

DLC coating on a plastic substrate for mechanical applications

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Abstract: In this final degree work, a coating of DLC was synthesised and characterized. With the PECVD process, we coated of DLC a PC substrate in order to improve its mechanical properties. With a DLC coating we are improving properties like the friction and the wear. In order to quantify those improvements, we characterized the sample with the nanotribometer to know its friction coefficient, and with the calorimeter to know its wear rate. Furthermore we did a transmittance to study the optical absorptions of the layer of DLC.

I. INTRODUCTION

The main objective of this work was to create a coating of DLC (Diamond-Like Carbon) over a substrate and study its mechanical properties and the transmittance of the system. This work wanted to find good mechanical properties of a layer.

The substrate was PC (polycarbonate), due to the intention of creating a low absorption coating. The coating was obtained with the PECVD (Plasma Enhanced Chemical Vapor Deposition) technique, and was DLC on its a-C:H form.

To understand this work, first of all, let us introduce what DLC is. DLC is a material made by carbon, so we are talking about a coating of carbon. Carbon is an abundant element in nature, and we can find it in different forms, depending on its electronic configuration. Carbon has different types of electronic configuration, depending on the atomic orbital, which is how carbon can be bonded with other atoms of carbon. Electrons have to be bonded with other atoms, in a type of bonds which can be s or p. In the case of carbon, it is a mixture of s and p, through the so-called hybridisation, producing the types of orbital sp , sp^2 and sp^3 [1]. Depending on this bonding configuration, carbon can be found on different types: graphite, diamond or amorphous carbon. DLC is a combination of $sp^3/sp^2/sp$ -hybrid bonds, and depending on that hybridisation, the coating has different properties more likely to the bulk material.

Moreover, the introduction of alloying elements in amorphous carbon improves specific properties of the film, depending on the added material. N, Si or metal incorporation reduces the internal stress of the material, giving a decrease of surface energy [2]. With F and Si-O the friction coefficient of the layer is reduced. And with metals, hardness is increased and friction reduced. Other metals, like Ta, W and Nb reduce films' intrinsic compressive stress. Al, Fe, Ni, Nb and Ti reduce surface free energy, and on the other hand, W increases it. The addition of hydrogen on the

thin film of DLC changes also the optical properties [2]. All these changes of the properties are only in a certain range. Introducing more one element does not mean that their properties are improved in all ranges.

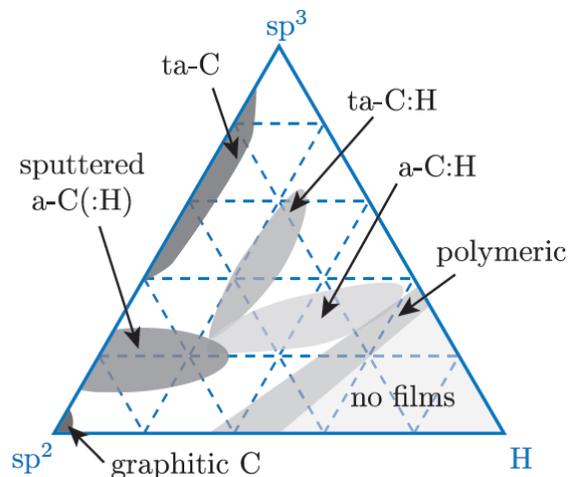


FIG. 1: Diagrame of the DLC types [3].

The applications of the DLC are many in different fields. For example, due to its very low friction coefficient and its high hardness, it is used in a lot of mechanical tools. In addition, DLC films are biocompatible and hemocompatible, so they are used for medical applications, like prosthesis, where a high wear resistance is also required [4]. DLC coatings reduce corrosion of the material and increase the lifetime of the material [2].

II. EXPERIMENTAL

A. Material

In this section, we are going to define the materials that we used to synthesise the layer and the techniques of deposition.

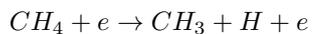
First of all, the layer grew up above a substrate which had to be transparent since we want to study the transmittance of the layer. Therefore, the sub-

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strate was a sample of PC. This substrate was designed for the ophthalmic industry, so it was pretreated with a hardening resin of polysiloxane, and with an anti-reflective multilayer.

Our layer is a DLC coating, and in particular it is amorphous carbon with hydrogen (a-C:H). Therefore, the precursor used to synthesise the layer is methane (CH_4). In the chamber of the reactor, once the methane has entered into the reactor's chamber, it collides with the electrons of the plasma, so some of the bonds of the molecule are broken, allowing the deposition of the CH_3 . That was the main molecule of the growing of our sample.

The reaction in the chamber is [1]:



B. Deposition technique

The deposition technique was a CVD (Chemical Vapour Deposition) process. In particular, we used the Radio Frequency Plasma Enhanced Chemical Vapour Deposition (RF PECVD) technique.

The reactor called PEDRO (Plasma Etching and Deposition ReactOr) is the one used to make the PECVD process. It belongs to the FEMAN group of the Applied Physics and Optics Department. Moreover, the reactor is used to make Magnetron Sputtering, Reactive Ion Etching and Ion Beam Etching, due the multiple arms that it has. The main chamber has a capacity of 80 litres and the vacuum can reach pressures about 10^{-6} Pa. The sample enters in the reactor through one arm, in this case for the one used to make a CVD process. Then, the sample remains into a pre-chamber in order to reach a primary vacuum until the gate to the high vacuum in the main chamber is opened. Once a mechanical pump has reached the primary vacuum in the pre-chamber, it enters to the big chamber where a turbomolecular pump makes the high vacuum until a prepressure of 10 Pa. After that, the chamber is ready to allow the entrance of the gases for the deposition. Thanks to a LabView interface, conditions such as pressure, gas flows or time of deposition are controlled [2].

Before the deposition, we used an Ar plasma flow in order to clean the sample of impurities. The sample was on the cathode of the chamber, allowing the plasma to be created on it.

Once we had the substrate clean, we defined the optimal experimental conditions in order to get a layer with good mechanical properties and a good transparency. We were looking for a layer with a low friction coefficient and a low wear rate. Therefore, if we are improving the transparency by reducing the thin of the layer, mechanical properties such as them can be reduced.

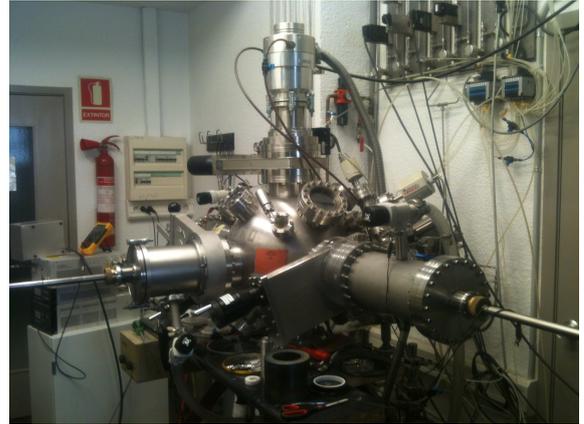


FIG. 2: PEDRO in the laboratory of the FEMAN group.

The first step of the PECVD technique is the transport of the reactants (in our case, it was methane, CH_4) to the reaction chamber. Then, the gas precursor and the by-products were formed. The plasma allowed the reactants and their products to be deposited on the substrate, thus the phase species were adsorbed. Before a correct deposition, the particles of the species were diffused on the surface and there were some chemical reactions. Also, the volatile by-products were desorbed and transported out of the chamber [2]. The cathode was refrigerated with water. This is important because our substrate was plastic, so it might be deformed due to the high temperatures.

The conditions in the chamber were:

Process	Cleaning	Deposition
Pressure (Pa)	10	10
Power of the plasma (W)	20	20
Bias (V)	-104	-178
Argon flow (sccm)	25	0
Methane flow (sccm)	0	25
Time of the process (min)	20	5

TABLE I: Working conditions in the main chamber of the reactor.

After the deposition process, the sample was taken out of the reactor through the same steps that it entered. The sample had to remain in the pre-chamber in order to keep the high vacuum in the main chamber.

C. Characterization techniques

The sample was characterized with the aim to know its mechanical and optical properties. The parameters studied were the friction coefficient, the wear rate, the thickness and the transmittance. Each parameter was

studied with a different technique and a different system.

Before starting the deposition, and regarding the measurement of the sample's thickness, 3 lines were painted with a marker on it. After the deposition, we removed the marker with acetone (lift-off), so the sample had a step with coating and non-coating and that allowed us to make a good measure of the thickness of the coating.

1. Thickness

This is the first step of our characterization, because it is not a destructive experiment and it gives us essential information of the coating.

The thickness was measured both with a contact and with a non-contact profilometer. The contact profilometer (named Dektak 30 30) is a device with a tip that touches the sample, goes over a few distance (usually 2 mm) and collects the information about the topography. This kind of profilometers has the disadvantage that it only shows a 2D plot, so it is necessary to make different scans to determinate the real thickness of the coating.

On the other hand, we have the non-contact profilometers. The device used in this case is a confocal microscope (named Sensofar), thanks to which we can get a 3D image of the sample and measure the thickness with an interactive interface.

Comparing the results of the profilometer and the confocal microscopy we can determinate the thickness of the coating.

In the following table, the parameters of the contact profilometer are shown:

Parameter	Value
Scan Length (mm)	2
Profile	Step
Measurement Range (nm)	65000
Stylus Force (mN)	0.20

TABLE II: Contact profilometer conditions.

2. Transmittance

That is also a non-destructive experiment.

Since our sample is transparent, we can measure the intensity of the light that passes through the coating and the substrate depending on the wavelength. The transmittance was measured in the Physics of Materials' Laboratory.

The white light of a W halogen lamp illuminates the sample. Then, a CCD camera placed on its other side collects the light that has passed through it, and with the computer's software we can get the plot of the transmittance. However that was not enough for the characterization of the coating: we have to compare

our results with the transmittance of the substrate in order to recognize which absorptions are caused by the coating, and which by the substrate.

The transmittance formula is:

$$T = \frac{I}{I_0} 100 \quad (1)$$

Where I is the intensity of light collected by the CCD camera with the sample, and I_0 without it.

Parameter	Value
Integration time (ms)	45
Scans to Average	20
Boxcar Width	7
Strobe/Lamp Correction	No
Electric Dark Correction	Yes
Nonlinearity correction	Yes
Stray Light Correction	Yes
External Trigger	Normal

TABLE III: Transmittance conditions.

3. Friction coefficient

This experiment damages the sample, so it has to be done after the non-destructive experiments.

The friction coefficient was measured with the nanotribometer machine (named CSM Nanotribometer). The nanotribometer is a device that uses a marble in order to scratch the surface and determinate the friction coefficient. The device applies a force to the substrate and scratches it during certain a time. The sample spins over itself and the marble makes a groove, while the software of the computer is calculating the friction coefficient of the surface at each point.

Parameter	Value
Radius (mm)	0.50
Lineal Speed (mm/s)	1.00
Total laps	100
Normal load (mN)	100.00
Acquisition rate (Hz)	5.0
Dimensions Ball (mm)	1.00
Environment	
Temperature (°C)	25
Humidity (%)	45.00

TABLE IV: Nanotribometer conditions.

If we are measuring for a long time, the layer can be trespassed, so then the nanotribometer will measure the friction coefficient of the substrate. Since the substrate has different layers, the nanotribometer can trespass them and measure the friction coefficient of

these layers. In this case, we will see different friction coefficient values in the plot while the nanotribometer is trespassing the layers.

4. Wear rate

The calotest (named CSM Calotest) is the device used to determinate the wear rate of the coating. A ball spins over the sample in order to scratch the surface and remove material of it, making therefore a hole. It is necessary an abrasive liquid made of a diamond suspension, in order to scratch the surface, because the ball was less hard than our coating of DLC, so diamond was needed to scratch the surface.

With the aim of measure the wear rate, we measure the hole made with the confocal microscope, the diameter of the hole and its deepness. The wear rate formula is:

$$K = \frac{V}{PS} \tag{2}$$

Where V is the removed material, S the sliding distance, and P the normal force applied to the sample [5]. In the Calotest manual it is shown how to calculate V, P and S [6].

Parameter	Value
Ball material	Polyoxymethylene (Delrin)
Ball mass (g)	18.817
Normal force (N)	0.369
Ball dimensions (mm)	30.00
Time (s)	20
Speed (rpm)	30

TABLE V: Calotest conditions.

In addition, we measured the wear rate of the substrate in order to know if our coating is harder than the sample without the coating.

III. RESULTS

In this section we are going to discuss all the results of the characterisations done to the sample.

In FIG. 3, sample 14C3102 is shown.

As we can see, the sample is transparent but it has a brown colour that will affect to the transmittance.

Acording to the profilometer, the thickness of the sample is **35 nm**. And acording to the confocal microscope, it is **38,5 nm**.

In order to know its optical properties, we measured a transmittance to the sample, and to the substrate without the coating, to compare the wavelengths affected with the layer.



FIG. 3: 14C3102 sample.

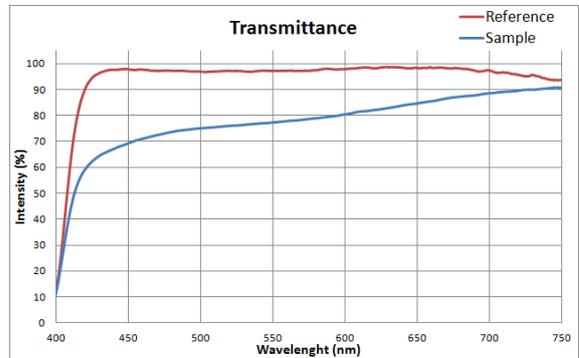


FIG. 4: Transmittance of the layer.

The transmittance (FIG. 4) shows that for low wavelengths there is absorption of the light. This is because of the colour of the sample, as the brown colour of the DLC.

For the friction coefficient we did the same. First of all, we did the characterization of the substrate, and then we compared it with the characterization with the coating.

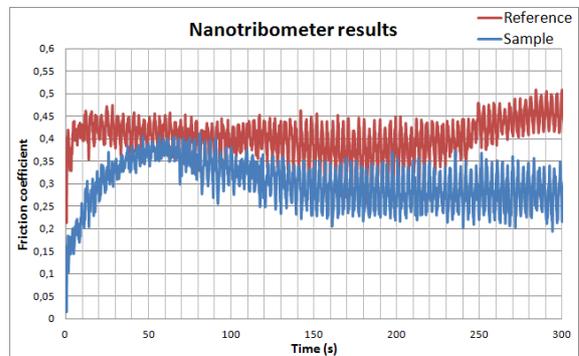


FIG. 5: Coefficient friction for the layer.

FIG. 5 shows the coefficient friction during the pro-

cess of the nanotribometer. The changes on the tendency of the friction coefficient are due to the different layers on the substrate. As we can see, in the first moments of the experiment, the friction coefficient is very low, around **0.15**, and then it increases until values like the ones from the substrate, **0.4**. At this moment, both have similar behaviour [5] because the nanotribometer is scratching the same material.

According to [7], layers between 300 and 700 nm have values of friction coefficient between 0.15 and 0.20. In our case, the friction coefficient is higher than these values because the layer is extremely thin. Nevertheless, in all the experiment, the friction coefficient of the DLC sample was always lower than the one of the substrate.

And finally, regarding the wear rate, we obtained a value of $1.1 \cdot 10^{-14} \text{ m}^3/\text{Nm}$. The hole considered has a diameter of $167 \mu\text{m}$ and a deepness of 143 nm. This means a volume of $3.132 \cdot 10^{-6} \text{ mm}^3$, according to the spherical cap formula.

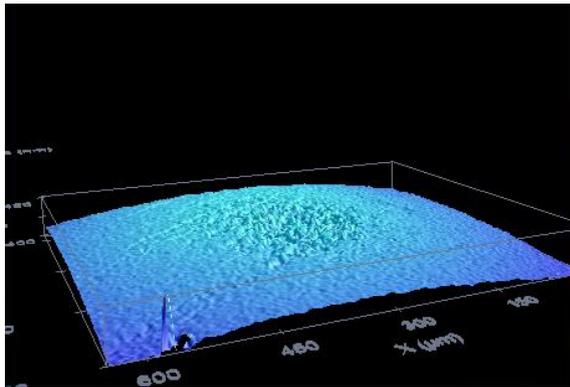


FIG. 6: 3D image of the sample with the confocal microscope, showing the hole made by the calotest.

Moreover, we measured the wear rate of the substrate. The deepness of the hole in this case was 773 nm. Hence the wear rate was $3.24 \cdot 10^{-13} \text{ m}^3/\text{Nm}$.

IV. CONCLUSIONS

- We synthesized a DLC coating of only 38 nm. The friction coefficient is around 0.20. This is lower than the expected because according to [2], we can get similar values but with layers of 200 nm.
- For the wear rate we obtained a value of $1.1 \cdot 10^{-14} \text{ m}^3/\text{Nm}$. According to [1], a typical wear rate is about $5 \cdot 10^{-16} \text{ m}^3/\text{Nm}$. We obtained a value higher than the expected, but despite that, the wear rate of our sample is lower than the one of the substrate. The result with the coating is a sample harder than the one we had without the DLC.
- Due to its brown color, the layer has a good transmittance, especially in the range of high wavelengths.
- We created a layer with many uses in the market, for example, in the ophthalmic market or as a coating for a mechanical tool, because it is transparent, hard and it has a low friction coefficient [8].

Acknowledgments

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