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Controlled Ag release from electrically conductive coating systems

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ABSTRACT

Nowadays, silver (Ag) coatings find widespread use in medical textiles, e.g. wound bandages, mainly due to their antibacterial properties related to the Ag ion release in aqueous media. Moreover, Ag-coated fibers offer excellent electrical properties, allowing their use for sensing applications such as electrocardiography (ECG) belts. Due to the potential cytotoxicity of Ag, electrically conductive coating systems need to be developed with reduced and time-controlled Ag release.

In this study, pure silver was continuously deposited onto a polyester (PET) fiber to optimize electrical conductivity for ECG application. The pure silver coated fibers, however, showed the typical initial burst release of Ag ions when immersed in an aqueous environment locally yielding cytotoxic conditions, i.e. high Ag ion concentrations. While the ion release can be favourable for antibacterial properties, it needs to be limited for medical devices. A diffusion barrier is thus required, while maintaining the electrical conductivity. Thus, different plasma polymer top coatings were applied onto the Ag-coated fibers using a continuous deposition process. The functional plasma polymerized films (a-C:H and a-C:H:O) were compared with an ultrathin titanium oxide layer (as recently investigated) regarding electrical properties and silver release. Ag release measurements demonstrated that an efficient control over the release properties (initial burst and long-term release) was achieved depending on the hydrophobicity and thickness of the plasma polymer films.

1. Introduction

Bacterial colonization and infection are of great concern in medicine, and also in daily products exposed to water or humidity. The antibacterial action of silver is used in numerous consumer products and medical devices. Metallic silver, silver salts, and also silver nanoparticles are commonly used for this purpose [1]. The state of research on the effect of silver on bacteria, cells, and higher organisms has already been well summarized, e.g., by Chernousova and Epple [2].

Antibacterial effects in general should be based on time-controlled release of substances to achieve a good balance between antibacterial activity and biocompatibility [3,4]. Silver particles are thus embedded within a matrix or are covered with a top-coating acting as a diffusion barrier [5]. Both methods restrict water diffusion to the silver reservoir as well as leaching of Ag ions into the solution. Several studies carried out over the past decades proposed the embedding of Ag ions or nanoparticles in various organic or inorganic matrixes in order to gain a better control over release properties [6]. For example, silver ions were embedded in Si-based sol-gel [7] or in spin-coated PMMA films [8], and silver nanoparticles were inserted in electrospun PMMA [9], PVA [10] or gelatin fibers [11]. More recently, plasma-based coatings, such as oxygen-containing [12] or nitrogen-containing [13] plasma polymer films as well as fluorocarbon, hydrocarbon and SiO_2-based plasma coatings [14,15] were used as matrix for silver particles.

The silver release from a surface depends on the exposed area used in the application and on the availability of the deposited silver. Especially fibrous substrates are suitable materials for long-time antibacterial effects as they have a large surface area, able to yield high Ag ion concentrations by leaching from the Ag-coated areas. Ag ions provide a broad activity against bacteria. High Ag ion concentrations (exceeding about 1 $\mu g\,ml^{-1}$) as they might locally occur by the so-called initial burst release, however, are known to be cytotoxic [4]. Such conditions are not suitable, e.g., for applications related to sensing and measurement of electrical body vital signals, such as electrocardiography (ECG) [16].

For textile electrodes a certain electrical conductivity of the applied coating system is essential. Silver shows a high conductivity and ductile behavior suitable for electrical application on fibrous substrates [17]. Due to its corrosion resistance and its ability to passivate a silver layer [18], titanium top-coatings were deposited onto silver-coated fibers. The obtained Ag/Ti metal layer systems had been studied towards their silver release, showing strong reduction of Ag release and high potential for ECG applications [16]. For measurements with dry skin an additional water environment dosed through a membrane can reduce the

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skin electrode contact resistance and improve the obtained ECG signal [19].

The current study aims to control the silver release from an Ag-coated fiber covered with hydrophobic a-C:H or hydrophilic a-C:H:O plasma polymer films to investigate functional diffusion barrier coatings. As the a-C:H:O plasma polymer matrix is rich in oxygen containing functional groups, noticeable water permeation can be expected. Besides effective control of the Ag ion release, the demanded electrical conductivity and contact resistance can be maintained over a rather wide range regarding the top coating thickness. Results obtained for the Ag-coated fibers with a-C:H and a-C:H:O top-layers are compared to previously observed results for titanium-passivated Ag fibers [16], in order to study their potential as surface functionalization of electrically conductive fibers.

2. Materials and methods

2.1. Substrate and surface area

Polyester (PET) fibers 150f48 comprising a silver coating with different amounts of deposited silver (Serge Ferarri Tersuisse SA, Switzerland) were used in this study. The nomenclature 150f48 indicates a fiber weight (fineness) of 15 mg m^{-1} (150 dtex) for the polyester fiber (with a density of 1.37 g cm^{-3}) made of 48 filaments. For comparison also a PET 167f134 (polyester 16.7 mg m^{-1} and 134 filaments) Ag-coated fiber material was considered. The specific fiber surface area A (per fiber length) can be calculated from Eq. (1):

$$A = 2\sqrt{\frac{m\ \pi\ F}{l\delta}} \quad (1)$$

where m is the mass (g), δ the density (g cm^{-3}), l the length (cm) and F the number of filaments of the fiber.

2.2. Silver and titanium coatings and film thickness determination

Silver and titanium layers were coated on the fibers by magnetron sputtering according to the protocol as reported in [16,20]. The mass of the applied silver and titanium coatings were analyzed by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) Optima 3000, Perkin Elmer. Silver-coated fibers of four meter length each were dissolved in concentrated nitric acid and diluted with water. The Ag-containing solution was then introduced into the ICP-OES and optically analyzed (Ag lines at 328.068 nm and 338.289 nm). The calibration was performed using an external silver standard solution of 1 $g \cdot l^{-1}$. A recovery rate between 98 and 101% was obtained. Silver detection limit is ≤ 0.075 $\mu g \cdot m^{-1}$. Titanium coatings were analyzed with the same method using the protocol as described in [16].

The theoretical (average) film thickness d_f of a homogeneous film over all 48 filaments was calculated from the measured mass of the deposited metal film. The Ag coating was deposited with either 1.7 mg m^{-1} (deposited Ag mass per fiber length) resulting in 62 nm Ag thickness (calculated average) or 4.5 mg m^{-1}, respectively 165 nm. For the Ti top-coatings a film thickness of 3 and 9 nm was applied.

2.3. Plasma polymer deposition

The plasma polymer coatings were performed within a capacitively coupled, radio frequency-driven (13.56 MHz) plasma reactor. A total fiber length of around 330 m was coated in each run by moving the fiber through the plasma zone at floating potential during the plasma treatment [21]. The deposition of the hydrocarbon (a-C:H) coatings was performed at 10 Pa pressure, 120 W power input and a gas flow rate of 30 sccm C_2H_4 (Carbagas, Switzerland) with 99.95% purity. Oxygen-containing a-C:H:O coatings were deposited at the same pressure and power input with a gas flow ratio of 4:1 of CO_2 (Carbagas, Switzerland), purity of 99.998%, and C_2H_4. To sustain the same total gas flow rate, 24 sccm CO_2 and 6 sccm C_2H_4 was used for the a-C:H:O coatings. A 100 nm thick reference coating was performed with the a-C:H and the a-C:H:O deposition conditions on a silicon wafer and subsequently measured by contact profilometer (Dektak Bruker, USA). Thinner coatings as applied on the fibers with a nominal thickness as observed for the reference coating were performed with the same plasma conditions by adjusting the deposition time accordingly. For instance, a nominally 25 nm thick a-C:H or a-C:H:O film was deposited within 3 min or 5 min, respectively (on 330 m fiber each). Note that only directly exposed filament surfaces collect the maximum film thickness, while shadowed areas obtain less deposition.

2.4. Resistance measurement

The sheet resistances of the coated fibers were measured along the fiber via two gold coated copper contacts type LK4-B/SIL (Stäubli Electrical Connectors, Switzerland) with 4 mm diameter and a spacing of 1 cm connected to the measurement unit Keithley 2100 (Keithley Instruments, USA). The fibers were loaded with 50 g weight on each side when guided over the two gold contacts. At least 20 measurements were taken from each sample over a fiber length of 1.5 m.

2.5. Analyses of the morphology

The surface morphology of the coated fibers were studied by scanning electron microscope (SEM) Amray 3200-C at 2 kV acceleration voltage and electron current of 10 μA.

2.6. Silver release

Silver release measurements were performed on silver coated fibers with a-C:H or a-C:H:O top coatings. Three samples of 4 m length were taken from each coated fiber and put in polystyrene test tubes. 4 ml ultrapure water (> 18 MΩ cm according to ISO 3696) from a Milli-Q plus System (Millipoor, USA) was added and stored between 6 h and 7 days at room temperature. After immersion in Milli-Q water, solutions were recovered, diluted in 2% nitric acid and then analyzed by ICP-OES using an Optima 3000 (Perkin Elmer) instrument (Ag lines 328.068 and 338.289 nm).

3. Results and discussion

The area of a fibrous structure is calculated according to Eq. (1). For the used fiber PET 150f48 with a fineness of 15 mg m^{-1} the total fiber surface was 26 cm^2 m^{-1}. The comparative fiber PET 167f134 with 16.7 mg m^{-1} and 134 filaments (almost same weight per meter but 2.8 times more filaments) had a surface area of 45 cm^2 m^{-1}. Fig. 1 shows a comparison of the electrical properties for the two considered PET fibers depending on the deposited Ag mass confirming that a higher surface area yields higher resistances for the same mass of silver applied. Fibrous structures are able to provide a high surface area. A larger amount of available surface area results in the distribution of the deposited silver over the surface yielding thinner coatings for the same applied Ag mass per fiber length. For thinner coatings film defects and non-uniformities between inner and outer filaments (Fig. 2) become more pronounced leading to higher resistance values.

The fibrous structure of the PET fiber 150f48 is shown in Fig. 2A which was further used throughout this study. Within the examined range of applied silver content of 1.7 and 4.5 mg m^{-1} (average film thickness of 62 and 165 nm, respectively) a similar (closed) film morphology was observed as can be seen in Fig. 2C and D. The granular surface indicates the typical columnar grain growth of the sputter-coated metal. Note that while the coating thickness is uniform along the fiber, a distribution in thickness was obtained over the cross-section with inner lying filaments collecting less coating.