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BIOMATERIALS

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PROPERTIES OF COMPOSITES WITH CALCIUM PHOSPHATE FILLED POLYMER MATRIX, OBTAINED USING STEREOLITHOGRAPHIC PRINTING FOR CERAMIC MATERIALS WITH PRESCRIBED PORE-SPACE ARCHITECTURE

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The process of removing an organic component from composites (photopolymer/calcium phosphate) with complex architecture, which are obtained by 3D-printing in order to create personalized bioceramic implants, was studied. Ceramic materials with complex pore-space organization were obtained by stereolithographic printing. It is shown that the degree of polymerization of the composite influences the final density of the calcium phosphate ceramic materials with complex architecture.

Key words: bioceramic, tricalcium phosphate, additive technologies, 3D printing, stereolithography, osteoconductivity, sintering.

The human body is capable of repairing minor bone damage but major damage, as in the past, requires additional intervention and creation of stimuli for regeneration. For bone implantation autografts — materials fabricated from the patient's own bone tissue — are considered to be the gold standard; they do not give rise to rejection and other adverse reactions by the body and promote acceleration of the regeneration process. At the same time the replacement of large bone defects by such materials is practically impossible without serious additional damage occurring in the course of autotransplantation [1, 2].

In this connection one of the tasks of material science is to develop an ideal synthetic material for bone implantation that in terms of characteristics would be comparable to autografts or even surpass them to a certain extent. A number of requirements exist for such materials [3 – 6]: biocompatibility and nontoxicity; bioactivity (capability of the material to promote effective intergrowth with the bone tissue and to stimulate its growth), incorporating the concept of osteoconductivity and osteoinductivity; bioresorbability (capability of dissolving in the body); and, adequate strength (at least 1 MPa).

Materials based on calcium phosphates ($0.5 \le Ca/P \le 1.67$) are characterized by biological compatibility with the body's tissues, and they also have the capability of resorption (dissolution), whose rate and degree increase with decreasing ratio Ca/P [7].

Osteoconductivity — the capability of a material to serve as a matrix in the process of growth of native bone tissue, maintaining the delivery of nutrients, adhesion and proliferation of bone cells, and penetration intergrowth of the bone itself — is an important parameter maintaining high biological activity of the material as well as the blood vessels and nerve fibers upon their penetration intergrowth with the implant [9]. It has been shown repeatedly that porous materials have advantages over dense materials. Such matrices possess high rates of resorption, promote better fixation of the implant, and create favorable conditions for cell colonization and high vascularization [5, 8, 10, 11].

The presence of a definite pore-space architecture [12] makes it possible to increase the penetrability and improve the osteoconductivity of the material and at the same time maintain adequate mechanical characteristics.

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Materials with a complex specified architecture and shape can be obtained only with use of additive technologies (3D printing). Ceramic materials with a predetermined complicated architecture can be obtained by heat-treatment of composites containing a polymer and an inorganic powder with a specified composition; they are formed by means of stereolithographic printing [13].

The heat-treatment of a printed composite must be carried out in accordance with a special program providing gradual removal of the polymer and preservation of the prescribed framework architecture at all stages of treatment, including the subsequent sintering of the ceramic [14, 15]. The development of such a program requires comprehensive thermal analysis of the removal kinetics of the polymer. In addition, factors such as the degree of polymerization, heat-treatment atmosphere, and others can influence the process of removing the organic components [16]. This ensemble of factors has a significant effect on the quality and characteristics of the obtained ceramic (density, strength, and so on), in connection with which the process of thermal removal of the polymer must be studied carefully and systematically.

In summary, the aim of the present work was to investigate the properties of the photopolymer matrix of composites, obtained by the method of stereolithographic printing, in order to develop ceramic bioimplants with a prescribed architecture based on calcium phosphates.

EXPERIMENTAL PART

Tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) was synthesized by the solid-phase method via the reaction

$$CaCO_3 + Ca_2P_2O_7 = \beta\text{-}Ca_3(PO_4)_2 + CO_2\uparrow. \qquad (1)$$

Calcium pyrophosphate $Ca_2P_2O_7$ was obtained by slow heat-treatment of freshly precipitated brushite $CaHPO_4 \cdot 2H_2O$. Next, weighed portions of $CaCO_3$ (reagent-grade) and synthesized calcium pyrophosphate were placed in the drum of a Pulverisette (Fritsche, Germany) planetary-type ball mill and homogenized for 15 min. The dried mixture was passed through a Saàtilåne HiTech polyester mesh screen with 220 μm cells. The obtained mass was heat-treated in a Nabertherm (Germany) muffle furnace.

The well-known procedure of [16] was chosen to prepare photocured suspensions for stereolithographic printing. The following composition was used: 1) Laromer 8889 monomer (BASF, Germany); 2) solvent (GDDA — hexanediol diacrylate); 3) TPO-L photoinitiator (BASF, Germany); 4) $Ca_3(PO_4)_2$; 5) Triaton X-100 surfactant (Sigma-Aldrich, Germany); 6) scattered UV-radiation absorber — sudan orange dye (India). The powder mass fraction in the suspensions ranged from 25 to 67%.

A three-dimensional stereolithographic DLP-printer Ember (Autodesk, USA) was used to print polymer/powder composites from photocured suspensions. Layer-by-layer partitioning and transmission of the model for printing to a printer were conducted with the aid of the free software Print Studio (Autodesk, USA). The thickness of a single layer in printing a three-dimensional object was equal to 50 – 200 μm.

The calibration depth-of-polymerization versus irradiation dose curves were constructed in order to determine the photosensitivity and critical energy of polymerization. A straight line was fit to the obtained relation in semi-logarithmic coordinates according to the Jacobs equation [18]:

$$C_d = D_p \ln\left(\frac{E_{\text{ir}}}{E_c}\right), \qquad (2)$$

where C_d is the polymerization; D_p is the photosensitivity; E_{ir} is the irradiation dose; and, E_c is the critical energy of polymerization.

A UV radiometer (G&R Labs Model 222, USA) with a 405 nm sensor was used to measure the radiation dose (mJ/cm^2).

A Spectrum One IR spectrophotometer (Perkin-Elmer, USA) was used to recorde the disrupted total internal reflection (DTIR) UV-spectra of the printed composites in the range $580 – 4000\ cm^{-1}$ with scanning step $1\ cm^{-1}$. The analysis of these spectra was performed on the basis of published data.

The relative density of the heat-treated ceramic samples was determined from the relation

$$\rho_{\text{rel}} = \frac{4m}{\pi d^2 h \rho_{\text{theor}}} \times 100\%, \qquad (3)$$

where m is the mass of the sample, g; d is the diameter of the pellet, cm; h is the thickness of the pellet, cm; and, ρ_{theor} is the theoretical density, g/cm^3.

Thermogravimetric (TA) and differential thermal (DTA) analysis of composites with polymer/powder composition were conducted with a STA 409 PC Luxx (Netzsch, Germany) simultaneous thermal analyzer with the sample loaded vertically. The mass of the weighed samples was 10 – 20 mg. Alundum crucibles were used for heat treatment.

A DIL 402 C (Netzsch, Germany) horizontal dilatometer was used to measure the linear shrinkage of the printed samples. The dilatometric data were analyzed with the aid of Proteas Analysis software.

A LEO SUPRA 50VP (Carl Zeiss, Germany) field-emission scanning electron microscope (SEM) was used to study the microstructure of the composites and the ceramic. A layer of chromium was deposited on the sample for the investigations (Quorum Technologies QT-150T ES Sputterer (Great Britain)). The accelerating voltage of the electron gun was 3 – 15 kV. A SE2-type detector was used to obtain images in secondary electrons with magnification to ×50,000.

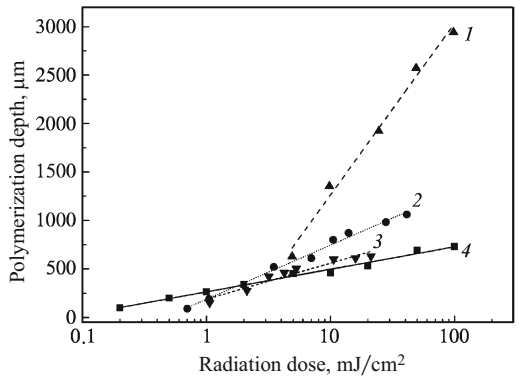

Fig. 1. Polymerization depth vs. radiation dose. Suspensions based on TCP $Ca_3(PO_4)_2$ and photosensitive polymers: *1*) TCP 0% by weight; *2*) 25%; *3*) 35%; *4*) 65%.

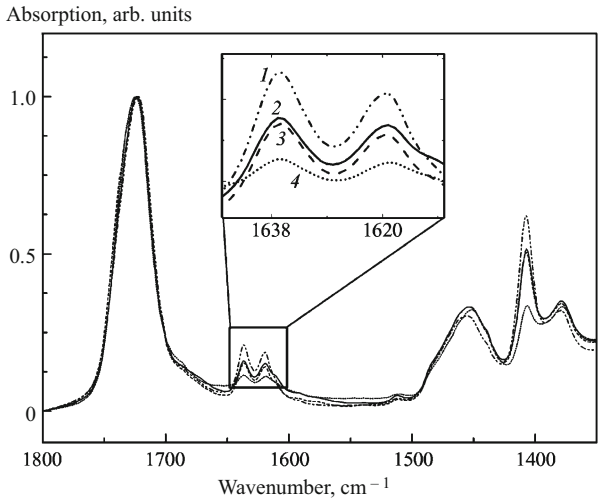

Fig. 2. Data from IR spectroscopy of polymer/TCP powder composites obtained with different radiation doses: *1*) 0.7 mJ/cm^2; *2*) 1.05 mJ/cm^2; *3*) 2.45 mJ/cm^2; *4*) 420 mJ/cm^2.

RESULTS AND DISCUSSION

To determine the required radiation dose for stereolithographic printing that is sufficient for polymerization of the running layer and bonding it with the proceeding layer the depth of polymerization of the suspension was studied as a function of the radiation dose and on this basis the optimal exposure time for a single layer was chosen.

Figure 1 shows the polymerization depth versus the radiation dose. These data were used to determine the stereolithographic printing parameters (Table 1). Increasing the powder content in the composition of the suspension has the effect of decreasing the photosensitivity and the critical energy of polymerization and therefore increasing the radiation dose needed for polymerization of a single layer during printing.

The removal of the organic component from the composites (polymer/powder) obtained by stereolithographic printing is one of the critical steps in obtaining ceramic materials. In addition the properties of the polymer matrix (thermoplasticity, thermoreactivity, degree of polymerization, and so on) influence the character of the compaction of the powder in the article in the process of its heat treatment and removal of the organic component from the composite.

A suspension with 25% weight content of $Ca_3(PO_4)_2$ powder was used to study the influence of the degree of polymerization of the organic component in the printed composite on the density of the green body after removal of the polymer. The method of stereolithography was used to obtain samples in the form of pellets, for which the exposure time of a single layer was varied.

According to IR spectroscopy, as the radiation dose increases doing printing, the area of the absorption peaks corresponding to vibrations of the double bonds C=C decreases (Fig. 2). This is associated with the opening of the double bonds in the polymerization process and the degree of polymerization of the organic matrix in the composite: in the wavenumber interval 1600 – 1650 cm^{-1} the absorption peaks correspond to stretching vibrations and in the interval 1390 – 1420 cm^{-1} to deformation vibrations.

The temperature program for the removal of the photopolymer matrix was developed using the widely used kinetic modeling approach [17] and the TG/DTA data. According to the thermal analysis data the removal of the polymer matrix occurs in the interval 150 – 550°C. Increasing the degree of polymerization of the organic matrix results in a reduction of the density of the obtained green body after heat-treatment for removal of the polymer before the sintering stage (Fig. 3). This fact was also confirmed by dilatometry data. It could be that during heat-treatment a larger quantity of free monomer in the makeup of the composite than in composites with a strongly polymerized organic matrix has the effect of increasing the mobility of filler powder particles as result of the capillary forces arising in the course of removal of the polymer, thereby increasing the density of the ceramic green body.

According to the SEM data (Fig. 4), the particles of TCP powder in the polymerized composite are distributed uniformly and could be separated by quite large distances from one another (at low weight content of the $Ca_3(PO_4)_2$ powder, %). The character of the removal of the employed polymer

TABLE 1. Photosensitivity and Critical Energy of Polymerization of Suspensions with Different Weight Content of $Ca_3(PO_4)_2$ powder

$Ca_3(PO_4)_2$ weight fraction, %	Photosensitivity D_p, μm	Critical energy of polymerization E_c, mJ/cm^2
0	770 ± 40	2.00 ± 0.50
25	240 ± 25	0.45 ± 0.05
35	170 ± 20	0.13 ± 0.03
40	140 ± 20	0.09 ± 0.03
65	100 ± 5	0.07 ± 0.01

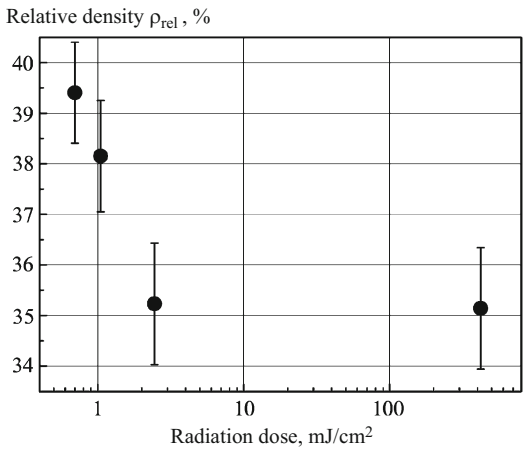

Fig. 3. Relative density ρ_{rel} of the green body (after removal of the photopolymer matrix) versus the radiation dose for suspensions based on TCP and photosensitive monomers (TCP weight fraction in the suspension 25%).

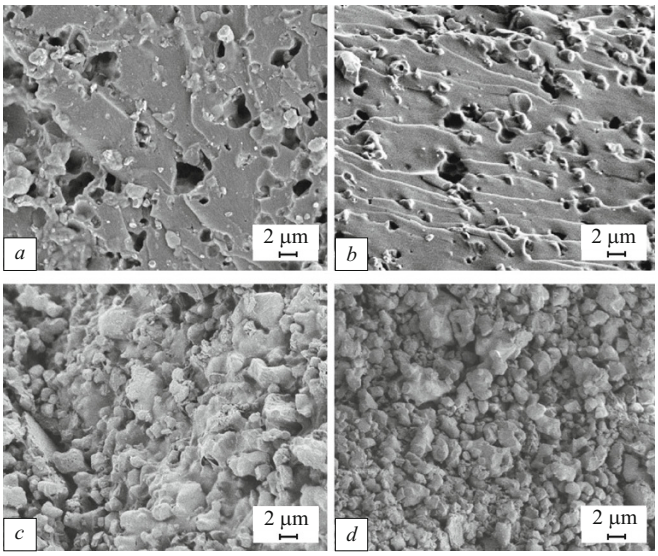

Fig. 4. Microstructure of printed composite with TCP powder content 35% by weight at different stages in the process of removing the organic component: *a*) without heat-treatment; *b*) with heat-treatment $T = 285$°C; *c*) $T = 355$°C; *d*) $T = 400$°C.

matrix (simultaneous presence of thermoreactive and thermoplastic properties) promotes convergence of the powder particles (see Fig. 4) during heat-treatment and makes it possible to preserve the prescribed shape and obtain ceramic materials with complex architecture.

CONCLUSIONS

The investigation of the properties of the photopolymer matrix of polymer/TCP composites with complex architecture, which were obtained by the method of stereolithographic 3D-printing has shown that the character of the polymer matrix (thermoplastic, thermosetting plastic) and its degree of polymerization make a considerable contribution in the density of the ceramic green body after removal of the organic part from the composite. Composites with a weakly polymerized photopolymer matrix make it possible to obtain ceramic green body density 40% with $Ca_3(PO_4)_2$ powder weight fraction 25% in suspension.

A low content of calcium phosphate in photocurable suspensions makes it possible to increase the resolution and detailing and also decrease the size of the elements of the finite ceramic body as result of shrinkage in the course of heat-treatment.

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