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Synthesis and structure of antibacterial coatings formed by electron-beam dispersion of polyvinyl chloride in vacuum

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ABSTRACT

A new antibacterial coating has been synthesized to modify implants with prolonged release of a medicinal antibacterial component (ciprofloxacin). Condensed in vacuum, the products of electron beam dispersion of PVC were used as one of the components of the target. It is shown that the repeated action of the electron flow on condensed destruction products of PVC is accompanied by the formation of poly-conjugated structures devoid of chlorine. Thermal treatment of the hydrocarbon layer (500 °C) leads to the formation of graphite-like structures and polyene fragments up to 8 units in length. The antibacterial coating (PVC_2-ciprofloxacin) is formed by the action of a low-energy electron flow on a mechanical mixture of ciprofloxacin and condensed PVC destruction products. It is shown that in comparison with the antibacterial layer PU - ciprofloxacin, the proposed coating is characterized by a higher resistance to abrasion. The PU - ciprofloxacin layer is completely worn out after 17 cycles. The worn-out areas of the proposed coating after 17 and 25 wear cycles are 47% and 53% respectively. Heat treatment of the coating, including standard sterilization, does not affect the kinetics of the release of ciprofloxacin from the hydrocarbon matrix. Unlike the PU layer - ciprofloxacin, the prolonged release (sustained release) of ciprofloxacin in PVC_2-ciprofloxacin is not ensured by intermolecular interaction but by the mechanical containment (confinement) of ciprofloxacin using a hydrocarbon matrix. Microbiological studies showed high antibacterial activity of the proposed composite layer in relation to *P. aeruginosa* and *E. coli*. The activity was maintained after abrasive coating treatment for 24 h.

1. Introduction

Nosocomial infection is a cause of serious postoperative complications, which in some cases may lead to the death of a patient [1–6]. The control of its consequences requires significant financial costs. Acute infections occur, in prosthetics, when the implants are introduced into the human body.

Currently, the main directions of the fight against bacterial adhesion and the subsequent formation of biofilms on the surfaces of the implants are formulated [1,2,5]. The most effective way of preventing postoperative complications is to use coatings maintaining a prescribed concentration of antibacterial substance near the implant surface for a long time. There are a number of requirements to these coatings, such as, biocompatibility, self-cleaning, programmable release of the drug component, strong adhesion to the implant surface, resistance to abrasion by soft tissues, etc. The deposition of antibacterial drugs onto a metal implant is not effective, since it may lead to bacterial resistance [5]. This is caused by the inability to maintain the drug concentration above the minimal inhibitory (MIC) for a particular microorganism near the implant surface over a long period of time.

The water-soluble (e.g., PEG) or biodegradable (e.g., polyactide) antibacterial polymeric coatings possess a good self-cleaning function, and can prolong release of the drug component, protect metal nanoparticles from leaching and reduce their cytotoxicity [7]. Physical processing methods, e.g., plasma make it possible to give the polymer coatings the surface energy necessary to stimulate the processes of

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tissue regeneration [8]. They make it easy to control the structure and, hence, the kinetics of the release of the drug component. The disadvantage of polymer coating systems is the low wear resistance and weak adhesion with metal surfaces, which probably leads to a rapid loss of coatings during the implant introduction into the body. One should note that all medical devices must undergo the obligatory standard procedure of thermal sterilization before being introduced into the body. This heat treatment may lead to notable structural changes of polymeric coating and thus the properties as well.

Carbon coatings (e.g., DLC) are characterized by high adhesion strength to metal surfaces, wear resistance and biocompatibility [9–11]. Only particles of metals (silver, copper, zinc, etc.) may be act as antimicrobial components of DLC coatings [9–13]. These metals are potentially toxic for cell cultures [1,3,5]. DLC coatings cannot be used as layers with programmable release of the drug component.

Many researchers have pursued various ways to deposit thin layers based on the advantages of carbon and polymer coatings. In particular, one of the methods for preparing such coatings is presented previously [6]. However, this technology cannot be effectively used to modify implants in a wide range of sizes and shapes because of the complexity and multi-stage processes.

The electron-beam polymers dispersion allows the formation of thin antibacterial layers with prolonged release of the drug component [7,14,15]. The plasma pre-treatment of metal substrates provides strong adhesion of coatings with the substrates.

In the work presented, the method of electron-beam formation of antibacterial coatings characterized by high adhesion and wear resistance is proposed. It is suggested to use mix condensed products of electron-beam dispersion of polyvinyl chloride PVC with medicinal compound as a target material. The deposited layer structure is midway between the structure of the polymer hydrocarbon and the DLC layers. Thus, the advantages of both polymer antibacterial layers and carbon layers can be preserved.

2. Methodology of the experiment

2.1. Methodology of forming coatings

The coatings were formed from the active gas phase generated by the action of a low-energy electron beam with 800–1600 eV energy and 0.01–0.03 A/cm^2 density on the target material in a vacuum. The initial pressure of the residual gases in the vacuum chamber was $\approx 4 \cdot 10^{-3}$ Pa.

The composite coatings were deposited from the gas phase formed by the action of electron beam on mechanical mixtures of PVC_1 and ciprofloxacin powders, as well as polyurethane and ciprofloxacin in a 1:1 weight ratio.

It should be noted that it is not possible to obtain a homogenous composite coating using the initial PVC powder. This is due to the fact that the process of electron-beam deposition of a coating, based on PVC, is implemented only after a deep dehydrochlorination of the polymer. This prevents the generation of the gas phase simultaneously containing the destruction products of all the components of the mixture target.

The article deals with the coatings of the same effective thickness. The effective thickness (which was 0.5 μm) of the formed layers was controlled directly during the deposition by means of a quartz thickness gage (QCM).

The substrate temperature at the coatings deposition corresponded to room temperature.

2.2. The material of coatings and substrates

The powder of polyvinyl chloride (Mw ~ 62.000; Mn ~ 35.000; Aldrich), polyurethane (PU, Desmopan 385) and ciprofloxacin (KRKA, Slovenia) was used as a target material.

The material of the coating deposited from volatile products of PVC dispersion (PVC_1) was used as a target subjected to re-electron-beam dispersion for the purpose of producing PVC_2 coatings. The production of PVC_1 was performed in two stages. At the first stage, during the action of the electron flow on the PVC powder, a coating on glass substrates was deposited. At the second stage, the formed layer was scraped off.

The substrates for deposition of the coatings based on PVC_2 were quartz plates (obtaining UV–Vis spectra), NaCl plates (IR spectroscopy studies), silicon (100) single crystal plates (XPS studies), titanium plates 50 × 50 × 0.5 mm (antibacterial studies, wear resistance studies), aluminum plates Ø 5 mm (antibacterial studies).

2.3. Features of the heat treatment of the formed coatings

The coatings were heat-treated in vacuum (10 Pa) and in air at 120 °C, 220 °C temperature for 60 and 120 min. Some coatings were annealed in vacuum at 500 °C for 120 min. The temperature range (120 ÷ 220) °C is used for thermal sterilization of medical devices, implants in particular. Heat treatment at a pressure of < 10 Pa is not possible. Heating the coating in high vacuum conditions is accompanied by decomposition of a thin layer and its transition to the gas phase.

2.4. Structure and morphology studies

The thermogravimetric analysis was carried out with DTG-60 (Shimadzu) under nitrogen atmosphere. The heating rate was 10 °C/min. The mass of the test material was 3 mg.

The molecular structure of the coatings was investigated on Vertex-70 (Bruker) using a standard transmission thermocell. PVC_1 was analyzed using the method of multiple frustrated total internal reflection (MFTIR). The scanning was performed in the range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1}. A band of stretching vibrations of C—H bonds in CH_2 groups (2920 cm^{-1}) was taken as an internal standard band. The optical density of the band 2920 cm^{-1} linearly depends on the layer thickness. The values of the optical densities of the analyzed bands were correlated with the absorbance of the internal standard band. The degree of oxidation of a thin layer was assessed in relation to the band of stretching vibrations of carbonyl groups C═O (1730 cm^{-1}) [16].

The UV–Vis spectroscopic studies were performed using a Cary-50 (Varian) spectrophotometer using a standard transmission thermocell.

The chemical composition of the deposited layers was determined by the XPS method. The measurements were done on a PHI Quantera II Scanning XPS Microprobe spectrometer using an Al Kα source of monochromatic X-rays ($h\nu$ = 1486.6 eV). The analysis results were processed using the OriginPro software package.

2.5. Microbiological studies

The antibacterial activity of the coatings was studied for the following microorganisms:

Pseudomonas aeruginosa ATCC 27853–0.5 μg/ml minimum inhibitory concentration (MIC) of ciprofloxacin 0.5 μg/ml (certified value);

Escherichia coli ATCC 25922–0.008 μg/ml minimum inhibitory concentration (MIC) of ciprofloxacin (certified value).

Initially, the titanium plates with a deposited coating were placed in cylindrical containers (80 mm diameter), coatings up, with addition of 35 g of glass beads (3 mm diameter) and 100 ml of bidistilled water (Fig. 1). The containers were incubated in Biosan ES-20 orbital shaker-incubator at 35 °C and 120 rpm for 1, 4 and 24 h. After treatment, each sample was rinsed with distilled water and sterilized by air: 160 °C temperature, 60 min. At the second stage, the sterile titanium plate was placed, coating up, in a Petri dish containing 20 ml of frozen Müller-Hinton agar (MHA). 18 ml of melted and cooled down to 45 °C MHA was poured by a pipette dispenser onto the plate surface as a second