Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Feature article

Reinforcement with reduced graphene oxide of bioactive glass scaffolds fabricated by robocasting

Siamak Eqtesadi[a], Azadeh Motealleh[a], Rune Wendelbo[a], Angel L. Ortiz[b], Pedro Miranda[b,*]

[a] *Abalonyx AS, Forskningsveien 1, 0373 Oslo, Norway*
[b] *Departamento de Ingeniería Mecánica, Energética y de los Materiales, Universidad de Extremadura, Escuela de Ingenierías Industriales, Avda. de Elvas s/n, 06006 Badajoz, Spain*

ARTICLE INFO

Article history:
Received 28 November 2016
Received in revised form
26 December 2016
Accepted 27 December 2016
Available online xxx

Keywords:
45S5 Bioactive glass
Robocasting
Graphene platelets
Mechanical properties
Pressureless sintering

ABSTRACT

45S5 bioactive glass composite scaffolds reinforced with reduced graphene oxide (rGO) were fabricated for the first time by robocasting (direct-writing) technique. Composite scaffolds with 0–3 vol.% content of rGO platelets were printed, and then consolidated by pressureless sintering at 550 or 1000 °C in Ar atmosphere. It was found that the addition of rGO platelets up to 1.5 vol.% content enhanced the mechanical performance of the 45S5 bioactive glass scaffolds in terms of strength and toughness. Best performance was obtained for 1 vol.% rGO, which yielded an enhancement of the fracture toughness of ~850 and 380% for sintering temperatures of 550 and 1000 °C, respectively, while the compressive strength increased by ~290 and 75%. rGO addition thus emerges as a promising approach for the fabrication of novel bioglass scaffolds with improved mechanical performance without deterioration of their bioactivity, which may then find use in load-bearing bone tissue engineering applications.

1. Introduction

The 45S5 bioglass (Bioglass®) is one of the most widely used and well studied bioactive glasses [1]. Its excellent bioactivity and fast surface reaction *in vivo* promote adhesion, proliferation, and differentiation of osteoblasts, and eventually vascularization and bone growth through gene expression triggered by their degradation products [2,3]. In spite of its good biological properties, the intrinsic brittleness of 45S5 bioglass as well as its low strength seriously limit the commercial applications of 45S5 scaffolds fabricated by conventional methods (e.g. foam replication technique) [4].

Robocasting, an extrusion-based additive manufacturing technique, has been recently used to enhance the mechanical properties of bioceramic scaffolds in general [5,6], and of 45S5 [7] and other bioglass compositions [8] in particular. The mechanical enhancement is achieved through the deposition of structures with uniform struts and pre-designed pore architecture, with the required pore size and interconnectivity but however a lower total porosity [9]. In particular, it has been found that the robocast 45S5 bioglass scaffolds exhibit much higher mechanical strength in comparison to other 45S5 scaffolds made by conventional techniques [7].

Although robocasting has mitigated the weakness of 45S5 scaffolds, the intrinsic poor sinterability of 45S5 bioglass still limits the mechanical performance of 45S5 robocast scaffolds, compared to other compositions, like 13–93, that are more densifiable [8]. This is because the micropores within the robocast struts act as starting flaws for crack propagation, thus deteriorating the strength of these robocast scaffolds. Moreover, although the compressive strength of 45S5 robocast scaffolds may still lie in the range of cancellous bone values, the toughness of these scaffolds is still far from cancellous bone performance [10].

The addition of a polymeric phase to the brittle robocast 45S5 bioglass scaffolds is a suitable solution for enhancing not only their strength but also their toughness [10–12]. However this approach is not exempt from some disadvantages, regardless of whether one uses biodegradable synthetic or natural polymers [13]. The synthetic biopolymers do not have natural sites for cell adhesion, and these often need to be added. Further, degradation of some synthetic polymers *in vivo* is accompanied by a hydrolytic reaction causing a local reduction in pH and possible inflammatory response. Natural polymers are another alternative for the fabrication of hybrid scaffolds, but unfortunately the natural polymers

* Corresponding author.
E-mail address: pmiranda@unex.es (P. Miranda).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.12.047
0955-2219/

undergo rapid degradation and loss of mechanical properties after implantation [14].

Graphene, a monolayer of carbon atoms arranged in a honeycomb lattice, has shown impressive thermal, mechanical, and electrical properties, and is a promising alternative as a reinforcement to tailor the material structure at nanometre scale in order to obtain stronger and tougher engineering ceramics [15–17]. In addition, it has been recently found that cells adhere to and proliferate better when cultured on graphene films rather than on SiO_2 substrates [18,19]. It has also been reported that electrically conductive nano-fillers, such as graphene, can be used in bone tissue engineering to facilitate cell growth and tissue regeneration with physioelectrical signal transfer [20]. Thus, the possibility of enhancing mechanical properties and simultaneously biological performance motivates the application of graphene as reinforcing phase in scaffolds, as discussed in some recent studies [20–22].

With these premises in mind, in the present study robocast 45S5 bioglass scaffolds were reinforced with reduced graphene oxide (rGO) in order to enhance their mechanical properties for bone tissue engineering applications. This study is novel because, to the best of our knowledge, there are very few reports devoted to the additive manufacture of graphene or of graphene-reinforced materials, none of which is specifically centred on graphene-reinforced 45S5 bioglass. This is also the case for the porous structures shaped by robocasting since the earlier work in this field is devoted to robocast structures without a biomedical purpose made of graphene nanoplatelets [23] or of SiC with graphene nanoplatelets [24]. In what follows, we therefore present the results obtained from an ample study covering aspect of processing, sintering, microstructural characterization, and mechanical performance conducted on robocast scaffolds with a fixed three-dimensional design made of 45S5 bioglass reinforced with rGO.

2. Experimental procedure

2.1. Materials and ink preparation

The bioactive glass with the 45S5 composition (BG), containing 45% SiO_2, 24.5% CaO, 24.5% Na_2O, and 6% P_2O_5 (in wt.%), was supplied by Mo-SCI Corporation (USA). Carboxymethyl cellulose (CMC; M_w = 35 000, Lamberti Iberia S.A.U., Spain) with a viscosity for a 2 wt.% aqueous solution in the range of η = 1–3 Pa s, as indicated by the supplier, was used as the sole processing additive [9].

The powder of rGO was supplied by Abalonyx AS (Norway). Graphene oxide (GO) was synthesized according to a modified Hummers method, and then thermally reduced to obtain rGO. Powders with only a partial degree of reduction were selected to limit their hydrophobicity, which may cause difficulties during ink preparation. The resulting platelets are either single layers or stacks of graphene nano-platelets (GNPs) about 6–8 nm in thickness and around 5 μm in diameter.

The as-received BG powder was milled for 3 h in an attrition mill (model 01-HD, Union Process, USA), using high-purity zirconia container and balls as milling media and ethanol as dispersing medium, to refine the particles to the 1–10 μm size range. The slurry was dried at 60 °C and the resulting powder was sieved through 106 and 75 μm stainless steel sieves to eliminate large particle agglomerates.

Concentrated inks containing 35 vol.% of the milled BG powder and rGO were prepared with 2 wt.% CMC, using the following procedure. CMC was first dissolved in deionized water and different amounts of rGO (i.e., 0, 0.5, 1, 1.5, 2, and 3 vol.%) were added. Then, the suspensions were further agitated for 10 min at 1000 rpm to break the possible rGO agglomerates. 45S5 BG powder was then added to these suspensions in small batches while continuously mixing. All mixing was performed in a centrifugal planetary mixer (ARE-250, Thinky, Japan) for a total mixing time of around 20 min.

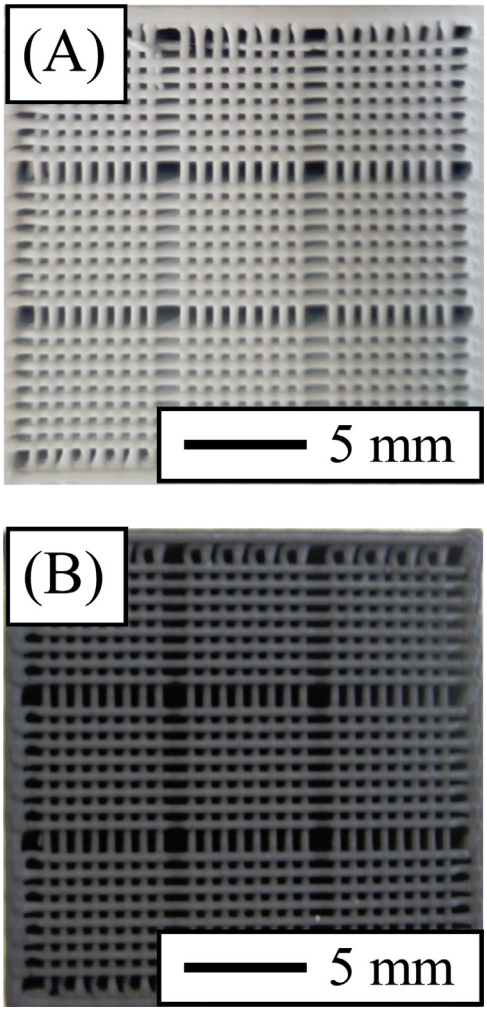

Fig. 1. Optical images of 3D porous scaffolds produced by robocasting from (A) 45S5 BG and (B) 45S5 BG-rGO inks, in their as-printed (non-sintered) condition. The difference in the color is due to presence of rGO in the 45S5 BG-rGO green body.

2.2. Robocasting of scaffolds

A robocasting device (A3200, 3D inks, USA) was used to fabricate three-dimensional structures of BG and BG-rGO from the inks. Each ink was individually housed in a syringe and extruded through a conical nozzle (inner diameter d = 410 μm) by the computer-controlled robotic system. The position of the nozzle moved following the CAD model designed previously in the control software (Robocad 3.0, 3D inks, USA). The scaffold design consisted of a tetragonal mesh with a center-to-center spacing between adjacent rods within a layer of $s = 2d$ = 820 μm and a layer height h = 287 μm. The external dimensions were 20 × 20 × 10 mm. Fig. 1 shows selected BG and BG-rGO scaffolds just after printing.

The ink flowed through the nozzle at the volumetric flow rate required to maintain a constant deposition speed of 20 mm s^{-1}. To prevent a non-uniform drying of the structure during assembly, the deposition process was carried out within a paraffin oil reservoir at room temperature. After deposition, the green bodies were removed from the bath and dried in ambient conditions for at least one day before sintering. The as-robocast scaffolds were all cut in nine pieces each, which were eventually used for the microstructural and mechanical studies.

Please cite this article in press as: S. Eqtesadi, et al., Reinforcement with reduced graphene oxide of bioactive glass scaffolds fabricated by robocasting, J Eur Ceram Soc (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.12.047