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New calcium carbonate-based cements for bone reconstruction

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Abstract

The feasibility of calcium carbonate-based cements involving the re-crystallization of metastable calcium carbonate varieties has been demonstrated. Two cement compositions were obtained by mixing either calcium carbonate phases (cement A) or a calcium carbonate and a calcium phosphate phase (cement B) with an aqueous media. These cements set and hardened after 30 minutes and 90 minutes respectively. The final composition of cement A was calcite and aragonite whereas cement B lead to a carbonated apatite analogous to bone mineral. Despite poor mechanical properties the presence of a high carbonate content in the final phase might be of interest to increase the cement resorption rate and to favour its replacement by bone tissue. First assays of implantation performed on fresh anatomical pieces (fresh cadavers) at 37°C revealed important advantages of such cement compositions: easiness of use, rapid setting, good adhesion to bone, very good homogeneity and stability of the cement.

Introduction

Calcium phosphate (CaP) bone cements have developed considerably in the last few years essentially as bone filling and bone reinforcement biomaterials [1-3]. However, the main challenge is to reach higher mechanical properties, higher rates of resorption and an improvement of bone formation.

Aragonite, a natural calcium carbonate (CaCO_3) from corals, has been shown to be a biocompatible and bioactive bone substitute and is being used for more than 15 years [4]. Considering that the resorption rate of bone substitute materials is related to their solubility, calcium carbonates, which exhibit a higher solubility than calcium phosphates, should show an improved biodegradation rate compared to CaP cements [5]. In addition, like in the case of the widespread BCP ceramics (biphasic calcium phosphate ceramics) made of HA and TCP, calcium carbonates could be used to produce biphasic cements with adaptable resorption rates.

This work is a preliminary study on new types of bone cements based on calcium carbonate and prepared by mixing either calcium carbonate phases or calcium carbonate and calcium phosphate phases with an aqueous media.

Materials and Methods

Calcium carbonate phases (aragonite, vaterite and a metastable calcium carbonate mixture comprising calcite, vaterite and amorphous CaCO_3) and dicalcium phosphate dihydrate (DCPD: $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) were prepared by double decomposition in aqueous media.

The cement powders were constituted by a mixture of several calcium carbonate phases (cement A) or a mixture of calcium carbonate (at least 40 % w/w) and calcium phosphate (cement B) (see Table 1). The cement paste was obtained by mixing the powders with an appropriate amount of liquid phase (either deionized water or a sodium chloride solution: 0.9% w/w). The wet paste was wrapped in wet paper and placed in a sealed container at 37°C for setting and hardening.

The setting rate of the cement was followed with a TA-XT2 Texture Analyser fitted with a cylindrical needle (0.7 mm in diameter). The setting time was reached when the paste developed a resistance force to needle penetration higher than 600 g/mm^2 . The cement compressive strength was evaluated on a Hounsfield Series S apparatus.

The cements were characterized by transmission FTIR spectroscopy on KBr pellets (Perkin Elmer FTIR 1600 spectrometer) and by X-ray diffraction (Inel CPS 120 diffractometer) using a Co anticathod.

Implantation tests were performed at 37°C on fresh anatomical pieces (fresh cadavers) at the Laboratoire d'Anatomie Médico-Chirurgicale Appliquée of the University of Bordeaux where surgeons in dentistry have evaluated the preparation of the cement, either with physiological serum or blood as liquid phase, and its implantation for odontostomatology applications.

Results

The composition of the initial solid phase and the range of the liquid on solid ratio (L/S) used for the two kinds of cement compositions are reported in Table 1.

Table 1: Cement A and cement B compositions

Cement A	Cement B
Solid phase: Aragonite + metastable CaCO_3 L/S = 0.25-0.50	Solid phase: Aragonite + vaterite + DCPD L/S = 0.5-1.0

The FTIR absorption spectra of the final phase for the two cement compositions are presented in Fig. 1. After hardening cement A appeared essentially composed of calcite and aragonite whereas cement B lead to a carbonated apatite analogous to bone mineral.

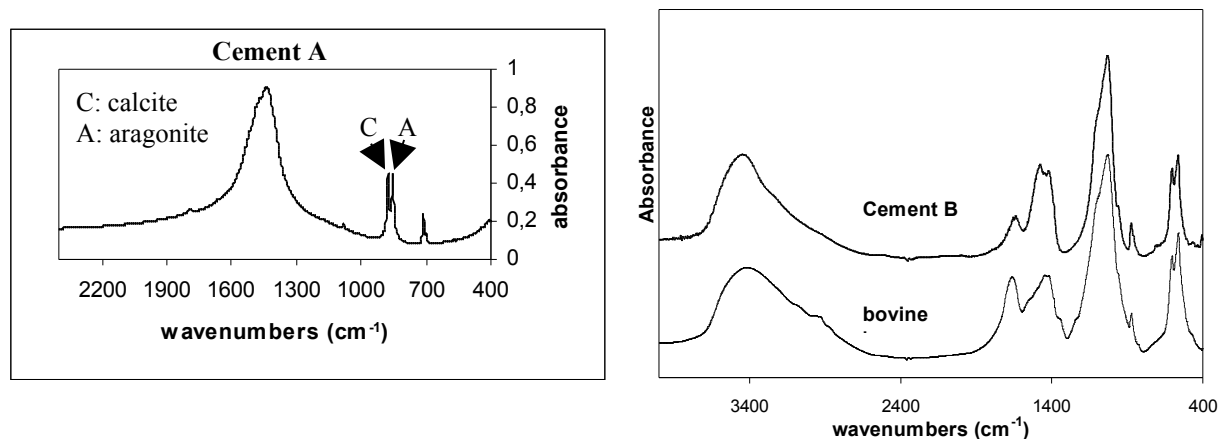
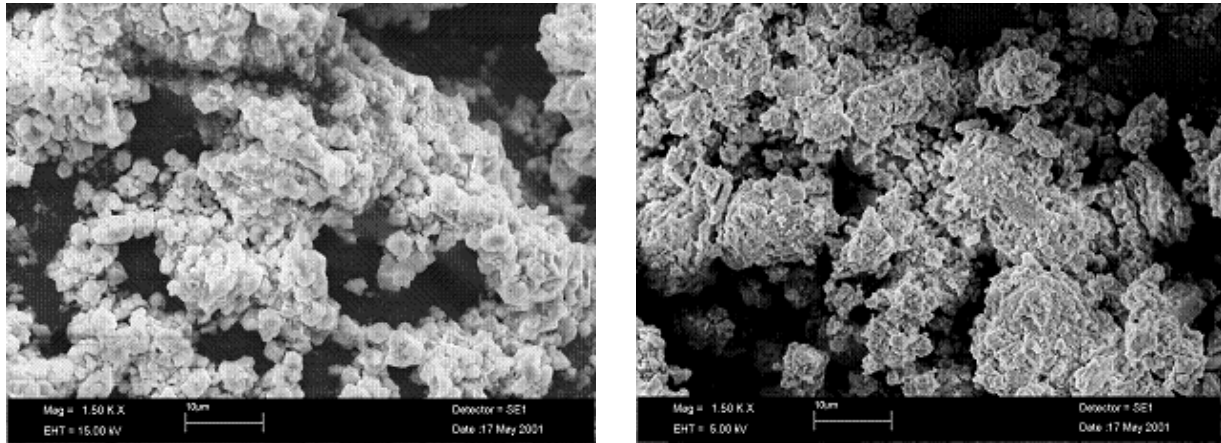


Figure 1: FTIR spectrum of the ending phase(s) of cement A and cement B

Moreover, a detailed study of various phase compositions of type A cement by FTIR spectroscopy and X-rays diffraction revealed that setting did not occur if vaterite, from the initial metastable CaCO_3 powder, remained in the ending cement and/or if the proportion of aragonite in the resulting cement was lower than 50 % (w/w) (data not presented). The carbonate content in the carbonated apatite of the type B cement depended on the proportion of calcium phosphate in the initial solid phase: the CO_3^{2-} content was around 10 % (w/w) for a cement prepared with 57 % (w/w) of DCPD and L/S=1.

Scanning electron microscopy (see Fig. 2) showed that the resulting cements were microporous. For, cement A, cubic or rhomboedral crystals characteristic of calcite were distinctly observed whereas cement B appeared mainly formed by a poorly crystalline phase.



a)

b)

Figure 2: SEM micrographs of the ending phase of a) cement A and b) cement B

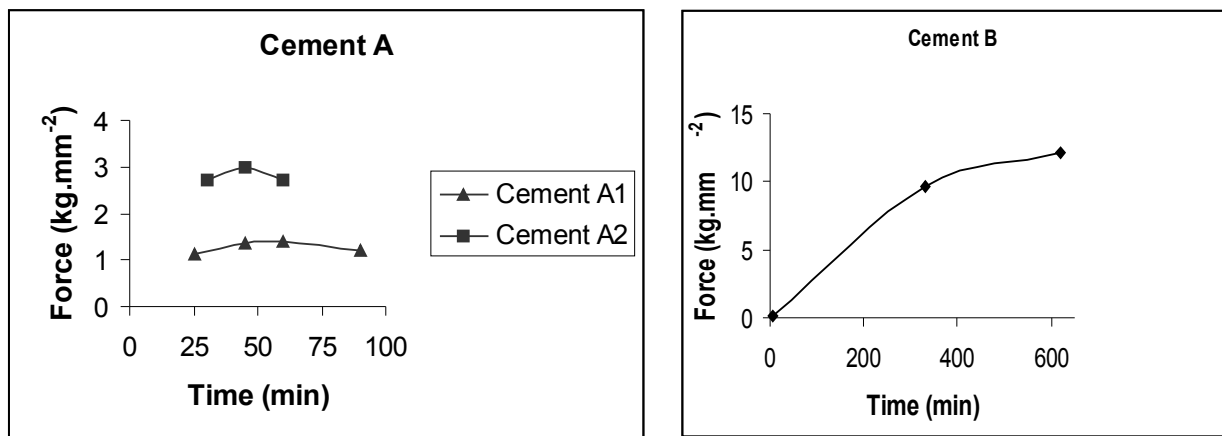


Figure 3: Setting time evaluation for cement A (A1: L/S = 0.38; A2: L/S= 0.25) and cement B (L/S = 0.71)

The setting kinetics of each cement is represented in Fig. 3. The setting of cement A and cement B occurred before 30 min and 90 min, respectively. As usually observed, a decrease of the proportion of liquid phase leads to a significant increase of the mechanical strength. After the setting time and during the hardening phase, a high increase of the mechanical strength of cement B occurred. This observation was confirmed by measurement of cement compressive strength which was higher for cement B than for cement A but remained poor in all cases: around 3 MPa for cement A and around 7 MPa for cement B.

Discussion and conclusion

FTIR and X-ray diffraction analyses revealed the presence of calcite and aragonite in the A-type cement paste after hardening. The follow-up of the phase composition during the setting and hardening periods evidenced the transformation of the initial metastable calcium carbonate phases into aragonite or calcite (data not presented). A detailed analysis of the data suggested that the hardening process resulted essentially from the transformation of vaterite from the metastable CaCO_3 phase into aragonite [6]. For cement B, the setting reaction appeared essentially related to the formation of a carbonated apatite phase by reaction of DCPD onto calcium carbonate.

Calcium carbonate materials from biological origin have been used and proposed as bone substitute materials. However, despite a good biological behaviour, question remains about the biological role of organic matter residues. Although several attempts have been made to produce synthetic calcium carbonate, sintering appears as a difficult technique and calcium carbonate cements seems an interesting alternative way. These cements, unlike sintered materials and natural materials could be associated with known biological active molecules. The formation of a poorly crystalline carbonated apatite analogous to bone mineral and the possibility to adapt the carbonate level in the resulting apatite is another interesting features of the type B biomimetic cement.

The proposed ionic cement formulae are biphasic (two calcium carbonate phases or calcium carbonate and calcium phosphate phases) which is an interesting characteristic enabling adaptation of the cement biodegradation properties depending on the surgical application. This feature can be compared to that of the well-known biphasic biomedical ceramics: HAP/TCP.

Even though the mechanical properties measured remained poor, they do not seem to be detrimental to in vivo application in locations under low mechanical stress and these properties can be improved by optimizing the L/S ratio.

First assays of implantation performed on fresh anatomical pieces (fresh cadavers) revealed important advantages of such cement compositions: easiness of use, rapid setting at 37°C , perfect adhesion to bone, very good homogeneity and stability of the cement. Before in vivo implantation, the cement compositions have to be evaluated for cytotoxicity and cytocompatibility in vitro. The expected rate of cement biodegradation and bone reconstruction after in vivo implantation of cement A and B would be a decisive advantage for the development of such formulations especially to improve bone regeneration in dental surgery (post-extractional and bone defect filling, stabilization during dental implant fitting).

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