

特约专栏

# The Progress of Special Lubricating Materials—A Brief Review

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**Abstract:** Lubricating materials generally include liquid and solid lubricants although in some cases gaseous lubricants are used. The types of lubricants could be divided into many classes based on the application environments or lubricants characteristics. Special lubricating materials mean the materials with properties superior to common lubricating materials. To enhance the lubricating performance via the design of molecular structure, bulk structure and the composite is always the main way to fabricate novel lubricating materials. For liquid lubricants and organic thin films, to design new molecular structure and reveal the tribochemistry mechanism are generally combined to develop novel lubricants. For example, the ionic liquids, as novel potential lubricants, are evaluated through different functional groups and tribochemistry during sliding process to guide the design and synthesis of ionic liquids with desired properties. The tribological performances of organic thin films heavily rely on their molecular structure and the film constructions. For typical solid lubricants, the design of bulk structure and composite are considered to be chosen to improve or adjust the frictional and wear resistance behaviors. The appearance of fullerene-like structure bestowed diamond-like carbon films much higher elasticity and much lower friction coefficient, while the introduction of metal elements reduced internal stress and improved the environment sensitivity in some cases. The blending and addition of inorganic nanoparticles are adopted to fabricate polymer lubricating materials with higher mechanical and wear resistance since it is not easy to design and fabricate novel polymers with desired lubricating properties. The development of high temperature lubricants is still a big challenge, in particular, lubricants with good consecutive lubricity from room temperature to high temperature (1 000 °C and higher). The addition of rare earth and ceramics, both with high temperature stability, to metal matrix is becoming a mainstream way to design and fabricate high temperature lubricants. The evaluation of lubricants could be done directly by the observation of friction and wear behaviors, which provide apparent judgment about the lubricants. The other way to get detail understanding about the lubricants applications is to see what happened on the surfaces during the sliding process, tribophysics and tribochemistry mechanisms, via the investigation of reaction products on the wear track, which in turn give some ideas or suggestion to adjust or design lubricants with desired properties.

**Key words:** materials; friction; wear; lubrication

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## 特种润滑材料研究进展简述

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**摘要:**虽然有些情况下使用气体润滑,但一般认为润滑材料主要包括液体和固体润滑材料。根据使用环境和润滑材料特性,润滑材料可以划分为许多类。特种润滑材料顾名思义是指具有比常规润滑材料更为优异特性的润滑材料。通过分子结构、体相结构设计和复合提升润滑特性一直是制备新型润滑材料的主要途径。对于液体润滑剂和有机分子薄膜,常常将新型分子结构设计和摩擦化学机理探讨结合在一起以发展润滑材料。比如,作为可能的新型润滑剂,离子液体的评价主要通过考察不同官能团和摩擦过程中发生的摩擦化学机制,以指导合成新型离子液体。有机薄膜的摩擦学特性强烈依赖于薄膜分子结构和构造结构。对于经典固体润滑材料,常考虑体相结构设计和复合方法提高或调整摩擦磨损特性。类富勒烯结构的出现赋予类金刚石薄膜更高的弹性和更低的摩擦系数,而金属掺杂能够降低内应力并在有些情况下改善薄膜环境敏感度。由于合成新型聚合物润滑材料比较困难,因此,共混和无机纳米颗粒的添加成为制备良好力学性能和耐磨损特性聚合物润滑材料所采取的方法。高温润滑材料,特别是从室温到高温(1 000 °C及以上)均具有良好润滑特性的润滑材料的发展依然是一个大的挑战。

具有高温稳定性的稀土和陶瓷填充金属是目前设计制备高温润滑材料的主流方法。通过摩擦磨损特性的考察可以获得对润滑材料的表观判断,而基于磨损表面反应物质的分析对摩擦过程中发生在表面的摩擦物理化学机制的探究则是了解润滑材料服役特性和机制的主要手段,也是设计制备新型润滑材料依赖的主要思想来源。

**关键词:** 材料;摩擦;磨损;润滑

## 1 Introduction

The friction and wear are commonly happened to mechanical contact moving parts, and are main factors leading to the failure of machines. Therefore, the efficient lubrication including liquid, solid and gaseous lubrication is demanded to be provided in order to ensure the mechanical motion stably and reliably. With the rapid development of mechanical systems to high speed, high loading, high temperature, extra high precision, lightweight, micromotion, longtime life, high performance lubricating materials with special functions are requested to support the need of industry. Special lubricating materials, namely, the lubricating materials to meet the harsh requirements from mechanical engineering that general lubricating materials are not able to satisfy. For instance, the super low volatility for liquid lubricating oils, good high temperature lubricating behaviors for metal lubricating materials, super low friction and wear for precision systems, low adhesive force and high durability for microelectromechanical systems (MEMS).

It is difficult to give a thorough review about the progress of special lubricating materials since they cover a wide range; we would like here to try to collect and organize some progress obtained recent years in heterocyclic compounds and ionic liquids, organic molecular films, polymers, carbon based thin films, and high temperature solid lubricants. In order to give the information as much as possible, the tables and figures are not included, if interested, please go to check the references listed below to get more details.

## 2 Heterocyclic compounds and ionic liquids

The additives of lubricating oils are always a key part to increase and ensure the performance. As a versatile additive, zinc dialkylthiophosphates (ZDDP) is widely used in lubricating oils for decades. However, under the pressure from environment protection, new additives for lubricating oils are urged to be developed to replace ZDDP. The precondition of designing and fabricating efficient additives is to understand the correlation of molecular structure and performance. Amid many studies, heterocyclic compounds are investigated extensively and gave much hope. There are two classic studies about the correlation of molecular structure and performance. First, Xue et al. probed the antiwear property of N-containing heterocyclic compounds with indole, indazole and benzotriazole as model molecules, which have the same ring structure except for the number of nitrogens, the results showed that the antiwear property of the compounds increases with the number of nitrogen increases. According to modern molecular orbital theory, indole, indazole and benzotriazole possess the same cyclic structure, which is a continuously close conjugated system composed of ten p-electrons, with two of them donated by the N-1 atom. In the indazole molecule, there is an N-atom such as that in the pyridine molecule, which possesses a basic lone electron pair. In the benzotriazole molecule, there are two basic N-atoms like that in pyridine. Thus the coordinate capacity of indazole with metal ions or metal surface is stronger than that of indole, and the coordinate capacity of benzotriazole is stronger than that of indazole. In addition, be-

cause of the strong electron withdrawing ability of the  $-N=N-$  grouping, the acidity of benzotriazole ( $pK_{a8.2}$ ) is the strongest in the three compounds, and benzotriazole can easily lose a proton to form the strongest coordinate ligand. In summary, the coordinating ability of the ring system increases as the number of nitrogen increases, so the antiwear properties of the N-containing cyclic compounds as oil additives increase as the number of nitrogen increases<sup>[1]</sup>. The second one is that Xue et al. revealed the correlation of tribological performance and molecular structure with 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole as model compounds, which possess 10p-electron conjugate system but different one-location atom. Due to the order of the electroaffinity:  $O > S > N$ , the degree of mercapto group lose proton and the acidity of three compounds is: 2-mercaptobenzoxazole > 2-mercaptobenzothiazole > 2-mercaptobenzimidazole, the coordinate capacity order is the same. The antiwear results demonstrated the same order mentioned above. That means there is a direct correlation between molecular structures and their tribological performance<sup>[2]</sup>.

However, it is a pity that novel additives based on the study of heterocyclic compounds with potential to replace ZDDP are yet commercialized. More researches about the multifunctional molecules are still under going, for instance, to combine multifunctional groups into one molecule. To find a compound which could meet the requirement and is able to replace ZDDP, of course, will be a milestone, but, seems, it will take longer time than expected. Talking about the development trend of the novel additives for lubricating oils, it might be reasonable and feasible to think about the combination of different materials with one or more functions to have multifunctions with multi components instead of one compound.

The interest of ionic liquids as lubricants study is aroused by their unique physical and chemical properties compared with general liquids and the space technology requirements for special performance lubricants as well as the high temperature lubrication. With the development of space technology, the general technology or materials used commonly on earth are no longer suitable to meet the harsh requirements due to the unique space environment. Therefore, special consideration with regard to the lubrication of the space equipment must be taken into account. For example, satellites are mounted with various drive mechanisms such as the posture control mechanism and the antenna drive mechanism, while many tribological elements are included in these drive mechanisms. The lubrication failure of these elements can cause serious damage to the satellites. The space environment is very severe to liquid lubricants. Generally, solid lubricants are widely used in high vacuum environment. Solid lubricants do not evaporate under high vacuum or change very much in physical and chemical properties in response to temperature. However, liquid lubricants always have many advantages over solid lubricants. For example, the lifetime of liquid lubricants is generally longer, which make the use of liquid lubricants more reliable, especially, in space. However, in the case of liquid lubricants to be used in space equipments, to maintain liquid state within a wide temperature range and to have good viscosity-temperature properties as well as to resist the oxidation degradation of atomic oxygen in space are all required.

Among many liquid lubricants, perfluoropolyether (PFPE)

and multiply-alkylated cyclopentane (MAC), both with very low vapor pressure, are used for space equipment<sup>[3]</sup>. Perfluoropolyethers (PFPEs) are used for many year in magnetic rigid disk due to their high thermal stability and extremely low vapor pressure. However, PFPEs are often out of action due to degradation catalyzed by strong nucleophilic agents and strong electropositive metals, for example,  $\text{Al}_2\text{O}_3$  of slider, moreover, the high cost of PFPEs limits further applications of PFPEs. From the commercial viewpoint, ionic liquids are cheaper than PFPEs. Ionic liquids (ILs) have received a growing interest as novel lubricant in the last decade<sup>[4-6]</sup>. Ionic liquid is defined as a material containing only ionic species without any neutral molecules. ILs have many attracting properties such as extremely low vapor pressure, a liquid state in a wide temperature range, non-flammability, excellent thermal stability, high electrical conductivity, interesting solvating properties, and high heat capacity<sup>[7-8]</sup>. Taking advantage of these characteristics, applications as lubricants are expected. Ye *et al.*<sup>[9]</sup> presented firstly the use of ILs as lubricants and showed excellent tribological performance of alkylimidazolium tetrafluoroborates for the contact of steel/steel, steel/aluminum, steel/copper, steel/ $\text{SiO}_2$ , steel/Si, steel/sialon ceramics, and  $\text{Si}_3\text{N}_4$ /sialon ceramics. Wang *et al.*<sup>[10]</sup> presented the excellent tribological behavior of alkylimidazolium hexafluorophosphate type ionic liquids for the contact of steel/steel both in air and vacuum. Based on the very low vapor pressure and excellent tribological behavior of RTILs, their use as liquid lubricants for the space equipments is expected, the results show in Fig. 1.

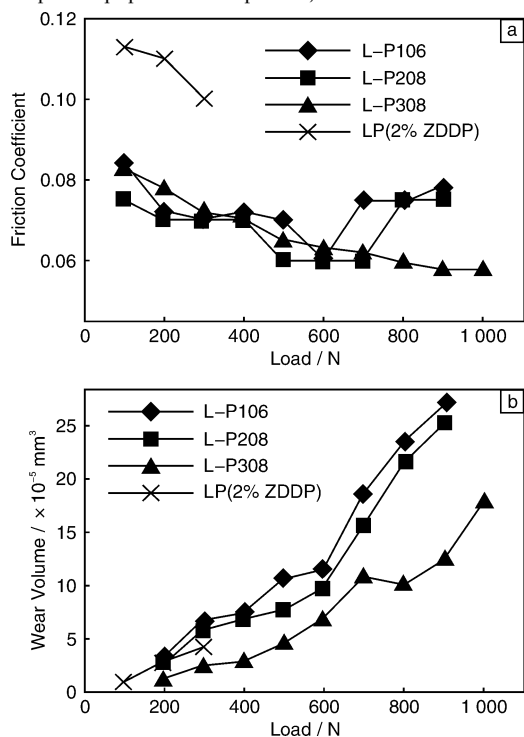


Fig. 1 Friction coefficient (a) and wear volume (b) of steel/steel contacts lubricated with L-P106, L-P208, L-P308, and LP-2% ZDDP at 100 °C

Ionic liquids could be used alone as lubricants or as lubricant additives. Jimenez *et al.*<sup>[11]</sup> reported the tribological properties of L-P106 and L102 ILs as 1% (mass fraction) base oil additives in synthetic esters and found that highly polar ILs could reduce the wear of aluminum at room temperature and all additives reduce both friction and wear at 100 °C. However, the improvement was very limited probably because of their poor solu-

bility in synthetic esters, especially at low temperatures. Qu *et al.*<sup>[12]</sup> found that mineral oil containing 10% (volume fraction)  $[\text{C}_8\text{H}_{17}]_3\text{NH}$ .  $\text{TF}_2\text{N}$  has demonstrated lower friction and wear than either the base oil or the neat IL on the aluminum flat. It is found that dicationic ILs as high-temperature lubricants showed excellent tribological properties and have a number of advantageous physical properties over the monocationic counterparts<sup>[13]</sup>.

Suzuki reported that imidazolium-based ionic liquids have high thermal stability, low volatility, and good viscosity-temperature characteristics, and retain liquid state in a wide temperature range. With these extreme good intrinsic properties, imidazolium-based ionic liquids demonstrated a low friction coefficient, good anti-wear performance, and a high load-carrying property under high vacuum<sup>[14]</sup>, as seen in Fig. 2.

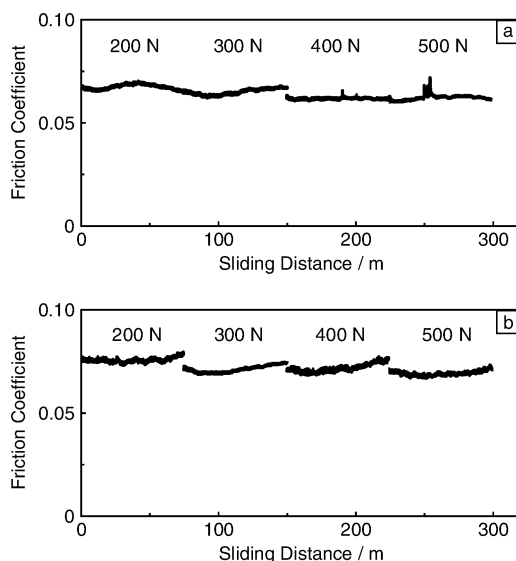


Fig. 2 Friction coefficient during the load-carrying test: (a) [hmim][BF<sub>4</sub>] and (b) [hmim][PF<sub>6</sub>] in high vacuum

Qu evaluated the lubricating properties of two ionic liquids (ILs) with the same anion but different cations, ammonium IL  $[\text{C}_8\text{H}_{17}]_3\text{NH}$ .  $\text{TF}_2\text{N}$  and imidazolium IL C10 mim.  $\text{TF}_2\text{N}$ , in neat form and as oil additives<sup>[15]</sup>. Substantial friction and wear reductions, up to 55% and 34%, respectively, were achieved for the neat ILs compared to fully formulated 15W40 engine oil. Adding 5% (volume fraction) ILs into mineral oil has demonstrated significant improvement in the lubricity. One blend even outperformed the 15W40 engine oil with 9% lower friction and 34% less wear.

Jimenez studied<sup>[16]</sup> two dialkylimidazolium ILs: 1-octyl-3-methylimidazolium tetrafluoroborate (L108) and 1-hexyl-3-methylimidazolium hexafluorophosphate (LP106), with long alkyl side chain and fluorine-containing anions as high temperature lubricants for titanium. Experimental data indicated that the tetrafluoroborate L108 IL failed just above room temperature, while the hexafluorophosphate LP106 IL showed an increasingly good performance with increasing temperature up to 200 °C. When the temperature was raised to 300 °C, severe wear was found also for LP106, due to IL decomposition and tribocorrosion. When the steel ball was substituted by a ruby sphere, a low friction coefficient and wear rate is obtained even at 300 °C for titanium due to the higher stability of the IL and the absence of metal tribocorrosion.

Xia tested two kinds of imidazolium ionic liquids (ILs) of 1, 2-dimethyl-3-hexylimidazolium bis (trifluoromethylsulfonyl) imide (L-F116) and 1-dimethyl-3-hexylimidazolium bis (triflu-

oromethylsulfonyl) imide (L-F106) as lubricant additives in poly (ethylene glycol) (PEG) for the steel – steel sliding pair. The results showed that, as seen in Fig. 3 corrosion phenomena of PEG containing ILs on pure copper are negligible compared to PEG at room temperature. The 2-substituted imidazolium IL L-F116 demonstrated excellent tribological performance and load-carrying capacity. The tribochemical products, detected to be sulfate, nitrides,  $\text{FeF}_2$ , etc., on the worn surface may contributed to lower friction coefficient and wear rate<sup>[17]</sup>.

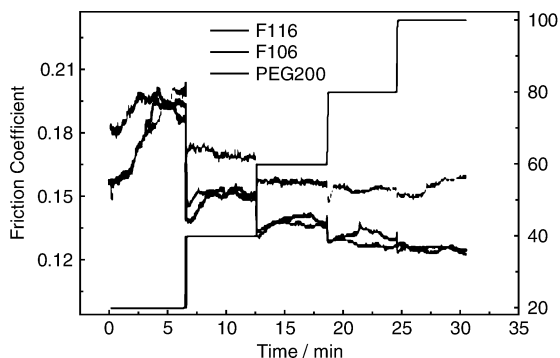


Fig. 3 The evolution of friction coefficient with time during a load ramp test from 20 to 100 N for different ILs additives and PEG at room temperature (stroke: 1 mm, frequency: 30 Hz, and duration: 30 min)

As a kind of pretty new compounds considered as potential lubricant with special functions, ionic liquids exhibited complete excellent properties demanded by lubricant, and much research work has been done to reveal and verify the potential of ionic liquids as special lubricants. However, a lot of problems remain there to be overcome before ionic liquids could be brought into real applications, such as severe corrosion to metals. Therefore, systematical investigation still needs to be done to setup the correlation of the molecular structure and the performance of ionic liquids. With that as fundament, to classify what kind of ionic liquids could meet the lubrication of what materials is the final step to finish the task of ionic liquids commercialization. The possible and easier way currently is to synthesize or find suitable compounds as additives to enhance the shortcomings of ionic liquids.

### 3 Organic thin films

Microelectromechanical systems (MEMS) is now mainly based on silicon materials that bring troublesome problems such as oxidation during micromachining and subsequent exposure to air, the oxidized layer in turn increases the stiction and friction of elements. More importantly, silicon based elements have poor wear resistance which limits the lifetime of the MEMS, that is the main reason why few MEMS are put in practice use until now. Due to the precision and the size control, it is impossible to apply general lubrication technology or liquid or solid lubricants to MEMS elements. As a middle course, many MEMS elements need to be encapsulated in vacuum environment to prevent the impact from impurities so as to improve the reliability and stability. Even encapsulated in vacuum environment, the MEMS contact moving elements still demand efficient lubrication. Based on the tons of research work screening, the feasible approach to provide stable and reliable lubrication is to deposit ultra-thin organic molecular layers on the surface of silicon based elements.<sup>[18]</sup>

The organic molecular layers lubricant, generally, can be mainly classified to: ① the LB films, ② the Self-Assembly

Monolayers (SAMs).

LB film is a molecular thick monolayer or multilayer of organic materials, which includes the form of monolayer at liquid surface and the transfer from liquid to solid substrate. The term of Langmuir-Blodgett comes from the names of a research scientist and his assistant, Irving Langmuir and Katherine Blodgett, who discovered unique structure thin film in early 1900's. LB films are the very early organic films considered and studied for the boundary lubrication purposes on metal surfaces<sup>[19]</sup>, mica<sup>[20]</sup> and Si surfaces<sup>[21]</sup>. Many organic compounds such as fatty acids, silanes, thiols, phospholipids and polymeric films have been studied. However, the drawbacks of LB films are obvious, firstly, it is difficult to prepare uniform non-polar molecules or high molecular weight polymers, and secondly, the durability of these monolayers is poor since they are bonded to solid substrate with the weak Van der Waals forces. Moreover, LB films are mainly concerned with flat surfaces and can not be formed on three dimensional surfaces<sup>[22]</sup>. To challenge the poor wear resistance of the LB films, many good ideas were proposed. For examples, introducing nano-particles into the LB film to improve load-carrying capacity or wear resistance<sup>[23]</sup>, using polymerization process to strengthen intermolecular cohesion forces to enhance film stability<sup>[24]</sup>. A typical case is to incorporate C60 into the ordered structure of LB film, the motivation was to use C60 as 'all bearings' between sliding surfaces<sup>[25]</sup>. As shown in Fig. 4, C60 molecules presented in the form of cluster about 100 nm in diameter but unevenly distributed, and the friction was lower at the locations of the C60 clusters. But, the problem is still there that the composited LB films did not show significant improvement in durability. Therefore, because of these limitations, LB films can hardly find applications in MEMS even though some LB films are very effective in reducing friction and wear to some extent.

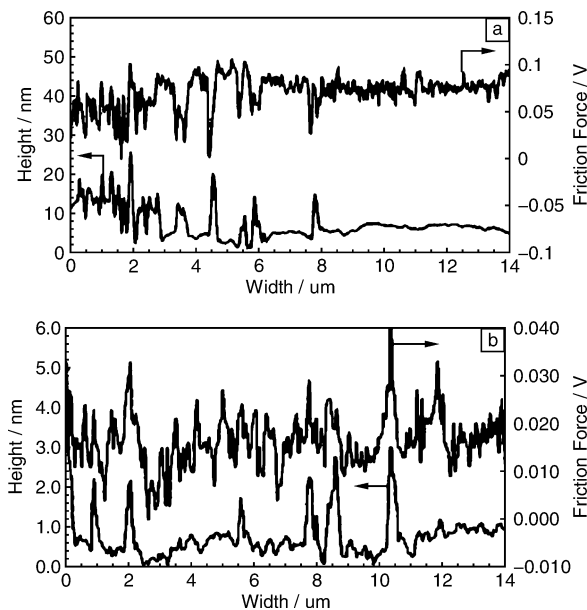


Fig. 4 (a) Heights and corresponding frictional force of C60/BA LB film, (b) Heights and corresponding frictional force of C60 derivative LB film

Since LB films do not provide higher wear resistance, SAMs have been proposed as prospective candidates for robust molecular lubricants<sup>[26-27]</sup>. These monolayers have been introduced in the 1980s for surface modification through chemical adsorption of functional organic molecules with the formation of chemical bonds

between reactive end groups and solid surfaces<sup>[28]</sup>. One of the important technological advantages of SAMs is that self-assembly processes are compatible with wet-chemistry processes in the micro fabrication industry.

Though there are many different types of SAMs, alkyl-silane SAMs have been extensively investigated as candidate lubricants for MEMS components since Si is the base material for MEMS components. Among the alkyl silane SAMs, OTS SAM is the most widely studied SAM and is regularly used in the industry as anti-stiction and anti-friction organic modifier<sup>[29]</sup>. These SAMs have shown higher durability than the classic physisorbed monolayers and decreased the friction coefficient for MEMS components to very low values ( $< 0.1$ ). Therefore, much attention has been paid to SAMs because of easy preparation and their excellent properties such as extremely low thickness (few nano-meters), steady chemical and physical properties and good covalent bonding with the substrate.

The tribological properties of SAMs are closely related to their intrinsic chemical composition and structures. The properties of the SAMs can be widely varied by changing the chain length<sup>[30]</sup>, chemical nature<sup>[31]</sup>, terminal group chemistry<sup>[32]</sup> and degree of cross linking within the layer, which makes them more attractive than the physisorbed LB films<sup>[28]</sup>. One of the example is shown in Fig. 5. Nanotribological investigations involving the study of the effect of chain length of silane SAMs on friction have shown that friction is higher with short chains when compared to longer chains<sup>[33]</sup>. SAMs with longer chains are generally densely packed, while the shorter-chain ones are not. With the same terminal groups, loosely packed SAMs generally possess higher friction force due to the larger energy dissipation during the sliding, and higher adhesive force as well due to the liquidlike disordered structure. On the other hand, altering the terminal groups, for instance, from a polar ( $-\text{CF}_3$  and  $-\text{CH}_3$ ) to polar ( $-\text{COOH}$ ,  $-\text{OH}$ , and  $\text{NH}_2$ ), could result in the increase of adhesion and friction. This is because SAMs with more polarized groups generally possess higher surface energy and a relatively strong interaction during the sliding, and therefore higher adhesion and more energy loss are expected, which leads to a higher friction force. Kim. *et al.*<sup>[32]</sup> have systematically studied the effect of the surface terminal group chemistry on frictional properties and found that the introduction of a small percentage of bulky groups such as  $\text{CF}_3$  and  $\text{CH}_2(\text{CH}_3)_2$  in the place of  $\text{CH}_3$ , dramatically increased the frictional forces. Even with similar struc-

ture, it was found that phenylacetic acid(PAA)/3-aminopropyltriethoxysilane (APS) with tail groups of  $-\text{C}_6\text{H}_5$  exhibited better wear resistance than propionic acid (PPA) /3-aminopropyltriethoxysilane (APS) terminated by the  $-\text{CH}_3$  groups, which could be assigned to the reconstruction of phenyls<sup>[34]</sup>.

Introducing a functional group, such as diacetylene, peptide, and sulfone, into straight hydrocarbon chains to construct robust SAMs is another alternative way to improve their tribological properties. It is hypothesized that, within the SAMs, the functional groups interact laterally taking the form of hydrogen bonding, dipole interaction,  $\delta$ -stacking, or covalent attachment, which may enhance the mechanical integrity and stability. To the best of our knowledge, only a few of studies have been engaged in the investigation on the frictional behaviors of the functional-group-embedded SAMs. The focused targets are the alkylthiols derivatives due to their convenient molecular synthesis and easy formation of the monolayer on gold surface, while the use of alkylsilanes is seldom reported. Because SAMs based on alkylsilanes are more suitable than alkanethiols SAMs as the potential lubricant layer for MEMS, more attention should be paid to SAMs derived from alkylsilanes. The interchain hydrogen bonds among the molecules enhance the stability of the monolayers against rubbing the counterpart ball and thus endow it an outstanding antiwear ability<sup>[35]</sup>.

It is also a good try to fabricate dual layer or multilayer with organic synthesis method or self-assembled approach to improve the wear resistance of the films. The formation of the overlayer on a monolayer seems to be effective to increase the durability and to reduce the friction coefficient. For instance, the self-assembled dual-layer film stearic acid/3-aminopropyltriethoxysilane (STA/APS) can greatly reduce the friction force and register much better load-carrying capacity than the OTS monolayer in sliding against the ceramic counterface<sup>[36]</sup>. It is clear that under-layer played a key role to determine the tribological properties of the films via dominating the order of the entire assembly<sup>[37]</sup>.

Most of the work has been conducted using AFM/FFM, which simulates single asperity surface interactions. Only few research results are currently available on the continuous sliding configuration (such as pin-on-disk) which simulates the actual rotating parts of MEMS, moving at much higher velocities than those achievable in AFM. By preparing silane SAMs on silicon surface, the coefficient of friction (COF) is reduced from 0.5 ~ 0.6 to 0.1<sup>[38]</sup> using reciprocating tribometer and from 0.15 to 0.018 reported by Tsukruk *et al.*<sup>[39]</sup> using FFM. Ruhe *et al.*<sup>[30]</sup> found that the initial dynamic coefficient of friction was independent of the length of the alkyl silane chains while the wear life extended as the chain length of the SAMs increased (Fig. 6). They

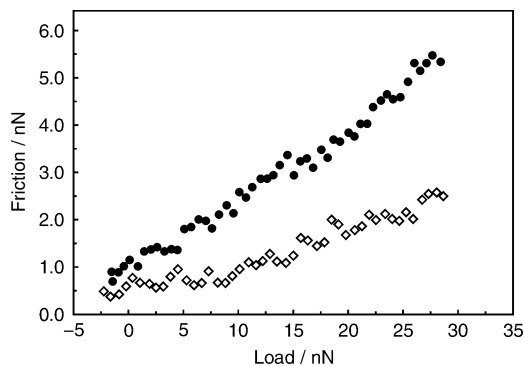


Fig. 5 From friction-load maps acquired on the two films, the average kinetic friction is plotted versus the external applied load. Negative loads arise from adhesive forces between the probe tip and the sample. The frictional response of the film is defined as the force of friction at a specified load. An approximate factor of 3 increase in the frictional response is observed upon moving from a methyl (open diamond) to a trifluoromethyl (closed circle) termination

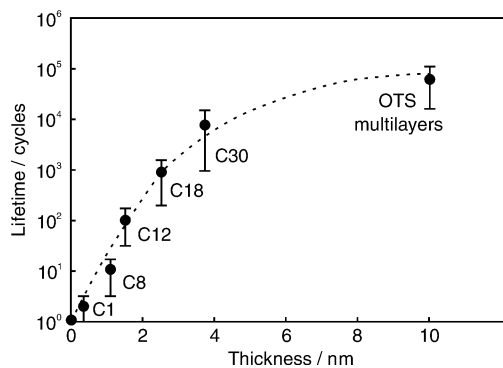


Fig. 6 Lifetimes to failure of interfaces modified with selfassembled films of silanes from Figure 1 as a function of the length of the alkyl chain; slider on disk experiments; silicon substrate

relate this behavior to the higher flexibility of the longer chains which can dissipate more mechanical energy by the shearing process than the short chain molecules and to the stronger inter-molecular interactions.

Clearly, neither LB films nor SAMs does currently satisfy the MEMS industry harsh demands due to the fatal weakness, very poor wear resistance. However, the successful application of SAMs to solve the lubrication of moving mirrors of Texas Instrument projector already gave us much hope to continuously probe the structure and tribology of SAMs. We propose here that probably there are two ways for tomorrow SAMs study; both of them rely on substrate materials. One is to focus on Si based materials, to design molecules with chemical bond and high degree density or multi scale films that mean longer chains together with shorter chains. The other is to shift attention to other kinds of materials different from Si, to find the lubrication problems and to solve them with current SAMs knowledge and technologies.

## 4 Polymers

With many merits such as self lubrication, lightweight, high impact resistance, easily designable, insulation, high corrosion resistance et al., polymers and polymer-based composites are widely used because of the combination of good mechanical and tribological properties, especially in dry friction conditions where lubricants cannot be used. Of course, there are some shortcomings such as low conducting coefficient, low temperature resistance, low irradiation resistance, low structural strength, compared with metals. In the past decades, the development of the applications of polymer based materials as self lubrication materials is fast, and more and more polymer based materials have been used to solve engineering problems that metals could not satisfy, for example, as self lubrication bearings. The main polymers investigated as wear resistance or self lubricating materials include polytetrafluoroethylene (PTFE), polyamide (PA), polyethylene (PE), polyformaldehyde (POM), Polyetheretherketones (PEEK), polyimide (PI), polyphenylene sulfide (PPS). In many cases, inorganic particles, fibers, clays are introduced into polymers to enhance some properties, such as wear resistance.

Polymers are usually mated with metal materials, however, there are some circumstances, in which it might be advantageous for polymers sliding against polymers rather than against metal materials, because polymers are light weight and they have very good electrochemical and acid or base corrosion resistance.

The friction between polymers can be attributed to two main mechanisms: adhesion and deformation<sup>[40-42]</sup>. If the interfacial bonding is stronger than cohesive of the weaker material, then this material is fractured and the polymer transfer takes place. Otherwise fracture occurs at the interface. The surface forces between polymer and polymer and forces acting between polymer chains are nearly equal and fracture often occurs in the bulk of polymers. It was observed for metal-polymer contact that metal is transferred to the polymer surface under certain conditions<sup>[43]</sup>. The results demonstrated that friction force of polymer-polymer combination was correlated with the adhesion hysteresis between two shearing polymer surfaces<sup>[44]</sup>, the friction coefficient of polymer-polymer combination increased with the increasing adhesive work between them<sup>[45]</sup>. Electrostatic attraction makes a contribution in partial to the adhesion of polymer contact when electric double layer is formed owing to transition of electron from one surface to another.

Chen et al.<sup>[46]</sup> stated that the population of chain "ends" at surfaces was the most important factor that determined the adhesion, adhesion hysteresis, friction and wear between two poly-

mer surfaces. During the sliding process, under the shear force and the friction heat, tribochemical reaction would take place to generate the groups OH, COOH, NHCO and others, which could induce hydrogen bond at very short distance between two polymer counterparts that two approaching atoms are linked together by a common proton providing a strong and stable compound.

The friction force is proportional to the normal applied load, the friction coefficient remains practically constant at load in the range 10 ~ 100 N when a steel ball of radius 6.35 mm slides over polytetrafluoroethylene (PTFE), polymethylmethacrylate (PMMA), polyvinylchloride (PVC), polyethylene (PE), and nylon<sup>[47]</sup>.

Dry sliding of polymer-polymer combinations always produced intermittent motion and seizure or stick-slip<sup>[48-49]</sup> due to adhesion, especially, under heavy load, while the adhesion might be considerably influenced or changed by some ways. The rough-on-rough surface sliding combinations had lower friction coefficients than those of smooth-on-smooth surface combinations<sup>[48]</sup>, due to capillary force, especially, under humid atmospheres. Adding solid lubricants to polymer matrix<sup>[50-51]</sup> is always a good choice to decrease adhesion of two sliding surfaces. Of course, external lubrication is also a useful method to reduce adhesion of two sliding surfaces. For example, Yamamoto and Takashina<sup>[52]</sup> reported that polyetheretherketone (PEEK) and polyphenylenesulphide (PPS) exhibited lower friction coefficients in water when they slide against themselves. It is generally agreed that the friction force is independent of sliding velocity, this is true but not completely true. The sliding velocity has a pronounced effect on friction when the tests are conducted near the glass-transition temperature (high mobility of polymer segments), whereas at lower temperature (segments of the main chain are frozen) friction hardly depends on the sliding velocity.

Wear is an intrinsic property of materials and also depends on the operating parameters<sup>[45]</sup>. The mechanisms of wear reported in sliding of polymers against counterfaces are adhesion and abrasion. An important characteristic of adhesive wear is the transfer of soft polymeric materials to the harder counterface<sup>[53]</sup>.

Though polymers possess lots of merits to make them as self lubricants in some cases, the disadvantageous of polymers are apparent, such as poor wear resistance because of weak strength compared to metals, high friction coefficient due to electrostatic force generated during sliding process. The blend of different polymers and the introduction of in/organic particles, fibers to polymers are two most approaches used to improve or enhance their friction and wear behaviors. For example, polyamide (PA) is well known for its excellent mechanical properties. However, its sensitivity to notched impact and poor dimensional stability limit its applications in a wet and low temperature environment<sup>[54-55]</sup>. Ultra-high molecular weight polyethylene (UHMWPE) possesses excellent self-lubrication properties and high impact resistance and high chemical stability, however, its low deformation temperature and difficult to be mould limit its wide engineering applications. The blend of PA and UHMWPE (PA/UHMWPE) can overcome the shortcomings of both polymers and at the same time, perhaps retaining good mechanical properties<sup>[56]</sup>. The wear resistance of PA is improved by blending with self-lubricating polymers such as UHMWPE<sup>[57]</sup>. Thus, offers strong potential in the field of lubricated sliding application. The proposed application of the PA/UHMWPE blend was that of cage for a roller bearing in a water pump and the wheel hub of an automobile, hence, the test conditions specified later.

With excellent intrinsic mechanical properties and relative chemical inertia, inorganic particles are added to polymers and

expected to enhance the mechanical properties of polymers. Definitely, the size of the particles plays an important role to improve, in particular, stiffness and toughness simultaneously. Reducing the particle size to a nanoscale level is assumed to reach a significant efficiency since smaller particles would disperse in polymer matrix much uniform to express the effect of dispersion strengthening. Nanoparticle filled polymers are very promising materials for various applications.

The incorporation of nanosize particles like  $\text{TiO}_2$ <sup>[58]</sup>,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$ <sup>[59]</sup> to polymer matrix has led to better enhancement in wear resistance (Fig. 7). There are some pretty reviews about the fillers effect on polymer friction and wear<sup>[60]</sup> and the tribology of polymers<sup>[61]</sup>

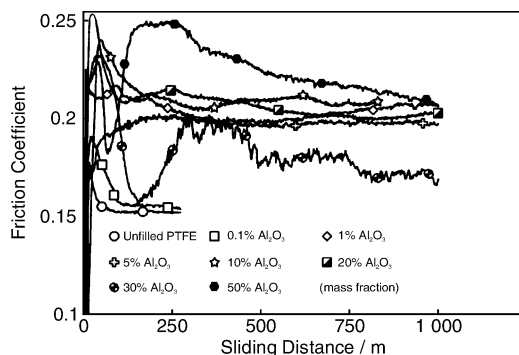


Fig. 7 A record of the friction coefficients as a function of sliding distance for the PTFE nanocomposite with various loading of  $\text{Al}_2\text{O}_3$

Xue *et al.*<sup>[62]</sup> found that various kinds of  $\text{SiC}$  particles, i. e., nano, micron and whisker, could reduce the friction and wear when incorporated into a PEEK matrix at 10% (mass fraction) or 4% (volume fraction). The results indicated clearly that compared with micro scale particles and whisker, nanoparticles resulted in the most effective reduction since nanoparticles were observed to be of help to the formation of a thin, uniform, and tenacious transfer film, which led to lower friction and lower wear. More details showed that  $\text{ZrO}_2$  nanoparticles from 10 to 100 nm showed a similar trend as most of the micron particles, i. e., the smaller the particles were applied, and the better was the wear resistance of the composites.<sup>[63]</sup>

To modify inorganic particles surface would make them more compatible with polymer, for example, the incorporation of  $\text{SiO}_2$  nanoparticles (9 nm), grafted with another polymer (polyacrylamide, PAAM) to enhance the adhesion of the particle agglomerates with the surrounding epoxy resin matrix<sup>[64]</sup>. The grafting polymerization technique increased the interfacial interaction between the nanoparticles and the matrix through chemical bonding, which in turn led to an improved tribological performance of these nanocomposites.

Xue *et al.* found that the wear rate of PTFE was decreased by 1 or 2 orders of magnitude and the size of wear debris became smaller when rare earth  $\text{CeO}_2$ ,  $\text{CeF}_3$  and  $\text{La}_2\text{O}_3$  were added<sup>[65]</sup>, the results is shown in Fig. 8.

Polymer clay nanocomposites have received considerable attention that polymer properties can be greatly improved by the presence of nanosized clay particles<sup>[66]</sup>. The coefficient of friction and wear loss decreases significantly on addition of organo-clay, whereas for conventional clay filled composites wear loss and coefficient of friction increase with increase in inorganic clay content. The nanocomposites exhibit a maximum of 85% improvement in wear resistance and 35% decrease in coefficient of friction. The highest wear resistance and least coefficient of fric-

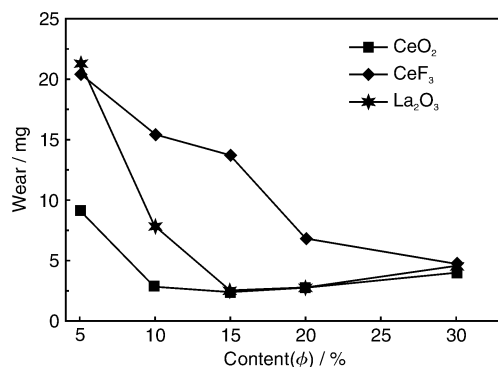


Fig. 8 Relationship between the wear of the PTFE composites and the content of  $\text{CeO}_2$ ,  $\text{CeF}_3$ , and  $\text{La}_2\text{O}_3$  in PTFE under the dry friction condition (sliding speed, 1.5 m/s; load, 100 N)

tion were observed in the nanocomposite with a clay content of 3% (mass fraction)<sup>[67]</sup>.

The blend and particles addition to polymer have been investigated extensively in the past decades and found many clues to strengthen the polymer tribology performance. In the early time for the study of polymer blending and the adding of particles, the research mainly focused on the particles addition effect screening. The interfacial interaction between added particle and polymer matrix was not put more attention. Based on the current research knowledge, to enhance the interfacial interaction via the particles surface modification might be a key point to improve the tribology performance of polymers.

## 5 Carbon based thin films

Generally, experience implies that hard materials are with higher friction and higher wear resistance such as stainless steel, and soft materials are with lower friction and lower wear resistance such as graphite, it seems difficult to combine low friction and high wear resistance together in most tribological applications. Carbon-based thin films have been the subject of extensive research over the last decade due to their excellent properties such as a low friction coefficient, chemical inertness, infrared transparency and high hardness,<sup>[68]</sup> and seem to meet the desire, providing not only low friction but also high wear resistance. They are usually harder than most metals and/or alloys, thus affording very high wear resistance and, at the same time, impressive friction coefficients are generally in the range of 0.05 ~ 0.2, and lower than 0.01 in some cases.

Since the family of carbon based films is very diverse and the lower friction was mainly found to diamond like carbon (DLC) films which generally including pure carbon and hydrogenated carbon films, we will hereby restrict the review to DLC films other than carbon based films such as carbon nitride films. DLC films possess low friction and excellent wear resistance, especially under dry conditions<sup>[69-70]</sup>, one of the typical results is show in Fig. 9, they are considered as candidates to ensure acceptable performance and low friction in systems that also operate under lubricated conditions but might undergo periods of temporary or even permanently poor lubrication conditions, characteristic for the boundary regime, for example, currently, DLC is hoped to be used as solid lubricant on the surface of elements of engine common rail system to reduce the friction to achieve the aims of energy saving and emission reduction as well as reliability. However, to achieve the appropriate performance under such conditions, some interactions between the films and the oils are necessary to be revealed for long lifetime, low friction and low

wear operation.

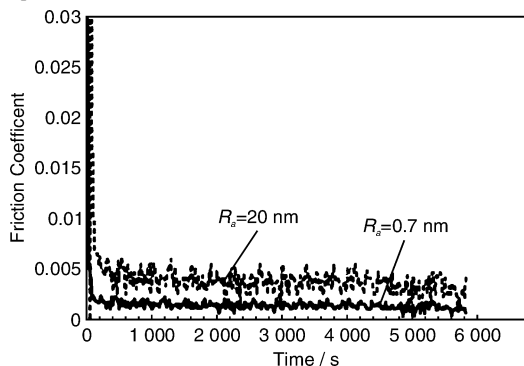


Fig. 9 Friction coefficients of a highly hydrogenated DLC film produced on rough ( $R_a = 20$  nm) steel and a very smooth ( $R_a = 0.7$  nm) sapphire substrate (test conditions: environment, dry nitrogen; load, 10 N; sliding velocity, 0.3 m/s)

DLC coatings are known as inert coatings with a low surface energy and are therefore considered not to react with the various oil additives and/or attract polar groups from the additives and the oil, which are the conventional mechanisms for the lubrication of steels and other metals<sup>[71–73]</sup>. These characteristics meet the requirement of engine common rail quite well where in some cases oil lubrication is efficient but not in others.

The hardness of carbon-based films is usually linked to the content of  $sp^3$  C–C bonds and these films are called diamond-like carbon (DLC) films. Recently, it has been shown that some nonhydrogenated carbon and carbon nitride films containing a large number of  $sp^2$  bonds possessed high hardness (up to 55 GPa) and extreme high elasticity (elastic recovery of 85%) concurrently<sup>[74–77]</sup> (Fig. 10). This unique character has been attributed to a ‘fullerene-like’ microstructure of DLC films, and the fullerene-like-structure DLC films without hydrogen incorporation have been generally prepared by physical vapor deposition (PVD). For instance, pure elastic carbon films have been synthesized by an anodic jet carbon arc<sup>[74–75]</sup>, while elastic carbon nitride films have been fabricated by reactive dc magnetron sputtering<sup>[76]</sup> and pulsed laser deposition<sup>[77]</sup>. However, the fullerene-like-structure DLC films without hydrogen incorporation exhibited poor friction behavior.

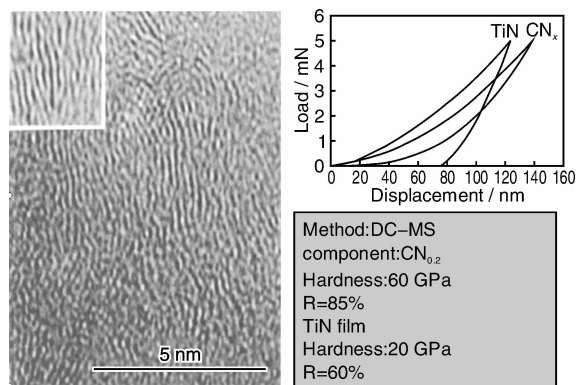


Fig. 10 HRTEM image and load-displacement curves for carbon nitride films containing a large number of  $sp^2$  bonds

Generally, hydrogenated amorphous carbon films displayed much lower friction coefficient compared with carbon nitride and pure amorphous carbon films, therefore, it would be very interesting to fabricate fullerene-like structure hydrogenated carbon

film. The presence of fullerene in hydrogenated carbon films would increase the hardness and reduce the internal stress, which means the fullerene or like structure would be of benefit to the mechanical characteristics of hydrogenated carbon films<sup>[78]</sup>. However, it is much difficult to construct fullerene-like structure in hydrogenated carbon films because this kind of structure is far away from equilibrium compared with that in pure carbon films and carbon nitride films. Zhang first reported<sup>[79–81]</sup> the fabrication of fullerene-like structure hydrogenated amorphous carbon films, compared with typical hydrogenated carbon ( $\alpha$ -C:H) films, the fullerene-like hydrogenated carbon (FL-C:H) films exhibit superior mechanical properties: higher hardness (20.9 GPa), better elasticity (elastic recovery of 85 per cent), and in particular, lower friction coefficient ( $\mu = 0.009$ ) when sliding against a  $Si_3N_4$  ball in ambient atmosphere with 20 per cent humidity. The super high elasticity is assigned to the five and seven-member rings presented in fullerene-like structure<sup>[82]</sup>. The low friction is believed to be due to the transfer film, which is not graphitized carbon but a kind of hydrocarbon film like hydrogenated carbon film observed on worn track of carbon films<sup>[80]</sup>. Further studies reveal that tribology behaviours of FL-C:H films are environment dependent, with highest friction coefficient (0.055) and lowest wear rate found from the tests in  $N_2$ <sup>[83–84]</sup>. Attempts have been made to understand the near-frictionless performance of hydrogenated carbon films reported in the literature, but few models are satisfactory in providing a convincing explanation to date.

Erdemir<sup>[85]</sup> has investigated the tribology of DLC films systematically and found that hydrogen in the DLC films played very important role to determine the films tribological behaviors. He used model experiments in inert gas environments and found a very close relationship between the hydrogen-to-carbon (HyC) ratios of source gases and the friction and wear coefficients of the resultant DLC films. The friction coefficient of films grown in source gases with very high HyC ratios (e. g. 10) was superlow (0.003), whereas that of hydrogen-free DLC films (with essentially zero HyC ratio) was very high (0.65). The friction coefficients of films grown in source gases with intermediate HyC ratios were between 0.003 and 0.65. Experiments also revealed that the frictional properties of these films were very sensitive to test environments. Specifically, when tested in open air, the friction coefficient of hydrogen-free DLC dropped to 0.25, whereas that of highly-hydrogenated DLC increased to 0.06. The elimination of strong covalent and  $p-p^*$  interactions at sliding DLC interfaces, plus better shielding of carbon atoms by di-hydration are proposed as the major mechanisms for the superlubricity of DLC films grown in highly hydrogenated gas discharge plasmas.

Though DLC films exhibited high hardness, low friction coefficient and chemical inertness, which make them feasible to be applied in many fields, high internal compressive stress (up to 10 GPa) is harmful to the adhesion of DLC film to substrate, and probably will lead to the peeling-off of the films from the substrate<sup>[86]</sup>. Therefore, element doping such as Ti, Cr, Mo, W, N, B, and Si was introduced to release the internal stress so as to improve the adhesion of DLC films<sup>[87–90]</sup>. In some cases, the doped elements present in the form of atomic in DLC films, in others, they would react with carbon matrix or to form nanocrystallite/amorphous structure. With high density of interfaces and high volume of grain boundaries, nanocrystallite/amorphous structure restricts initial crack occur and cracks expansion. As a result, DLC films embedded with nanocrystals, such as nanocrystalline carbides ( $TiC$ ,  $WC$ )<sup>[91]</sup>, dichalcogenides ( $MoS_2$ ,  $WS_2$ )<sup>[92]</sup>, demonstrated excellent and stable tribological performance. Wang reported that<sup>[93–94]</sup> with 2.8% (atom fraction)

tungsten doping, the residual compressive stress of hydrogenated amorphous carbon films decreased by 50%, without significant deterioration in the mechanical properties. When the W concentration was  $< 2.8\%$  (atom fraction), the W atoms were dissolved in the amorphous carbon matrix without forming a  $WC_{1-x}$  phase. The reduced directionality of the W–C bonds in the W-incorporated amorphous carbon matrix relaxes the stress caused by the distorted bonds. However, amorphous and crystalline  $WC_{1-x}$  nano-particles appeared when the W concentration was  $> 2.8\%$  and  $> 3.6\%$  (atom fraction), respectively, the segregation of the W atoms at higher concentration increased the residual stress significantly. At higher W concentrations, the nanosized  $WC_{1-x}$  crystallites evolved resulting in a gradually decrease in the residual compressive stress. It is clearly that the mechanism and effect of metal doping into carbon films are much complex, with the different doping concentration, different structure or chemical bond or new phase would appear, which determine the mechanical properties of the carbon composite films. To achieve the aim of reducing internal stress of the carbon films, not only doping concentration is a key factor, but also structure and chemical bond evolution of the carbon composite films.

The counterpart is also an important factor to affect the tribological behaviors of DLC films, for example, DLC films self mated or sliding against with steel. Kalin<sup>[95]</sup> investigated self-mated DLC contacts to study the “pure” effect of doping elements and additives by eliminating possible interactions with counterbodies, such as steel. Under such well-defined conditions, DLC films, particularly doped ones, are also strongly affected by additives and actual boundary “metal-like” lubrication can be achieved without steel in the contact<sup>[96]</sup>. Moreover, more positive results were observed when lubricated by the oil with very polar characteristics and a large amount of nonsaturated molecules<sup>[97]</sup>.

However, the tribological behaviors of DLC films are much different when sliding against steel because oils would form a thin film on steel surface very easily and react with steel. The tribological behaviors of DLC films are dependent on a variety of selected counterparts, the physical and mechanical properties of the DLC films, the oils and the additives.

DLC films with very low friction and high wear resistance as well as chemical inert properties are really promising as novel solid lubricant to be applied in harsh environment such as space, engine, MEMS, vacuum *et al*. Before they are brought into practical applications, some problems have to be solved such as humidity and gaseous sensitivity, high internal stress, poor adhesion to metal substrates, poor high temperature resistance, and the compatibility with liquid lubricating oils. It is believable that with the appearance of fullerene-like structure, elements doping, nanocrystalline/amorphous structure as well as new deposition techniques, above questions could be overcame in near future.

Besides the effectivity of lubricants could be reflected directly by the friction and wear behaviors, the deeper insight of the lubricants applications could also be revealed indirectly from the investigation of tribochemistry via the observation of tribochemical products left on the wear track, which in turn provides the guidance to the design and fabrication of lubricants<sup>[98]</sup>. The history of lubricants is the history of machines and mechanicals, while the history of solid lubricants is the history of space technology and high technology. The demands from industry are always the driving force to push the development of solid lubricants going ahead. The solid lubricants materials are related with chemistry, physics, materials science and engineering, mechanical engineering, it is hard to develop or fabricate novel solid lubricant

just with one field knowledge. The composition and chemical state of solid lubricants materials relies on chemists and material scientists, the structure and its evolution need the contribution from physicists and material scientists, the tribological performance of the solid lubricants materials is the task of chemists, physicists, material scientists and tribologists as well as lubricating engineers. Along with the application environment become more and more harsh, the design, fabrication, evaluation of solid lubricants materials would be more complex. Therefore, there are many different aspects in the study and development of solid lubricants materials, which require the synergetic work.

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