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Review

Dicalcium phosphate cements: Brushite and monetite

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A R T I C L E I N F O

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A B S T R A C T

Dicalcium phosphate cements were developed two decades ago and ever since there has been a substantial growth in research into improving their properties in order to satisfy the requirements needed for several clinical applications. The present paper presents an overview of the rapidly expanding research field of the two main dicalcium phosphate bioceramics: brushite and monetite. This review begins with a summary of all the different formulae developed to prepare dicalcium phosphate cements, and their setting reaction, in order to set the scene for the key cement physical and chemical properties, such as compressive and tensile strength, cohesion, injectability and shelf-life. We address the issue of brushite conversion into either monetite or apatite. Moreover, we discuss the in vivo behavior of the cements, including their ability to promote bone formation, biodegradation and potential clinical applications in drug delivery, orthopedics, craniofacial surgery, cancer therapy and biosensors.

1. Introduction

Brushite cements were discovered by Mirtchi and Lemaître in 1989. These materials were prepared by mixing water with a powder consisting of an acidic calcium phosphate (monocalcium phosphate monohydrate) and a basic calcium phosphate (β-tricalcium phosphate). The result of this mixture was a moldable paste that eventually solidified in an exothermic reaction forming a hard material that was composed mainly of dicalcium phosphate dihydrate, also known by the mineral name "brushite" [1].

Subsequent studies showed that brushite cement is biocompatible and it has a unique advantage over the other calcium phosphate cement system (hydroxyapatite cement), which is its ability to be resorbed under physiological conditions. However, the original formula of brushite cement resulted in a material that was difficult to handle, set too fast (∼30 s) and had low mechanical properties (∼1 MPa diametral strength) [2,3].

During the past two decades many studies have been aimed at improving the properties of brushite cement systems. In the current study we discuss all the developments that have been introduced in brushite cements to improve their setting time, mechanical properties, biocompatibility, bioactivity and bioresorption. Moreover, we also present the most relevant biomedical applications of this material.

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2. Cement composition

The main constituents of dicalcium phosphate (DCP) cements are an alkaline calcium source, an acidic phosphate source and water, as well as other additives to prolong the cement setting time, increase its mechanical properties and improve its handling. In Table 1 we present the different compositions that have been evaluated in the literature [1,4–50].

2.1. Alkaline calcium source

The alkaline calcium source in DCP cements can be very basic, such as calcium oxide [49] and calcium hydroxide [50]. These two components have the main advantage of being easy to manufacture and inexpensive. On the other hand, brushite has a calcium to phosphate ratio of 1, therefore calcium phosphate compounds with higher calcium to phosphate ratios can be used as alkaline calcium source in brushite cements. For instance, tetracalcium phosphate (TTCP) has a calcium to phosphate ratio of 2, which is ideal for DCP cements. However, its preparation is highly energy demanding, and its use in DCP cements has been very limited [44]. Hydroxyapatite (HAp) has a calcium to phosphate ratio of 1.67, and its ions can be easily substituted [51]. Therefore, introducing HA into a brushite cement setting system allows modulation of the cement setting reaction through ionic substitution [19,46]. Nano-crystalline HAp (nHAp) has also been used to prepare DCP cements [44].

The most common basic calcium source in brushite cements is tricalcium phosphate (TCP) (calcium to phosphate ratio 1.5). This

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