



Evolution of the sp^2 content and revealed multilayer growth of amorphous hydrogenated carbon (a-C:H) films on selected thermoplastic materials



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ABSTRACT

Amorphous hydrogenated carbon (a-C:H) films were gradually deposited on high-density polyethylene (HDPE), polyethylene terephthalate (PET) and polyoxymethylene (POM) via an indirect (f-type) and a direct (r-type) plasma-enhanced chemical vapor deposition (PECVD) process with acetylene plasma. The surface morphologies of the thicker r-depositions on the three different thermoplastics have been analyzed by atomic force microscopy (AFM) at varying micrometer scales. Absorbance spectroscopy has been used to characterize the optical properties of all coatings. Intrinsic stress release phenomena are revealed on thicker layers through the detection of characteristic surface corrugations. Based on contact angle measurements, the different size of these morphological entities is discussed in terms of different surroundings at the formed sp^2 clusters in the films. Superimposed structures developed between coalescence grains have been furthermore observed on top of the thicker layer on PET, demonstrating that the growth of a-C:H material on plastics occurs by a multilayer mode. For all coatings, the total sp^2 content increases with increasing f- and r-deposition. Even if thinner layers show dissimilar sp^2 contents and even if different specific sp^2 organizations exist between the developed coatings on POM compared to HDPE and PET, for thicker r-depositions the total sp^2 content assimilates for all films.

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1. Introduction

One of the most efficient methods to improve plastics' performances such as hardness, abrasion resistance, light and heat endurance is the coating with amorphous hydrogenated carbon (a-C:H) films [1]. This material combination is widely used to produce food and beverage containers [1] as well as medical related devices [2–4] due to their excellent gas barrier, biocompatible and anti-bacterial behaviors [1].

The a-C:H material is composed by π -bonded sp^2 carbon clusters arranged in plane and embedded in a sp^3 matrix of carbon and hydrogen atoms [5]. The properties of the coatings can be widely manipulated depending on the specific deposition method used [3]. For instance, Markwitz et al. [6] have recently shown that the

fraction of sp^2 sites can be easily adjusted by varying the molecular ion energy in a range between 3 kV and 10.5 kV. The sp^2 content is in fact directly proportional to the acceleration energy since the number of six-fold carbon rings in the a-C:H network increases [6]. The enhanced sp^2 fraction is favored by the increase of hydrogen content from the near-surface region towards the bulk [7]. Nevertheless, to address appropriate properties for particular applications, an enhanced understanding of the occurring a-C:H growth processes on plastic is needed.

In a previous study two types of a-C:H films have been grown on polyethylene (PE) by plasma-enhanced chemical vapor deposition (PECVD) with acetylene plasma [8]. The films have been classified as hydrogenated diamond-like carbon (DLC) films and named respectively as f-DLC (f- meaning more flexible) and r-DLC (r- meaning more robust) [8]. A pronounced interlayer was observed in this composite material enabling a strong attachment between DLC and plastic substrate [8]. Interlayer formation was found as well for corresponding layers on high-density polyethylene (HDPE)

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[9] and polyethylene terephthalate (PET) [10]. Moreover, from Raman analysis the same sp^2 clustering as well as hydrogen content were revealed for the 1000 nm r-depositions on HDPE [9], PET [10] and silicon (100) [11], used as harder material for comparison. To release intrinsic stress, a transition between polymer-like to a more cross-linked DLC network occurs by the growth of sp^2 carbon clusters and parallel dehydrogenation of the coating regardless of these different substrates [10]. Dehydrogenated carbon atoms from $=CH_2$ groups fold together by forming closed sp^2 clusters [10]. In addition, a similar growth behavior of grains was revealed for DLC films on both HDPE [9] and PET [10]. Contrary to depositions on silicon (100) [11], the specific growth process results in a coalescence phenomenon for both 1000 nm r-depositions on these plastics, leading to similar surface morphologies [9,10]. On the other hand, no pronounced interlayer formation was found for analogous f- and r-depositions on polyoxymethylene (POM) [12], giving only weakly attached coatings on this substrate. For thin f- and r-depositions both the chemical and morphological film growth on POM [12] is different from HDPE [9] and PET [10]. However, with increasing r-deposition the same trend of dehydrogenation of the coating and coalescence of grains at 1000 nm have been observed [12]. Nevertheless, the developed sp^2 clusters are smaller and the film is more hydrogenated compared to the corresponding layers on HDPE and PET [12].

In the present study the surface morphology of the 1000 nm r-depositions on HDPE, PET and POM are investigated in detail with three different magnifications down to the sub-microscale by atomic force microscopy (AFM). No further examinations are carried out for films deposited on silicon (100) because their morphological growth leads to incomparable surface morphologies at 1000 nm r-deposition [11]. The Tauc gap and the total sp^2 content of the various f- and r-depositions on the three different thermoplastics are determined from absorbance spectra. To enable comparisons with a previous study on PET [10], contact angle measurements are done for the 1000 nm r-deposition on HDPE. With the present setup, the wettability examination of the corresponding film on POM is not possible because of delamination processes with thicker layers [12].

2. Materials and methods

2.1. Sample preparation and coating

After oxygen plasma cleaning (65 sccm/min, 1 Pa, 20 meV, 200 W), the deposition of both the f- (indirect deposition method: samples' surfaces are not in line to the plasma source) and r-type film (direct deposition method: samples' surfaces are in line to the plasma source) on HDPE, PET and POM was performed via an industrial radio frequency RF-PECVD process using acetylene plasma (65 sccm/min, 0.65 Pa, 20 meV, 107 W). Briefly, the different incidence path as well as energy of plasma species for the f- and r-type deposition processes lead to the more flexible or more robust nature of the coating [8,10]. The series of the f-deposition ranges from 2 nm up to 200 nm, whereas that of the r-deposition from 2 nm up to 1000 nm. Details about both deposition processes can be found in Refs. [8,10].

2.2. Surface characterization by AFM

Images of $(3 \times 3) \mu m^2$, $(1 \times 1) \mu m^2$ and $(0.5 \times 0.5) \mu m^2$ area were recorded on the surfaces of all 1000 nm r-depositions at ambient air conditions by atomic force microscopy (AFM, Omicron Nano Technology GmbH, Germany) and displayed herein as normal force signals (F_N). The lateral force signals (F_L) does not show differences with respect to the here presented F_N images. Height information is

available in the [Supplementary Data](#). Detailed experimental settings can be found in Ref. [10].

Image analysis was done using the commercial Scanning Probe Image Processor software (SPIP version 4.6.1, Image Metrology A/S, Denmark). All images were plane corrected using a LMS fit of degree 3. From the $(0.5 \times 0.5) \mu m^2$ squared images the dimensions of small particles and bulges found on the 1000 nm r-deposition on PET were evaluated using the threshold and watershed methods, respectively. Furthermore, the roughness of all 1000 nm r-depositions on HDPE, PET and POM was calculated for each magnification. Both the size of surface features as well as roughness values were calculated as an average of at least three individually recorded images.

2.3. Absorbance spectroscopy

The optical properties of the different f- and r-depositions were investigated by absorption measurements. The coated samples were illuminated by using a combined light source of Deuterium discharge tube and Tungsten iodine lamp. The Jasco V-560 UV/VIS spectrophotometer was used in a spectral range between 190 nm and 900 nm with a bandwidth of 2 nm. The measurements were carried out by a double beam instrument with 0.5 nm step, a response time of 0.25 s and a scan speed fixed to 200 nm/min. The illuminated spot size is about $3 \text{ mm} \times 1 \text{ mm}$.

2.4. Contact angle investigation

The surface wettability of the 1000 nm r-deposition on HDPE was examined by contact angle measurements. The wetting angle for the corresponding r-type film on PET [10] is reported below to enable comparison. The wettability of the 1000 nm r-deposition on POM could not be analyzed since the film delaminates in contact with the wetting liquid [12]. The experimental equipment was the OCA 15 plus contact angle goniometer (DataPhysics Instruments GmbH, Filderstadt, Germany). By the sessile drop technique five individual water drops (HPLC grade, 1 μl) were automatically dropped from a dispensing needle across the entire sample surface. The measurement was conducted under ambient air conditions. The contact angle was calculated as the average of the angles on both sides of each drop.

3. Results

3.1. Surface morphology of the 1000 nm r-depositions

Fig. 1 shows the representative surface morphology of the 1000 nm r-deposition on HDPE (Fig. 1a–c), PET (Fig. 1d–f) and POM (Fig. 1g–i) for magnifications at $(3 \times 3) \mu m^2$ (Fig. 1a,d,g), $(1 \times 1) \mu m^2$ (Fig. 1b,e,h) and $(0.5 \times 0.5) \mu m^2$ (Fig. 1c,f,i).

As reported in previous studies [9,10,12], for the $(3 \times 3) \mu m^2$ scale coalesced grains dominate the surfaces for all 1000 nm r-depositions on HDPE (Fig. 1a), PET (Fig. 1d) and POM (Fig. 1g). At this scale the surface morphology of the coated HDPE (Fig. 1a) results overall similar compared to the coated PET (Fig. 1b), composed by nearly circular grains. In contrast, the corresponding film on POM (Fig. 1g) is apparently different compared to HDPE (Fig. 1a) and PET (Fig. 1d), since bigger grains assemble with more irregular forms. The average height and area of coalesced grains is respectively: $(21 \pm 3) \text{ nm}$ and $(0.06 \pm 0.01) \mu m^2$ for HDPE [9], $(12 \pm 1) \text{ nm}$ and $(0.06 \pm 0.01) \mu m^2$ for PET [10], $(28 \pm 2) \text{ nm}$ and $(0.11 \pm 0.02) \mu m^2$ for POM [12]. Besides the different grain size, the 1000 nm r-deposition on PET shows in a detailed view additional smaller particles typically present at boundaries between adjacent grains (Fig. 1e and Fig. 1f, indicated by arrows). Furthermore, at these

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