



Structure–property–processing correlations in freeze-cast composite scaffolds



Philipp M. Hunger^{a,b}, Amalie E. Donius^b, Ulrike G.K. Wegst^{a,*}

^a Thayer School of Engineering, Dartmouth College, 14 Engineering Drive, Hanover, NH 03755, USA

^b Department of Materials Science and Engineering, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA

ARTICLE INFO

Article history:

Received 24 July 2012

Received in revised form 21 December 2012

Accepted 1 January 2013

Available online 12 January 2013

Keywords:

Composites

Porosity

Biopolymers

Scaffolds

Biomimetics

ABSTRACT

Surprisingly few reports have been published, to date, on the structure–property–processing correlations observed in freeze-cast materials directionally solidified from polymer solutions, or ceramic or metal slurries. The studies that exist focus on properties of sintered ceramics, that is materials whose structure was altered by further processing. In this contribution, we report first results on correlations observed in alumina–chitosan–gelatin composites, which were chosen as a model system to test and compare the effect of particle size and processing parameters on their mechanical properties at a specific composition. Our study reveals that highly porous (>90%) hybrid materials can be manufactured by freeze casting, through the self-assembly of a polymer and a ceramic phase that occurs during directional solidification, without the need of additional processing steps such as sintering or infiltration. It further illustrates that the properties of freeze-cast hybrid materials can independently be tailored at two levels of their structural hierarchy, allowing for the simultaneous optimization of both mechanical and structural requirements. An increase in freezing rate resulted in decreases in lamellar spacing, cell wall thickness, pore aspect ratio and cross-sectional area, as well as increases in both Young's modulus and compressive yield strength. The mechanical properties of the composite scaffolds increased with an increasing particle size. The results show that both structure and mechanical properties of the freeze-cast composites can be custom-designed and that they are thus ideally suited for a large variety of applications that require high porosity at low or medium load-bearing capacity.

© 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The first detailed studies on “freeze casting”, the directional solidification of a polymer solution and the mechanisms by which a well-controlled and complex cellular architecture can be created, are probably those published by Ezekwo et al. [1] and Tong et al. [2,3]. They studied in detail the physical phenomena of directional solidification in water-based agar solutions and observed the effect of freezing-front velocity and diffusion conditions on the geometry of the ice-templated structure, drawing on extensive literature concerned with the directional solidification of metals and alloys. The first reports on the freeze casting of porous ceramics appeared at the turn of the millennium [4,5], followed by publications that described the potential of freeze-cast ceramic scaffolds for biomedical applications due to an attractive combination of connected porosity and mechanical properties [6–8].

Interestingly and despite the fact that both ceramics and metals are freeze-cast using polymeric binders to stabilise the green body

before sintering, no studies have been published to date that report property values for freeze-cast ceramic composites solely glued with a polymeric phase and not further processed by sintering. One important advantage of such materials design is that multiscale composite materials can be created, which emulate the hierarchical composite structure found in stiff and strong, yet tough, natural materials such as nacre and bone [9–11]. Another advantage is that this cold processing route permits the addition of functional groups and components to the polymeric phase during scaffold formation to create functionalised biomaterials, whose activity is not compromised due to high temperature processing steps. A third advantage is that freeze casting is a highly versatile process with which highly connected and aligned porosity can be created [12]. It provides excellent control across several length-scales over the pore size and geometry as well as the pore wall architecture [13]. Thus, hierarchical scaffold architectures, including those with gradient properties in composition, structure and properties, can be produced [14].

Currently, applications of particular interest for freeze-cast materials range from hard and soft tissue scaffolds to solid oxygen fuel cells, and from catalyst carriers to electrodes in electrochemical cells [5,7,15–17]. Though little explored, great potential for

* Corresponding author. Tel.: +1 603 646 3148; fax: +1 603 646 6584.

E-mail address: ulrike.wegst@dartmouth.edu (U.G.K. Wegst).

freeze-cast materials also exists in applications that require the porosity of the scaffold to be filled with a second phase. Overall, freeze casting is a process with great promise for the synthesis of hierarchical materials that combine high porosity with excellent mechanical performance and whose properties can be tailored to a specific application.

For the custom design of materials, it is important to gain a fundamental understanding of how material composition and processing affect structure and mechanical properties. The work presented here is a first attempt to explore these with a model material consisting of alumina particles in a biopolymer matrix. From it, hierarchically structured composites with a highly aligned, honeycomb-like porosity were prepared by freeze casting.

At the first hierarchical level, pore size and geometry were modified through variation of the freezing rate and studied at a constant overall porosity and composition. At the second level of hierarchy, the effect of particle size and single vs. bimodal particle size distribution on the cell wall's mechanical properties and performance were investigated, while keeping the overall cell wall material composition constant.

2. Materials and methods

2.1. Solution preparation and properties

Low molecular weight chitosan (75–85% deacetylated, Sigma Aldrich, St. Louis, MO) and type B gelatin from bovine skin (Sigma Aldrich, St. Louis, MO) were used as received. Chitosan and gelatin solutions were prepared by dissolving 2.4% (w/v) chitosan and 5.5% (w/v) gelatin in 1 vol.% glacial acetic acid (VWR International, West Chester, PA). The chitosan solutions were mixed thoroughly by magnetic stirring at 60 rpm for 24 h. Gelatin solutions were mixed by magnetic stirring at 60 rpm for 12 h at a temperature of 35 °C. After initial stirring, chitosan and gelatin solutions were mixed in a volume ratio of 4:1 in a high shear SpeedMixer (DAC 150 FVZ-K, FlackTek, Landrum, SC) at a speed of 1600 rpm for 60 s to blend a 3% (w/v) polymer solution consisting of 63 wt.% chitosan and 37 wt.% gelatin [18].

The viscosity of the chitosan–gelatin solution was determined at room temperature (25 °C) on an AR 2000ex rheometer (Rheology Advantage Version 5.5.0 data analysis software, TA Instruments, New Castle, DE) [19]. A concentric cylinder geometry with a stator inner radius of 15 mm, a rotor outer radius of 14 mm, a cylinder immersion height of 42 mm and a gap of 5920 µm was used to measure the viscosity. Approximately 20 ml of the solution was pipetted into the stator of the concentric cylinder system, and the viscosity was measured in a shear rate range of 40–1100 s⁻¹. The viscosity of the 63/37 wt.% chitosan–gelatin in 1% acetic acid solution, which has a density of 1.01 g cm⁻³, was found to be 0.0689 Pa s at room temperature.

2.2. Slurry preparation and properties

Ceramic slurries of identical composition, but of three different particle size distributions, were prepared by suspending 27% (w/v) alumina particles of two different sizes in the aforementioned chitosan–gelatin solution using the SpeedMixer at a speed of 2500 rpm for 60 s for mixing and degassing. The particle diameter in slurry 1 was small (S), $d_{50} = 400$ nm (Sasol North America Inc. – Ceralox Division, Tuscon, AZ); the particle diameter in slurry 2 was large (L) $d < 10$ µm (Sigma Aldrich, St. Louis, MO). Slurry 3 had a bimodal (B) particle size distribution with 70 wt.% of $d < 10$ µm particles and 30 wt.% of $d_{50} = 400$ nm particles. All three slurries resulted in a final dry composition of 75 vol.% alumina, 16 vol.% chitosan and 9 vol.% gelatin.

2.3. Freeze casting and lyophilisation

Polymer solutions and ceramic slurries were directionally solidified using the freeze casting system detailed in an earlier publication [20]. Briefly, 10 ml of the polymer solution or ceramic slurry was poured into a polytetrafluoroethylene (PTFE) mould, which was sealed with a copper bottom plate and degassed at 1600 rpm for 60 s in a DAC 150 FVZ-K SpeedMixer. For freezing, the filled mould was placed with its copper bottom on the temperature-controlled copper cold finger of the freeze-caster, while the top of the mould remained open to atmospheric conditions. After precooling the slurry to 5 °C, the cold finger temperature was reduced at a constant freezing rate of either 1 or 10 °C min⁻¹ to directionally solidify the sample. Once fully frozen, the sample was removed from the cold finger, demoulded with a punch and placed for at least 72 h in a FreeZone 4.5 Liter Benchtop Freeze Dry System (Labconco, Kansas City, MO) to sublimate the ice.

To determine the velocity at which the freezing front travels along the sample for a given applied cold finger cooling rate, the temperature profile was monitored and recorded during freeze casting by a mould equipped with six thermocouples mounted along its height at a spacing of 6.35 mm. To avoid any physical disturbance of the freezing process, the thermocouples were positioned in 640 µm diameter holes drilled from the outside into the PTFE mould wall, maintaining a wall thickness of 170 µm between the thermocouple and the inside of the mould. The freezing front was assumed to be positioned at the 0 °C temperature contour and the freezing front velocity calculated as the speed at which this travels along the height of the mould. Local cooling rates were determined for each thermocouple position.

The density of the samples was determined by weighing each sample cube for mechanical testing and dividing it by the sample volume of 25 mm³. The relative density was calculated as the ratio of the measured density to the density of the solid wall material. The overall porosity P of the scaffolds was determined as $P = 1 - \rho_{rel}$.

2.4. Sample preparation for structural and mechanical characterisation

After lyophilisation, the dry cylindrical samples were fixed with their bottoms on a ceramic plate for cutting into predetermined shapes and sizes for structural and mechanical characterisation. Cutting was performed by hand with a 220 µm diameter diamond-decorated steel wire and a wire speed of 0.7 m s⁻¹ on a Well 4240 saw (WELL Diamond Wire Saws, Inc., Norcross, GA). For structural and mechanical characterisation, cubes with a side length of 5 mm were cut at three standard heights, measured from the bottom of the sample with cube centres at 7, 17.5 and 28 mm, respectively. For each sample, four cubes were prepared and tested per sample height, and at least three samples of each composition were prepared and investigated mechanically and structurally.

2.5. Structural characterisation through microscopy and nitrogen sorption (BET)

To determine the overall porosity of the entire cylinder before cutting and to measure the density of each specimen before structural characterisation and mechanical testing, the samples were weighed on a high precision balance (± 0.01 mg; XP105 Delta Range, Mettler Toledo Inc., Columbus, OH). The 5 mm cubes were precision cut with the diamond wire saw, whose wire was positioned for cutting with a micrometre screw of 0.5 µm accuracy.

The structure of the freeze-cast scaffolds was quantified using scanning electron microscopy (SEM) with a Zeiss Supra 50VP (Carl Zeiss NTS LLC., Peabody, MA, USA) at accelerating voltages between

Download English Version:

<https://daneshyari.com/en/article/10159891>

Download Persian Version:

<https://daneshyari.com/article/10159891>

[Daneshyari.com](https://daneshyari.com)