Modification with natural biopolymers of the surface of porous titanium-based materials produced by powder metallurgy

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INTRODUCTION

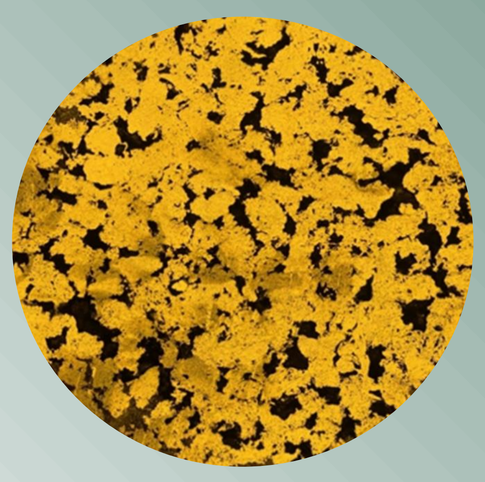


Fig. 1 Microscopic image of the sample surface under study.

The demand for new materials used in medical implantology is increasing yearly. Nowadays, implants not only function as a replacement or support for living tissue, but provide features that prevents future complications connected with inflammation followed by rejection of an implant. Currently, biomaterials that combine appropriate mechanical properties, high biocompatibility and bioactivity are sought. Introducing porosity into the material makes it possible to reduce Young's modulus, thereby minimizing damages related to mechanical mismatch of bone and implant material. The pores in the implant could promote bone cells ingrowth into the material, thus stabilizing the whole element.

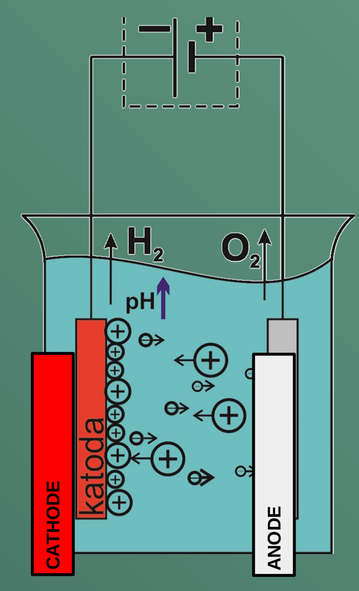
One of the most interesting natural materials for modifying the surface of medical implants is chitosan - a natural polymer characterized by high biocompatibility, biofunctionality, and non-toxicity. It is widely used in medical applications such as tissue engineering, drug delivery, or wound dressing, as chitosan is also known for its antibacterial and antifungal properties, as well as promoting bone regeneration. Moreover, chitosan coatings are biodegradable and bioresorbable, which means that after fulfilling their function, the coatings decay and are absorbed by the body.

MATERIALS AND METHODS

The porous biomaterial was prepared from commercial titanium with the powder metallurgy method. The surface of obtained porous titanium was modified by the electrophoretic deposition (EPD) of chitosan coatings. The EPD process was conducted for various time-voltage conditions (Table 1).

Table 1. Parameters for EPD coating process

T (5 min)	2.5 V	5 V	7.5 V	10 V	20 V
U (10 V)	2. min	5 min	10 min	20 min	30 min



Solutions for the EPD coating deposition process were prepared using chitosan (Sigma-Aldrich), citric acid (Acros Organic; 99.6%), distilled water and ethyl alcohol (anhydrous 99.8%).

The electrophoretic coating deposition process was carried out from four different solutions:
1. **starting solution:** 2% citric acid solution containing 1 g/dm³ of chitosan,
2. **solution 1 (25% ethanol)**: 2% citric acid solution in 25% ethanol containing 1 g/dm³ of chitosan,
3. **solution 2 (50% ethanol)**: 2% citric acid solution in 50% ethanol containing 1 g/dm³ of chitosan,
4. **solution 3 (75% ethanol)**: 2% solution of citric acid in 75% ethanol containing 1 g/dm³ of chitosan.

OBSERVATION AND ANALYSIS OF COATINGS

As mentioned earlier, the morphology of the coatings depends on the solution used in the EPD process. The above study showed a significant effect of ethanol concentration on the homogeneity of the obtained biopolymer coatings. Coatings of the most satisfactory quality were obtained for the chitosan starting solution and solution 1 (Fig. 2, 3). Increasing the ethanol concentration to 50% resulted in cracking and peeling of the applied coating (Fig. 4). This was probably due to too rapid evaporation of the alcohol from the coating, which contributed to its rapid shrinking and cracking. In contrast, a solution with a 75% ethanol concentration affected the deposition of thin coatings (Fig. 5). It is possible that such high ethanol concentration in the solution affected the solubility of chitosan in the solution, which adversely affected the performance of the EPD process. The thickest coatings were obtained in 30 min at a deposition voltage of 10 V. However, it should be noted that hydrogen was released at these deposition parameters, which caused the formation of bubbles and pores in the chitosan coating. The pores present in the biocoating may promote osseointegration. The SEM study also showed the effect of changing time and voltage on the morphology of the deposited biopolymer coatings.

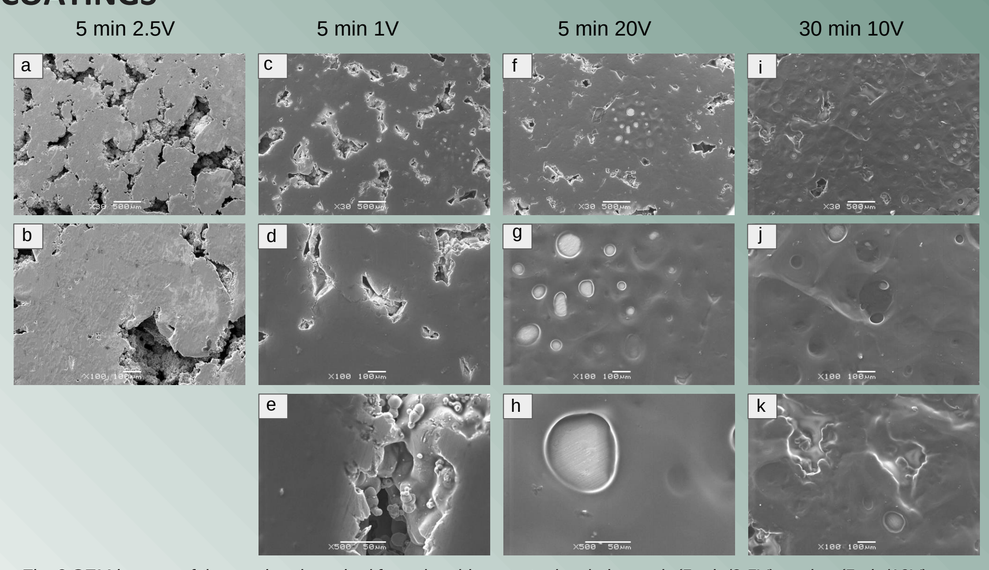


Fig. 2 SEM images of the coating deposited from the chitosan stock solution: a, b (5 min/2.5V); c, d, e (5min/10V); f, g, h (5min/20V); i, j, k (30min/10V).

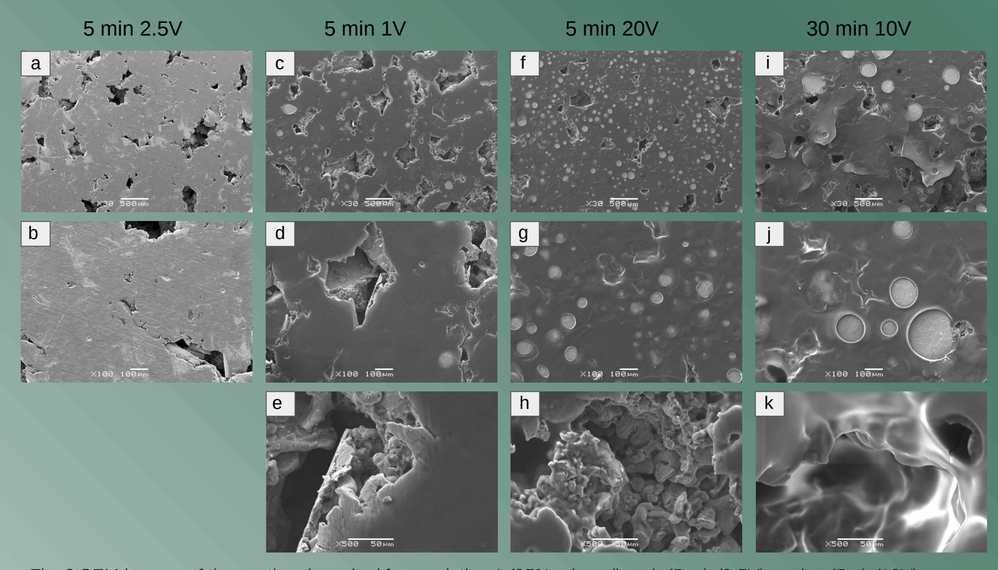


Fig. 3 SEM images of the coating deposited from solution 1 (25% ethanol): a, b (5 min/2.5V); c, d, e (5min/10V); f, g, h (5min/20V); i, j, k (30min/10V).

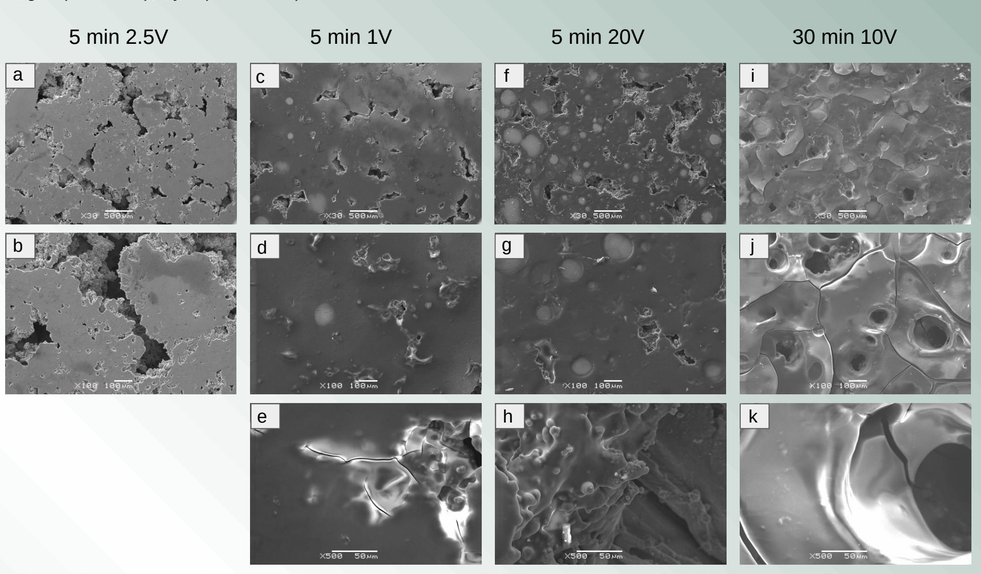


Fig. 4 SEM images of the coating deposited from solution 2 (50% ethanol): a, b (5 min/2.5V); c, d, e (5min/10V); f, g, h (5min/20V); i, j, k (30min/10V).

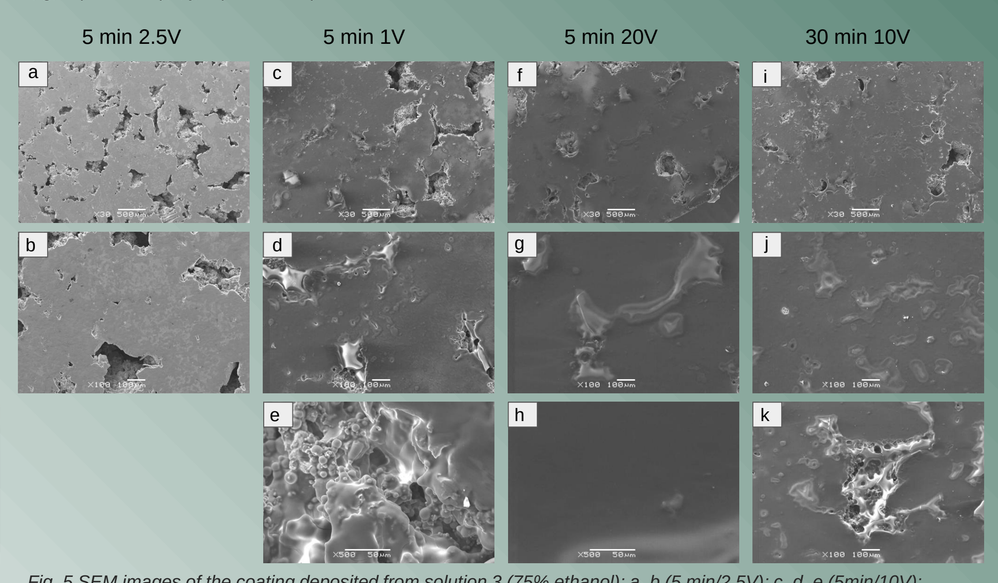


Fig. 5 SEM images of the coating deposited from solution 3 (75% ethanol): a, b (5 min/2.5V); c, d, e (5min/10V); f, g, h (5min/20V); i, j, k (30min/10V).

CHARACTERISTICS OF BIOCOATING

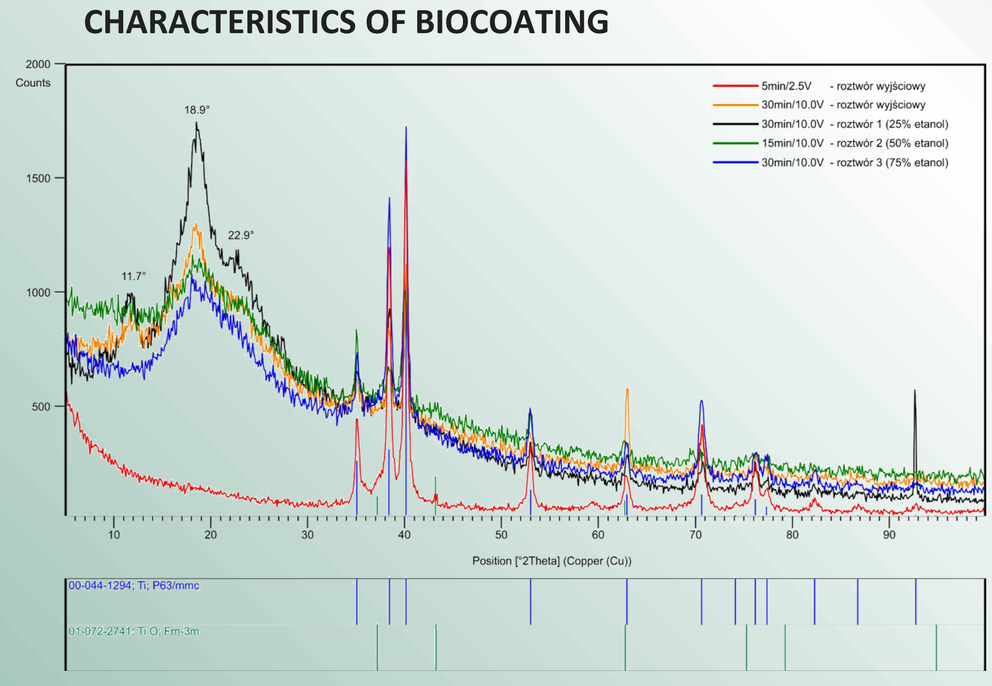


Fig. 6 Diffractograms of chitosan coatings.

Based on the summary of the diffractogram (Fig. 6), the sample deposited for 30 min at 10 V in solution 1 with 25% ethanol has the highest thickness. The diffractogram of the sample deposited in the starting solution using the parameters of 5 min/2.5 V does not contain reflections from chitosan. This may indicate the absence of a chitosan coating or the formed coating is too thin to be recorded.

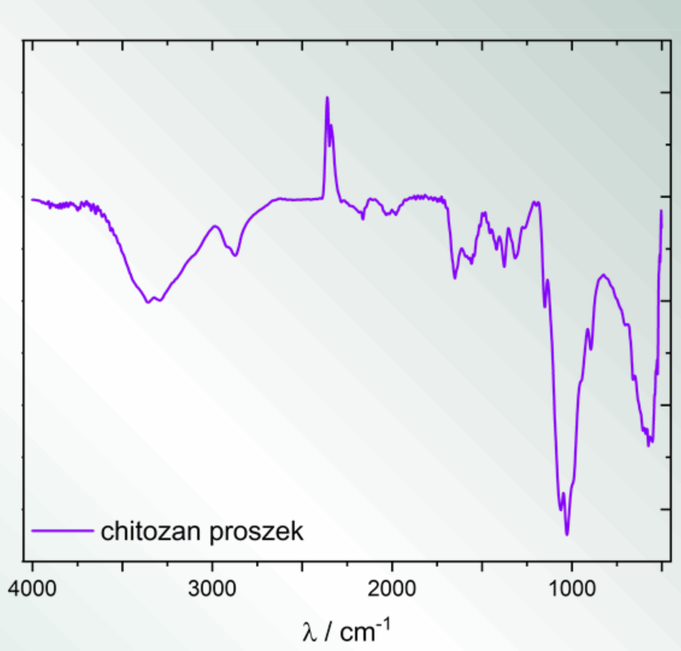


Fig. 7 FTIR spectrum of chitosan powder.

The FTIR spectrum of chitosan powder is shown in Fig. 7. FTIR analysis revealed the presence of characteristic functional groups of chitosan. It thus confirms the presence of deposited coatings on the porous titanium substrate (Fig. 8).

The characteristic bands for chitosan have the following values: 3359 cm^{-1}, 2920 cm^{-1}, 1651 cm^{-1}, 1558 cm^{-1}, 1456 cm^{-1}, 1377 cm^{-1}, 1315 cm^{-1}, 1151 cm^{-1}, 1062 cm^{-1}, 1028 cm^{-1}, and 895 cm^{-1}.

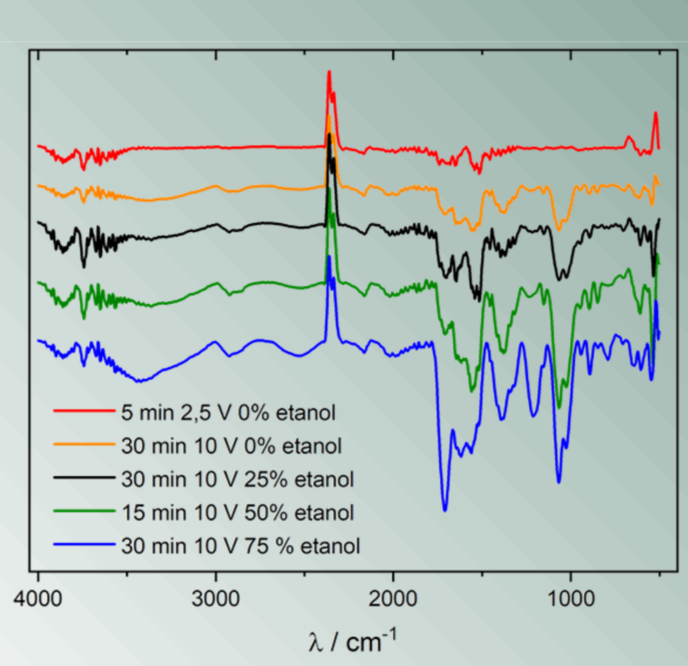


Fig. 8 FTIR spectra of chitosan coatings.

CYTOTOXICITY

Fig. 9 Cytotoxicity results. Fibroblast viability observed microscopically at x100 magnification. Cell viability for samples with ethanol (A), for samples without ethanol (B), and control sample (C).

Statistical analysis of the results using the one-way ANOVA (after checking the normality of the distribution) confirmed the lack of cytotoxic effect of obtained material.

RESULTS AND DISCUSSION

The EPD method makes it possible to obtain chitosan-based biopolymer coatings on porous titanium substrates. Studies have shown that the developed deposition parameters allow the penetration of the coating material into the pores of the substrate. It was shown that it is possible to control the thickness and morphology of the coatings by selecting the deposition conditions.

It was found that as the deposition time and voltage increase, the coatings are thicker. An increase in voltage in the electrophoretic deposition process promotes the formation of bubbles and gas pores in the chitosan coating. An increase in ethanol concentration in the solutions increases the likelihood of cracking and peeling of the coating. The best coatings were obtained for process parameters: 30 min/10 V.

Vital staining showed a high cell survival rate of 99.71%. Biological tests also show the absence of cytotoxic effects of the produced biomaterial on fibroblasts.