JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 57 (2016) 347–358

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jmbbm

Research Paper

Effects of oxygen plasma treatment on interfacial shear strength and post-peak residual strength of a PLGA fiber-reinforced brushite cement

Stefan Maenz[a,e,1], *Max Hennig*[a,1], *Mike Mühlstädt*[a], *Elke Kunisch*[b], *Matthias Bungartz*[c], *Olaf Brinkmann*[c], *Jörg Bossert*[a], *Raimund W. Kinne*[b,1], *Klaus D. Jandt*[a,d,e,1,*]

[a]*Chair of Materials Science, Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Germany*
[b]*Experimental Rheumatology Unit, Department of Orthopedics, Jena University Hospital, Waldkrankenhaus "Rudolf Elle", Eisenberg, Germany*
[c]*Chair of Orthopedics, Department of Orthopedics, Jena University Hospital, Waldkrankenhaus "Rudolf Elle", Eisenberg, Germany*
[d]*Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Germany*
[e]*Jena School for Microbial Communication (JSMC), Friedrich Schiller University Jena, Germany*

ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form
25 January 2016
Accepted 27 January 2016
Available online 5 February 2016

Keywords:
Calcium phosphate cement
Fiber reinforcement
Plasma treatment
Interfacial shear strength
Mechanical properties

ABSTRACT

Biodegradable calcium phosphate cements (CPCs) are promising materials for minimally invasive treatment of bone defects. However, CPCs have low mechanical strength and fracture toughness. One approach to overcome these limitations is the modification of the CPC with reinforcing fibers. The matrix-fiber interfacial shear strength (ISS) is pivotal for the biomechanical properties of fiber-reinforced CPCs. The aim of the current study was to control the ISS between a brushite-forming CPC and degradable PLGA fibers by oxygen plasma treatment and to analyze the impact of the ISS alterations on its bulk mechanical properties.

The ISS between CPC matrix and PLGA fibers, tested in a single-fiber pull-out test, increased up to 2.3-fold to max. 3.22 ± 0.92 MPa after fiber oxygen plasma treatment (100–300 W, 1–10 min), likely due to altered surface chemistry and morphology of the fibers. This ISS increase led to more efficient crack bridging and a subsequent increase of the post-peak residual strength at biomechanically relevant, moderate strains (up to 1%). At the same time, the work of fracture significantly decreased, possibly due to an increased proportion of fractured fibers unable to further absorb energy by frictional sliding. Flexural strength and flexural modulus were not affected by the oxygen plasma treatment.

This study shows for the first time that the matrix-fiber ISS and some of the resulting mechanical properties of fiber-reinforced CPCs can be improved by chemical modifications

*Corresponding author at: Chair of Materials Science, Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany. Tel.: +49 3641 947730; fax: +49 3641 947732.
E-mail address: k.jandt@uni-jena.de (K.D. Jandt).
[1]These authors have equally contributed to the study.

http://dx.doi.org/10.1016/j.jmbbm.2016.01.030

such as oxygen plasma treatment, generating the possibility of avoiding catastrophic failures at the implant site and thus enhancing the applicability of biodegradable CPCs for the treatment of (load-bearing) bone defects.

1. Introduction

Minimally invasive augmentation techniques with injectable cements, i.e. kyphoplasty and vertebroplasty, have become standard surgical techniques for the treatment of vertebral body fractures. Despite their lack in bioactivity and biodegradability, injectable poly(methyl methacrylate) (PMMA) cements are most frequently used, especially in load-bearing bone areas. In addition, there is a controversial discussion about the possible connection between supra-physiological strength and Young's modulus of the PMMA cements and subsequent fractures in adjacent vertebral bodies following kyphoplasty/vertebroplasty (Hulme et al., 2006; Nouda et al., 2009; Trout et al., 2006; Uppin et al., 2003).

Calcium phosphate cements (CPCs), as first described by LeGeros et al. and Brown/Chow (Brown and Chow, 1983; LeGeros et al., 1982), may be a promising alternative to PMMA cements since they are biodegradable and have a Young's modulus comparable to that of cancellous bone (Burguera et al., 2006). However, injectable and resorbable brushite-forming CPCs exhibit low mechanical strength and low fracture toughness, leading to premature damage of the cement at the implant site (Blattert et al., 2009; Wilke et al., 2006).

One possibility to increase the mechanical strength and fracture toughness of CPCs is the modification with reinforcing fibers. In this context, different studies describe the use of non-resorbable fibers consisting of aramide (Xu et al., 2000; Xu et al., 2001b), polyamide (dos Santos et al., 2000), polypropylene (Buchanan et al., 2007), glass (Xu et al., 2000) or carbon (Xu et al., 2001a; Xu et al., 2000), as well as the application of resorbable, biodegradable fibers, such as polycaprolactone, polylactide, polyglycolide or different copolymers thereof (Burguera et al., 2005; Canal et al., 2014; Dagang et al., 2007; Gorst et al., 2006, 2006; Losquadro et al., 2009; Maenz et al., 2014; Nair and Laurencin, 2007; Weir and Xu, 2010; Xu et al., 2007a; Xu et al., 2007b; Xu et al., 2000, 2000; Xu et al., 2006, 2006; Zhang and Xu, 2005; Zhao et al., 2010a; Zhao et al., 2010b). Detailed reviews about fiber-reinforced CPCs can be found elsewhere (Canal and Ginebra, 2011; Krüger and Groll, 2012).

For a resorbable CPC, biodegradable fibers in conjunction with degradable calcium phosphate phases are desirable. Biodegradable poly(L-lactide-co-glycolide) acid (PLGA) suture materials with yarn diameters of 200–350 μm have been used as biodegradable fiber reinforcement for CPCs in several studies (Burguera et al., 2005; Dagang et al., 2007; Gorst et al., 2006; Weir and Xu, 2010; Xu et al., 2007a; Xu et al., 2007b; Xu et al., 2000; Xu et al., 2006; Zhang and Xu, 2005; Zhao et al., 2010a; Zhao et al., 2010b). In general, the addition of PLGA fibers results in increased strength and work of fracture (WOF) with an increased fiber volume fraction (Gorst et al., 2006; Xu et al., 2000; Xu et al., 2006) or fiber length (Xu et al., 2000). However, the large diameter of commercial PLGA suture material limits their application in injectable CPCs.

In a recent study, our group for the first time described an injectable, PLGA fiber-reinforced, brushite-forming CPC, whose injectability mainly depended on the length of the applied PLGA fibers (diameter of 25 μm, Maenz et al., 2014). The mechanical strength showed a maximum at a fiber content of 5% (w/w), while the WOF was further augmented with increasing fiber content up to 7.5% (w/w). In general, the CPC's mechanical properties rose with increasing fiber length, suggesting that the interfacial shear strength (ISS) between the two components of the composite may be of critical importance for the efficacy of the reinforcement.

To the best of our knowledge, a modification of the fiber surface in a fiber-reinforced CPC has so far only been described in one study (Canal et al., 2014), in which polylactide (PLA) fibers treated by low-pressure oxygen plasma were incorporated into an apatite-forming CPC. The plasma treatment resulted in increased flexural strength and WOF compared to a CPC reinforced with untreated fibers. The authors suggested that the augmented mechanical properties may be due to an increased ISS between CPC and oxygen plasma-treated PLA fibers, but did not actually measure the ISS.

Therefore, the present study aimed at specifically enhancing the matrix-fiber ISS in a PLGA fiber-reinforced brushite-forming CPC and at analyzing the impact of the fiber modification on the CPC's bulk mechanical properties. To this end, oxygen plasma treatment of the PLGA fibers increased the ISS between CPC matrix and fibers up to 2.3-fold in a single-fiber pull-out test and significantly augmented the post-peak residual strength of the CPC at biomechanically relevant, moderate strains (up to 1%), suggesting that matrix-fiber ISS and the resulting mechanical properties of fiber-reinforced CPCs can be fine-tuned for future clinical applications.

2. Materials and methods

2.1. Materials

Two different types of PLGA fibers were used. PLGA fibers with a diameter of 25 μm were prepared and characterized as described in our recent study (Maenz et al., 2014). In brief, the fibers were extruded from the granulate material PURASORB PLG 1017 (Purac, Gorinchem, Netherlands) by using a mini extrusion system (RANDCASTLE EXTRUSION SYSTEMS INC, Cedar Grove, USA). Fibers were then cut using a cutting mill PULVERISETTE 19 (FRITSCH GmbH, Idar-Oberstein, Germany) with 1 mm sieve inserts. The fiber length after cutting was determined using a Zeiss Auriga 60 scanning electron