Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 323–329

INFRARED AND NUCLEAR MAGNETIC RESONANCE STRUCTURAL STUDIES *vs*. THERMAL TREATMENT OF GEOPOLYMERS/BIPHASIC CALCIUM PHOSPHATES

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In biomaterial field, the introduction of new types of composites presents a great interest for orthopaedic surgeons. In this work, geopolymers which are a family of aluminosilicates were synthesised and mixed with biphasic mixture (hydroxyapatite and of tricalcic phosphate).

The optimised thermal treatment causes the reduction of pH to 7 units and favours the expansion of composites. Consequently, the increasing of porosity percentage was induced. These properties offer a good opportunity for applied composite as potential osseous biomaterial. To study the consequences of thermal treatment in the initial amorphous structure of composites some physico-chemical techniques like SEM, MAS-NMR and FTIR were employed. These methods permitted to evaluate the porosity, different links in composites and contributions of different groups of Si and Al before and after thermal treatment.

Keywords: *aluminosilicate, biphasic, hydroxyapatite, orthopaedic surgeons, porosity, structure, thermal treatment, tricalcic calcium*

Introduction

Geopolymers noted GPS result from the synthesis of an alkali silicate and powdery oxides of aluminium and silicon at a temperature lower than 100°C [1]. The geopolymers can be assimilated to mineral polymers that present a good stability and good mechanical properties with respect to the temperature, and withstand well to acids and several potentially damaging liquids [2]. They are characterised by a polymeric structure, which represent a succession of SiO_4 and AlO_4 tetrahedrons [3]. This network is related to one of some zeolites but defer by an amorphous structure [4].

The different types of geopolymers are characterised by the Si/Al ratio. The addition of loads to the geopolymer matrix reinforces their mechanical properties.

In this work, we were interested in the associations between the GPS and the calcium phosphates (Hydroxyapatite HA: $Ca_{10}(PO_4)_6(OH)_2$ and phosphate tricalcic TCP: $Ca_3(PO_4)_2$) in order to determine the possibilities to use geopolymers as precursor to biomaterials [5]. The calcium phosphates present some biological advantages. They are widely applied as osteoconductors ceramics [6, 7].

The compounds studied in this work are made of geopolymers GPS associated to a biphasic mixture 13% mass of calcium phosphate (HA and TCP). Compounds have been stocked previously to –10°C during at least 6 h. Synthesis of the composites was described in our previous works [8].

Different synthesised compounds were heat treated at two temperatures and studied by several physico-chemical methods in order to determine the best composite destined for the ‘in vitro’ and the ‘in vivo’ evaluations for applications in biomaterials field.

The characterisation of the composites geopolymers/calcium phosphates used in this work has been done by a measure of the granulometry in different materials, by the morphology survey achieved by scanning electronic microscopy (SEM) and by structural studies insured with nuclear magnetic resonance (MAS-NMR) and with Fourier transformed infrared (FTIR).

Experimental

Materials and method

Geopolymers were characterised by molecular ratios of K_2O/SiO_2 and Si/Al. The resulting GPS was mixed with 13% mass of biphasic material composed by HA and TCP, respectively, at 60 and 40%. In this work, K_2O/SiO_2 ratio was 0.54 and Si/Al ratio of 21. The following notation was applied in this work: pure geopolymers: G54 and composite G54HT. Obtained samples present a pH of about 10 units. To reduce this parameter near physiological pH of about 7, com-

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1388–6150/$20.00

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pounds were heat treated at 250 and 500°C. To evaluate the influence of thermal treatment, compounds were studied by several physico-chemical methods like laser granulometry, MAM-NMR and FTIR.

Laser granulometry measurements

Laser granulometry used in this work permits to define the middle size of the elementary particles of powders used for the synthesis and to present their statistical distribution.

Analysed powder was mixed to a chemical dispersing and track to the ultrasonic sounds in order to break the agglomerates. The suspension is then placed in the device of the granulometer, which contains water. A laser beam is directed toward the particles. COULTER granulometer LS 130 was employed for this study.

Results permit to get the distribution of the number of particles according to their occupied volumes. The software assimilates the grains in spheres whose diameter is indicated in the abscissa axis.

Thermal treatment

Composites geopolymers/calcium phosphates present pH values superior than 10 after the synthesis. For use like biomaterial, it is suitable to have pH values of about 7 units which is the physiological value. In our previous works [5, 8], compounds of PSS with a ratio Si/Al=2, associated to calcium phosphates had a pH>10. They were heat treated at 750° to obtained pH value neighbouring of 7 units. At this temperature, there are partial fusion of the geopolymer matrix and apparition of new crystalline phases [8].

A thermogravimetric analysis was achieved on the composite G54 (Si/Al=21) associated to the calcium phosphates HA and TCP (noted HT). The goal was being to study the loss in water of the materials *vs*. thermal treatment. This study permitted to refine the research of the adequate temperatures of thermal treatment landings.

The GPS compounds have been weighed then placed in skiffs made of platinum under nitrogen flux. Interval of temperature understood between the ambient temperature and 800°C was investigated in order to avoid the compound vitrification area. The temperature ramp rate has been set to 5°C per minute. Measurements have been made with thermobalance Setaram Labsys TG-DSC 1600.

Morphology

The percentage of porosity is an important criterion for assessing of the potential use of these compounds as biomaterials. The percentages of porosity were studied in the pure geopolymers and composites according to the thermal treatment.

The percentages of porosities have been calculated according to the following relation:

$$P=(1-dg/dr)\cdot 100$$

where P – percentage of porosity, dg – geometric density calculated for cylindrical samples with diameter of 6 mm and height of 12 mm, dr – real density of the material measured with the help of a pycnometer to helium Battery PYC 1330.

MAS-NMR method

Compounds were ground and introduced into zirconia rotors of 4 mm in diameter. High-resolution solid state NMR experiments were achieved at room temperature and pressure using a Bruker MAS spectrometer ASX300(7T). Different experimental parameters were described in our previous works [9]. The shifts (ppm) have been calculated from various references. ^{29}Si and ^{27}Al spectra have been fitted with dm 2002, a MAS-NMR software developed by Massiot [10].

FTIR principle

The infrared method permits to define the different types of links in the compounds. The different constituent groups of matter possess levels of vibrations *vs*. energies.

Compounds have been ground finely, mixed to 90% in mass of KBr then hurried in order to obtain transparent samples. An infrared incidental beam is sent through the sample. The obtained spectra present bands which correspond to the absorption bands characteristic of different links in the compound. FTIR method permits to have a systematic survey of the present links in our composites. It permits to discover possible modifications following the thermal treatments at 250 and 500°C.The infrared studies have been achieved on an interferometer to transmission of Fourier Bomem-Michelson 100.

Results and discussion

Laser granulometry measurements

The obtained curves present the occupied volume by each class of particles noted (volume diff%) and the total occupied volume by the powder noted (volume cum%).

Figure 1 (thermal silica) presents the curve of the distributions according to the particles size (noted volume diff%). This curve presents a distribution that spreads on about hundred μm (0.3–100 μm). Most of the grains are about 10 μm in diameter. The curve shouldering toward 100 μm indicates the presence of big particles (visible on the SEM pictures).

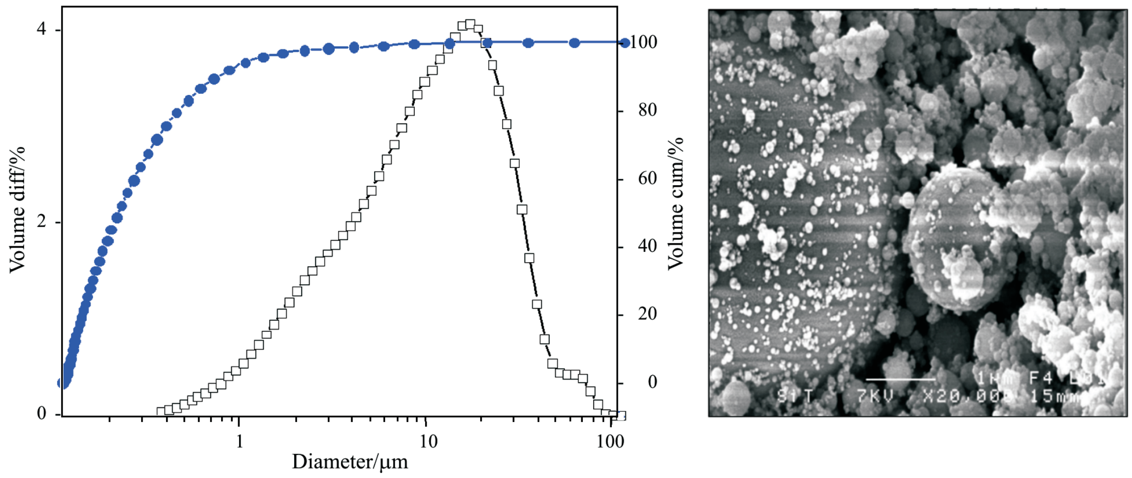

Fig. 1 Granulometry and morphology SEM (×20 000) of thermal silica

Figures 2 and 3 (respectively, TCP and HA) present less large distributions than the thermal silica with diameters from about 0.3 to 40 µm. HA presents the finest granulometry, with most particles with a diameter between 3 and 4 µm. Particle sizes of about 10 µm of diameter subsist after the ultrasonic treatment (Fig. 2).

TCP presents a medium granulometry of 10 µm, the sizes distribution of the grains is more regular than HA.

The set of the powders used have some granulometries lower to the hundred of µm. The values representation of the volume accumulated in % (noted volume cum%) for each of the three figures present the similar rates, the least strong slope is observed for the thermal silica.

Determination of thermal treatment temperatures

Figure 4 represents the evolution of the mass linked to a departure of water according to the temperature. It shows three different zones:

- From 25 to 110°C, the geopolymer looses a first part of its water. This region will not be studied any more in detail because there is not increase of the porosity percentage.
- From 110 to about 350°C, the material undergoes a second loss of water. In this zone the expansion of the materials was observed.
- Above 350°C, the material undergoes further modifications.

Some exploratory tests highlight that the geopolymers characterized by a ratio Si/Al=21 is expanded by heating thus to materials with a porosity of about 90%. This expansion takes place at 250°C, it decreases as a function of the added calcium phosphate HT. This porosity present some advantages for applications as biomaterials. In this work, the choice of the thermal treatment has been conducted by three criteria:

- the pH of the composite geopolymers/calcium phosphates HT
- the maintenance of the composite structure
- the porosity percentage advantage.

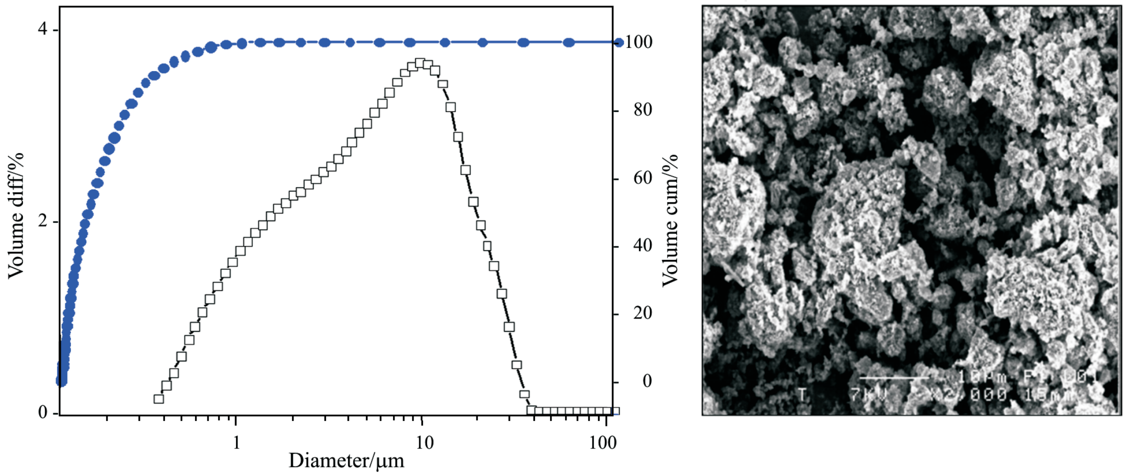

Fig. 2 Granulometry and morphology SEM (×2000) of tricalcic phosphate TCP

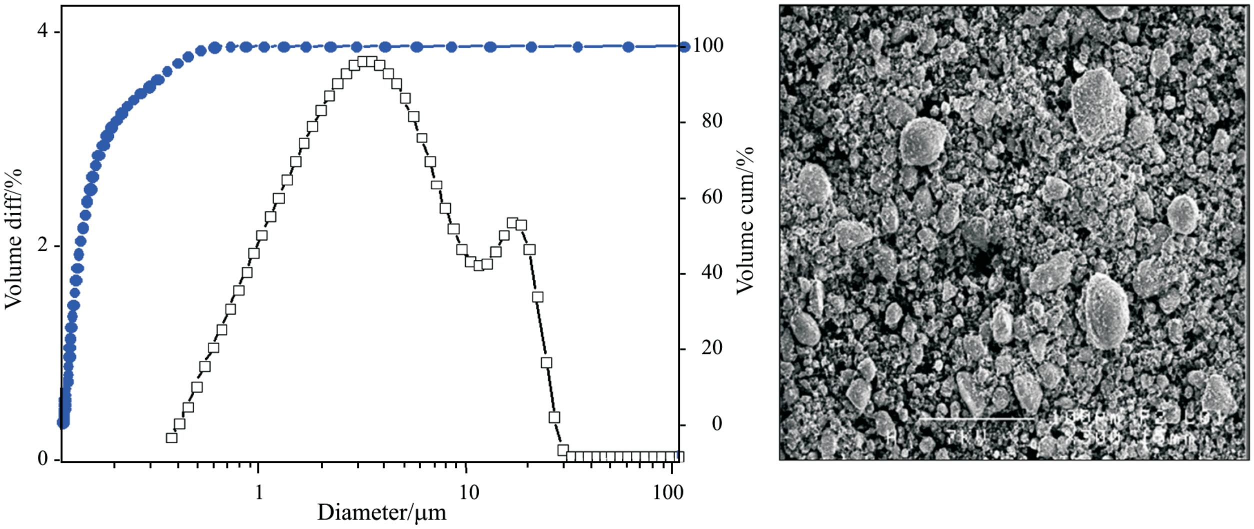

Fig. 3 Granulometry and morphology of HA

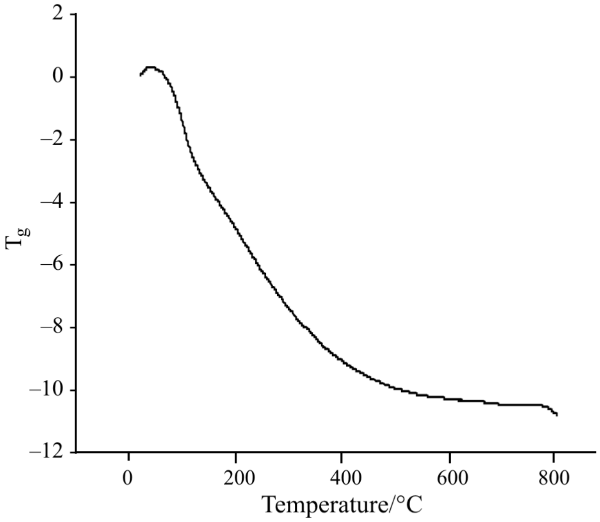

Fig. 4 Thermogravimetric analysis of pure geopolymer from 15 to 800°C

Two thermal treatment temperatures have been chosen. They permit to keep the initial amorphous geopolymer matrix (identical to the structure before thermal treatment).

The first temperature of treatment has been set to 250°C, this temperature permits the expansion of the composite. In this condition compounds are noted G54HT_250.

The second temperature of treatment was 500°C. This temperature is low enough to permit the expansion of the geopolymers without crystallization of the matrix. Under these conditions, compounds are noted G54HT_500.

The two thermal treatments applied in this work 250 and 500°C are described in Table 1.

SEM and morphology evaluation

The K_2O/SiO_2 ratio of 0.54 applied to the composite G54HT present percentages of porosities lower than the values of the pure geopolymers G54.

After the thermal treatment at 250°C, the morphology of the composite G54HT_250 is very close to the one of the pure geopolymers G54 (Figs 5 and 6). The composites present numerous cavities in the compact partitions. The pore size spreads from some µm to a few hundreds µm.

After thermal treatment at 500°C, the partitions of the geopolymers are porous, the pore sizes are of about some µm (for the partitions) to a few hundreds microns (for the cavities) (Fig. 6).

The morphology of the composite G54HT_500 is very close to the one of the pure geopolymers G54. Composites present numerous cavities in the partitions become porous. Compounds present micro and macro porosity (Figs 3, 10).

The elevation of the thermal treatment induces the increasing of this important parameter in all samples.

Table 1 THT 250 and THT 500 thermal treatments

	T_{start}/°C	Launching 1	Landing 1	Launching 2	Landing 2	Launching 3
THT 250	25	2°C min^{-1}	250°C 180 min	free	–	–
THT 500	25	2°C min^{-1}	250°C 120 min	2°C min^{-1}	500°C 180 min	free

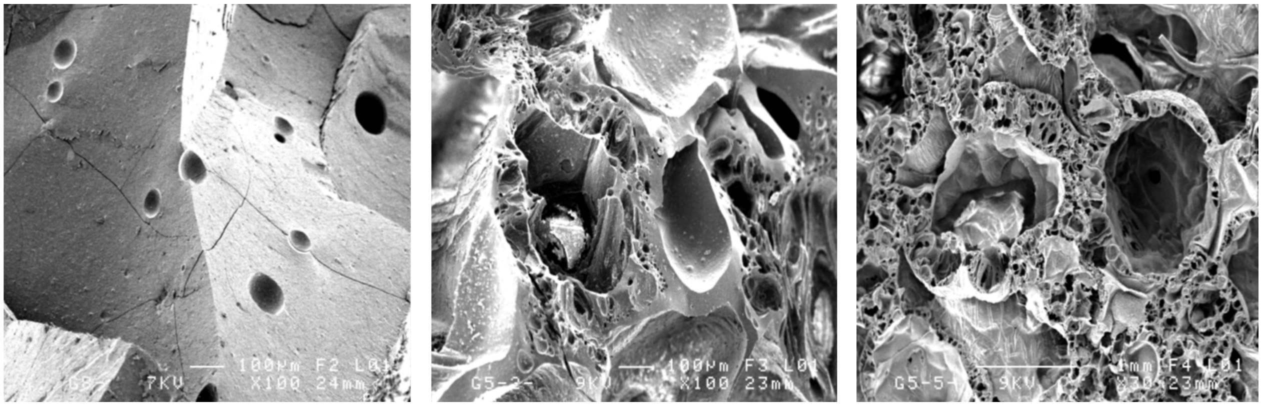

Fig. 5 Pure geopolymer G54 and thermal treatment: G54_250 and G54_500

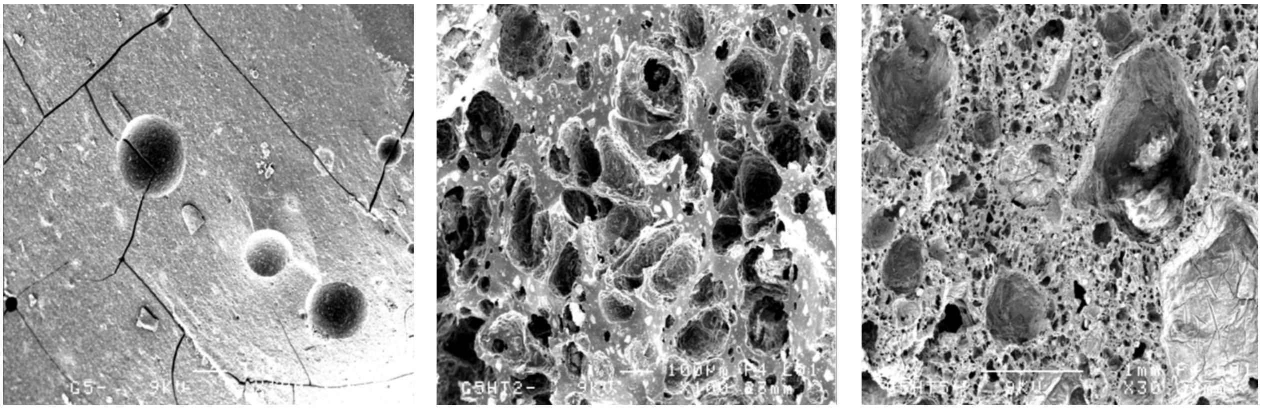

Fig. 6 Composite G54HT and thermal treatment G54HT_250 and G54HT_500

Structural studies vs. thermal treatment by MAS-NMR method

MAS-NMR of silicon

Figure 7 shows that after thermal treatment at 250°C, the order of abundance of the different contributions is identical to the one of the untreated composites (Q_4(Q_{4-4} and Q_{4-3})>Q_3>Q_2) for the composite G54HT.

The increase of the treatment temperature at 500°C induces an important modification of the structure. An inversion of proportions was observed, the Q_3 groups become minority.

The spectrum of the composites G54HT_500 (treated at 500°C). The model presented on the same figure is the sum of four contributions already observed for the composites before thermal treatment.

MAS-NMR of aluminium

The comparison between untreated and treated composites shows that the proportion of AlO_4 increases *vs*. the thermal treatment temperature (AlO_4 (G54HT) = 48.9%, AlO_4 (G54HT_250) = 73% and AlO_4 (G54HT_500) = 89.6%) (Fig. 8).

In the spectrum of the composite G54HT_500 after a thermal treatment at 500°C, three contributions (AlO_4, AlO_5 and AlO_6) observed already for the compounds before thermal treatment permitted to get the model.

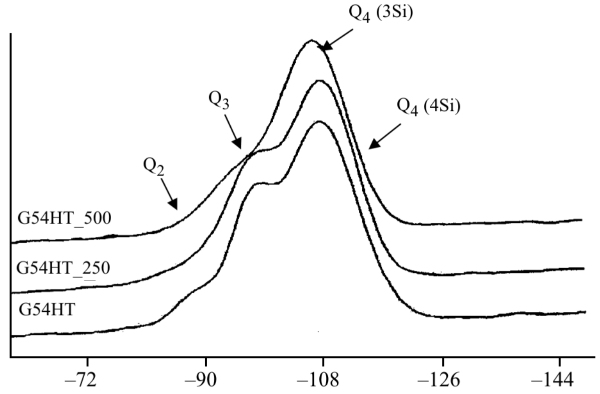

Fig. 7 MAS-NMR of Si in G54HT, G54HT_250 and G54HT_500

By comparison with the pure geopolymers in the same conditions of thermal treatment, the composites present a number more important of AlO_4 and AlO_6.

The two thermal treatments 250 and 500°C applied to the geopolymers and to the composites do not modify significantly the silicon and aluminium environments. The Si Q_4 and the AlO_4 remain majority.

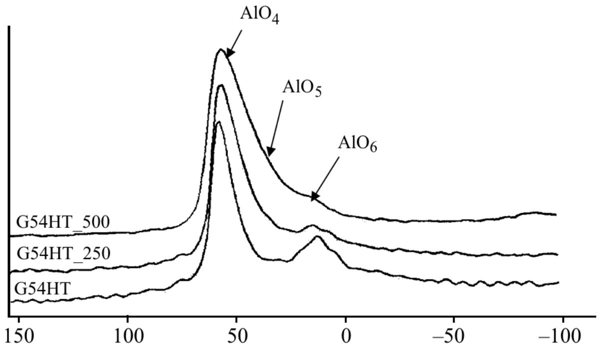

Fig. 8 MAS-NMR of Al in G54HT, G54HT_250 and G54HT_500

The increase of the treatment temperature induces a rearrangement between the ramifications and the chains (reduction of the Si Q_3 instead of the Q_2 units).

At 250°C the samples undergo expansion and offer a high percentage of porosities, superior to 60%. This phenomenon is accompanied with a reduction of the quantity of protons in the samples (not presented in this work).

This phenomenon is amplified for the compounds, which had been submitted to thermal treatment at 500°C.

After the thermal treatment at 500°C, the composite G54HT_500 presents a high proportion in AlO_4 and Si Q_4. It also presents the weakest proportion in AlO_5.

Structural studies vs. thermal treatment by FTIR method

The bands at 3500 and 1600 cm^{-1} presented in Fig. 9, show the hydration of compounds G54.

The other bands are located in the region of the weak wavenumbers (1100–450 cm^{-1}). The bands of vibration towards 1040 and 785 cm^{-1} is assigned to the asymmetric and symmetrical vibrations respectively (strenching mode) Si–O–(Si,Al) of the AlO_4 tetrahedrons and SiO_4 [11, 12].

The absorption band observed for each compound toward 470 cm^{-1} is assigned to the vibrations (bending mode) of Si–O–Si and Si–O–Al [13].

Figure 10 presents the absorption spectra of the different composites geopolymers/phosphates of calcium G54HT. The absorption bands observed are classified in several categories:

- The absorption bands characteristic for the structure of the constituent aluminosilicate in the matrix 1040, 800 and 470 cm^{-1}.
- The absorption bands corresponding to the hydration of the compounds, to 3500 [13] and 1600 cm^{-1} [14]. These bands were present in the pure geopolymers.
- The absorption bands characteristics for the calcium phosphates HT. The absorption band at 1080 cm^{-1} characteristic for the links (strenching fashion) P–O of the PO_4^{3-} groups [15, 16] superposed with absorption band toward 1040 cm^{-1} of the geopolymers. The absorption bands 603 and 566 cm^{-1} appear with the introduction of the calcium phosphates HT.

The FTIR spectra of pure geopolymers treated at 250 and 500°C show the same absorption bands before the thermal treatment was observed.

The increase of the thermal treatment temperature induces the reduction of the intensities of the bands toward 3500 and 1600 cm^{-1} (OH groups).

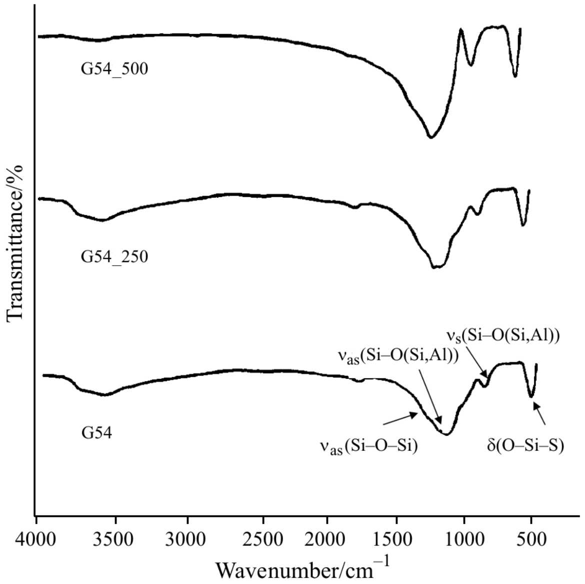

Fig. 9 Infrared spectra of G54 and thermal treatment G54_250 and G54_500

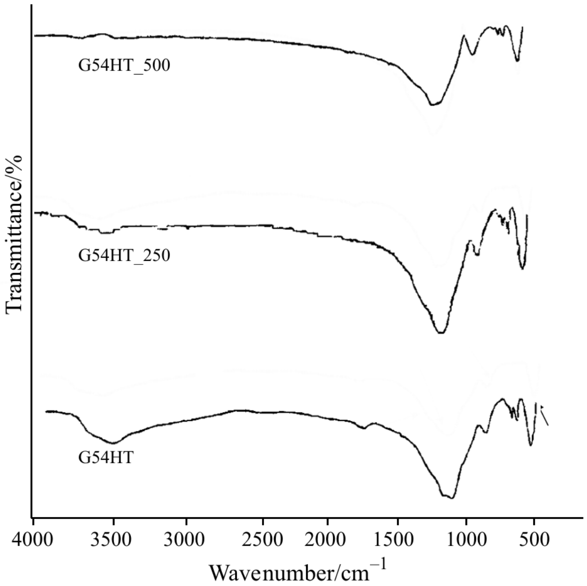

Fig. 10 Infrared spectra of G54HT and thermal treatment G54HT_250 and G54HT_500

The influence of the thermal treatment is negligible, the composites treated at 250 and 500°C present the same bands as the samples before thermal treatment.

- The absorption bands at 1040, 800 and 470 cm^{-1} are characteristic for the aluminosilicate structure.
- The absorption bands 1080, 603 and 566 cm^{-1} appear with the introduction of the calcium phosphates HT.

The influence of the thermal treatment is observed in the intensity of the characteristic bands of the OH groups (3500 and 1600 cm^{-1}).

According to other studies [17, 18], obtained result of structural studies show the importance of thermal treatment of composites. Applied of geopolymers as potential biomaterials offer significant opportunity and broaden the field of applications for filling or substitution materials [19–22].

Conclusions

In this study, we were interested in the synthesis and the characterization of geopolymer material (characterised by molar ratios $K_2O/SiO_2=0.54$ and Si/Al=21) and of composites geopolymers associated with biphasic calcium phosphate HT.

The main results concerning the geopolymer are pH value remaining higher than 10 after synthesis without any detectable structural modification. The geopolymers present an amorphous structure consisting in catenated SiO_4 tetrahedrons, which are reticulated by tetracoordinated aluminium.

Following the thermal treatments, physico-chemical characterisation of pure geopolymers and composites were carried out with SEM, MAS-NMR and FTIR techniques.

MAS-NMR studies of the compounds confirm the departure of water and highlight a rearrangement of the silicon atoms. These modifications observed by MAS-NMR are associated to an important increase of the percentage of porosity, in relation with the thermal treatment undergone by the compounds. FTIR spectra show that the thermal treatment at 250 and 500°C offers some advantages corresponding the decreasing of pH value and the increasing of porosity necessary for applications of these materials as biomaterials without any alteration of their initially macroscopic amorphous structure.

The preliminary ‘in-vitro’ and ‘in vivo’ experiments were carried out with G54 and G54HT_500 compounds. The first results present good bone bonding and some encouraging phenomena.

References

1 J. Davidovits and M. Davidovits, Patent n° EP 0815064 B1, 1996, p. 1.
2 J. C. Swanepoel, Stridum Appl. Geochem., 17 (2002) 1143.
3 J. Davidovits, International Conference on Alkaline Cements and Concretes, (1994) 131.
4 J. G. S. Van Jaarsveld and J. S. J. Van Deventer, Miner. Eng., 10 (1999) 659.
5 A. C. Derrien, H. Oudadesse, J. C Sangleboeuf, P. Briard and A. Lucas, J. Therm. Anal. Cal., 75 (2004) 937.
6 M. Vallet Regi, J. Chem. Soc., Ed. by Dalton Trans., (2001) 97.
7 K. De Groot, The centennial Memorial Issue of the Ceramic Society of Japan, 99 (1991) 943.
8 M. Zoulgami, Thèse d’Université, N° 2534, Université de Rennes 1, Septembre 2001.
9 M. Zoulgami, A. Lucas, P. Briard, J. Gaudé and H. Oudadesse, Eur. Phys. J. AP, 19 (2002) 173.
10 A. C. Derrien, Thèse d’Université, N° 3042, Université de Rennes 1, Octobre 2004.
11 J. J. Videau, J.Etourneau, J. Rocherulle, P. Verdier and Y. Laurent, J. Eur. Ceram. Soc., 17 (1997) 1955.
12 L. G. Hwa, S. L. Hwang and L. C. Liu, J. Non-Cryst. Solids, 238 (1998) 193.
13 E. M. Flanigen, H. Khatami and H. A. Szimanski, Infrared Advances in Chem. Series, R. F. Gould Ed., Amer. Chem. Soc., 101 (1971) 201.
14 A. M. Efimov and V. G. Pogareva, J. Non-Cryst. Solids, 275 (2000) 189.
15 R. Ternane, M. Cohen-Adad, G. Panczer, C. Goutaudier, N. Kbir-Ariguib, M. Trabeloi-Ayedi, P. Florian and D. Massiot, J. Alloys Compd., 333 (2002) 62.
16 A. Belkebir, J. Rocha, A. P. Esculcas, P. Berthet, B. Gilbert, Z. Gabelica, G. Llabres, S. Wijzen and A. Rulmont, Spectrochim. Acta A, 56 (2000) 435.
17 M. Ciecinska, J. Therm. Anal. Cal., 72 (2003) 199.
18 I. Wacławska and L. Stoch, J. Therm. Anal. Cal., 65 (2001) 141.
19 E. Chassot, H. Oudadesse, J. Irigaray, E. Curis and S. Benazeth, J. Appl. Phys., 90 (2001) 6440.
20 H. Oudadesse, J. L. Irigaray, Y. Barbotteau, V. Brun and Ph. Moretto, NIM, 190 (2002) 458.
21 A. C. Derrien, H. Oudadesse, S. Martin, A. Lucas-Girot, G. Cathelineau, T. Sauvage and G. Blondiaux, NIM, 226 (2004) 281.
22 H. Oudadesse, A. C. Derrien, A. Lucas-Girot, S. Martin, G. Cathelineau, T. Sauvage and G. Blondiaux, Instrum. Sci. Technol., 32 (2004) 545.

Received: January 28, 2005
In revised form: March 3, 2005

DOI: 10.1007/s10973-005-6890-6