Carboxyl-rich coatings deposited by atmospheric plasma co-polymerization of maleic anhydride and acetylene

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ABSTRACT

Carboxyl coatings are extensively used for adhesion promotion, bio-immobilization and surface reactions thanks to their reactivity towards nucleophilic groups and high wettability. The deposition of relatively stable carboxyl-rich coatings using low-cost atmospheric pressure plasma processes is still challenging. This work is aimed at the investigation of the plasma copolymerization of maleic anhydride (MA) and C_2H_2 by atmospheric pressure dielectric barrier discharge. The quantification of the carboxyl groups is performed by X-ray photoelectron spectroscopy (XPS) C1s curve fitting and by derivatization with trifluoroethanol. The layer synthesized at optimized monomer flow rate and plasma power contains 5 at.% of carboxyl groups (determined by derivatization combined with XPS) and exhibits the thickness loss below 5% after 128 h in water. The influence of the MA:C_2H_2 ratio on the layer chemistry, morphology and stability is analyzed.

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1. Introduction

The deposition of functional organic thin films by plasma polymerization has become a promising technique able to prepare reactive surfaces for adhesion promotion [1–3], gas sensing [4,5], biosensing [6–8], immobilization of antibodies [6,9,10], peptides [11,12] and DNA [13,14], or cell adhesion enhancement [15–18]. The chemistry and morphology of plasma polymerized layers (PPLs) can be adjusted independently from the substrate nature by tuning the discharge parameters. For most applications, a sufficiently high surface concentration of functional groups as well as the layer stability in aqueous media is required [19–23]. Hegemann et al. showed that unstable plasma coatings release toxic oligomer poisoning the media and, therefore, cannot be used for biomedical applications [24,25]. Regardless of the nature of functional groups, carboxyls, amines, hydroxyls, epoxy and the like, a good stability of the PPLs requires a strong polymer cross-linking. In low pressure plasmas, it can be achieved by bombardment of energetic species formed in plasma [26,27]. Additionally, a stronger cross-linking can be obtained by an increase of the input power or a decrease of the monomer flow, i.e. by an increased energy invested per monomer molecule leading to higher dissociation [23,28–31]. Unfortunately, higher dissociation also means degradation of the functional groups due to the stronger monomer fragmentation [19,32,33]. Hence, the deposition of PPLs combining a high stability and a high density of functional groups is always challenging. It is even more difficult when the plasma polymerization is carried out at atmospheric pressure. The attractive energy-efficient and low-cost atmospheric pressure plasma polymerization generally leads to the deposition of PPLs that exhibit a lower water stability for a similar amount of functional groups compared to low pressure discharges [34–39]. The difficulties in obtaining a uniform gas distribution complicate achieving uniform coatings in terms of thickness and chemistry using atmospheric discharges. Moreover, the filamentary nature of dielectric barrier discharges (DBDs) causes local film non-uniformities or defects [40] and can lead to damage of temperature sensitive polymer substrates [41]. Therefore, it is advantageous to find a monomer whose admixture will lead to the ignition of DBD in a homogeneous mode. Recently, Eliáš et al. demonstrated that the so called atmospheric pressure glow discharge (APGD) can be ignited in the mixture of Ar and C_2H_2 [42].

Among the different reactive groups deposited by atmospheric pressure plasma polymerization, carboxyls (COOH) are the most widely used for bioapplications thanks to their reactivity as well as high stability at air. One of the most widely used monomers for the atmospheric pressure plasma polymerization of carboxyl-rich coatings is acrylic acid [8,36,37,41,43] but other monomers like acetic acid [44] or maleic anhydride (MA) co-polymerized with vinyltrimethoxysilane (VTMOS) [45–47] are used too. However, the investigation of carboxyl-rich PPLs deposited at atmospheric pressure has been quite limited. Carton et al. showed that carboxyl-rich PPLs deposited from He/acrylic acid plasma

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jet suffered large mass losses after immersion in water although the surface chemistry characterized by XPS was not significantly affected [36]. Morent et al. reported that the DBD plasma polymerization of acrylic acid led mostly to the deposition of soluble coatings [41]. According to Fourier transform infrared spectroscopy (FT-IR), the PPLs significantly dissolved after 5 min in water unless the maximum power was used.

Recently, Donegan et al. also confirmed the solubility of PPLs deposited from acrylic acid by the PlasmaStream He/N₂ plasma jet [37]. However, the authors demonstrated that very thin (<30 nm) films containing 0.23 carboxyl groups per carbon atom and exhibiting a relatively good thickness and functional stability can be prepared by acrylic acid plasma polymerization in air using the PlasmaTreat jet. It should be noted that authors did not report the complete elemental composition of the surface or atomic density of carboxyl groups. Of course, the often observed incorporation of nitrogen atoms during the atmospheric plasma polymerization in air [48] can decrease the effective carboxyl density.

The important parameter for the bioapplications of carboxyl films is the concentration of carboxyl groups that is often estimated on the basis of XPS C1s curve fitting. However, it is impossible to distinguish the positions of the carbon peaks related to the carboxyl and ester groups and, therefore, the reported values include also "non-reactive" ester groups. Since Voronin et al. demonstrated that a high concentration of the carbon contribution at 289.2 eV in plasma polymerized acrylic acid films does not always correspond to a high carboxyl group concentration, the chemical derivatization of carboxyl moieties is necessary [49]. As the derivatization of the carboxyl groups in the PPLs deposited at atmospheric pressure has not yet been reported, it is still debatable if a stable carboxyl-rich coating can be deposited by the atmospheric pressure plasma polymerization.

The copolymerization approach seems to be a promising method for tuning the carboxyl group density and the layer stability thanks to an additional control parameter, the ratio of two monomers. The first monomer is aimed at the incorporation of reactive carboxyl group (e.g. acrylic acid or MA) while the second must provide the branched and well cross-linked network enhancing the layer stability (e.g. VTMOS, ethylene or acetylene). Hence, in theory, the cross-linking enhancement will not require an increased energy invested per monomer molecule and much higher structural retention of the first monomer can be expected. Nevertheless, the reported investigations of the carboxyl-rich plasma copolymer stability are very limited and often based only on IR spectroscopy measurements in attenuated total reflection (ATR) mode. Furthermore, the reported layers were immersed into water for short time periods only [46].

In this work, the MA and C₂H₂ (acetylene) co-polymerization using homogenous DBD is studied in order to optimize the carboxyl density and thickness stability of the PPLs. The influence of the MA:C₂H₂ flow rate ratio on the layer stability and carboxyl group density is analyzed. For the first time the chemical derivatization combined with XPS analysis (CD-XPS) is employed to determine the carboxyl density in PPLs deposited at atmospheric pressure.

2. Material and methods

2.1. Plasma polymerization and diagnostics

The deposition of thin films by DBD plasma co-polymerization of MA and C₂H₂ was carried out in a metallic cube chamber (500 × 500 × 500 mm). The discharge was ignited between planar metallic electrodes covered with Al₂O₃ ceramics, 1 mm in thickness. The top electrode, connected to the high voltage source, was divided into two rectangular pieces, each 20 × 55 mm. The bottom electrode, 150 × 60 mm, was grounded. The gases were supplied by a 1 mm slit placed between the high voltage electrodes. The gap between the top and bottom ceramics was 1.6 mm. The polished crystalline silicon (c-Si) substrates were put on the bottom ceramics. The deposition

uniformity was improved by moving the DBD top part with the gas mixture supply as schematically shown in Fig. 1.

The MA pellets (Sigma-Aldrich, 99%) were placed in a bubbling system and MA vapors were delivered into the discharge by Ar flow (Messer, 99.998%). The flow rate of the second monomer, C₂H₂ (Messer, 99.6%) was regulated directly by a flow controller in the range 2–3 sccm. The Ar flow rate through the bubbler, Q_{Ar-MA}, was 0.25–1.5 slm. The flow rate of MA, Q_{MA}, was calculated as $Q_{MA} = Q_{Ar-MA} P_{MA}/P_{at}$, where P_{MA} and P_{at} are vapour pressure of MA at 20 °C, i.e. 22.3 Pa, and atmospheric pressure, respectively. The total Ar flow rate ($Q_{Ar} + Q_{Ar-MA}$) was kept constant at 1.5 slm thanks to the additional injection of Ar process gas passing MA bubbler. The deposition conditions are reported in Table 1. A hypothetical scheme of the MA/C₂H₂ co-polymerization for the example of 1:3 MA:C₂H₂ ratio is drawn in Fig. 2. The scheme highlights a possible free radical co-polymerization and illustrates simply its expected mechanism.

Before the deposition the discharge chamber was pumped down to the pressure of 100 Pa and then filled up to 96 kPa with a desired deposition gas mixture. The discharge was ignited by a sinusoidal high voltage from the generator with tunable frequency, 5.0–6.6 kHz. The power supplied by the generator was 8 W.

The discharge voltage and current were monitored by the Agilent Technologies DSO1022A oscilloscope. Optical emission spectra (OES) of the discharge at various deposition conditions were recorded by the Avantes Sensline (AvaSpec-ULS2048LTEC) spectrometer in the wavelength range 330–1050 nm. The signal at the wavelengths below 330 nm was limited by a thick glass window used as the view port. High resolution emission spectroscopy was performed with the spectrometer Horiba Jobin-Yvon FHR 1000 for an unambiguous identification of emission molecular bands.

2.2. Characterization of thin films

The film thicknesses were characterized by ellipsometry using a phase modulated Jobin Yvon UVISEL ellipsometer in the spectral region of 1.5–6.5 eV at the angle of incidence of 65°. Since the coatings exhibited very high roughness of upper boundaries and granular structure (see Morphology of MA/C₂H₂ PPLs section) it was necessary to evaluate the film thickness in a manner useful for the film stability characterization. Therefore, we report the optical thicknesses (optical path lengths) [50] divided by the typical film refractive index ≈ 1.56 as the effective film thicknesses.

The transmittance in the spectral range from 370 to 7500 cm⁻¹ was measured using Fourier Transform IR (FTIR) Bruker Vertex 80v spectrophotometer with a parallel beam transmittance accessory. The data were collected at pressure of 250 Pa with a resolution of 4 cm⁻¹ and 500 scans. The transmittance of the films on Si substrate was divided by the transmittance of bare Si substrate in order to calculate a relative transmittance.
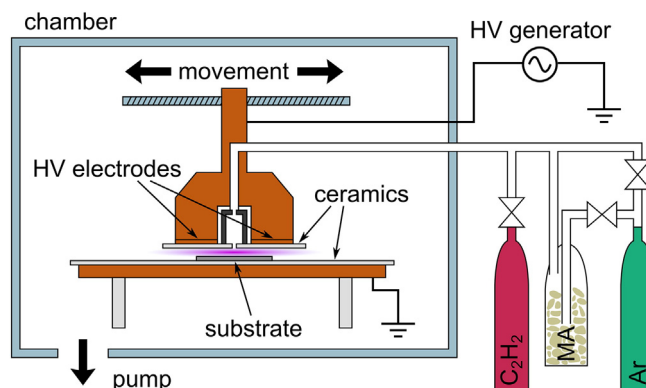

Fig. 1. Schema of DBD setup.