Designing Tribological Interface for Efficient and Green DLC Lubrication: The Role of Coatings and Lubricants

Mitjan Kalin*

Faculty of Mechanical Engineering, University of Ljubljana
Aškerčeva 6, 1000 Ljubljana, Slovenia
*Corresponding author: mitjan.kalin@tint.fs.uni-lj.si

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DLC coatings are low friction and low wear coatings and thus inherently possess some of the characteristics that may be beneficial or even enable green lubrication requirements. In particular, their low wear behavior may represent a potential for different, less harmful and more environmentally adapted lubrication compared to conventional materials, which may become an attractive approach for novel green technologies in various mechanical systems. In this work, we present some of several possible strategies for designing green lubrication, focusing only on concepts that are well-suited and enabled in a combination with specific properties of DLC coatings. These may include approaches through predominantly chemical-based interactions, physical-based lubrication technologies, and a combination of both, i.e. physical-chemical properties.

Keywords: green lubrication, DLC coatings, additives, nanoparticles, wetting, surface energy

1. Introduction

DLC coatings are nowadays frequently used in applications under high stress and/or under boundary or mixed oil lubrication [1-5] and the range of uses for DLC coatings continue to grow rapidly. DLC coatings inherently possess some of the properties that may be beneficial or may even enable new green lubrication technology without using strong additives typical for heavy-loaded metallic surfaces that critically affect environmental emissions. In particular, DLC’s well-recognised low wear behaviour may represent a potential for more environmentally adapted lubrication, which may become an attractive approach for novel green technologies in various mechanical systems. In this work we present some of several potential strategies that may be used to design green lubrication through use of DLC coatings in combination with various lubrication techniques and technologies. We present and discuss potential approaches through predominantly (i) chemical-based interactions, for example using conventional additives, but with ambition to use milder additives with more environmental-adapted chemistry, (ii) physical-based lubrication technologies by employing self-lubricating nanoparticles, and (iii) an approach that benefits from a combination of physical and chemical interactions that are based of particular solid-liquid interface properties rather than additives.

2. Lubrication based on chemically-active additives

In the last decade, mainly chemically-based interactions between different additives and DLC coatings were studied. Most often, strong EP additives or the most effective types of AW additives were investigated. Less than a decade ago, it was still doubted whether DLC coatings can react with additives, however, some early works have claimed and empirically showed [6] what became obvious in several studies in the last 5-6 years through direct chemical evidences for these reactions. The problem with the lubrication of the DLC coatings is in their low reactivity [7], which makes their tribochemical interactions with lubricants and additives quite limited [8,9]. Nevertheless, as mentioned above, it has been shown that different conventional additives affect the friction and/or wear performance of DLC coatings, both in contact with steel and in self-mated contacts. Direct chemical evidences of interactions between additives and DLC surfaces have been obtained using different surface sensitive techniques [10-14]. An example of AES spectra from a study presenting evidence of reaction via S, P and O on DLC is shown in Fig. 1. Indeed, these interactions were weaker than on steel and occurred in lower amounts. SEM image of an
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example of a weakly adhered tribofilm on DLC coating is shown in Fig. 2.

Moreover, these studies showed also a variety of different influences of additives in DLC/DLC contacts. Sometimes it was observed that extreme pressure and the anti-wear additives decreased wear in DLC/DLC contacts (Figure 3), but increased friction [6,8,10,14]. Another study [11] presented evidence that MoDTC and ZDDP additives react directly with DLC surface, proposing possible enhanced formation of MoS\(_2\) by ZDDP, and beneficial effect of MoS\(_2\), both on friction and wear. A better reactivity with hydrogen containing DLC was found. The suggested mechanism is presented in Figure 4.

The effect of DLC doping with different elements is also not yet fully clear. It was proposed and shown empirically with several coatings [6] and also by chemical analyses [11,15] that doped elements can enhance the steel-like behavior in self-mated DLC/DLC contacts, but tribocorrosion and lubrication mechanisms are still unknown. This is true also for exact effects of the types of doping elements, but often Ti-containing DLCs were found quite beneficial [11,15] and more reactive compared to W-containing DLC [15].

Accordingly, several evidences on chemical reactivity of DLC coatings with relatively strong additives (mainly S-containing, as well as P-containing) were presented in literature, showing that wear is always reduced, while friction can be increased, or reduced, obviously affected by type of additives used and their combinations. However, validated tribochemical mechanisms were not yet presented.

It can thus be concluded from the past studies that any differences in results and sometimes contradictory effects may also be due to lack of un-doubt evidences, which results from weakly adhered tribofilms, and less remaining evidence in the form of surface boundary films and tribochemical reactions at the contacting surfaces.

In view of the above studies it seems that very strong interactions between the DLC and additives will hardly be possible with current-day additives. Requirements for reducing the harmfulness of the substances used, i.e. need for much greener lubrication, is another reason that further seeking and developing stronger and new
DLC-tailored additives, may not be the optimal route towards the best DLC lubrication solutions. Namely, such potential additives that would firmly interact with DLC, should probably be even more reactive toward surfaces and more chemically active, which are typically the ones that are less environmentally acceptable.

It is very important to note that DLC provides both low wear and friction also with the base oils only. Accordingly, although strong reactive additives were found to further improve wear behaviour of DLC, they may not be required for DLC-coated systems, especially since sometimes they also increase friction, and the wear of the coatings is already low compared to steel surfaces. From this point of view, milder additives, such as low- or no-SAPS additives may be sufficient to protect even the most heavy-loaded contacts, when coated by DLC, while being able to maintain other non-coated surfaces in the system at satisfactory tribological conditions (i.e. without coatings and strong chemical-based additives). Our current research, together with several companion companies, universities and institutes, already targets these phenomena in a dedicated European project about interactions between no/low SAPS additives and DLC coatings.

Furthermore, our recent studies also show that even the base oils with their physical and rheological properties are far from being optimized for DLC contacts, although these properties show significant influence on friction and wear [16] that can be further designed to improve the lubrication without any chemical-based action, but instead - with purely green technology relying on oils rheology.

3. Lubrication by employing nanoparticles

Since it has become clear that DLC coatings are not adequately active toward chemical-based additives, other concepts that are predominantly physical-based seem very welcome as potential lubrication solutions for DLC green technology. Self-lubricating nanoparticles are thus an interesting lubricating concept to be explored from various points of view.

The idea of nanoparticle-assisted lubrication has been proposed as a promising concept quite some time ago. However, despite the numerous types of nanoparticles that have already been tested and some that have already been used in practical applications, the actual tribological mechanisms and the relevant influential parameters under different contact conditions have yet to be determined.

Following the advances in conventional solid lubrication and the established theory of the transfer films [17,18], research has focused on the tribology of graphite-like nanostructures, i.e., C60 fullerenes [19,20], carbon nanotubes [21,22] and carbon nano-onions [23,24]. In lubricated conditions, however, nanoparticles used were mainly fullerene-like structures of IF-MoS2, and IF-WS2, where it was revealed that these inorganic nanoparticles perform very effectively as additives in lubrication fluids [25-28].

The proposed low friction mechanisms of the nanoparticles are similar to their macro-scale structures, i.e. based on low shear basal planes of layered materials, such as MoS2, WS2, and/or graphite. There have also been other mechanisms proposed, most frequently rolling of the nanoparticles, and this mechanism, again does not include any chemical reactions with elements and compounds associated with environmental emissions. It should be stressed that MoS2, which is one of the best known solid lubricants, it is also very chemically stable compound – accordingly, it is not likely to contribute in emissions.

Accordingly, it seems that nanoparticles, once placed in lubricated mechanical system, can form protective nano-sheets at the surface and provide low friction and wear with limited environmental impact, representing a potential for novel green lubrication technologies.

However, the nanoparticle lubrication mechanisms are not yet agreed and understood, and the research still tackles some fundamental problems related to dispersion, agglomeration/aggregation and sedimentation of nanoparticles in oils. For this reason, available studies and results with nanoparticles in oils are still mainly in combination with steel or other metal surfaces, and these results suggest huge improvements in friction and wear performance, such as, for example, those in our own work [29] by using MoS2 nanotubes in PAO oils, Figures 5 and 6.

In a recent work [30] about lubrication of DLC coatings with IF-MoS2 (fulleren-like) nanoparticles it was, however, contrary reported - that there was no effect on friction reduction by using DLC coating with nanoparticle-containing lubricant. The reason for such behaviour was suggested to be lack of (chemical) reactive sites for MoS2 sheets to be able to attach to the surface. Although the primary well-accepted effect of the layered solid lubricants is considered as primarily

![Fig. 5](image-url)
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The Role of Coatings and Lubricants for Tribological Interfaces

In spite of the above results, the nanoparticle concept appears promising for future green lubrication. Especially because of the low chemical reactivity of DLC and lack of effective chemical solutions, as well as due to possible compensation for non-ideal nanoparticles effectiveness in these contacts through the DLC inherent low wear and low friction behaviour.

4. Lubrication with slip at the solid-liquid interface

Another concept for green lubrication may be realized through tailored physico-chemical interactions at the solid-liquid interfaces that induce slip at the lubricated contacting surfaces, Figure 7.

We have recently showed that based on modified surface wetting properties and/or surface energies, friction can be significantly reduced - up to 20% or more - and lubrication design could be modified based on these parameters. A dedicated paper describes a new procedure to implement this new concept in lubrication design [31]. DLC coating was used as a model material, since DLC coatings are known to have lower surface energy than steel and often also poorer wetting. Figure 8 shows the friction reduction in EHL regime (and elsewhere) only due to use of surfaces where at least one surface possesses poorer wetting and/or surface energy – compared to steel. It should be stressed, that all other parameters in EHL were the same (viscosity, temperature, load, roughness), and no major influence of any asperity interaction could be considered. Moreover, similar results supporting this concept were found also in some other studies [32,33].

We have further verified this suggestions and concept also by purposely using several different DLC coatings, having a variety of different surface characteristics, and the same conclusion was always confirmed [34]: DLC surfaces result in lower friction than steel in EHL regime, and also at transition from mixed to EHL. Moreover, when only one such surface is in contact, friction is higher than in the case of two such surfaces, but it is lower than with both steel surfaces (steel/steel) contact (see Figure 8). The results in boundary regime appear the same, but further tests need to be done to confirm the behavior in this regime.

Although the concept of solid-liquid slip is well-known and was previously already observed to reduce friction drag under different circumstances, primarily theoretically, using various model materials or experiments at the nano scale [35-39], this was not comprehensively investigated at the macro scale with engineering materials and lubricants, with exception of only few studies [31-34]. Accordingly, it turns out that although the relevance of solid-liquid interface properties is well-accepted, a model that would correlate these parameters and friction does not yet exist, and only indirect, empirical correlations to establish these parameters are available today [31].

Nevertheless, DLC coatings offer a great potential for large variation in surface properties through different compositions, use of various doping elements and
deposition parameters and are thus ideal candidates to further explore this area. However, even so far, all results using DLC that have focusing in this subject clearly support the suggestion that friction can be significantly reduced by modifying the wetting and/or surface energy of DLC coatings, thus providing reduced friction in a green way, without any additives.

5. Discussion

This paper propose and discuss few potential new strategies that may lead to green lubrication technologies, specifically focusing on those that include use of DLC coatings.

These strategies can employ chemical-based additives, but with reduced environmental emissions impact. These additives may be less strong and probably will not need to consist from very successful, but environmentally undesirable elements, such as S, P and Zn. Namely, DLC with its high wear resistance and low friction may not need these additives for adequate protection even for the most heavy-loaded contacts. Moreover, current results show that these additives are not equally effective on DLC, as are on the steel surfaces anyway. Accordingly, milder additives, such as low- or no-SAPS may be suitable for the systems incorporating DLC coatings, even though used at high loads and high temperatures, and this may become one of the new green lubrication technologies in future mechanical systems.

Other potential green lubrication technologies are nanoparticles incorporated in oils and greases, especially those based on WS2 and MoS2. They are effective on steel surfaces, but still, there are many issues opened related to proper dispersion and sedimentation of these nanoparticles. However, a combination with DLC coatings may be welcome due to DLC’s non-reactivity with classical additives, as well as may allow some inefficiency in such lubrication, which can be compensated with DLC low wear and friction behavior. Namely, a recent study on these nanoparticles with DLC is not the most optimistic; however, there are many details to be further explored.

The third concept discussed in this work is based on modification of solid-liquid interface and affecting friction and wear through wetting and surface energy properties. DLC coatings are good candidates for this green lubrication technology, because their properties can be tailored in many different ways. So far, it is quite clear that friction with DLC is lower in EHD and mixed/EHD regime compared to steel, but mechanisms are not yet confirmed. We have proposed that slip occurs at DLC surfaces, which causes film thickness reduction and so the viscous friction [31,34] and this suggestion agrees with some other studies, as well [32,33]. However, it is not obvious whether wetting or surface energy affects this behavior and research in this area is currently ongoing. However, by employing proper surface-lubricant interface, additives that cause emissions today may be substantially omitted, and again, DLC with its inherently low wear and low friction may be an ideal surface to compensate some of the drawbacks in such cases. In fact, we have recently showed that friction with low amounts of lubricant and low viscosity oils and/or oils with short chain lengths actually reduce friction, not increase, as is typical for steels – if the contact severity is low enough so that DLC remains at the contacting surfaces during operation [16].

6. Conclusions

There exist several potential solutions for green lubrication technologies, and only few are discussed in this work. Namely, DLC coatings may be good candidates for some of the most promising and available solutions for green lubrication already at today’s state of the art of science and technology. These include the following.

Mild additives without components based on S, P and Zn that cause emissions, such as low- or no-SAPS, may be possible to use with DLC coatings and promote greener lubrication. The reason is DLC’s high wear resistance that does not require as much additive protection as conventional steel surfaces.

Self-lubricating nanoparticles based on WS2 or MoS2 are promising concept for green lubrication with oils and greases, because their lubrication mechanisms are mainly based on physical concepts, which are not suppressed with DLC lower chemical activity.

DLC coatings offer many possibilities for surface modifications and thus enable reduced friction and green lubrication through modified solid-liquid interface behavior, namely tailored wetting and surface energy of the contacting surfaces, and in this way inducing slip. This concept has already been proved and is getting more attention in current research.

References


