

Fabrication of Porous n-HA/PA66 Composite for Bone Repair

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Abstract. Using nano-hydroxyapatite/polyamide66 composite (n-HA/PA66) and a special foamer as start materials, a porous species for bone defect repair was successfully developed by thermal-pressing method. The resulting material presented: (1) high compressive strength which reached 13~46MPa; (2) excellent porous structure, the average diameter of pores in the matrix was in range of 280 μ m to 500 μ m and porosity of 36% to 57%. The porous architecture could be adjusted by the combination of processing parameters such as the weight of start mixture used per mold and the ratio of composite to foamer as well as n-HA content in the composite. No apparent change in composition and structure of n-HA/PA66 composite was found by XRD and IR determination before and after formation of porous species. According to Sherrer equation, the value of D(002) of n-HA crystals in porous material and start powder were about 70nm, indicating no occurrence of change in size of n-HA during the thermal-pressing procedure. Additionally, no foamer residual was detected in porous species.

Introduction

In recent years, synthetic hydroxyapatite [HA, Ca₁₀(PO₄)₆(OH)₂] with similar composition and crystal structure to natural bone, known to directly bond to bone and teeth *in vivo* has been developed in a variety of forms used in hard-tissue substitutes and regeneratives because of its excellent bioactivity and osteoconductivity [1-3]. However, it is highly brittle and stiff and applications have been dramatically limited, especially as bone substitute in load-bearing repair. A composite of two components, the polyamide66 and HA, has potential because of their combined benefits, that is, the osteoconductivity and bioactivity of HA and the strength and shape availability of polyamide66. Compared to dense body, the porous type of the same species is more proficient for blood and nutrient circulation as well as for cell and tissue ingrowth, as it supplies open space and high surface area [1-3, 6]. In the present study, a porous n-HA/PA66 composite for bone repair was developed by thermal-pressing method.

Materials and Methods

The preparation method of n-HA/PA66 composite powder was described elsewhere in detail [4]. To fabricate porous material, a special foamer was dissolved into ethanol and n-HA/PA66 composite powder was added into the solution with vigorous stir to obtain homogeneous mixture. After dried, the mixture powder was pressed into a 50×30×10mm cube mold, keeping the mold pressure at about 3-5MPa at 300°C for 1h, and then cooled to room temperature. After fully washing and drying

procedure, the porous material was obtained. Various specimens, which summarized in Table 1, were prepared to evaluate their properties and to discuss the effect of the ratio of composite to foamer (C/F, w/w) and the ratio of n-HA to PA66 (n-HA/PA66, w/w) as well as the weight of mixture used per mold (W, g) on the final performances of porous species.

Table 1. Experimental design and different parameters

series	Ratio of composite powder to foamer (C/F, w/w)	Weight of mixture used per mold (g)	Ratio of n-HA to PA66 (n-HA/PA66, w/w)
A1	100:2	9.5	3:7
A2	100:2	11.5	3:7
A3	100:2	13.5	3:7
B	100:1	11.5	3:7
C	100:2	11.5	4:6

After preparation, the morphology of the porous material was observed by SEM (Hitachi S-450) at an accelerating voltage of 20kV. The total porosity, P_t , of the porous material was calculated according to the ratio between its measured mass and volume of the sample as described by Hou et al. [5]. The compressive strength was conducted with REGER 30-50 mechanical testing machine (Shenzhen Reger Co. Ltd). The specimens were rectangular in shape with the dimension of 15×10×30mm. The cross-head speed was 5mm/min, and the load was applied until the specimen was crushed completely. XRD (X'Pert pro-MPD, Philips) and FT-IR (Thermo Nicolet 170SX FT-IR Spectrometer) were employed to investigate the influences of the thermal-pressing procedure on the properties of n-HA/PA66 composite after formation of porous species.

Results and Discussion

The SEM micrographs given in Fig.1 show that the pores have different structure, both interconnective and disconnective, and that the average pore's diameter in the matrix is between 280µm and 500µm. The pores of sample A1 (Fig. 1a, 1b) and A2 (Fig. 1c, 1d) are well-interconnected in the matrix, whose structure are considered to be suitable for tissue ingrowth, diffusion of nutrients and clearance of wastes in previous studies [2]. However, in the case of sample A3 (Fig. 1e), a linear aperture structure and preferential orientation in one direction is observed. Moreover, in sample A series, the average size of pores decrease inversely with the increased weight of the mixture used per mold from 9.5g to 13.5g. These results suggest that the weight of the mixture used per mold is one of the key factors affecting pore structure and porosity. For sample B (Fig. 1f), it exhibits both linear aperture and nonlinear holes, which indicates that C/F ratios also result in different pore structure, as different amount of gas produced by the degradation of foamer. By comparing sample A2 with C (Fig. 1g), it is found that less pores but larger pore size were for the later. The reason is that the melted composite with higher n-HA content has higher viscosity, thus affects diffusion of the gas during formation of pores [6].

Table 2 summarizes the results of compressive strength and total porosity. It can be noticed that compressive strength of the porous blocks is in a range of 13~46MPa, higher than that of cancellous bone (2~12MPa) and typical porous HA (1~3MPa) [7]. In sample A series, it is obvious that compressive strength weaken inversely to its porosity. However, sample B and C, with lower porosity than that of sample A1, present a lower compressive strength than that of samples A1. Moreover, sample A2 has higher compressive strength compared to B, although they are of the

same porosities. Those might result from different pore structure in the matrix. The results above mentioned show that not only porosity but also pore structure affect the mechanical performance of porous material dramatically.

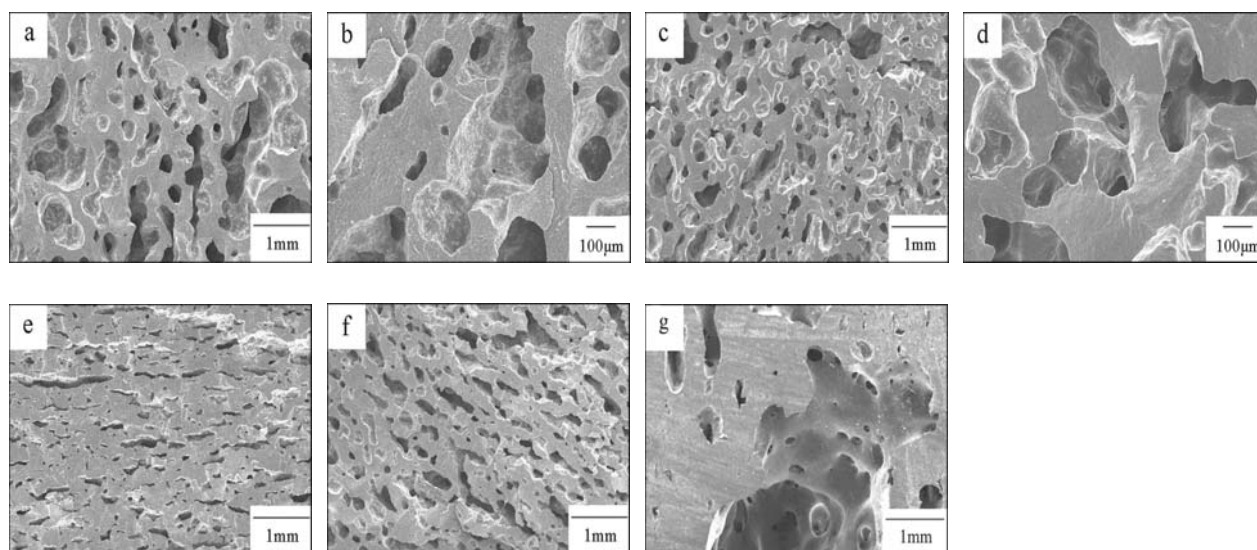


Fig. 1 SEM micrographs of porous species: a)A1, $\times 22$; b)A1, $\times 100$; c)A2, $\times 22$; d)A2, $\times 100$; e)A3, $\times 22$; f)B, $\times 22$; g)C, $\times 22$

Table 2. Results of porosities and mechanical properties of porous materials measurements

Series	Total porosity Mean (%)	Compressive strength Mean \pm standard deviations (MPa)
A1	57	22.4 \pm 3.2
A2	44	43.2 \pm 2.1
A3	36	46.3 \pm 2.4
B	44	19.6 \pm 1.7
C	50	13.2 \pm 2.6

The XRD patterns obtained for the n-HA/PA66 composite powder before and after formation of porous species are shown in Fig. 2. No apparent changes of the shape of peaks are found. Peaks at about 26° , 32° , 40° , 47° and 50° in 2-Theta are ascribed to HA. Two additional peaks are seen around 20° and 24° in 2-Theta corresponding to PA66. According to Scherer equation: $D = K\lambda/\beta_{1/2}\cos\theta$ (Where D is the crystal size; K, the constant 0.9; θ , glancing angle; λ , X-ray wavelength and $\beta_{1/2}$ is the half width of diffraction peak), the values of D (002) of HA in the initial composite and porous block are about 70nm, indicating no changes in the size of n-HA crystals and that it is still in nanometer scale after the thermal-pressing procedure. This may result from the complex between n-HA and PA66, as their combination has higher binding energy compared to that of blend of the two materials [4, 8].

The FT-IR spectra of initial composite and porous block are given in Fig. 3. The spectrum of porous material (Fig. 3a) is consistent with that of start material (Fig. 3b). The PO4³⁻ peaks at about 564, 962, 1035 and 1094cm⁻¹ are notable. The OH⁻ are recorded at about 3571 and 631cm⁻¹. Bands at around 3304, 1535 and 1636cm⁻¹ are the characteristic peaks of PA66. Bands are observed at around 2924 and 2851 cm⁻¹ representing carbon-hydrogen vibration. From the results of XRD and FT-IR analysis, it is found that no apparent changes of the composition and structure of n-HA/PA66 composite occurred during the thermal-pressing procedure and no foamer residual was detected in

the porous material.

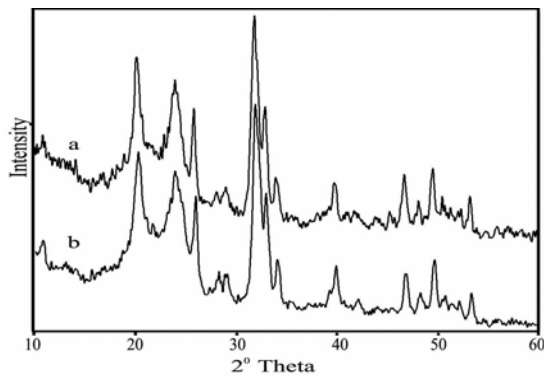


Fig. 2. XRD patterns of porous material with 30/70 n-HA/PA66 ratio (a) and initial powder with 30/70 n-HA/PA66 ratio (b).

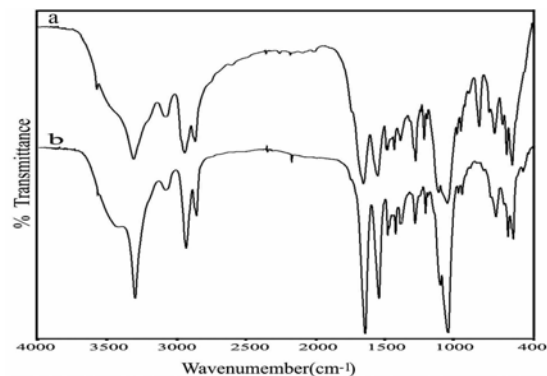


Fig. 3. FT-IR spectra of porous material with 30/70 n-HA/PA66 ratio (a) and initial powder with 30/70 n-HA/PA66 ratio (b).

Conclusions

Porous n-HA/PA66 materials were obtained from the thermal-pressing method. The porous materials present good compressive strength (13~46MPa) and excellent pore configuration with controllable interconnectivity and average diameter as well as porosity by varying the combination of different processing parameters. It has potential as bone prosthesis for clinical application.

Acknowledgments

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References

- [1] B.S. Chang, C.K. Lee, K.S. Hong, H.J. Youn, H.S. Ryu, S.S. Chung, W. Park: *Biomaterials* Vol. 21 (2000), p.1291
- [2] O. Gauthier, J. Bouler, E. Aguado, P. Pilet, G. Daculsi: *Biomaterials* Vol. 19 (1998), p.133
- [3] D. Walsh, T. Furuzono, J. Tanaka: *Biomaterials* Vol. 22 (2001), p.1205
- [4] J. Wei, Y.B. Li: *Eur. Polym. J* Vol. 40 (2004), p.509
- [5] Q. Hou, DW Grijpma, J. Feijen: *Biomaterials* vol.24 (2003), p.1937
- [6] X.D. Wu, Y.C. Peng, C.M. Guo: *Light Industry Machinery* Vol. 2 (2005), p.22
- [7] D.L. Shi, G.W. Jiang: *Mater. Sci. Eng C* Vol.6 (1998), p.175
- [8] X.J. Wang, Y.B. Li, J. Wei, K. de Groot: *Biomaterials* Vol. 23 (2002), p.4787