Journal of the European Ceramic Society 36 (2016) 2403–2409

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Mechanical characterization of glass-ceramic scaffolds at multiple characteristic lengths through nanoindentation

Mohamad Shahgholi[a], Sara Oliviero[d], Francesco Baino[b], Chiara Vitale-Brovarone[b], Dario Gastaldi[a], Pasquale Vena[a,c,*]

[a] Department of Chemistry, Materials and Chemical Engineering, Laboratory of Biological Structure Mechanics (LaBS) – Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
[b] Institute of Materials Physics and Engineering, Department of Applied Science and Technology, Politecnico di Torino, 10129 Torino, Italy
[c] I.R.C.C.S., Via R. Galeazzi 4, 20161 Milano, Italy
[d] University of Sheffield, Department of Human Metabolism, United Kingdom

ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form 18 January 2016
Accepted 27 January 2016
Available online 17 February 2016

Keywords:
Glass-ceramic
Scaffold
Nanoindentation
Micro-CT

ABSTRACT

The mechanical behaviour of implantable scaffolds is of relevant interest in all applications which require load-bearing capability. This study aims at establishing a quantitative relationship between the mechanical properties of glass-ceramic scaffolds for bone repair and the nano/micro-scale properties of their constituent materials. A nanoindentation study is carried out spanning different penetration depth on bulk (pore-free) glass-ceramic samples and on the walls of porous scaffolds. Micro-tomographical investigations allow assessing small-scale porosity of the scaffold walls. A simple homogenization model is used to establish the relationship between the elastic modulus of the bulk material and that of the micro-porous walls of the scaffolds. The elastic modulus of scaffold walls was found to be approximately 50% lower than that of the bulk glass-ceramic. The properties estimated experimentally on the walls of the scaffolds are quantitatively consistent with the analytical predictions provided by the homogenization model and the micro-porosity measured through tomographical analyses.

1. Introduction

The increase in average life expectancy is a great achievement of scientific findings; meanwhile, with ageing population over the last decades, now bone repair is one of the major clinical needs which requires significant research efforts [1,2]. Several studies have suggested the use of bioceramics, which include biocompatible glasses, glass-ceramics and (crystalline) ceramics, for bone defect healing and bone fracture treatment [3] in different regions of the body, i.e. in vertebrae, maxillofacial reconstruction [4], hearing restorations (ear prosthesis) [5], orthopaedics, dental implants [6–8], etc. Bioactive ceramics and bioactive glasses are able to create a stable interface with host tissue, and some of them can even stimulate new tissue growth, which is crucial to pursue clinical success in their applications [9]. In the early 1970s, Hench and coworkers showed bioactivity of 45S5 bioglass [10]; from then various formulation of bioglasses have attracted the interest of the researchers in different tissue repair applications [11–14], and in the specific field of bone repair [14–18]. In this regard, the most important role played by the scaffolds in bone tissue repair is the recovery of natural bone functions [19,20]. Specifically, major attention was devoted to optimizing the design, composition and mechanical behaviour of porous bioactive glass-based scaffolds for hard tissue recovery.

Often a three-dimensional (3-D) porous scaffold structure is fabricated by using bioactive glasses in order to direct and support bone tissue growth and regeneration [21,22]. Bioactive glasses are reported to stimulate more bone regeneration compared to other bioactive ceramics but they lag behind other bioactive ceramics in terms of clinical success [15]. Hence, the number of research activities on bioactive glasses is growing due to their unreached potential in the market. In this work we deal with 3-D bioceramic sintered scaffolds fabricated from the SiO_2-based glass formulation CEL2 which was demonstrated to be highly bioactive in vitro [23] and biocompatible with osteoblasts that expressed the typical markers of osteogenesis [24,25].The method selected

* Corresponding author at: Department of Chemistry, Materials and Chemical Engineering, Laboratory of Biological Structure Mechanics (LaBS) – Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy.
E-mail addresses: mohamad.shahgholi@gmail.com (M. Shahgholi), sara.oliviero@libero.it (S. Oliviero), francesco.baino@polito.it (F. Baino), chiara.vitale@polito.it (C. Vitale-Brovarone), dario.gastaldi@polimi.it (D. Gastaldi), pasquale.vena@polimi.it (P. Vena).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.01.042
0955-2219/

for scaffold fabrication, i.e. sponge replication, is able to produce highly-interconnected 3-D network of open macropores [26] and trabecular structures characterized by micro and nanopores. These peculiar features at different length scales substantially affect the mechanical properties of the scaffold. It is therefore of great relevance to establish a characterization method that is able to determine the real mechanical properties of the glass-ceramic scaffold. This method must explicitly account the features of the material which are peculiar for the specific manufacturing approach: namely, micro-porosity of the scaffold walls originated by the sintering process. The specific aim of this study is to establish a quantitative relationship between the mechanical properties of the glass-ceramic scaffold and the nano and micro-scale properties of the constituent material with specific reference to the material stiffness. This aim is achieved through an experimental and analytical approach to the mechanical characterization of the scaffolds carried out at multiple characteristic lengths. A nanoindentation study carried out at multiple penetration depths (indentation loads) is integrated with analytical homogenization models and voxel-specific micro-CT data on 3-D porous scaffolds.

Very few papers are available on the application of nanoindentation tests on ceramic scaffolds, among them Vivanco et al. [27] used nanoindentation to characterize the mechanical properties of the scaffold walls with specific reference to the effect of the compliance of the micro-struts. More papers are available on micro-CT scan data used to assess the micro-porosity of the ceramic microstructures. Scheiner et al. [28] used micro-CT data to assess the microporosity of the same glass-ceramic material investigated in this study. To the authors' knowledge, the approach presented in this paper which puts together the micro-CT data and the nanoindentation data gathered at multiple characteristic lengths is novel. The mechanical characterization of the constituent glass-ceramic in a bulk form was the starting point of this study. Unlike its bulk form, sintered glass-ceramic scaffolds exhibit small scale porosity which may heavily affect the mechanical properties of the scaffold wall. Thereby, the nanoindentation study carried out on the microstructure of the sintered scaffold will determine in a quantitative fashion the effect of the sintering process on the mechanical properties of the scaffold structural features. Well-established analytical homogenization models are used to correlate the mechanical properties of the sintered structures with their nano- and micro-porosity. The porous structure as estimated through the analytical approach will be validated by making use of the attenuation data of micro-CT scans carried out on the glass-ceramic scaffolds.

2. Materials and methods

2.1. Preparation of CEL2 bulk samples and scaffolds

An experimental SiO_2-based glass formulation (CEL2; molar composition: 45% SiO_2, 3% P_2O_5, 26% CaO, 15% Na_2O, 7% MgO and 4% K_2O) was selected to produce the samples investigated in the present work. The glass was prepared by melting the required quantities of high-purity reagents (powders of SiO_2, $Ca_3(PO_4)_2$, $CaCO_3$, Na_2CO_3, $(MgCO_3)_4$ $Mg(OH)_2$ $5H_2O$ and K_2CO_3 purchased from Sigma–Aldrich and used as received) in a platinum crucible in air (1500 °C for 0.5 h to ensure homogeneity of the melt; heating rate 10 °C min^{-1}). The melt was poured in stainless steel moulds (about 50 mm × 10 mm × 10 mm) and an annealing treatment (500 °C for 12 h) was applied for glass thermal stress relaxation. The obtained glass bars were cut into 2-mm thick slices by using a diamond wheel (Accutom 5, Struers); these slices will hereafter be referred to as "bulk samples". The porous samples were obtained by means of the procedure described below. The melt was quenched into cold water to obtain a "frit" that was ground by ball milling (a six-ball zirconia milling machine was used), and the glass powders were eventually sieved through stainless steel sieves (Giuliani Technologies, Italy) to obtain a powder with a particle size below 32 μm. The 3-D scaffolds were produced by the sponge replication method, which was shown to be very effective to obtain porous ceramics with a highly-interconnected 3-D network of open macropores [26]. Small cubic blocks (10 mm × 10 mm × 10 mm) of a commercial open-cell polyurethane (PU) sponge (45 ppi; density of the porous PU ≈ 20 kg/m^3) were coated with CEL2 powder by impregnation into a water-based glass slurry (glass:distilled water:poly(vinyl alcohol) (PVA) = 30:64:6 wt.%). After PVA hydrolysis under continuous magnetic stirring at 80 °C, CEL2 powder was added to the solution; the water evaporated during PVA dissolution was re-added to the slurry to restore the correct weight ratios among the slurry components. After further stirring for 15 min at room temperature to ensure slurry homogeneity, the sponge blocks were immersed in the slurry. The slurry infiltrated the porous network of the PU template, that after 1 min was extracted from the batch and subsequently compressed (≈50 kPa for 1 s) up to 60% in thickness along three orthogonal spatial directions, in order to homogeneously remove the excess slurry; this infiltration/compression cycle was repeated for three times and a final cycle of impregnation alone was performed. The glass-coated sponges were dried at room temperature overnight and afterwards thermally treated at 950 °C for 3 h (heating and cooling rates set at 5 and 10 °C min^{-1}, respectively) in order to burn-off the polymeric template and to sinter the inorganic particles. A glass-derived replica of the starting PU template was finally obtained. As reported elsewhere [26], two crystalline silicate phases develop during the above-mentioned heat treatment; however, for the sake of simplicity, the expressions "CEL2 scaffold" or "CEL2 sample" will be hereafter adopted, without further specifying the glass-ceramic nature of the sintered materials. Consistently, the bulk samples were heat-treated according to the same conditions used to produce the scaffolds in order to obtain a material with the same crystalline phases.

2.2. Embedding and polishing

Bulk and CEL2 samples were embedded in epoxy resin (Epofix, Struers) in order to facilitate the polishing procedure. Subsequently, a metallographic polishing wheel (Buehler) was used to perform 7 consecutive steps of polishing: 4 steps were performed using SiC sandpapers (grit sizes 600, 1200, 2500 and 4000) and 3 steps using adhesive papers (Alulap and Polilap) with alumina (Al_2O_3) suspensions (particle sizes 1 μm, 0.05 μm and 20 nm). Each step was performed at 100 rpm speed for 4 min in clockwise direction and 4 min in counterclockwise direction. After polishing, samples were immersed in ultrasonication bath (SONIC A) with deionized water for 7 times, 5 min each, in order to remove polishing debris. A contact profilometry procedure was used to assess the average roughness over a 20 μm × 20 μm square area of the polished surface. This was performed by using the Nanotest Platform described below and a tiny contact load (0.05 mN); an average roughness of approximately 100 nm was achieved. The heterogeneous nature of the sample surface did not allow us to obtain smoother surfaces. Due to this specific nature of the sample surface, indentation sites were selected manually on the basis of the microscopic imaging of the surface.

2.3. Nanoindentation tests

Three bulk samples and four porous samples underwent nanoindentation tests. Nanoindentation tests were performed on Nanotest Platform 3 (MicroMaterials) at controlled temperature of 28 °C using a Berkovich diamond indenter. Load-controlled