

## TRIBOLOGICAL BEHAVIOR OF DLC FILMS IN PAO 5W30 OIL UNDER BOUNDARY LUBRICATION

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### ABSTRACT

*This paper reports the influence of PAO 5W30 synthetic oil in contact with DLC films. These films were deposited on 316L stainless steel substrates using PECVD technique. The addition of synthetic oil has been proposed as the controlling mechanism that can lead to super low friction coefficients and wear. Tribological behavior under hybrid lubrication was investigated. The results clearly show that when synthetic oil was added to DLC/DLC pair, the friction coefficient did not change compared to DLC/DLC pair in air conditions. However, for 316L/DLC pair, the friction coefficient decreased 75% compared to 316L/DLC pair in air conditions. The wear rate of DLC/DLC did not change, when the 5W30 oil was added, the wear rate of 316L/DLC pair decreased 37%, while 316L/316L pair decreased 71% compared to the same pairs in air conditions. This can be related to polar additives contained in 5W30 oil which leads to reducing wear in 316L pairs.*

### 1. INTRODUCTION

Nowadays, dynamic wear and friction coefficient conditions have been studied with large interest in scientific community and industry [1]. Advances in coating technologies allow new deposition techniques of diamond-like carbon (DLC) films, with higher deposition rates, high degree of hardness, adherence, and wear resistance and with decreasing friction coefficient. These properties open further possibilities in improving tribological performance and reliability of different machine components [1-2]. Improving DLC tribological behavior depends mainly on the film properties and its adhesion to the substrate as well as loading and environmental conditions [3]. However, despite of the low friction coefficients normally observed for DLC-coated surfaces under dry sliding conditions, only a few DLC-coated components are likely to be operated completely without a lubricant [4]. With the introduction of DLC-coated surfaces in existing systems, the major concern is the compatibility with the existing lubricants [5]. In particular, the addition of synthetic oil has been proposed as the controlling mechanism that can lead to super low friction coefficients and wear [4].

The current manuscript is a study of the tribological behavior under hybrid lubrication of DLC films with PAO 5W30 motor synthetic oil. The main objective of this paper

is to understand DLC friction and wear as function of hydroxyl number, according to ASTM E 1899 and DIN 53240-2 norms and water content of PAO 5W30 synthetic oil

### 2. EXPERIMENTAL PROCEDURE

DLC films with 20% hydrogen concentration were deposited on 316L stainless steel substrates using a pulsed-DC discharge under controlled conditions [2-3,6]. For all tribological tests, the disk specimen surfaces were previous polished to a final finish of  $\sim 0.02 \mu\text{m}$  average roughness ( $R_a$ ). The original ball  $R_a$  was  $\sim 1.81 \mu\text{m}$ . Both of them were ultrasonically cleaned in acetone bath. The substrates were additionally cleaned by argon discharge with 1 sccm gas flow at 11.3 Pa working pressure and a discharge voltage of  $-700 \text{ V}$  for 30 min prior to deposition. The 316L stainless steel surface was modified by diffusion process during one hour at  $430^\circ\text{C}$  using  $\text{N}_2$ ,  $\text{H}_2$  e  $\text{CH}_4$  gas to form an adhesion interlayer [7]. This carbonitride interlayer has around 8 GPa of hardness and  $10 \mu\text{m}$  of thickness [7]. The DLC film 20% hydrogenated was deposited using methane to a thickness of  $\sim 2.0 \mu\text{m}$ . The deposition was performed using 1 sccm of gas flow ( $\text{CH}_4$ ), during 2 h at 11.3 Pa using a discharge voltage of  $-700 \text{ V}$ .

The tribological tests were performed for 316L pair coated and uncoated with DLC films. The 50 mm-diameter disks and 4 mm-diameter balls were used for the tribological tests. The friction and wear tests were carried out using a UMT-CETR ball-on-disk tribometer in rotational mode at 120 mm.s<sup>-1</sup> sliding speed under 2 N of applied load during 3000 cycles. The environment during the tests was strictly controlled to keep humidity at  $40 \pm 2\%$  and temperature at  $23 \pm 1^\circ\text{C}$ . The tests were repeated five times for each pair combination in order to confirm the reproducibility. A new position on the ball/disk was used for each test, and the friction coefficients were collected from the steady-state region [8]. The initial average Hertzian contact pressure ranged from 0.73 to 1.09 GPa. For lubricated tests, it was used 5W30 commercial Poly-Alpha-Olefin (PAO) synthetic oil (SAE, 5W30 API SL/CF), see Tab. 1, at room temperature. After friction measurements, the ball wear rate was measured and calculated automatically through the profilers, NT1100.

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**Table 1 – Oil Properties [9]**

Properties	5W30
Density (20 °C) g/cm <sup>3</sup>	0.84
Viscosity (40 °C) cSt	60

### 2.1 Hydroxyls number

The hydroxyl number (HN) is defined as the amount of potassium hydroxide in milligrams that is equivalent to the hydroxyl amount of one gram of the sample. The most frequently described method to determining hydroxyl number is the reaction with acetic anhydride in pyridine with subsequent titration of the free acetic acid. A potentiometric titration technique was carried out on PAO 5W30 synthetic oil before and after tests in contact with DLC/DLC and 316L/DLC pairs, in order to determine changes in the oil's number of hydroxyl. The instrument used was an 814 USB Sample Processor with two towers, 120 mL PP beakers with covers, 809 Titrand, 741 Magnetic Stirrer and 800 Dosinos from Metrohm International. The chemicals used for these experiments were N-methylpyrrolidone (1-methyl-2-pyrrolidone, NMP), acetic anhydride 4-N-dimethylaminopyridine, 1-Octanol as reference material, Ethanol (electrode rinsing solution), purity > 99.8% and Water deionized (electrode rinsing solution).

### 2.2 Water determination by Karl Fisher

A Karl Fisher titration was carried out on three samples of the mobile and the stationary phase. The instrument used was an 841 Titrand including titration cell and indicator electrode from Metrohm International. The chemicals used for these experiments were methylene chloride, stabilized Karl Fisher reagent, and diluents for stabilized Karl Fisher reagent. All these chemicals were obtained from Fisher Scientific.

### 2.3 Contact angle analysis

The contact angles of deionized water and 5W30 oil on the disk surface coated and uncoated with DLC film were measured with sessile drop method, using a contact angle measuring instrument EasyDrop, KRÜSS - DSA20E model. Drop Shape Analysis System in atmospheric condition at room temperature. It was repeated at least five times for each sample before and after tests under oils and environment air. A droplet with a volume of 2.5 µL was released over the sample surface from a syringe needle.

### 2.4 Microstructure analysis of DLC films

The atomic arrangement of the films was analyzed using Raman scattering spectroscopy (Renishaw 2000 system) with an Ar<sup>+</sup>-ion laser ( $\lambda = 514$  nm) in backscattering geometry. The laser power on the sample was ~0.6 mW and the laser spot had 2.5 µm diameter. The Raman shift was calibrated in relation to the diamond peak at 1332 cm<sup>-1</sup>. In order to evaluate the coating homogeneity, several measurements were performed from different areas of the

coated samples before and after the tests. All measurements were carried out in air at room temperature.

## 3. RESULTS AND DISCUSSION

As a matter of nomenclature the tribological pairs coated and uncoated with DLC film used in this work are nominated DLC/DLC to both parts covered with DLC film and 316L/DLC to counter-body without DLC and body recovered with DLC film.

### 3.1 Friction and wear under oil

The friction coefficient and wear rate after 3000 cycles under environmental air (40% RH), and 5W30 oil can be seen in the Fig. 1. The 316L/DLC pair showed an increase in friction coefficient in environment air at 100% compared to DLC/DLC. The same occurs with 316L/316L compared to 316L/DLC pair in the same condition. Under 5W30 oil, the friction coefficient of 316L/DLC pair decreased 48% compared to DLC/DLC, while the 316L/316L pair showed an increase in the friction coefficient at 195% in same condition. However, comparing with environment air, the addition of oil decreased 36% the friction coefficient for 316L/316L pair. It is interesting to note that when 5W30 oil is added to DLC/DLC pair, the friction coefficient did not change compared to DLC/DLC pair in air conditions. However, for 316L/DLC pair, the friction coefficient decreased 75% compared to 316L/DLC pair in air conditions.

These results show that wear rate for 316L/DLC pair in environment air decreased 19% compared to DLC/DLC pair in the same condition, while the wear rate of 316L/316L pair increased one order of magnitude compared to 316L/DLC pair (Fig.1(b)). However, when the 5W30 oil was added, the wear rate of DLC/DLC did not change, while the wear rate of 316L/DLC pair decreased 37% and of 316L/316L decreased 71% compared to the same pairs in air conditions. The lowest friction coefficient and wear rate was obtained to 316L/DLC pair under synthetic oil. The reduction mechanism of friction

and wear for 316L/DLC pairs can be attributed to the effect of long chain polar (amphiphilic) molecules. In the so-called "Self-Assembled Monolayer" (SAM) or "Monolayer" model, the polar extremity of the molecule is strongly chemisorbed on the native oxide layer present on the steel surface while the paraffinic moiety extends outside the metal surface. The amphiphilic molecules must have at least 10 carbons in their aliphatic chain in order to promote the formation of a crystal-like structure in the SAM layer. Then, low friction is generally attributed to easy sliding of methyl groups over each other, in a way described and also simulated by Molecular Dynamics in the literature by Harrison [10], for example.

### 3.2 Raman Scattering Spectroscopy

The Raman scattering spectra fitted using two Gaussian lines and their integrated intensity ratio of the D and G peaks

(ID/IG-ratio) were compared. All DLC films of the present study before friction tests revealed a similar ID/IG-ratio around to 1.37 (Fig. 2 (a)). The spectra were fitted with Gaussian distributions associated with the peaks commonly found in amorphous hydrogenated carbon and labeled as G (graphite) and D (disordered), with bands between 1100 and 1750  $\text{cm}^{-1}$ , typical of amorphous hydrogenated carbon [10]. However, Raman spectra obtained from the ball after friction from experiments in environment air, and oil showed some important and indicative changes. It is well known that the relative intensity of the D peak is related to the microcrystalline size of the graphitic cluster, where less-graphitic amorphous films have a lower ID/IG value [11]. This transformation is strongly dependent on thermal and/or straining effects, as it was observed and reported previously by others [12]. DLC ID/IG-ratio before and ID/IG-ratio of DLC/DLC pair after tribological tests under boundary-lubricated conditions can be seen in Tab. 2.

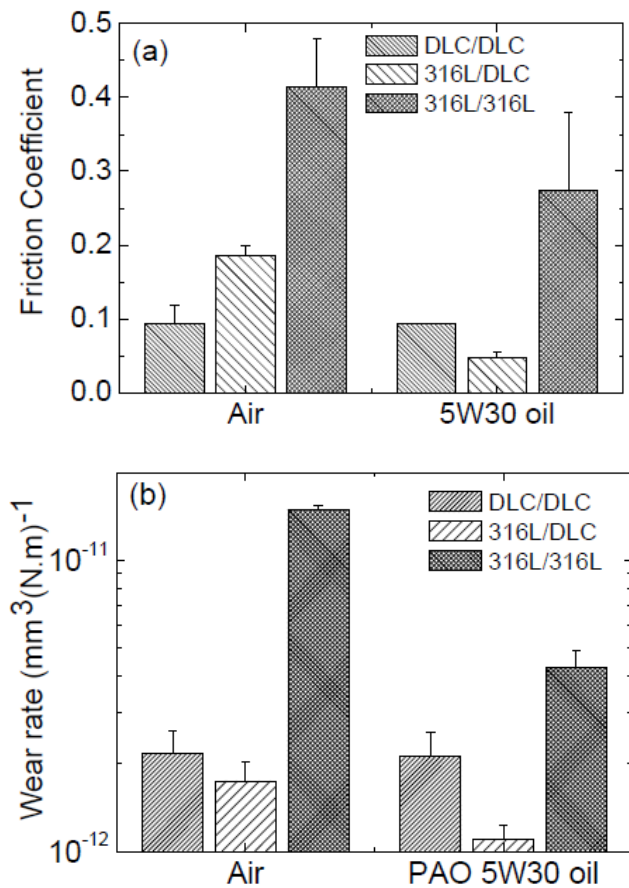


Figure 1 - (a) Friction coefficient and (b) wear rate of DLC film, under environment air and 5W30 oil

Table 2 - ID/IG-ratio of DLC film before and after tests under boundary lubricated conditions

	DLC (before)	Air	5W30 oil
ID/IG	1.37	1.72	1.08

Friction tests in environmental air show an additional T band centered at 1008.7  $\text{cm}^{-1}$ , see Fig 2 (b).

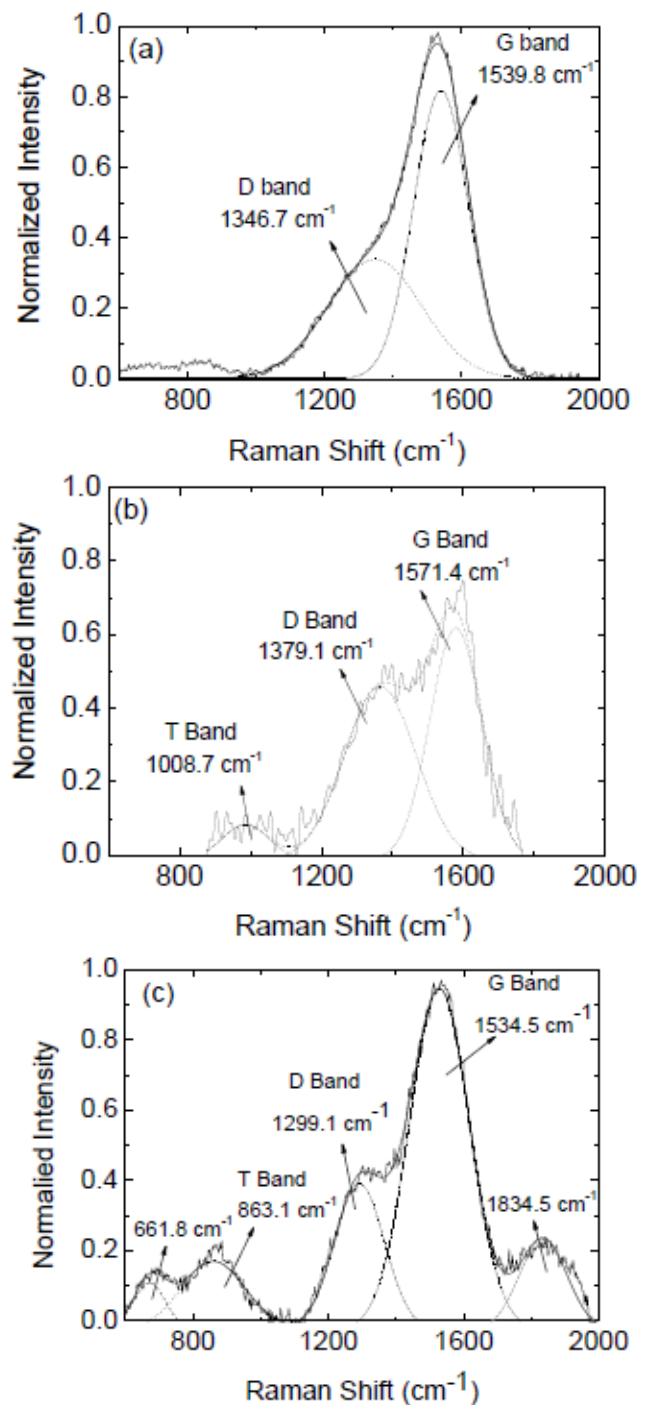


Figure 2 - DLC film spectra: (a) before and after tests in (b) environment air, and (d) 5W30 synthetic oil.

It is a consequence of the 316L stainless steel wear, increasing ID/IG-ratio to 1.72. Researches confirm that the tribolayer is composed of wear particles from both 316L substrates, with the presence of CrNi and DLC films [13,14]. Friction tests with 5W30 oil revealed a decrease in ID/IG-ratio to 1.08 compared to tests in environmental air. It is also showed two additional bands centered at 661.8 and 1834.5  $\text{cm}^{-1}$ , respectively, that can be seen in Fig. 2(c). This can be related to the formation of a tribolayer scattered in the oil.

### 3.3 Water Determination

Owing to the low water content in 5W30 oil, the coulometric Karl Fisher method was used. In this analyze, methanol was used as solvent and vigorous homogenization of the solution was required. For this oil, became necessary to heat the oil until 160°C and N<sub>2</sub> as drag gas due to precipitation of Karl Fisher solution. The result showed that 5W30 oil has 952.4 ppm of water in 30 mL of oil, corresponding to 3.17x10<sup>22</sup> of H<sub>2</sub>O molecules. Compared to 1.33x10<sup>24</sup> of H<sub>2</sub>O molecules contained in 40% RH (relative humidity), the 5W30 oil has 2.38% H<sub>2</sub>O molecules.

### 3.4 Contact Angle

The wettability effect of water and 5W30 oil was examined on disks coated and uncoated with DLC film, see Fig. 3. The DLC film showed water contact angles around 80.5±0.5° and 29.7±0.5° for 5W30 synthetic oil. The 316L stainless steel surface showed water contact angles around 53.9±0.5° and 27.2±0.5° for 5W30 synthetic oil.

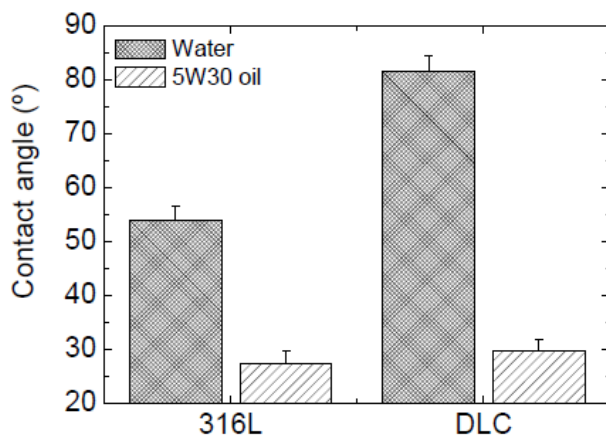


Figure 3 – Contact angle of DLC coatings and 316L stainless steel with deionized water and 5W30 oil.

The high wettability of DLC and 316L surface can be explained by polarity of the oil. The polarity of the oil directly affects its adhesion to the parts it is supposed to lubricate. Highly polar oil displays greater adhesion, resulting in greater boundary layer thickness and higher film rupture strength. 5W30 oil is very non-polar, without polar additives and it would exhibit a lower degree of wetting on engine parts. This is one of the reasons that 5W30 synthetic oil is formulated with the addition of another more polar base stock, such as a polyol ester. The addition of a polar additive such as a detergent or an anti wear additive such as ZDDP would also increase the overall polarity of this oil [15].

### 3.5 Hydroxyl numbers

The hydroxyl group is an important functional group and knowledge of the hydroxyl number, i.e. the hydroxyl group content, is required for the production of intermediate and finished products such as polyols, resins, paint resins and lubricants (petroleum industry) [7]. Investigations have

shown that the terminal hydroxyl groups and intermolecular hydrogen bonding may be expected to play a part in such equilibrium with DLC film surface. Also, the stability of metallo-organic compounds varies greatly and it is dependent on the nature of the OH groups and other products that may be formed during friction [16]. However, special production techniques are required to obtain hydroxyl numbers. The use of a fully automatic system for this type of analysis is highly recommended, because in this way, contact with toxic solvents is minimized. Unfortunately, the 5W30 oil showed small hydroxyl numbers that could not be determined with accuracy by this method, so that, it was not possible to conclude if the hydroxyl numbers reacted with free dangling bonds in DLC film surface.

Table 3 - Results obtained from potentiometric determination of the hydroxyl number as per ASTM and DIN to 5W30 oil

DLC/DLC	316L/DLC
6.504	5.439
8.764	5.555
18.490	11.368
11.252 ± 6.368	7.454 ± 3.390

## 4. CONCLUSIONS

Tribological performance of the DLC film under 5W30 oil was investigated. Transferred materials on the DLC surface was examined using Raman spectroscopy and contact angle. The main conclusions can be drawn as follows:

1. The 5W30 oil has 2.38% H<sub>2</sub>O molecules compared to 1.33x10<sup>24</sup> H<sub>2</sub>O molecules contained in 40% RH, leading to conclude that the presence of water is not responsible to affect the friction and wear in these conditions.
2. Wettability behavior of 5W30 lubricant oil on DLC and 316L stainless steel surface is dependent on the polar additives contained in this oil.

It is clear that more investigations are necessary to understand about triboreactions between 5W30 oil and DLC film surface and the role of the additives under higher temperatures.

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