule attracts a polar molecule, and a nonpolar molecule attracts a nonpolar molecule. The dipole interaction is the electrostatic interaction between polar molecules. Nonpolar molecules interact with each other by van der Waals forces.

These interaction forces were the origin of driving force of swelling. The difference in polarity of the rubber and lubricant leads the difference the compatibility and swellability between rubber materials and lubricants. The swellability and polarity were investigated by following experiments and simulations in this section.

4.1.7.2 Estimations of the polarity

Here, in order to understand the concept of what the word "polarity" refers to, the several simulation and experiment were carried out. In the case of molecular simulation such as DFT calculation, it is possible to model the small molecule instead of the polymer structure.

The chosen model molecules were methane for n-hexadecane, acetonitrile for ACN in NBR, and methyl acetate for MO. Firstly, the electronic state calculation was conducted with the structural optimization such as chemical bond lengths and bond angles were calculate. Finally, the deviation of the charge was discussed. The simulation was conducted using Gaussian09 with ω B97X-D for the parameter[62], cc-pVTZ for the basis function, and NPA (natural population analysis) for the electron density.

The results are shown in Fig. 4-4. The electron density of methane showed that the single C-H bond was polar because the carbon 1 was negative. However, methane was not polar because of its symmetry. On the other hand, ACN in acetonitrile was polar because nitrogen 6 in ACN was negative, and the ester group was also polar because carbon 5 bonded with oxygen was positive and oxygen 6 and oxygen 7 was negative. Namely, the electronegativity difference between atoms in a bond and the asymmetry of the molecules made the bond polar. Therefore, nitrile and ester were more polar than alkane.

The potential energy is also possible to be calculated with this simulation for evaluating interaction among molecules. The potential energy calculated with the molecules of methane and acetonitrile is shown in Fig. 4-5. The lowest energy of methane/nitrile pair is lower than that of methane/methane pair. Namely, methane/nitrile pair needs more energy to separate two molecules than methane/methane pair.

The polarity was evaluated with vaporized rate of lubricant by TGA (thermal degradation analysis) instead of the boiling point. For the aim of comparing the polarity and the forces of attraction in between lubricant and rubber, desorption of lubricant from the rubber was measured. The results are shown in Fig. 4-6. (b) lead that both MO and HD had evaporated at 80 °C, as indicated by the negative DTA value. The larger absolute value of the DTA for MO indicated that more heat was required to vaporize MO. (c) indicated that the volatile speed of HD was faster than that of MO. From these facts, the attraction forces between molecules were larger for MO than those for HD. In other words, polar molecules have a stronger cohesive force than non-polar molecules.

Another method to estimate the interaction between molecules was the solubility parameter. The solubility parameter was used as a semi-empirical parameter to predict the solubility of the interactions. The solubility parameters indicated the strength of the intermolecular forces. This basic theory was proposed by Hildebrand in 1919. After his study, the several types of solubility parameters had been proposed. The widely accepted one was the Hansen solubility parameter (HSP), which is mainly known as a three-dimensional solubility parameter. In HSP, intermolecular interaction was divided into three parts: dispersion, polarity, and hydrogen bonding. They were able to be calculated from experimental data such as the heat of vaporization and vapor pressure [63]. It has been widely operated in academic and industrial use, for example in order to find the solvent of a polymer or to predict the absorption of molecular on the polymer surface or compatibility of rubber and lubricant. It was recently reported that HSP was able to be obtained by Molecular Dynamic simulations [64][65].

The calculation of HSP was done by commercially available software, which is called as HSPiP 4th Edition. The parameters are shown in Fig. 4-7. The HSP of the polymer was calculated by following equation with the parameters of monomer:

$$\delta_{(D \text{ or } P \text{ or } H)mixture} = \delta_{(D1 \text{ or } P1 \text{ or } H1)} \Phi_1 + \delta_{(D2 \text{ or } P2 \text{ or } H2)} \Phi_2 + \dots \quad (4-2)$$

where Φ is a ratio of each ingredient[66]. From the calculated parameter, the polarity of NBR2 was higher than that of NBR1 and the polarity of MO was higher than that of NBR2.

Besides Eq. (4.2) also shows that the solubility parameter is consist of three components. It means that not only the polarity but also the others component influenced on the solubility.

4.1.7.3 Measurement of the swelling ratio

The swelling test of rubber was carried out as an index of the magnitude of interaction. Each rubber test piece was immersed in the lubricant until swelling was saturated. The volume of each test piece was measured, and the swelling ratio was calculated in the comparison of those in the initial state. The procedure in detail was described in Section 2.1

The results of the swelling tests are shown in Fig. 4-8. The vertical axis represents the swelling ratio, and the horizontal axis represents the swelling time, namely immersing time. Initially, NBR1 was swollen in the 24 hours, and after that, the swelling speed decreased. NBR1 became saturated at the swelling time of about 48 hours. The swelling ratio of NBR2/MO increased slower than that of NBR1. However, after 96h of swelling, NBR2/MO also saturated. NBR2/HD was not swollen at all.

As mentioned in the previous section, the polarity of NBR2 was higher than that of NBR1 and the polarity of MO was higher than that of HD. NBR1 and NBR2 was swollen larger than HD because the polarity of MO was more similar to the NBR 1 and NBR2. High polar rubber NBR2 did not swollen at all by non-polar lubricant.

4.1.8 Cause of the decrease in COF

As above, the rubber was swollen by lubricant due to interaction between the rubber and lubricant and the interaction strongly related to the polarity of the molecules of the rubber and the lubricant. In the light of that the change in the sliding surfaces differed depending on the combinations of rubber/lubricant, the chemical structure of the rubber, that of the lubricant, or/and their interaction affected on the generation of the lubricant film. The polarity of the rubber, in other words the amount of ACN group in NBR rubber and the presence or absence of polar

groups in lubricant had a great influence on generating of the lubricant film. It was mainly driven by the interaction between rubber molecules and lubricant molecules.

4.1.9 Summary of change in COF and sliding surfaces

The discussion up to this point is summarized as below. It was clarified that the polarity of rubber and lubricant influenced on the boundary lubrication of rubber in the following two points.

- A) Increase in COF at initial stage of sliding: Lose of lubricant from contact interface.
- B) Decrease of COF during sliding: Filling of lubricant into contact interface

Further evidence of A) is provided in the next section with the observation results of optical interferometry. Understanding of A) is useful for practical use of the oil seals. It is because there is a possibility that the low sliding speed or the high load generate poor lubricated part in the sliding surface and caused extremely high torque. Then, we enter to the main part of this thesis related to B), why COF changed and how the polarity of the rubber and the lubricant effect on the change. this will be discussed in the following sections.

4.2 Quantitative evaluation of lubricants using in-situ FT-IR

4.2.1 Changing spectrum through sliding and baseline distortion

In Fig. 3-13, the peaks of the C-H bond around 3000 cm^{-1} increased, and it corresponded to the increase of lubricant at sliding surfaces. Namely, the change of lubrication in the sliding surface could be examined qualitatively the in-situ of FT-IR measurement. Furthermore, FTIR can correlate to the amount of lubricant in it. This information is enormously useful to interpret the mechanism of boundary lubrication.

However, the baseline distortion made a quantitative evaluation difficult. By clarifying the cause of the distortion and evaluating the spectrum, it was possible to grasp the change in the sliding surface in more detail.

In the next section, before starting the discussion of boundary lubrication, how the spectrum changes with increasing of the sliding speed, in other words, changing of the lubrication condition. Then, the obtained knowledge was applied to understand the mechanism of boundary lubrication.

In this section, the quantitative analysis was done. Since the characteristic peaks were not appeared in the spectra, it could be concluded that the chemical change did not take place during

sliding, but the main dominant factor of change can be the physical interaction of the rubber and the lubricant.

4.2.2 Interpretation of FT-IR spectra obtained on the film thickness

In Fig. 3-17 (a)-(4), negative peaks appeared at 0 μm gap (4). This was because the anomalous dispersion of the refractive index occurred since the light was specular reflection from the rubber.

As the gap was increased, positive peaks of HD appeared, while the baseline was still skewed. This was led by that the transmitted reflection light was stronger than specular reflection from the rubber. A gap between the rubber and the disc delivered the peak around 3000 cm^{-1} which was obtained as the overlap of the specular reflection light from the rubber and the transmitted reflection light from the lubricant.

As would be expected from these facts, the shape of spectra changed also due to sliding speed, in other words due to lubricating condition. It was described schematically in Fig. 4-9. At the condition which the lubrication was not enough to avoid direct contact between the rubber and the disc, only negative peaks of anomalous dispersion were detected. In this case, KK transformation was explained in Section 2.3 to the spectra enables to obtain k value spectra corresponding to the absorbance spectra. However, regarding under the fluid lubrication, KK transformation had not to be applied because it was not a simple anomalous dispersion spectrum. Infrared light irradiated on the sliding surface, absorbed by the lubricant. and then reflected on the rubber. With the reflection, it was absorbed by the rubber and showed the anomalous dispersion. The anomalous dispersion light was again absorbed by the lubricant and returned to the direction of detector. Hence the final detected light was the mixture of the transmitted reflection light of the lubricant and specular one of anomalous dispersion spectra of the transmitted reflection light of the lubricant reflected on the rubber.

It enables us to determine the lubrication regime by the shape of the FT-IR spectra. The concrete example is shown in Fig. 4-10. The spectrum of (1) was HD on the glass coated by gold so as to obtain better transmitted reflection light. (2) NBR1/HD with the no gap between the disc and the rubber at no sliding. (3) NBR1/HD during sliding at 520 mm/s and (4) NBR1/HD during sliding at 0.5 mm/s. The spectrum (3) was mixture of the transmitted reflection light originated by HD (1) and specular reflection light from rubber surface (2), whereas the spectrum from the rubber surface (4) has only negative peak due to anomalous dispersion. These results showed that the sliding condition of (3) was fluid lubrication and (4) was boundary or mixed lubrication. Thus, it is possible to determine the boundary lubrication or/not with the shape of the spectrum.

In the Fig. 3-16 (b) and Fig. 3-17 (b), the differential spectra have positive peaks so that it could determine that there was under fluid lubrication. The film thickness could be calculated from the peak height at 2915 cm^{-1} . However, the negative peaks were detected in the spectra at 0.52 mm/s for NBR1/HD and at 0.52 mm/s for NBR2/HD. It was indicated that in this sliding speed it was under the boundary lubrication. In this regime, the film thickness could be calculated not by subtracting background spectrum but by KK transformation.

COF and the film thickness were plotted in Fig. 3-18 (c) and (d). COF also indicated that it was under the mixed and boundary lubrication regime at 0.52 mm/s for NBR1/HD and at 0.52 mm/s for NBR2/HD. The Gc point of NBR1 was around 50 mm/s and NBR2 around 130 mm/s .

Regarding the condition of the boundary lubrication at 0.52 mm/s for NBR1/HD and at 0.52 mm/s for NBR2/HD, KK transformation was conducted for the spectra, and the peak height was calculated at 2930 cm^{-1} . The results were shown in Fig. 4-12. The increase in the peak height through increasing of the sliding speed under boundary lubrication was very small compared with that under fluid lubrication. With the FT-IR it is able to determine whether the fluid lubrication film was generated or not.

4.2.3 Measurement of lubricant in sliding surface under boundary lubrication

In this section, the change in the amount of lubricant under boundary lubrication during sliding was focused. The measurements were made at five points on the sliding surface. Fig. 4-13 (a) was the microscopic image of sliding surface. The sliding speed was 0.5 mm/s .

The FT-IR spectra were measured every five minutes at each point. COFs were measured every one second. The spectra at the measuring points except for 0 to 10 min at the y-coordinates of $-100\text{ }\mu\text{m}$ and all at y-coordinates of $-200\text{ }\mu\text{m}$ were an anomalous dispersion spectrum at all sliding times. That is, they were in contact with the disk during sliding. The spectra at the y-coordinates of $+200\text{ }\mu\text{m}$ were a mixture of transmitted and specular reflection at all points. The $+200\text{ }\mu\text{m}$ point was considered to be outside of the contact surface and was excluded with the following data analysis.

The increase / decrease of the peak height corresponds to the increase / decrease of the amount of HD inside the rubber. The amount of HD at $-200\text{ }\mu\text{m}$ point has been greatly decreased soon after starting of sliding. The $-100\text{ }\mu\text{m}$ point showed little change throughout the sliding time. At the 0 and $+100$ points, the amount of HD was larger than the other measurement points, and it decreased gradually from the initial stage.

The -200 μm point had the highest pressure among the measuring points[57] and the amount of HD at this point was greatly reduced. The -100 μm point showed little change throughout the sliding time. The 0 and + 100 points decreased gradually from the initial stage.

The decrease of HD on the sliding surface contributes greatly to the increase in COF. In the early stage of sliding, the amount of HD at 0 and + 100 μm point was larger, which were the points closer to the oil inlet region.

The difference in the amount of HD between these measurement points converges to the same level with 25 h sliding. This suggests that firstly HD penetrate into the rubber at the + 100 and 0 points at oil inlet region and diffused to the point of -200. By diffusing of HD to the -200 point, the lubricant existed enough over the entire contact surface, and COF decrease.

4.3 Investigations of swollen rubber

In previous section, it could be led that swelling over the entire contact surface decreased COF. In this section, the influenced factors on the friction of swollen rubber were investigated. The sample was pre-immersed in the lubricant for more than one week at room temperature in order to reach a saturation point.

4.3.1 Boundary lubrication of swollen rubber

COF measured by the pin-on-disc friction tester with the swollen samples are shown in Fig. 4-14 (b) and Fig. 4-15 (b). By swelling, COF did not increase significantly in the early stage of sliding in the comparison with non swollen sample (a) and (b). This indicated that the lubricant did not penetrate the rubber because the swelling of the rubber had been already saturated. COF was low except for NBR2/HD. Especially, COF lowered, when it swelled in MO. Among them, NBR2/MO shows very stable low COF. NBR2/HD was not swollen at all, and COF did not change. As mentioned above, both of NBR2 and MO had polarity and the intermolecular interaction was strong. This effect could influence on the formation of the lubricant film.

4.3.2 Sliding surface of swollen rubber

The sliding surface of the swollen rubber was observed by means of total reflection method. The change in COF of swollen rubber was shown in Fig. 4-16 and Fig. 4-17. The images of the sliding surfaces are shown in Fig. 4-18. From Fig. 3-8, the contact area was larger than that of non-swollen rubber because of softening by swelling. The elastic modulus after swelling was lower than that of non-swollen rubber, which is shown in Fig. 4-19. Even if it was taken into account, the thickness

of soft EHL film was estimated in the nanometer scale for any of the swollen rubber/lubricant combinations tested[57]. It indicated that the fluid lubrication with the swollen rubber was still insufficient as well as non-swollen rubber in this test conditions.

However, the increase in COF due to the full direct contact as occurred with the non-swollen rubber did not occur, and it was suggested that a lubricant film had been formed from the initial stage. Besides, the cavities were not observed with swollen samples, which were observed with non-swollen samples. Instead of that, the whole surface was observed to be gray, while COF was stable and the curve was smooth, especially with MO. The observation image of the sliding surface suggests the formation of a thin film which was observed in gray on the sliding surface. The lubricating film prevented direct contact between the rubber and the counterpart. Especially for NBR2/MO, the gray area did not change during sliding. These results indicated that the lubricant stably existed on the surface of the swollen rubber, and this played a role as a lubricant film.

On the other hand, NBR1/HD and NBR2/HD after certain period of the sliding vibrated finely in parallel to the sliding direction from the middle of the sliding. NBR2/HD vibrated with a larger amplitude, indicating that stick-slip occurred. At the moment of the slip, the lubricant flows into the sliding surface due to the increase in the relative velocity between the rubber and the counterpart. And then the lubricant flows out from the sliding surface and the rubber stick onto the disc until the rubber slip again. In this cycle, the lubricant existed on the sliding surface on a time-averaged basis, and COF was low, though the curve was spiky. The turbulence of COF curve and the value of COF became larger with the swollen NBR2/HD than that before swelling. However, the cause of the increase in the value is unknown. It was suggested that some change occurs near the surface even when the bulk is hardly swelled by soaking in the lubricant in advance.

4.4 Evaluation of the interaction between rubber and lubrication

4.4.1 Contact angle and surface free energy

The contact angle measurements of non-swollen and swollen rubber were conducted. The results are shown in Fig. 4-21. NBR1 was more wettable than NBR2 with nonpolar liquids. NBR2 was more wettable with polar liquids such as water. This was because NBR2 has a higher proportion of polar ACN groups than NBR1. Swelling with MO resulted increasing wettability with both non-polar and polar liquid. Swelling with HD caused little change.

The surface free energy calculated from the contact angle is shown in Fig. 4-22. Swelling with MO increased the polar component and the surface free energy. This was supposed to be the reason why the wettability of rubber swelled with MO was high. High wettability may lead to the

formation of a lubricant film on the surface. It was suggested that the property of the liquid could be added to the surface of the rubber by swelling with liquid.

4.4.2 Measurement of dispersion coefficient by gas permeation test

In order to investigate the diffusion coefficient of liquid in rubber, a liquid permeation test of rubber was performed. A summary of the study is given in Section 2.1.1 and Fig. 2.2. The calculated permeation rates and time-lag from the weight changes are compared in Fig. 4-23. As diffusion theory showed that the permeation rate was proportional to the swelling rate[67], this study also confirmed that the larger the swelling rate, the higher the permeation rate. On the other hand, the time-lag was longer in MO than in HD, independent of the swelling rate. The time-lag was inversely related to the diffusion coefficient, indicating that MO diffused slowly in rubber.

One of the reasons for this was presumed to be that the mobility of the molecular chain was suppressed by the electrical interaction between the polar ACN in NBR and the ester group in MO. Previous friction test results suggested that MO was less prone to stick-slip than HD and that the lubrication film was thicker due to more swelling comparison with MO.

4.5 Summary

Firstly, it could be categorized as three different systems such as NBR1/MO and NBR1/HD: the rubber / lubricant combination with fast swelling, NBR2/MO: a system with small amount and slow speed of swelling, and NBR2/HD: a system with no swelling at all.

The boundary friction of rubber varied with these combinations. It is shown in Fig. 4-24.

In case of well swelling systems, in the early stage of sliding, COF increased with the generation of a cavity on the sliding surface. This was revealed by the newly developed in-situ FT-IR. In situ FT-IR showed that the oil film thickness would be quantitatively evaluated by the peak size under hydrodynamic lubrication, and whether direct contact occurs would be evaluated by the anomalous dispersion spectrum. It was also possible to detect the presence of direct contact by the spectra with KK transformation under boundary lubrication.

In addition, it was found that the amount of lubricant varied with time dependency and had spatial distribution on the sliding surface. The results indicated that the lubricant diffused through the rubber under boundary lubrication. Besides, the amount of lubricant in the rubber correlated the boundary friction. The diffusion speed in rubber could be estimated by the liquid permeation test.

The pretreatment of soaking test was conducted to fill enough lubricant in the rubber and the boundary friction coefficient came to low and stable. In particular for NBR2/MO, where both

rubber and lubricant are polar, had this tendency. This would be delivered that the attraction of polar molecules to lubricate the sliding surface. The polarity of the molecule was estimated by MO simulations, vaporized rate, and contact angle measurements.

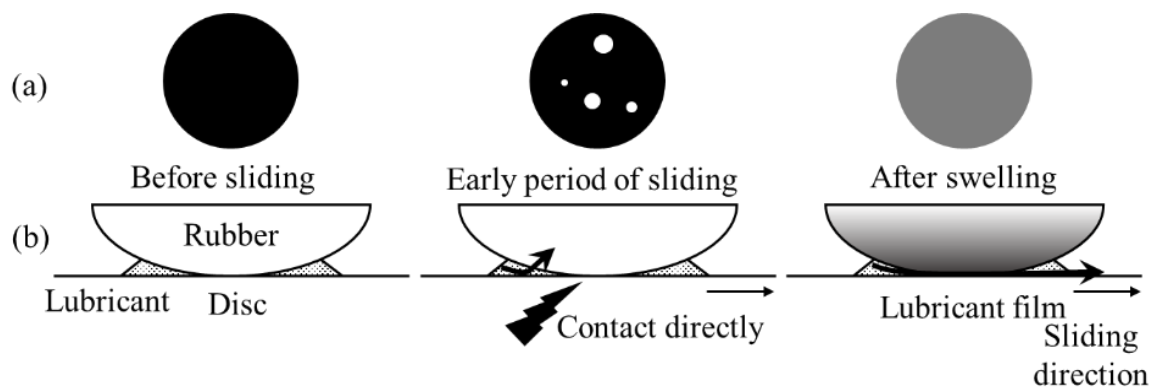


Fig. 4-1 Schematic images of (a) the appearance of the sliding surfaces observed with the total reflection method (black indicates contact area and white indicates non-contact area) and (b) proposed mechanism of boundary lubrication of rubber.

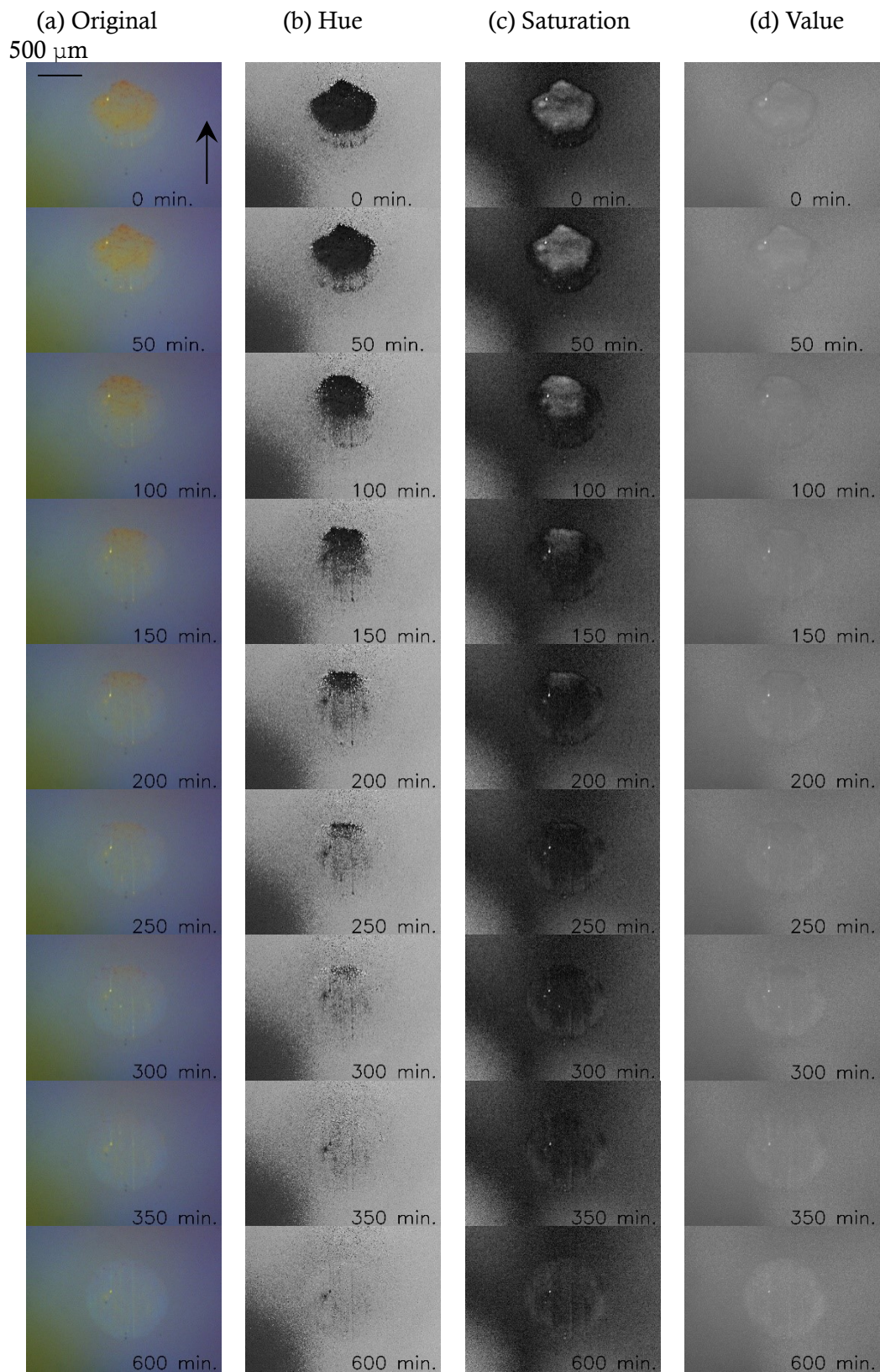


Fig. 4-2 Interferometry images of the sliding surface of NBR1 lubricated HD. (a) are the original images and (b) Hue, (c) Saturation and (d) Value were obtained from components of (a) with digital processing.

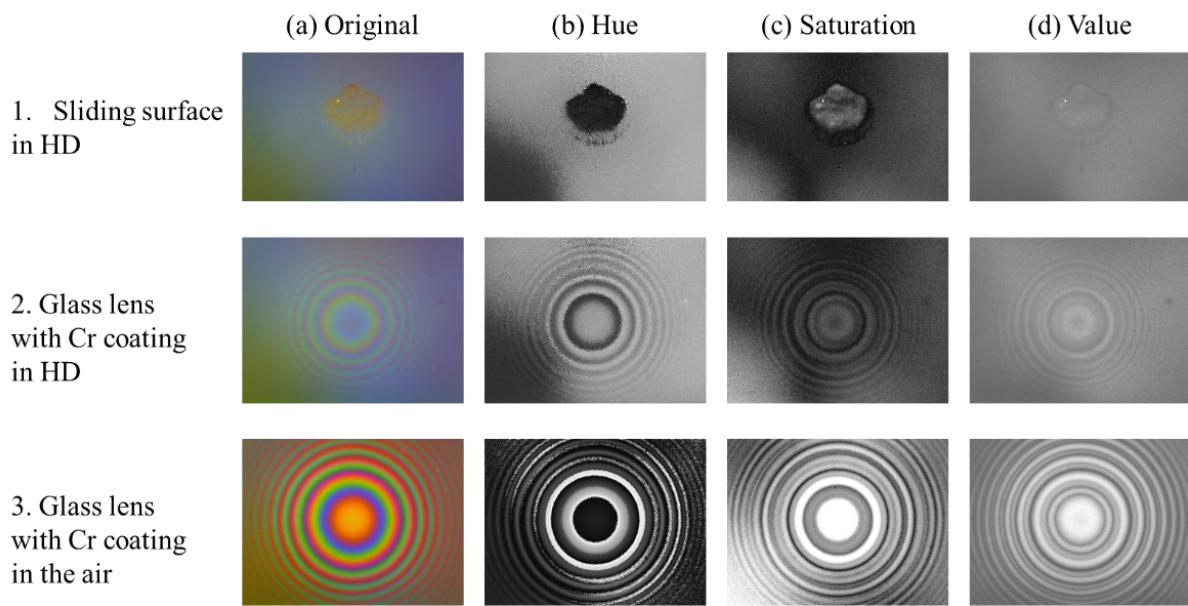
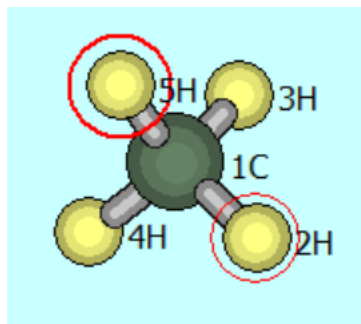


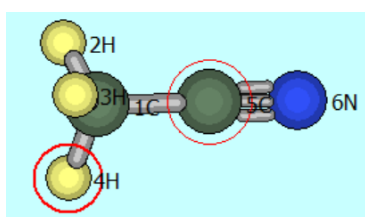
Fig. 4-3 Interferometry images the sliding surface of NBR1 lubricated HD (1), and the images of Newton's rings observed when the glass lens contacted to the glass disc in HD (2) and in the air (3). (a) are the original images, and (b) Hue, (c) Saturation and (d) Value were obtained from components of (a) with digital processing.

(a)

Electron density

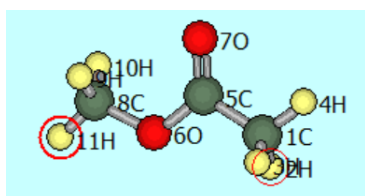
Atom	Number	Charge
C	1	-0.81434
H	2	0.20358
H	3	0.20358
H	4	0.20358
H	5	0.20361

(b)

Electron density

Atom	Number	Charge
C	1	-0.69267
H	2	0.24411
H	3	0.24407
H	4	0.24407
C	5	0.29191
N	6	-0.33151

(c)

Electron density

Atom	Number	Charge
C	1	-0.69140
H	2	0.22548
H	3	0.22854
H	4	0.22488
C	5	0.80702
O	6	-0.51125
O	7	-0.59667
C	8	-0.23366
H	9	0.18124
H	10	0.18278
H	11	0.18305

Fig. 4-4 Results of molecular orbital simulation over stabilized structure and the electrondensity of (a) Methane, (b) Acetonitrile, and (c) Methyl acetate.

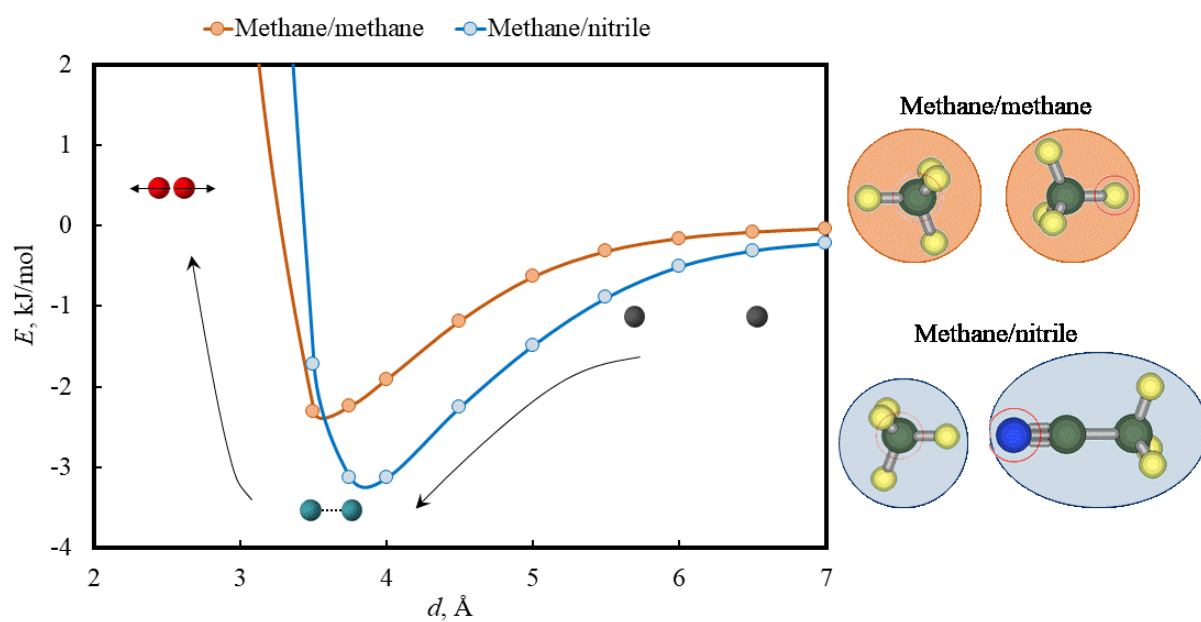


Fig. 4-5 The graph of molecular simulation result. The horizontal axis shows the atomic distance, and the vertical axis shows the potential energy.

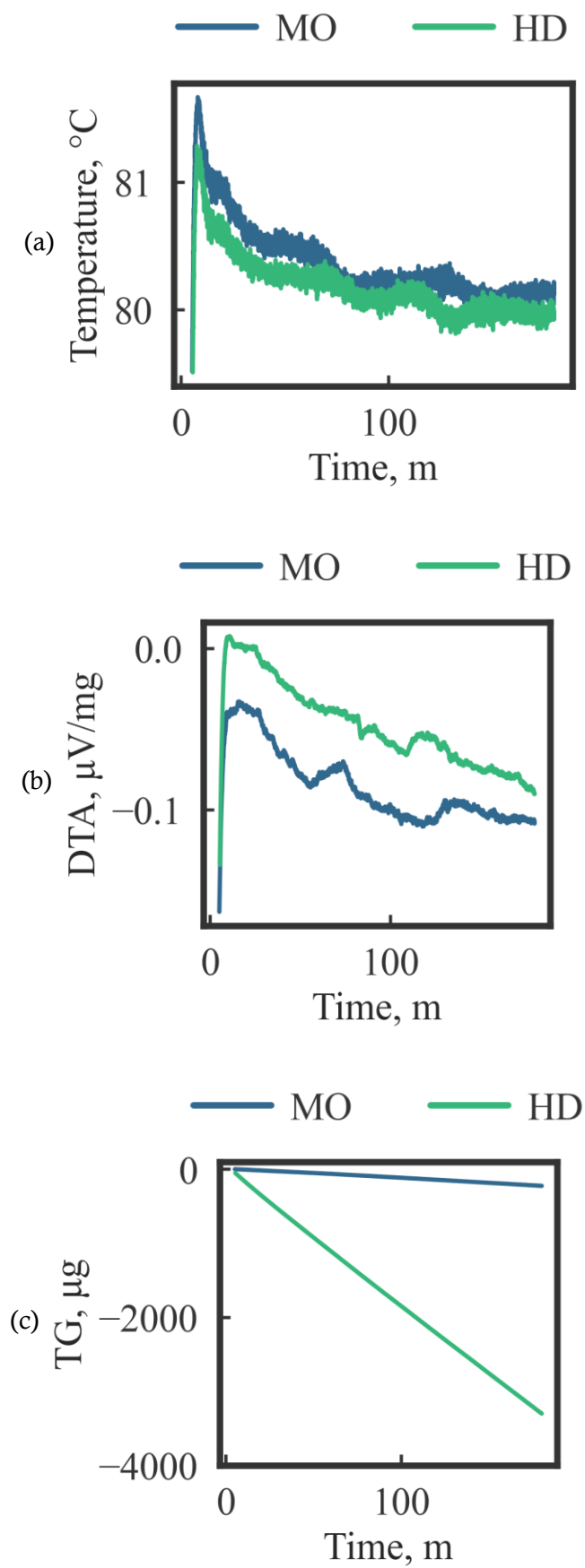
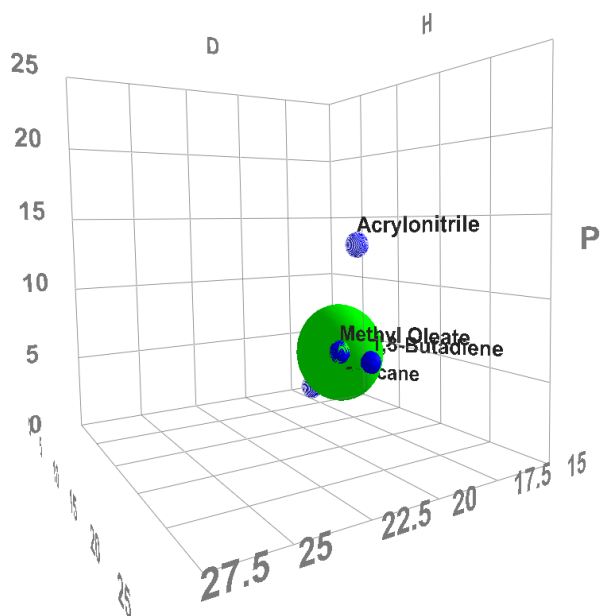


Fig. 4-6 (a) Temperature, (b) Differential thermal analysis, and (c) Thermogravimetric analysis.

(a)

	δD	δP	δH
HD	16.3	0.0	0.0
MO	16.2	3.8	4.5
NBR1	15.0	4.8	5.8
NBR2	15.2	6.8	6.1

(b)



(c)

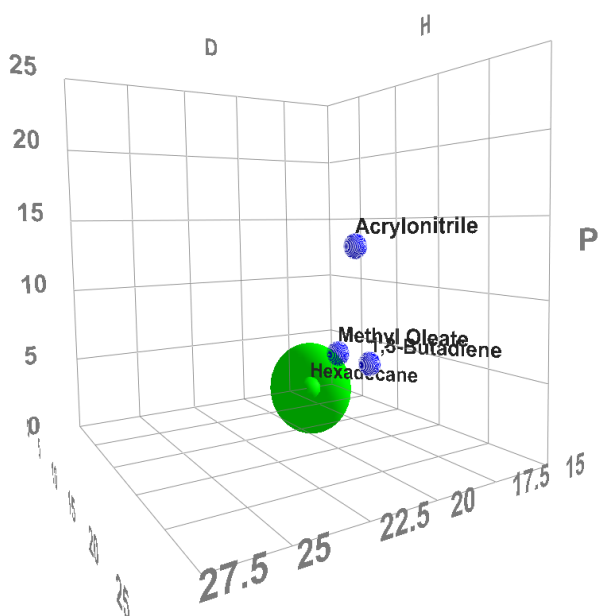


Fig. 4-7 (a) Hansen solubility parameter calculated with the software (HSPiP 4th Edition). The green sphere represents (b) HD and (c) MO in the three dimensional coordinate system of D, P, and H.

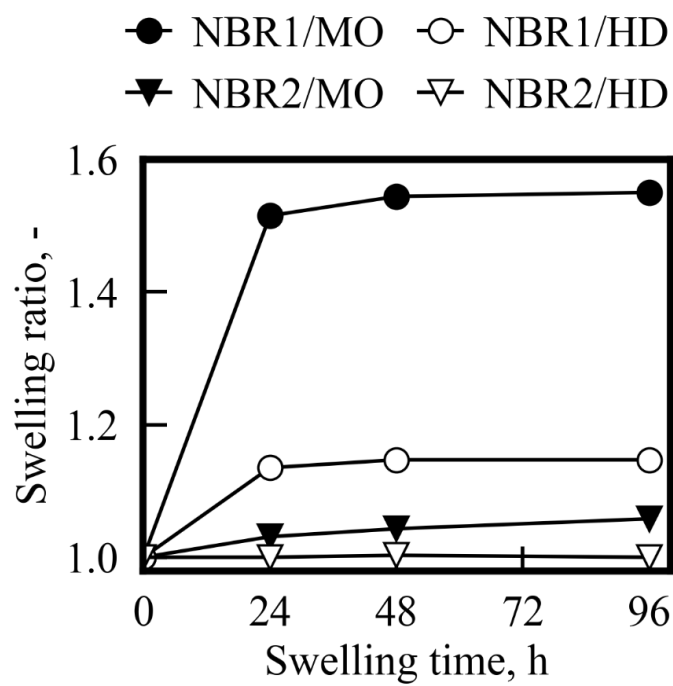


Fig. 4-8 Swelling ratio in the weight calculated from weight change with the various combinations of rubber/lubricant at 60 °C

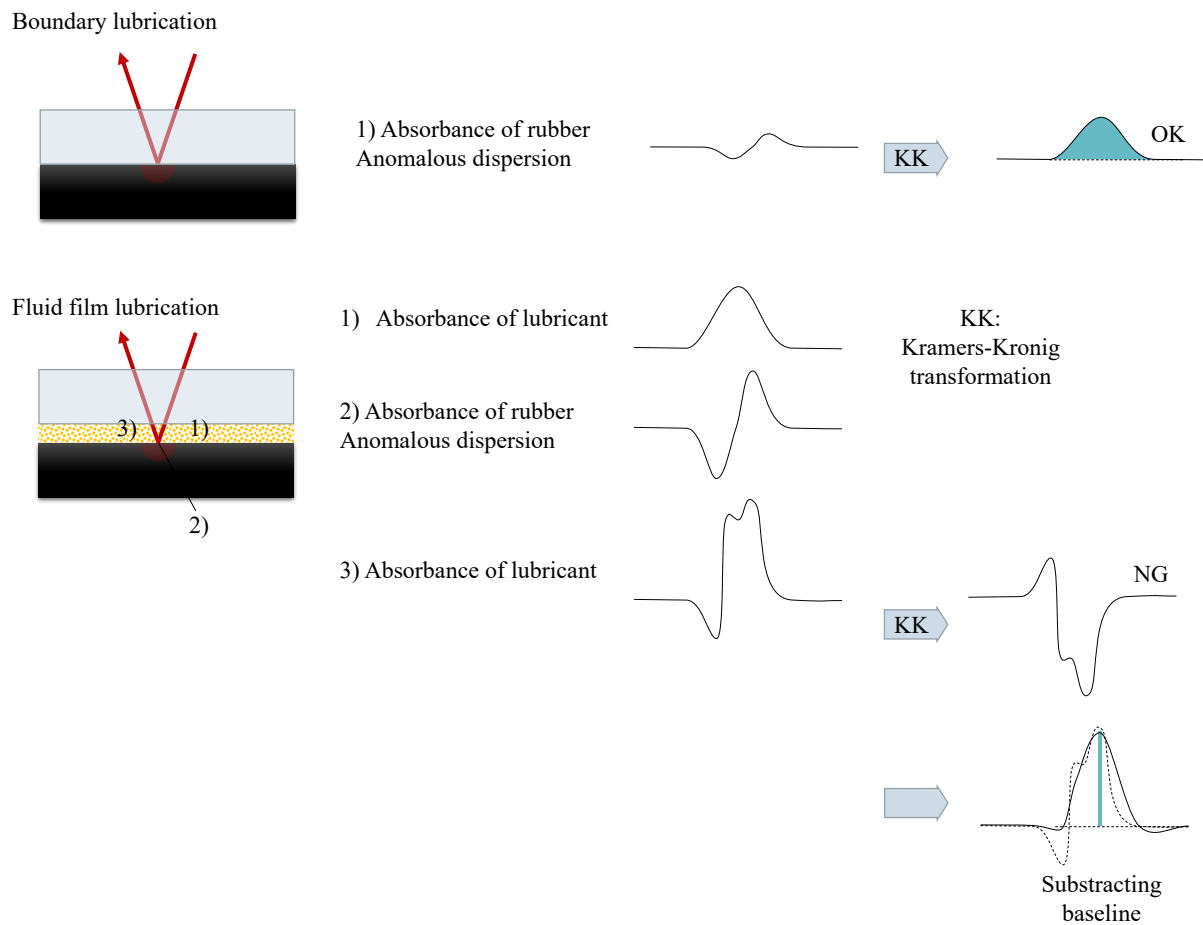


Fig. 4-9 Shape of FT-IR spectra under fluid lubrication and boundary lubrication.

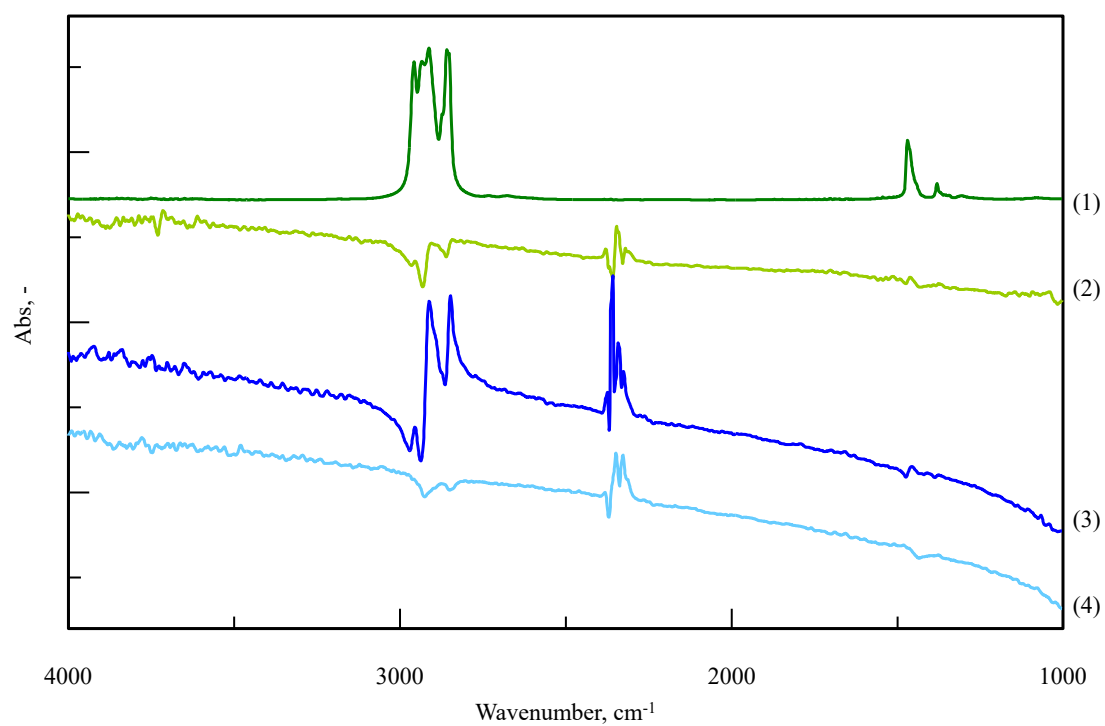


Fig. 4-10 The spectrum of (1) HD on the glass coated by gold, (2) NBR1/HD with the gap between the disc and the rubber was 0 μm ., (3) NBR1/HD during sliding at 520 mm/s and (4) NBR1/HD during sliding at 0.5 mm/s.

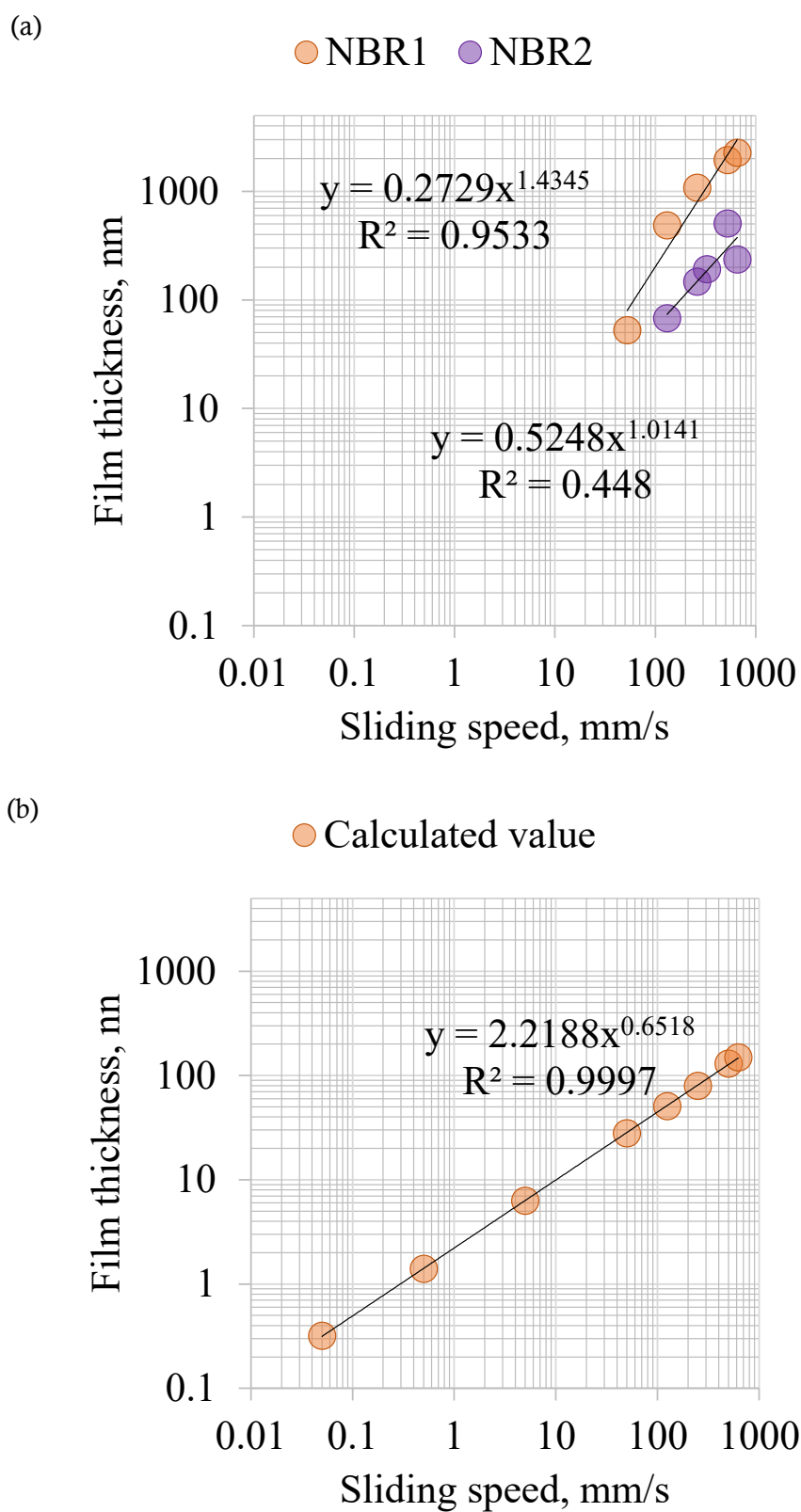


Fig. 4-11 (a) The film thickness calculated from FT-IR spectra and (b) the film thickness calculated from Soft EHL.

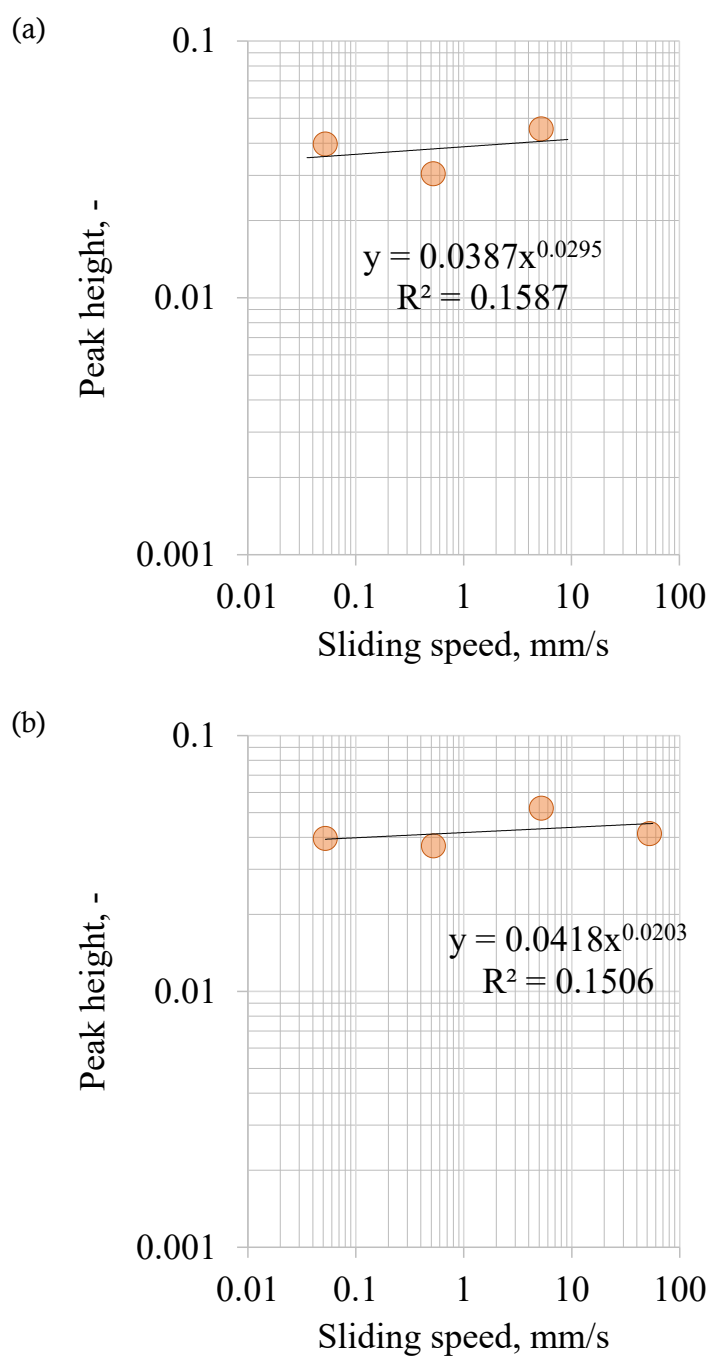


Fig. 4-12 The Peak height at 2930 cm^{-1} of (a) NBR1/HD and (b) NBR2/HD fitted in a power function.

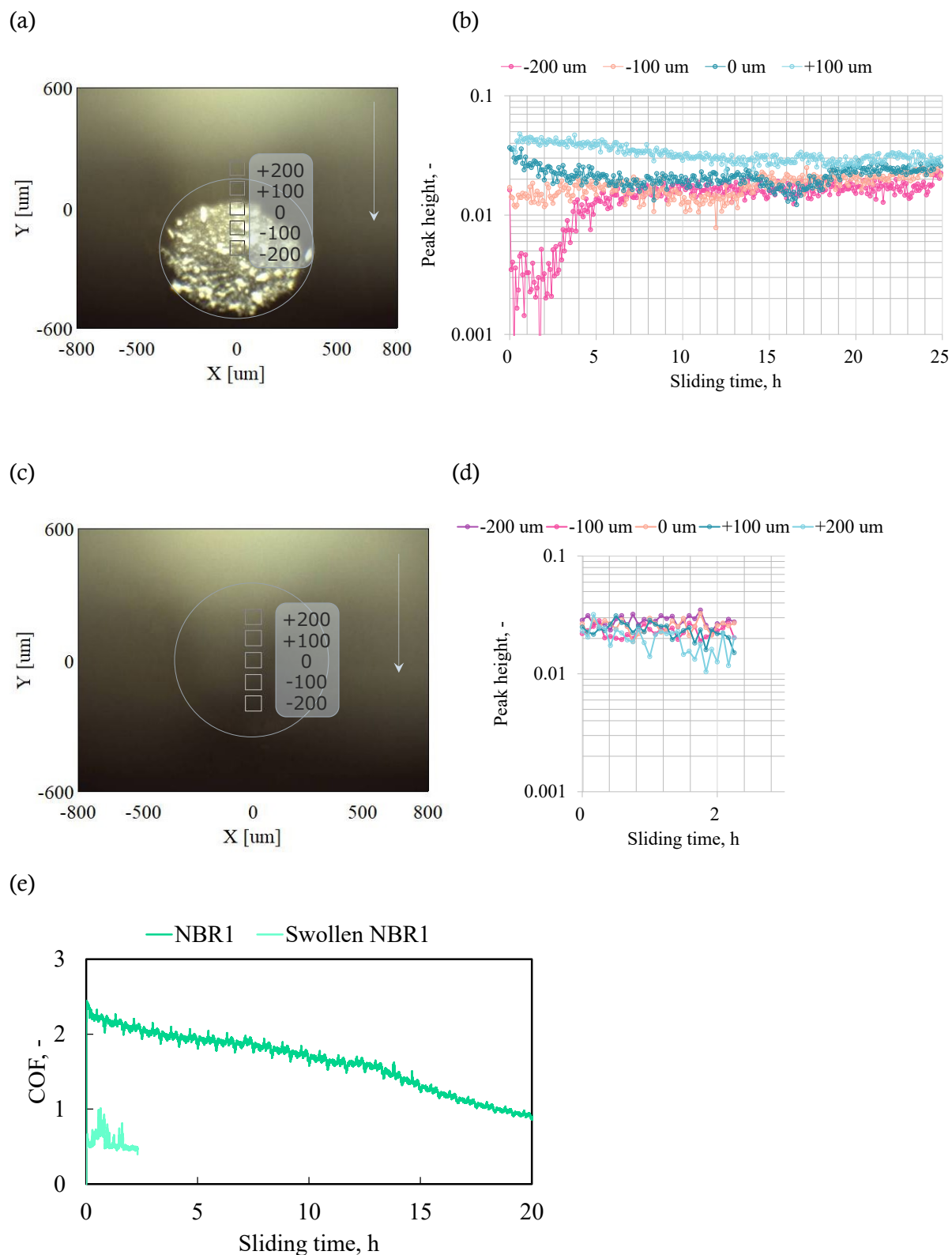


Fig. 4-13 .(a) The microscopic images of (a)NBR1/HD and (c) swollen NBR1/HD. The numbers indicated Y coordinates of the measuring points. The Change in peak height at 2930 cm^{-1} during sliding of (b) NBR1/HD and (d) swollen NBR1/HD. The arrows on the upper right of the images indicated the sliding direction of the disc. The sliding speed was 0.5 mm/s .

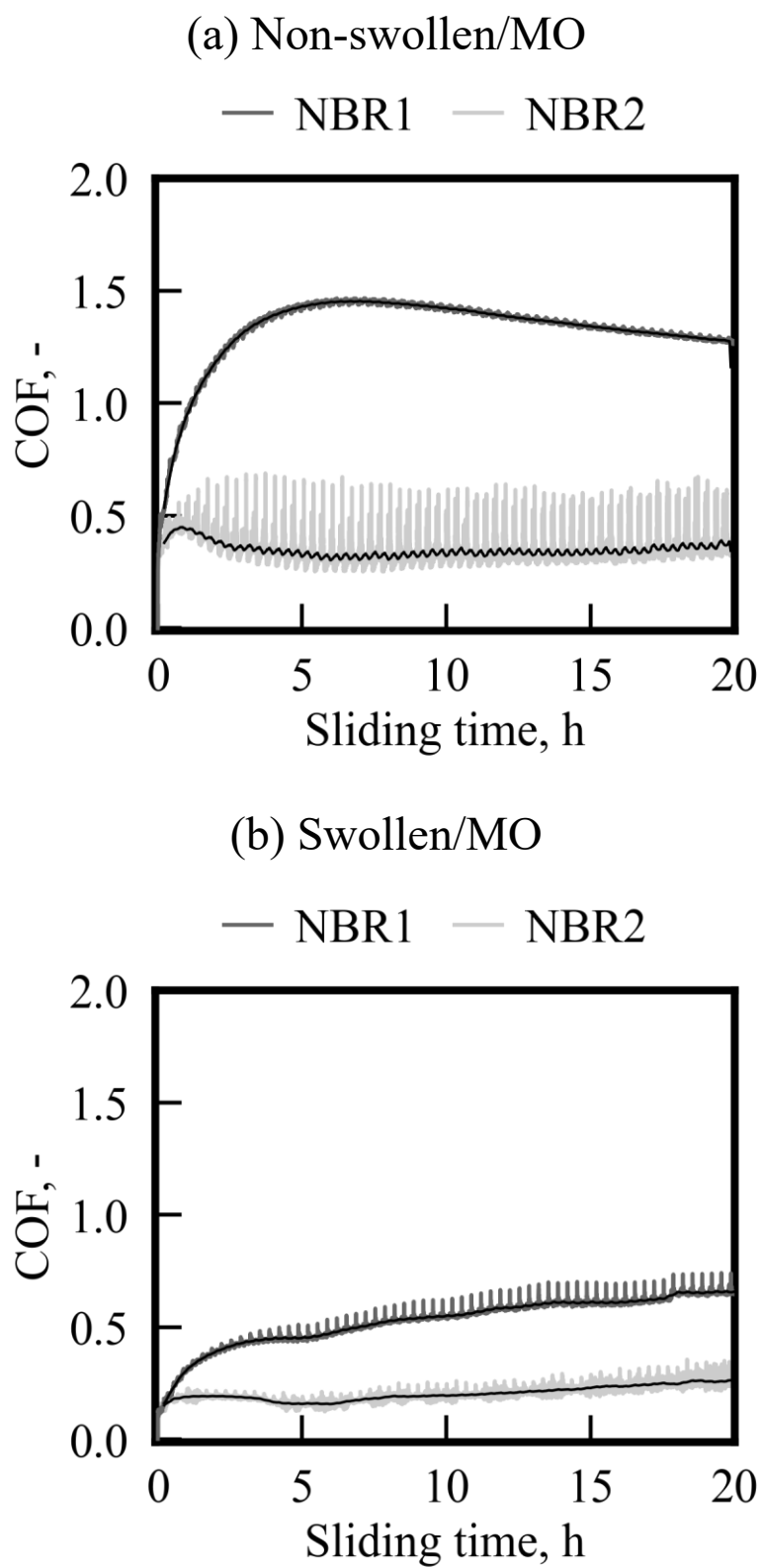


Fig. 4-14 Change in COF of (a) non-swollen and (b) swollen rubber lubricated with MO.

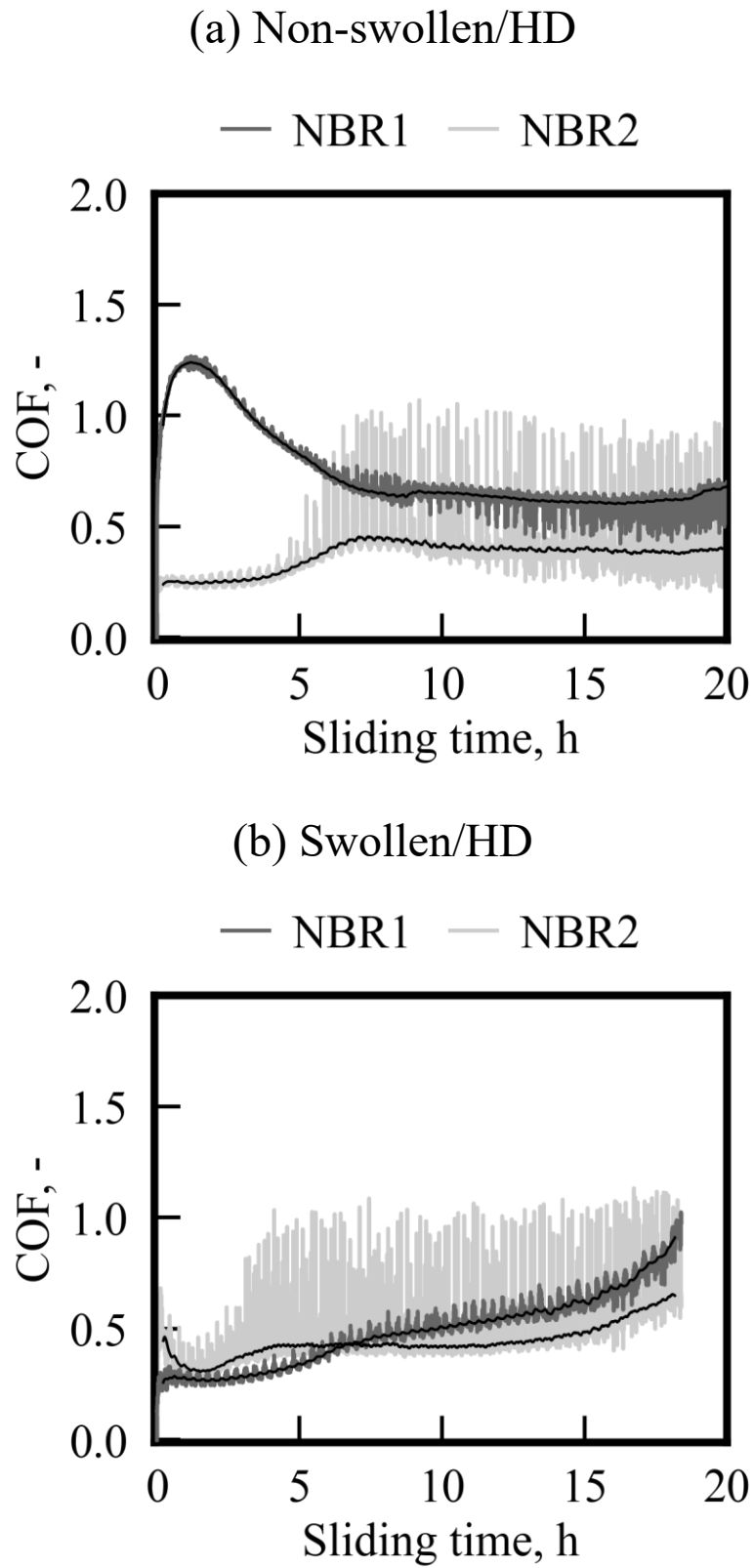


Fig. 4-15 Change in COF of (a) non-swollen and (b) swollen rubber lubricated with HD.

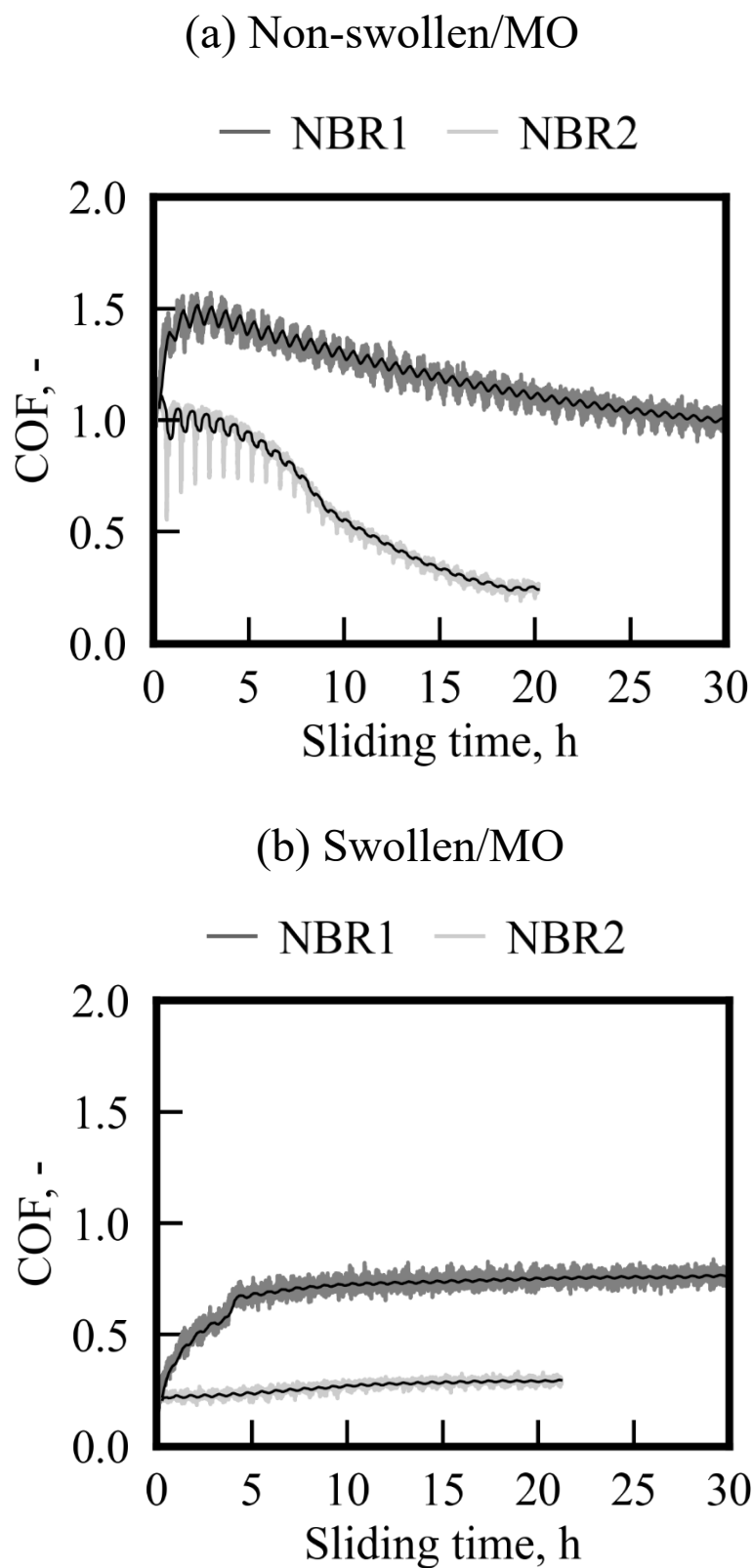


Fig. 4-16 Change in COF measured under the observation of total reflection method. (a) Non-swollen and (b) swollen rubber lubricated with MO.

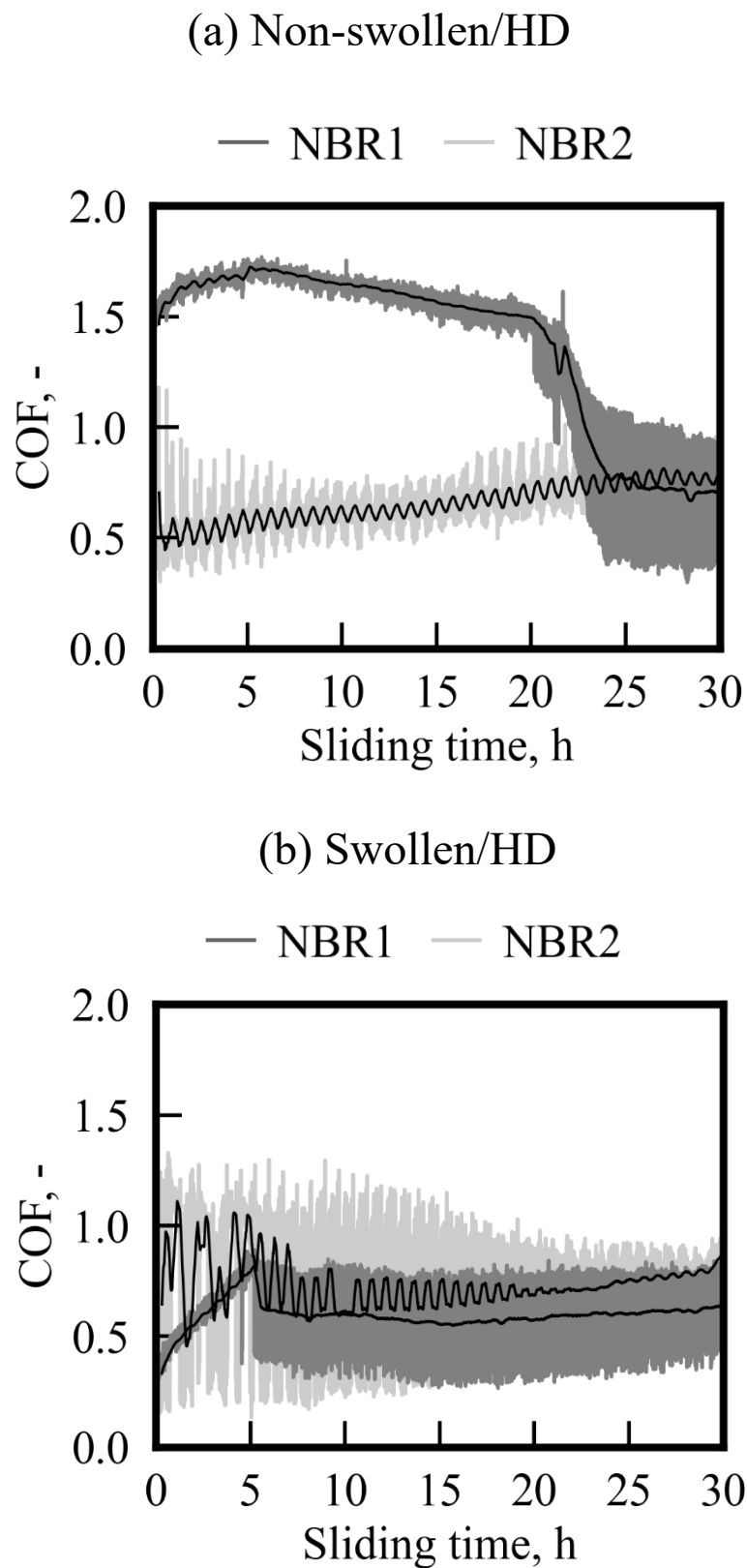


Fig. 4-17 Change in COF measured under the observation of total reflection method. (a) Non-swollen and (b) swollen rubber lubricated with HD.

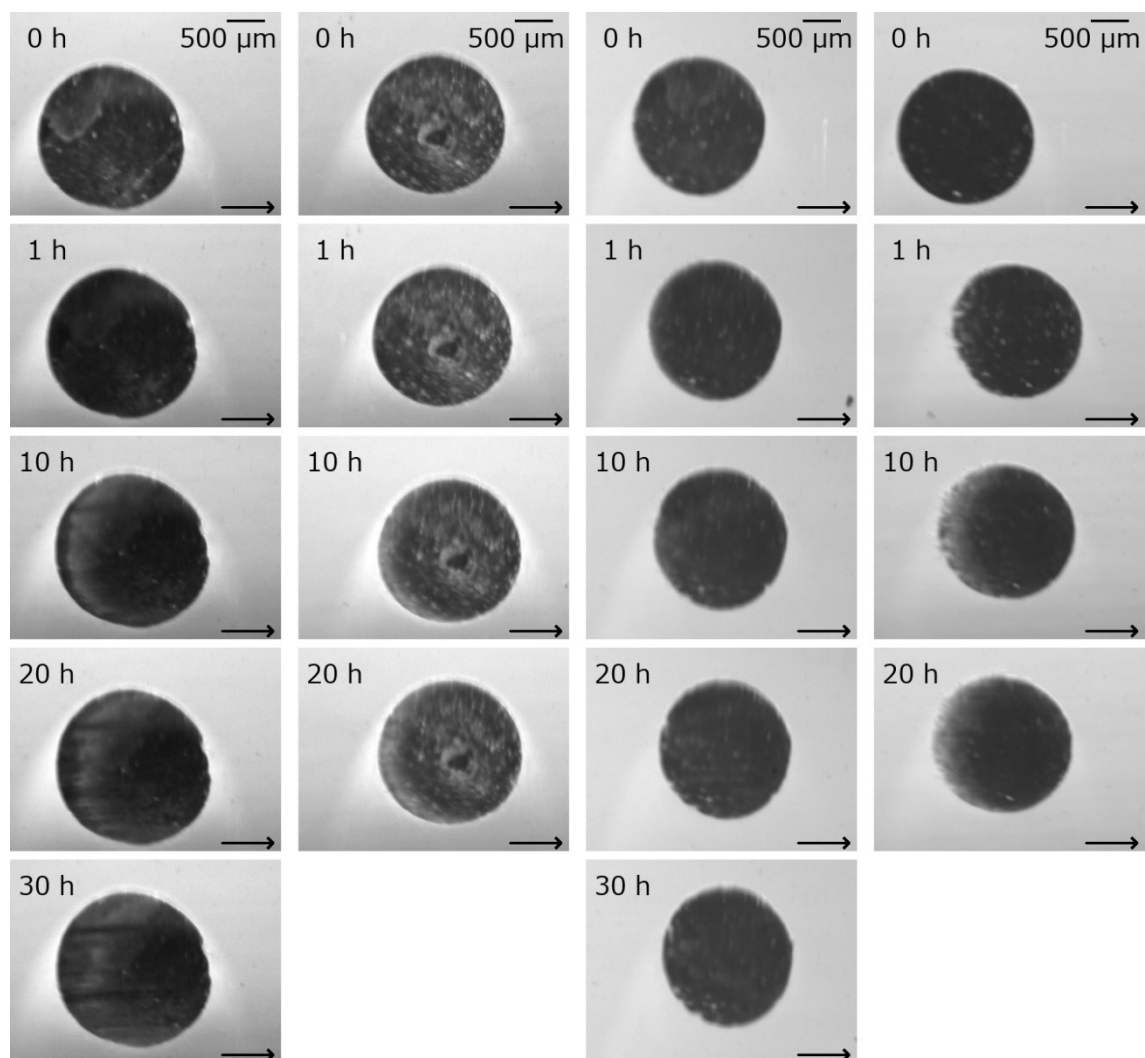


Fig. 4-18 Images obtained by the total reflection method machine. The numbers on upper left of images indicate the sliding time and the arrows on lower right of images indicate the sliding direction of the disc.

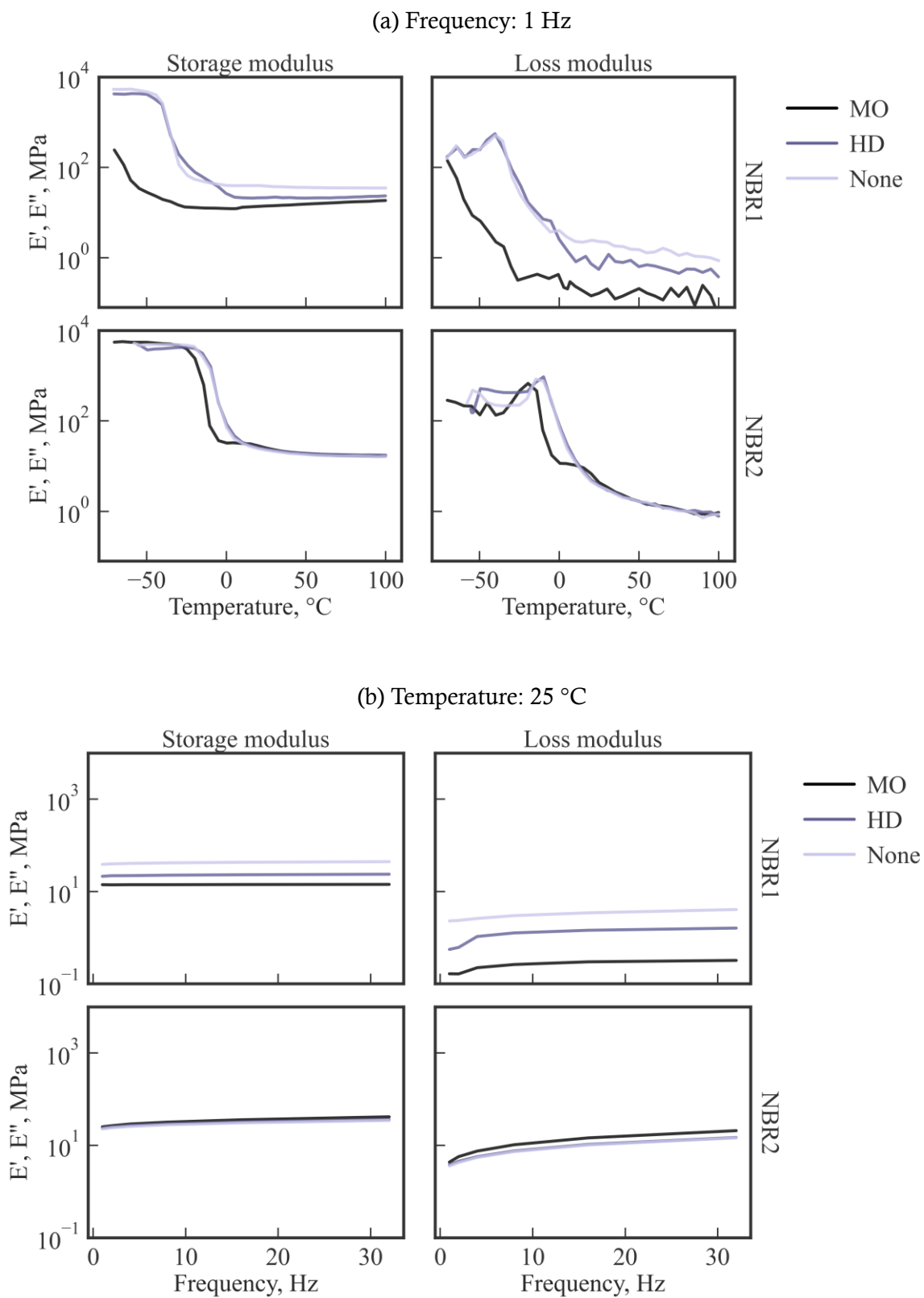


Fig. 4-19 Storage modulus (E' , MPa) and loss modulus (E'' , MPa) measured by dynamic mechanical analysis. (a) shows the temperature dependency at 1 Hz. (b) shows the frequency dependency at 25 $^{\circ}\text{C}$

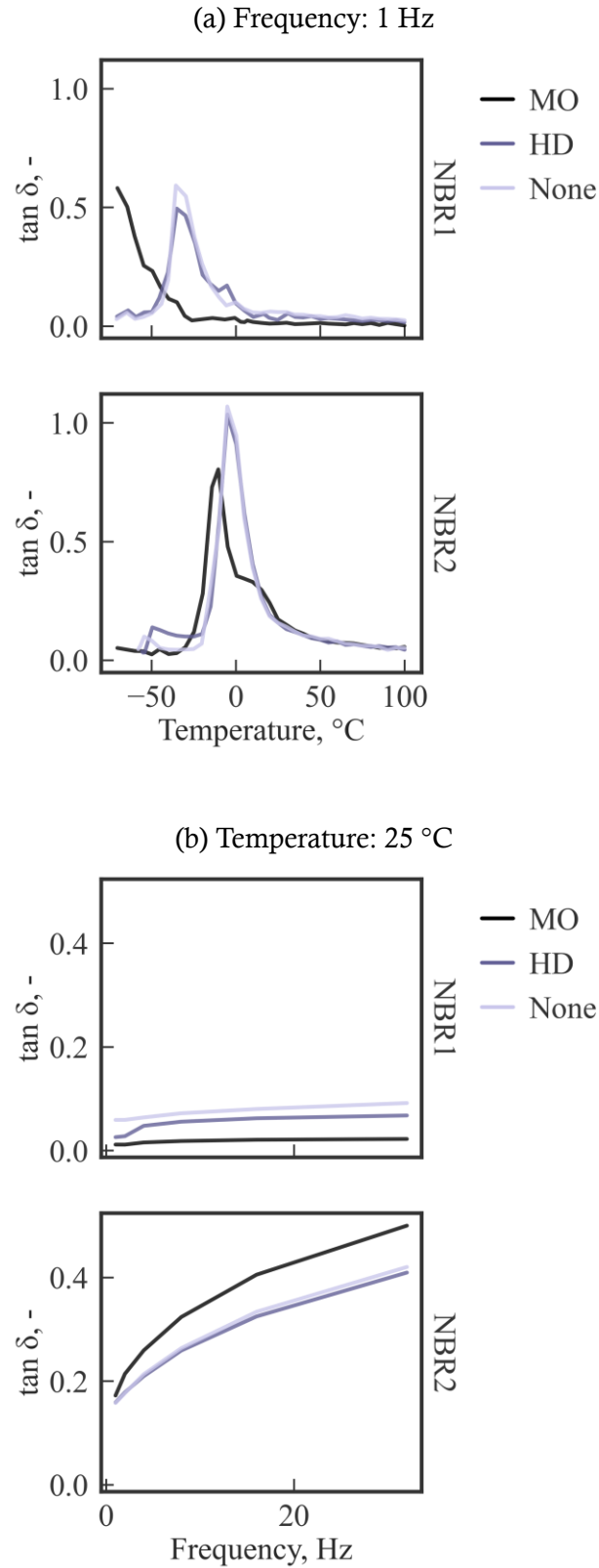


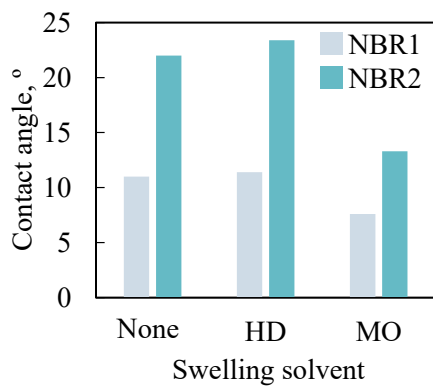
Fig. 4-20 Loss factor ($\tan \delta$) measured by dynamic mechanical analysis. (a) shows the temperature dependency at 1 Hz. (b) shows the frequency dependency at 25 °C

(a)

Swelling liquid	Probe liquid	NBR1		NBR2	
None	HD		11.0		22.0
HD	HD		11.4		23.4
MO	HD		(Spreading) 7.6		13.3
None	Water		96.4		90.8
HD	Water		96.1		87.7
MO	Water		80.8		78.1

(b)

Probe liquid: HD



(c)

Probe liquid: Water

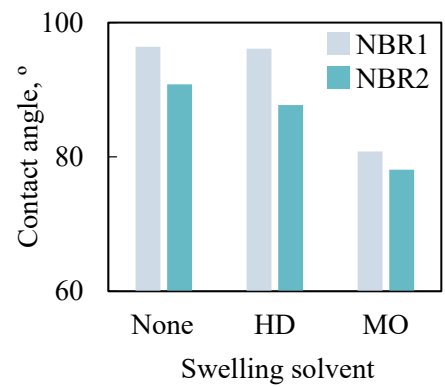


Fig. 4-21 Contact angle of non-swollen and swollen rubber plates. (a) Images of the droplets and contact angle. The graphs of the contact angle (b) with HD and (c) with water as the probe liquid.

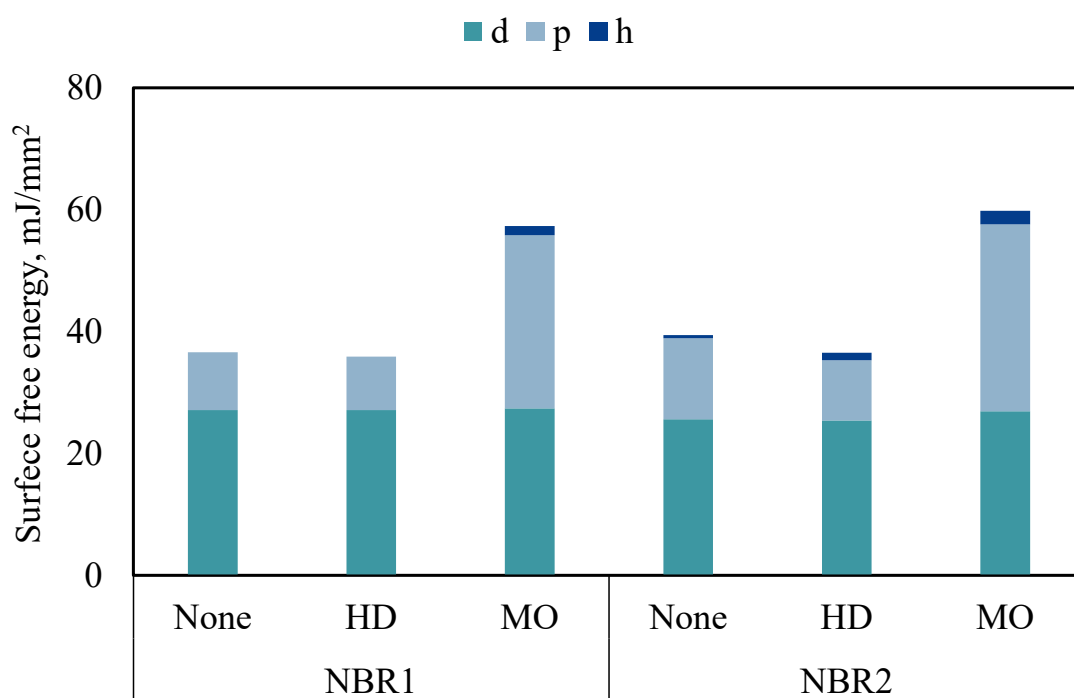


Fig. 4-22 Surface free energy of non-swollen and swollen rubber plate calculated from the contact angle in three components. (d: dispersion, p: polar, and h: hydrogen bond)

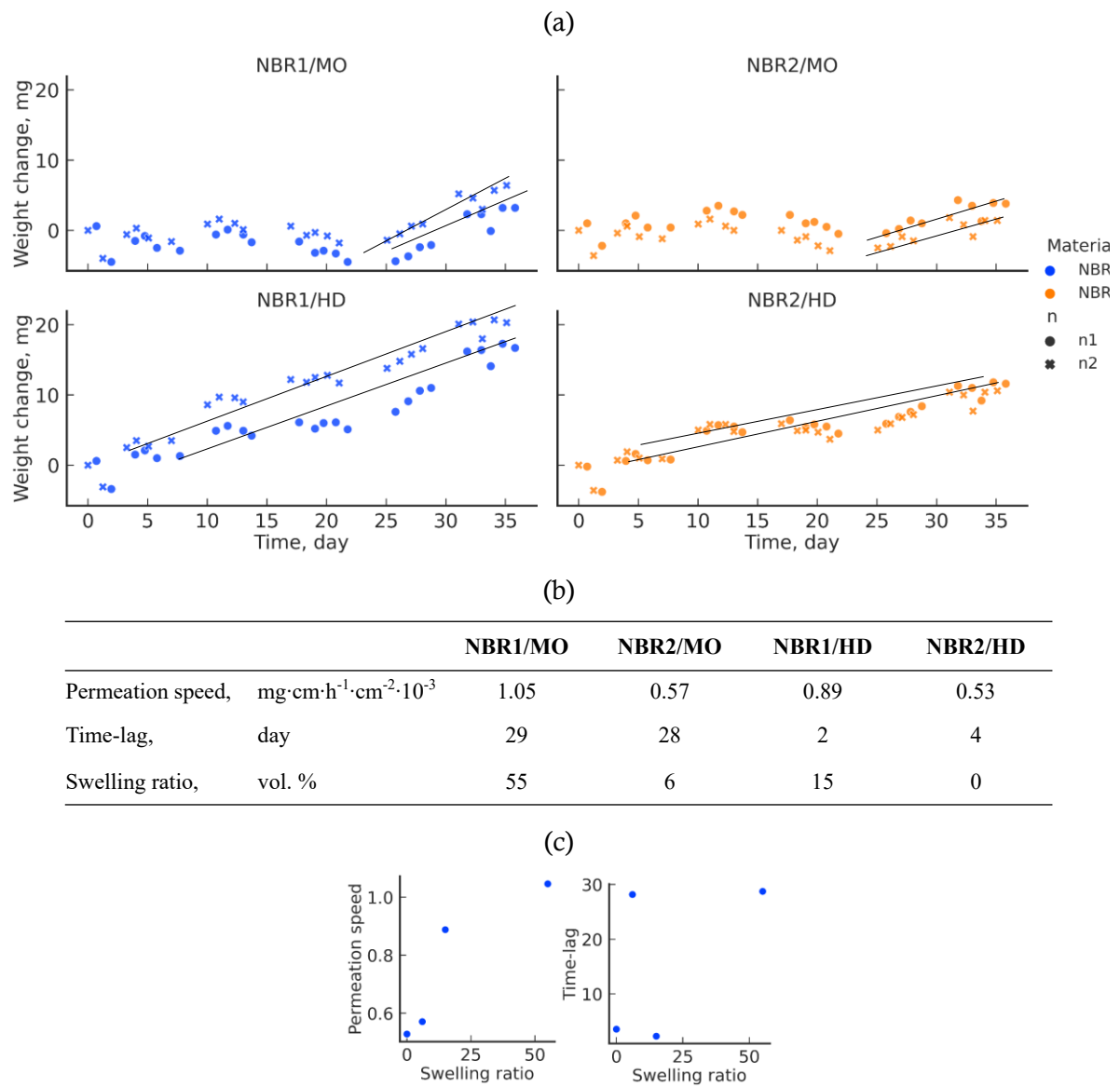


Fig. 4-23 Results of liquid permeation test. (a) Weight change, (b), (c) permeation speed and time-lag calculated from the weight change.

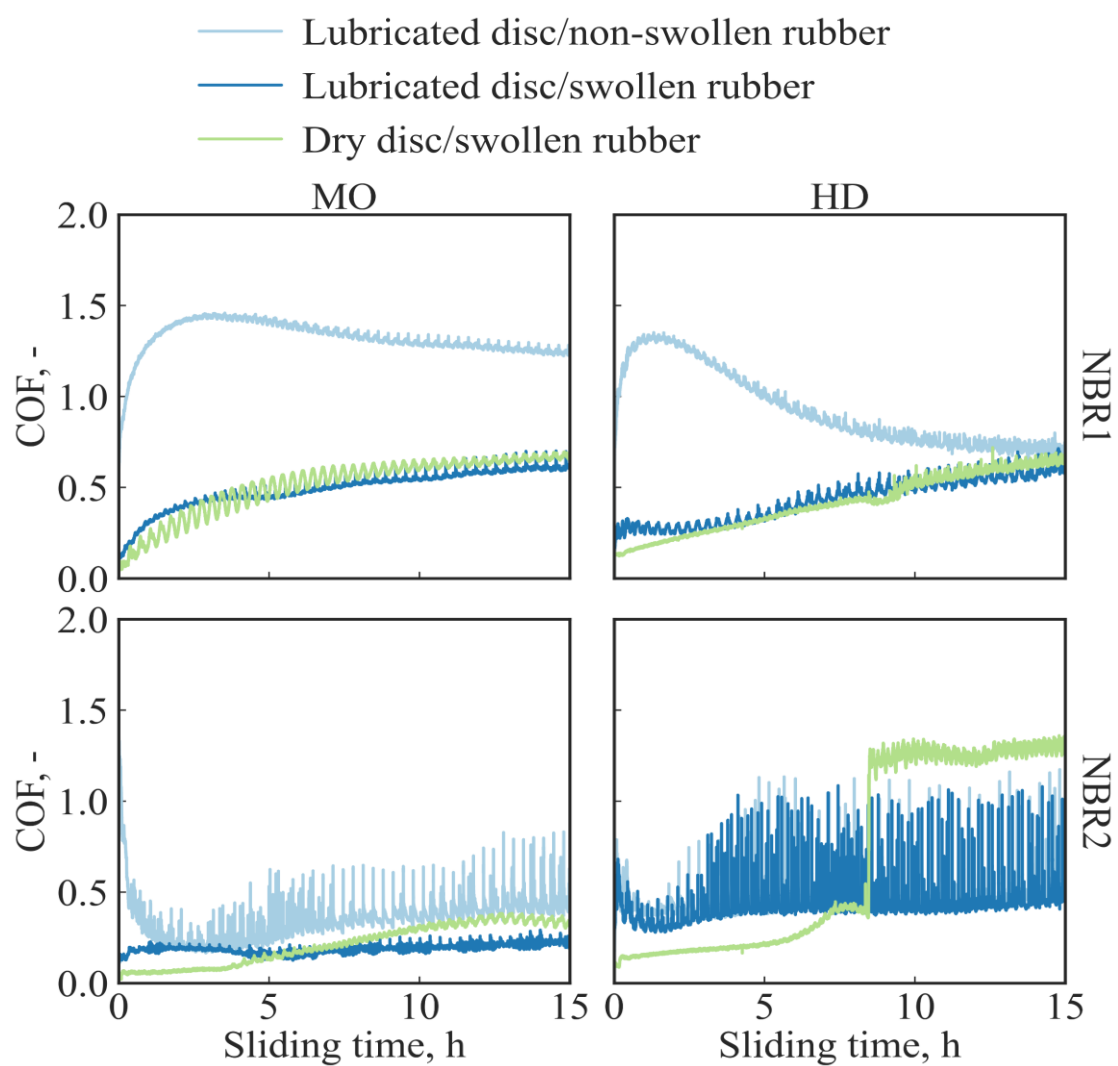


Fig. 4-24 COF at various conditions.

5 A model of boundary lubrication of the rubber

As described in Chapter 1, in the numerical analysis of the oil seal, the contribution on COF of the radial shaft seals at the boundary friction regime was not clarified, and COF was treated as a constant value because the detail of the mechanism has not been clarified.

This study showed that the lubricating condition was not uniform but changed according to the amount of lubricant, which was influenced by friction conditions and combination of the rubber/lubricant. The compatibility of rubber/lubricant depends on the polarity of rubber and lubricant.

In this chapter, a model of boundary lubrication is proposed, in which a lubricant film is formed by balancing of lubricant into and out of the sliding surface.

5.1 Lubrication mechanism inferred from experimental results

The change in COF of rubber in the region where hydrodynamic lubrication was lost is shown in Fig. 5-1. These results could be divided into three groups as shown in Table 5-1.

NBR2/HD is the non-swelling system. This system is usually used for radial shaft seals. NBR1/MO and NBR1/HD are the swelling systems with low-polar rubber. They have a large swelling amount of more than several ten percent volume change and a high swelling rate, that is, they reach saturated swelling ratio in several day even at room temperature. NBR2/MO is the swelling system with the high-polar rubber. Its swelling ratio saturates about + 5 % and has a lower swelling rate than the swelling system with the low-polar rubber.

Fig. 3-4 non-swelling system has a low friction coefficient on average over time, but the friction force curve is spike-like. From the in-situ observation, it was revealed that it caused by the stick-slip and scratches on the disc. In consideration of this fact, it is assumed that the non-swelling system prevents excessive friction by stick-slip, but the boundary lubrication layer is thin.

COF of the swelling system with low-polar rubber increased with sliding but decreased after a certain period of time. This mechanism is illustrated in Fig. 5-2. The swelling system with low-polar rubber has a high swelling rate. Therefore, rubber started to be swollen with sliding. This means that the part of lubricant on the sliding surface was absorbed by the rubber immediately after sliding started. Besides, the other part of lubricant adsorbed onto the disk and is carried out from the sliding surface. These two phenomena could cause the increase of COF. Several hours after sliding started, the swelling reached saturation and

COF decreased. Namely, it is because the rubber surface was sufficiently filled with the lubricant and the lubricating action was exerted. The swelling process of the rubber causes initial increased and subsequent decreased in COF.

The swelling system with high-polar rubber showed almost the same tendency as the non-swelling system because the low swelling rate resulted that the lubricant could not be absorbed in the rubber during the experimental time.

What will happen if rubber reaches equilibrium and swell in advance by pre-immersing?

COF changed with swollen rubber, which was pre-immersed in the lubricant is shown in Fig. 5-1. COF of the pre-immersed swelling systems were lower than that of initial state, while COF of the pre-immersed non-swelling system is as same as that of initial state. In particular, COF of the swelling system with high-polar rubber had the lowest friction for the long sliding time, while COF of the pre-immersed swelling system with low-polar rubber gradually increased with sliding.

This indicates that the swelling system with high-polar rubber had the strong effect of retaining the lubricant on the sliding surfaces when it was filled with the lubricant by pre-immersing. From the investigation about polarity of the rubber and the lubricant mentioned in Chapter 4, the polarity and its interaction led the formation of stable lubrication film. For example, COF of swollen NBR2/MO was stable low. NBR2 was a highly polar rubber compared with NBR1 because NBR1 has more ACN group than NBR2. Besides MO also has a polar group, ester group. The attraction force acted between the polar groups of NBR2 and MO could effect on the stable formation of lubricant film.

5.2 A model of boundary lubrication

As described in the previous section, under the boundary lubrication, a lubricant film could be maintained on the surface by balancing the movement of lubricant into and out of the rubber in addition to the movement of lubricant out of the sliding surfaces.

Pre-immersing to fill the rubber with lubricant, the lubricant produces the boundary lubrication. The absorption of lubricant to the rubber network and the diffusion of the lubricant in the rubber were dominant.

Fig. 5-3 shows the illustration of the rubber which absorbs lubricant. The size of the rubber chain network was in nm to sub μm . It is called correlation length of the network. The size of the network chain can be determined by the interaction parameter of the rubber and the

lubricant, and the swelling ratio [68]. The network is gradually filled with lubricant by the swelling of rubber.

As a comparison, the approach of conventional boundary lubrication for metals is shown in Fig. 5-3. The boundary lubrication of metals is mainly based on the adsorption of molecular films and chemically reacted films. In comparison with this, in the case of rubber, not only surface but also internal diffusion is the important factor.

As another comparison, the gel is also a mixed state of three-dimensional network and liquid like rubber. Since the structure of gel varies depending on the type of gel, only an example is shown in Fig. 5-3. The rubber can be more similar to the gel rather than metals in boundary lubrication. The biggest difference between gel and rubber is that the amount of liquid contained in gel. It is larger than that contained in rubber. Besides, in the case of rubber, since it swells after cross-linking, the lubricant is always subject to the pressure caused by elastic deformation of rubber network. In addition, liquids in gels such as water are lower molecules than oil in many cases. Therefore, the mobility of the liquid in the gel is more active. Hence, the mesh transmission and interstitial fluid load support is clarified as main lubrication mechanism[69][70]. In the case of rubber, the condition of the sliding surface and the rubber changes gradually and dynamically. In some cases, there is no lubricant in the rubber, and in other cases, the lubricant enters the rubber by being immersed for a long time. It is necessary to have parameters and a model to discuss these comprehensively. In next section, a mathematical model is proposed, and the results of the analysis based on the model will be discussed.

5.3 A conceptual model of lubricant flow

Boundary lubrication of rubber is different from that of metals but is similar to that of gels. However, it has characteristic feature. That is, the degree of the swelling and the properties of the swelling liquid had the strong effect on the boundary lubrication. If we understand how the wide range of possible combination of rubber and lubricant affect boundary friction, we will be able to use the knowledge to estimate friction in given conditions, and also to design low friction materials.

Based on the above discussion, the following conceptual mode is proposed. The model is shown in Fig. 5-4, where V is the entrainment speed of the lubricant, p is the pressure, T is the temperature, B is the length of the sliding surface, L is the length of the sliding surface in the direction that is vertical to the sliding, c is the concentration of the lubricant in the rubber, c_s is the saturated concentration of lubricant in the rubber, D is the virtual

thickness of the surface lubrication layer in the rubber, and h is the thickness of the lubricant film that corresponds to the amount of the lubricant in the sliding surface.

The lubricant flow into sliding surface at a rate of q_{in} kg/s and flow out of the sliding surface at a rate of q_{out} , kg/s. The lubricant is also absorbed into the rubber at a rate of q_a kg/s and emitted at a rate q_e kg/s. For the sake of simplicity, it is assumed that q_a and q_e is in the certain ratio independent of q_{out} . In practice, q_a and q_e influence on q_{out} .

The amount of lubricant flowing into the sliding surface per unit time q_{in} is

$$q_{in} = k_{in}pVLh \quad (5-1)$$

and the amount of lubricant flowing out of the sliding surface per unit time q_{out} is

$$q_{out} = k_{out}pVLh \quad (5-2)$$

q_a is assumed to be proportional to the difference between the concentration at surface and saturated concentration of the lubricant and independent of h , which represents the amount of lubricant. From this, h and c can be given independently.

The amount of the absorption into the rubber q_a , kg/s is

$$q_a = k_aBLD(c_s - c) \quad (5-3)$$

The amount of the emission from the rubber q_e per unit time is assumed to be proportional to the product of p and c .

$$q_e = k_eBLDcp \quad (5-4)$$

It is to be noted that the definition of the four flow rates is based on the following assumptions:

- A) The friction force is not directly determined. For convenience, the reciprocal of h is regarded as friction force because it is in the boundary lubrication regime. The validity of this method should be further investigated in the future works.

- B) All variables and constants are given as concepts, with their units not unified, and no direct relationship with actual physical quantities is derived, such as time, dimensions, velocity, pressure, heat, diffusion coefficient, and concentration distribution.

For the derivation of h and c , the following relationships are obtained. Firstly, from the law of conservation of mass :

$$\begin{aligned}\frac{d(BLh)}{dt} &= q_{in} - q_{out} - q_a + q_e \\ &= (k_{in} - k_{out})pVLh - BLD\{k_a(c_s - c) - k_e cp\}\end{aligned}\quad (5-5)$$

Secondly, the following equation is obtained from the change in the concentration of the lubricant at rubber surface:

$$\frac{d(BLDc)}{dt} = q_a - q_e \quad (5-6)$$

$$\frac{dc}{dt} = k_a(c_s - c) - k_e cp = -(k_a + k_e p)c + k_a c_s \quad (5-7)$$

$$\frac{dc}{dt} + (k_a + k_e p)c = k_a c_s \quad (5-8)$$

By solving this differential equation, the following relation is obtained:

$$c = \frac{k_a c_s}{k_a + k_e p} + \left(c_0 - \frac{k_a c_s}{k_a + k_e p}\right) e^{-(k_a + k_e p)t} \quad (5-9)$$

where c_0 is the concentration of the lubricant at $t = 0$.

Here the following relationship is derived,

$$\lim_{t \rightarrow \infty} C = \frac{k_a c_s}{k_a + k_e p} = c_s \times \frac{1}{\frac{k_a + k_e p}{k_a}} = c_s \times \frac{1}{1 + \frac{k_e}{k_a} p} \quad (5-10)$$

Hence, the concentration of the rubber surface converges to the value which is proportional to the saturated concentration and associated with the ratio between the absorption constant and the emission constant in this model.

Eq. 5-5 and Eq. 5-7 with appropriate arrangement yield the following:

$$\frac{dh}{dt} = \frac{pV}{B} (k_{in} - k_{out})h - D \frac{dc}{dt} \quad (5-11)$$

By substituting Eq. 5-9 into Eq. 5-11 and integrating it, the following is derived:

$$h = \frac{D\{c_0(k_a + k_ep) - k_ac_s\}}{\frac{pV}{B}(k_{in} - k_{out}) + (k_a + k_ep)} \left(e^{\frac{pV}{B}(k_{in}-k_{out})t} - e^{-(k_a+k_ep)t} \right) + h_0 e^{\frac{pV}{B}(k_{in}-k_{out})t} \quad (5-12)$$

where $h = h_0$ at $t = 0$.

Numerical simulation is conducted by giving various sets of constants in order to see how this conceptual model can reasonably describe the actual boundary friction behavior of the rubbers.

First, the influence of the sliding speed is shown in Fig. 5-5 and that of absorption rate is shown in 5-6. With non-swollen rubber, COF increased during sliding at the low speed. This decrease of k_a reduces the rate of increase in COF. Namely, if the absorption speed of lubricant into rubber is faster than the speed of introduction of lubricant, COF would increase. This result expressed well the experimental result in Fig. 3-3 and Fig. 3-4.

Next, the influence of the saturated concentration is shown in Fig. 5-7. The larger c_s is, the larger COF is. This is because the absorption rate is assumed to be proportional to the difference between the concentration at surface and saturated concentration of the lubricant. In other words, higher c_s caused the large rate of absorption which resulted in the increase of COF. This calculation explains well the experimental result that NBR1/MO with large saturated swelling ratio showed high COF. In other words, when the saturated swelling ratio is large, there is much room in the rubber for the lubricant to be absorbed. Therefore, the lubricant on the sliding surface decreases, and the friction increases. It can also explain that when the saturated swelling ratio is too large, a cavity was generated.

In this model, the flow of liquid is well represented. In contrast, the model does not explicitly include the influence of cohesion described in Chapter 1, or the relationships with

surface energy, interaction, and polarity described in Chapter 4. These factors are particularly relevant when h is small and this corresponds to the state of high friction in the experimental results. It also relates to the swelling and emission rate. It is necessary to determine the relationship between the parameters, such as k_a and k_e , and physical properties. Furthermore, understanding the relationship between the thickness D of the surface layer and COF will make the model more realistic and more widely applicable.

As seen above, this conceptual model explains reasonably well the experimental results in Chapters 3 and 4. The combination of rubber /lubricant shown in Table 5-1 used in the experiments will now be discussed. The parameters are determined as shown in Table 5-2. As forementioned, these parameters have no direct relationship with any physical properties. Hence, the parameter is determined relatively among the rubber/lubricant combinations. k_a is determined from the order of diffusion coefficient and c_s is determined from the order of swelling ratio. k_{ep} is determined from the order of polarity investigated by the surface free energy and MO simulation.

The results of calculation are shown in Fig. 5-8 and Fig. 5-9. (a) corresponds to NBR1/MO, (b) NBR2/MO and (c) NBR1/HD. (a) shows the increasing COF at early period and decreasing during sliding. (b) and (c) are similar at friction but concentration of lubricant in (b) is higher than that in (c). This implies that the stable coefficient of NBR2/MO is more stable than that of NBR2/HD.

5.4 Summary

A mechanism of boundary lubrication of rubbers in lubricated sliding was proposed based on the experimental findings in Chapters 3 and 4. Friction strongly depended on the amount of lubricant left on the contact surface, which in turn depended on transportation of the lubricants in and out of rubber and lubricant flows in and out of the contact. These flow characteristics depended on the combination of compatibility and polarity.

A conceptual mathematical model was built in order to qualitatively described the changes in the amount of lubricant at the contact surface. The numerical simulation with different combination of flow characteristics revealed that this model could reasonably describe a variety of frictional behaviors that were actually observed experimentally.

Table 5-1 Swelling and polarity of each combination of rubber/lubricant

Swelling system	Polarity of rubber: low	NBR1/MO
		NBR1/HD
	Polarity of rubber: high	NBR2/MO
Non-swelling system	Polarity of rubber: high	NBR2/HD

Table 5-2 Parameters for the calculation with the model

	Polarity of rubber	Lubricant	k_{in}	k_{out}	k_a	$k_e p$	c_s	D
Swelling	Low	Non-polar	1	0.99	1	1	0.5	0.02
Swelling	High	Polar	1	0.99	0.5	0.2	0.1	0.01
Non-swelling	High	Non-polar	1	0.99	0.1	1	0.01	0.001

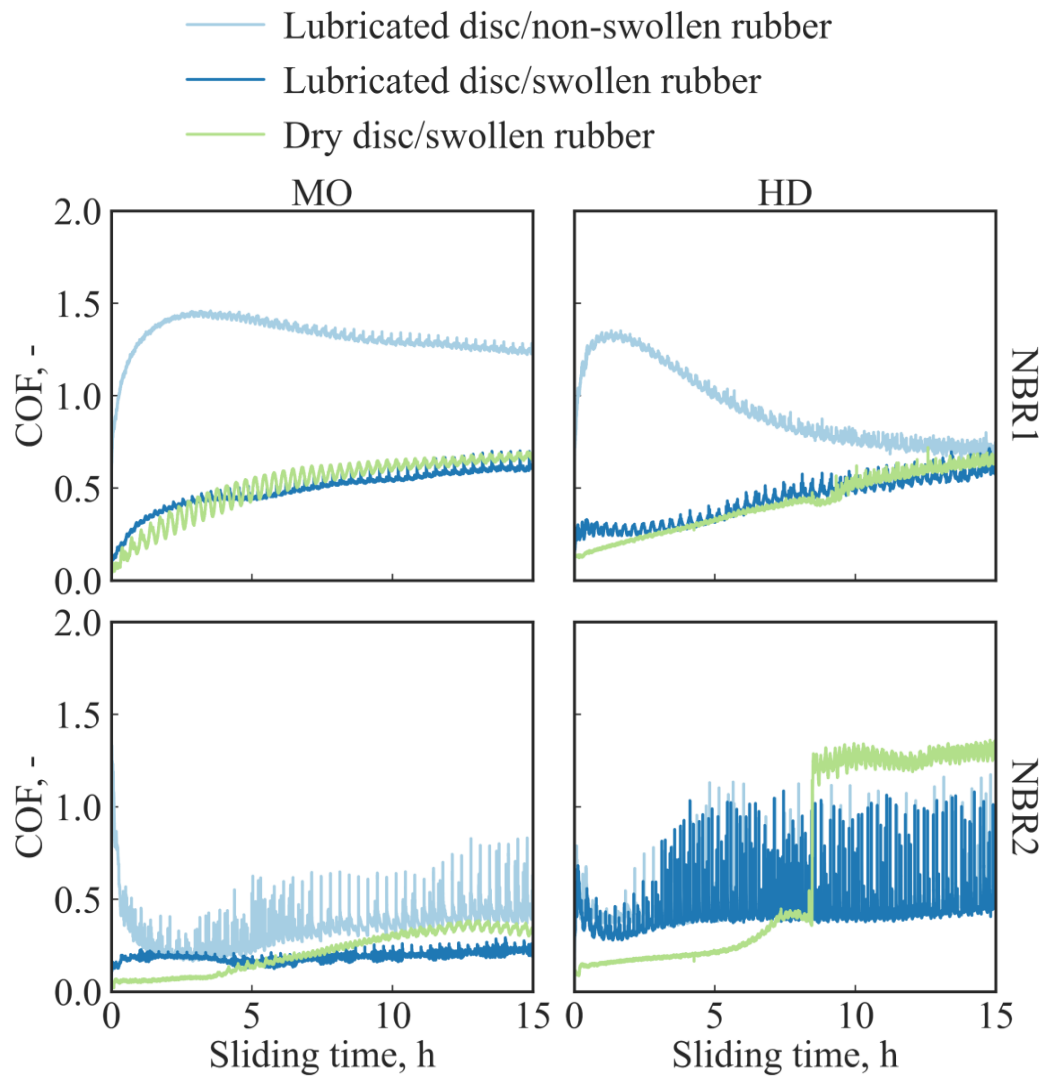


Fig. 5-1 COF at various conditions.

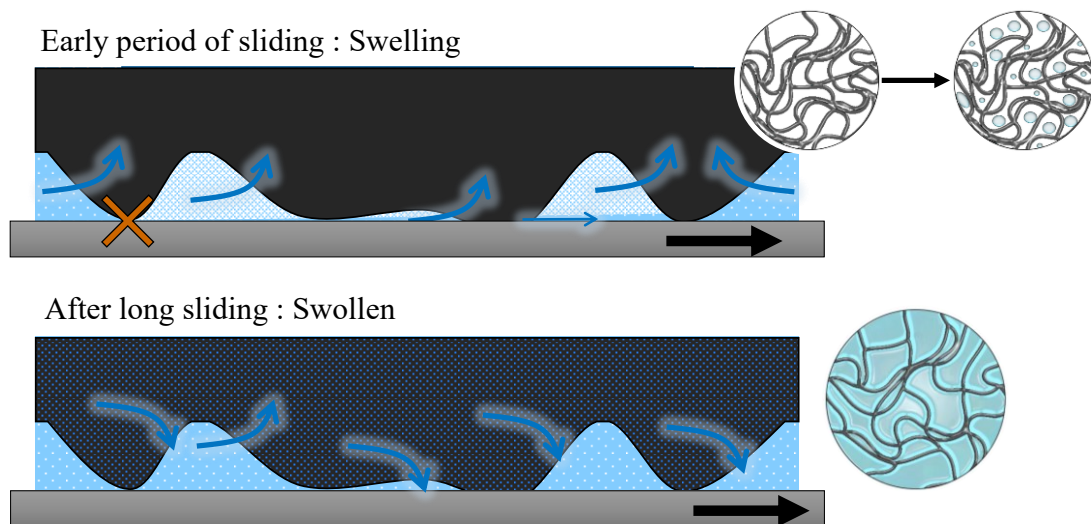


Fig. 5-2 Schematic diagram of lubrication mechanism of swelling system.

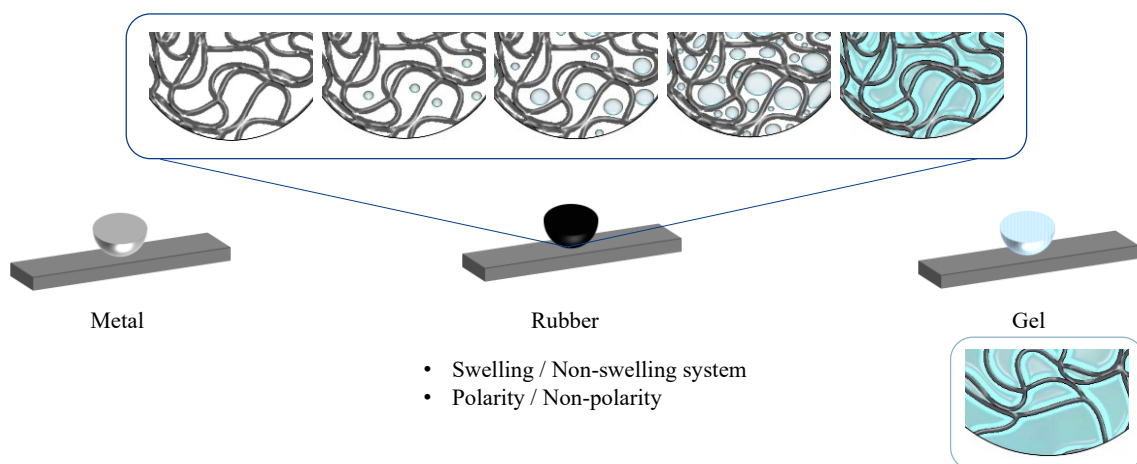


Fig. 5-3 Illustration of the model for the boundary lubrication of the rubber.

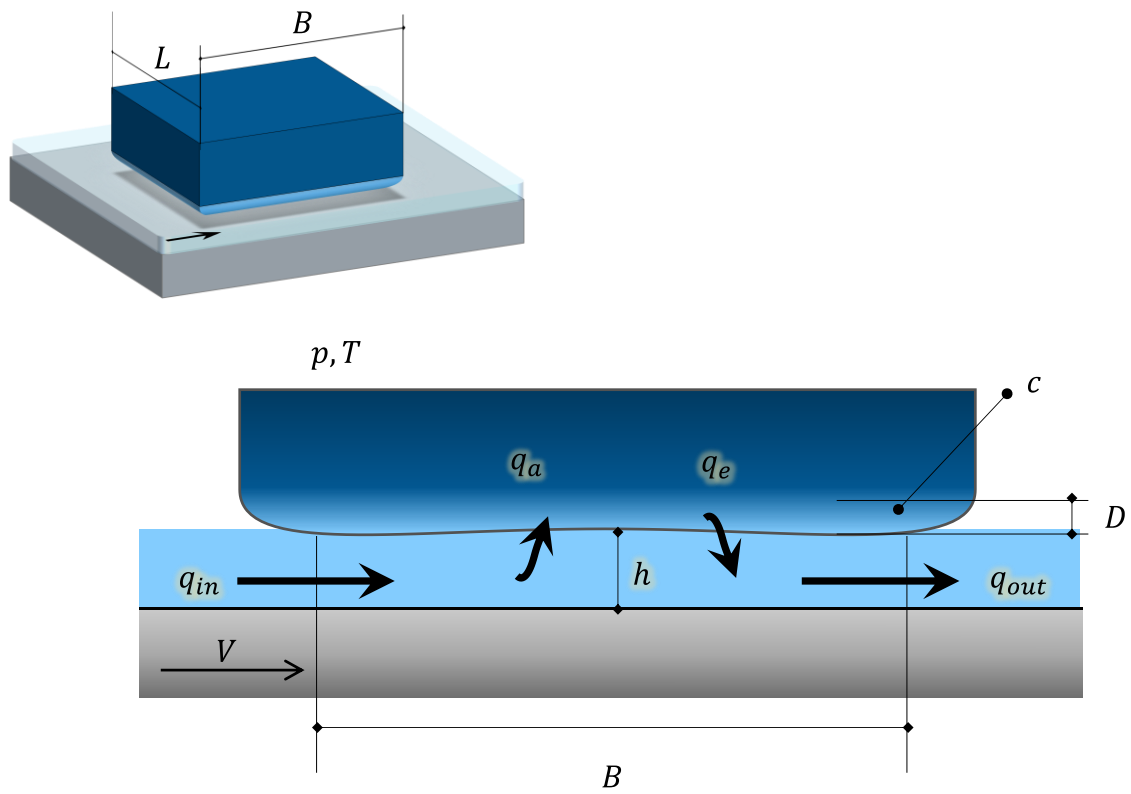


Fig. 5-4 Conceptual model of lubricated sliding contact of rubber.

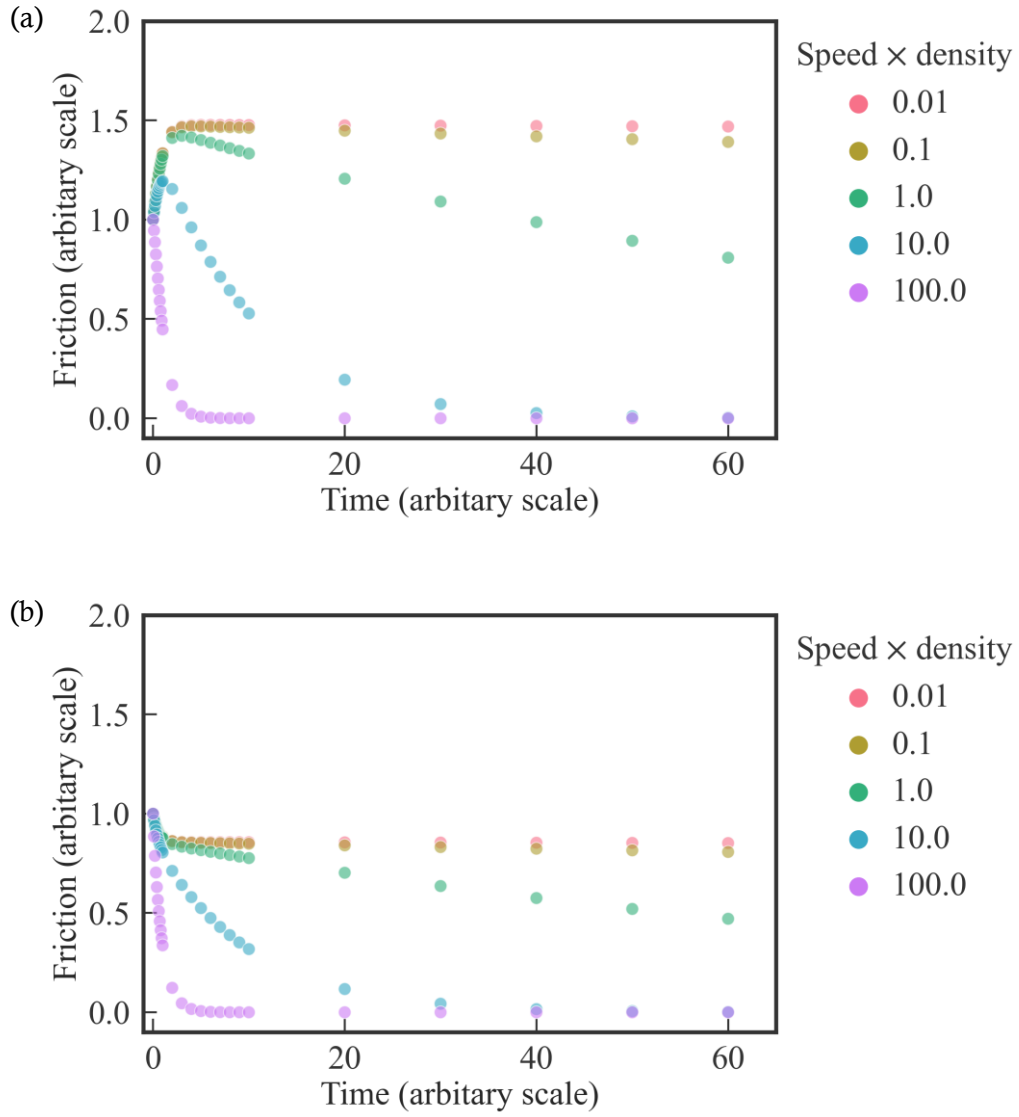


Fig. 5-5 Effect of entrainment speed on friction; (a) non-swollen $c_0 (= 0.01)$ and (b) Swollen state ($c_0 = 0.5$). The other parameters are follows: $k_{in} = 1$, $k_{out} = 0.99$, $k_a = 1$, $k_{ep} = 0.5$, $c_s = 0.5$, and $h_0 = 0.01$.

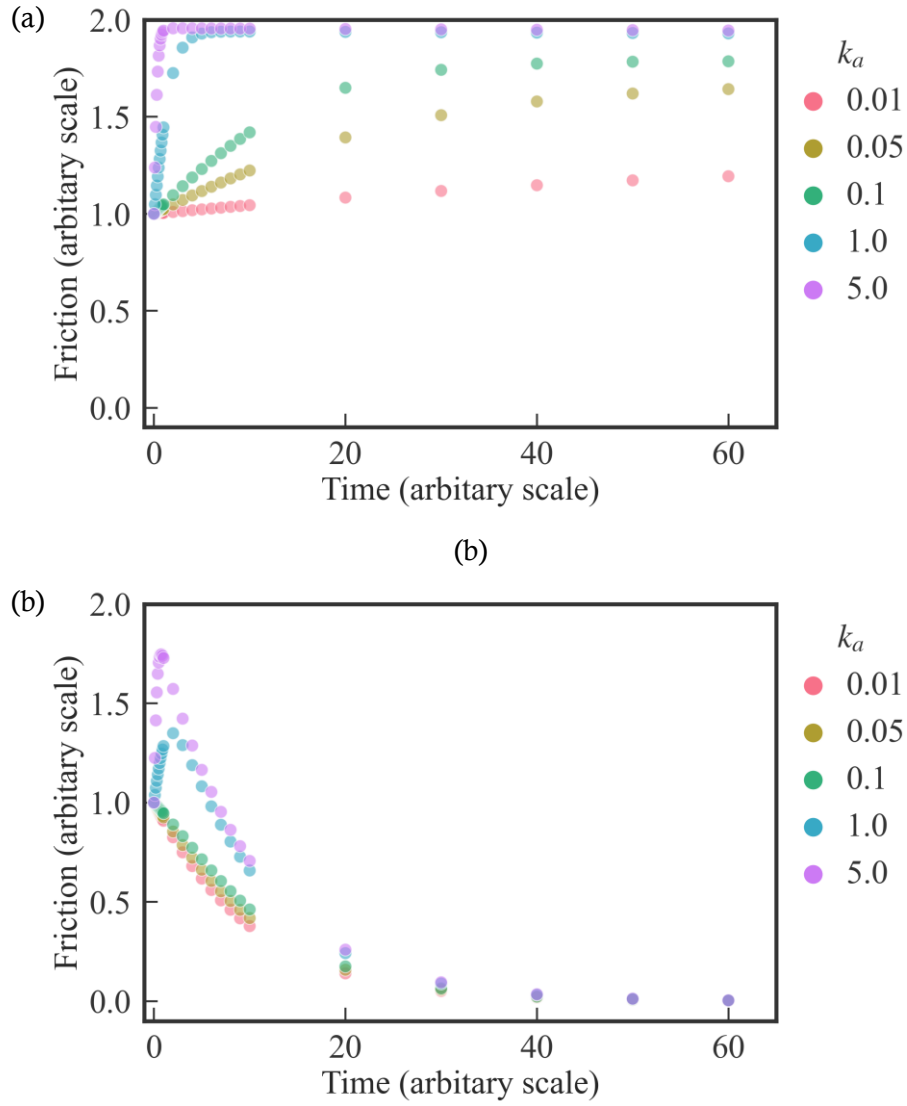


Fig. 5-6 Effect of lubricant absorption rate on friction for different entrainment speed; non-swollen with different k_a when V = (a) 0.1 and (b) 10. The other parameters are follows; $k_{in} = 1$, $k_{out} = 0.99$, $k_{ep} = 0.01$, $c_s = 0.5$, $h_0 = 0.01$, and $c_0 = 0.01$.

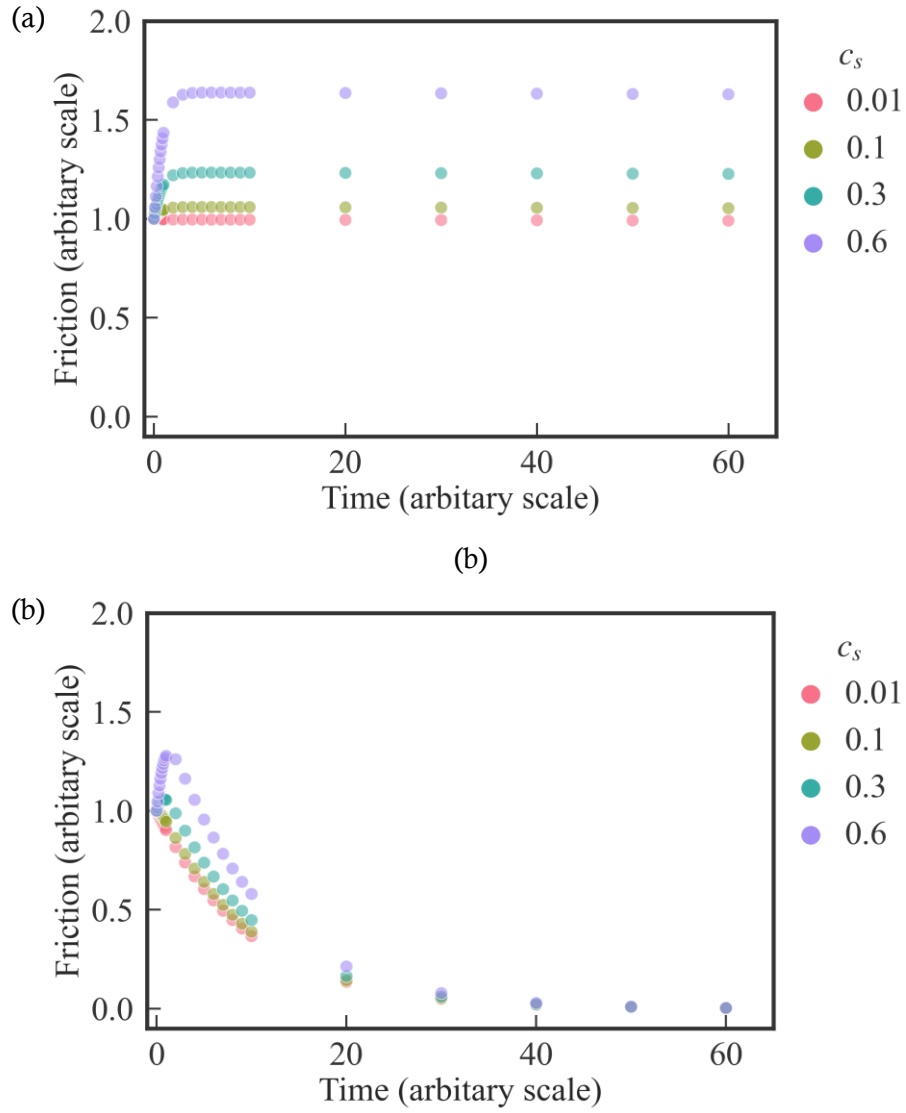


Fig. 5-7 Effect of saturation concentration on friction for different entrainment speed; non-swollen with different c_s when $\rho_v =$ (a) 0.1 and (c) 10. The other parameters are follows $k_{in} = 1$, $k_{out} = 0.99$, $k_a = 1$, $k_{ep} = 0.5$, $h_0 = 0.01$, and $c_0 = 0.01$.

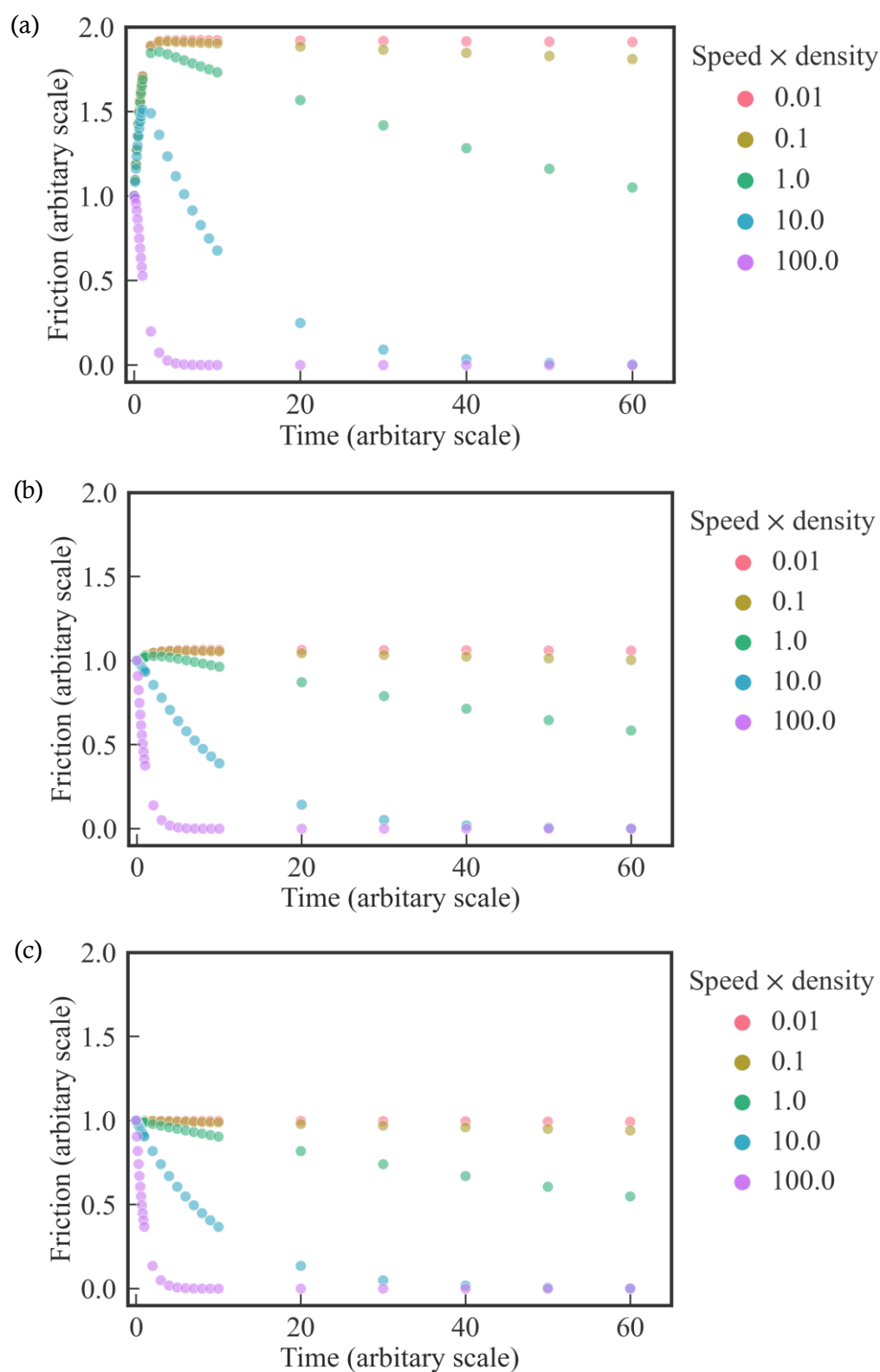


Fig. 5-8 Effect of entrainment speed on friction for swelling system with; swelling system with (a) non-polar lubricant and low polarity rubber and (b) polar lubricant and high polarity rubber, and (c) non- swelling system.

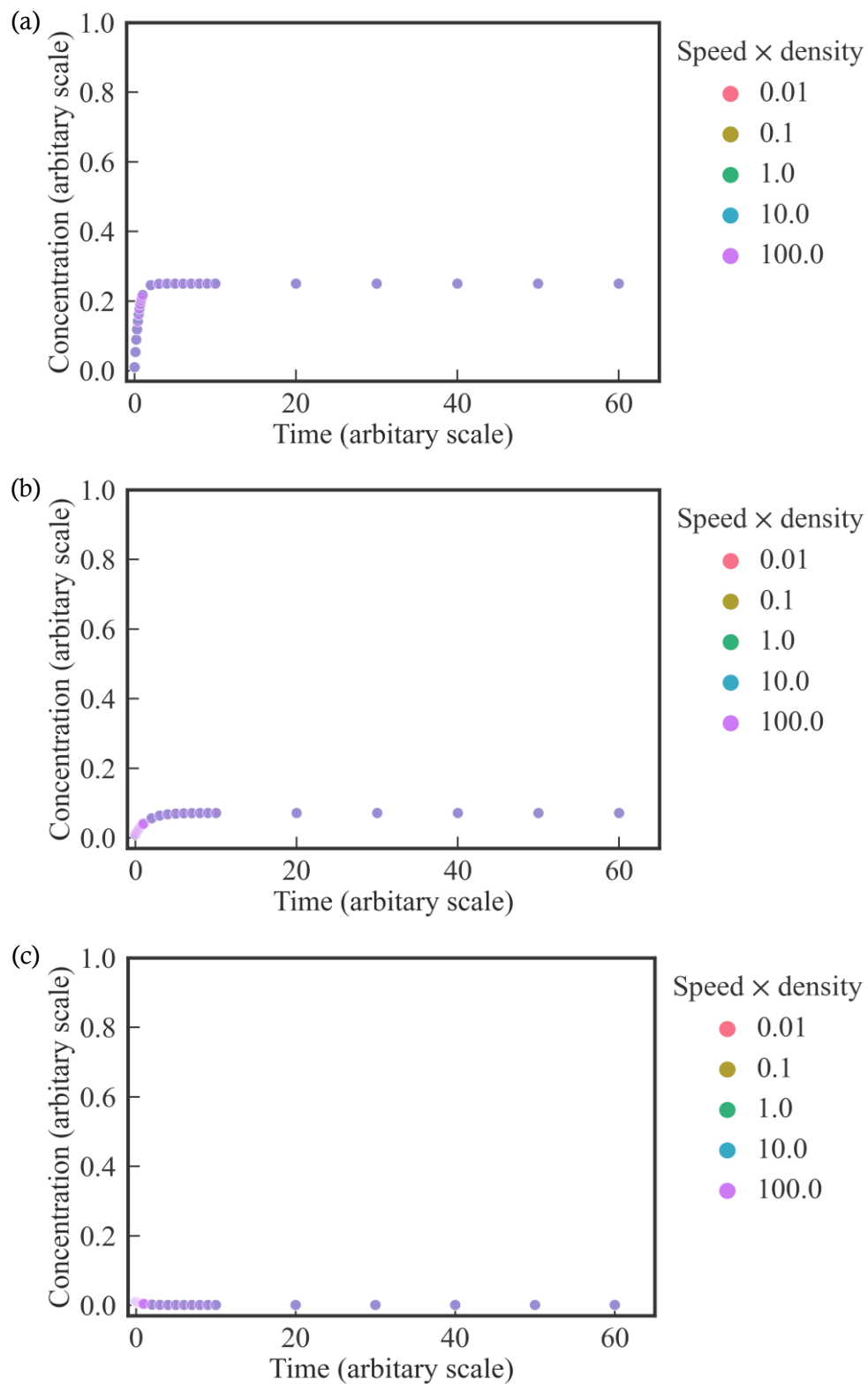


Fig. 5-9 Variation of concentration with time for different k_a , c_s and k_{ep} of Swelling system with; (a) non-polar lubricant and low polarity rubber and (b) polar lubricant and high polarity rubber, and (c) non-swelling system.

6 Conclusions

It is known that boundary friction contributes to the friction of radial shaft seals. However, since the details of mechanism or influential parameters are unknown, the friction coefficient of oil seals is assumed to be a constant value at the numerical analysis of COF. However, it is actually affected by the type of rubber and oil. The purpose of this study was to establish a model for the boundary friction of rubber for the estimation of COF for the radial shaft seals.

6.1 Experimental results and discussion

The friction was investigated by pin-on-disc friction tests, and observation by the total reflection method, using two kinds of the rubber and two kinds of lubricant which had different polarity. The experimental results are summarized as follows.

- (i) When the sliding speed was low, the change of COF during sliding was greatly different among the several combinations of rubber and lubricant. This region was assumed to be the boundary lubrication regime.
- (ii) In-situ FT-IR microscopy showed that the lubricant of the sliding surface increased as the sliding continues.

6.2 Mechanism and conceptual model

Based on these results, and with the additional analysis, the following mechanisms were revealed, and models were proposed.

- (i) A mechanism was proposed in which lubricating film is formed by a movement of lubricant into and out of the rubber. When the compatibility between rubber and lubricant is high, the lubricant is absorbed in the rubber, the boundary lubrication function is lost, and COF becomes high.
- (ii) The swellability influenced the boundary friction. Swelling rate and saturated swelling ratio was found to play an important role. It was clarified that COF was low when

swelling saturated, and the formation of boundary lubricating film was indicated. The compatibility between rubber and lubricant influenced on the swellability. It was evaluated by the measurement of diffusion coefficient measured with permeability test and the calculation of Hansen solubility parameter.

- (iii) Besides, an attraction force generated by polarity of the rubber and the lubricant was also important to maintain the boundary lubricating film. The polarity evaluated by contact angle measurement, and molecular orbital simulation. The polarity resulted the strong intermolecular interaction. The interaction is evaluated by TGA analysis.
- (iv) It was also proven that the boundary lubricating film is maintained when the polarity of rubber and lubricant is high because the rubber and lubricant with high polarity showed stable low COF.
- (v) The boundary lubrication of rubber can be correlated with the movement of the lubricant into/outward sliding surface. The influencing parameters of the friction are the flow rate of lubricant into the sliding surface, flow rate outward the sliding surface, absorption rate into the rubber and emission rate out of rubber. With these factors, a conceptual mathematical model was built in order to qualitatively describe the changes in the amount of lubricant at the contact surface. The numerical simulation with different combination of flow characteristics revealed that this model could reasonably describe a variety of frictional behaviors that were actually observed experimentally
- (vi) The flow into the rubber is induced by the interaction between the rubber and lubricant. It is evaluated as swelling ratio, diffusion coefficient, and solubility. When these parameters are high, the lubricant film is formed. However high interaction between the rubber and the lubricant also causes loss of lubricant depending on the sliding speed. The flow outward the rubber influenced by the attraction force between the rubber and the lubricant induced by the polarity of the molecules. The attraction force helped the maintaining the lubricant film. In the boundary lubrication regime, the intermolecular interaction is important

6.3 Future works

Following points are necessary to achieve in order to clarify details of the mechanism of the boundary lubrication and apply to the practical application

(i) Numerical analysis

The factors of proposed model would be investigated to be described by the physical properties so that COF of radial shaft seals can be estimated quantitatively.

(ii) Method development for thickness measurement of boundary lubrication film FT-IR analysis showed that the thickness of the boundary lubrication film was less than about 100 nm order, but it is not clear whether it is at the molecular level or in the bulk of the order of nm. It would achieve by the further improvement of optical interferometry. The problem to be solved are low reflectivity on rubber, low saturation of the resulting image, and accuracy of calibration. Improvement of optical system and development of data analysis method by programming are necessary.

(iii) Application to products

By focusing on the polarity of rubber and lubricant, the possibility of preventing the loss of the lubricant and the stick-slip on the sliding surfaces was indicated. It is possible to create low-friction parts by applying this to products. The next tasks are that the optimization of the swelling ratio and physical properties because the mechanical properties of rubber deteriorate as it swells.

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Acknowledgement

I am extremely grateful to my supervisor, Prof. Dr. Joichi Sugimura for his continuous support during my PhD study. His wealth of knowledge and experience ,and international mind always guided me through this work. He motivated and inspired me with his invaluable advice and the fruitful discussion.

I would like to express my gratitude to the directors of NOK Co., Ltd., for permission to publish this paper, in particular Dr. Yuki Sato for giving me the chance to obtain my doctorate.

I thank to colleagues in FTI who had a helpful discussion and gave me heartfelt encouragement for the success of my work.

I thank to my family. Yuichi encouraged me as a great husband and also gave me an inspiration as a specialist of rubber chemist. The cheerful nature of Anne and Yugo gave me courage and strength. I hope your life is filled with smiles and happiness. Finally, I am forever grateful for my parents.