



# Amorphous hydrogenated carbon (a-C:H) depositions on polyoxymethylene: Substrate influence on the characteristics of the developing coatings

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## ABSTRACT

After oxygen plasma treatment polyoxymethylene (POM) material was exposed to acetylene plasma to progressively deposit two different types of amorphous hydrogenated carbon (a-C:H) films. Radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD) was used to generate both plasma processes. The surface morphology of the coated samples has been investigated by atomic force microscopy (AFM) and their chemical composition by Diffusive Reflectance Infrared Fourier Transform (DRIFT) and Raman spectroscopy. Results revealed the absence of a solid interlayer formation between the a-C:H films and POM. The in sequence exposure of oxygen and acetylene plasma on POM substrate prevents a sufficient intermixing between both materials. Furthermore, it is proven that the a-C:H network developed on POM is remarkably different compared to identically deposited films on high-density polyethylene (HDPE) and polyethylene terephthalate (PET). This demonstrates that the different plastic substrates together with the diverse effects of both plasma exposures on them can strongly affect the resulting structure of the coating.

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## 1. Introduction

One of the most used industrial methods to improve plastic materials' properties like hardness and abrasion resistance, as well as to enhance biocompatibility and antibacterial behavior is the deposition of amorphous hydrogenated carbon (a-C:H) films [1–7]. Due to the enormous number of possible combinations concerning the linkage and different amounts between C and H-atoms, these films exhibit an extreme variety of arrangement [8]. Therefore, several categories are distinguished by their position in the ternary diagram of  $sp^3$ ,  $sp^2$  and H content [8]. The cluster model assumes that the  $sp^3$  network is composed by C-C and C-H bonds surrounding  $\pi$ -bonded  $sp^2$  carbon clusters arranged in plane [8].

The a-C:H materials are also denoted as diamond-like carbon (DLC) [3,8], but in this study only a specific category of these materials is named as DLC. These are the a-C:H containing between 20% and 35% of  $sp^3$  bonds and between 20% and 40% of hydrogen (see Ref. [8] for details).

To enable a proper attachment of a-C:H films on plastic materials, they are first exposed to oxygen, hydrogen, argon or nitrogen plasma [9,10]. These treatments create dangling bonds on the polymeric surface by removing contaminants as air pollutants, additives, short hydrocarbon chains and oxide layers, making the plastic appropriate for a-C:H deposition [11–17]. However, during such exposures undesirable modifications of the plastic as well as possible surface passivation from vacuum residual must have to be considered not to compromise the adhesion of the film [9].

As first approximation, the properties of the coating depend on the  $sp^3/sp^2$  ratio of carbon hybridizations and the amount of present hydrogen [8]. In addition, they strongly depend on the size and distribution of the  $sp^2$  carbon clusters, the specific chemical organization of the  $sp^3$  matrix, the type of interconnection between the various C-H molecular groups therein and the type of interlinking established between film and substrate [8]. The resulting film morphology mainly depends on the working temperature, surface diffusion, developing stress and possible recrystallization occurring during film evolution [8].

It is still controversial if and how a different gas feed used for deposition affects the resulting a-C:H network. In literature it is largely assumed that a-C:H films have properties more similar to diamond (superior hardness, chemical inertness and high electrical resistance)

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or closer to graphite (softness and good electrical conductivity) depending on both the specific deposition process (present temperature, pressure, flux, bias voltage, etc.) and the precursor type (specific H/C ratios, carbon bond configurations, energy of the plasma species, chemical reactions within the plasma, etc.) [8,18]. Some researchers instead suggested that the chemical precursor has only a little influence on the film properties, because they are mainly governed by the energy of the species involved in film growth [19,20]. Recently, Thiry et al. demonstrated that also the branching degree and clustering of the network have a strong impact on the film properties [21]. The authors have shown that a-C:H films deposited from methane have less  $sp^3$  bonding and similar hydrogen content compared to layers obtained from acetylene, but the coatings developed from methane are harder [21]. It was concluded that films deposited from methane are less branched and have a higher cross-linking degree compared to depositions from acetylene, enabling the formation of a denser network with increased hardness [21].

This brief scenario shows that a common understanding of a-C:H films' properties and their development is not trivial. Therefore, to gain an enhanced understanding of the a-C:H growth process and to address specific film properties, a detailed inspection on the complete film deposition processes is necessary.

In a previous study a pronounced interlayer formation was observed between DLC films and polyethylene (PE) [22]. The films have been grown by plasma-enhanced chemical vapor deposition (RF-PECVD) in acetylene plasma [22]. The interlayer is formed because the impinging plasma species and the developing film intermixes towards a stable combination with the plastic material at the first stages of the deposition process [22]. The epitaxial DLC growth starts only after this interlayer formation ends [22]. Further studies of DLC depositions on high-density polyethylene (HDPE) [23] and polyethylene terephthalate (PET) [24] revealed interlayer formation as well. With increasing film thickness a transition between a polymer-like to a more cross-linked DLC network was also detected [23,24]. This transition occurred independently from the used substrate as proven by comparing the results of identical DLC depositions on HDPE, PET and silicon (100) as harder substrate [23–25]. During such chemical evolution the DLC network changes via dehydrogenation of  $=CH_2$  groups and folding of the dehydrogenated  $sp^2$  chain parts into more stable  $sp^2$  clusters, to release the intrinsic stress caused by the increasing deposition [24].

In the present study commercial polyoxymethylene (POM) material is coated by two different types of a-C:H films. In line with previous studies [22–25], the resulting coatings are obtained respectively by the f- (= more flexible) and r-deposition (= more robust) processes. POM is a semi-crystalline polymer with high abrasion resistance, low friction coefficient and high heat resistance widely used to assemble mechanical gears, insulin pens, inhalers, food containers etc. [26]. The polymeric chains in POM are composed by repetitions of methylene groups connected via oxygen atoms [26]. Therefore, the repetitive units in POM differ by an additional oxygen atom compared to PE and HDPE [22,23]. POM was chosen as substrate to investigate if and how the different chemical composition changes the properties of the deposited films. As done in previous studies [22–25], POM is coated by RF-PECVD technique with acetylene plasma after a prior exposure to oxygen plasma. The surface morphology of the resulting composites was studied *ex situ* by atomic force microscopy (AFM), while Diffusive Reflectance Infrared Fourier Transform (DRIFT) and Raman spectroscopy were used to investigate their chemical composition.

## 2. Experimental details

### 2.1. Sample preparation and coating

POM plates with 1 mm thickness were purchased in best commercially available quality (OX303010, Goodfellow GmbH, Bad Nauheim, Germany). Before plasma exposures, circular POM samples were cut

out (10 mm diameter), cleaned with isopropanol in an ultrasonic bath and dried in ambient air at room temperature. Afterward, they were mounted on a homemade aluminum sample holder with commercial carbon pads (Plano G3347, Plano GmbH, Wetzlar, Germany). POM samples were coated by two different types of a-C:H films in various depositions: 2 nm, 5 nm, 10 nm, 20 nm, 50 nm, 100 nm and 200 nm for the f-type, and 2 nm, 5 nm, 10 nm, 20 nm, 50 nm, 100 nm and 200 nm, 500 nm and 1000 nm for the r-type. The coating of both types was done via a RF-PECVD process with a RF-driven (13.6 MHz) plasma source (COPRA DN 400, CCR GmbH, Troisdorf, Germany) [27,28].

Briefly, POM is first cleaned with oxygen plasma (65 sccm/min, 1 Pa, 20 eV, 200 W) [22–25] and then exposed to acetylene plasma (65 sccm/min, 0.65 Pa, 20 eV, 107 W) in a high vacuum chamber [22–25]. During plasma exposures the temperature inside the chamber never exceeded 40 °C [4]. The r-type is obtained via a direct deposition (sample surfaces are in line of sight with the plasma source), whereas the f-type is achieved via an indirect deposition (sample surfaces are not in line of sight with the plasma source) [22–25,28–31]. The various films were realized by varying the duration of acetylene plasma exposure. The deposition rate is 2 nm/min for the f-type and 10 nm/min for the r-one. The obtained depositions were checked using a profilometer (Veeco Instruments Inc., Dektak3 surface profile measurement system, Plainview, NY, USA) on deposited silicon wafers partially covered by aluminum foil additionally mounted on the sample holder [22–25].

### 2.2. Surface characterization by AFM

The surface morphology of all samples was studied *ex situ* by atomic force microscopy (AFM, Omicron Nano Technology GmbH, Taunusstein, Germany). AFM images were recorded in contact mode in air and at room temperature, using standard silicon nitride PNP-TR cantilevers (Nano And More GmbH, Wetzlar, Germany). The entire scanned area was a square of  $5 \mu\text{m} \times 5 \mu\text{m}$ . The microscope was regularly calibrated by a cellulose acetate replica (Pelco, calibration specimen for atomic force microscopy, 607-AFM) of a 2160 lines/mm waffle pattern diffraction grating to secure the correctness of the measurements. To ensure reproducibility, at least three different positions were recorded on the surface of each sample and all the individual measurements were repeated in continuous scans until their accuracy was ensured [22–25]. By using the commercial Scanning Probe Image Processor software (SPIP version 4.6.1, Image Metrology A/S, Hørsholm, Denmark) the average height and average area of grain-like particles on the topmost layer and well-formed grains on top of it were respectively calculated with the watershed and threshold method for all f- and r-depositions showing such morphological features [23–25]. The mean values are calculated as the average from the respective  $5 \mu\text{m} \times 5 \mu\text{m}$  AFM measurements for each sample with according errors as their deviation [23–25].

### 2.3. DRIFT spectroscopy and analysis

Infrared (IR) measurements were performed via Diffusive Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy. The measuring system was a Shimadzu Fourier Transform Infrared Spectrophotometer (IRPrestige-21, Kyoto, Japan) equipped with the diffuse reflectance measuring apparatus DRS-8000 [24,32,33]. The measurements were carried out at room temperature in a flow of argon gas to eliminate ambient air contaminations [24]. All spectra were recorded with 300 repetitive scans in the  $CH_x$  stretching zone from  $3050 \text{ cm}^{-1}$  to  $2800 \text{ cm}^{-1}$  [24,34,35]. To ensure reproducibility, at least three different positions on each sample were examined to probe samples' homogeneity and the metrological correctness. No useful information was extractable from other spectral ranges (for more details please see the Supplementary Content). Spectra were analyzed with a commercial IR Solution – FTIR Control Software (software version 1.30, Shimadzu Corporation, Kyoto, Japan). The spectra were line corrected using the baseline-multipoint manipulation tool and successively refined by smoothing [24].

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