Consiglio Nazionale
delle Ricerche

1ST BIENNIAL CONFERENCE

BioMaH

a cura di

Julietta V. Rau e Antonio Ravaglioli

PROCEEDINGS

1ST BIENNIAL CONFERENCE

BIOMA

BIOMATERIALS FOR HEALTHCARE

BIOMATERIALS FOR TISSUE AND GENETIC ENGINEERING AND
THE ROLE OF NANOTECHNOLOGY

a cura di
Julietta V. Rau e Antonio Ravaglioli

OCTOBER 17TH-20TH, ROME, ITALY

Consiglio Nazionale
delle Ricerche

BioMaH is endorsed by the following International Institutions:

BioMaH Is Endorsed By Biomaterials Societies:

Silver Sponsors:

Sponsors:

P.le Aldo Moro, 7 00185 Roma
www.edizioni.cnr.it
bookshop@cnr.it
ISBN 978 88 8080 214 3
Ottobre 2016

BIOCOMPOSITES AND BIOCERAMICS BASED ON RESORBABLE CALCIUM PHOSPHATES WITH CA/P≤1.5

E.S. Klimashina*[a,b], D.M. Zuev[b], P.V. Evdokimov[a,b], V.I. Putlayev[a,b], Ya.Yu. Filippov[c]

[a] *Lomonosov Moscow State University, Faculty of Chemistry, GSP-1, 1-3, Leninskie Gory, Moscow, 119991, Russia, tel: +7(495)9391682, fax: +7(495)932-88-20, e-mail: lunin@direction.chem.msu.ru*

[b] *Lomonosov Moscow State University, Faculty of Materials Science, GSP-1, 1-73, Leninskie Gory, Laboratory Building B, Moscow, 119991, Russia, tel: +7(495)9328877, +7(495)9328533, fax: +7(495)9390998, e-mail: teach@hsms.msu.ru*

[c] *Lomonosov Moscow State University, Research Institute of Mechanics, 1, Michurinsky Pr., Moscow, 119192 Russia, tel: +7(495)9393121, fax: +7(495)9390165, e-mail: common@imec.msu.ru*

**e-mail: klimashina@inorg.chem.msu.ru, alenakovaleva@gmail.com*

Keywords: biocomposites, 3D printing, calcium phosphates, resorbability, osteoconductivity

INTRODUCTION

Modern regenerative medicine has a great need in resorbable bioactive composite materials for bone implants. Biodegradable polymers (polycaprolactone (PCL), polylactide (PLA)) filled with resorbable calcium phosphate (with the ratio Ca/P ≤ 1.5, e.g., amorphous mixed-anionic and tricalcium phosphates) can serve as such implants. Imperative feature of the materials is specific macroporous architecture (osteoconductivity) created by 3D-printing. In the case of thermal extrusion technique of 3D-printing (or, fused deposition modeling – FDM™), it is necessary to fabricate composite cords polymer/calcium phosphate filler with uniform distribution of phosphate particles inside thermoplastic prior to printing and to elaborate printing regimes [1]. Another thrust of problems is structured around hydrophobicity of the vast majority of the polymers and, therefore, the need in modification of their surface. The aim of this work is to create bioactive macroporous composites based on calcium phosphate and biopolymers, as well as ceramic implants of predetermined complex shape, based on the mixed anionic calcium phosphates. The tasks of the work included

(i) synthesis and physico-chemical studies of amorphous ($Ca_9(PO_4)_6xH_2O$, ACP) and amorphous mixed anionic ($Ca_{3-x}(P_2O_7)_x(P_6O_{18})_{1-x}$, x = 0.2, 0.4, 0.6, 0.8, maACP) calcium phosphates, (ii) fabrication multiphase dense bioceramics based on maACP, (iii) 3D-printing of macroporous biocomposites (β-TCP/poly(ε-caprolactone), β-TCP/poly(D,L-lactide) for bone implantation, and (iv) modification of the composite surface.

RESULTS AND DISCUSSION

ACP and maACP were obtained by precipitation from solutions by the following reactions at 10°C, pH > 10:

1. $9Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 6NH_4NO_3 \rightarrow Ca_9(PO_4)_6 \cdot yH_2O\downarrow + 18NH_4NO_3 + 3H_2O$
2. $9CaCl_2 + 6Na_2HPO_4 + 6NaOH \rightarrow Ca_9(PO_4)_6 \cdot yH_2O\downarrow + 18NaCl + 3H_2O$
3. $(3\text{-}x)CaCl_2 + (1\text{-}x)Na_6P_6O_{18} + xNa_4P_2O_7 \rightarrow Ca_{1-x}(P_2O_7)_x(P_6O_{18})_{1-x}\downarrow + 2(3\text{-}x) NaCl$

It was found that ACP particle agglomerates obtained by precipitation from the "chloride" solution method, have a smaller average size (6.4 times) compared to the "nitrate" synthesis method. By thermal treatment (with T = 500°C, 700°C and 900°C in during 10 hours) of pressed pellets maACP multiphase dense bioceramics were obtained. Composite cords were molded with a different ratio of β-TCP to biopolymers. Using Fused Deposition Modeling (FDM) technology of 3D-printing, 3D periodic structures with mesh size 16.5×16.5×4.5 mm; 30×30×3.5 mm, 10×10×2 mm, and more complex shape implants were fabricated. It was demonstrated hydrophilicity changing of the composite surface modifed by plasma treatment (500V, 5mA, AC, 5-15 minutes) and soaking in 5•SBF-solution as well as by combination of methods above.

CONCLUSIONS

Thus, we obtained macroporous bioactive composites based on calcium phosphate and biopolymers as well as ceramic implants based on mixed-anionic calcium phosphates with predetermined complex architecture. It was shown that osteoconductive composite implants made of degradable polymer and bioresorbable calcium phosphate can be fabricated by FDM™ 3D-printing technique.

This work was supported by RFBR, project 15-08-99597, 15-38-70047, 15-03-09387, and with the financial support of the RF President Grant, MK-8668.2016.8., and also with the financial support of the MSU, project NMWUP N°013-09/16.

REFERENCES:

1 Ievlev V M, Putlyaev V I, Safronova T V, Evdokimov P V; Additive Technologies for Making Highly Permeable Inorganic Materials with Tailored Morphological Architectonics for Medicine; Inorganic Materials; 51 13 (2015) 1297.

1ST BIENNIAL CONFERENCE

October 17th-20th
Rome – Italy

ISBN 978 88 8080 214 3