ADVANCES IN STUDIES ON THE TRIBOLOGY OF ULTRATHIN FILMS

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SUMMARY
An advance in studies on the tribology of ultrathin films over the years is presented, in which the researches on tribological properties of the Langmuir-Blodgett films, and self-assembled monolayers, as well as the molecular deposition films investigated by the authors and co-workers are primarily introduced. The emergence of atomic force microscope has promoted the development of ultrathin films; especially the Langmuir-Blodgett film is studied extensively. Firstly the research results on various factors affecting the tribological properties of Langmuir-Blodgett films and the progress in molecular dynamics simulation in application to the mechanisms of friction and lubrication are introduced. Secondly a review of the experimental and theoretical researches on self-assembled monolayers is given. Finally the recent advances in the investigation of tribological properties of molecular deposition films deposited on different substrates (Au, Si and Silica rock surfaces) are presented; moreover, the prospect on the tribological application of this ultrathin film is approached.

Keywords: Tribological properties; LB films; self-assembled monolayers; molecular deposition films; molecular dynamics simulation

1 INTRODUCTION
Understanding the tribology of ultrathin films, in particular of ordered molecular films, is of importance for many technologies such as micro-electromechanical systems (MEMS) and magnetic storage systems. The tribological properties of such films have been investigated extensively by atomic force microscope (AFM), friction force microscope (FFM) and surface force apparatus (SFA)[1~15], as well as molecular dynamics (MD) simulations [16~23].

In this paper, the progress in studies on tribological properties of the Langmuir-Blodgett (LB) films and self-assembled monolayers (SAMs), as well as molecular deposition (MD) films is reviewed.

2 LB FILMS
2.1 Experimental studies on the tribological properties
2.1.1 Effect of velocity and load
The dependence of friction and wear on sliding speed for the arachidic acid LB films has been investigated by AFM [1]. It has been found that under the condition of constant normal pressure and temperature, the value of either of wear or friction is a function of low speed scanning on ultrathin organic films. Wear occurred randomly at defective sites is mainly caused by shear forces, and wear occurred in defect-free areas is resulted from adhesive forces.

Hohno and co-workers [24] showed that when the thickness of LB film is beyond a monolayer, the frictional coefficient bears basically no relation to load within the range of given load, which is in accord with the classic theory. In the case of a monolayer, the frictional coefficient is independent of load and decreases with increase in load on condition that the load is much small.

Fujuwara and co-workers [12] have investigated the microscopic frictional properties of two kinds of LB films using FFM. It is found that in case of the normal force being small, the friction force is directly proportional to the normal load. When the normal load is relatively large, the friction load is increased as the 2/3 power of the normal load increases.

2.1.2 Effect of the number of layers
For a given environment and substrate, accumulated number of layers of LB film has a minimum value, less than this number of layers, the more the number of layers, the better the lubrication performance of LB film. Moreover, Fujihira et al [2] found that the frictional coefficient of the five-layer-o-dodecosenoic acid LB film is approximately equal to that of the three-layer LB film, but for the monolayer LB film, this value is lower.

2.1.3 Effect of Chain lengths
n early studies of boundary lubrication, it has been shown that the frictional coefficient of the carboxylic acid film with 6~14 carbon atoms was decreased with the increase in the number of carbon atoms. However, no obvious change in the frictional coefficient was observed while the carbon atoms are more than fourteen [25].

Later, Dominguez et al. [26] investigated the frictional properties of long-chain carboxylic acid monolayers with 12~26 carbon atoms deposited on glass and steel surfaces. It has been observed that the chain length independence of the frictional coefficient is a consequence of the fact that all monolayers have surface densities equal to or greater than 5 molecules /nm². Recently, Fan and coworkers [27] also found that the frictional coefficient of the fluoriated polymer LB films decreases with increasing fluoroalkyl chain length.

2.1.4 Effect of substrates
Adsorptive state and intensity of LB films on substrates are dependent on the physical and chemical properties
of substrates. The adsorption of carboxylic acid on glass is better than that on steel. The frictional coefficient on glass is approximately half of that on steel surface [26]. The thiolipids are covalently bound on gold and physisorbed on mica. The tribological properties of the former are obviously better than that of the latter [28].

2.1.5 Effect of subphase
On increasing pH value, both the Yong's modulus and friction force were found to be decreased [29]. The reason is partly that pH value on the subphase of LB film influences the film forming density as well as the ordered state and the roughness of molecule.

2.1.6 Effect of Electric Field
Liu et al [30] found that in a DC field, the frictional force increases with the DC voltage and wear-life is significantly shorter. On the other hand, in an AC field, the AC voltage and frequency can influence the frictional force.

2.1.7 Effect of Film Forming Substances
The tribological properties of the LB films of fatty acids were systematically investigated [31, 32]. It has been found that both the LB films of fatty acids and surface-modified MoS2 nanoparticles decrease the frictional coefficient of a glass/steel friction pair. Compared to the fatty acid LB films, MoS2 nanoparticles-modified with diacyl-dithiophosphate LB film has a higher antiwear life and load-carry capacity. This is attributed to the good load-carrying capacity of MoS2 nanoparticles.

2.2 Application of MD simulations to the research on tribological properties
MD simulations were used to simulate the sliding of a model bilayer LB film to investigate the friction between two-LB monolayers of model alkane chains [16]. The results showed that there are two kinds of energy dissipation mechanisms, one is continuous, and called 'viscous mechanism' which is similar to the energy dissipation of liquid viscosity, and the other is discontinuous and called 'plucking mechanism' which is followed a simple thermal activation model, in which stored strain potential energy is converted into thermal energy.

Subsequently, Koike and Yoneya [17] carried out the MD simulation of sliding friction of LB monolayers of perfluorocarboxylic and hydrocarboxylic acid on SiO2 and found that the frictional coefficient of the former was about three times as large as that of the latter correspond to the known experimental results. They further suggested that difference of the frictional coefficient was mainly caused by the difference of 1-4 van der Waals’ interaction.

3 SAMS
3.1 Experimental studies on the tribological properties
3.1.1 Effect of chain length
It has been found that the frictional coefficient decreases with the increasing chain length, but when once the chain length is big enough, the frictional coefficient is not change any more [33]. Moreover, longer chain molecules can provide a crystalline structure and enhance lateral cohesion [34]; thus they are better candidates for stable and robust coatings than the shorter chain molecules. However, the longer chain surfactants are less compliant toward shearing and show higher frictional force as compared with shorter chain molecules in a melted state.

In a study conducted by Xiao et al [3] on the friction of a SAM of alkylsilanes on mica, was found to be a strong function of the alkyl chain length, with the shorter chains exhibiting the highest friction.

Recently, a similar conclusion drawn by Lio [4] has been shown that, with more than 8-11 carbons in the chain, the frictional behavior is very similar and independence of long-range order and head group linkage.

3.1.2 Effect of End Groups
The connection between chemical nature, adhesion and friction has established by Frisbie et al [35], they demonstrated different adhesion between surfaces (tip and substrate) coated with molecules exposing a variety of end groups. The adhesive forces were found to be in the order COOH/COOH > CH3/CH3 > COOH/CH3 with the corresponding frictional forces following the exact same order. The interaction between hydrophilic groups, which can form hydrogen bonds, will be stronger than that between hydrophobic groups, whereas the cross-interaction should be weakest.

Moreover, frictional forces are also dependent on the functional groups at the solid/air interface [34]. The terminal functional groups can affect the wettabilities of the surface. Under the condition of high humidity, for the hydrophilic surfaces, the frictional force is decreased through enhancing the lubrication effect of water; as for the hydrophobic surfaces, the friction force is increased through increasing adhesion in the contact zone.

3.1.3 Effect of Film Substances
Blushan et al. [5] studied microtribological characterization of self-assembled monolayer by AFM and FFM and observed that high area density leads to a strong chain-chain interaction, thereby improving the microtribological performance of the monolayer. The C18 double-grafted film on the SiO2/Si (100) surface shows superior microfrictional behavior (the reduction of the friction coefficient from 0.03 to 0.018). Moreover, the nanoindentation studies show that the C18 double-grafted films are much more rigid than the LB films.

Tribological properties of molecular films composed of a C60-SAM, CH3-SAM, as well as an N3-SAM were studied by FFM [13]. These results show that high friction is observed between surfaces that adhere strongly (hydrophilic-hydrophilic) and the lowest friction forces are observed between weakly interacting surfaces (hydrophilic-hydrophobic). The difference in frictional properties of the monolayer films studies may be attributed to the variation of adhesion forces between
hydrophilic SFM tip and film surfaces with different hydrophilicity and roughness.

The frictional characteristics of several types of organic films were tested by scanning probe microscopy [36]. It has been found that the monolayer organic films on inorganic substrates can reduce the frictional coefficient significantly, and the composite NBI/STA monolayers are much more stable and do not damage by high-applied load.

3.1.4 Effect of Load and Velocity

Klein and co-workers [14] have been found that at high shear velocity, the repulsive forces between lubricated surfaces increase with the increasing velocity; however, the frictional forces decrease with the increase in shear force. Late on, they [15] proposed a concept of ‘molecular brush’ to explain the superlubrication phenomena, i.e. the frictional coefficient between mica surfaces bearing end-grafted chain of polystyrene is reduced to 0.001.

The variation in frictional force between self-assembled surfactant monolayers on mica and a silicon tip under the action of dynamic shear was investigated by lateral force microscope [37]. It has been observed that at a fixed shear velocity, the friction force is increased linearly with applied load for both the substrate mica and the monolayer-coated surfaces. At a fixed load, the frictional force increases monotonically with shear velocity for bare mica surfaces, however, for the monolayer surfaces, frictional force initially increases with velocity to a peak and then tends towards stability.

3.2 Application of MD simulations

Tupper and Brenner [18, 19] simulated friction in self-assembled monolayers of alkanethiols on gold by the same way. The results yield a friction force that is proportional to the applied load, in agreement with Amontons' law. Furthermore, they [20] have simulated the effect of surface asperities upon self-assembled monolayers under compression. The results show that the asperities are able to get closer to the substrate relative to the flat surface at comparable loads without completely disrupting the film and that at higher loads the monolayer film disorders by creating a large number of gauche defects in order to accommodate the asperities.

Bonner and Baratoff [21] have performed isothermal MD simulations of CH$_3$(CH$_2$)$_{10}$S self-assembled monolayers on Au (111). With the tip increasing penetration, continuous sliding is followed by stick-slip, leading to net friction, either extrinsic or intrinsic. Molecules close to the tip are strongly deformed, and the simulated SAM domain can be collectively tilted towards the scan direction. Defects in the chemisorbed S-layer are formed and are dragged beyond a critical load. These results provide an insight into the molecular origin of friction and viscoplastic response of model lubricant film.

Recently, MD simulations are used to interpret the difference in wearless friction observed between two monolayers with CH$_3$ and CF$_3$ terminal groups of the same alkyl chains bound at their ends to rigid substrates [22, 23]. The model suggests that the frictional difference can be qualitatively interpreted by the difference in slopes of the corrugated interfacial potentials between two films at the repulsive regions.

4 MD FILMS

MD films [38], a layered and ordered self-assembled monolayer or multilayer ultrathin film, is prepared through electrostatic attraction between opposite charges from cationic and anionic compounds. MD method is a simple and effective approach to make ultrathin films, and is not limited by the shape or size of the substrate. Because of its stronger bonds compared with those of SA monolayer and LB film, the MD film is more durable to heat and more time-stable than the SA monolayer and LB film. However, there are few results reported for the nanotribological properties of MD film.

Wang et al. [6 ~ 11] have systematically investigated the nanofriction features of different MD films on the Au substrate by AFM. The experimental results with a constant scan rate of 20 µms$^{-1}$ indicated that the effects of the load on the frictional force exerting on the various surfaces were different (Figure 1(a)). When the load keeps constant at 25 nN, the effects of the scan rate on the frictional force were also found to be different for various surfaces (Figure 1 (b)) [9].

![Fig. 1: Frictional force vs load (a) and scan rate (b) for different surfaces: ■ clean Au substrate; ● anioned Au surface; ○ alkyl-terminated anioned Au surface; ▼ monolayer MD film; ♦ alkyl-terminated monolayer MD film](image)
It has been concluded that the process of the anioning and the deposition of a monolayer MD film can reduce the frictional force which is under the influence of both the load and scan rate, however, the activities of the charged surfaces make the nanofriction characteristics of the samples unstable. After being decorated with alkyl terminals, the frictional forces of the anioned Au surface and the MD film decrease obviously, and the inactivity of the alkyl terminal makes the nanofriction characteristics of the samples stable. As a result, the frictional forces increase slightly proportionally to the load and the scan rate.

In addition, the micro-friction properties of a MD film on silica rock have been studied with AFM. It has been found that the MD film has lower coefficient of friction as compared with the original surface of silica rock and its value is decreased with the increase in lateral load, which shows that the MD film could improve the friction properties of silica rock surface. Moreover, based on the analyses of the surface force versus distance curves, photographic image, friction force image, and modulated force image, it is concluded that the effect of reduction in friction of MD film on silica rock is attributed to its action of reduction in adhesion and micro-modification.

5 CONCLUDING REMARKS

Despite the fact that the tribological properties of some ordered molecular films (such as LB film) have been studied extensively, their actual application for tribological purpose is still pending further work. Especially, the study on the tribological properties of MD film justly begins. However, the present studies have been shown that some ordered molecular films have an alluring foreground in the tribological application field. Therefore, so long as we persevere, the nano-lubrication technique of these films should be developed in the near future.

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7 REFERENCES