THERMAL BEHAVIOUR OF COMPOSITES ALUMINOSILICATE–CALCIUM PHOSPHATES

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Abstract

A new type of aluminosilicate matrix calcium phosphate crystallites composites (ACPC) was synthesized and studied for osseous bone applications. The room temperature synthesis of the aluminosilicate matrix and composites was described. Thermal treatments of compounds allowed the adaptability of some parameters (pH, porosity and mechanical properties). Structure of heat treated composites were characterized by XRD and FTIR. The influence of thermal treatment on the mechanical properties, the porosity and the pH was studied for two temperatures (250 and 500°C). Results evidenced the ability to control the pH, the high level of porosity ($\approx$70%) and the good mechanical properties, allowing to consider that ACPC are potential biomaterials for osseous bone application.

**Keywords:** aluminosilicate, mechanical properties, mineral composition, porosity, synthesis, thermal treatment

Introduction

In order to develop new type of potential biomaterials, we focused on the synthesis and the characterization of an aluminosilicate matrix calcium phosphate crystallites composites (ACPC). The influence of added calcium phosphate to an aluminosilicate matrix *vs*. thermal treatment was studied. Thermal treatments of those compounds highlight their behaviour at 250 and 500°C. The aluminosilicate belong to the geopolymer family and named GPS (GeoPolymer with high ratio of silicate Si/Al=21). The main idea was the optimization of the mechanical properties of compounds with calcium phosphate (well known for their good biological behaviour [1–3]. The choice of the aluminosilicate matrix was based on some previous works [4–6] which already demonstrated their utility. GPS presented an inorganic polymeric materials definited by an

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amorphous zeolitic framework because of their 3-D network structure [7, 8]. These materials were characterized by molecular ratios K/Si and Si/Al corresponding to a geopolymer with the following formulation:

$$Mn\{(-SiO_2)z-AlO_2\}n, wH_2O$$
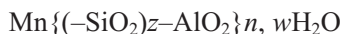
In this relation, M is a mono or divalent cation (like Na^+, K^+, Ca^{2+}…), z corresponds to the Si/Al ratio and varied between 1 and 35, n is the polycondensation degree and w varies as a function of hydratation of the aluminosilicate.

At room temperature, a depolymerized solution of potassium silicate was blended with SiO_2 and Al_2O_3. The resulting GPS was mixed with 13 mass% of calcium phosphate: TCP, HA, or an association of HA and TCP (60 and 40 mass%, respectively). Composites were polycondensed at 60°C. At this stage, composites presented high basic character which was a real disadvantage for future biological applications. For this reason, composites undergo thermal treatments at 250 and 500°C, the influence of these 2 temperatures of thermal treatment on the structure and on properties of pure GPS and composites was studied.

Materials and methods

GPS synthesis

The synthesis of the aluminosilicate matrix composite $Mn\{(-SiO_2)z-AlO_2\}n, wH_2O$ took place in three stages [8, 9]:

1 – 100 g of a potassium silicate solution K_2O, $3SiO_2$, $21H_2O$ was depolymerized by addition of 23.1 g KOH, using the following molar ratio [10] involving the molecular reactants $K_2O/SiO_2=0.8$. The complete depolymerization of the silicate by the action of KOH was obtained 24 h after at least, (t=0 corresponded to the addition time of KOH into K_2O, $3SiO_2$, $21H_2O$).

2 – 135 g of thermal silice (powder which contained 28.75 mass% Si and 1.72 mass% Al) was mixed with 100 g of previous depolymerized silicate solution, 10 mL of distilled water was also added, in order to optimized the homogenization. A silicate characterized by the following molecular ratio was obtained:

$$Si/Al=21 \text{ and } H_2O/K_2O=10$$

3 – This mixture stay 24 h long at –10°C, allowing to get a polycondensed silicate.

Composites (GPS/calcium phosphate) synthesis

Various composites were synthesized and named by the following notation: GPS X Y where X represents the calcium phosphate added and Y corresponds to the thermal treatment temperature (250 or 500°C). In this first study one of the main objective was to keep the geopolymer matrix properties (amorphous framework, porosity and mechanical properties) and to observe the influence of the addition of small mass of

calcium phosphate on the structure. Two commercial calcium phosphates were studied: hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and tri-calcium phosphate $Ca_3(PO_4)_2$.

Three composites (GPS/calcium phosphate) were made and heat-treated at two temperatures: 250 and 500°C.

– GPS with 13 mass% of hydroxyapatite (HA): GPS H

– GPS with 13 mass% of tri-calcium phosphate (TCP): GPS T

– GPS with 13 mass% of an association (60 mass% of HA and 40 mass% of TCP): GPS HT

The 13 mass% of each calcium phosphates (TCP, HA and their association) was added to the polycondensed silicate. After a good mixing, resulting composites were casted in Teflon® mould, covered with polyethylene thin films and heated at 60°C during 150 min for polymerization.

After polymerization, composites presented a high level of basicity due to the very basic conditions of synthesis. To be used as potential biomaterials, pH values of these composites must be close to the physiological pH values (maximum 8 pH units) to avoid luckless reactions in organisms. For this reason composites were submitted to two different thermal treatments [19, 20]:

– Thermal treatment at 250°C during 150 min: compounds named GPS X 250 (high and low rates of 2°C min^{-1}).

– Thermal treatment at 250°C for 150 min followed by heating at 500°C for 180 min: compounds named GPS X 500 (high and low rates of 2°C min^{-1}).

Physico-chemical characterizations

To characterize these materials, we studied their pH, crystalline structure and mechanical properties linked to their percentage of porosity.

– pH measurements of composites were obtained by immersion of 15 mg of fine grounded materials into distilled water. The solution was stirred and pH values were performed on pHmeter Orion 730. The influence of the addition of 13 mass% of several calcium phosphates and the action of thermal treatment on this parameter were studied.

– X-ray diffraction analyses were recorded on an INEL CPS120 diffractometer with a cured position sensitive detector ($CuK_{\alpha 1}$ radiation). X-ray diffraction was used to check the absence of any crystallized phases impurities which were the signature of a non complete reaction of polymerisation.

– Infra-red spectroscopy was performed on a Bruker Equinox 55/S Spectrometer. Samples were ground into fine particles about 300 to 500 meshes and pressed in KBr disks (mixture of 10 mass% of grinded material with 90 mass% of KBr). FTIR spectra were taken in the 4000–400 cm^{-1} region. This spectrometry gave information about the different chemical links which characterize the structure. We observed the calcium phosphate action and the influence of thermal treatment on the structure.

– The general morphology of composites was ascertained by JEOL 6301F Scanning Electron Microscope (SEM). SEM allowed a visual estimation of the interval of porosity size distribution, the shape and interconnection of pores.

– Mechanical tests were performed on cylinders of 6 mm diameter and 12 mm length in a compressive mode, on a Lloyd Instruments LR 50 K machine, using a piston displacement speed of 0.2 mm min^{-1}. The ratio of the maximal load value $F(N)$ to the surface $S(mm^2)$ gives the compressive strength σ_s (MPa).

– Percentage of open porosity was obtained by the following ratio :

$$\% \text{ porosity} = (1 - V_{geom}/V_{real}) \times 100$$

where V_{geom} (mm^3) is the geometric volume (6 mm diameter and 12 mm height for samples) and V_{real} (mm^3) is the real volume of sample, given by measurements in a helium gas pycnometer (Accupyc 1330, Micromeretics). The mistake due to potential closed porosity could be neglected because of the very high percentage of porosity of composites.

Results and discussion

pH measurements as function of thermal treatment (TTH)

TTH 250°C: Composites obtained after this thermal treatment presented pH values lower than pH value of reference (composites after polycondensation at 60°C were taken as reference). Any significant difference on pH values as a function of kind of calcium phosphate was observed (Fig. 1).
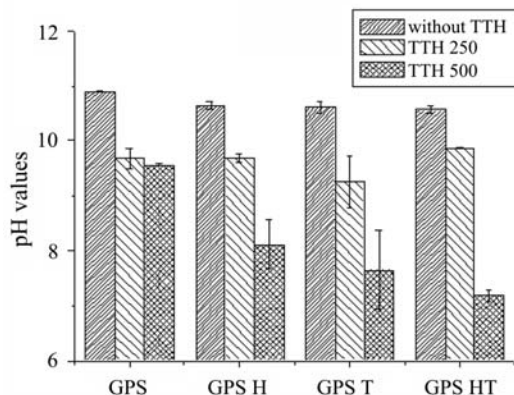

Fig. 1 pH of pure GPS matrix and composites as a function of thermal treatment

TTH 500°C: Results presented pH values (pH<8) lower than pH value of composites treated at 250°C. It could be explained by a dehydration of composites apart from the kind of calcium phosphate.

The synthesis of GPS matrix required very basic conditions, and the potential application of these materials as biomaterials compelled us to reduce pH values. On Fig. 1, pH values decreased with thermal treatment (TTH). The addition of various

calcium phosphates did not influence pH values neither at 250 or 500°C. The TTH at 500°C permitted to get composites with pH values near to the physiological pH, especially HT500 composite.

Crystalline structure of pure GPS and composites

Previous works [7, 11] have already shown that Geopolymer structure consisted in a disordered 3D-Network of short-range order materials. This high degree of disorder preclude the structure characterization. X-ray diffraction permitted to check the eventual presence of impurities phases. Moreover, X-ray diagram gave informations on the influence of thermal treatment on the structure of composites (polysialate/calcium phosphate).
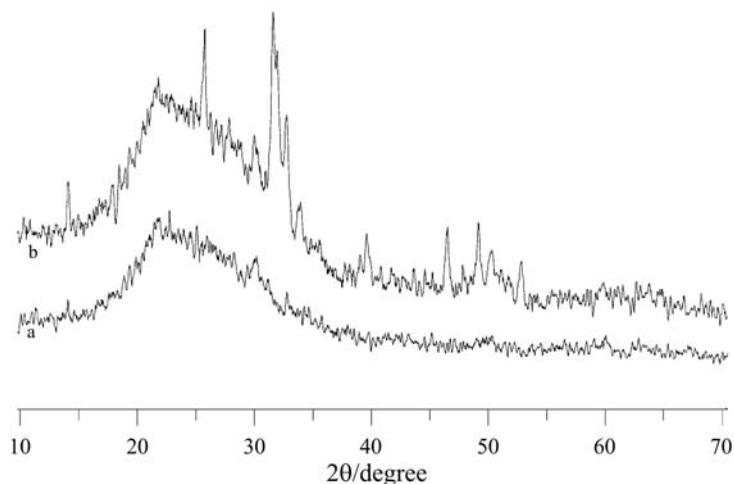

Fig. 2 XRD of a – pure GPS matrix and b – calcium phosphate composite GPS H after thermal treatment at 500°C

X-ray diffraction of the aluminosilicate (pure GPS) presented a diagram of an amorphous material, characterized by a diffuse halo between 16 and 38° 2θ and a weak SiO_2 impurity reflection (JCPDS 82-1561). Various thermal treatments were accountable of the leave of H_2O, but did not influence the structure of GPS, there was no crystallization even after the thermal treatment at 500°C (Fig. 2). The initial structure of pure GPS was not altered by the action of those two thermal treatments.

X-ray diffractograms of synthesized composites all presented a base line characterized by a diffuse halo between 16 and 38° 2θ corresponding to the amorphous matrix (GPS), the X-ray pattern of crystallized phosphate, and the weak SiO_2 impurity reflection (JCPDS 82-1561). The comparison between X-ray diffraction data of pure calcium phosphate (HA, TCP or their association) and diagram of corresponding composites did not shown any modifications of the structures of phosphate after their association with GPS. Composites structures were not influenced by thermal treat-

ments. Synthesized composites kept a two phases structure (a crystallized calcium phosphate phase into an amorphous GPS matrix) in the whole range of temperature studied. Figure 2 presented X-ray diagram of composite GPS H 500 to illustrate the association of GPS and calcium phosphate, GPS T 500 and GPS HT 500 were very similar and were not presented. To complete the structure characterization, samples were studied by FTIR in order to evaluate the eventual influence of calcium phosphate on the geopolymer structure.

Fourier transform infra red spectrometry of pure GPS and composites

FTIR spectra presented few absorption bands gathered in two ranges of wavelength: around 3500 and under 1700 cm^{-1}.

For pure GPS and composites, the main absorption bands observed were 3600, 1080–1040, 785 and 470 cm^{-1}, they characterized the GPS matrix. The broad band 1040 cm^{-1} was attributed to asymmetric stretching mode Si–O–(Si, Al) in SiO$_4$ and AlO$_4$ tetrahedra [12, 13]. The thermal treatment induced a change of the band position, due to a beginning of modification of the structure. The band at about 785 cm^{-1} related with the symmetric stretching mode of Si–O–(Si, Al) bond in SiO$_4$ and AlO$_4$ tetrahedra [12]. Bands located at 470 cm^{-1} corresponded to Si–O–Si or Si–O–Al bending mode [13, 14]. The OH band at 3600 cm^{-1} (stretching mode of vibration) [15] and bound water band at 1600 cm^{-1} [12] depended on thermal treatment: the decrease of their intensity was proportional to the increase of temperature of thermal treatment.

Moreover, for composites, the strong band at 1080 cm^{-1} corresponded to the superposition of the asymmetric stretching mode of Si–O–(Si, Al) of the GPS matrix with the asymmetric stretching mode of P–O of PO$_4^{3-}$ groups [16]. The absorption bands at 603 and 566 cm^{-1} due to the presence of phosphate [16, 17]. Positions of various bands did not move with the temperature, the structure of phosphate in the composite did not seem to be modified by thermal treatment. The main information was the verification of the dehydration of composites and the agreement with the XRD. This characterization would not be complete without the determination of porosity and mechanical properties in compression. These characteristics would determine the best composite for a forthcoming biologic evaluation (studies in-vitro and in-vivo) for potential applications in maxillo-facial or orthopedic surgery.

Porosity and mechanical properties studies vs. thermal treatment (TTH)

Porosity of pure GPS and composites

We focused on the variation of porosity and mechanical properties *vs*. thermal treatment. The statistical distribution of percentages of porosity has been realised using 15 samples for each compound at least.

After the thermal treatment at 250°C (TTH 250), pure GPS and composites presented a connected porosity composed of microporosity (pore sizes of few micrometers) and macroporosity (pores size up to 700 μm). Cavities partition were strong and compact, the size of pores was determined by SEM, Fig. 3 presented the morphology

of composite GPS H (GPS T and GPS HT were not presented because they were similar). The repartition of number of sample *vs*. percentage of porosity were presented on Fig. 4, distributions of percentages of composites porosity were analysed by a normal statistical distribution. The percentage of porosity of pure GPS was distributed between 74 and 84% with main values about 76 to 78% (Fig. 4). Calcium phosphates addition permitted the decrease of the range of porosity from [74–84%] to [68–78%]. The dispersion of results was due to the very big size of some pores, those pores were not present in the same proportion in each sample. Statistical curves permitted to underline that for composites, maximum distribution values were between 72 and 77% of porosity and distributions were very large (up to 20% of porosity).
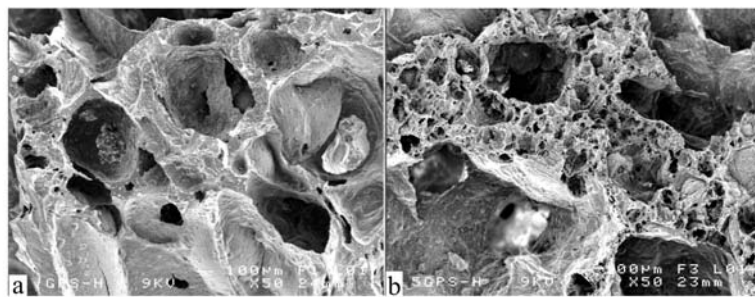

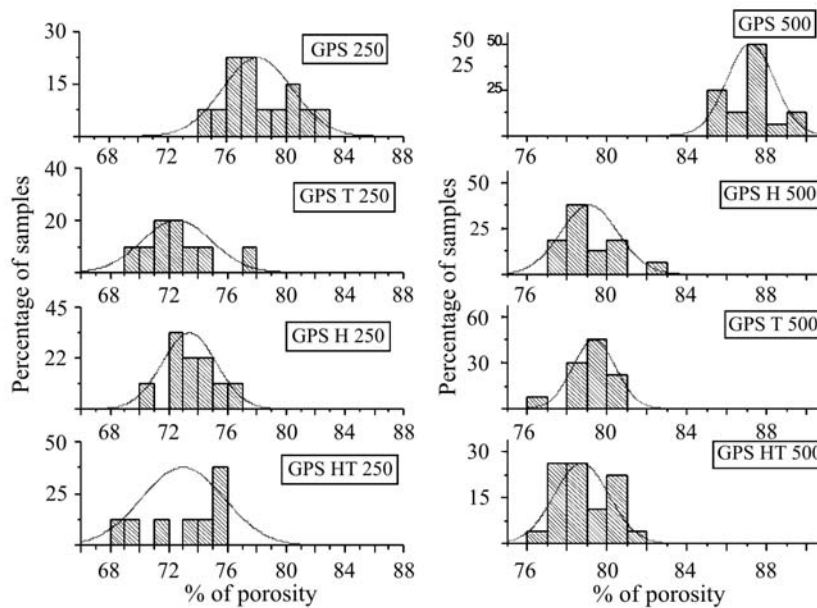**Fig. 3** SEM of composite GPS H a – after TTH 250 and b – after TTH 500

Fig. 4 Number of sample and normal distribution for pure GPS and composites *vs*. percentage of porosity after a thermal treatment at 250 and at 500°C

Thermal treatment TTH 500 produced pure GPS and composites always with connected porosity and with a wide range of pore size (less than 10 μm to more than 700 μm), but cavities partitions were now porous (Fig. 3), especially for composites. After the TTH 500 samples presented a better distribution of sample number *vs*. percentage of porosity. Microporosity development (due to the start of water) increased the percentage of porosity of composites (main values between 78 and 80% of porosity) and pure GPS (main value at 88% of porosity) (Fig. 4). After thermal treatment TTH 500, percentage of porosity distributions of composites were superposed and the distribution domain was 6% of porosity large. The type of calcium phosphate (HA or TCP) and their association did not influence the percentage of porosity. The addition of calcium phosphate to the GPS matrix precluded a total expansion and the thermal treatment at 500°C permitted the homogenization of the porosity of compounds.

Mechanical properties of pure GPS and composites

The compressive strength of composites as a function of TTH was given in Fig. 5. The addition of calcium phosphate to the GPS increased the compressive strength values after thermal treatment at 250 and 500°C, this augmentation was linked to the decrease of percentage of porosity. After the thermal treatment at 250°C, composites presented large percentage of porosity distribution, which explained the important distribution in compressive strength measurements. For a same percentage of calcium phosphate, GPS H 250 presented the most interesting result (1.9±0.6 MPa). For this temperature of thermal treatment, differences in the distributions of percentage of porosity (Fig. 4) did not allow a real comparison between composites. Composites which were heat treated at 500°C presented better mechanical results than those treated at 250°C, excepted for the pure GPS. Similar maximum of percentage of porosity (Fig. 4) enabled the comparison of their mechanical properties in compression. Higher compressive strengths were obtained for composite GPS H 500 (2.0±0.4 MPa) and GPS HT 500 (1.8±0.5 MPa). The study of mechanical property *vs*. temperature showed best results after the
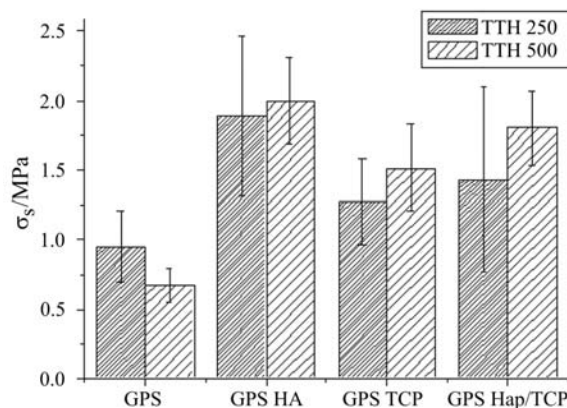

Fig. 5 Values of mechanical strength in compression as a function of thermal treatment

TTH 500 for all composites, the increase of percentage of porosity due to the higher temperature of treatment did not lower the mechanical behaviour of compounds. Thermal treatment at 500°C permitted to obtain very homogeneous composites whereas the thermal treatment at 250°C produced composites with irregular porosity. The very high level of porosity was accountable of low compressive strength values for all composites. According to the comparison between these values and [18], we suppose that with an appropriated porosity, mechanical properties would be very interesting. This preliminary mechanical study was one of our criteria to define the most interesting thermal treatment and the best association between GPS and calcium phosphate.

Conclusions

In order to characterize the influence of the thermal treatment and the addition of calcium phosphate into amorphous aluminosilicates, we studied physico-chemical properties of various compounds. The basicity was an important disadvantage and has been reduced significantly by the thermal treatment at 500°C. This TTH permitted to get homogeneous materials with high degree of macroporosity (higher than 70%). This first study of the association between GPS and calcium phosphate and the thermal treatment was useful to definite the best compromise percentage of porosity/mechanical properties. We yet for see to study the influence of molecular ratio K_2O/SiO_2 and the mass% of among calcium phosphate on the structure, mechanical properties and porosity. Best composites (from a physico-chemical view point) would be next assess by biological experiments, their cytotoxicity would be appraised by an in-vitro biological test, before an in-vivo evaluation.

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