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**Osteoconductive bioceramics based on resorbable calcium phosphates**

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## INTRODUCTION

The most important properties of materials for bone implantation are biocompatibility, resorbability and osteoconductivity. Calcium phosphates with the Ca/P ratio less than 1,67 are biocompatible due to the similarity of native bone tissue, and their resorption ability increases with a decrease in this ratio; therefore, calcium phosphates with the ratio of 0,5≤Ca/P≤1 are especially promising.

Creation of porous ceramic materials with good osteoconductive properties (high penetration, porosity) is possible by means of additive manufacturing (3D printing). Stereolithography is one of the most universal and perspective methods, in which 3D-object is created using photopolymerization of special suspensions.

In this way the scope of our research was to create and investigate macroporous bioresorbable ceramic materials for bone implants in the system of $Ca(PO_3)_2 – Ca_2P_2O_7$.

## EXPERIMENTAL METHODS

Three research objects were chosen in the framework of this work: calcium polyphosphate $Ca(PO_3)_2$ (Ca/P=0,5), calcium pyrophosphate $Ca_2P_2O_7$ (Ca/P=1) and the mixture of these compounds in the 1:1 ratio (Ca/P=0,75). Powders of amorphous hydrated calcium phosphates with these Ca/P ratios were obtained by means of wet precipitation method using ion exchange from solutions of sodium poly- and pyrophosphates and calcium acetate. Then, dried powders were heat treated under different temperatures.

In order to obtain ceramic material using stereolithography, it is necessary to use suspensions containing powder of the demanded phase composition and a light-cured monomer. Three parameters were varied in the study of the suspensions for further stereolithography application: composition of powder (Ca/P=0,5; 0,75; 1), the temperature (500, 700, or 900°C) of preliminary heat treatment of the CPP powder and the content of powder (2–40 vol.%) in the slurry.

The samples of macroporous composite materials were printed by means of the stereolithography. The structure with the architecture of gyroid was chosen for stereolithographic printing, since it is one of the most promising models for producing osteoconductive materials. Macroporous ceramic samples were obtained after the heat treatment of these composites.

## RESULTS AND DISCUSSION

Amorphous powders of hydrated calcium phosphates $Ca(PO_3)_2*H_2O$ and $Ca_2P_2O_7*2H_2O$ were obtained. Powders obtained by the heat treatment of those powders under T<900ºC were inherently grey due to the presence of residual carbon. Using of these powders for suspensions for stereolithography allowed to increase the printing resolution.

The relations between depth and radius of polymerization and the radiation dose were established. Basing on the obtained data, photosensitivity and critical energy of polymerization of the studied suspensions were identified.

Rheological study of suspensions indicated that all slurries with the powder loading of 20-40% exhibited the low viscosity and non-Newtonian (pseudoplastic) flow behaviour.

2–40% of calcium pyrophosphate powder in the composite material ("polymer/inorganic powder" composite) provided for the retention of shape and continuity of the ceramic sample after the removal of polymer and sintering during the thermal treatment.

Predetermined architecture of macroporous ceramic materials was retained after the heat treatment. The porosity of the prepared ceramic material (more than 86%) is sufficient to provide high osteoconductive properties.

## CONCLUSION

The method of amorphous hydrated calcium phosphates synthesis using ion exchange was elaborated. The properties of the suspensions (viscosity, photosensitivity, and critical energy of polymerization) were explored. It was shown that the variation of the photosensitivity of suspensions by changing the colour of powder could sufficiently improve the resolution of stereolithographic printing. Ceramic materials with high osteoconductive properties were obtained using stereolithographic printing. Created porous ceramics based on calcium poly- and pyrophosphated exhibit good resorbability and osteoconductivity and are suitable for medical applications.

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