Composite Coating with Controlled Bioactivity for Medical Applications

The aim of this doctoral dissertation was the development and comprehensive characterization of multifunctional composite coatings intended for surface modification of biomaterials and implants with low bioactivity. It was hypothesized that a hybrid coating combining a polymer phase (PVP:PEG with collagen and glutathione) with a ceramic phase (HAp) and modified with active substances (clindamycin, VEGF-165, TGF-β1) could simultaneously support bone tissue regeneration, reduce the risk of infection, and promote a favorable healing microenvironment.

In the first stage, calcium phosphates with different molar Ca/P ratios (HAp, TCP, brushite) were synthesized using the wet precipitation method. XRD/FTIR/SEM+EDS analyses confirmed phase purity and controlled morphology. The powders were modified with clindamycin, and the drug release profile was found to depend on the Ca/P molar ratio and the specific surface area. All carriers exhibited antimicrobial activity against Staphylococcus aureus, with the lowest MIC99 observed for brushite. Subsequently, a composition of a ceramic-polymer coating and a two-step deposition process on substrates (PLA, PLLA/HAp) were developed. It was observed that an increased HAp content enhanced surface roughness and surface energy, potentially promoting cell interactions; however, at 15% HAp, tribological wear intensified. Collagen increased the sorption capacity and reduced the coefficient of friction. The optimal compromise of mechanical, sorption, and tribological properties was found in the coating containing 5% HAp. Incubation studies in simulated biological fluids demonstrated chemical stability of the materials and the ability to induce the growth of new apatite layers already at 5% HAp content. The coatings were modified with clindamycin, which was released more rapidly from polymeric than composite materials. Drug-loaded materials effectively inhibited the formation of Staphylococcus aureus biofilm. The selected composite coating variant with 5% ceramic phase content was further functionalized with the growth factors VEGF-165 and TGF-β1, which exhibited biphasic, diffusion-controlled release, consistent with the Higuchi model. The safety and biological activity assessment included in vitro studies using L929 and hFOB 1.19 cell lines, as well as two-stage in vivo models including subcutaneous implantation and a cranial defect model. No inflammatory response was observed, the levels of pro-inflammatory cytokines IL-1β and TNF-α were comparable to control, while the level of anti-inflammatory IL-10 was elevated. Histological and fluorescence analyses confirmed the initiation of mineralization at the implant–bone interface, and increased expression of the bone formation marker OPN was noted in groups with growth factors and antibiotic.

The obtained results confirm that the designed composite coatings combine bioactivity with antimicrobial properties and stimulate the mineralization of new bone tissue. Particularly promising is the composite coating containing 5% HAp, modified with clindamycin and VEGF-165 and TGF-β1. This solution constitutes a multifunctional drug delivery system that can be used to coat implants with low bioactivity to provide additional functionalities. The presented results confirm the relevance of the conducted research and form the basis for further development towards potential clinical applications.