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DLP printing of viscoelastic hydrogel/calcium phosphate composites for bone tissue replacement

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Mr. Ilya Preobrazhensky [1], ***Mr. Andrey Tikhonov*** [1], ***Dr. Pavel Evdokimov*** [2], ***Prof. Valery Putlayev*** [2]

1. *Department of Materials Science, Lomonosov Moscow State University, Moscow, 119991, Russia,* ***2.*** *Department of Chemistry, Lomonosov Moscow State University, Department of Materials Science, Lomonosov Moscow State University*

3D-printing, and more specific, stereolithography, is a promising technique to fabricate materials for the restoration and regeneration of different tissues. Photopolymerization of different materials underlying the technique and combining biodegradable, osteoconductive, osteoinductive and required mechanical properties, allowing easily managing architecture and macroporosity of the material, is very attractive for regenerative medicine purposes. All of the parameters are extremely significant in the case of bone healing implants. This work was aimed at obtaining of viscoelastic hydrogel/calcium phosphate composites with complex architecture («gyroid»-type) through DLP 3D-printing assuming personalized bone tissue regeneration.

Hydrogels based on polyethylene glycol derivatives (PEG-diacrylate or PEGDA (M=575 Da), PEG-methacrylate or PEGMA (M=350 Da)), were chosen as one of the most commonly used and biocompatible synthetic polymers for biomedical applications, with adjustable viscoelastic mechanical and swelling properties, and applicable for DLP printing. Reinforcement and functionalization of hydrogel matrices were carried out by filling with calcium phosphates with various micromorphology and resorbability, *viz*. brushite ($CaHPO_4 \cdot 2H_2O$), octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, OCP), or ceramic particles of tricalcium phosphate ($Ca_3(PO_4)_2$, TCP). Such biocomposites were obtained through light exposure with UV-lamp or with 3D-printer Ember (Autodesk, USA) of the slurries containing biocompatible photoinitiator Irgacure® 819 (BASF, Germany).

Based on the results of the work, the optimal ratio of the monomers and the filling fraction of calcium phosphates in hydrogels were found. It was shown that the increase of methacrylate content allows obtaining composites with a higher swelling ability (up to *ca.* 4 times in terms of mass gain) and faster biodegradation behavior. Reinforcement of the hydrogels with the calcium phosphate particles led to greater stiffness as well as to the growth of the phase shift between shear loss and storage modules.

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