

# Nano-Lubrication: A Review

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*Lubrication is essential for proper and reliable operation of mechanical systems as it is vital to reduce friction and wear of moving components to assure high quality performance. Particularly, with continued development of precision devices the need to acquire effective lubrication technology for micro-systems continues to rise. The challenge lies in the fact that conventional lubrication methods cannot be applied to micro-systems due to viscosity effects. Thus, driven by the needs of precision devices, stringent operating conditions and environmental preservation, numerous alternatives to conventional liquid lubricants have been proposed. In this paper, various lubrication methods to replace or improve conventional liquid lubrication and their characteristics are reviewed. Fundamental mechanism and tribological characteristics of minimum quantity lubrication (MQL), vapor phase lubrication (VPL), and self-assembled monolayer are discussed.*

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## 1. Introduction

Friction is a resistive force that must be overcome to generate relative motion between two components in contact. Combating friction has been an essential task to efficiently transport resources and operate mechanical components. Considering that a wheel is regarded as one of the most valuable inventions of mankind, reduction of friction has been essential to improve the efficiency of machinery and to promote the convenience of common tasks.<sup>1-7</sup>

Generally, friction is attributed to shearing junctions produced at the interface of contacting asperities and deformation of the asperities which accommodates relative motion. Since interaction between two or more than two contacting surfaces dominates the frictional characteristics, an ideal method to reduce friction and wear is to detach the contacting surfaces in relative motion with ease.<sup>8</sup> For this purpose, liquid lubricants have been widely exploited to minimize friction and wear at the interface by separating the contacting surfaces.<sup>9-12</sup>

There are generally three different regimes of lubrication depending on the operating condition: boundary, mixed, and hydrodynamic lubrication. Among them, hydrodynamic lubrication, which is the regime where the lubricant sustains sufficient pressure to prevent direct contact of asperities, exhibits the lowest friction and wear.<sup>9,13</sup> Considering the number of benefits, application of lubricants is regarded as the simplest and the most effective strategy to reduce friction and

wear of mechanical components.

It has been reported that one of the earliest evidence of lubricant usage was found in Egypt about 4000 years ago. This claim was based on the figure that was found in Egypt that showed a large statue being pulled by dozens of men. In the figure, a man pouring some sort of a liquid in front of the statue could be found. It was presumed that the liquid was a lubricant used to lower friction between the statue and the ground. Since then, application of lubricant to numerous machinery has become essential and it is believed that lubricants have significantly contributed to industrial development.<sup>8,9,14,15</sup>

However, exceptional cases where liquid lubricants cannot be applied have emerged with development of new technologies and operating conditions such as micro-electric-mechanical systems (MEMS), high vacuum systems, high temperature/cryogenic systems, and ultra-clean systems. With decreasing dimension of mechanical components, the ratio of surface area to volume increases drastically. In such cases, liquid lubricant may interfere with relative motion rather than reduce friction because of capillary force generated from liquid surface tension. For high vacuum and high temperature operating conditions, application of liquid lubricants is limited because of evaporation. Furthermore, in harsh operating conditions, liquid lubricant can be exhausted immediately and the contacting surfaces may not be protected by the lubricant.<sup>16-18</sup>

In addition to the limitations of using liquid lubricants in extreme conditions, the motivation to decrease the use of lubricants is becoming

more important as environmental issues arise. Since enormous amount of lubricants and cutting fluids are consumed and wasted during manufacturing processes the concern for environmental pollution has been growing with increasing production.<sup>19-27</sup>

Considering the above mentioned issues, an alternative strategy to reduce the use of liquid lubricants or entirely replace it has been in great demand. In this regard, much effort has been devoted in recent years to achieve friction reduction by adopting nano-scale lubrication techniques. Since asperities of the surfaces come on direct contact with each other in the absence of a liquid lubricant, thorough comprehension regarding the behavior of materials at nano-scale is required to minimize friction and wear.

In this paper, lubrication at nano-scale including applications of minimum quantity lubrication and vapor phase lubrication techniques are discussed. Furthermore, the effectiveness of using a self-assembled monolayer, which is an ultra-thin organic film, to reduce stiction and wear in micro-scale contacts is presented. Tribological issues related to these topics, such as the degree of friction and wear reduction and the mechanisms involved are reviewed based on various experimental works reported by researchers.

## 2. Minimum Quantity Lubrication (MQL)

### 2.1 Introduction to MQL

Conventional manufacturing processes consume a massive amount of cutting fluids as coolants and lubricants to reduce heat generation and friction which are significantly related to the quality of product. For several decades, consumption of cutting fluid has increased drastically with increasing amount of production. Mass production systems require faster manufacturing processes which lead to more heat generation owing to increased friction and high rate of chip production at the interface between the cutting tool and the workpiece. Accordingly, more lubricants must be used in order to prevent these problems.<sup>28,29</sup>

However, it also has been reported that liquid lubricants may cause environmental pollution and economic loss. This is because using a large amount of cutting fluid during machining implies tremendous expenses in supplying, cleaning and disposing the fluid. For example, more than 70000 tons and 350 million liters of oil are consumed in a year in Germany and U.S.A., respectively.<sup>30</sup> In order to machine a workpiece using conventional cutting fluid, several equipments for filtering, recirculating, and coolant treatment are required to treat the fluid during the manufacturing process. Considering the operation of these equipments, it has been reported that more than 50% of mechanical energy is consumed during the machining process. Fig. 1 represents the total power consumption during machining processes by applying various methods such as wet, laser assisted machining (LAM), cryogenic, dry, and MQL. Among these processes, it can be readily recognized that wet machining method consumes the highest amount of energy during the process as shown in Fig. 1. This outcome was attributed to the requirement of numerous equipments such as coolant pump for circulate and recycling device for cutting fluids. On the contrary, the MQL process consumes only about half of the energy that is wasted by the wet machining process.<sup>31-33</sup>

Another source of expense is related to the issue of lubricant use.

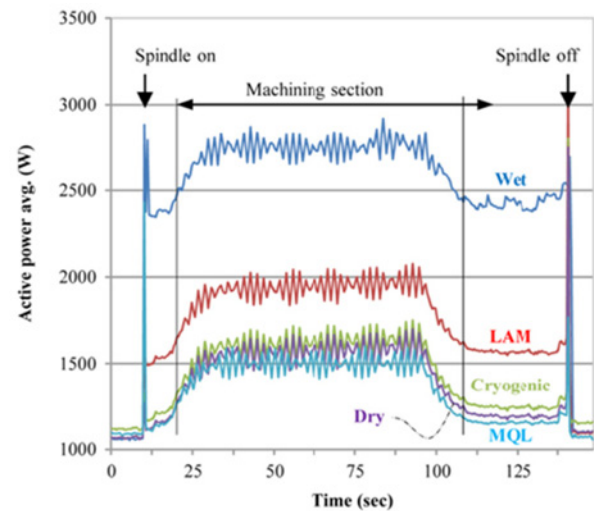


Fig. 1 Power consumption during machining process with respect to machining technique involving with cutting fluid.<sup>31</sup> Reprinted from 31, Copyright 2014, with permission of Springer

Machining processes always produce chips from the workpiece and the chips that are excreted get mixed with the cutting fluid. After the process, cutting fluid must be disposed and cannot be reused as it is, since the fluid is contaminated with chips. In addition, it is also required to clean the workpiece before going on with the next manufacturing process when excessive cutting fluid is utilized. The post cleaning processes lead to additional expenses and environmental pollution. Moreover, cutting fluids typically contain pesticides and preservatives, and hence, contact by the operator may cause negative health effects.<sup>34-37</sup>

The problems associated with excessive use of cutting fluids may be mitigated by MQL technique. MQL process refers to the process of injecting a small amount of cutting fluid as a mist form with compressed air into the spacing between the cutting tool and the workpiece. Particle size of the mist is typically less than  $0.5 \mu\text{m}$  that is small enough to be penetrated into the part with complicated geometry which cannot be readily lubricated by cutting fluid even for high speed machining process. Therefore, it has been reported that heat generation and chip removal at the interface between the cutting tool and the workpiece are minimized and enhanced, respectively, through application of MQL technique.

Although the MQL process utilizes relatively expensive ester vegetable oil, the total cost of coolant is quite low since the amount of oil consumption is less than 1/10000 of that used in a traditional machining process. In addition, there is no need to incur extra costs for storage, recycling, pumping, filtration, and cooling equipments. Furthermore, since workpiece post cleaning is not necessary, it has been reported that the total cost is saved by 15% using the MQL technique.<sup>38</sup> Since the chips produced during the machining process are exhausted without cutting fluid (less than 2%), it can be deduced that MQL reduces industrial waste, prevent environmental pollution and eliminate the health hazard of the operator.

From the view point of environmental pollution and operating cost, there is an obvious advantage of the MQL technique over the conventional method that uses excessive cutting fluid. Additionally,

lifetime of machines is expected to significantly extend because the workplace and machines can be kept clean.<sup>39,40</sup> Based on the advantages of MQL, overall enhancement of machinability can be expected.<sup>41,42</sup>

## 2.2 Characteristics of MQL method

MQL system is classified into external and internal methods with respect to the method of oil supply. The external method refers to supply of oil mist through a nozzle placed closely to the tool surface. Although it is difficult to determine the optimum position of the nozzle, which significantly influences the performance of MQL technique, the external method has a distinct advantage that can be applied to an arbitrary machining systems.

Alternatively, the internal method provides oil mist through the cutting tool which can help supplement the disadvantage of the external method. Through this method, optimum injection of the oil mist can be achieved because it is supplied to the exact interface where the cutting tool and the workpiece are in contact. One concern may be that the setup cost of the internal method is relatively higher than that of the external method.<sup>38</sup>

Typically, two types of lubricants are used in MQL technique. The first is synthesized esters of vegetable oils. They are considered as good lubricants owing to their high ignition point, high boiling point, low viscosity, good lubricity, and high corrosion resistance. Therefore, these types of oils are often used for machining operations in which reducing friction is regarded to be more important than heat dissipation. The other type of lubricant that is used in MQL technique is fatty alcohol made of natural materials or mineral oil. It has been reported that fatty alcohol is quite effective to cool the machined surface and cutting tool while its lubricity is not as good as the synthetic ester oil. Therefore, it is frequently exploited for machining operations that require effective heat dissipation rather than friction reduction. Both types of lubricants are known to be environmentally stable, biodegradable, and nontoxic.<sup>43</sup>

Milling process is generally regarded as an interrupted cutting operation which tend to dry readily since the workpiece and the cutting tool are directly exposed to air. This is unlike other processes such as tapping or drilling where the cutting tool penetrates into the workpiece to preserve the lubricant at the contact interface. Therefore, optimization of conditions to apply the MQL technique to interrupted cutting operations is needed.<sup>38</sup> Application of MQL technique is readily done to machining of casting materials since they are not significantly affected by the cutting fluid. Particularly, gray cast iron can be machined using the MQL technique due to self-lubricating characteristics of carbon in the material.<sup>44</sup> However, it is reported that aluminum is not a suitable material to be machined using the MQL technique.<sup>45</sup>

## 2.3 Tribological investigation of MQL

Since the introduction of the MQL technique numerous studies have been conducted to optimize the technique for various machining operations. Many papers related to MQL are devoted to optimization of MQL parameter of various materials such as cast iron, steel, titanium alloy, aluminum alloy, nickel based alloy (Inconel). Cast iron is relatively easy to convert flood machining to MQL machining. Shen et al. (2008) used MQL technique for grinding of cast iron and added water-based  $Al_2O_3$  and diamond nanofluids to the coolant for enhancing the cooling effect. To investigate the wheel wear and tribological phenomena with

respect to different lubrication condition in MQL grinding, the effects of grinding force, wheel wear ratio, surface roughness, and grinding temperature were assessed. From the result it was derived that dispersed solid particles ( $Al_2O_3$  and diamond) played an important role for decreasing the wheel wear, grinding force, and surface roughness. Especially in the case of  $Al_2O_3$  nanofluid, it was found that higher concentration of nanofluid has better protection of wheel surface. In terms of G-ratio (low wheel wear rate), difference between 4%  $Al_2O_3$  nanofluid and 1%  $Al_2O_3$  nanofluid was 2 times (32 and 16).<sup>46</sup>

In case of steel, there has been a lot of researches about this material since it is one of the most important materials used in a variety of applications. Dhar et al. (2006) investigated the turning process of AISI-4340 steel (C=0.36%, Cr=1.45%, Mn=0.92%, Mo=0.52%, Ni=2.87%, V=0.20%) with carbide tool (SNMM 120408). The turning process was conducted with cutting velocity ( $V_c$ ) 110 m/min, feed rate ( $S_o$ ) 0.16 mm/rev, and depth of cut (t) 1.5 mm in dry, flood, and MQL conditions. After the cutting tests, average principal flank wear ( $V_B$ ), average auxiliary flank wear ( $V_S$ ), surface roughness ( $R_a$ ) were investigated. As expected,  $V_B$  increased with increasing machining time in all cases. However, it was found that the wear incurred in the MQL condition was lower than that of dry and wet conditions. Furthermore,  $V_S$  and  $R_a$  were lower for the MQL condition than for other cutting conditions.<sup>47</sup>

Dhar et al. (2007) also investigated with various conditions of cutting velocity and feed rate for AISI 1040 steel and carbide tool (SNMM 120408). Chip-tool interface temperature, chip reduction coefficient, main cutting force, feed force, average principal flank wear, average auxiliary flank wear, surface roughness, and dimensional deviation were observed in this study. It was found that most parameters such as cutting temperature, cutting force, chip-tool interface, tool wear, surface roughness, and dimensional deviation decreased in MQL condition. Especially, average principal flank wear, average auxiliary flank wear, surface roughness, and dimensional deviation decreased significantly at levels of 40%, 50%, 25%, and 50%, respectively. These results clearly demonstrated that MQL machining leads to lower wear and friction of tool surface and enhancement of tool life.<sup>48</sup>

Ji et al. (2014) investigated the effect of MQL on machining force, temperature, and residual stress of AISI 4130 steel. Tool material used in this study was carbide coated by PVD and cutting was conducted under cutting speeds of 1.049 m/s, 2.098 m/s, and 3.147 m/s; feed rates of 0.0508 mm/rev, 0.1016 mm/rev, and 0.1524 mm/rev. The width of cut was kept constant at 4.775 mm. The performance of cutting was compared with dry and flood cooling conditions with respect to different flow rate of lubricant and three different air-oil mixture ratios. It was shown that flood cooling condition resulted in significant reduction in the cutting force and cutting temperature compared to the dry condition. However, there was no major change between the performance of MQL and flood cooling machining conditions.<sup>49</sup>

Numerous studies employed Taguchi method and ANOVA to optimize the parameters of machining in MQL condition. Dureja et al. (2015) examined the performance of coated carbide tool in turning of stainless steel (AISI 202) under MQL condition. MQL lubricant flow rates of 50, 100, 150 mL/h and adequate cutting speed were selected to minimize tool wear based on Taguchi method. Flank wear of the tool and surface roughness of the stainless steel workpiece were examined after the machining tests. The optimum conditions of MQL parameters

were 58 m/min of cutting speed, 0.06 mm/rev. of feed rate and 100 mL/h of MQL flow rate for minimum flank wear and 23 m/min of cutting speed, 0.07 mm/rev. of feed rate and 150 mL/h of MQL flow rate for lowest surface roughness.<sup>50</sup> Rubio et al. (2014) and Duchosal (2015) also performed optimization of MQL parameters using the Taguchi method and ANOVA.<sup>51,52</sup> They also showed that these techniques are quite effective to identify the optimum conditions for MQL.

Numerous studies on grinding steel have also been conducted with various types of steel and operating conditions. Rabiei et al. evaluate the performance of MQL technique by using two soft steels (CK45 and S305) and two hard steels (HSS and 100Cr6). Two soft steels were CK45 with a hardness of  $90 \pm 3$  HRB (mild carbon steel) and S305 with a hardness of  $25 \pm 2$  HRC (raw HSS). These materials have soft and ductile properties with high elongation rate before fracture. The hard steels used in this work were 100Cr6 hardened steel with a hardness of  $58 \pm 2$  HRC (bearing steel) and HSS with a hardness of  $62 \pm 2$  HRC (tool steel). These materials are hard with low malleability and have low elongation rate before fracture. The grinding wheel composed of aluminum oxide was used in this work. The effects of MQL technique for two different kinds of steel were significantly different. For hard steel, the MQL method was effective to reduce friction which led to less frictional heat generation. The result of hard steel is displayed in Fig. 2. In all cases of specific removal rate, the force ratio ( $F_t'/F_n'$ ) or friction coefficient decreased in MQL condition. This indicated that the small droplet of oil lubricant works as effective lubricant to reduce friction between the contacting surfaces. In addition, surface roughness of hard steel also decreased significantly in MQL condition.

Contrary to hard steels, MQL technique was not effective for grinding of soft steels. In case of soft steel material, both friction coefficient and surface roughness were worse in MQL condition than in dry and flooding conditions.<sup>53</sup> The difference in the performance of MQL technique for the two types of steel materials was attributed to difference in the mechanical properties such as hardness and ductility. As a result, further optimization of parameters for grinding soft steel is required to utilize the MQL technique.

Recently, studies on optimization of MQL technique to machine difficult-to-cut materials such as titanium alloys and nickel based alloy (Inconel), which is a high-tech material, have also been actively conducted.<sup>54-58</sup> Though the MQL technique has not yet been fully developed for a wide spectrum of materials, it is expected that with continued research, MQL technique will be widely employed in the future.

### 3. Vapor Phase Lubrication (VPL)

#### 3.1 Introduction to VPL

Vapor phase lubrication (VPL) is an effective method to reduce friction in harsh conditions where liquid lubricant cannot be applied. As well known, evaporation of lubricants in extremely high temperature systems such as gas turbines and bearings in engine is inevitable. Therefore, preservation of lubricant is essential to maintain adequate lubrication of the mechanical systems in those applications and sealing of the lubricants in such environments is a challenging task.<sup>59</sup> In the case of mechanical systems with small dimensions such as MEMS,

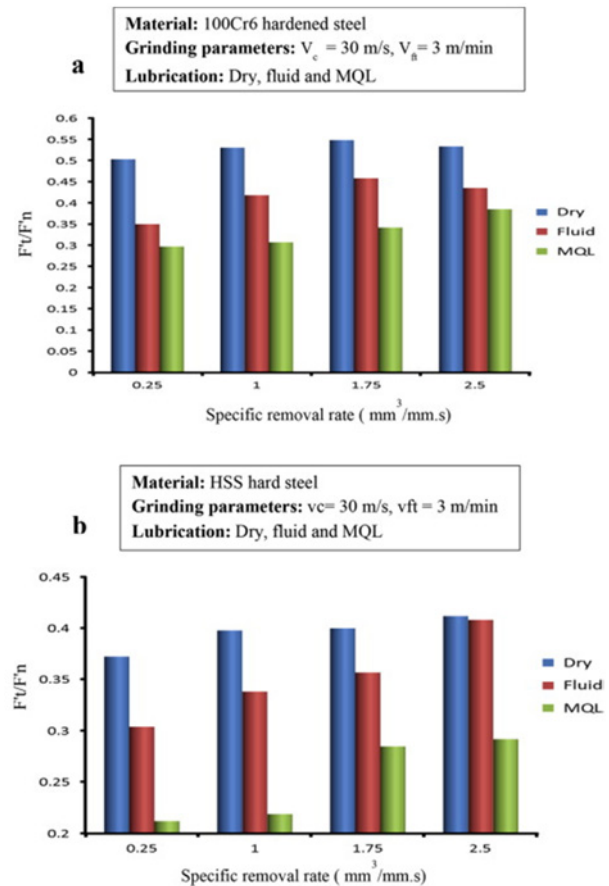


Fig. 2 Friction coefficient of (a) 100Cr6 hardened steel and (b) HSS hard steel with respect to lubrication condition.<sup>53</sup> Reprinted from 53, Copyright (2015), with permission from Elsevier

application of liquid lubricant is limited due to stiction induced by capillary force which makes the system unable to operate.<sup>60</sup> In this regard, practical MEMS devices that involve relative motion between the components typically have been designed to utilize lubricants in solid phase.<sup>61</sup> Considering the limitation of liquid lubricants, demand for an alternative lubricating method has been increasing. VPL is one of those methods that is able to provide sufficient lubricity by transforming a liquid lubricant to a vapor phase.

The first VPL was suggested by Fein and Kreuz in 1965. They reported that cyclohexane hydrocarbon vapor exhibited better lubrication performance than liquid phase. Polymeric deposits which aided in considerable reduction of wear were found when lubrication was done with gaseous cyclohexane hydrocarbon.<sup>62</sup> Since the first report on VPL, applicability of conventional lubricant such as oils, natural fatty acids or phosphate esters for vapor lubrication has gained significant attention.<sup>63</sup>

Vapor phase condensation (VPC), carbonaceous vapor lubrication, and vapor phase deposition (VPD) are the most representative categories of vapor phase lubrication. They are different from each other in terms of lubrication mechanism, but have similarity in delivery method of lubricant, which is in gas phase.<sup>64</sup> For high temperature applications, sealing of lubricant is essential to maintain uniform lubrication condition. On the contrary, condensation of gaseous lubricant may cause serious

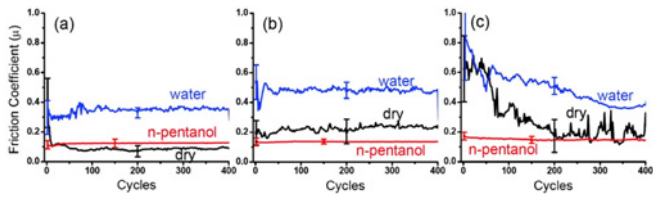


Fig. 3 Friction coefficient in 50% relative humidity (blue), dry argon (black), and 50% relative vapor pressure ( $P/P_{sat}$ ) of n-pentanol (red), where the normal load were (a) 0.1, (b) 0.3, and (c) 0.7 N.<sup>67</sup> Reprinted with permission from 67. Copyright (2009) American Chemical Society

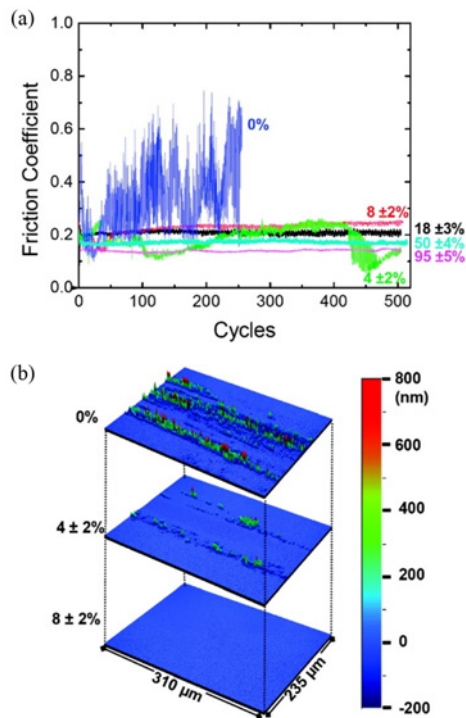


Fig. 4 (a) Friction coefficient and (b) surface profile of wear track on (100) silicon wafer with respect to relative vapor pressure ( $P/P_{sat}$ ) of 1-pentanol.<sup>66</sup> Reprinted with permission from 66. Copyright (2008) American Chemical Society

problem in operating micro-scale device such as MEMS due to stiction.<sup>65</sup> Therefore, attaining balanced condition of lubricants is important, and for this purpose low weight molecules such as (isopropyl) alcohol, methanol, n-propanol, and n-pentanol are usually used since these molecules can be evaporated easily in working conditions or even in ambient room temperature conditions.<sup>66</sup>

The effectiveness of VPL in reducing the friction of  $\text{SiO}_2$  was examined under dry argon, 50% relative humidity, and n-pentanol as shown in Fig. 3. From the figure, it was obvious that friction coefficient of n-pentanol maintained a stable and low value for all the conditions.<sup>67</sup> Fig. 4 displays friction and wear characteristics with respect to the relative vapor pressure of 1-pentanol. It was clearly demonstrated that friction and wear could be improved by providing lubricant in the gaseous phase.<sup>66</sup>

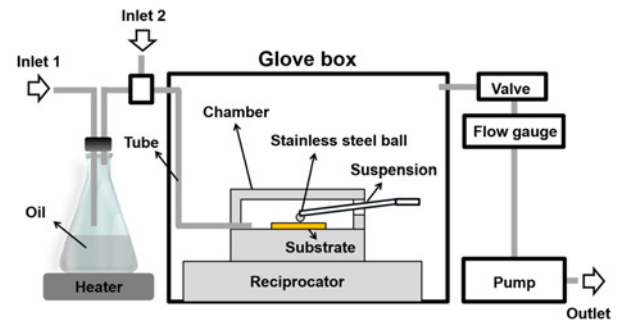


Fig. 5 Schematic of typical VPL system for microscale tribological test. In this system, vapor phase lubricant (oil) was constantly flowed into the chamber, making atmosphere near the sample fresh and steady, while vapor outside of the chamber was flowed out.<sup>64</sup> Reprinted from 64, Copyright 2014, with permission of Springer

In order to sustain stable lubrication for MEMS device through VPL, adequate amount of gas phase lubricant must remain in the system. For this purpose, lubrication systems with a chamber in which lubricant gas is periodically injected are commonly used as shown in Fig. 5.<sup>64</sup> As mentioned, identifying the optimum conditions of VPL to balance the degree of condensation and evaporation of the lubricant in MEMS application is essential since adsorption of gas phase molecules on the component surface significantly influences the lubrication effectiveness.<sup>68-70</sup>

### 3.2 Tribological characteristics with respect to VPL application

There have been a lot of experimental investigations of VPL to better understand the underlying lubrication mechanisms and to optimize the technique. Boehm et al. (2001) assessed the effectiveness of VPL on aluminum surface using a custom in-situ ultrahigh vacuum tribometer with either single species of low-weight molecule (1-hexene and 1-hexanol) or a mixture with oxygen gas. A normal load of 0.5 N and a reciprocating speed of 0.5 mm/s were used in the sliding tests. It was found that a tribofilm formed by chemical reaction in oxygen mixed environment resulted in a friction coefficient as high as 0.7 but the wear resistance was better than that of the single species case in which the friction coefficients were below 0.2.<sup>71</sup>

Sawyer and Blanchet (2001) conducted experiments involving a high speed bearing that operated under severe conditions where the temperature was 540°C and the normal load was 100 N. The corresponding Hertzian contact pressure was about 1.3 GPa. Acetylene was utilized as a vapor lubricant in nitrogen atmosphere on M50 steel specimen. It was found that the friction coefficient decreased to 0.01 with 2.0 m/s rolling and 0.1 m/s sliding combined condition. In this work, they reported that increase of acetylene partial pressure ensures sufficient area of deposition, which is beneficial for reducing the friction.<sup>72</sup>

Strawhecker et al. (2005) investigated the effect of VPL on friction and adhesion reduction at the nano-scale. For this purpose, n-propanol in argon was utilized as the vapor phase lubricant. A normal load from 0 to 100 nN was applied in room temperature using an atomic force microscope (AFM). They reported that the varying tendency of friction coefficient was very similar to that of the adhesion force (pull-off force). This outcome was attributed to the fact that both friction and

adhesion varied proportionally to the contact area. Also, the results showed that increasing the partial pressure of n-propanol lowered the friction force significantly.<sup>73</sup>

Asay et al. (2008) succeeded to operate a MEMS device under contact sliding condition without failure up to 17,000 times longer in VPL condition than in dry sliding condition. In the MEMS experiments, the applied load was 500 nN and reciprocated at 100 Hz with 18  $\mu$ m stroke in room temperature. They employed 1-pentanol vapor with dry nitrogen as a vapor phase lubricant and assessed the lifetime of MEMS sidewall devices with respect to the partial pressure of the alcohol. Also, adhesion and static friction forces were measured at the initial state as well as after the failure. During dry nitrogen atmospheric condition, the friction coefficient increased significantly which led to accelerating the failure of the MEMS device.<sup>60</sup>

In a tribochemical study of VPL done by Barnette et al. (2009), the effects of three different argon based lubricant conditions (dry, 50% relative humidity, and 50% partial pressure of n-pentanol vapor) on the chemical properties of SiO<sub>2</sub> surface were assessed. Contact load was set to 0.1 to 1 N which corresponded to Hertzian contact pressure of 0.19 to 0.4 GPa. The sliding speed was set to 0.3 cm/s and the experiments were performed at room temperature condition. It was found that adsorption of the alcohol molecules on the surface enhanced the wear resistance significantly. Overall, the lowest wear was achieved with VPL using n-pentanol at 50% partial pressure.<sup>67</sup>

Martin et al. (2010) assessed the tribological properties of hydrogen-free tetrahedral amorphous carbon under VPL conditions. They conducted tribological experiments under the condition of 345 MPa maximum contact pressure and 1 mm/s reciprocating speed in 80°C temperature environment. The best results were achieved with hydrogen peroxide hydroxylated (10,000 Pa) ta-C surface exposed to 1 Pa of glycerol vapor, rather than in ultrahigh vacuum or 100 Pa of glycerol vapor condition. It was concluded that H/OH-terminated surfaces attributed to either hydrogen peroxide hydroxylation or glycerol dissociation that led to low frictional behavior with unmeasurable wear.<sup>74</sup>

In the study conducted by Marino et al. (2011), alternating high and low frictional behavior appeared in dry argon ambient condition with hydrogenated diamond-like carbon (DLC). Pin-on-disk tribological experiment were performed with 1 N of normal load and 2 mm/s of sliding speed in room temperature. The alternating frictional behavior could be suppressed in n-pentanol vapor environment. Furthermore, in terms of wear characteristics, n-pentanol vapor environment showed ultrahigh wear resistance compared to those of dry argon and humid conditions.<sup>75</sup>

Recently, Yoo and Kim (2014) investigated the effects of using high molecular weight lubricants for VPL. In this work, canola and silicone oils were used to lubricate aluminum and copper specimens. The experiments were performed with a normal load of 10 mN and 5 mm reciprocating stroke at 1 Hz in room temperature. Experimental results showed that both oils were effective for reducing and stabilizing the friction force. For aluminum specimen with canola oil VPL, the friction coefficient decreased significantly from 1.17 to 0.32. On the contrary, it was found that silicone oil could be decomposed during the sliding process which led to noticeable increase in the friction coefficient.<sup>64</sup>

From the results presented by numerous researchers on the effectiveness of VPL technique, it may be concluded that it is a viable

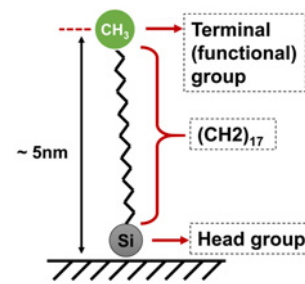


Fig. 6 Schematic of self-assembled monolayer (octadecyltrichlorosilane)<sup>76,77</sup>

method to reduce friction and wear in conditions where conventional liquid lubrication method cannot be readily applied. However, for wider application of VPL, more studies are needed to identify the types of lubricants that can be utilized for this purpose as well as the scope of materials that can be used for VPL.

## 4. Self-Assembled Monolayers (SAMs)

### 4.1 Tribological characteristics of SAMs

Self-assembled monolayers usually refer to a layer of molecules adsorbed on a substrate with molecular order. Assembly of the molecular structure is based on the chemical reaction that takes place at the surface of the substrate to acquire a stable energy state.<sup>76</sup> SAMs consist of head group, alkyl chain, and terminal group as shown in Fig. 6. The figure represents a schematic of octadecyltrichlorosilane (OTS), which is one of the common SAMs used to lower the surface energy of the substrate. SAMs have been extensively studied since they possess attractive characteristics such as low friction, low wear, and low surface energy.<sup>78</sup> Particularly, applications of SAMs have been focused on MEMS and precision mechanical devices where conventional lubrication methods cannot be employed.

SAMs are generally attached to a solid surface by the chemisorption of the head group. Since different head groups are adsorbed on different surfaces, SAMs are usually classified with respect to the head group. In this regard, to attain maximum positive effect, proper SAMs have to be utilized for a certain solid surface with respect to the application and purpose. In addition, tribological characteristics of SAMs with different head groups also have to be assessed. Because of their many advantages, numerous studies on the tribological behavior of various SAMs have been reported. Several types of self-assembled monolayers such as thiols, silanes, fatty acid, stearic acid, and sulfides have been exploited for various purposes and examined to investigate their friction and wear characteristics.<sup>79-82</sup> The studies are mostly involved with friction and wear characteristics of SAMs with respect to the normal force, humidity, temperature, and velocity of the sliding system.

### 4.2 Tribological characteristics of SAMs base on silane head group

Several studies related to the tribological characteristics of silane films have been reported since they adsorb readily to Si surface which is the base material used for MEMS. Rhe et al. reported the tribological behavior of various SAMs using a tribometer in macro-

scale. In this study, they used various alkylsilane films including hexamethylenedisilazane (C1), dimethyloctylchlorosilane (C8), dimethyldodecylchlorodane (C12), dimethyloctadecylchlorosilane (C18), dimethyltriacontylchlorosilane (C30), ethyloctadecyldichloro-silane (ODS), and OTS. The alkylsilane films coated on Si wafer with native oxide were examined to investigate their durability. The sliding tests were conducted with a normal force of 0.15 N and a speed of 1 m/s in rotational motion. It was found that OTS showed the longest lifetime compared to the others. This outcome was attributed to the fact that OTS had the longest chain length among all of SAMs. The experimental results showed that SAMs with short chain length such as C1 and C8 did not provide sufficient lubrication effect and they were readily deteriorated during the tribological experiment.<sup>83</sup> Srinivasan et al. compared the adhesion characteristics between OTS and perfluorodecyltrichlorosilane (FDTS) using a cantilever beam array (CBA). They assessed the adhesion properties of SAMs by observing the release behavior of the cantilever from the surface. Since both of the SAMs were non-polar, water contact angle of the SAMs were above 110°. However, when a non-polar liquid such as hexadecane was dropped on the surface, the contact angle was below 70°. They suggested that higher contact angle of FDTS than OTS when hexadecane was used was due to lower polarity of C-F bond than C-H bond. It was also revealed that adhesion of SAMs was significantly lower than the bare Si surface. Moreover, thermal stability of SAMs was found to be degraded with respect to temperature increase, particularly in air environment.<sup>84</sup>

Tian et al. reported the frictional behavior of N-Octadecyltriethoxysilane (OTE) using an AFM. In this study, normal force, relative humidity, and temperature were varied to assess their effects on the frictional behavior. The results showed that friction of mica decreased with increasing level of relative humidity. It was presumed that the water molecules condensed readily on the mica surface since mica was hydrophilic and the condensed water provided the lubricious property. Interestingly, the influence of humidity was apparent even though the SAMs were hydrophobic. The reason for the humidity dependence of the SAMs could be explained by penetration of the water molecules between the OTE/mica interface since the alkylsilane monolayer was not compactly packed. When the relative humidity was sufficiently low (5%), friction increased with increasing temperature. However, when the humidity was high, friction was independent at low temperature while it was dependent at high temperature.<sup>85</sup>

Choi et al. examined the frictional characteristics of heptadecafluoro-1,1,2,2-tetradecyltriethoxysilane (FTE) and PFPE. The films were coated on DLC surface by the immersion process. Friction experiments were conducted using an AFM with normal force ranging from 5 to 45 nN. It was found that water contact angle on FTE coating was about 100° and lower friction was exhibited when FTE and PFPE was deposited on DLC compared to the bare DLC surface. In addition, it was revealed that friction force increased proportionally with increasing normal force which indicated that the friction coefficient was quite stable over the range of normal forces used in the experiment.<sup>86</sup>

Tribological studies using AFM has also been conducted using perfluoroalkylsilane (PFTS) and alkylsilanes (ODMS and ODDMS). These films were coated on Si wafer with native oxide and glass disk

with pure SiO<sub>2</sub> coating. Adhesion, friction, and wear of the SAM coatings were investigated using an AFM and compared with the results obtained using a tribometer in macro-scale. For the experiments conducted using an AFM, the normal force applied ranged from 5 to 100 nN and the scan speed and area were 1 Hz and 1×1 μm, respectively. As for the water contact angle measurement, PFTS showed the highest contact angle and that of ODDMS was the lowest regardless of the substrate material. It was found that adhesion decreased when SAM coating was deposited on the Si surface compared to the bare surface.

As for the frictional behavior, PFTS exhibited slightly higher friction than the other SAMs. This was attributed to the stiffness of the perfluorinated chain of PFTS which was higher than that of the alkylcarbon chain. The C-C bond of alkylcarbon was presumed to rotate easily and this behavior may lead to low friction force. On the contrary, when the experiments were carried out in macro-scale, PFTS showed a relatively lower friction unlike the results of the nano-scale experiments.

Wear tests using the SAMs showed that degradation of the substrate surface occurred over a certain normal force that could be regarded as the 'critical load' while wear of the Si surface without SAM coating was proportional to the normal force.<sup>87</sup>

Tambe et al. also performed a comprehensive tribological investigation of SAMs using an AFM for a variety of material combinations. They used various thin films such as octylphosphonate (OP) and octadecylphosphonate (ODP) for Al, n-octyldimethyl (dimethylamino)silane (ODMS) and n-octadecyldimethyl (dimethylamino)silane (ODDMS), perfluoroalkylsilane (PFTS), pentafluorophenyltriethoxysilane (PFPTES) and fluorinert for Si. Substrates used in the experiments to deposit the thin films were Al and Si with native oxide. In this study, the adhesion and friction forces were measured with an AFM and the influence of environmental conditions was examined by controlling the relative humidity. Adhesion and friction forces of the films were found to be smaller than those of the bare substrate. Furthermore, it was found that friction of bare Al surface and SAMs on Al surface exhibited lower friction than that of bare Si surface and SAMs on Si surface. This outcome was presumed to be due to the relatively high roughness of Al and packing density of the SAMs on Al. In addition, friction of SAMs with fluorocarbon backbone chain was higher than that of SAMs with hydrocarbon backbone chain. This was due to the higher stiffness of fluorocarbon chain as explained previously.<sup>77</sup>

Friction coefficient of SAMs based on silane head group with respect to contact pressure and sliding velocity is displayed in Fig. 7. As shown in the figure, it was apparent that friction coefficient of SAMs was mostly less than 0.2 and it varied with respect to contact pressure, sliding velocity, and molecular structure of SAMs.

### 4.3 Tribological characteristics of SAMs base on thiol head group

Kim et al. reported a nano-scale frictional study on various SAMs such as n-octyltrichlorosilane, 1H,1H,2H,2H-perfluorodecyltrichlorosilane, tridecanethiol, 13,13,13-trifluorotridecanethiol using an AFM. Normal force applied during the friction experiment ranged from -5 to 30 nN. The results showed that high friction force was measured when the thin film consisting of fluorinated alkyl chain was examined. Among the SAMs, tridecanethiol exhibited the lowest friction.<sup>91</sup>

Bhushan and Liu reported the tribological behavior of thiol thin films

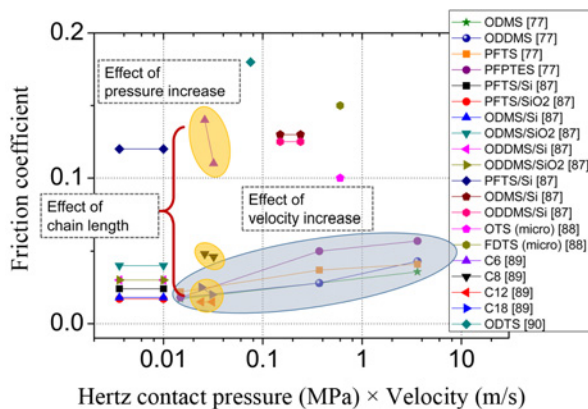


Fig. 7 Friction coefficient of various types of SAMs based on silane head group with respect to contact pressure and sliding velocity<sup>77,87-90</sup>

such as Hexadecane thiol (HDT), 16-mercaptohexadecanoic acid thiol (MHA), 1, 1'-biphenyl-4-thiol (BPT), cross-linked BPT (BPTC) deposited on Au (111) and 4,4'-dihydroxybiphenyl (DHBp) film deposited on a hydrogenated Si(111) surface. They examined the adhesion and friction characteristics using an AFM and also measured the water contact angle. Through the experimental results, it was verified that HDT showed the lowest adhesion and friction force and the highest contact angle due to low adhesion characteristics of  $\text{CH}_3$ , the terminal group of HDT. Furthermore, it was found that molecular spring constant of the SAM chain affected its frictional behavior in nano-scale. The wear properties of the SAM films were also measured by obtaining the wear depth. It was determined that DHBp showed the best wear resistant characteristics due to its biphenyl structure with high stiffness and strong interfacial bond between Si and oxygen.<sup>92</sup>

Liu et al. reported a study regarding the tribological behavior of biphenyl thiol investigated using an AFM. In this study, thin films such as 1,1'-biphenyl-4-thiol monolayer (BPT) and cross-linked BPT monolayer (BPTC) on Au(111) were assessed. Adhesion of the SAMs was found to be smaller than that of bare Si(111) and Au(111) surfaces. For the friction tests, a normal force from 5 to 100 nN was applied. It was found that friction increased proportionally with respect to the normal force. In addition, friction force for BPTC was found to be higher than that of BPT since more energy was required for orientation of the BPTC molecules due to cross-linking of biphenyl.<sup>93</sup>

Sung et al. exploited thiol thin film as the resist layer for fabrication of micro patterns. For this purpose, experiments were carried out to assess the tribological characteristics thiol films using an AFM. In this study, four types of thiol thin films such as 1-heptanethiol (HT), 1-decanethiol (DT), 1-dodecanethiol (DDT), and 1-hexadecanethiol (HDT) were examined. According to the experimental results, it was found that SAMs with short chain length showed lower friction than those with long chain length due to difference in the recovery time.<sup>88</sup>

Qian et al. investigated the tribological properties of SAM with respect to various environment. In this work, octadecyltrimethoxysilane (OTE) on  $\text{SiO}_2$  and N-alkanethiols ( $n=9, 17$ ) on Au(111) surface were chosen to be examined. In this study, it was found that friction of Si and Au without SAM coating increased at low humidity and decreased at high humidity. However, there was no significant difference in friction

of SAM coatings with respect to relative humidity. It was suggested that in the case of Si and Au surfaces, high viscosity of the water molecules due to confinement effect at the contact point resulted in high frictional interaction. Furthermore, relatively low friction at high humidity was attributed to low viscosity of water multilayers. On the other hand, influence of relative humidity on the friction of SAM coatings was significantly decreased due to their hydrophobic properties.<sup>94</sup>

#### 4.4 Tribological characteristics of multi layer of SAMs

Recently, In addition to monolayer SAMs, several studies have been reported that are related to the tribological characteristics of multi-layer SAM coatings. Ren et al. reported a study regarding the frictional behavior of dual layer SAM consisted of polyethyleneimine (PEI) and stearic acid (STA). In this study, the tribological behavior of the SAMs were investigated using an AFM as well as a tribometer in macro-scale. Experimental results showed that Si without coating exhibited the highest friction and STA-PEI showed the lowest friction. It was suggested that friction of STA-PEI was low since the long chain of STA allowed for ease of shear and rearrangement of the molecules along the sliding direction. When the macro-scale friction was assessed, early failure of PEI was observed while STA-PEI maintained low friction for a relatively long time. The good wear resistance of STA-PEI was attributed to various reasons such as elastic behavior of STA and hydrogen bond in STA-PEI that made the molecular structure recover readily after deformation.<sup>83</sup>

Tribological study using 3-aminopropyltriethoxysilane (APS) and perfluorododecanoic acid (PFDA)-APS dual layer film was reported by Mo et al. They measured the adhesion and friction forces using an AFM and showed that adhesion and friction of Si was the highest followed by APS and PFDA-APS dual layer film. The reason of the low friction of PFDA-APS dual layer film was explained based on the compliant behavior of PFDA that allowed rotation and rearrangement of the molecules due to its long chain length. When the friction experiments were conducted in macro-scale, it was revealed that friction of APS was the highest and that of LA-APS was the lowest. It was suggested that PFDA-APS showed relatively higher friction than LA-APS because of the high stiffness of the fluorocarbon backbone chain.<sup>95</sup>

Zhao et al. reported a study conducted using an AFM to investigate the tribological behavior of a dual layer self-assembled film. In this study, (3-mercaptopropyl) trimethoxysilane (MPTMS) and octadecyltrichlorosilane (OTS) were used. For fabrication of the dual layer film, OTS was assembled on the MPTMS film that was deposited on an Au substrate. Tribological characteristics such as adhesion, friction and wear of the films were investigated using an AFM. From the adhesion measurement results, it was determined that the adhesion force of MPTMS was higher than that of the bare Au surface. This unexpected result was attributed to the formation of a hydroxyl group which caused the formation of hydrogen bonds between the  $\text{Si}_3\text{N}_4$  AFM tip and the MPTMS surface. The adhesion force of the OTS-MPTMS dual layer was the lowest. This outcome was attributed to the hydrophobic property of OTS SAM. When the frictional behavior was examined, it was shown that friction decreased drastically with the SAM coatings. In addition, it was also revealed that OTS-MPTMS dual layer displayed better wear resistance. It was presumed that high load carrying capacity provided by the rigid and cross-linked layer of



MPTMS and lubricious characteristics of OTS reduced the friction and wear significantly.<sup>96</sup> Zhao et al. also investigated the tribological characteristics of self-assembled triple layer films using an AFM and a macro-scale tribometer. In this study, 3-glycidoxypropyltrimethoxysilane (GPTMS), 3-aminopropyltriethoxysilane (APTES), and octadecyltrichlorosilane (OTS) were combined and examined to assess the characteristics of the triple layer film. First, GPTMS was deposited on a Si surface and then APTES was coated on the GPTMS film. For fabrication of the triple layer film, OTS was finally deposited on the APTES-GPTMS layers. It was found that the adhesion force of APTES-GPTMS was the highest and that of OTS-APTES-GPTMS was the lowest. In the case of GPTMS coating alone on the Si surface, the adhesion force was higher than the bare Si surface due to the oxygen atoms in the terminal epoxy group of GPTMS. In addition, APTES-GPTMS dual film showed a high adhesion force due to the alkoxy-silane-terminated group (Si-OCH<sub>2</sub>CH<sub>3</sub>) that was hydrophilic at the surface.

As for the frictional behavior, it was proposed that OTS-APTES-GPTMS triple layer showed much lower friction coefficient than the Si surface since the long chain of the triple layer exhibited molecular spring effect that allowed the ease of orientation and compression of the molecules which aided in lowering the friction force. When experiments were conducted in macro-scale, it was found that friction of GPTMS increased abruptly at the initial stage and the OTS-APTES-GPTMS triple layer maintained a low friction coefficient for a long time. Based on these results, it was apparent that the triple layer film provided good lubrication and wear resistant properties compared to single or dual layer thin film.<sup>97</sup>

Extensive studies on the nano-lubricating properties of SAMs suggest that these thin organic films are very effective in reducing friction and wear at the micro/nano-scale. Furthermore, since the chemical structure of the SAMs can be customized with respect to terminal groups, head groups, and chain length, their physical properties may be varied widely. Combined with the ability to form more than one layer, SAMs show great potential to be used as low friction and high wear resistant film for precision devices.

## 5. Conclusions

With advancement and development of precision mechanical systems, the need to lower friction and wear of the moving components continue to arise. Since liquid lubricants cannot be utilized in certain systems such as in MEMS, novel lubrication techniques need to be sought. In this regard, understanding the current capabilities of nano-lubrication techniques is important.

MQL technique which may be a substitute for conventional lubrication method during a machining process has been developed to minimize economic loss and environmental pollution. The principal mechanism of MQL technique is injection of compressed air with pulverized oil as a form of a mist between the machining tool and the workpiece. It has been reported that MQL technique can effectively reduce friction and cost during the machining process. VPL is an alternative method to overcome the shortcomings of liquid lubricants for certain applications such as high temperature systems and MEMS devices. It has been demonstrated that VPL can extend the lifetime of the MEMS device by

providing continuous lubrication and eliminating the stiction problem. Furthermore, SAM, which is an organic thin film has been extensively investigated for nano-tribological applications. These ultra-thin layers have low adhesion and friction properties and show great promise as a nano-lubricant for micro-scale systems.

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