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ORIGINAL ARTICLE

Functional graded scaffold of HDPE/HA prepared by selective laser sintering: microstructure and mechanical properties

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Abstract This paper presents a study on the effect of hydroxyapatite (HA) content on the microstructure and mechanical properties of high-density polyethylene (HDPE)/HA composites and the fabrication of functional graded scaffold of HDPE/HA by selective laser sintering (SLS). The microstructure of the sintered composite scaffolds had interconnected pores with diameters of 30–180 μm and porosity of 45–48 %. The HDPE/HA composite scaffolds had a flexural modulus of 36–161 MPa and ultimate strength of 4.5–33 MPa. The maximum loss modulus peak tended toward lower temperature values for HDPE/HA composites with 10 and 20 % of HA content, indicating that the α_χ relaxation was slightly affected by higher quantities of HA. The HA particles reinforced the matrix and minimized the plastic and definitive deformation under the test conditions. HDPE/HA functional graded scaffold fabricated using SLS with controlled microstructure and properties showed considerable potential for biomedical applications, being suitable for bone and cartilage tissue engineering.

Keywords HDPE/HA scaffold · Selective laser sintering · Microstructure and properties

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1 Introduction

The reconstruction of complex joints represents a challenge in bone tissue engineering. The scaffolds employed must fit into the anatomic defect, possess mechanical properties that will bear in vivo loads, enhance tissue in-growth, and not produce toxic degradation byproducts [1–4]. The success of tissue engineering will rely on the ability to generate complex 3D structures. Therefore, methods that can be used to precisely engineer the architecture and topography of scaffolding materials will represent a critical aspect of functional tissue engineering [5]. Due to the lack of control on architecture and porosity, produce complex scaffolds structures can involve both bottom-up and top-down overall micro and nanomanufacturing approaches [6].

Selective laser sintering (SLS) is a solid free-form fabrication method that may be used for creating bone tissue scaffolds to match the complex anatomical geometry [7–10]. SLS enables the design and fabrication of controlled microstructure and properties, thereby allowing control over pore size, porosity, permeability, mechanical properties, and material composition [11, 12]. Control over these characteristics may enhance cell infiltration and mass transport of nutrients and metabolites throughout the scaffold.

The use of nonbiological materials can cause adverse reactions. High-density polyethylene (HDPE) is a biologically inert polymer with known clinical performance related to mechanical behavior [13–15]. The fabrication and characterization of HDPE scaffolds with varying internal pore architectures and porosities produced through SLS has been reported [12]. Hydroxyapatite (HA) is a typical bio-active material and it occupies 75 wt% of human bone regardless of the water content [16]. It has excellent biocompatibility and nontoxicity and is capability of promoting bone growth and of conjoining with human bone [17–20]. Animal tests

[21, 22] showed that there was no inflammation around implanted HA, and that the HA was surrounded by bone tissues and formed an osseous combination with bone tissues. These results indicate that HA plays the roles of support and filler in bone and can become a part of the bone skeleton. Thus, if HA is used as the filler for HDPE, the bioactivity of HDPE might be improved to promote bone growth. The presence of HDPE might overcome the brittleness problem of HA and the fact that dense HA is not easily absorbed. Selective laser sintering has been investigated for the production of bioactive implants and tissue scaffolds using composites of HDPE reinforced within 30 and 40 % HA presenting pores within the optimal sizes for tissue regeneration [23]. This study investigates the effect of HA content on the microstructure and mechanical properties of HDPE/HA functional graded scaffold fabricated by SLS.

2 Experimental part

2.1 Materials

The powder polymer used in this study was HDPE, HD7555 Ipiranga, with a melting temperature of 127.7 °C (according to differential scanning calorimetry). The particle size range used was 150–212 μm. HA with a particle size of 5–10 μm was supplied by Sigma-Aldrich.

2.2 Design and fabrication of porous scaffold and composites specimens

The HDPE scaffold specimen (35×5×1.4 mm size) was designed in CAD software and then exported to the SLS machine. The periodic porous architectures were designed through the selection of powder particle size and processing parameters as previous described [12]. Composites of HDPE and HA were mixed by mechanical powder mixing using a Y cylindrical blender for 70 min at 90 rpm. SLS processing of the materials was conducted by preheating the powder to 95 °C. Specimens were built by SLS using the previously determined processing parameters. The specimens were manufactured with a CO_2 laser at 5 W of power, 250 μm of beam focus diameter, and scan speed of 57 mm/s. The chamber temperature was 80 °C. The building layer thickness used was 200 μm and the spacing between the laser scans was 125 μm. Specimens with pure HDPE and composite material were manufactured using the optimized processing parameters. Functional graded scaffold with the composite compositions were fabricated based on the optimized processing parameters. The scaffold plate with functionally graded composition was manufactured by the automatic dispersion of different blends in a Y-direction graded layer before sintering due by the SLS powder delivery device.

2.3 Characterization

The composite specimens and the functional graded scaffold were inspected with a Phillips XL30 scanning electron microscope (SEM) in order to investigate the microstructure. The specimens were coated with gold in a Bal-Tec Sputter Coater SCD005. Dynamic mechanical analyses were performed on a TA Instruments analyzer, model Q800, with single cantilever mode. Stress–strain curves were obtained at a loading rate of 2 $Nmin^{-1}$ and 30 °C. The storage modulus (E′) and the loss factor (tan δ=E′/E″) at fixed frequency equal to 1 Hz were determined in the temperature range of 0–150 °C at a heating rate of 3 °C min^{-1}. Fatigue experiments were conducted at 30 °C and 1 Hz applying 50 % of the maximum strain amplitude determined in the stress versus strain curves for each specimen.

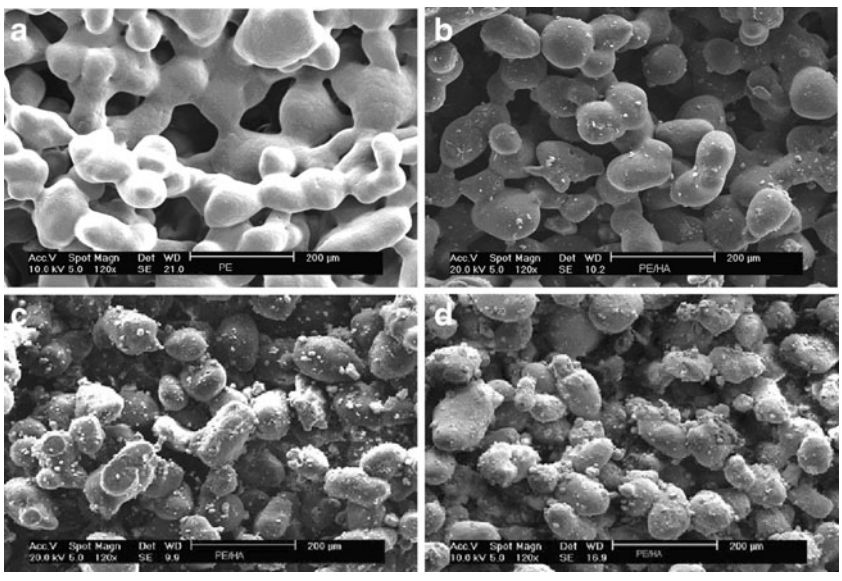

Fig. 1 Micrographs of HDPE (**a**) and HDPE/HA composites with HA content of 5 % (**b**), 10 % (**c**), and 20 % (**d**)

Table 1 Flexural mechanical properties of HDPE and HDPE/HA composite scaffolds

	Flexural modulus (MPa)	Ultimate strength (MPa)	Elongation (%)
HDPE	456±88	51±6	7.8±2
HDPE/HA 5 %	161±36	33±4	8.6±1
HDPE/HA 10 %	62±17	31±3	7.3±1
HDPE/HA 20 %	36±7	4.5±1	3.8±2

3 Results and discussion

With the processing parameters used in the SLS, the HDPE specimen showed a microstructure with a higher sintering degree than the composite specimens, with particles joined by extensive neck formations, as can be observed in the micrographs shown in Fig. 1a. The composite scaffold microstructures show the presence of different quantities of HA powder with average sizes of 10 μm, proportional to the designed composite composition, in the HDPE-sintered matrix (Fig. 1b–d). Nevertheless, the HA particles tend to agglomerate at higher concentrations.

The porosity, which refers to the percentage fraction of voids in the scaffold specimen volume and the internal pore architectures, in relation to the designed pore diameter, was analyzed by density measurements and SEM images, in order to evaluate the manufactured scaffold morphologies. The scaffolds were designed with volumetric porosity ranging from 35 to 45 %. The manufactured scaffolds had porosity values of 45–48 %, which can be considered as consistent with the scaffold design. The microstructure of sintered scaffold specimens had irregular distributions of interconnected pores with average size being related to the particle size and shape of the original HDPE powder. However, the scaffold specimens had pore diameters predominately between 30 and 180 μm, which is a wider range than expected (designed pore diameter was around 130 μm).

Table 1 shows the average values for the flexural modulus, ultimate strength and elongation for the pure HDPE and HDPE/HA composite specimens. The pure HDPE specimens had an average flexural modulus of 456 MPa and ultimate strength of 51 MPa. The flexural modulus, ultimate strength, and elongation values for the HDPE/HA composite specimens decreased as a function of the HA content, probably due to the low chemical affinity between the polymeric and the ceramic phases, which strongly affected the mechanical properties of the porous composite specimens. The presence of HA particles also affects the sintering degree of the HDPE matrix, by spacing the HDPE particles and dissipating heat. The mechanical modulus values of human bone range from 1 to 5,000 MPa, with strength values ranging from 0.10 to 27 MPa [24–29], and mean values of approximately 194 and 4 MPa, respectively [27]. The HDPE/HA scaffolds exhibited flexural modulus values ranging from 161 to 36 MPa and strength values of 33 to 4.5 MPa, depending on the scaffold composition. Both of these ranges fall within those for human bone.

In order to evaluate the dynamic mechanical properties of HDPE and HDPE/HA scaffold specimens, DMA analyses were carried out. The variation in the E′ and E″ as a function of temperature for HDPE and HDPE/HA composites measured at a frequency of 1 Hz are shown in Figs. 2 and 3. At ambient temperature (20 °C), E′ decreased with increasing HA content, which is coincident with the quasistatic mechanical testing (Table 1).

The loss modulus of HDPE decreased after the addition of HA, suggesting that there is no significant interaction

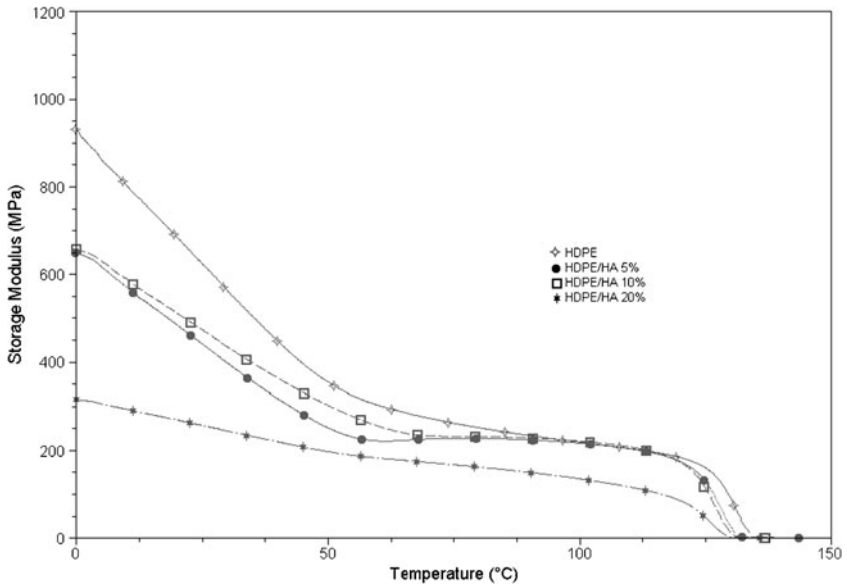

Fig. 2 Storage (E′) modulus as function of temperature for HDPE and HDPE/HA composites

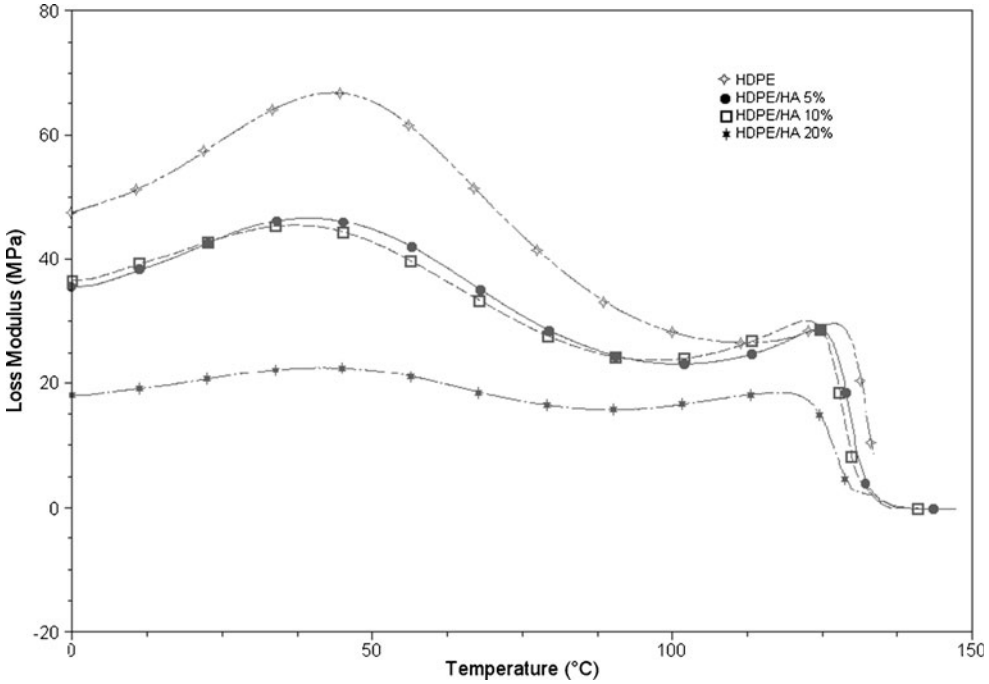

Fig. 3 Loss (E′) modulus as function of temperature for HDPE and HDPE/HA composites

between the two components. The maximum loss modulus was obtained at between 45 and 50 °C. The maximum loss modulus peak showed a trend toward lower temperature values for the HDPE/HA composites with 10 and 20 % of HA content (Fig. 3), indicating that the α_c relaxation process in HDPE was slightly affected in these cases, i.e., the addition of greater quantities of HA can modify the mobility of the polymer chains in interlamellae regions of the semicrystalline HDPE matrix. Previous X-ray diffraction studies have provided evidence that thermoplastic composite matrices, when processed by SLS, tend to undergo rapid heat exchange and there is the formation of kinetic phases like amorphous and gamma phases [11].

For the HDPE and HDPE/HA composite scaffolds, the fatigue curves obtained at 50 % of the maximum strain amplitude (Fig. 4) showed stress variation as a function of the number of cycles. The fatigue curve for HDPE showed a large stress variation (2.8 MPa) for up to 760 cycles. With the mechanical loading of the HDPE matrix plastic deformation (irreversible deformation) occurs, leading to fatigue by creep. However, the HDPE/HA 5 and 10 % samples showed greater fatigue strength than undiluted HDPE due to the presence of HA in the scaffold specimen. The HA particles reinforce the matrix and minimize the plastic and definitive deformation under the test conditions. The HDPE/HA with 20 % of hydroxyapatite showed the same tendency in the fatigue behavior as the other HDPE/HA composites, i.e. an increase in the fatigue strength with HA content. The variation in the strength of the HDPE/HA 20 % composites was practically null for up to 800 cycles, consistent with the influence of HA observed in the composite fatigue strength under the test conditions.

Figure 5 shows the scaffold plate with composition gradient (5–20 % of HA in HDPE), which was obtained by laser sintering using the processing parameters previously defined. The HDPE/HA scaffold with composition gradients showed an increase in pore size and a decrease in strength as the HA content increased, as observed for individual specimens. The use of SLS to prepare parts and components with

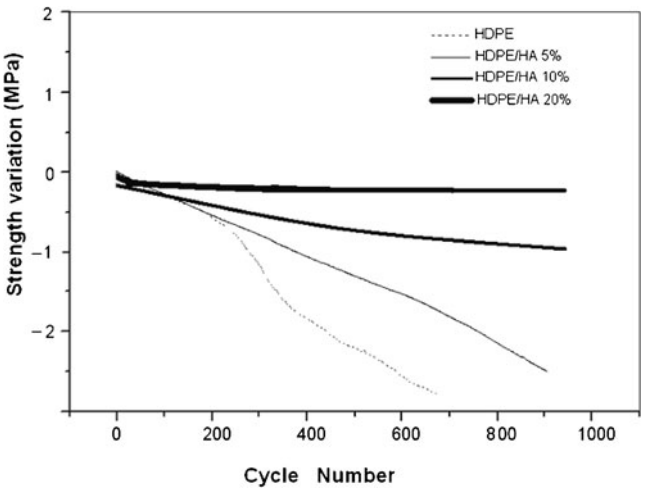

Fig. 4 Fatigue strength as a function of cycle numbers for HDPE and HDPE/HA composites

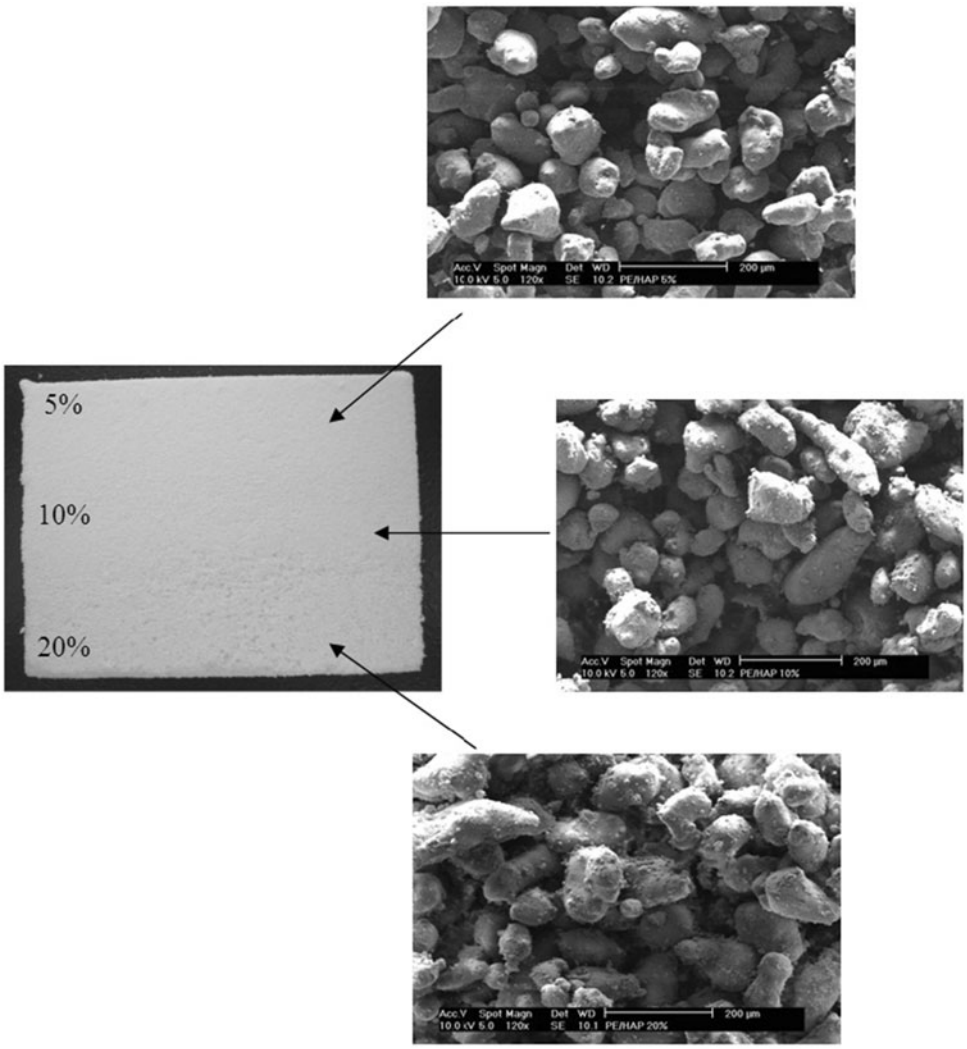

Fig. 5 Functional graded scaffold of HDPE/HA manufactured by selective laser sintering

gradients of structures and properties can improve the development of new applications in areas, such as cartilage and bone tissue.

4 Conclusions

The HDPE/HA composites showed a microstructure with a high sintering degree and particles united by neck formations. The presence of HA particles affects the sintering degree of the HDPE matrix, by spacing the HDPE particles and dissipating heat. The microstructure of the sintered composites had irregular distributions of interconnected pores with diameters of 30–180 μm. The manufactured composite scaffolds had porosity values of 45–48 %, which can be considered as consistent with the designed scaffolds. The HDPE/HA composite scaffolds had flexural modulus values from 36 to 161 MPa and ultimate strength from 4.5 to 33 MPa, which are compatible with bone tissue properties.

The storage modulus of the composite scaffolds decreased with increasing HA content, which is in agreement with the quasistatic mechanical testing. The maximum loss modulus peak showed a trend toward lower temperature values for HDPE/HA composites with 10 and 20 % of HA content, indicating that the α_c relaxation was slightly affected by higher quantities of HA due to the modification of the interlamellae regions caused by rapid heat exchange. The addition of HA to the HDPE matrix resulted in a reduction in the cyclic fatigue compared to the pure HDPE. The HA particles reinforced the matrix and minimized the plastic and definitive deformation under the test conditions. HDPE/HA functional graded scaffold fabricated using SLS with controlled microstructure and properties showed considerable potential for biomedical applications, such as in bone and cartilage tissue engineering.

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References

1. Mercuri LG (1998) Alloplastic temporomandibular joint reconstruction. Oral Surg Oral Med Oral Pathol Oral Radiol Endod 85 (6):631–7
2. Langer R, Tirrell DA (2004) Designing materials for biology and medicine. Nature 428(6982):487–92
3. Agrawal CM, Ray RB (2001) J Biomed Mater Res 55(2):141–50
4. Das S, Hollister SJ (2003) Tissue engineering scaffolds. In: Buschow KHJ, Cahn RW, Flemings MC, Ilschner B, Kramer EJ, Mahajan S (eds) Encyclopedia of materials: science and technology. Elsevier, Amsterdam
5. Gauvina R, Chena Y, Leed JW, Somand P, Zorlutunaa P, Nichola JW, Baea H, Chend S, Demhosseinia AK (2012) Biomaterials 33 (15):3824–3834
6. Chryssolouris G, Stavropoulos P, Tsoukantas G, Salonitis K, Stournaras A (2004) Int J Mater Prod Technol 21(4):331–348
7. Taboas JM, Maddox RD, Krebsbach PH, Hollister SJ (2003) Biomaterials 24(1):181–94
8. Landers R, Pfister A, Hubner U, John H, Schmelzeisen R, Mulhaupt R (2002) J Mater Sci 37(15):3107–16
9. Das S, Hollister SJ, Flanagan C, Adewunmi A, Bark K, Chen C, Ramaswamy K, Rose D, Widjaja E (2003) Rapid Prototyp J 9 (1):43–9
10. Sachlos E, Czernuska JT (2003) Eur Cells Mater 5:29–40
11. Salmoria GV, Leite JL, Ahrens CH, Lago A, Pires ATN (2007) Pol Testing 26:361–368
12. Salmoria GV, Ahrens CH, Klauss P, Paggi RA, Oliveira RG, Lago A (2007) Rapid manufacturing of PE with controlled pore gradients using SLS. Mat Research 10:214–221
13. Moro T, Kawaguchi H, Ishihara K, Kyomoto M, Karita T, Ito H, Nakamura K, Takatori Y (2009) Biomaterials 30(16):2995–3001
14. Saikko V (1994) Wear 176(2):207–212
15. Edidin AA, Kurtz SM (2000) J Arthroplast 15(3):321–331
16. Chu CL, Wang SD (1999) J Mater 13:51–54
17. Akita S, Tamai N, Myoui A, Nishikawa M, Kaito T, Takaoka K, Yoshikawa H (2004) Tissue Eng 10:789–795
18. Morita S, Furuya K, Ishihara K (1998) Biomaterials 19:1601–1606
19. Furukawa T, Matsusue Y, Yasunaga T, Okada Y, Shikinami Y, Okuno M, Nakamura T (2000) J Biomed Mater Res 50:410–419
20. Wang M, Joseph R, Bonfield W (1998) Biomaterials 19:2357–2366
21. Huang M, Feng JQ, Wang JX (2003) J Mater Sci- Mater M 14:655–660
22. Ural E, Kesenci K, Fambri L (2000) Biomaterials 21:2147–2154
23. Hao L, Savalani MM, Zhang Y, Tanner KE, Harris RA (2006) J Eng Med 220:521–531
24. Porter BD, Oldham JB, He SL, Zobitz ME, Payne RG, An KN, Currier BL, Mikos AG MJY (2000) JBiomech Eng 122(3):286–8
25. Lang SM, Moyle DD, Berg EW, Detorie N, Gilpin AT, Pappas NJ Jr, Reynolds JC, Tkacik M, Waldron RL (1988) J Bone Jt Surg Am 70(10):1531–8
26. Lotz JC, Gerhart TN, Hayes WC (1990) J Comput Assist Tomogr 14(1):107–14
27. Goulet RW, Goldstein SA, Ciarelli MJ, Kuhn JL, Brown MB, Feldkamp LA (1994) J Biomech 27(4):375–89
28. Mow VC, Hayes WC (1997) Basic orthopaedic biomechanics. Lippincott, Philadelphia, pp 88–89
29. Ouyang J, Yang GT, Wu WZ, Zhu QA, Zhong SZ (1997) Clin Biomech 12(7/8):522–4