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PROCEEDINGS

OSTEOCONDUCTIVE BIOCERAMICS BASED ON CALCIUM PYROPHOSPHATE

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INTRODUCTION

Modern regenerative medicine requires the creation of new materials for bone implantation. The most important properties of such materials are biocompatibility, resorbability, and osteoconductivity. When implanted at the damaged area of bone, the material should be gradually dissolved and replaced with the growing native bone tissue. Being dissolved, such material serves as the source of elements required for the bone formation. Calcium phosphates with the $0{,}5 \le Ca / P \le 1{,}67$ ratio are biocompatible, and their resorption ability increases with a decrease in the Ca / P ratio; therefore, calcium pyrophosphate (CPP) with a ratio of Ca / P = 1 is especially promising.

Osteoconductivity of material for implantation is the ability to provide the proliferation of blood vessels and nerves into the implant. Porous materials with porosity above 60% and pore size not less than 100 μm demonstrate good osteoconductive properties. Creation of porous ceramic materials with high penetration is possible by means of rapid prototyping techniques. Stereolithography is one of the most universal and perspective methods, in which 3D-object is created using photopolymerization of special suspensions.

In order to obtain ceramic material, it is necessary to use suspensions containing powder of the demanded phase composition and a light-cured monomer. However, the printing quality of such suspensions with ordinary white inorganic powders is very poor due to the light scattering at the powder particles. Addition of colorants allows increase in the printing resolution; however, calcium phosphates obtained by heat treatment (T < 900°C) of amorphous calcium phosphate synthesized from solutions of phosphoric acid and calcium acetate, are inherently grey due to the presence of residual carbon.

The aim of our research was to create macroporous calcium phosphate bioresorbable ceramic materials for bone implants with the pre-defined architecture using stereolithography for molding.

This work was divided into several steps. First, we developed a method to synthesize colored powders of calcium pyrophosphate and studied the product properties; second, we obtained and characterized the suspensions for stereolithographic printing containing those powders and light-cured monomer; third, we examined the printing resolution; then, we obtained the "polymer - calcium pyrophosphate powder" composite materials; and, finally, we manufactured the samples of macroporous resorbable ceramics via the heat treatment of those composites and characterized the final product properties.

RESULTS AND DISCUSSION

XRD analysis of the powder after synthesis confirmed the formation of X-ray amorphous product. According to thermogravimetric analysis data, the total mass loss (about 30%) on heating that powder from 20 to 1000°C chiefly occurred over the 40–600°C range. According to mass spectrometry data, the mass loss was associated with the elimination of water (up to 200°C) and the release of the decomposition products of ammonium acetate (at higher temperature). The form of nano-sized particles of the obtained powders was close to isometric. The phase composition of the powders after heat treatment at 500 to 900°C was represented of biocompatible β- and γ- phases of calcium pyrophosphate.

Two parameters were varied in the study of the suspensions for further stereolithography application: the temperature (500, 700, or 900°C) of preliminary heat treatment of the CPP powder and the content of powder (10–40 vol.%) in the slurry. To characterize the properties of the light-sensitive suspensions, they were exposed to different radiation doses through a special mask. The so obtained "polymer-powder" composites were examined by means of light microscopy. 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 non-Newtonian (pseudoplastic) flow behaviour. At the higher concentration of the powder in the suspensions, the flow can become dilatant, i.e. the viscosity grow with the increase in shear rate. To provide the homogenization of suspensions when printing, the low viscosity is required for moulding of prefabricated ceramic unit by means of stereolithography.

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

Macroporous prefabricated ceramic unit (Figure 1, left) were printed by means of the stereolithography from the suspension containing 10 vol.% of calcium pyrophosphate powder obtained at 700°C. That suspension was selected for printing of prefabricated ceramic unit because of its low viscosity, fairly high depth of polymerization, and the high printing resolution. 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. Composite macroporous ceramic samples (Figure 1, right) were obtained after the heat treatment of prefabricated ceramic unit. Predetermined architecture was retained after the heat treatment. The porosity of the prepared ceramic material (more than 86%) is sufficient to provide high osteoconductive properties.

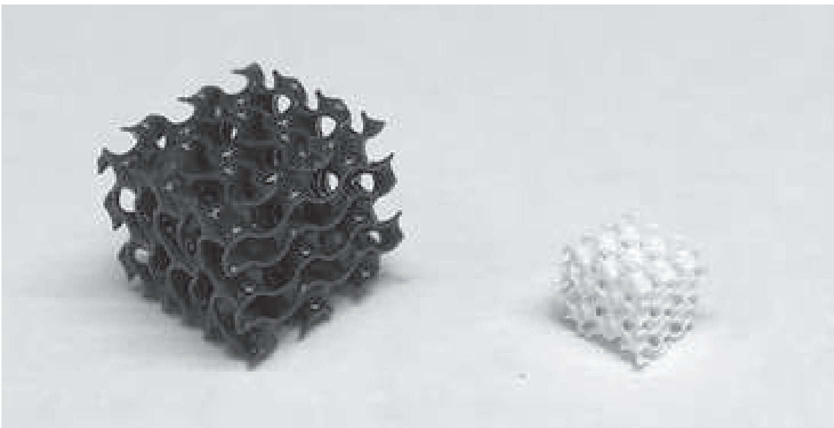

Figure 1: The view of the composite preform obtained by stereolithography from suspension containing 10 vol.% of colored CPP powder (at the left side) and macroporous ceramic sample obtained via heat treatment of that preform (right side)

CONCLUSIONS

The method of amorphous hydrated calcium phosphates synthesis using ion exchange was elaborated. Stable and homogeneous suspensions based on coloured CPP powders and light-cured monomer suitable for stereolithographic printing were obtained. Macroporous ceramic materials with a predetermined architecture were created by means of stereolithographic printing from suspensions based on the coloured CPP powders and the light-curing monomer. 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 the CPP powder sufficiently improved the resolution of stereolithographic printing. Ceramic materials with high osteoconductive properties were obtained using stereolithographic printing as a method for moulding the prefabricated ceramic units. Created porous ceramics based on calcium pyrophosphate exhibit good resorbability and osteoconductivity and are suitable for medical applications.

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