



Diamond-like carbon coating of a pure bioplastic foil

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ABSTRACT

Bioplastic materials are a promising replacement for petroleum-based plastics. Coating is an often used method to improve characteristics of traditional plastic materials. We present results of the coating of a 50 μm thick pure bioplastic foil, a mixture of 92% polyhydroxybutyrate and 8% polyhydroxyvalerate, with diamond-like carbon (DLC) via a radio frequency plasma enhanced chemical vapor deposition process. Two different types of DLC are deposited on the foil, an sp³-rich (r-DLC) and an sp²-rich (f-DLC). The first type results in a more robust the second in a more flexible kind of coating. The surface morphologies of layers with various thicknesses are examined, r-DLC up to 1000 nm, f-DLC up to 200 nm. DLC layers up to around 450 nm are intact, further deposition results in cracking and exfoliation of the DLC coating. The exfoliated DLC flakes roll up during the ongoing plasma process. This process is observed again on the thereby newly exposed substrate between the flakes. Rolling of the DLC flakes shows the presence of internal stress in the deposited DLC coating.

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1. Introduction

Up to now the main part of plastics is produced on a crude oil basis. Overall production of plastics on the basis of crude oil is approximately 260 million tons per year worldwide [1]. Considerations to save resources are of great importance as fossil raw materials will not be available infinitely [2,3]. In addition there are also economic reasons as a scarce amount of oil will lead to an increase in price. This is why there are worldwide efforts to broadly replace the petroleum-based economy by a biologically based economy in the long run. In the case of plastics new materials are developed by using renewable raw materials [4,5]. Apart from the economic use of energy and raw materials, resulting in an ecofriendly production, also the environmentally compatible degradation of plastics as well as the recycling of the increasing waste masses is in the focus of research. It is the overall target to minimize environmental contamination [4,5]. In many ways bioplastics are a good alternative to replace petroleum-based plastics. They have the potential to avoid or to decrease the two above mentioned problems of scarce resources and waste disposal from the beginning [6].

According to the widely used definition bioplastics are polymer materials that consist of bio-based (renewable) raw materials and/or can be biologically degraded [1]. Consequently they can be classified into three different bioplastic groups [1]. Firstly, biodegradable plastics; they can be made of renewable as well as petroleum-based raw materials (e.g. plastics of polyvinyl alcohol or polycaprolactone) [1]. Secondly, biobased polymers; not all of them are at the same time biodegradable (e.g. highly substituted cellulose acetate, polyethylene made of sugar

cane) [1]. Degradability of biopolymers exclusively depends on the molecular structure, not on the raw material it was produced of. Thirdly, biobased and biodegradable plastics as the overlap of these two properties. Only the last group will solve the indicated problems. In the following only this third group of biopolymers will be described and named bioplastics in terms of this article. This limitation excludes also blends (mixtures of bioplastics and petroleum-based plastics), which are nowadays often sold as to be a bioplastic material.

There are especially three types of bioplastics according to the previous declaration with economic significance: biodegradable biobased starch plastics (thermoplastic starch), polylactides and polyhydroxyalkanoates [1,7–10].

In this article a commercially available polyhydroxyalkanoate foil is examined. The substrate used for this study is a mixture of polyhydroxybutyrate (PHB 92%) and polyhydroxyvalerate (PHV 8%), both biogenerable and biodegradable substances [11].

In order to systematically optimize the performance profile i.e. to generate additional functions and fields of application plastics are usually refined by admixing additives or mixing of various plastics. The use of non biodegradable polymers as additives or material components not only leads to an increased stability of the bioplastics but also ends up in a decreased degradability of these polymer blends. It also results in a loss of compostability which is an economic and environmentally beneficial way of disposal in some fields [4,5,12–14]. Although composting means that the energetic and material resources are lost forever, collecting and recycling of these materials is practically not feasible in some fields and the additional energetic expenses would be too high [1].

Deposition of protective thin layers on the surface extends the properties of plastics allowing application for additional fields [15,16]. Especially the low abrasiveness and scratch resistance can be compensated

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or at least improved by this kind of coating. For hard materials, like metals, inorganic coatings like nitride, oxide or carbide layers (e.g. TiN, Al₂O₃, TiCN) are widely used in industry. The most obvious alternative for soft materials, like plastics, are modern carbon layers – so called diamond-like carbon films (DLC). They can easily be adapted to many fields of application with an expected preservation of compostability at the same time.

DLC films are amorphous carbon layers that show a disordered network (only short range order, no long range order) of bonds between sp²- and sp³-hybridized carbon atoms as well as hydrocarbon bonds. The hydrogen content and the mixture in hybridization of the carbon atoms mainly determine the properties (e.g. abrasiveness, elasticity, color, transparency) of the amorphous carbon layers [17]. A high percentage of sp³-hybridized carbon atoms as well as a low hydrogen content leads to a rather linked and therefore more robust carbon layer [18]. Throughout this manuscript DLC is used in wide definition given in [18] ranging from almost all carbon atoms that are sp²-hybridized (glassy carbon, graphitic carbon) to almost all carbon atoms that are sp³-hybridized (diamond-like) combined with any amount of hydrogen incorporated in the film (from none to the limit of hydrocarbon polymers).

DLC layers only consist of carbon and hydrogen, the essential components of the polymer basic material. The degradable bioplastics include oxygen as an additional content. Degradation up to 90% of the material in an industrial composting plant within 90 days is the legal requirement [12]. Since the DLC layers normally account for less than 1% of the overall material, the composite of DLC and compostable bioplastics will anyway fulfill these general legal requirements of compostability.

Herein we show that by the use of plasma enhanced chemical vapor deposition (PECVD) with a proper parameter set DLC layers can be conducted in a low temperature process on the bioplastic of interest PHB92/PHV8. The required properties of the DLC layer can be modified by choosing adequate coating parameters. Layers of a few nanometers are preferred for soft basic materials, like plastics [19]. In this article the coating of a pure bioplastic foil (PHB92/PHV8) with two types of DLC is examined, a more robust (r-DLC) and a more flexible (f-DLC) one.

2. Experimental details

The biopolymer foil used is a mixture of two biodegradable polyhydroxyalkanoates, 92% of polyhydroxybutyrate and 8% of polyhydroxyvalerate (PHB92/PHV8 biopolymer film). This pure bioplastic foil is 50 µm thick and bought in best commercially available quality (Goodfellow BV301050).

For the experiments samples of 9 mm diameter are stamped out of the delivered foil with a steel punch. Each sample is cleaned by isopropanol and properly dried in ambient air. Thereafter each piece is bonded to homemade aluminum trays with regular carbon pads as used for electron microscopy (Plano G3347). On such a tray up to 43 samples are arranged and this set is coated with the same type and the same thickness of the DLC layer. For the presented analysis two types of amorphous DLC coatings were deposited in seven (f-DLC) respectively nine (r-DLC) different thicknesses.

The coating was done using radio frequency PECVD (RF-PECVD). A detailed description of the RF-driven (13.6 MHz) commercially available plasma source (model COPRA DN 400, CCR GmbH, Troisdorf, Germany) is given by Weiler et al. in [20,21].

For the deposition of the DLC layers the samples are placed at a distance of 275 mm in front of the plasma source in a high vacuum chamber. In a first process step they are exposed to an oxygen plasma for 10 min at about 1 Pa of pressure and 200 W of RF irradiation power to remove remaining surface contaminations. Afterwards the samples are exposed to an acetylene plasma at 0.65 Pa and 107 W. A self-bias voltage of –20 V (mean value) develops on the sample during the deposition process. Earlier studies by Kleinen et al. using the same

setup have determined ion energies between 15 eV and 25 eV and current densities between 0.1 and 0.2 µA cm⁻¹ [22,23]. Possible changes in sample temperature during the deposition process for both types of DLC were monitored by non-reversible temperature labels (OMEGALABEL® TL-10-105). The temperature of the samples has never exceeded 40 °C, which is the lowest determinable value. By adjusting the ion energy and the ion flux as well as changing the sample position with respect to the plasma source different types of DLC coatings can be deposited. Many ion species impinge on the substrate surface when direct deposition is used, therefore the sample plate is located in direct line of sight to the plasma source. Since more subplantation processes prevail, a higher degree of cross-linked sp³-carbon centers are present in the coating [21]. This type is called, following the notation in [24], r-DLC, r for more robust. When a more indirect deposition is chosen, the sample's face is therefore presented to the plasma without being in line of sight with the plasma source, and less energetic ions appear, a more flexible coating, so called f-DLC develops, following also the notation in [24]. In this case mainly radical species are present and diffuse on the substrate surface [25].

The thickness of the deposited carbon layer is determined by the deposition time and monitored by pieces of a silicon wafer additionally mounted on the tray. Due to the different deposition strategies deposition rates of 2 nm/min for f-DLC and 10 nm/min for r-DLC evolve.

For the electron microscopic analysis the coated samples including the carbon pad were carefully transferred to typical scanning electron microscopy (SEM) sample holders (Plano G301). Uncoated samples were mounted in the same way. The pure bioplastic material is even much less conductive than other more common plastics, like polyethylene. All samples on their holders were additionally coated with a few layers of gold (Au) to avoid electron charging effects. Damages by the electron beam due to the initial measurement routine could be found on images with DLC layers up to 5 nm in height.

The specific surface morphologies of the raw and the differently coated pure bioplastic foils were observed by SEM (Philips SEM515). Throughout these experiments the SEM was always operated by an acceleration voltage of 20 kV.

3. Results and discussion

The process of coating starts with an oxygen plasma procedure to remove contaminations and to reveal a reproducible surface of the substrate. The properly cleaned pure bioplastic foil is coated with DLC in a second step of the coating process. In Fig. 1 the changes in surface morphology during these single initial steps are shown. Fig. 1A shows the pure bioplastic foil (substrate) after mechanically removing dust by wiping with an isopropanol wetted paper towel. The appearing cloud-like structure is due to the production process, where small biopolymer particles (in this specific foil the average diameter is around 12 µm) are merged together in a melting process. Between these particles small trenches are seen, sometimes even deep holes. Small white dots (less than 1 µm in diameter) are remaining dust particles. Worm-like bright structures (up to 3 µm in length and less than 0.5 µm in width) are found in up to 10% of the biopolymer particles. They are obviously also remnants of the production process.

Fig. 1B shows the situation after the above described oxygen plasma cleaning process. The initially smooth surface appears considerably rougher. Trenches and holes are more pronounced since the arranged particles of biopolymer are more clearly visible. The worm-like structures are still observable and additionally very small dots (around 0.3 µm in diameter) appear in a large number on top of the biopolymer particles.

Fig. 1C contains images taken after the r-DLC deposition of 50 nm. All the structural elements seen before and described above show there-in DLC coverage. The surface appears smoother and small dots and worm-like structure therefore enlarged, while their number is not increased during the coating process. Trenches and holes on the other

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