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Direct ink writing of wollastonite-diopside glass-ceramic scaffolds from a silicone resin and engineered fillers

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ABSTRACT

Wollastonite-diopside scaffolds have been successfully developed by direct ink writing of an ink made of silicone polymer and inorganic fillers. The main reason for using a silicone in the ink formulation consisted in its double effect, in controlling the ink rheology and in developing of wollastonite and diopside crystalline phases upon heat treatment. The obtained 3D wollastonite-diopside scaffolds featured regular geometries, and a high compressive strength (3.9–4.9 MPa) when considering the large amount of porosity (68–76 vol.%). A glass with the same oxide composition as the silicone-based ink and crystallizing into wollastonite and diopside, was produced and used as additional filler. This addition enabled the fabrication of even stronger 3D printed scaffolds (~8 MPa for a porosity of 67 vol%), owing to the enhanced viscous flow upon firing which reduced the micro-cracks in the scaffold struts generated by the preceramic polymer decomposition. The obtained highly porous wollastonite-diopside glass-ceramic scaffolds are suitable candidates for bone tissue engineering.

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1. Introduction

Ca-rich Silicate bioceramics, such as CaSiO_3 (wollastonite) and Ca–M–Si (M = Mg, Zn, Ti, Zr), have received a great attention for bone tissue regeneration applications [1,2]. It has been reported that their mechanical strength, especially the fracture toughness, is generally higher than that of HAp ceramics [3]. The incorporation of elements (such as Zn, Mg, Ti, Zr and Sr) into calcium silicate ceramics has shown great potential to further promote their orthopaedic application. The addition of these elements improved the mechanical characteristics and controlled dissolution rates, which provide an indication for stability and bioactivity (i.e. apatite formation and mineralization) of the material [4–10]. However, it is necessary to remind that there are also some limitations for silicate bioceramics in terms of development and sintering [1].

Recent studies demonstrated the possibility to develop high purity silicate ceramics (including bioceramics), using the approach of polymer-derived ceramics (PDCs), i.e. considering silicone resins containing oxide fillers as additives [11]. Oxide or oxide-precursor powders (especially if nano-sized) react easily with the amorphous silica provided by the oxidative decomposition of silicones, at rela-

tively low temperatures. The preceramic polymer technology does not only enable the synthesis, but also contributes positively to the shaping of the ceramic components, allowing to obtain quite complex morphologies in the shaped product. In particular, highly porous structures, which are extremely useful in the biomaterial field for bone tissue regeneration, can be easily achieved. As an example, porous akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) [12] hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$) [13] and wollastonite-diopside (CaSiO_3 – $\text{CaMgSi}_2\text{O}_6$) [14–16] ceramics were successfully fabricated from silicone-based mixtures first subjected to a low temperature foaming (not exceeding 350 °C) and later fired at high temperature (above 1000 °C). The low temperature foaming was due to gas released when the silicone was still in polymeric state, due to the decomposition of added organic compounds [11,13], or by decomposition of the same fillers if they were added in the form of hydrated compounds, such as $\text{Mg}(\text{OH})_2$ and sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) or sodium phosphate dibasic heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) [12,14–16]. The latter fillers can be seen playing a multifunctional role, since they contribute to both foaming, by water release, and to the development of the desired crystalline phases and sintering, by forming a liquid phase upon firing which favours ionic interdiffusion. As previously observed [16], since the liquid phase provided by the secondary filler remains as a glass phase after cooling at room temperature, the resulting product (comprising crystalline silicates dispersed within a glass phase), although not derived from a homogeneous glass,

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may be considered as a new kind of glass-ceramic (i.e. a 'polymer-derived glass-ceramic').

The preceramic polymer route enables to use additive manufacturing (AM) techniques, such as powder-based 3D printing and direct ink writing (DIW), for the fabrication of components, e.g. porous scaffolds, of complex geometry, exhibiting both an ordered macro-porosity and a homogenous micro-porosity in the struts. We recently investigated two different AM approaches: in the first one (powder-based indirect printing), bioglass powders were mixed with a silicone and oxide fillers. The silicone behaved as an active binder, incorporating and binding both glass and filler powders at low temperature, and contributing to phase development, at high temperature, by reacting with the filler powders. The crystal phases thus resulted both from the devitrification of the bioglass and from the silicone-filler reaction [17]. In the second approach (DIW), a silicone mixed with fillers was used directly in the formulation of an ink suitable for the fabrication by direct printing of hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$) bioceramic scaffolds. The use of a preceramic polymer in the formulation allowed to achieve suitable pseudoplastic rheological properties of the ink, and to form the desired crystalline phases upon heat treatment, by its reaction with the fillers (CaO and ZnO precursors) [18].

In this paper, we investigated the fabrication of wollastonite-diopside bioceramic scaffolds by direct printing (DIW) starting from an ink based on a preceramic polymer plus fillers (to produce a bioceramic) but also containing some bioglass powder. Unlike powder-based indirect 3D printing, glass powders were used in a limited amount, with the specific aim of enhancing the formation of liquid phase upon firing in order to achieve denser struts and better mechanical properties, with respect to a formulation based only on preceramic polymer and fillers.

2. Experimental procedure

a) Direct ink writing of wollastonite-diopside scaffolds

First of all, inks not containing added glass particles were prepared, to fabricate reference samples (later referred to wollastonite-diopside or W-D scaffolds). A commercially available silicone resin, MK (supplied as a fine powder $<100\ \mu\text{m}$, Wacker-Chemie GmbH, Munich, Germany). The MK silicone was considered as the main silica source due to its high ceramic yield (84 wt%), upon thermal decomposition in air (the polymer transforms into highly reactive amorphous silica, SiO_2). To produce the ink, MK was initially dissolved in isopropanol (IPA) and then mixed with fumed silica (FS, Aerosil R106, Evonik, Essen, Germany), in an amount corresponding to a weight ratio between MK-derived silica and FS of 9:1. The mixing was carried out by means of a ball mill for 1 h at a speed of 200 rpm/min, in an alumina jar with alumina balls (diameter $\sim 1\ \text{cm}$). In this way, it was possible to obtain a homogeneous mixture free of aggregates. Fumed silica was added to control the rheology of the ink, as demonstrated in a previous work [18].

After mixing MK and fumed silica with IPA, active oxide fillers (CaCO_3 and $\text{Mg}(\text{OH})_2$, both $<10\ \mu\text{m}$, Industrie Bitossi, Vinci, Italy) were added in amounts corresponding to a CaO:MgO:SiO₂ molar ratio equal to 2:1:3, which enables to obtain wollastonite ($\text{CaO}\cdot\text{SiO}_2$) and diopside ($\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) in a molar ratio equal to 1 [14–16]. Finally, anhydrous sodium phosphate (sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, Sigma Aldrich, Gillingham, UK) was introduced as extra filler (5 wt% of the theoretical ceramic yield of the other components). The ink which was again ball-milled for 4 h at 400 rpm and finally loaded into a syringe and extruded through a conical nozzle ($D = 410\ \mu\text{m}$, Nordson Italia S.p.A., Milano, Italy). 3D printing was performed at room temperature, using a commercial printer equipped a syringe extruder (Powerwasp Evo, Wasp, Massa Lombarda, Italy). The printed scaffolds had the following geometry:

$5 \times 5 \times 5$ and $15 \times 5 \times 5\ \text{mm}^3$, with 1 mm spanning length between the center of two contiguous filaments. The z-axis displacement (i.e. the layer thickness) was $350\ \mu\text{m}$, while the diameter of the nozzle was $410\ \mu\text{m}$, which led to a certain overlapping and increased the adhesion between the scaffold layers. The printing process was carried out in sunflower oil in order to prevent nozzle clogging due to drying phenomena. After printing, the scaffolds were left to dry in ambient conditions and then subjected to a crosslinking process at $200\ ^\circ\text{C}$ for 1 h.

b) Preparation of wollastonite-diopside glass and scaffolds from glass-containing ink

The overall oxide composition of the adopted silicone-based mixture (SiO_2 : 51.7 wt%; CaO: 32.1%; MgO: 11.5%; Na₂O: 2.2%; P₂O₅: 2.5%) was considered also for developing a glass (later referred to wollastonite-diopside or W-D glass) to be used as further filler. W-D glass was produced from pure minerals and chemicals (silica, dolomite, calcium carbonate – all in powders $<10\ \mu\text{m}$, Industrie Bitossi, Vinci, Italy – and sodium phosphate – same as above), by melting in a platinum crucible at a temperature of $1400\ ^\circ\text{C}$ (heating rate of $10\ ^\circ\text{C}/\text{min}$).

The mixture led to a homogeneous glass, despite the short holding time (15 min at $1400\ ^\circ\text{C}$), that was suddenly cooled by direct pouring on a cold metal plate. The glass fragments were easily reduced into fine powders by ball milling and were later manually sieved; only the particles passing through the smallest available sieve aperture (below $45\ \mu\text{m}$) were kept.

A second ink was produced adding the above mentioned fine W-D glass powders to the previous formulation (glass content corresponding to 10 wt% of the total ceramic yield of all other reactants). Scaffolds were produced according to the same conditions applied before.

c) Preparation of monolithic wollastonite-diopside tablets

In order to further assess the impact of glass as reactive filler, monolithic wollastonite-diopside tablets were prepared using $\text{Mg}(\text{OH})_2$ and CaCO_3 micro-particles, mixed with MK, sodium-phosphate and W-D glass (in an amount varying from 0 to 70 wt% of the theoretical ceramic yield of the other components). MK was dissolved in isopropanol (15 ml for 10 g of final ceramic) and then mixed with the micro-sized fillers. The mixing was performed under magnetic stirring, followed by sonication for 10 min, which allowed to obtain stable and homogeneous dispersions. The mixtures were poured into glass containers and dried at $80\ ^\circ\text{C}$ overnight. After drying, the silicone-based mixtures were in the form of solid fragments, later converted into fine powders by ball milling at 350 rpm for 30 min. The powders were cold-pressed in a cylindrical steel die applying a pressure of 20 MPa for 1 min, without using any additive. Specimens of 0.5 g, having 16.6 mm in diameter and approximately 2 mm in thickness, were obtained. For comparison purposes, tablets of glass-free formulation were also prepared.

d) Ceramization and characterization of glass-ceramics

W-D glass powders were subjected to differential thermal analysis (DTA, Netzsch STA 429, Selb, Germany), with heating rate of $10\ ^\circ\text{C}/\text{min}$ up to $1100\ ^\circ\text{C}$ in air, according to previous experiences on wollastonite-diopside foams [14,15]. Silicone/fillers/glass pellets were fired at $900\text{--}1100\ ^\circ\text{C}$, for 1 h in air, with a heating rate of $10\ ^\circ\text{C}/\text{min}$, whereas wollastonite-diopside scaffolds, with and without W-D glass, were fired at $1100\ ^\circ\text{C}$ for 1 h both in air and flowing nitrogen (99.9%).

Microstructural characterization on both pellets and scaffolds were conducted on the ceramized scaffolds by means of optical stereomicroscopy (AxioCam ERc 5s Microscope Camera, Carl Zeiss Microscopy, Thornwood, New York, USA) and scanning electron microscopy (FEI Quanta 200 ESEM, Eindhoven, Netherlands) equipped with EDS.

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