Journal of Physics: Conference Series

PAPER • OPEN ACCESS

3D-printed scaffolds based on PLA/HA nanocomposites for trabecular bone reconstruction

To cite this article: K V Niaza *et al* 2016 *J. Phys.: Conf. Ser.* **741** 012068

3D-printed scaffolds based on PLA/HA nanocomposites for trabecular bone reconstruction

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Abstract. In the present work porous PLA scaffolds filled with micro- and nano- HA were studied. Both composites with micro- and nano-HA were obtained by extrusion in the same conditions. Scaffolds were obtained by 3D-printing by fused filament fabrication method. Structure of porous scaffolds was pre-modeled by computer software. Compression and three - point flexural tests were used to study mechanical properties of the scaffolds.

1. Introduction

Reconstruction of the structural integrity of the damaged bone tissue is an urgent problem for people with traumas or bone diseases. Polylactide (PLA) is a bioresorbable polymer which is widely used for medical applications, especially bone implants [1]. Some works [2, 3] revealed the need to reinforce PLA matrix to reach mechanical properties of human bone tissue. Bioactive ceramics like hydroxyapatite (HA) may be used to increase mechanical properties and osseointegration [4]. In case of increasing mechanical properties in compression it is more preferable to use nanoparticles as it was observed by *Senatov et al* [5]. Nanocomposite system with nano-HA in the form of nanorods is able to mimic a natural morphology of bone apatite. Due to the fact that HA is identical to the bone tissue and is actually a source of minerals for bone cells, it leads to the regeneration approach. In case of nano-HA such a bioactivity increases. Composite materials with the addition of ceramic nanoparticles showed a significant increase in polymer degradation rate compared with the unfilled polymer [6]. This indicates the improvement in osseoconductive properties of nanocomposites. Rapid prototyping structures shows mechanical properties significantly higher than those structures fabricated by other well – known techniques such as solvent – casting and particle leaching, thermal-induced phase separation and gas foaming, among others [4-8]. In this work 3D-printing as an actively developing method for formation of polymer implants was used to produce highly-porous scaffold [1].

2. Materials and methods

Pellets of polylactide (PLA) (Mw = 60 000 g/mol, Aldrich) were used as a material for bioresorbable matrix. Hydroxyapatite (HA) powders with the average particle size of 90 nm and 1 micron produced by JSC "Polystom" (Russia) were used as the bioactive fillers.

Mixing of PLA and 15% weight HA powder was carried out in a screw extruder HAAKE MiniLab II Micro Compounder (Thermo Fisher Scientific, USA) for 15 min at 30 rev / min and temperature of 185 °C. Structure of 3D scaffold (Figure 1,2) was modeled using SolidWorks 2015 software (SolidWorks Corporation,USA). 3D-printing of porous scaffolds was performed using Picaso Designer Pro-250 (Picaso 3D, Russia) by fused filament fabrication (FFF) at nozzle temperature of 220 °C.

Studies of PLA/HA nanocomposites and scaffolds were conducted by scanning electron microscopy (SEM). SEM was performed with Hitachi TM-1000 (accelerating voltage 5kV). To

Journal of Physics: Conference Series **741** (2016) 012068 doi:10.1088/1742-6596/741/1/012068

investigate non-conductive polymer samples, the surface of the samples was covered with a layer of platinum (10 – 20 nm) by Auto Fine Coater JFC-1600 (Jeol, USA). Structural characterization of HA nanoparticles was performed by transmission electron microscopy (TEM). TEM was performed with JEM 1400 (accelerating voltage 120kV). Mechanical testing was studied in compression and three-point flexural test. Mechanical testing was performed in a universal testing machine Zwick/Roell Z 020, (Zwick GmbH & Co.KG, Germany) using rectangular samples of scaffolds with the cross-sectional dimensions of 24 x 12.5 mm for compression tests (ASTM D695) and 80 x 10 x 4 mm for three point flexural test (ASTM D790).

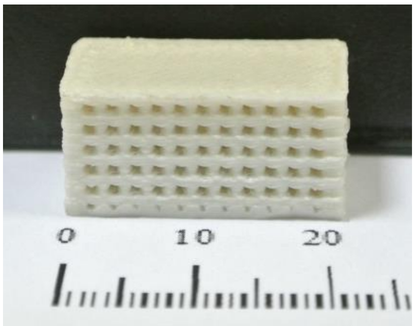

Figure 1. 3D-printed scaffold based on bioactive nanocomposite PLA/HA

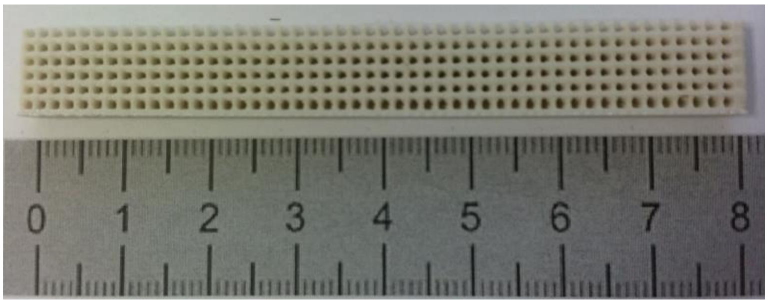

Figure 2. 3D-printed scaffold for three-point flexural test

3. Results and Discussion

Figure 3 shows TEM image of HA nanoparticles. The particles have an elongated non-equiaxed shape. The average length is 90 nm, the average diameter – 20 nm. Nanoparticles have a porous structure, which is shown in Figure 3a. The pore size is less than 5 nm. All pores are mainly open and belong to meso- and micropores. This indicates an increased specific surface of nanoparticles.

It was shown, that nanocomposites had higher mechanical properties such as Young's modulus, ultimate strength than composites with micro-HA in compression test, as shown on Figure 4. The mean value of Young's modulus was 4.0±0.2 GPa and 2.8 ±0.2 GPa for PLA/nano-HA and PLA/micro-HA, respectively. Young's modulus of biocomposite with nano-HA is closer to the Young's modulus of human bone tissue, than modulus of composite with micro HA. It is known, that modulus of trabecular bone is in the range from 3 to 5 GPa [12]. Incorporation of HA nanoparticles into PLA matrix led to higher mechanical properties, than in case of micro-HA. Therefore, PLA/nano-HA scaffolds demonstrated mechanical properties of a trabecular bone tissue preserving highly porous structure.

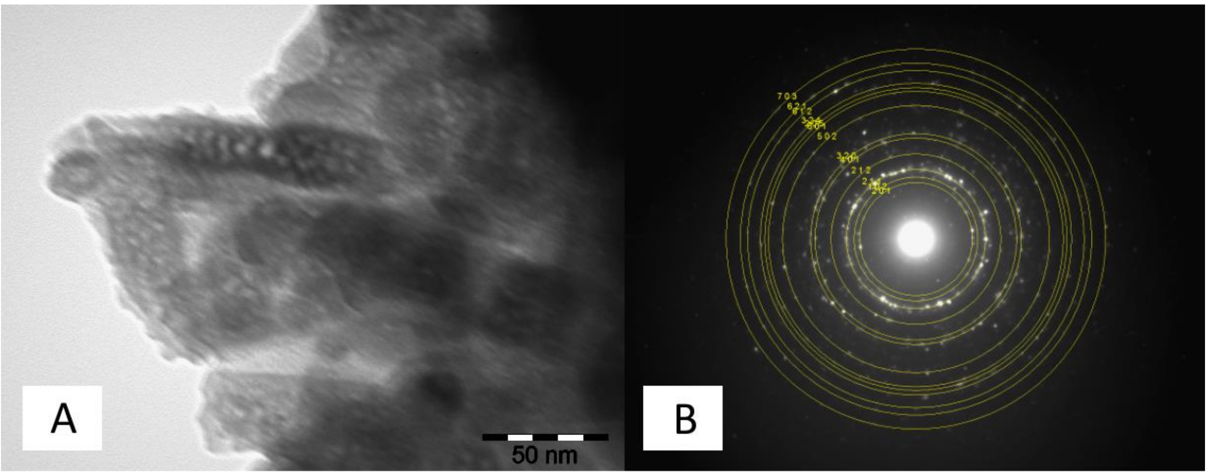

Figure 3. TEM image (A) and electron diffraction pattern (B) of HA nanoparticles

Three-point flexural test confirmed previous results. Flexural modulus is 1.93±0.11 and 1.57±0.11 GPa for PLA/nano-HA and PLA/microHA, respectively (Figure 5). This is the result of greater surface interaction between nanoparticles and polymer matrix. Porous scaffold is a construction, that can withstands not only compressive loadings, but also flexural up to 30 MPa, which are inherent in the trabecular bone.

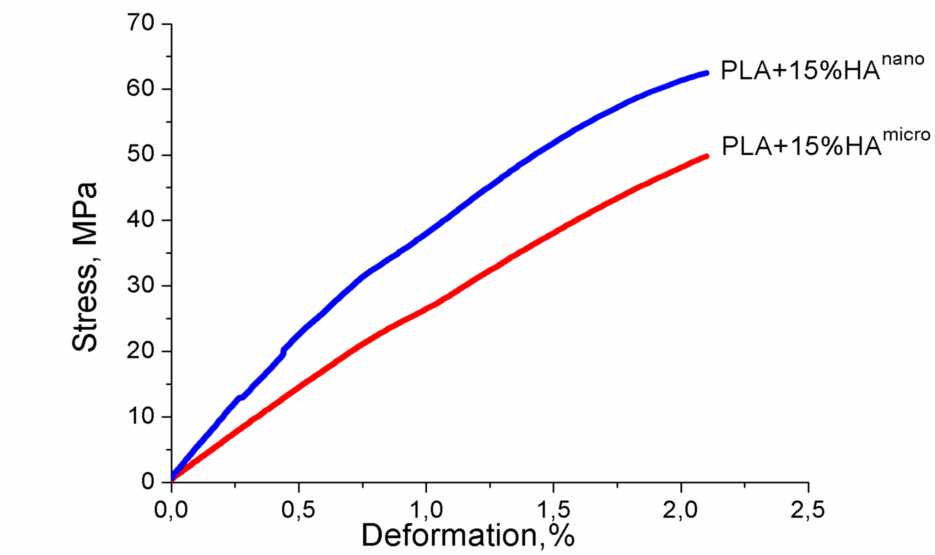

Figure 4. Typical stress-deformation curves of compression test for PLA-based composites

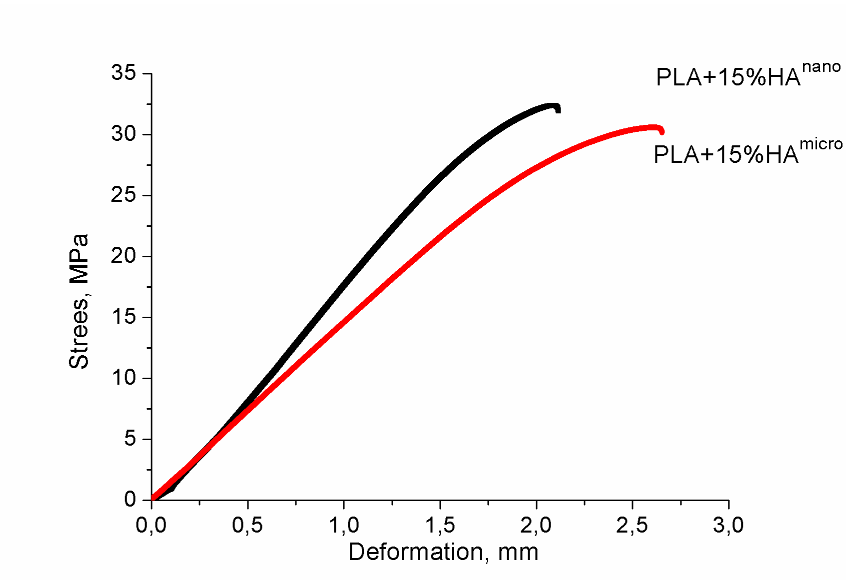

Figure 5.Typical three-point flexural curves for PLA-based composites

Figure 6 shows SEM image of fracture surface after three-point flexural test for scaffold with micro- and nano-HA. The brittle fracture in all cases was observed. The main difference in the microstructure lies in the character of the particle distribution. Nanoparticles did not form agglomerates more than 10 μm in diameter and showed better distribution in the polymer matrix in contradistinction to micro-HA particles, which formed agglomerates more than 100 μm. The presence of the plastic flow regions (Figure 5b) after destruction of the nanocomposites indicates better adhesion of nano-HA to the polymer matrix.

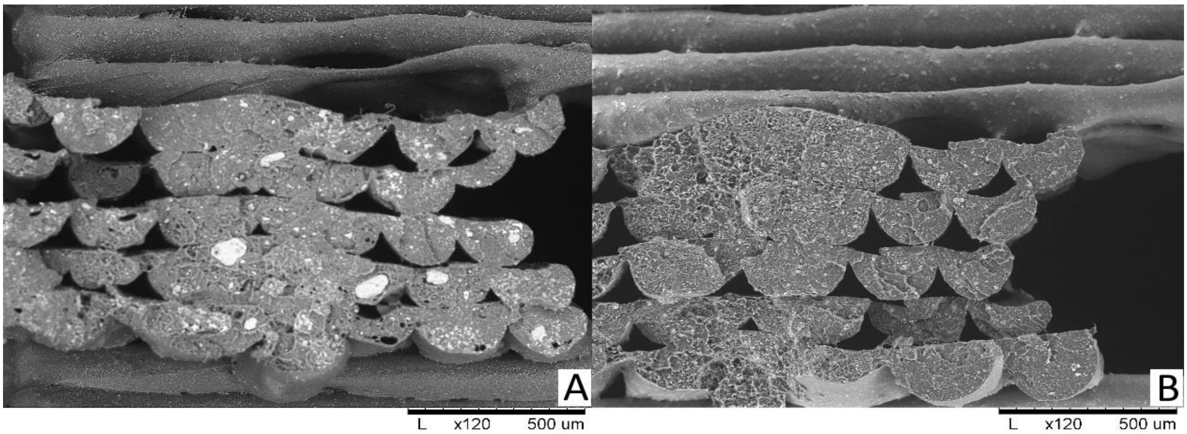

Figure 6 –SEM imager of fracture surface of PLA-based scaffold after three-point flexural test
A - PLA / micro-HA
B - PLA / nano-HA

Incorporation of the nano-HA into the polymer matrix instead of micro-HA led to a hardening of the material and more regular microarchitecture because of greater interfacial surface by formation of ultrafine structure.

Theoretical porosity of scaffolds is 30 vol. %, however, real porosity is higher, because of pore formation during 3D-printing. This is the result of special character of sintering between the layers. This character is single-point and the size of such pores is about 100 μm.

The strength of construction is also achieved by solid sintering of perpendicular layers.

Conclusions

PLA-based porous scaffolds with porosity of 30 vol. % for bone implants were prepared by 3D-printing based on fused filament fabrication. Hydroxyapatite nanorods with the average length of 90 nm and the average diameter of 20 nm increased mechanical properties of the scaffolds due to the higher Young's modulus similar to the trabecular human bone tissue. The architecture of porous scaffolds mimics structure of trabecular bone. Mechanical properties of scaffolds are in range of mechanical properties of bone tissue. 3D-printed scaffolds based on PLA/HA nanocomposites may be perspective constructions for trabecular bone reconstruction.

Acknowledgments

This work was supported by the Federal Targeted Program "Research and development in priority directions of development of scientific technological complex of Russia in 2014–2020", with the funding from the Ministry of Education and Science of Russian Federation: agreement 14.575.21.0088, 21 October 2014, RFMEFI57514X0088

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