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Calcium aluminate cement-based compositions for biomaterial applications

R.M. Parreira [a], T.L. Andrade [a], A.P. Luz [b], V.C. Pandolfelli [b], I.R. Oliveira [a,*]

[a] Institute for Research and Development, University of Vale do Paraíba, Av. Shishima Hifumi, 2911 São José dos Campos, SP, Brazil
[b] Materials Engineering Department, Federal University of São Carlos, UFSCar, Rod. Washington Luiz, km 235, São Carlos, SP, Brazil

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ABSTRACT

Calcium aluminate cement (CAC) Calcium aluminate cement (CAC) is classified as a hydraulic binder presenting various advantages, such as fast hardening at room temperature and suitable rheological properties, when compared to traditional materials. Based on this, CAC has been investigated as an alternative biomaterial in order to overcome some drawbacks presented by commercial products usually applied in the dentistry (mineral trioxide aggregate=MTA and glass ionomer) and orthopedics (polymethyl methacrylate=PMMA) fields. In this work, the properties of CAC-based compositions containing different amounts of additives (i.e., alumina, zirconia, zinc oxide, hydroxyapatite, tricalcium phosphate, chitosan and collagen) were evaluated and the attained results were compared to those of MTA, PMMA and two glass ionomers (Meron and Vidrion F). The characterization of the selected materials comprised their particle size distribution, as well as the cold crushing strength, apparent porosity, pore size distribution and radiopacity. Plain CAC presented higher crushing strength than the commercial products used in dentistry and the blend of this cement with 4 wt% of additives (alumina, zirconia, zinc oxide, tricalcium phosphate or hydroxyapatite) resulted in improved mechanical performance when compared to PMMA (cement for bone repair). The addition of zinc oxide and hydroxyapatite to CAC also gave rise to samples with low porosity levels and smaller pore sizes after their contact with simulated body fluid solution over 7 days at 37 °C. Conversely, collagen and chitosan-containing compositions showed higher porosity and lower mechanical strength. Regarding the radiopacity results, the evaluated compositions presented better results than the commercial products, except for MTA.

1. Introduction

Cements used in orthopedics must fulfill many requirements, such as low curing temperature (to prevent thermal necrosis of the bone tissue during setting), suitable setting time and high crushing strength (in order to withstand the compressive load developed during daily activities). The most used cement for bone repair is comprised mainly by polymethyl methacrylate (PMMA), which presents excellent mechanical properties when compared to other polymeric materials [1]. However, this product still presents drawbacks regarding its handling behavior (too low consistency and strong odor) and biocompatibility. Additionally, the reactions associated to this cement are exothermic, resulting in local heat increase which can damage the surrounding tissue. Based on these aspects, the aim is to find and develop new alternative sources to overcome these limitations [1].

Other classes of materials that have been investigated for dentistry and orthopedic fields are the chemically-bonded ceramics (CBC), whose setting behavior is controlled by specific chemical reactions that can take place at room temperature [2]. For instance, calcium phosphates and calcium sulfates are extensively used to fill bone defects and stabilize fractured vertebrae [1,2]. Zinc phosphate, on the other hand, is commonly used as dental cement, despite its low mechanical strength, poor chemical stability and esthetics for a permanent filling product [2]. It must be highlighted that dental materials must present improved mechanical performance under compressive strength in order to withstand the stresses derived from the long term application.

Calcium silicate (CSC) and calcium aluminate (CAC) cements (also classified as CBC materials or hydraulic binders that form hydrates after its dissolution in water) can be used as dental restorative products [1,3]. The latter presents a suitable performance as a root-end filling component, as it can overcome some drawbacks of commercial CSC-based compositions and MTA (mineral trioxide aggregate), such as: long setting time, high porosity and

* Corresponding author.
E-mail address: ivoneregina.oliveira@gmail.com (I.R. Oliveira).

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low mechanical strength. CAC also presents interesting features as a biomaterial, for example: (i) better flowability and handling properties [4,5], (ii) adjustable rheology and a setting time at room temperature, resulting in high initial mechanical strength [2], (iii) biocompatibility when tested in subcutaneous tissues of rats without inflammatory reactions [6,7], (iv) ability to induce in situ hydroxyapatite generation [2,8], (v) it can act as a barrier preventing bacterial microleakage [9], and (vi) low expansion favoring good retention and adhesion to the teeth [2].

CAC also has the potential to be used in orthopedic applications due to its high viscosity (which injects the prepared mixture just after the mixing step), low heat release associated to the chemical reactions of this product with aqueous solution during setting and high biocompatibility [1,10].

Some studies have reported on calcium aluminate cement applications to repair bone defects, based on the fact that its chemical composition and thermal expansion coefficient are similar to teeth and human bones [3,11]. CAC-based zirconia-containing materials has also been developed to stabilize compressive vertebrae fractures, leading to mechanical strength values similar to PMMA, good stability after 6 months in contact with phosphate buffer solution and porosity levels in the range of 10–15%. When evaluated in sheep vertebrae, CAC-based mixtures showed less inflammation and better adaptation to the bone tissue than PMMA [1].

Alumina, zinc oxide, calcium phosphates, collagen and chitosan are other alternative additives that can be incorporated into CAC-based compositions. In addition to suitable biocompatibility, corrosion and wear resistance, chemical stability and high crushing strength, zirconia and alumina have the advantage of acting as bioceramic reinforcements for cements [12]. Some investigations have focused on the development of biphasic calcium phosphate composites containing alumina, as they can present improved mechanical properties, biocompatibility and bone formation in combination with adjacent hard tissues [13]. Zinc oxide presents antibacterial ability and biocompatibility [14] allowing for the design of engineered zinc-containing ceramic composites for bone tissue repair, and it has the following benefits: (i) the presence of apatite in tricalcium Zn-phosphate may induce cell proliferation [15], and (ii) it can stimulate osteoblast cells in aluminate-based materials, favoring the mineralization process [16].

Calcium phosphate ceramics are used to repair bone defects, increase and maintain alveolar bone crests, relocation of dental root, ear implants, lining metallic implants, and others. Hydroxyapatite and tricalcium phosphate are the most common compounds of this category [17]. As reported by Roemhildt et al. [18], cement-based compositions (presenting high mechanical strength) comprising a blend of calcium phosphates+calcium aluminate have been developed for bone and joint repair. In this case, calcium phosphate improves the biological activity of the material, whereas calcium aluminate is responsible for increasing the mechanical strength of this composite.

Collagen and chitosan are biopolymers [19,20] that have received great attention. The increasing use of the former is related to the low immunological reaction index and its ability to generate fibers from soluble mixes, whose properties are similar to the ones found in tissues. On the other hand, chitosan presents non-toxicity, biocompatibility, antioxidant and antimicrobial abilities, as well as healing and anti-inflammation characteristics. These features make the later able to be used in surgical sutures, dental implants, bone reconstruction, contact lenses, controlled drug delivery, encapsulation material, etc. [21]. Kishen et al. [22] stated that the addition of chitosan nanoparticles to dental cements led to a major improvement in antimicrobial properties and leaching ability of the antibacterial components in the evaluated systems. However, chitosan also has some drawbacks regarding its mechanical strength and biological performance, which requires blending inorganic materials (i.e., hydroxyapatite, calcium phosphate and silica) with this biopolymer [23].

Considering these aspects, this paper focuses on the preparation of various CAC-based mixtures containing different amounts of additives (alumina, zirconia, zinc oxide, hydroxyapatite, tricalcium phosphate, chitosan and collagen) in order to evaluate and compare their properties with commercial products commonly applied in dentistry (MTA and glass ionomers) and orthopedics (PMMA).

2. Materials and techniques

The following materials were used in this work: CACH, prepared using the dry-mixture of calcium aluminate cement (Kerneos Aluminates, France [5]) with a polyglycol-based dispersant (0.6 wt%, Basf, Germany) and a plasticizer $CaCl_2 \cdot 2H_2O$ (2.8 wt%, Labsynth, Brazil) in a ball mill for 1 h, and the additives: (1) calcined alumina (CT3000SG, Almatis, USA), (2) monoclinic zirconia (CC-10, Saint-Gobain, France), (3) zinc oxide (Synth, Brazil), (4) hydroxyapatite (Sigma-Aldrich 21,223, USA), (5) tricalcium phosphate (Cadisa, Brazil), (6) chitosan (Polymar, Brazil) and (7) bonive collagen (type I, JBS, Brazil). The selected compounds presented high purity and their particle size distribution was evaluated using S3550 equipment (Microtrac, USA) after keeping the samples for 15 min in an ultrasonic bath (Sonics Vibra-cell, USA, model VCX 500) for the powder deagglomeration. Additionally, commercial products were analyzed and used as reference materials: ortophedic PMMA cement (Bio mecânica, Brazil) and dentistry cements, such as white MTA, (Angelus, Brazil), glass ionomers for base and lining (Vidrion F, SS White, Brazil) and for cementing and restoration (Meron, Voco, Germany).

A total of 1, 2, 4, 6, and 10 wt% of the selected additives were added to CACH and these compositions were mixed in a ball mill for 1 h. After that, aqueous suspensions (80 wt% of solids) were prepared using a lab mixer and molded as cylindrical samples (diameter=16 mm and height=18 mm). Collagen and chitosan-containing compositions required extra water to mold the samples. Table 1 shows the resulting solid content for each prepared suspension with these additives.

The samples were kept at 37 °C for 24 h in a water saturated environment, demolded and dried at 110 °C for another 24 h. Apparent porosity measurements were carried out in dried materials, which were classified as “without treatment” tests. Other cast cylinders were also placed in contact with simulated body fluid (SBF) [24] solution at 37 °C for 7 days. Humid samples were then subjected to uniaxial compression tests, whereas others were dried at 110 °C for 24 h and their apparent porosity was evaluated (“after SBF treatment” measurements).

Table 1
Additives and total solid contents in the prepared suspensions containing collagen and chitosan.

Additives	Content (wt%)	Solid content in the prepared suspension (%)
Collagen	1	73
	2	68
	4	63
	6	58
	10	53
Chitosan	4	77
	6	75
	10	72