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Sol–gel derived alumina–hydroxyapatite–tricalcium phosphate porous composite powders

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Abstract

In this study, alumina–hydroxyapatite–tricalcium phosphate (α-Al_2O_3–HA–TCP) porous composite powders were produced and characterized. At first, boehmite sol (AlOOH) was obtained via sol–gel process by using aluminium isopropoxide ($Al(OC_3H_7)_3$) as the starting material. Bovine hydroxyapatite (BHA) powders derived from deproteinized bovine bones were added as 10, 20, 30 and 50% weight of the starting material to each boehmite sol. Also Na-alginate was added to the boehmite sol as the dispersive agent. Subsequently, gelation for 3 h at 110 °C was applied to each sol mixture. Finally, gelated samples were heat treated for 2 h at 500, 800, 1000 and 1300 °C. DTA–TGA, XRD, FTIR and SEM-EDS analyses were used to characterize the obtained composite powders composed of α-Al_2O_3–HA–TCP phases. In order to investigate porosity properties, powders were pressed with hydraulic manual press and formed into pellets. Later these pellets were sintered for 2 h at 1300 °C. Apparent porosity and bulk density tests were applied to the pellets. The evaluation of these tests results indicate that a novel α-Al_2O_3–HA–TCP composite material with ~38–44% apparent porosity has been produced.

Keywords: Sol–gel processes; Composites; Al_2O_3; Hydroxyapatite

1. Introduction

Materials used in the regeneration or reparation of fully or partially damaged organs/tissues of the body are known as ''biomaterials''. Bioceramics, an important class of biomaterials, can be conveniently applied in orthopedic and dental surgery due to their remarkable properties such as high biocompatibility and stability [1–7]. Bioceramics are classified mainly into three groups on the basis of the interactions between the implant material and the tissues. These groups are called bioinert, bioactive and bioresorbable bioceramics respectively. Alumina and zirconia belongs to bioinert ceramics while hydroxyapatite (HA) to bioactive and tricalcium phosphate (TCP) to bioresorbable ceramics [1,3,5,8–12]. Although alumina is famous for its high chemical and mechanical strength, it cannot form biochemical interfacial bonds with the tissues. HA is chemically and crystallographically similar to the mineral in human bones and teeth. On the contrary to alumina, HA has an ability of interfacial bonding to bone owing to its highly bioactive character. TCP can replace the body tissues when implanted depending on its bioresorbable properties and is one of the decomposition products of HA. These materials can be employed in different hard tissue applications like total hip joints, bone cement, tooth implants, etc. [11–19]. Recently, porous bioceramic materials have drawn interest since pores in the structure provide prosperous spaces for the tissue and implant contraction which makes the materials potentially suitable for cell/tissue ingrowth/development [1,12].

HA can be obtained either from natural sources such as bovine bones, egg shells, sea shells, and corals or with chemical methods like hydrothermal precipitation, sol–gel technology, solid-state reactions. Several researchers have reported results about producing hydroxyapatite from natural sources [20–24] and in this experimental study, bovine hydroxyapatite (BHA) powders derived by Oktar et al. were used [23]. Sol–gel method is the most reliable way for providing alumina with very high purity [25–27]. Previous studies based on alumina–HA

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composite material production tried to apply HA as a bioactive coating on alumina substrates and prepare composites from alumina and HA powders through various processes [28–31]. In this study, it is aimed to produce alumina–HA composites by assembling the two phases at different states which were boehmite sol and the BHA powders.

2. Materials and methods

2.1. Preparation of the composite powders

At the first part of the experimental procedure; boehmite sol (AlOOH) was obtained via sol–gel process by using aluminium isopropoxide (AIP ($Al(OC_3H_7)_3$), Aldrich ≥98%) as the starting material. Distilled water/AIP molar ratio was determined as 100 depending on Yoldas [27] principle. Firstly, 40 mol of distilled water was heated up to 90 °C, in a glass reactor with a heater equipped magnetic stirrer. The temperature was arranged to ∼90 °C and controlled by a pH meter continuously. When the temperature was reached to 90 °C 0.4 mol of AIP was added to the distilled water so hydrolysis reactions started. After stirring for 1 h, HCl (Merck, 37%) diluted up to 10%, was added to the solution for peptization. At the end of the preparation process, pH of the boehmite sol (AlOOH) was measured as ∼2.5 [32].

Deproteinization of the bovine bones in NaOH, washing the deproteinized bovine bones, calcination of the deproteinized-washed bones and grinding these calcinated bones are the steps that were applied respectively for producing BHA powders from bovine bones [23].

At the second part of the experimental procedure; BHA powders derived from bovine bones were added in proportions of 10, 20, 30 and 50% weight of the starting material to each

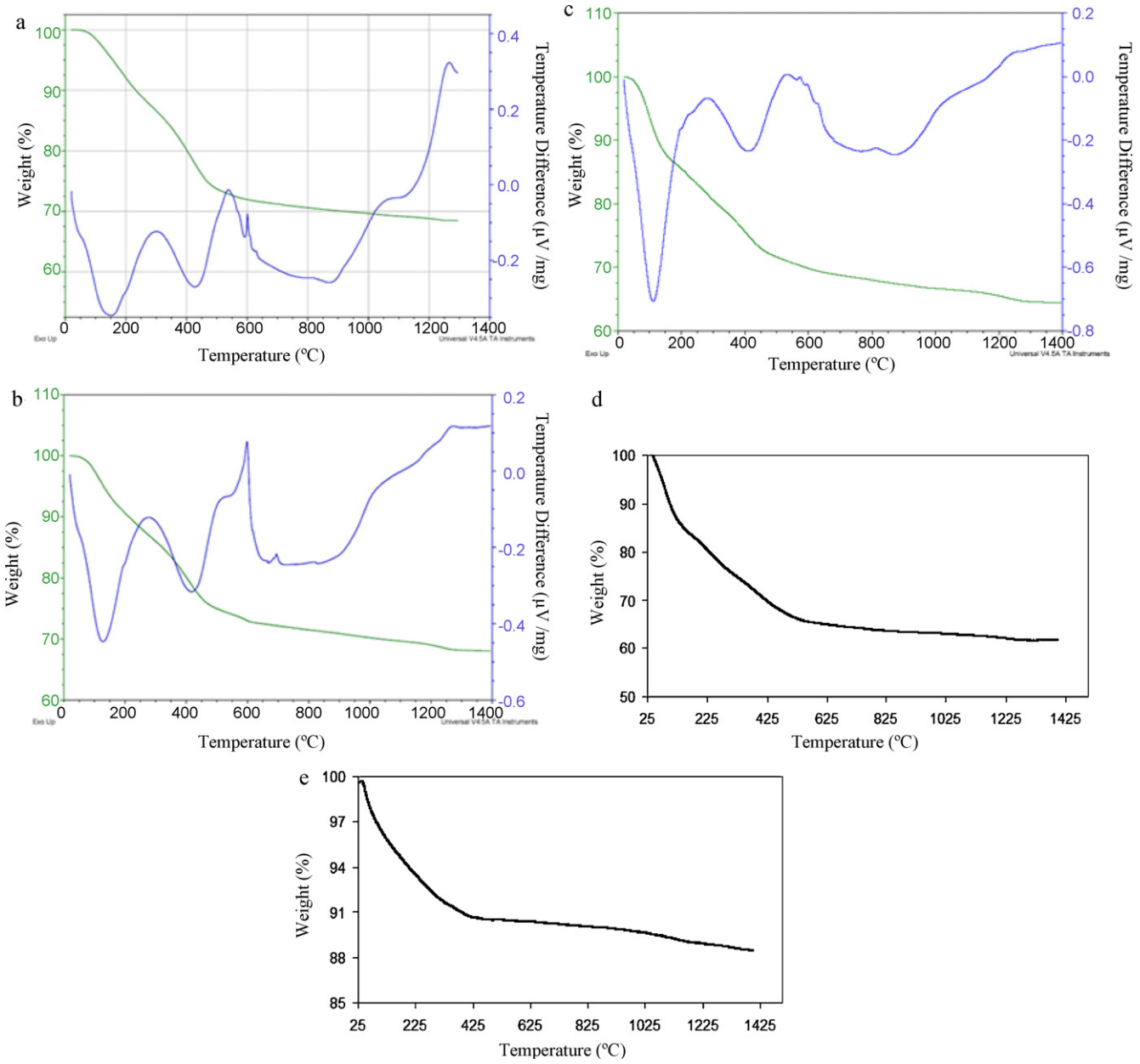


Fig. 1. DTA–TGA results of (a) AH10, (b) AH20 and (c) AH30 samples and TGA results of (d) AH50 and (e) pure BHA samples.

Table 1
Composite powder samples.

Sample code	Heat treatment temperature (°C)	BHA addition (wt.%)
500AH10	500	10
800AH10	800	10
1000AH10	1000	10
1300AH10	1300	10
500AH20	500	20
800AH20	800	20
1000AH20	1000	20
1300AH20	1300	20
500AH30	500	30
800AH30	800	30
1000AH30	1000	30
1300AH30	1300	30
1300AH50	1300	50

boehmite sol. However it was observed from the pre-experiments that BHA particles tended to precipitate and did not show a homogenous dispersion in the boehmite sol. Hence, a dispersive agent, sodium alginate (Na-alg, $NaC_6H_7O_6$, Aldrich) was used and added as 1, 2, 3 and 5% weight of its own molecular weight to the solution. Na-alginate enhances the viscosity and reduces the flow properties of boehmite–BHA mixture. After mixing these components for 1 h with a mechanical stirrer, gelation for 3 h at 110 °C was applied to each sol mixture. Gelated samples were heat-treated in alumina crucibles for 2 h at 500, 800, 1000 and 1300 °C with 10 °C/min heating speed by using a high temperature laboratory furnace, Nabertherm LHT 08/17. Finally white, irregularly shaped composite powders were obtained [32]. These composite powder samples are listed in Table 1 (A: alumina phase and H: BHA phase).

At the last part of the experimental procedure; 1300AH10, 1300AH20, 1300AH30 and 1300AH50 powder samples were pressed with hydraulic manual press in stainless steel molds and formed into pellets. These pellets were sintered for 2 h at 1300 °C with 10 °C/min heating speed by using a high temperature laboratory furnace [32].

2.2. Characterization of the composite powders

Ca/P molar ratio of BHA powders was determined with Panalytical Axios Minerals branded X-Ray Fluorescent (XRF) device. Equal pieces taken from each boehmite sol were dried at 110 °C for 4 h and subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) by using TA branded SDT Q600 model device in order to examine the phase transformations of alumina and HAs behaviour against high temperature. DTA–TGA analyses were carried out under atmospheric conditions with 10 °C/min heating speed and 100 ml/min gas flow speed. Phases in the composite powders were detected by X-ray diffraction (XRD) analyses through monochromatic Cu-K_α radiation ($\lambda = 0.154$ nm) at Rigaku D/Max-2200/PC branded device. Fourier transform infrared spectroscopy (FTIR) analyses were performed with Perkin Elmer Precisely Spectrum One device and the KBr method. Microstructure images were obtained with Jeol branded JSM

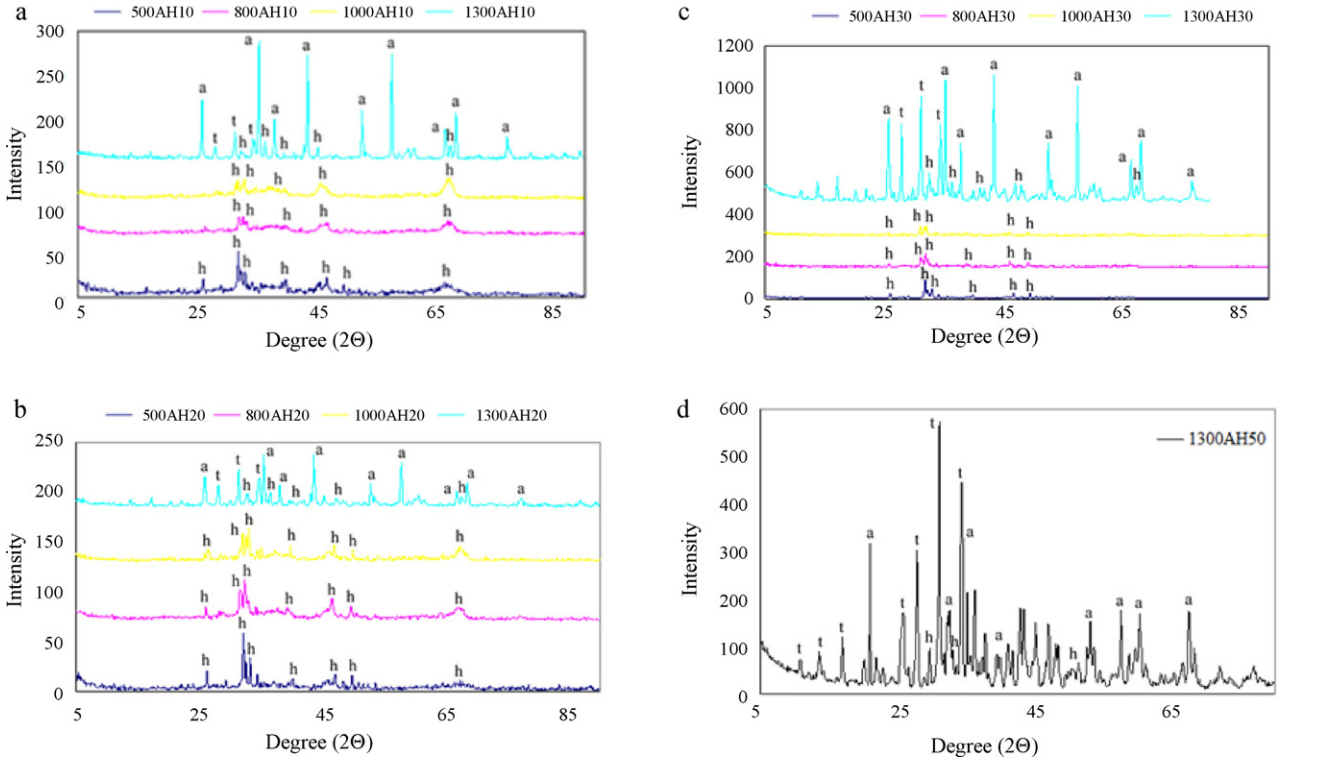


Fig. 2. XRD results of (a) 500AH10–800AH10–1000AH10–1300AH10, (b) 500AH20–800AH20–1000AH20–1300AH20, (c) 500AH30–800AH30–1000AH30–1300AH30 and (d) 1300AH50 samples. (a: alpha-Alumina, h: Bovine hydroxyapatite, t: Tricalcium phosphate) (a: PDF 74-1081, h: PDF 76-0694 and 89-6438, t: PDF 09-0169 and 70-2065).

6335F (field emission) model scanning electron microscobe (SEM) and phases in these images were identified with Inca branded energy dispersive spectroscopy (EDS) semi-quantitative elemental analysis system. Apparent porosites and bulk densities of the sintered composite pellets were determined with the experiments based on Archimedes principle.

3. Results and discussion

XRF chemical analysis results of the natural bone powders derived from bovine bones showed that; 19.74 wt% P and 39.12 wt% Ca elements were detected in the structure. With reference to this result, Ca/P weight ratio was calculated as 1.98 and this ratio is close to the Ca/P weight ratio of the stoichiometric hydroxyapatite which is 2.15.

From the DTA–TGA results as shown in Fig. 1, it was determined that at ∼150 and 450 °C evaporation of the solvent, organic groups, surface adsorbed water in the composite gel and crystal water of the boehmite (AlOOH) phase and at 200–600 °C removal of the Na-alginate organic phase from the system occurred. When the DTA–TGA results were compared with the literature data; transformation of boehmite phase to γ-alumina happens at 500–650 °C, γ-alumina phase to δ-alumina occurs at ∼800 °C, δ-alumina phase to θ-alumina happens at 900–1050 °C and θ-alumina phase to α-alumina, which is the only stable phase of alumina, is realized at 1250–1300 °C were proved. At 1250–1300 °C, a small amount of BHA decomposed and transformed into bioresorbable β-tricalcium phosphate (β-TCP). From the TGA curve of BHA in Fig. 1, it was observed that a rapid weight loss took place until ∼425 °C. With the increase of temperature, BHA partially dehydrated and transformed into oxyapatite ($Ca_{10}(PO_4)_6O$) at 1250–1300 °C. Oxyapatite decomposed with time so that TCP phase formed [33].

When the results of XRD analyses as shown in Fig. 2 were examined, only hydroxyapatite phase was detected in the powders obtained after the heat treatments at 500, 800 and 1000 °C. Since γ-Al_2O_3, δ-Al_2O_3, θ-Al_2O_3 are amorphous and unstable phases, they could not be detected with XRD analyses and hence were evaluated with DTA–TGA results and general literature data. HA, β-TCP and α-Al_2O_3 phases were identified in the powders produced after the heat treatment at 1300 °C. As seen from the results, there was not a chemical structure formed between alumina and HA. Stable α-Al_2O_3 phase was obtained at 1300 °C. However at this heat treatment temperature; a large amount of HA remained in its own structure while the rest of it decomposed, hence transformed into β-TCP. This decomposition reaction developed through the oxyapatite phase. Oxyapatite is a phase which forms by the slowly dehydration of HA at ∼1300 °C. Oxyapatite keeps its stability in dry environment conditions but it tends to transform into HA in moist environment conditions [33,34]. When oxyapatite decomposes, TCP and tetracalcium phosphate (TTCP) phases are formed. TTCP phase was not found in the powders obtained

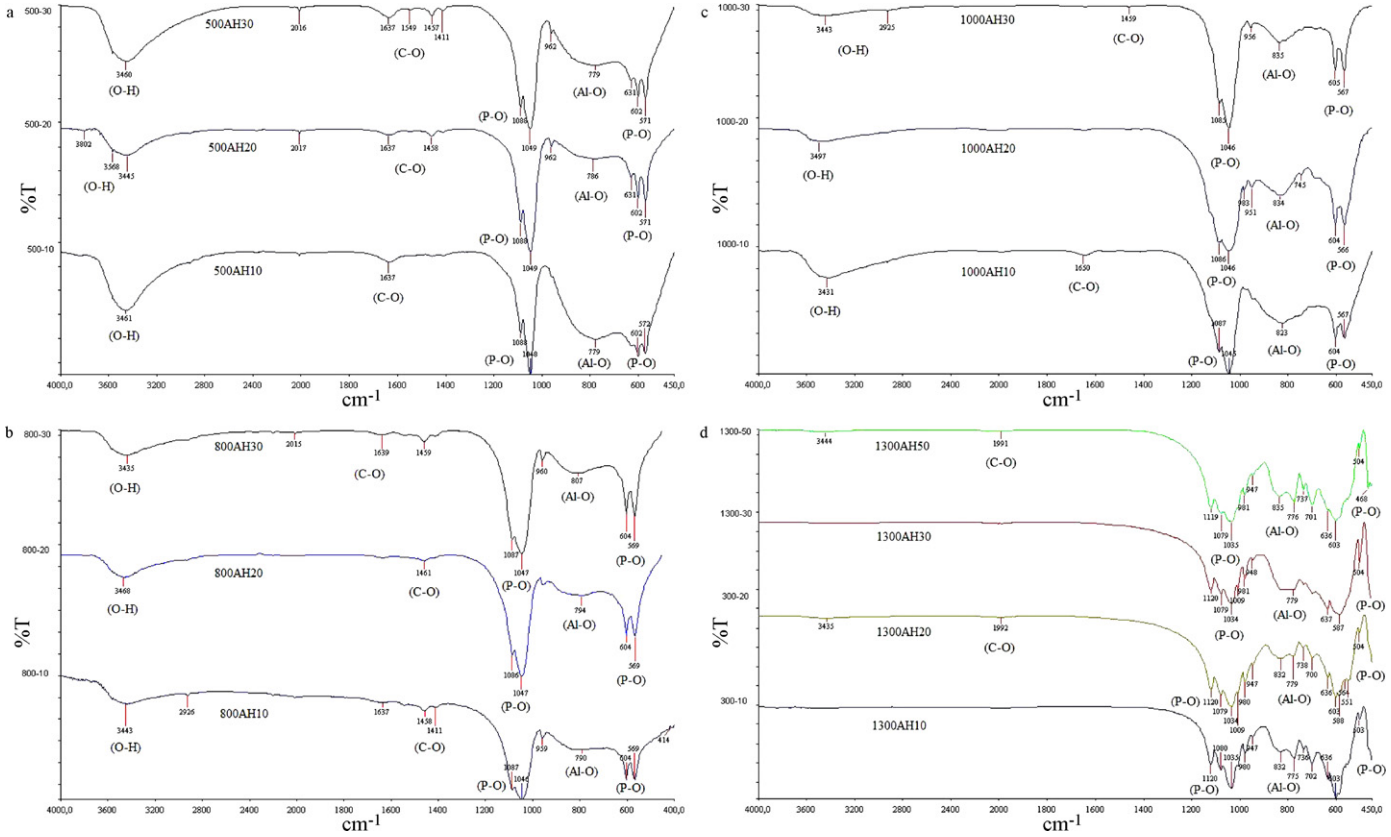


Fig. 3. FTIR results of composite powders; (a) 500AH10–500AH20–500AH30, (b) 800AH10–800AH20–800AH30, (c) 1000AH10–1000AH20–1000AH30 and (d) 1300AH10–1300AH20–1300AH30–1300AH50 samples.

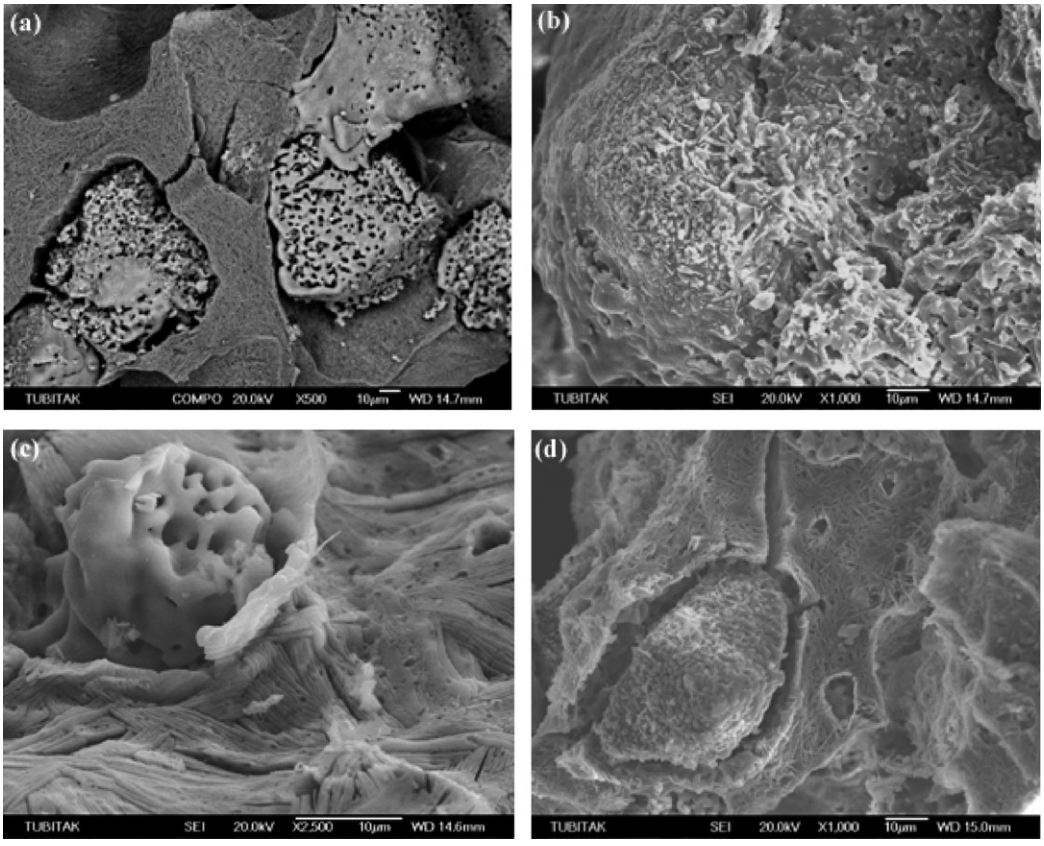
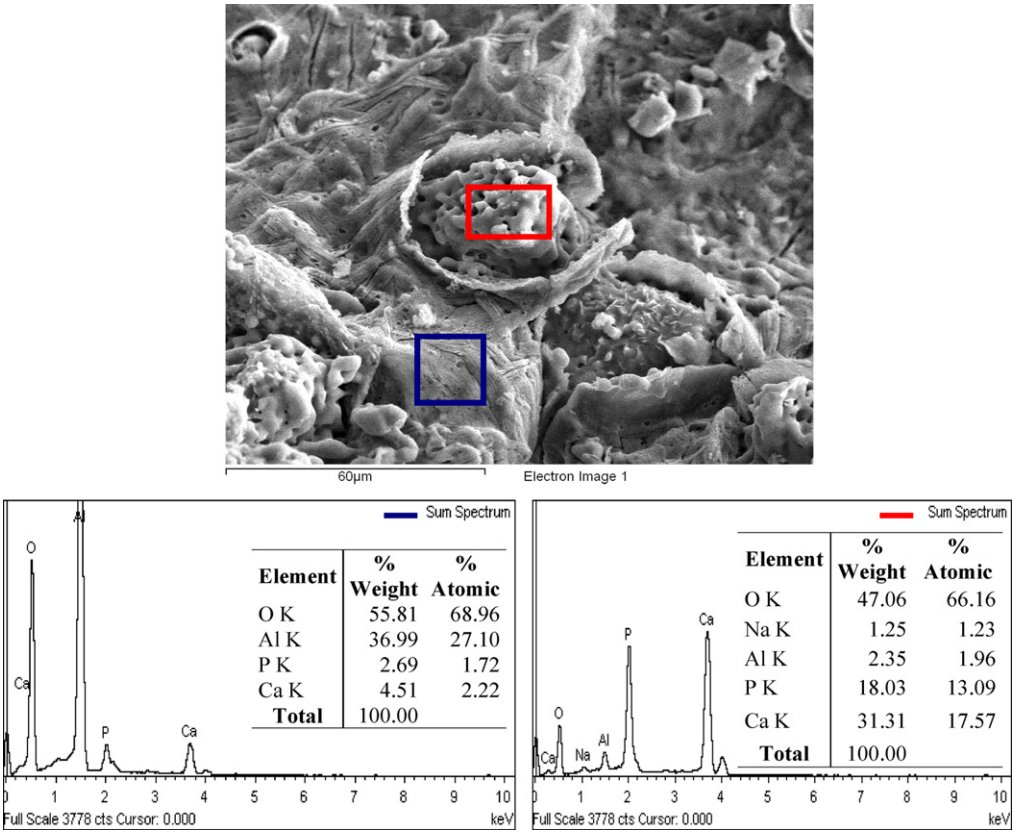


Fig. 4. SEM micrographs of composite powders; (a) 1300AH10 (×500), (b) 1300AH20 (×1000), (c) 1300AH30 (×2500) and (d) 1300AH50 (×1000).



Element	% Weight	% Atomic
O K	55.81	68.96
Al K	36.99	27.10
P K	2.69	1.72
Ca K	4.51	2.22
Total	100.00	

Element	% Weight	% Atomic
O K	47.06	66.16
Na K	1.25	1.23
Al K	2.35	1.96
P K	18.03	13.09
Ca K	31.31	17.57
Total	100.00	

Fig. 5. SEM micrograph and EDS results of 1300AH30 composite powders.

Table 2
Apparent porosities and bulk densities of 1300AH10, 1300AH20, 1300AH30 and 1300AH50 pellet samples and pure BHA pellets.

Sample	Apparent porosity (%)	Bulk density (g/cm^3)
1300AH10	38.29	2.046
1300AH20	43.43	1.971
1300AH30	43.33	1.977
1300AH50	39.00	1.937
BHA	3.40	2.603

after the heat treatment at 1300 °C. Therefore it can be reported that the decomposition stage was partially completed. β-TCP is a bioresorbable apatite based structure and can be used in biomedical applications. HA, the part that did not decompose, was composed of a composite structure with α-Al_2O_3 and β-TCP. In addition, according to the FTIR analyses as shown in Fig. 3; vibration peaks of (O–H), (C–O), (P–O) and (Al–O) bonds were determined.

SEM images of the composite powders are given in Fig. 4 and EDS analyses of 1300AH30 sample are shown in Fig. 5. With respect to the SEM images and EDS analyses; it was observed that alumina got a crater-like appearance in the alumina–BHA interface. It is thought that the removal of OH ions from the structure during the transformation of boehmite to alumina induced this type of appearance. Based on the same reason, big gaps were seen at the interfaces separating the phases. This indicates that the composite powders possess a porous structure due to these gaps remained between BHA particles and alumina matrix phase. The same case also clarifies the irregular and porous morphology of the alumina–BHA composite powders.

According to the apparent porosity and bulk density test results given in Table 2; it was found out that alumina–BHA composites possess a high amount of apparent porosity (∼38–44%) and relatively low densities (∼1.93–2.04 g/cm^3), as expected.

4. Conclusions

In this study, firstly a composite gel was obtained by the addition of BHA powders to the sol–gel derived boehmite sol and then porous composite powders were produced resulting from the heat treatments applied to the gel mixtures. Transformation to α-Al_2O_3 phase starting from boehmite sol was seamlessly completed and despite the presence of HA in the mixture, no chemical reactions were observed between HA and α-Al_2O_3 during this experimental period.

Porous materials can be used especially in the implants where load bearing capacity is not required such as in bone cement materials, in prostheses produced from bioresorbable materials and in drug–protein delivery/releasing systems [12]. It can be concluded that, the most important result of this study is the production of a highly porous biocomposite material composed of bioinert alumina, bioactive HA and bioresorbable β-TCP phases.

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