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Surface and interface investigation of aluminosilicate biomaterial by the "*in vivo*" experiments

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ABSTRACT

Porous mixtures of aluminosilicate/calcium phosphate have been studied for biomaterials applications. Aluminosilicates formed with an inorganic polymeric constitution present amorphous zeolites because of their 3D network structure and present the ability to link to bone matrix. Amorphous geopolymers of the potassium–poly(sialate)–nanopolymer type were synthesised at low temperature and studied for their use as potential biomaterials. They were mixed with 13% weight of calcium phosphate like biphasic hydroxyapatite and β-tricalcium phosphate. In this study, "*in vivo*" experiments were monitored to evaluate the biocompatibility, the surface and the interface behaviour of these composites when used as bone implants. Moreover, it has been demonstrated using histological and physicochemical studies that the developed materials exhibited a remarkable bone bonding when implanted in a rabbit's thighbone for a period of 1 month. The easy synthesis conditions (low temperature) of this composite and the fast intimate links with bone constitute an improvement of synthetic bone graft biomaterial.

1. Introduction

In the biomaterials field, some silicates like bioactive glasses [1], calcium phosphate [2,3], aragonite [4], are successfully applied in bony surgery. The numerous synthetic aluminosilicates [5,6], possess chemical properties which offer employment as bone graft biomaterial. In this work, amorphous geopolymers of the potassium–poly(sialate)–nanopolymer type with a mole ratio Si/Al = 31 were studied for their use as potential biomaterials in collaboration with CORDI society (France). Obtained aluminosilicates are in the amorphous zeolite form because of their 3D network structure made by the succession of SiO_4 tetrahedral periodically replaced by an AlO_4 tetrahedron. This study is focused on composite resulting from associations between aluminosilicate with molecular ratio Si/Al = 31 and 13 wt.% of calcium phosphates like a biphasic hydroxyapatite (HA) and tricalcium phosphate (β-TCP) chosen for its high biocompatibility and because it well mimic the mineral composition of bone [7]. The weight percentage of calcium phosphate was fixed at 13% in order to get good compromise between porosity and compressive strength after heating. There are notified G54HT_500 [5,8]. Surfaces and interfaces of obtained compounds were characterised by several physicochemical and histological studies after the "*in vivo*" experiments.

2. Materials and methods

2.1. Material synthesis

Aluminosilicates were prepared at ambient temperature by mixing dehydrated kaolinite (metakaolin), potassium silicate, concentrated potassium hydroxide and water. The resulting product of this chemical reaction is a strongly basic bulky solid polymer. The synthesis of aluminosilicate named also geopolymer took place in three parts. At first, KOH was added to a potassium silicate (K_2O, $3SiO_2$, $21H_2O$). The resulting solution was mixed with SiO_2 and Al_2O_3. The obtained compounds were characterised by the K_2O/SiO_2 ratio of 0.54 taking into account the potassium already present in the silicate and KOH added. The Si/Al molecular ratio was of about 31. Then, the resulting aluminosilicate, was covered with Teflon tops and treated at 60 °C for 150 min. The final composition corresponds to the following chemical formulation: $K\{-(SiO_2)_z\text{-}AlO_2\}_n, wH_2O$; z values: 1–35 and w values 1 or 2. Following this, 13% of the biphasic calcium phosphate (60% of HA and 40% of β-TCP) was added. To reduce pH values from 11 to physiological pH values around 7 and increase the porosity, the composites were heat treated at 500 °C for 180 min.

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2.2. Surface and interface bone–implant biomineralisation

Scanning electron microscopy (SEM) was applied to investigate evolution of the morphology of the aluminosilicate matrices. Good compromise between the porosity and the compressive strength after heating at 500 °C of each composite was established [5]. SEM, studies require transverse cuts of 250 μm thick sections of extracted composites embedded in resin and plated with a gold–palladium layer.

The particles induced X-ray emission (PIXE) method is based on the interactions between a proton beam and atoms. The Van de Graaff accelerator beam energy used in this work is of 3 MeV. The proton beam size is about 250 μm in diameter adapted for our porous compounds [9]. This method requires a plane surface to realise cartographies via concentrations measurements of certain atomic elements in different surfaces areas. Proton beam displacement was achieved in 3D from the implant to the bone through the interface implant–bone. Concentrations of some atomic elements were measured and calculated with the help of GUPIX software. Bone–implant interface was studied by determination of mineral composition in each extracted composite. Biomineralisation of the composite surfaces and on the bone–composite interface was evaluated versus time after implantation.

2.3. In vivo experiments

Studies of composites biocompatibility and bony bonding were highlighted. Cylinders of aluminosilicates-HA/β-TCP of 6 mm in diameter and 4 mm in height were sterilised and inserted in the transcortical sites of the rabbits tibia of 16–18 weeks old and weight of 3–4 kg. Experiments were carried out on five rabbits at 1 month and on three rabbits at 3 months after implantation. Samples were then cut into two parts, one destined for the physicochemical studies and other for the histological studies. The *in vivo* experiments were carried out on composites with a porosity of 63%, a pore size of 250 μm and a compressive strength of 6 MPa [5].

3. Results and discussion

Heating at 500 °C retains the initial amorphous geopolymer matrix similar to the structure before thermal treatment. This temperature is low enough to permit the expansion of the geopolymers without crystallisation of the matrix. XRD patterns were presented in our previous works [4,5]. Obtained diagrams confirm clearly the initial amorphous compounds.

The biomineralisation of surfaces and bone–implant interface was studied by SEM, EDS (energy dispersive spectrometry) and PIXE method in all samples extracted from rabbit's thighbone versus time after implantation. EDS and PIXE techniques are complementary methods. EDS permits to realise cartographies by obtained graphs when PIXE permits to realise quantitative mapping by scanning surfaces and interfaces of materials. Atomic elements analysed in this work were: Ca, P, Zn, Al, K and Si. They present a high physiological interest [10]. In Fig. 1, the graph presents the morphology of non-implanted composite aluminosilicate/HA-TCP. It permits comparison between the two cartographies achieved on samples extracted after 1 and 3 months after implantation, one with SEM and other with EDS (Fig. 2). Histological graphs show composite–bone interface. Obtained results are compared to a bony mineral composition at different stage. Al was not released in the surrounding environment (analysed by ICP-OES) [6]; it is present in our compounds at an amount which does not induce effects on the bone healing. PIXE

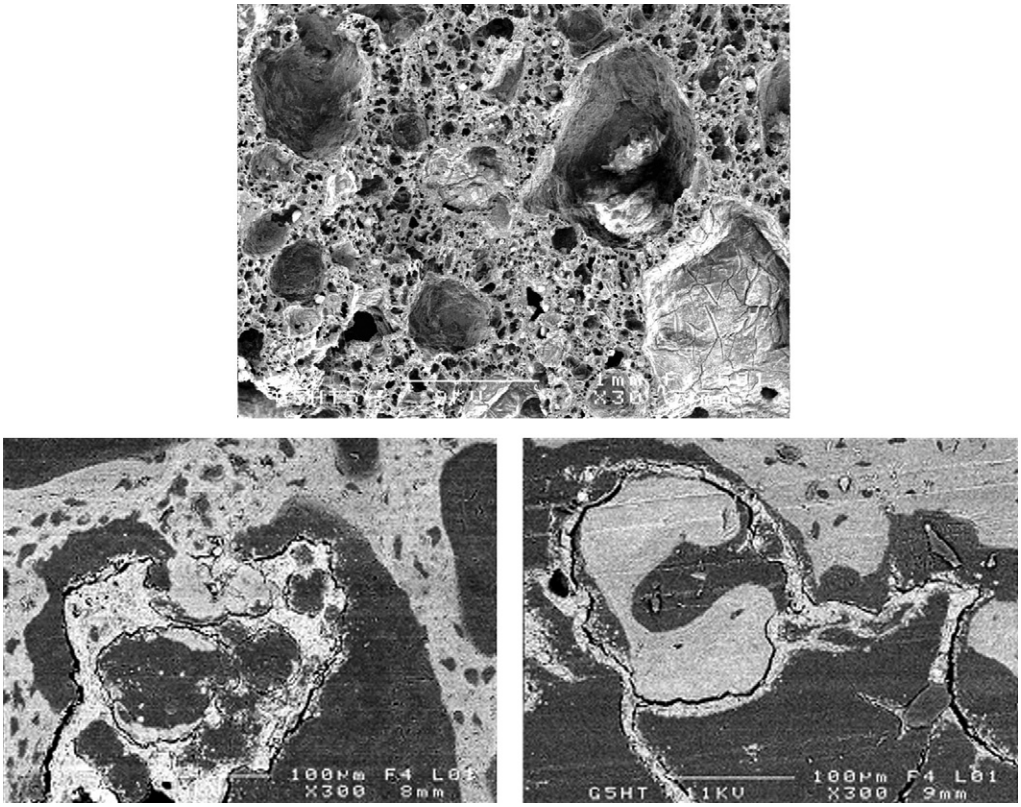

Fig. 1. SEM (300×), pure composite G54HT_500, bone–implant (G54HT_500) interfaces. Sampling at 1 month (left) and 3 months (right). SEM dumps in electrons retrodiffusion: differentiation between the bone and the implant (white).