Summary

Implant prosthetics is the most dynamically developing field of dentistry. The use of the latest technologies in modern prosthetic rehabilitation of missing teeth ensures long-term effects and allows you to avoid many complications, even in the case of diseases such as diabetes or osteoporosis. However, despite the high effectiveness of implant treatment, implantation failures still occur. For this reason, new design and material solutions in implantation systems are constantly being developed so that the implantation procedure becomes the least invasive, the osseointegration process is accelerated and the risks associated with inflammation (*periimplantitis*) are eliminated.

Based on the analysis of the literature and own preliminary research, this doctoral thesis has a thesis that the modification of the surfaces of titanium dental implants by producing hybrid phosphate-polymer coatings improves their biocompatibility, bioactivity, bactericide, tribological wear, and resistance to pitting corrosion in a biological environment, and the obtained coatings constitute a universal carrier of medicinal substances for use in intelligent drug delivery systems. The main goal of this study was to develop an innovative method of producing multifunctional hybrid coatings on the surface of commercial titanium implants, made of an amorphous calcium phosphate sub-coating and an outer fibrous polymer coating consisting of type I collagen and polycaprolactone. The scope of the research also included the physico-chemical characteristics of the obtained coatings and the assessment of their shaped properties.

The multi-stage modification of the surface of titanium implants included sandblasting with an abrasive in the form of noble corundum, sterilization in a steam autoclave, production of amorphous calcium phosphate subcoatings using the electrochemically assisted deposition method from a newly developed acetate bath (Patent No. 233784) and the production of fibrous polymer coatings by blowing a polymer solution. (Patent application No. P.439307). Phosphate subcoatings were obtained according to a multi-stage deposition mechanism, where in the first stage oxygen reduction took place, in the second stage - phosphate reduction, and the third stage was related to water reduction. The local increase in pH at the cathode surface was caused by the cathodic polarization, which led to the formation of hydroxide ions. The calcium ions migrated from the bath to the negatively charged cathode surface and reacted with the phosphate ions, causing the synthesis of amorphous calcium phosphate on the titanium surface.

The physicochemical characteristics of the obtained phosphate-polymer coatings included structural tests carried out using the X-ray qualitative phase analysis method and the grazing incidence X-ray diffraction method, surface morphology studies by scanning electron microscopy, local chemical composition analysis by energy dispersion spectroscopy, coating thickness tests by amplitude-sensitive eddy currents, surface roughness tests by confocal microscopy and profilometric method, functional group analysis by attenuated total reflection - Fourier transform infrared spectroscopy, and thermal analysis by differential scanning calorimetry. It was shown that the physicochemical properties of the obtained phosphate subcoatings depend on the bath temperature and the current-time conditions of the deposition process. The porosity and thickness of the fibrous polymer coating were controlled by the concentration of the polymers used and the parameters of the polymer solution blowing process. Based on the conducted research, the optimal conditions for producing the phosphate

subcoating and the outer polymer coating were selected for applications in implantoprosthetic treatment.

Hybrid phosphate-polymer coatings obtained in optimized production conditions were subjected to the evaluation of tribological and micromechanical properties. The tribological tests were performed in a reciprocating motion in a ball on flat system in the environment of artificial saliva. The wear analysis of the samples after tribological tests was carried out based on the profilometric analysis of the wear scars. The wear analysis of the counter-sample was performed by measuring the diameter of the wear scar using optical microscopy. The evaluation of the micromechanical properties of the deposited coatings was carried out in the microhardness tests using the Vickers method, and their adhesion to the titanium substrate was assessed in the scratch test. The obtained hybrid coatings were tested for local contact voltage by the scanning Kelvin probe method and for surface wettability tests by the sitting droplet in the air method. The in vitro evaluation of the corrosion resistance of the tested coatings was carried out in the artificial saliva using the open circuit potential and polarization curves. A complementary method of electrochemical impedance spectroscopy was used to determine the mechanism and kinetics of pitting corrosion and to conduct quantitative tests of water absorption in the obtained coatings. The research on bioactivity of the obtained biomaterials was determined in an immersion test in a cell-free simulated body fluid. The in vitro biological evaluation included the study of cytotoxic properties and the examination of the bactericidal properties of the obtained coatings. Two cell lines were used to assess cytotoxicity using the cell metabolic activity assay (MTT test): human osteoblast CRL-11372 (ATCC, CRL-11372, Lot: 63791506) and the mouse fibroblast cell line L-929 (Sigma, L929, Lot: 10i019). The assessment of bactericidal effectiveness was performed on hybrid coatings saturated with the antibiotic in the form of tetracycline using the Kirby-Bauer disc diffusion method. In the bactericidal study, the titanium substrate in the initial state was also taken into account as a control sample. The test system consisted of *Staphylococcus aureus* culture plates (ATCCR 6538) and *Pseudomonas aeruginosa* strain (ATCC 9027). The release kinetics of tetracycline implemented in hybrid coatings was determined by UV-VIS spectroscopy.

Based on the conducted research, it has been shown that the developed method of modifying the surface of titanium endosseous implants allows to increase their resistance to tribological wear and rise corrosion resistance in the environment of artificial saliva. Phosphate subcoatings show greater bioactivity compared to the titanium substrate which increases with the deposition temperature. Obtaining calcium phosphate subcoatings with a chemical composition similar to the composition of bone tissues makes a significant contribution to the development of material engineering thanks to the possibility of deposition at ambient temperature and physiological pH of the bath with a Ca:P ratio of 1.67, which will allow for the production of composite coatings based on calcium phosphate in the future, containing inorganic and/or organic components. The obtained phosphate subcoatings may accelerate the process of osseointegration and reconstruction of bone tissues surrounding titanium implants, and thus shorten the time of implantoprosthetic treatment. It has been shown that microfibrous polymer coatings do not exhibit cytotoxicity, and the tetracycline incorporated into the microfiber is gradually released from the coating. The obtained polymer coatings, after being saturated with an antibiotic, show bactericidal properties, which will allow to eliminate inflammation around the neck of implants (*periimplantitis*).

The obtained hybrid phosphate-polymer coatings with increased osteoinductive properties with the possibility of intelligent and controlled drug delivery will be able to be used in implantoprosthetic treatment. The developed innovative technology of titanium implant surface modification allows the use of naturally occurring polymers in the human body, which may reduce post-implantation complications. The use of the produced polymer microfibers as a drug carrier will result in a milder course of treatment in patients and a reduction in the amount of anti-inflammatory drugs they take. Targeted drug delivery will have a positive effect on the immune response of the body by maximizing the concentration of the drug in the infected tissue and limiting the systemic toxicity of the therapeutic. The obtained coatings can be a source of tissue-forming elements and constitute a universal drug carrier meeting the requirements of the progressive development of civilization, which forces the design of the latest generation biomaterials with high durability and supporting the regeneration process.