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Review article

Fibre-reinforced calcium phosphate cements: A review

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ARTICLE INFO

Article history:
Received 23 April 2011
Received in revised form
18 June 2011
Accepted 23 June 2011
Published online 14 July 2011

Keywords:
Calcium phosphate cement
Fibres
Yarns
Textile laminar structures
Composites
Bone substitutes
Reinforcement

ABSTRACT

Calcium phosphate cements (CPC) consist of one or more calcium orthophosphate powders, which upon mixing with water or an aqueous solution, form a paste that is able to set and harden after being implanted within the body. Different issues remain still to be improved in CPC, such as their mechanical properties to more closely mimic those of natural bone, or their macroporosity to favour osteointegration of the artificial grafts. To this end, blends of CPC with polymer and ceramic fibres in different forms have been investigated. The present work aims at providing an overview of the different approaches taken and identifying the most significant achievements in the field of fibre-reinforced calcium phosphate cements for clinical applications, with special focus on their mechanical properties.

Contents

Abbreviations: CPC, calcium phosphate cement; DCPA, dicalcium phosphate anhydrous, $CaHPO_4$; DCPD, brushite, dicalcium phosphate dihydrate $CaHPO_4{\cdot}2H_2O$; HA, hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$; α-TCP, alpha tricalcium phosphate, α-$Ca_3(PO_4)_2$; β-TCP, beta-tricalcium phosphate, β-$Ca_3(PO_4)_2$; TTCP, tetracalcium phosphate, $Ca_4(PO_4)_2O$; PLA, polylactide; PLLA, poly-L-lactide; PGA, polyglycolide; PLGA, poly (lactide-co-glycolide); PCL, poly-ε-caprolactone; PA, polyamide.

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doi:10.1016/j.jmbbm.2011.06.023

1. Introduction

Calcium phosphate cements (CPC) are able to harden *in vivo*, through a low-temperature setting reaction. The products formed in this setting reaction have many similarities with the mineral phase that constitutes 70 wt% of the bone tissue. However, their mechanical properties are far from those of the cortical or even the cancellous bone. Not only in terms of strength, but especially in terms of toughness, ductility and fatigue resistance. The similitude of CPC with the bone mineral arises from their origin. Both are obtained by precipitation in aqueous solutions at physiological temperature. When set, CPC consist of a network of calcium phosphate crystals, with a chemical composition and crystal size that can be tailored to closely resemble the biological hydroxyapatite occurring in living bone (Morgan et al., 1997; Ginebra et al., 2010).

A number of CPC formulations are currently available. They consist of mixture of one or several calcium phosphate powders with water or an aqueous solution. Either hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) or brushite (dicalcium phosphate dihydrate; DCPD: $CaHPO_4.2H_2O$) can be formed in the cement setting reaction. One of the main advantages of CPC is their in vivo hardening ability. Bone defects can be reconstructed by filling with CPC mouldable pastes, which in some instances can be injected in the surgical site by minimally invasive surgical procedures (Ginebra et al., 2001; Ishikawa, 2008), with significant benefits for several clinical situations such as the treatment of osteoporosis related fractures, unstable fractures, maxillofacial defects and deformities, and more recently for other specific applications such as vertebroplasty (Lewis, 2006). Moreover, the possibility of loading them with drugs or growth factors has open new perspectives in their application as drug delivery systems (Ginebra et al., 2006).

However, their poor mechanical performance has limited their applicability to non-stress-bearing applications. Their compressive strength, when no pre-compaction is applied, ranges from 10 to 90 MPa (Ginebra, 2008), the apatitic cements being stronger than brushite cements. These values overcome those of trabecular bone, which range between 1.5 and 45 MPa (Carter and Hayes, 1977), or fall in the lower range of the compressive strength of cortical bone, that varies between 90 and 209 MPa (Ontañón et al., 2000; Burstein et al., 1977). Nonetheless, the major constraints of the mechanical performance of CPC arise from the intrinsic brittleness derived from their composition and microstructure. CPC are in fact intrinsically porous ceramics, with porosities that vary between 20% and 50% depending on the liquid to powder ratio used in their preparation (Espanol et al., 2009). Thus, the bending strength values reported for CPC, typically in the range of 5–15 MPa (Martin and Brown, 1995; Ginebra et al., 2001) are well below that of cortical bone, which is close to 200 MPa (Currey and Butler, 1975). With respect to the fracture properties of CPC, Morgan et al. (1997) reported a fracture toughness of 0.14 MPa $m^{1/2}$ for a carbonated apatite CPC, comparable to other brittle cellular materials such as chalk or Portland cement (Maiti et al., 1984), and far from the fracture toughness of human cortical bone, 2–5 MPa $m^{1/2}$ (Nalla et al., 2003).

The development of CPC with enhanced toughness would considerably broaden the field of potential applications, such as the repair of multiple fractures of long bones, fixing of cemented articulation prostheses or substitution of vertebral bodies among others (Dos Santos et al., 2000). It is true that the mechanical limitations of CPC can be balanced with the effects of progressive remodelling that eventually is expected to lead to the replacement of the CPC with new bone. However, even if the material is completely transformed in newly formed tissue, at the initial stages after implantation it would be desirable to have CPC with enhanced mechanical properties. This has led to the development of fibre-reinforced CPC. In fact, fibre reinforcement has been extensively explored in the field of hydraulic cements and concretes for civil engineering and building applications. The incorporation of fibres into a brittle cement matrix has been proven to increase the fracture toughness of the composite by the resultant crack arresting processes as well as the tensile and flexural strengths (Beaudoin, 1990). Fibre reinforcement has proven also to be effective in other types of brittle cements, such as the acrylic bone cements used for orthopaedic or dental applications (Schreiber, 1974; Pal and Saha, 1982; Puska et al., 2004).

However, in cements intended for medical applications such as CPC, specific requirements arise in the selection of the fibres; on one hand, they must be biocompatible. On the other hand, they can be used not only as a reinforcement for the cement matrix but also as pore-generating agents. In this second approach, fibres, in addition to being biocompatible, must also be biodegradable.

It is the aim of the present work to provide an overview of the different approaches taken in the development of fibre-reinforced CPC for clinical applications and to identify the kind of fibres used and the most significant achievements.