Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jmbbm

Research Paper

The effect of water on the mechanical properties of soluble and insoluble ceramic cements

Ilsoo Koh[a,*], *Alejandro López*[b], *Ana B. Pinar*[c], *Benedikt Helgason*[a], *Stephen J. Ferguson*[a]

[a]*Institute for Biomechanics, ETH-Zurich, Zurich, Switzerland*
[b]*Division of Applied Materials Science, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Uppsala, Sweden*
[c]*Laboratory of Crystallography, ETH-Zurich, Zurich, Switzerland*

ARTICLE INFO

Article history:
Received 4 May 2015
Received in revised form
24 June 2015
Accepted 30 June 2015
Available online 15 July 2015

Keywords:
Ceramic cement
Gypsum
Brushite
Xray-diffraction
SEM
Mechanical testing

ABSTRACT

Ceramic cements are good candidates for the stabilization of fractured bone due to their potential ease of application and biological advantages. New formulations of ceramic cements have been tested for their mechanical properties, including strength, stiffness, toughness and durability. The changes in the mechanical properties of a soluble cement (calcium sulfate) upon water-saturation (saturation) was reported in our previous study, highlighting the need to test ceramic cements using saturated samples. It is not clear if the changes in the mechanical properties of ceramic cements are exclusive to soluble cements. Therefore the aim of the present study was to observe the changes in the mechanical properties of soluble and insoluble ceramic cements upon saturation. A cement with high solubility (calcium sulfate dihydrate, CSD) and a cement with low solubility (dicalcium phosphate dihydrate, DCPD) were tested. Three-point bending tests were performed on four different groups of: saturated CSD, non-saturated CSD, saturated DCPD, and non-saturated DCPD samples. X-ray diffraction analysis and scanning electron microscopy were also performed on a sample from each group. Flexural strength, effective flexural modulus and flexural strain at maximum stress, lattice volume, and crystal sizes and shape were compared, independently, between saturated and non-saturated groups of CSD and DCPD. Although material dissolution did not occur in all cases, all calculated mechanical properties decreased significantly in both CSD and DCPD upon saturation. The results indicate that the reductions in the mechanical properties of saturated ceramic cements are not dependent on the solubility of a ceramic cement. The outcome raised the importance of testing any implantable ceramic cements in saturated condition to estimate its in vivo mechanical properties.

*Correspondence to: *Institute for Biomechanics, ETH Zürich, HPP-O14, Hönggerbergring 64, CH-8093 Zürich, Switzerland*. Tel.: +41 44 633 4440.
E-mail address: ikoh@ethz.ch (I. Koh).

http://dx.doi.org/10.1016/j.jmbbm.2015.06.030
1751-6161/

1. Introduction

A bone fracture is a frequently diagnosed clinical condition, especially with increasing fragility in an ageing population. Fractured bone initiates its healing process through the formation of granulation tissue, which is slowly converted into a cartilaginous callus with time (Carter et al., 1988; Diamond et al., 2007). The progenitor cells (chondroblasts and osteoblasts) in the cartilaginous callus differentiate to form either chondrocytes or osteocytes. The degree of proliferation and differentiation of each type of cell is dependent on the local mechanical stimuli. The formation of osteoblasts occurs when the progenitor cells in the callus experience low shear strains while the formation of chondrobalsts occurs when the cells experience comparably higher shear strains (Claes and Heigele, 1999; Isaksson et al., 2006; Lacroix et al., 2002; Prendergast et al., 1997). The formation of osteoblasts, which promote mineralization, can thus be promoted at the site of fracture by stabilizing the fractured bone to control local tissue strain.

Ceramic bone cements are considered as potential candidates for the stabilization of fractured bones. This is due to their ease of application and biological advantages (Heini and Berlemann, 2001; Huan and Chang, 2007; Liu et al., 2013; Nilsson et al., 2003; Yang et al., 2012). Calcium sulfate dihydrate (CSD, gypsum) and dicalcium phosphate dihydrate (DCPD, brushite) are self-setting, biocompatible, bioresorbable, osteoinductive and non-toxic injectable pastes. Therefore both materials are commonly used to fill the fracture gaps in injured bones and to act as scaffolds for bone ingrowth. The bioresorbability of the filling material is an important property. The bioresorbable filling material can undergo resorption during the formation of bone, with a gradual replacement of the material by bone over time. Thus, a ceramic cement used to fill bone defects should be able to: 1) accommodate bone ingrowth and 2) degrade/resorb over the time period of bone healing. The healing of bone defects can take up to 2 months (Claes et al., 1998; Lacroix and Prendergast, 2002). As CSD has typical resorption time of 2 months (Barinov and Komlev, 2011), CSD may not be a suitable material to fill large defects. On the other hand, DCPD was shown to take 6 months to convert into poorly crystalline carbonated apatite (Penel et al., 1999). Therefore, DCPD is clinically preferred over CSD as a filler material (Barinov and Komlev, 2011; Tamimi et al., 2012). A disadvantage of DCPD is its inadequate mechanical properties (Mirtchi et al., 1989).

Adequate mechanical properties of a filler ceramic cement are: 1) primary strength to sustain the applied loads, 2) optimal stiffness to transfer sufficient mechanical stimuli for the formation of bones, and 3) toughness and durability to support the damaged bone until mineralization has progressed. Over the past decades, strengths of newly developed ceramic cements have been frequently reported (Charriere et al., 2001; Drosos et al., 2012; Huan and Chang, 2007; Lewis et al., 2006; Liu et al., 2013; Morgan et al., 1997; Van Lieshout et al., 2011; Yamadi and Kobayashi, 2009; Yang et al., 2012, Zhang et al., 2011). Stiffnesses of ceramic cements are reported sporadically (Charriere et al., 2001, Drosos et al., 2012; Morgan et al., 1997; Van Lieshout et al., 2011; Welch et al., 2002, Zhang et al., 2011), while only limited reports are available on the toughness and durability of ceramic cements (Morgan et al., 1997; Zhang et al., 2011). Although the strength of ceramic cements is commonly tested using water-saturated (wet) samples, the stiffness of ceramic cements is frequently determined using non-water-saturated (dry) samples. The discrepancy in testing methods underlines the lack of a standardized protocol to test ceramic cements. Considering that ceramic implants are exposed to human body fluids, it seems critically important to perform the experiments under relevant conditions, i.e. using water-saturated samples, to resemble in vivo conditions.

Our previous investigation has reported the significant differences in the strength and apparent modulus of CSD upon water-saturation (Koh et al., 2014). It was suggested that these changes may be due to: 1) dissolution of CSD crystals, and/or 2) inter-crystal water lubrication, however the exact mechanism remain unclear. Since CSD has a high solubility, it may be more reasonable to state that the reduction in the strength and apparent modulus were purely due to crystal dissolution. This uncertainty justifies testing also non-degrading ceramic or insoluble ceramic cements in both a water-saturated (wet) and non-water-saturated (dry) state.

The aim of the current study was to better understand the cause of the changes in the mechanical properties of ceramic cements upon water-saturation. To achieve the aim, a ceramic cement with high solubility (CSD, $K_{sp}=2.4\times10^{-5}$ in water) (Issleib, 2013) and low solubility (DCPD, $K_{sp}=2.47\times10^{-7}$ in water) (Issleib, 2013) were mechanically tested in water-saturated and non-water-saturated conditions. The composition and crystal structure of the samples were also obtained to relate it to the mechanical properties. It is hypothesized that the change in mechanical properties are independent to the solubility of ceramic cements. The study was designed as an inter-group comparison study. The changes in the mechanical properties of CSD and DCPD due to saturation were analyzed independently.

2. Methods

2.1. Sample preparation

A set of stainless steel molds ($90\times8\times6\,mm^3$) were manufactured according to the tolerances outlined in ASTM standard (ASTM, 2013). The molds were used to cast two types of ceramic cements (CSD and DCPD) into beams. The stainless steel molds were coated with a lubricant (Diverses Multigliss, Molykote, Dow Corning GmbH, Wiesbaden, Germany) to ease the removal of the prepared sample (Charriere et al., 2001).

2.1.1. Preparation of CSD samples

The CSD slurry was produced by mixing β-$CaSO_4\cdot½H_2O$ (purum ≥97.0%, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland) and distilled water (0.67 mL/g) with a spatula for 5 min. The stainless steel molds were filled with the slurry using a spatula and placed on a vibration table (KV-26 plus, Wassermann Dental-Maschinen GmbH, Hamburg, Germany). The molds were vibrated at 6000 rpm for further 5 min to