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Shape memory effect in 3D-printed scaffolds for self-fitting implants

F.S. Senatov[a,*], M.Yu. Zadorozhnyy[a], K.V. Niaza[a], V.V. Medvedev[a], S.D. Kaloshkin[a], N.Yu Anisimova[a,b], M.V. Kiselevskiy[a,b], Kai-Chiang Yang[c]

[a] National University of Science and Technology "MISIS", 119049, Leninskiy pr. 4, Moscow, Russian Federation
[b] N.N. Blokhin Russian Cancer Research Center, 115478, Kashirskoye sh. 23, Moscow, Russian Federation
[c] School of Dental Technology, College of Oral Medicine, Taipei Medical University, No. 250, Wu-Hsing Street, Taipei City 11031, Taiwan

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ABSTRACT

3D-printed porous scaffolds based on polylactide (PLA)/15% wt. nano-hydroxyapatite (HA) with shape memory effect (SME) for self-fitting implants were studied. Introduction of HA nanoparticles into the PLA matrix had an effect on the ordering of polymer molecular chains. The presence of HA nanoparticles caused a change in friction between molecular chains during the glass transition. Apparent activation energies of SME for PLA and PLA/HA 3D-printed samples were 490 and 555 kJ/mol, respectively. HA nanoparticles acted as centers for the formation of additional rigid fixed phase that governed shape memory properties. The maximum recovery stress was observed in case of shape programming in the glass transition interval at 64 °C. However, cyclic SME tests showed that the increase in number of cycles "programming – SME activation" led to decrease in shape recovery rate and recovery stresses due to accumulation of defects. It was demonstrated that 3D-printed porous PLA/HA scaffolds support mesenchymal stromal cells (MSCs) survival, and stimulate active proliferation of the cells as well. Such scaffolds with SME colonized by MSCs have the potential to be used as self-fitting implants for bone replacement and could also be beneficial in the engineering of complex tissues. MSCs colonization of scaffold favors vascularization of the implant, which is essential for the successful bone prosthesis.

1. Introduction

People with traumas or bone diseases are in need for reconstruction of bone defects. The most common and conventional methods to repair complex bone defects involve allografts with different fixators [1] or metal implants [2]. Nowadays polymer-based scaffolds for the regeneration of the damaged or missing bone are gaining popularity due to high biocompatibility, absence of stress shielding effect [3] after implantation and biodegradation ability. Polymers with a shape memory effect (SME) may be used in self-fitting implants to fill the space of the 3D defect with reliable fixation and integration to the surrounding bone [4–7]. Shape memory polymers (SMP) have a potential advantage over the metallic shape memory alloys (SMA) due to much higher recoverable strains [8]. Usability of SMPs in space filling scaffolds has been demonstrated for different polymers like polylactide (PLA), polycaprolactone (PCL), polyurethane (PU) and copolymers [9–11].

Initial shape of SMP may be transformed (deformed) into the temporary shape at the temperatures below the temperature of SME

* Corresponding author.
E-mail address: Senatov@misis.ru (F.S. Senatov).

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initiation. Temporary shape corresponds to a temporary spatial configuration having higher order and higher internal energy than initial shape. The recovering force in SMPs is the result of changing both - internal energy and entropy. The recovery of initial shape becomes noticeable at temperatures above the temperature of SME initiation (melting or glass transition temperature) which corresponds to the temperature sufficiently high to release the motion of the polymer chain segments. SMPs suppose concurrence of a fixed phase like solid fillers, crosslinks or entanglements and amorphous phase [14,15].

PLA is a well-known medical thermoplastic SMP. Entanglements of polymer chains can be regarded as zones of fixed phase whereas the temporary stretched chains constitute the soft deformable phase. Such property of SMPs like stress of recovering can be enhanced by incorporation of dispersed inorganic particles [16,17], which play the role of extra amount of fixed phase. For this it is especially interesting to use bio-resorbable hydroxyapatite (HA) nanoparticles for bone reconstruction purposes [18,19].

3D-printing by fused deposition modeling (FDM) is a perspective technology for porous polymer scaffolds formation with premodeled shape and size. SMP porous scaffolds could be (1) 3D-printed with larger dimensions than the bone defect, (2) compressed to the temporary shape at the programming temperature around the transition temperature, (3) installed into the defect, and then (4) heated to recover the permanent shape. Such grafts were used in different biomedical applications by Gogolewski and Gorna [12] and Yakacki et al. [13].

3D-printed PLA/HA porous scaffolds (700 µm pores, 30% vol. porosity) with a larger crack-resistance and the potential to be used as self-fitting implants for trabecular bone defects replacement were developed in our previous studies [16,17]. Such 3D scaffolds should also be a platform for cells that can be precursors for the newly formed bone. Therefore, 3D-printed porous PLA/HA scaffolds can be colonized by recipient's cells *in vitro* before implantation. It is known that mesenchymal stromal cells (MSCs) derived from bone marrow are perspective cells to use for colonization of porous scaffold [20].

In this paper the effect of programming temperature on stresses formed during deformation of scaffold by compression to a temporary shape and activation of SME was studied in static and cyclic tests, and the apparent activation energy of SME was determined. Also structural characteristics and MSCs adhesion on the 3D-printed porous PLA/HA scaffolds were investigated.

2. Materials and methods

2.1. Samples preparation

Polylactide (PLA) (molecular weight of 110 kg/mol, Ingeo 4032D, Natureworks LLC) was used as a SMP matrix. Hydroxyapatite (HA) nanopowder (90 ± 10 nm, JSC "Polystom", Russia) was added to increase amount of fixed phase and increase bioactivity of scaffolds.

Filaments of PLA/HA nanocomposites (∅1.6 ± 0.2 mm) for 3D-printing were prepared in the following regime discussed in previous study [16]: (1) drying of initial PLA pellets and HA nanopowder (T = 80 °C, t = 4 h), (2) mixing of PLA and 15 wt.% HA nanopowder in a screw extruder HAAKE MiniLab II Micro Compounder (T = 180 °C, t = 15 min, ν = 30 rev/min).

"SolidWorks 2015" software (SolidWorks Corp., USA) was used to make a 3D-model of a scaffold, as shown in Fig. 1A. Correction of STL files before 3D-printing was performed by Netfabb Basic 5.2 software.

3D-printing of porous scaffolds was performed using Picaso Designer Pro-250 (Picaso 3D, Russia) with Polygon 2.0 software by FDM-method at a nozzle temperature of 180 °C and 220 °C for PLA and PLA/HA scaffolds, respectively. PLA scaffolds without HA nanoparticles were printed to compare structural, mechanical, and shape memory properties of the scaffolds. A nozzle with a diameter of 350 µm was used. The thickness of a single layer was 150 µm. The printing rate was 30 mm/s. The porous samples were treated for 30 min in an ultrasonic bath to remove residual surface particles and ledges after 3D-printing. The pore size was 700 µm. All the pores were interconnected. Porosity of the scaffolds was at a level of 30 vol.%. Generally, a range of pore sizes 50–800 µm is required for tissue cells penetration into the structure of implant [21,22].

Specimens of 3D scaffolds with rectangular samples for shape-memory studies (Fig. 1B) and dynamic mechanical analysis (DMA) tests were prepared by 3D-printing.

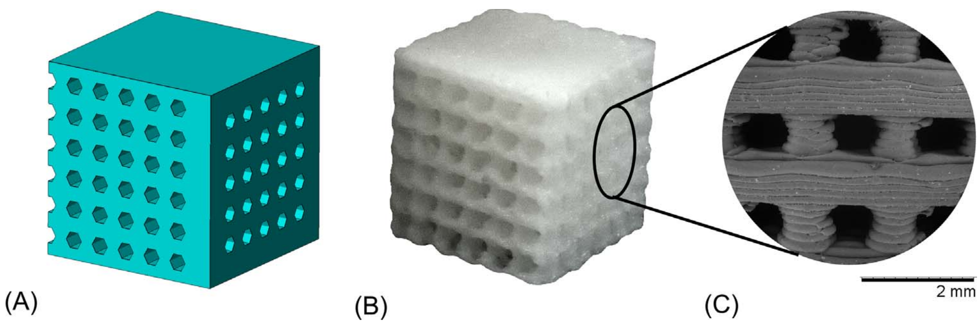

Fig. 1. 3D model of a scaffold (A), 3D-printed PLA/HA scaffold (B) and SEM image of its structure (C).