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Manufacturing of Porous Ceramic Spheres Using Calcium Phosphates, by a Mechanical Method Without Additives or Binders

Kalan Bastos Violin [1, a], Tamiye Simone Goia [1,b], Kunio Ishikawa [2,c], José Carlos Bressiani[1,d] and Ana Helena de Almeida Bressiani[1,e]

[1]Av. Professor Lineu Prestes, 2242, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP, Brazil

[2] 3-1-1 Maidashi, Higashi-ku, Fukuoka, 815-8582, Kyushu University, Faculty of Dental Science, Department of Biomaterials, Japan

[a]kbviolin@ipen.br, [b]tsgoia@ipen.br, [c]ishikawa@dent.kyushu-u.ac.jp, [d]jcbressia@ipen.br, [e]abressia@ipen.br

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Abstract. The processing of porous ceramics spheres (PCS) has been developed for biphasic calcium phosphates (BCP), hydroxyapatite (HAp) and beta tricalcium phosphate (β-TCP) in order to be used mostly as bone fillers and drug delivery systems. The importance of the PCS is due to better accommodation of them in order to fill empty spaces and also because is more friendly to cells and bone tissue growth. Also is important to obtain a surface roughness to increase the surface area in contact with the living tissue and their fluids. There are several methods used to achieve the PCS form and most of them use suspensions based on liquids immiscibility effect or additives. The aim of this work was to achieve PCS of BCP, HAp and β-TCP with rough surface and varying size without using solutions or additives. The method developed is based on a mechanical continuous movement of the particles, relying on the normal ability of the ceramic powders to aggregate themselves while rolling in a cylindrical container for long periods. The physical forces involved in the process, gravity, particle attraction, centripetal force and shocking make the ceramic rounds with golf ball appearance on its surface. With this method it was possible obtain PCS with 30% of porosity with rough surface and size between 1 to 4 mm in diameter.

Introduction

The ceramics spheres are used in several fields of application such as food industry, pharmaceutics, and agriculture. This particular shape has been used commonly in medical industry, specifically orthopedics and dentistry, as hydraulic cements or as bone substitutes. The calcium phosphates (CaP) materials are used as biomaterials by the similarities in composition with the bone tissue, thus helping in the process the new bone formation. The raw materials used for this purpose are hydroxyapatite (HAp; $Ca_5(PO_4)_3OH$), β-tricalcium phosphate (β-TCP; $Ca_3(PO_4)_2$), and their mixtures called biphasic calcium phosphates (BCP). These materials have an excellent biocompatibility, osteoconductivity and osteoinductive potential [1].

The interaction of the materials and cells are related with chemical, physical and mechanical properties. Besides their compositions and properties being very close to the mineral part of the bone tissue, the CaPs materials can be obtained in the form of granules with increased specific surface area, another aspect that is of great interest, due to roughness and microporosity that will promote an increased surface area, which in contact with the living tissue and their fluids, supports the protein adsorption and consequently cell attachment [2, 3].

Despite granules had been used widely as bone fillers with a high range of particle size, based on a low complexity process and low production cost, the particles present low microporosity and sharp edges. Different from irregular shaped granules, spheres can improve the accommodation of the particles and drug delivery capability, besides having a higher surface area, which also helps tissue growth, are more friendly to cells and present better outcome on tissue response. [4, 5]

The manufacturing of CaP spheres has been increasingly investigated nowadays. There are many methods to produce those mentioned ceramic spheres with different routes, following a combination of various aspects, considering the starting materials (solutions, slurries, pastes, and solids), the dispersion phases (gas, solution, solid), the dispersion tools (nozzles, propellers, sieves, molds), and the consolidation methods (drying, precipitation, gelling, freezing) [6, 7].

In a production process, many aspects should be considered, among them, the steps of manufacturing should be avoided to reduce costs and contamination; furthermore environmental friendly process should be pursued in order to develop greener technologies. The objective of this paper is to present a novel simplified procedure to obtain PCS by a mechanical process, without additives and near net shape, with a low cost and environmental friendly procedure.

Experimental Procedure

The commercial ceramic powders of HAp and β-TCP were HAP-200 and β-TCP-100, respectively, both purchased from Taihei Chemical Industrial Co. Ltd., Osaka, Japan. The BCP is a composition with 1:1 by weight of HAp and β-TCP. The ceramic powders were added in a plastic cylinder container of ~1000ml (9cm x 17cm), and the closed container was put in a small ball mill device for transverse mixing, following the weigh, speed and time presented on Table 1.

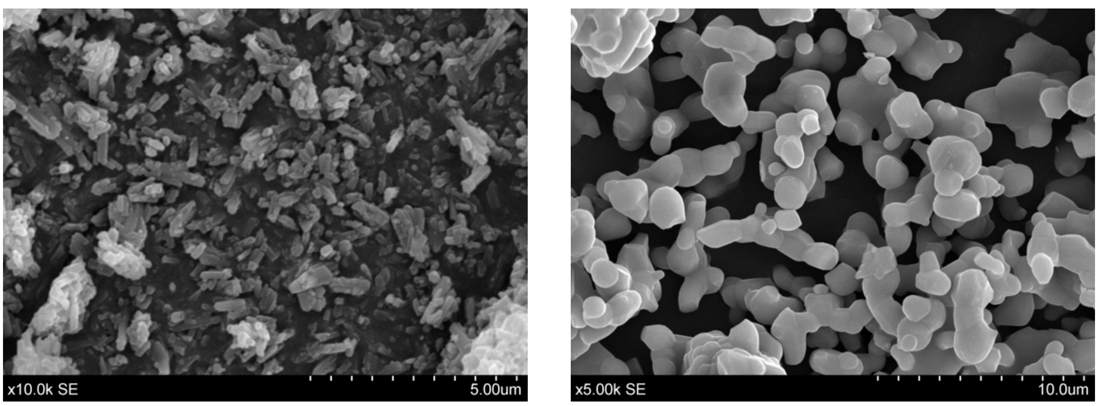
Table 1

Powder	Weigh	Speed (rpm)	Time
HAp	50g	60~85 rpm	2~6 hours
β-TCP	50g	60~85 rpm	2~6 hours
BCP	β-TCP (25g) + HAp (25g)	60~85 rpm	2~6 hours

The size of the spheres was determined based on these parameters and the final shape was selected by sieve ranging from 1 to 4 mm in diameter. The sintering was performed at 1100ºC/60 minutes for β-TCP, 1150ºC/60 minutes for BCP and 1300ºC/60 minutes for HAp, all in oxidant atmosphere. The ceramics powders and the sintered spheres were characterized by scanning electron microscopy (SEM) S-3400N, Hitachi and X-ray diffraction (XRD) D8 Advance, Bruker. The apparent porosity of the sintered spheres was calculated by Archimedes' method according to the standards of ASTM C20-00 [8].

Results and Discussion

The materials' phases were confirmed by XRD before and after sintering, no contamination was observed on raw materials, and in the sintered samples there was no phase transformation. The HAp powder characterization by SEM shows a smaller particle size with large distribution, raging about less than 5μm, and weak aggregates (Fig.1A). The β-TCP powder appears with larger particle size with homogenous distribution, ranging around 10μm, and fewer aggregates (Fig. 1B)



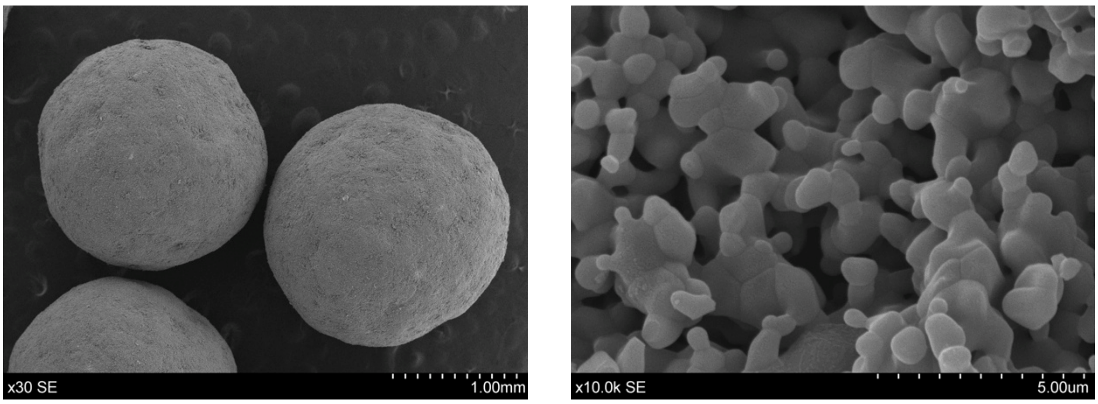
A B

Figure 1. Morphological SEM of powders: A) HAp, B) β-TCP.

The method proposed is based on a mechanical continuous movement of the particles, relying on the normal ability of the ceramic powders to aggregate themselves while rolling in a cylindrical container. This process is based on the forces present and generated on the system. The forces involved are gravity, particle attraction and charging and centripetal force. The centripetal force is generated by the spinning and movement of the cylinder container, this movement forces the particles against the wall of the container while gravity pulls the particles to the lower point, bottom, of the cylinder, then inflicting particles to roll in perpetual motion. As small aggregates begin to nucleate and roll continuously through time, more loose particles present in the container are added to the rolling aggregate, layer by layer until the sphere is formed. The shocks between the spheres and towards the container also produced subtle surface modifications increasing the roughness of spheres. The analogy of this process is related with the formation of a snowball downhill, thus we propose to call the process "Snowballing technique". The element controlling the growth of the spheres with the limited amount of powder inside the container was the speed of the spinning vessel, combined with the inherent characteristics of these materials used, as density and particle size, the speed of revolutions defined if the spheres grow or disintegrate.

The speed and time presented on Table 1 show how to control the size of the spheres considering the given amount of powder inside the container for any of the three materials used. The higher speed with shorter time produced smaller spheres around 1mm in diameter as shown on Figure 2A, lower speed and longer time produced larger spheres around 4mm in diameter as presented on Figure 3A, and intermediate speed and intermediate time produced intermediate spheres around 2mm in diameter as presented on Figure 4A. The shocking and rolling of spheres, during the Snowballing process, also produce spheres with golf ball appearance on their surface, as shown on Figure 4A.

The amount of powder inside the container was around ~10% from the total capacity of the container which allows the free turnover of the powder [9] and thus leading to the formation of spheres. The sintering temperature parameters were sufficient to allow the formation of neck between the ceramic particles and promoted good mechanical strength, allowing the free handling of them, and without phase transformation, as shown on Figure 2B, Figure 3B and Figure 4B.



A B

Figure 2. SEM of HAp spheres, produced at higher speed and shorter time. A) Morphology, B) Structural surface appearance with microporosity.

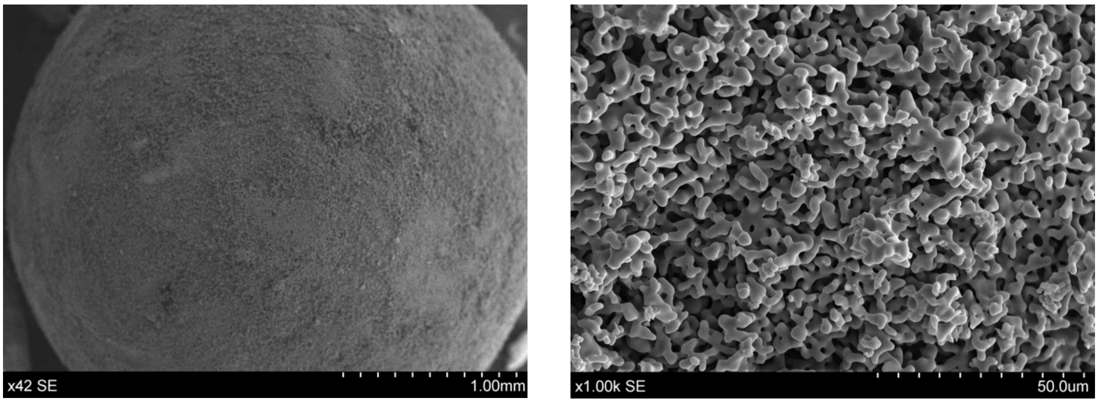


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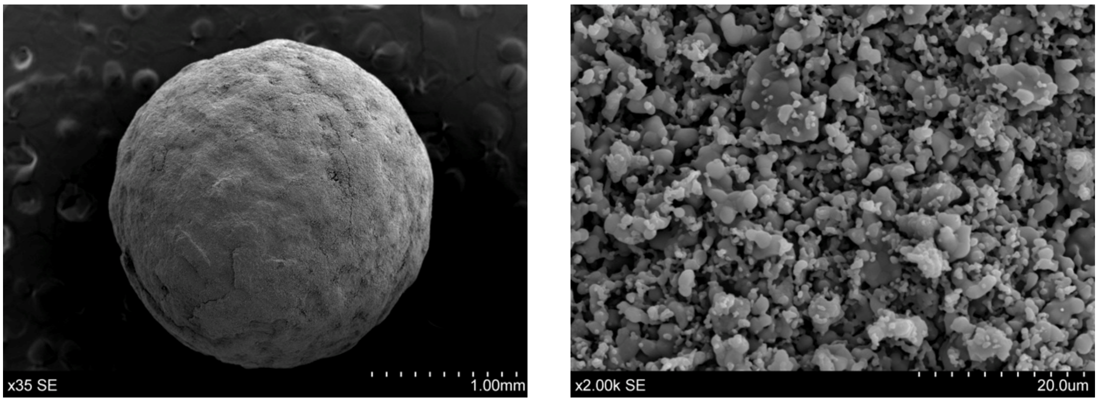
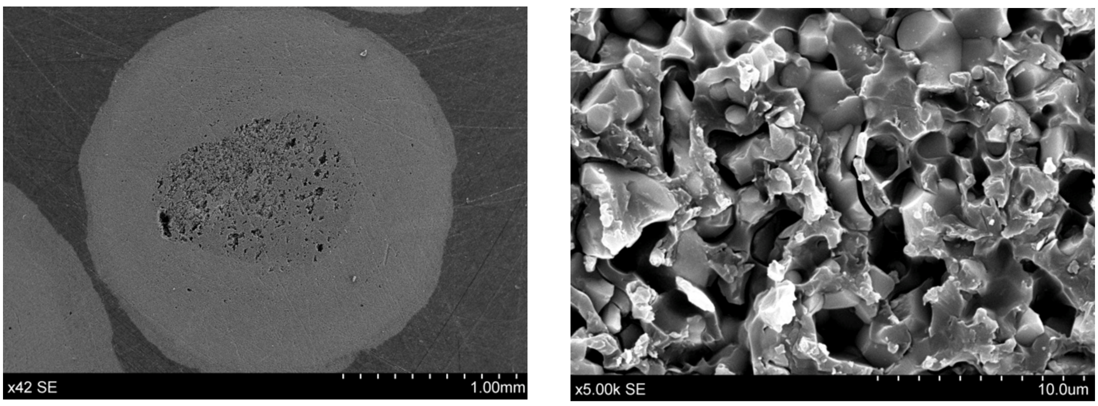
Figure 3. SEM of β-TCP spheres, produced at lower speed and longer time. A) Morphology, B) Structural surface appearance with microporosity.



A B

Figure 4. SEM of BCP spheres, produced at intermediate speed and intermediate time. A) Morphology, B) Structural surface appearance with microporosity.

The apparent porosity obtained by Archimedes' method was 30%, it can be observed by the cross-section of a BCP sphere (Fig. 5). The core of the PCS is more porous than its outer part, this feature is expected since as the sphere grows, its weight also increases, and thus the loose particles aggregated will be more densely packed to it, because of gravity, although still remaining with high microporosity as observed by SEM (Fig. 5B).



A B

Figure 5. SEM of BCP spheres' cross-section, produced at intermediate speed and intermediate time. A) Morphology, B) Structural outer part appearance with microporosity

The environmental friendly aspect of the technique is based on the fact that without the use of additives or binders the powder inside the container is the same of the powder raw material. Thus no waste is produce since if for any reason the process fail the powder can be easily separated again by handling with mortar or vigorous shaking, because the energy maintaining the particles together are low energy electrostatic forces.

Conclusions

The new developed Snowballing technique, successfully produced PCS with varying size, 1mm to 4mm in diameter, without additives or binders from HAp, beta-TCP and BCP.

The Snowballing technique is simple, low cost, involving low energy, without use of hazardous chemicals and with clean recyclable waste.

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References

[1] S. V. Dorozhkin, Bioceramics of calcium orthophosphates, Biomaterials 31 (2010) 1465-1485

[2] R.Z. Legeros, S. Lin, R. Rohanizadeh, D. Mijares, J.P. Legeros, Biphasic calcium phosphate bioceramics: Preparation, properties and applications, Journal of Materials Science: Materials in Medicine 14 (2003) 201-209.

[3] G. Daculsi, Biphasic calcium phosphate concept applied to artificial bone, implant coating and injectable bone substitute, Biomaterials 19 (1998) 1473-1478.

[4] D.J. Misiek, J.N. Kent, R.F. Carr, Soft tissue responses to hydroxylapatite particles of different shapes, Journal of Oral and Maxillofacial Surgery 42 (1984) 150-160.

[5] O. Gauthier, E. Goyenvalle, J.M. Bouler, J. Guicheux, P. Pilet, P. Weiss, G. Daculsi, Macroporous biphasic calcium phosphate ceramics versus injectable bone substitute: A comparative study 3 and 8 weeks after implantation in rabbit bone, Journal of Materials Science: Materials in Medicine 12 (2001) 385-390

[6] M. Bohner, S. Tadier, N. Garderen, A. Gasparo, N. Döbelin, G. Baroud, Synthesis of spherical calcium phosphate particles for dental and orthopedic applications, Biomatter 3:2 (2013) e25103-1-e25103-15.

[7] D.H. Kim, H.H. Chun, J.D. Lee, S.Y. Yoon, Evaluation of phase transformation behavior in biphasic calcium phosphate with controlled spherical micro-granule architecture, Ceramics International 40:4 (2014) 5145-5155.

[8] ASTM C20-00. Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water.

[9] R. Hogg, Mixing and segregation in powders: evaluation, mechanism and processes, KONA Powder and Particle Journal 27 (2009) 3-17.

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[1] S. V. Dorozhkin, Bioceramics of calcium orthophosphates, Biomaterials 31 (2010) 1465-1485.
http://dx.doi.org/10.1016/j.biomaterials.2009.11.050
[3] G. Daculsi, Biphasic calcium phosphate concept applied to artificial bone, implant coating and injectable bone substitute, Biomaterials 19 (1998) 1473-1478.
http://dx.doi.org/10.1016/S0142-9612(98)00061-1