

Dispersed hydroxyapatite bioglass 45S5 composites: comparative evaluation of the use of bovine bone and synthetic hydroxyapatite

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Abstract: The bovine bone and sintetic hydroxyapatite (HA) bioceramics are reference materials to employment as a bone substitute, however, their slow rate of degradation and its low rate of bioactivity index (Ib) are presented as limiting factors for application as bone graft. In contrast, the bioglass is a resorbable and osteoinductive material. the present work objective the development of composites of dispersed bovine bone or sintetic HA in silicate-phosphate bioglass, seeking to obtain a biomaterial with properties suitable for application as bone grafts. The composites were prepared by mixing between the powder components followed by sintering for 1h. Were used HA and bioglass (45S5) with particle size <240µm. The tested proportions of HA/45S5 were 20/80, 30/70 and 40/60 (wt%). The composites characterization was made employing scanning electron microscopy, Infra-Red Spectrometry and hydrolytic resistance test. The test results indicate the potential use of the materials developed for applications such as bone graft.

Introduction

The bioceramics are obtained and processed to provide specific physiological behavior for applications as bone grafts. bioceramics should be resorbable, thus acting as temporary material, gradually being replaced by new bone^(1,2,4).

The hydroxyapatite (HA), a calcium phosphate bioceramic, is the main material for applications in bone replacement because it is a material that exhibits absence of local and systemic toxicity, absence of inflammatory responses and apparent ability to bind to host tissue. However, despite their promising biological properties, its low rate of bioactivity index (Ib) and its slow rate of degradation is presented as limiting factors for its application as bone graft⁽⁵⁾.

Unlike HA, the bioglass is a resorbable biomaterial which has a high Ib, and osteoinductive propriety, which allows intracellular and extracellular interface response occurs in the living tissue, allowing the surface to be colonized by stem-cells free as result of surgical interventions.

In this context, the present work objective was to compare the use of bovine bone HA with synthetic HA (calcium triphosphate) in silicate-phosphate bioglass (45S5) with HA dispersed composites, seeking to combine the osteoconductive and osteoinductive properties of both materials, resulting in a biomaterial with properties suitable for application as bone grafts.

Experimental Procedure

Bioglass 45S5 obtention

The composition of bioglass 45S5⁽⁶⁾ was prepared using analytical grade reagents and fused at 1500 ° C for 2 hours in vertical kiln. The bioglass was quenching and cast in 10x10x50 mm bars. The annealing was performed at 500°C for 2 h, and part of the material was milled to powder (≤ 250µm).

Hydroxyapatite

Bovine hydroxyapatite and synthetic hydroxyapatite, both high purity for use in bone implants were used. These materials were kindly provided by the company Critéria Ltda.

Hydroxyapatite/Bioglass composites obtention

The raw materials were milled to fine powder (60 mesh - $\leq 250\mu\text{m}$) and the composites were formulated in the following proportions : 20/80, 30/70 and 40/70 wt% of HA and bioglass respectively. The samples using the bovine HA are identified by HAB / BV and the samples using Synthetic HA by HAS / BV, followed by its mass proportions (For exemple: HAB/BV 30/70 for the composite using bovine HA 30 wt% and bioglass 70 wt%). The homogenization was performed in agate mortar. For each composition five 5.0 mm in diameter cylinder test were (approximately 0.2 g of material) uniaxially compacted (1000Kgf loaded). The sintering of the green cylinders arranged in zirconia navicular crucible was held in muffle type furnace at 1100 ° C for 2 h with 15°C /min heating rate and following natural cooling inside the oven.

Samples characterization

The composites characterization was performed using the techniques of X-ray diffraction (XRD) for powdered samples (Bruker AXS D8 Advance, USA). The measurements of the infrared spectra were performed using Thermo Nicolet - Nexus 870 FT-IR spectrometer. USA, for powdered samples (dispersion in KBr pellets, spectrophotometric grade - Merck PA). The scanning electron microscopy - SEM were performed using Jeol 6400 apparatus (Japan). The chemical resistance evaluation (hydrolytic resistance test) was performed as described by Day ⁽⁹⁾.

Results and Discussion

The developed composites XRD patterns are show in Figure 1. In these diffractograms is possible to observe crystalline materials characteristic for all HA/Bioglass composite, showing that the sintering period was sufficient for the occurrence of the evolution of crystalline phases.

The composites shows peaks relating to the HA and β -tricalcium phosphate (β -TCP) and glassy phase crystallization characteristic peaks, such as silica in form of cristobalite (SiO_2), calcium silicate (CaSiO_3) and devitrite ($\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$). In general way, the peaks for β -TCP, are better defined for the composites obtained using the synthetic HA. These results are HA degradation to β -TCP sintering effect indicative. This fact is more interesting in composites where the bovine hydroxyapatite was used, because in the composites containing sintetic hydroxyapatite, β -TCP is already introduced with raw materials.

The use of β -TCP has become the object of interest in the area of biomaterials due to their behavior resorbable. The use of β -TCP with the HA has been a viable alternative to increase the speed of assimilation of the latter ⁽⁵⁾.

Table 1 it can be seen that occurs in composition of HAB / BV 20/80 a small contraction after sintering, whereas with increasing concentration of HA, there is the occurrence of the expansion of HAB / BV 30/70 and HAB / BV 40/60 compositions . Thus, there is the occurrence of the contraction phase represented by the bioglass (devitrificação efect), as a sintering reaction result, and an volume increase for higher concentrations of bovine HA due the degradation to β -TCP. ⁽¹⁰⁾. However the composites HAS/ BV 20/80, HAS / BV 30/70 and HAS / BV, 40/60 the occurrence of contraction due to bioglass devitrificação , is not compensated by the expansion due to degradation of HA to β -TCB.

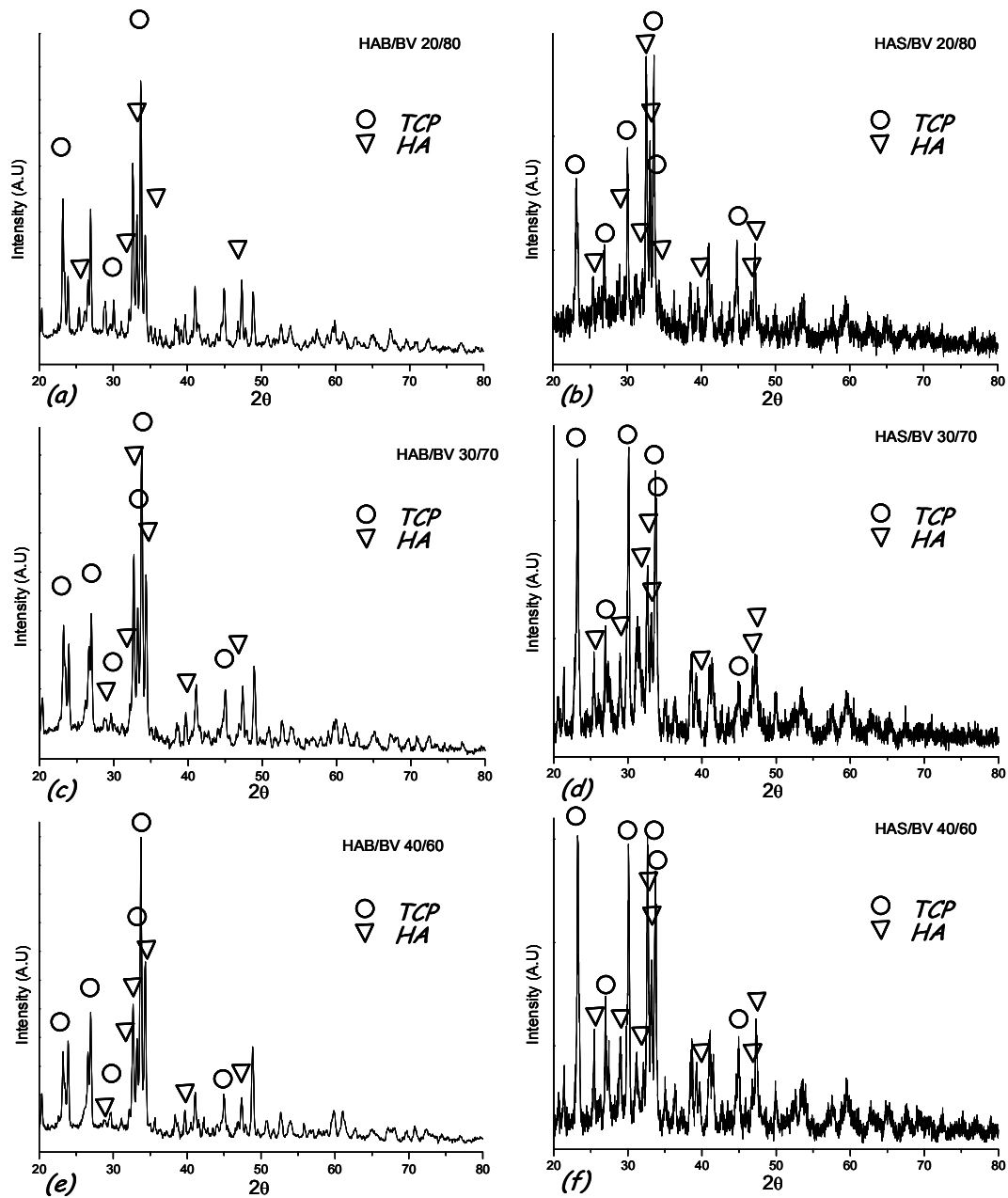
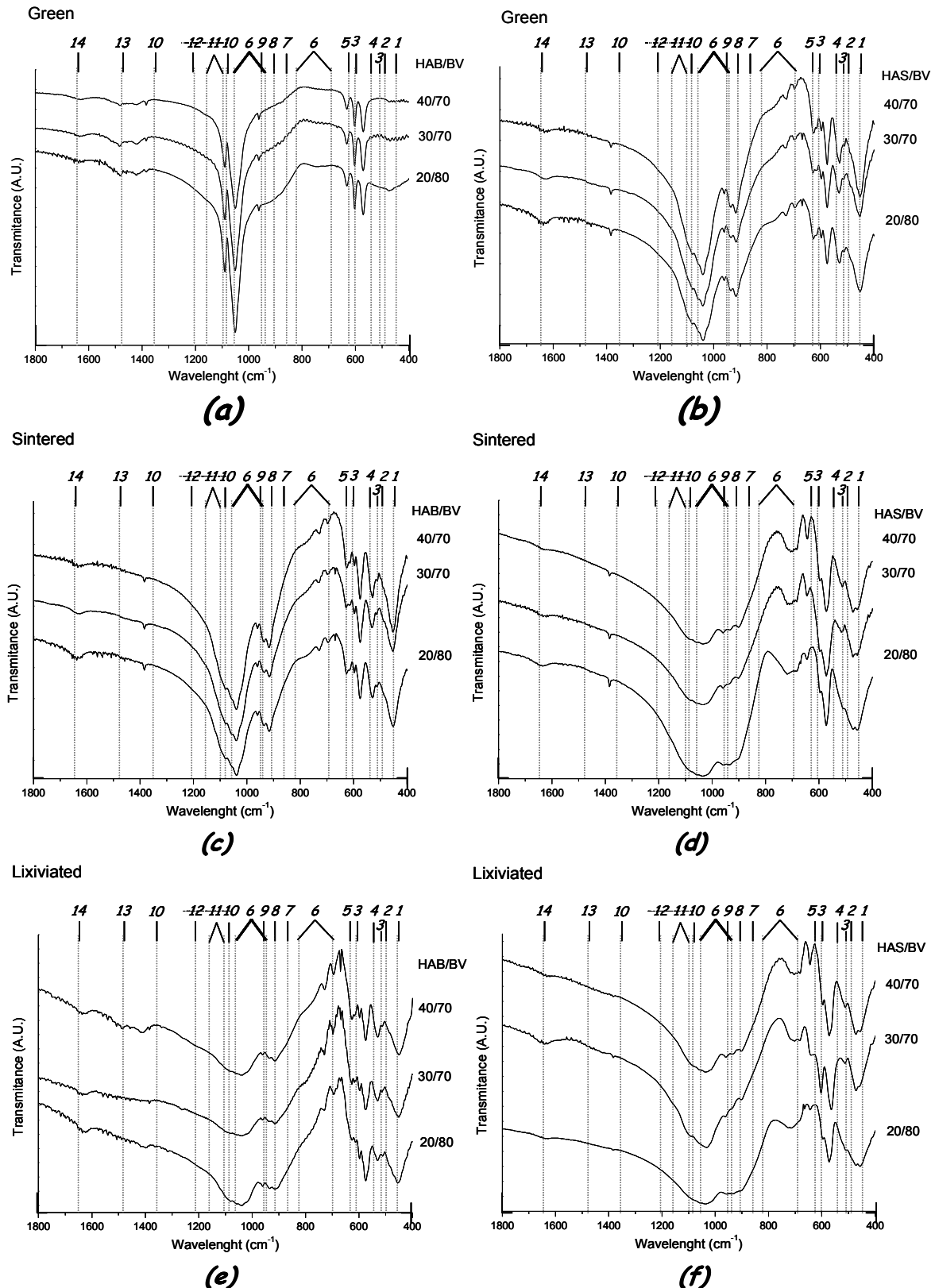


Fig. 1 - XRD patterns corresponding to: (a) HAB/BV 20/80, (b) HAS/BV 20/80, (c) HAB/BV 30/70, (d) HAS/BV 30/70, (e) HAB/BV 40/60 e (f) HAS/BV 40/60

Table 1 - Fire contraction observed in the composite HA / Bioglass (vol.%)

Composition [HA/Bioglass]	20/80		30/70		40/60	
	Bovine	Sintetic	Bovine	Sintetic	Bovine	Sintetic
Contraction [vol. %]	4,3	8,5	-5,4	9,0	-31,7	7,5



1 - Si-O-Si [Q⁴]; 2 - Segregated metal oxides; 3 - P-O Crystalline; 4 - P-O Vitreous; 5 - OH Hydroxyapatite;
 6 - Silicate; 7 - Si-O[NB],[Q⁰]; 8 - Si-O[NB],[Q¹]; 9 - Si-O[NB],[Q²]; 10 - P=O; 11 - Si-O[NB],[Q³];
 12 - Si-O,[Q⁴]; 13 - Na-O; and 14 - Structural water

Fig. 2 - FTIR spectra corresponding to *HAB/BV* and *HAS/BV* series: (a) and (b) are green compositions ; (c) and (d) sintered ; and, (e) and (f) after hydrolytic attack.

The FTIR spectra for all composites in green, sintered and after hydrolytic attack are show in fig. 2. Comparing the green compositions (fig. 2-a and 2-b) with sintered composites, (fig. 2-c and 2-d) a 45S5 bioglass depolymerization were observed. The bioglass depolymerization assist in the

HA interface formation. This fact is observed by reducing the peak indicates Si-O-Si [Q^3] and the increase of the peaks indicative of Si-O-Si [Q^4], Si-O-Si [Q^1], Si-O-Si [Q^0] after sintering, i.e, the initial random network structure of glass, mainly composed of silica tetrahedra by Q^3 , which are a typical occurrence for this type of glass, started to segregate into clusters of silica Q^4 , which tend to crystalline phases formation and by other hand, silicates Q^1 and Q^0 , probably are associated with phosphorus, as suggested by the peaks indicative of connections typical of silicates. In this sense, there is also reducing the intensity of the peaks indicative of the P-O vitreous bonds and increased P-O crystalline bonds. The peak OH functional group in HA indicative, Shows that at least part of this material remains without degrading after burning.

After leaching (Fig. 2-e and 2-f) in all materials the glassy phase homogeneous dissolution were observed in FTIR spectra. The crystalline phases corresponding to the PO and OH functional group in the HA peaks remain after leaching, indicating the composite bioactivity index. The comparison of SEM micrographs of the synthesized material (Fig 3-a and 3-c for HAB/BV 30/70 and HAS/BV 30/70 respectively) and same material after 336h (14 days) of hydrolytic attack (Fig 3-b and 3-c) indicate material compaction and a bioglass liquid phase formation during sintering that contributed to obtaining a material with low apparent porosity. This observed behavior is similar for all composites.

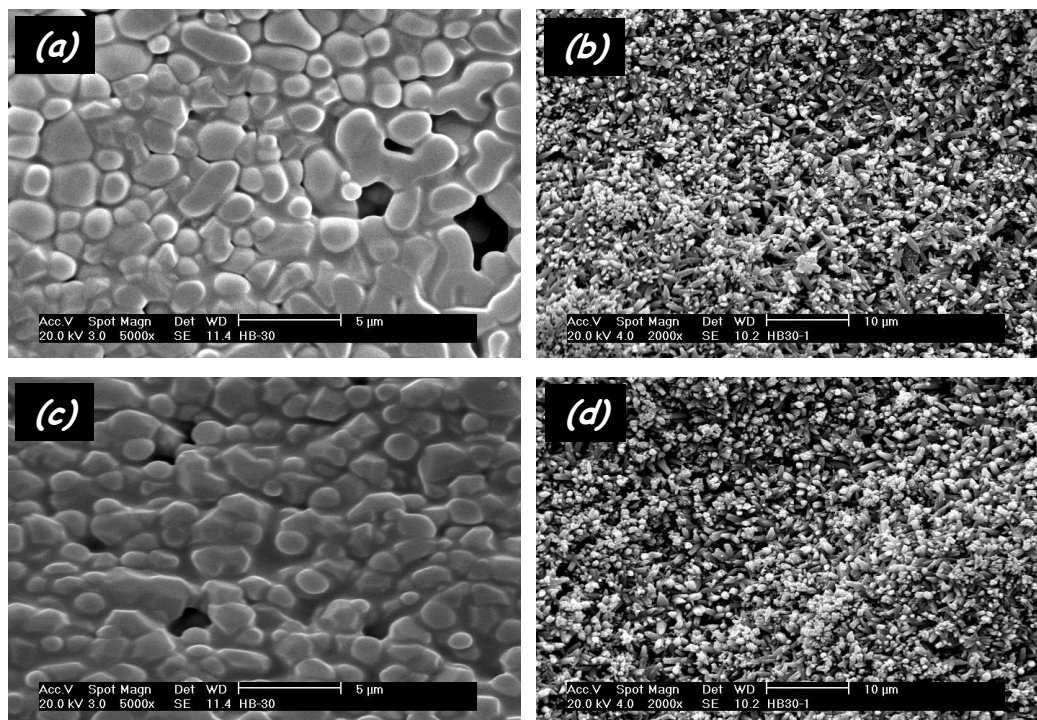


Fig. 3 - HAB / 30/70 BV and SAH / BV 30/70 SEM micrographs after sintering (a and c, respectively) and after 336 hours hydrolytic attack (b and d, respectively).

After the hydrolytic attack, there is an intense dissolution of the bioglass phase. Thus, when implanted in living organism, the dissolution of bioglass and also the β -TCP, which is resorbable, will lead to formation of a porous material. The formed channels will receive a response in the intracellular and extracellular interface with living tissue enabling them to be colonized by stem cells free, due to the osteoinductive character of bioglass. It is hoped that with the glassy phase and β -TCP phase dissolution progress the bone tissue formed involving the HA particles remnants and interacting with them as result of HA osteoconductive character.

4. Conclusions

The addition of bovine or synthetic HA to the bioglass was able to produce potentially resorbable composites, which will allow the combination of osteoconductive and osteoinductive properties of the each materials. The presence of β -TCP in the composites is presented as an advantage because it is a resorbable apatite phase and with biological interest. The behavior of both (bovine or sintetic HA) materials when dispersed in the bioglass is similar in most parameters examined, however during the sintering behaviors they exhibit different expansion / contraction, and the HA Bovina, inducing to volume expansion due to the degradation of β -TCB.

From these results it is possible the development of composite HA / bioglass where interest in the properties of both materials can be combined resulting in appropriate biomaterials for bone graft.

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