



Glass powders and reactive silicone binder: Interactions and application to additive manufacturing of bioactive glass-ceramic scaffolds



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ABSTRACT

A novel concept for the additive manufacturing of three-dimensional glass-ceramic scaffolds, to be used for tissue engineering applications, was based on fine glass powders mixed with a reactive binder, in the form of a commercial silicone. The powders consisted of ‘silica-defective glass’ specifically designed to react, upon firing in air, with the amorphous silica yielded by the binder. By silica incorporation, the glass was intended to reach the composition of an already known $\text{CaO-Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ system. Silica from the binder provided up to 15 wt% of the total silica. With the same overall formulation, silicone-glass powder mixtures led to nearly the same phase assemblage formed by the reference system, crystallizing into wollastonite (CaSiO_3) and Ca-borate (CaB_2O_4). Samples from silicone-glass powder mixtures exhibited an excellent shape retention after firing, which was later exploited in highly porous reticulated scaffolds, obtained by means of direct ink writing (DIW).

1. Introduction

Among preceramic polymers (i.e. polymers yielding a ceramic residue after firing), silicones are particularly interesting as raw materials for silicate ceramics [1]. In fact, oxides dispersed in a silicone matrix, directly in form of oxide powders, carbonates, hydroxides etc., easily react with the silica-rich amorphous residue formed by the polymer (upon heating above 500–600 °C). Then, the desired silicates (corresponding to a specified molar balance between metal oxide and silica) may be achieved in conditions of low processing temperature and high phase purity [1]. Polymer-derived silicates are advantageous also for the processing, since the use of silicones enables the application of plastic-forming techniques, often supported by the same fillers. Besides providing oxides to be combined with the silica-rich residue, the fillers may be used also to release some water vapour upon heating (e.g. using hydrated borates) [2], at low temperature (300–350 °C), i.e. with silicones still in the polymeric state, in order to achieve highly porous foams (transformed into ceramic foams at higher temperatures).

Glass powders represent a quite particular class of oxide fillers. Glass may remain substantially inert, embedded in a polymer-derived matrix, as recently shown by Francis et al. [3], who explored silicone/

bioglass coatings, fired at temperatures not exceeding 500 °C, i.e. with silicones are still at the early stages of ceramic conversion. As an alternative, glass may interact with the matrix, in different ways. Glass (in limited amounts) may ‘correct’ some issues of ceramics from silicone-oxide filler mixtures, especially the formation of micro-cracks. These cracks could be ascribed to the gas release from ceramic conversion and to the volumetric changes in the crystallization of silicates within a rigid matrix. Glass powders, as additional fillers, enhance the formation of liquid phase upon firing (offering some stress relaxation), with no negative impact on the phase assemblage, if the chemical composition of the glass additive matches with that of silicone-oxide filler mixtures [2,4]. In some cases, glass particles are mainly used, combined with ceramic particles, to limit the shrinkage in the course of polymer-to-ceramic conversion, with limited impact on sintering. Parchovianský et al. as an example, used special aluminosilicate-zirconate glasses ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-ZrO}_2$), prepared in the form of microspheres (by flame synthesis), in batches for developing relatively thick, protective, dense and well adherent coating system on steel (the authors actually used an un-filled polysilazane to form a bond coat, in turn covered by a top coat from the same polymer mixed with fillers) [5].

The ‘integration’ of the ceramic residue of preceramic polymer and

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glass fillers, used in significant amounts, was first discussed in the pioneering work by Ohl et al. [6]. These authors introduced borax in a silicone matrix, embedding Duran® glass powders as main fillers; the interaction between polymer-derived silica with Na₂O and B₂O₃ (from borax) was intended to form a glass with a chemical composition approaching that of the commercial boro-silicate glass. Although a homogeneous glass was not achieved (silicone/glass/borax mixtures led to partially crystalline samples, featuring some cristobalite), the approach led to transparent ceramic foams. A second example concerns the use of silicone as ‘non-sacrificial’ binder, i.e. not subjected to complete burn-out, in analogy to what already done with advanced ceramics [7]. More precisely, Zocca et al. [8] successfully manufactured porous bioceramics by means of powder-based 3D printing of AP40 bioglass powders mixed with a silicone, exhibiting a distinctive binding action. In fact, the mixture was selectively consolidated by injection of a liquid (mixture of 1-hexanol and hexylacetate), which partially dissolved the silicone; the silicone ‘glued’ the glass powders once activated by the printing liquid. The extra silica provided by the silicone was counterbalanced by the introduction of calcite powders, so that the final glass-ceramic featured apatite, from the crystallization of AP40, and wollastonite, from both crystallization of AP40 and polymer-derived silica/CaO (from CaCO₃) interaction.

An even more advanced concept of preceramic polymer/glass integration has just been tested in glass-ceramic joints for planar solid oxide fuel cell (SOFC) designs [9]. Instead of compensating the extra silica from the a silicone matrix (e.g. with borax or calcite, as done by Ohl et al. and Zocca et al. respectively), the approach consists of considering ‘silica defective’ glasses, i.e. glasses with a chemical composition approaching that of glasses already applied for SOFC glass-ceramic joints, except for a reduced silica content. Silica-defective glasses ‘recover’ the original silica content by reaction with the silica provided by a silicone binder; owing to the identity in the overall chemical formulation, the new glass/silicone mixtures lead to nearly identical glass-ceramics than those formed by sintering and crystallization of the starting glass, with significant advantages in the manufacturing. Unlike conventional binders, the silicone does not simply glue glass powders and substrates (YSZ and Crofer layers), at low temperature, but keeps a binding action up to the firing temperature (operating with conventional binders, there is no practical binding action in the interval between binder burn-out and sintering of glass powders).

The present paper aims at presenting the latest approach as a tool for the additive manufacturing of bioactive glass-ceramic scaffolds starting from a ‘problematic’ glass. In particular, we referred to a glass belonging to the CaO–Na₂O–B₂O₃–SiO₂ system, crystallizing into a glass-ceramic with excellent biocompatibility and bioactivity (testified by cell tests) [10]. This glass was not suitable for the manufacturing of highly porous reticulated scaffolds, combined with a conventional sacrificial binder: after burn-out of the binder, ‘free’ glass powders exhibited an excessive viscous flow when processed in the firing conditions originally applied, on bulk samples, for crystallization of wollastonite and calcium borate. Instead of modifying the heat treatment, with risks of significant changes in the phase assemblage, we processed a silica-defective glass variant, “printed” mixed with a silicone binder. The interaction between glass and binder, upon firing, was successful in yielding the expected phase assemblage, in samples showing an excellent shape retention (see scheme in Fig. 1). This shape retention could be ascribed to the fact that softened glass, at the early stages of interaction, was supported by a rigid silica skeleton offered by the ceramic transformation of the silicone.

2. Experimental procedure

Table 1 reports the chemical composition of the reference glass [10], named WB (corresponding to the molar formula (0.05Na₂O·0.35CaO·0.20B₂O₃·0.40SiO₂), and of the ‘silica-defective’ variant, named WB-15. The new glass was designed to achieve the composition of the

reference glass once interacting with silica from a commercially available silicone, MK (Wacker-Chemie GmbH, Munich, Germany). Silica from MK was expected to provide 15 wt% of the overall silica content, combined with WB-15, as shown by Table 1. The amount of silicone, to be mixed with WB-15, was carefully calibrated, considering the silica yield of MK once fired in air (84 wt%) [1].

Glass batches were prepared was prepared from analytical grade purity oxides and carbonates (SiO₂, CaCO₃, H₃BO₃ and Na₂CO₃) and melted in Pt–10%Rh crucible in a laboratory furnace with superkanthal heating elements. WB was processed at 1400 °C for 1 h in a Pt–Rh crucible; the variant “WB-15”, due to the lower silica content, could be processed even at 1100 °C, again for 1 h. The heating rate was 10 °C/min. Coarse glass fragments, from the direct pouring of glass melts on a cold metal plate, were easily ground into fine powders by ball milling and later manually sieved; only the particles with a diameter below 75 µm were kept.

Dilatometric analysis (402E Netzsch Gerätebau GmbH, Selb, Germany) was performed on residual glass fragments, operating at 10 °C/min heating rate, to assess the transition temperature, T_g, and the dilatometric softening temperature, T_d (reported in Table 1).

Monolithic pellets were prepared using glass (WB-15) particles mixed with MK. In the latter case, the preceramic polymer was first dissolved in isopropanol (15 ml for 10 g of final ceramic) and then mixed with glass powders. The mixing was performed under magnetic stirring, followed by sonication for 10 min, leading to stable and homogeneous dispersions. The mixtures were poured into large glass containers and dried at 80 °C overnight. After drying, the silicone-based mixtures were in the form of solid fragments, subsequently ball milled 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. Disc-shaped pellets having approximately 16.5 mm in diameter and 3 mm in thickness were obtained. Analogous pellets were prepared by pressing fine powders of WB and WB-15 glasses without any binder.

The pellets were subjected to a two-step heat treatment, with 1 h at 700 °C and 1 h at 800 °C. The applied heating rate was 5 °C/min and natural cooling occurred after the final holding stage at 800 °C. The treatment on pellets were useful for preliminary tests on shape retention and phase evolution.

Direct ink writing was performed using the reference WB glass and WB-15 glass combined with MK. In all cases, inks were loaded into a syringe and extruded through a conical nozzle (D = 410 µm, 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 dimensions of 15 × 5 × 5 mm³, with 1 mm spanning length between the centre of two contiguous filaments. The layer thickness was 0.35 mm to increase the adhesion between the scaffold layers. The printing process was carried out in open air at room temperature. After printing, the scaffolds were left to dry in ambient conditions and later subjected to heat treatment, in the same conditions applied for pellets.

The ink based on the reference WB glass was made by loading of WB powders into carboxymethyl cellulose (CMC) solution, based on the direct ink writing process described in a previous works [11–13].

For the preparation of an ink comprising a silicone resin, MK was initially dissolved in isopropanol and then mixed with fumed silica (FS, Aerosil R106, Evonik, Essen, Germany). The mixing was carried out by means of a ball mill for 1 h at a speed of 200 rpm/min. In this way, it was possible to obtain a homogeneous mixture free of aggregates. The fumed silica was introduced to control the rheology of the ink, as done in a previous work [4], and replaced 10 wt% of the silica provided by the MK polymer. The MK/FS mixture was added with WB-15 glass powders and then ball-milled for 4 h at 400 rpm. After printing and drying, scaffolds were subjected to a crosslinking process at 200 °C for 1 h, before firing.

Fired pellets were subjected to preliminary morphological analysis

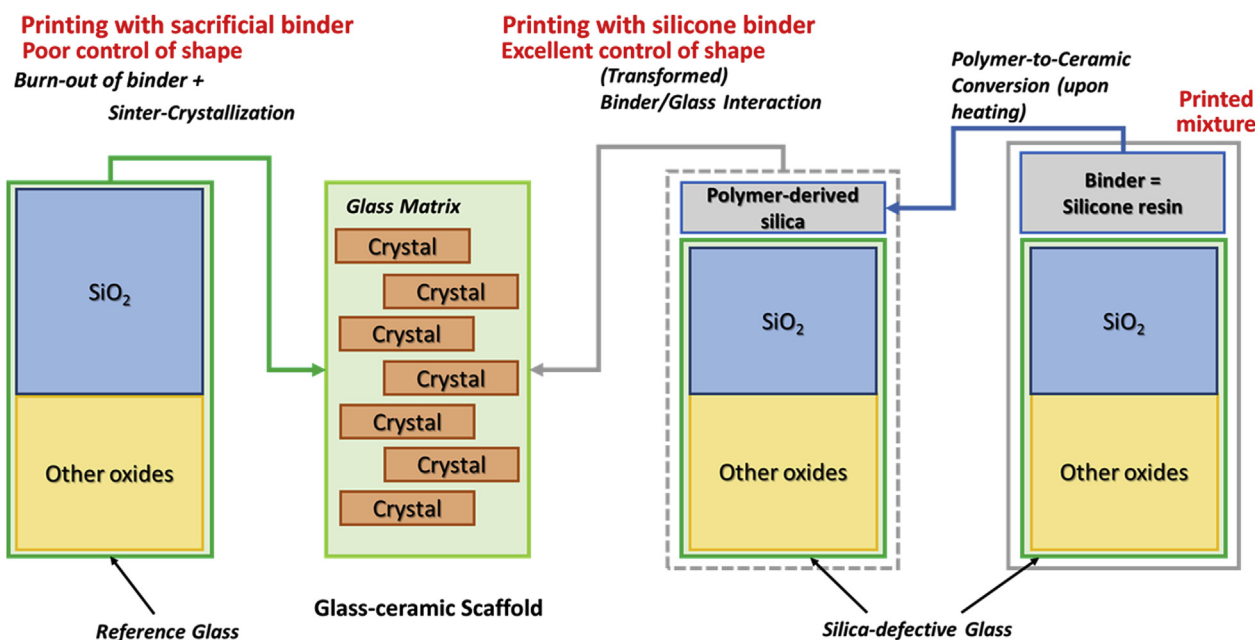


Fig. 1. Processing schemes for glass-ceramics: conventional devitrification (left) compared with heat treatment of silicone/silica-defective glass mixtures (right) [updated from Ref. [9]].

Table 1

Chemical composition (wt%) and characteristic temperatures of the studied glasses.

Glass name	Glass composition, oxides(wt%)				Characteristic temperatures($^{\circ}$ C)	
	SiO ₂	CaO	B ₂ O ₃	Na ₂ O	T _g	T _d
Reference glass	40	32	23	5	622 ^a	n.d.
WB					618 ^b	654 ^b
Silica-defective glass WB-15	29.4	37.7	27.1	5.9	590 ^b	620 ^b

^a Data from previous investigation [Ref.10].

^b Data from current investigation.

and to X-ray diffraction analysis (performed on powdered samples, by means of Bruker AXS D8 Advance, Karlsruhe, Germany). A semi-automatic phase identification was conducted by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA). Scaffold samples were subjected to the same X-ray diffraction analysis and to microstructural analysis, 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, the Netherlands) equipped with EDS. Fourier-transform infrared spectroscopy (FTIR, FTIR model 2000, Perkin Elmer Waltham, MA) were also made.

The apparent and true densities of scaffold samples were measured by means of a helium gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA), operating on samples in bulk (3D printed scaffold) and powder forms. The density of the ceramized scaffolds was measured geometrically using a digital caliper and by weighing with an analytical balance. The compressive strength was evaluated at room temperature, by means of an Instron 1121 UTM (Instron Danvers, MA) operating with a crosshead speed of 0.5 mm/min. Each data point represents the average value of at least 10 individual tests.

3. Results and discussion

The first tests concerned the firing of pellets of glass/silicone (WB-15/MK) mixture. From Fig. 2a we can note that the sample from silicone-glass mixture, according to the adopted heat treatment schedule, exhibited a very good shape retention after cooling: the firing caused just a homogeneous shrinkage (of ~8%), with no rounding of the edges (observed for pellets from the two glasses, WB and WB-15). This could be explained by the formation of a rigid silica-based ‘skeleton’, from the firing of the non-sacrificial silicone binder, progressively interacting with the silica-defective glass (WB-15). The sample, as shown by Fig. 2b, actually contained a multitude of internal pores (the porosity is ~17 vol% and pore size between 10–50 μm). The porosity was reasonably caused by the release of moieties from the oxidative transformation of the silicone, occurring up to high temperature; gas bubbles were in turn trapped by the increase of viscosity associated with an abundant crystallization, inferable from Fig. 2c and d. The same Fig. 3c demonstrates also that the WB-15/MK interaction did not lead to structural gradients, i.e. silica-rich amorphous zones (ascribable to oxidized MK) clearly separated from crystallized zones (ascribable to WB-15).

The actual mixing between polymer-derived silica and silica-defective glass is further testified by the mineralogical analysis, shown in Fig. 3a. The diffraction pattern of a pellet from pure WB glass is nearly identical to the pattern reported in the reference paper [10], with calcium silicate (wollastonite, W, CaSiO₃, PDF#84–0655) and calcium borate (CaB₂O₄, B, PDF#76–0747) as the only crystal phases. The silica-defective variant (WB-15), after sintering without any additive, led to interesting changes: first, as expected from the reduced silica content, the intensity of the peaks of the borate phase had a substantial increase; second, calcium silicate was present also in the form of a second polymorphic variant (pseudowollastonite, PsW, PDF#89–6485). The change in the balance between silicate and borate phase is illustrated also by Table 3, displaying estimations on the relative weight balance between crystal phases, provided by the Match! software, based on the Reference Intensity Ratio method (RiR-method). Although simpler than Rietveld refinements, the method is known to be quite affordable [14].

The sample from WB-15/MK featured an enhanced content of pseudowollastonite but, interestingly, exhibited a nearly identical

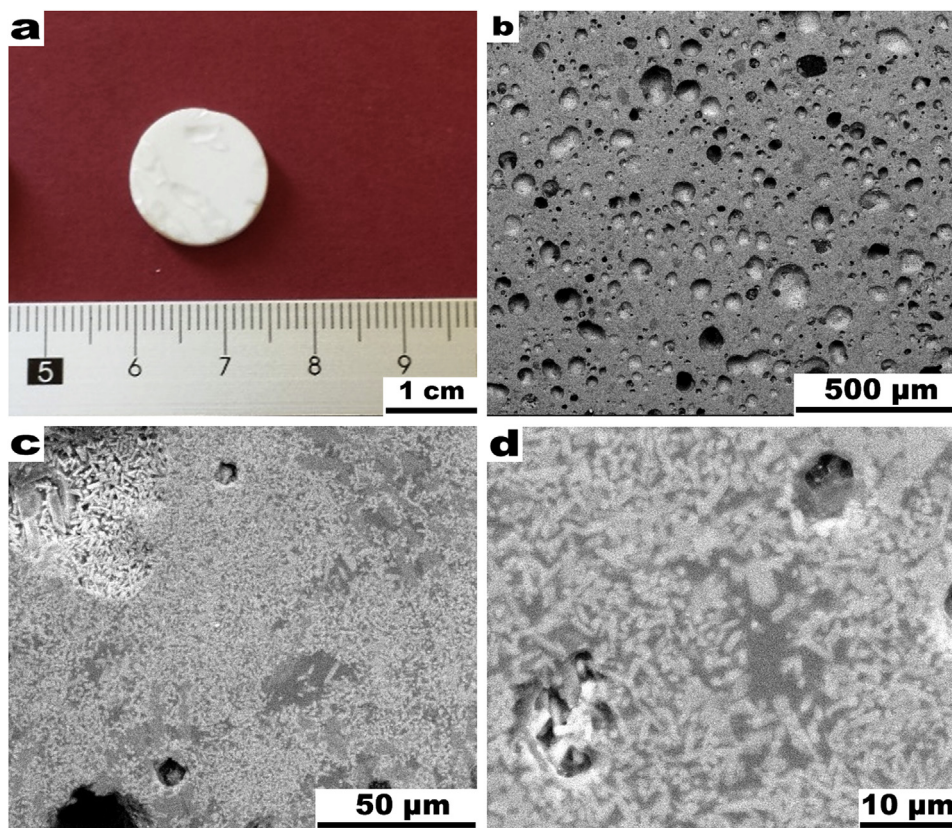


Fig. 2. Results from the firing of pellets from WB-15/MK mixture: a) morphology; b, c) cross-section details.

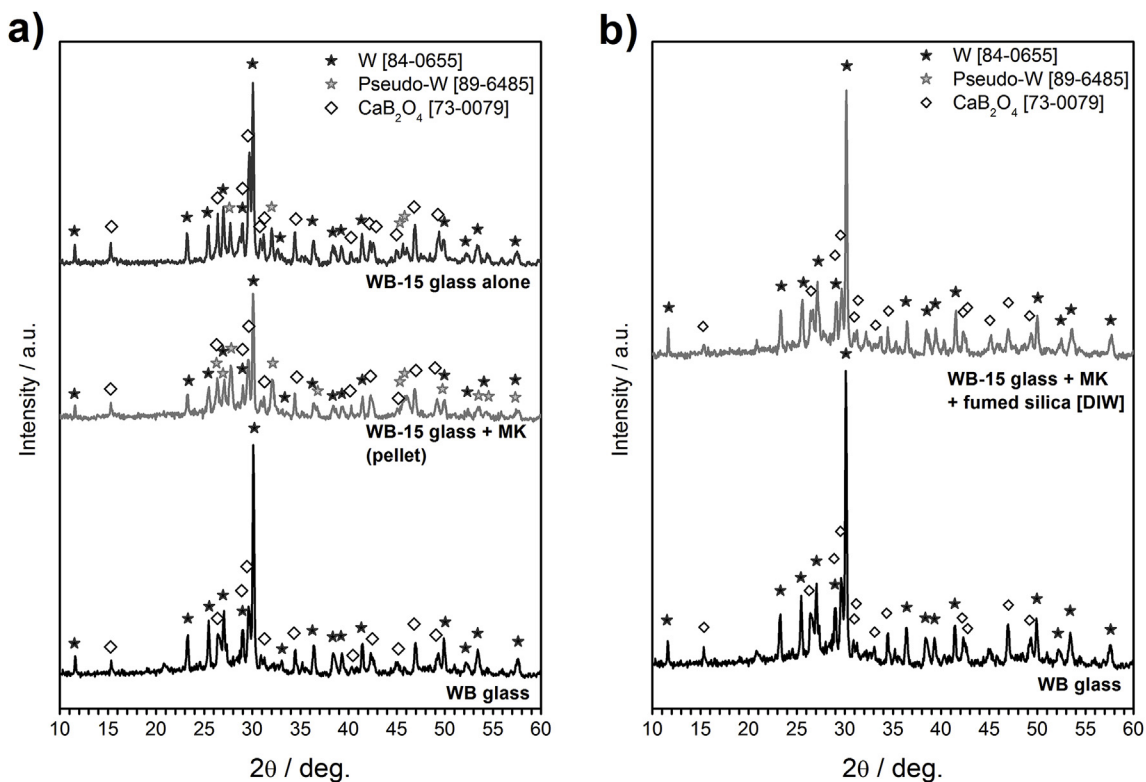


Fig. 3. a) comparison between glass-ceramics from WB glass and from WB-15 glass, combined with MK and alone; b) comparison between the reference glass-ceramic and glass-ceramic scaffold from DIW of silicone/WB-15/colloidal silica mixture.

Table 2
Formulations of glass/silicone batches (wt %).

	Silica-defective glass WB-15	Silicone	Oxide distribution WB-15-silicone mixture	Reference glass WB
Chemical compositions (wt %)				
Oxide	SiO ₂	100(as ceramic residue)	(29.4 × 0.85) + (100 × 0.15) = 40	40
	CaO		37.7 × 0.85 = 32	32
	B ₂ O ₃		27.1 × 0.85 = 23	23
	Na ₂ O		5.9 × 0.85 = 5	5
Oxide yield (%)	85	15		100
Batch formulations (wt %)				
Reference glass-ceramic				100
Pellet	82.6	17.4 (MK)		
3D Scaffold [DIW]	82.8	15.6 (MK) + 1.6 (FS)		

Table 3
Estimated weight proportions between crystal phases according to the Match! Software (and Reference Intensity Ratio method).

Formulation	Starting materials	Phase (wt%)			
		W	PsW	Total CaSiO ₃ (W + PsW)	CaB ₂ O ₄
WB	WB glass, alone	65.7	–	65.7	34.3
	WB-15/MK [pellets]	39.8	25.3	65.1	34.9
	WB-15/(MK + fumed silica) [DIW]	69.6	–	69.6	30.4
WB-15	WB-15 glass, alone	46.4	8.7	55.1	44.9

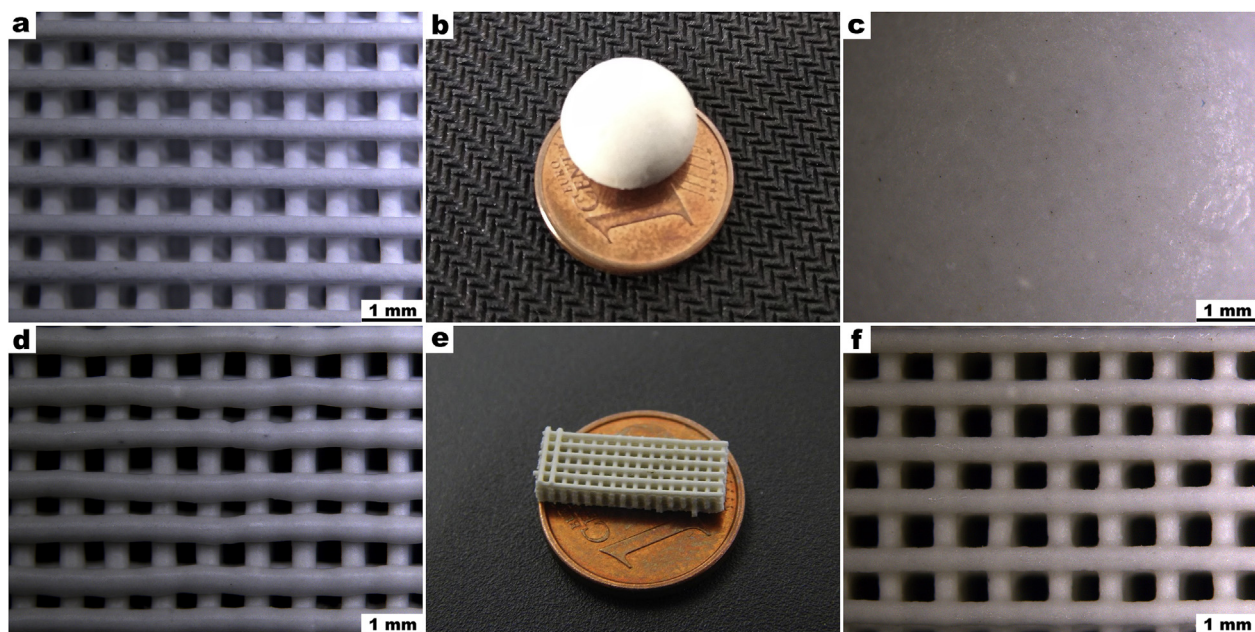


Fig. 4. SEM images of 3D glass-ceramic scaffolds obtained by DIW, before and after firing (a–c: WB glass with sacrificial binder; d–f: WB-15 with silicone binder).

weight balance between silicate and borate phases compared to the glass-ceramic from the original glass (the sum of wollastonite and pseudowollastonite equals the amount of wollastonite in the sample from pure WB). The formation of pseudowollastonite, instead of wollastonite, was not reputed to be a problem, considering the abundant literature on the biocompatibility and bioactivity of this less common variant of CaSiO₃ [15,16].

For the reference glass, the relatively large gap between dilatometric softening (a well-recognized threshold for significant viscous flow sintering [17]) and crystallization (WB featured two crystallization peaks, the most remarkable being placed at 827 °C [10], more than 170 °C above T_d), had a significant drawback in 3D printing. Fig. 4a shows the highly uniform structure of samples from WB glass before firing; Fig. 4b, on the contrary, clearly shows the viscous collapse, which transformed reticulated scaffolds into smooth beads (see surface

detail in Fig. 4c).

The above mentioned rigid ‘silica skeleton’, offered by MK, was effective in keeping the cellular structure imparted by DIW, illustrated by Fig. 4d, substantially unaltered, except for minor shrinkage (6%), as shown by Fig. 4e and f.

Fig. 5 reports some microstructural details of scaffolds developed using MK as reactive binder. In particular, overlapped filaments remained parallel in the x-y plane (Fig. 5a) and did not undergo any deflection in the z plane (Fig. 5b). Higher magnification details (Fig. 5c) do not reveal any microcrack; the struts (cross-section in Fig. 5d) are well densified. The reduced thickness of the struts, compared to the thickness of pellets (Fig. 2a) likely favoured the evolution of gasses from ceramic conversion of the silicone binder. The absence of cracks and the good densification justify the observed very good compressive strength (16.9 ± 1.8 MPa), with a density of 0.93 ± 0.11 g/cm³

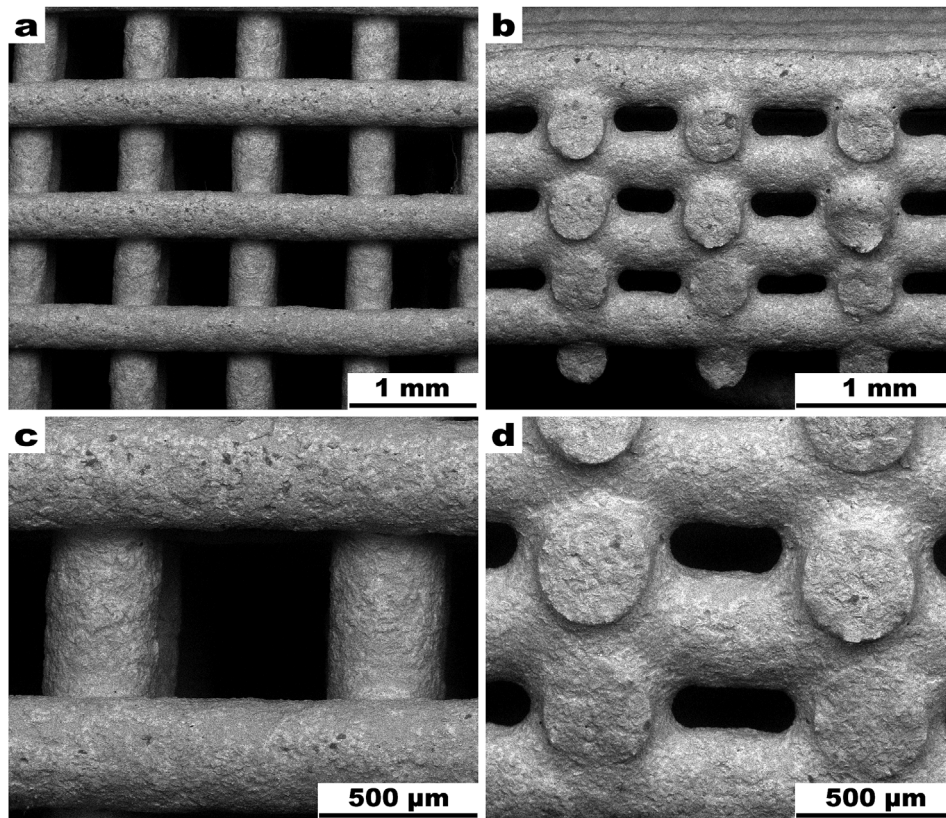


Fig. 5. Morphology and microstructural details of 3D scaffolds obtained by means of DIW (on inks from WB-15 glass mixed with MK silicone and fumed silica).

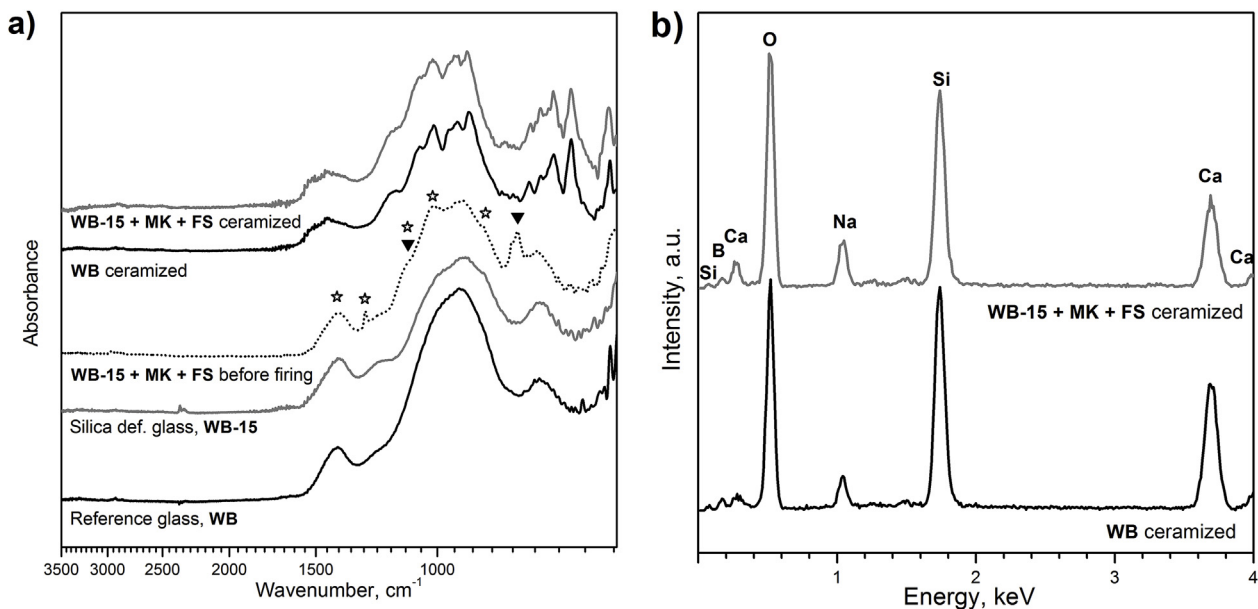


Fig. 6. a) FTIR spectra of studied glasses and glass-ceramics; b) comparison of EDX spectra of glass-ceramics from the reference glass (WB) and from silica-defective glass (WB-15) mixed with silicone binder.

(corresponding to 58% total porosity, mostly open).

The spectacular match with the glass-ceramic from WB glass, in term of phase assemblage, obtained by using WB-15 combined with MK, in pellets, was even improved with the material used for direct ink writing experiments. As shown by Fig. 3b, the silicate/borate balance is nearly identical to that of the reference, and wollastonite is the only calcium silicate variant. The inks for DIW experiments evidently benefited from the inclusion of some fumed silica (slightly reducing the

silica provided by MK, see Table 2), not present in MK-based pellets, known for its significant reactivity [4].

Fig. 6 provides further proofs of the successful integration between silica-defective glass and silicone binder, from infrared spectroscopy and energy dispersive X-ray spectroscopy. Passing from WB to WB-15 determined some changes in the infrared spectra, shown in Fig. 6a, associated with the reduction of silica (see the reduction of the band at $800\text{--}1100\text{ cm}^{-1}$). The mixing of WB-15 with MK and fumed silica is

testified by the appearance of additional bands (800 and 1100 cm^{-1} for fumed silica [18] and; 1400 , 1270 , 1120 , 1040 , 840 cm^{-1} for MK silicone [19], see black triangles and stars in Fig. 6a respectively). Finally, the infrared spectra of glass-ceramics (samples after heat treatment) from pure WB and from WB-15/MK/FS are practically identical. The identity is also confirmed in terms of overall chemical compositions, according to the EDX spectra shown in Fig. 6b (collected on areas of $300 \times 300\text{ }\mu\text{m}^2$).

The present findings can be considered as just a starting point. Future work will undoubtedly concern the extension to other additive manufacturing techniques, such as powder 3D printing and digital light processing (stereolithography), and other geometries, in order to explore the strength-to-density correlation at different porosity levels. Finally, the absence of any negative impact, on biocompatibility and bioactivity, from the adoption of preceramic polymers should be assessed by means of cell tests (positive biological responses have been already achieved from MK-derived ceramics [8,20,21], but need confirmation).

4. Conclusions

We may conclude that:

- The chemical interaction between a silicone resin and glass powders, inserted as fillers, was confirmed as an effective method for the manufacturing of sintered glass-ceramics;
- With the same overall composition, the sinter-crystallization of a glass and the interaction between a silicone resin and a 'silica-defective' variant of the same glass may lead to nearly identical phase assemblages;
- The use of a silicone reactive binder enabled the use of direct ink writing (not successfully applied to the reference glass with a sacrificial binder), for the manufacturing of highly homogeneous reticulated scaffolds exhibiting very good to compressive strength; the use of colloidal silica as extra filler in the ink formulation implied a refinement of the phase assemblage.

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References

- [1] E. Bernardo, L. Fiocco, G. Parciannello, E. Storti, P. Colombo, Advanced ceramics from preceramic polymers modified at the nano-scale: a review, *Materials* 7 (2014) 1927–1956.
- [2] L. Fiocco, H. Elsayed, J.K.M.F. Daguano, V.O. Soares, E. Bernardo, Silicone resins mixed with active oxide fillers and Ca–Mg silicate glass as alternative/integrative precursors for wollastonite-diopside glass-ceramics foams, *J. Non-Cryst. Solids* 416 (2015) 44–49.
- [3] A. Francis, R. Detsch, A.R. Boccaccini, Fabrication and cytotoxicity assessment of novel polysiloxane/bioactive glass films for biomedical applications, *Ceram. Int.* 42 (2016) 15442–15448.
- [4] H. Elsayed, P. Colombo, E. Bernardo, Direct ink writing of wollastonite-diopside glass-ceramic scaffolds from a silicone resin and engineered fillers, *J. Eur. Ceram. Soc.* 37 (2017) 4187–4419.
- [5] M. Parchovianský, G. Barroso, I. Petříková, G. Motz, D. Galusková, D. Galusek, Polymer derived glass ceramic layers for corrosion protection of metals, ceramic for energy conversion, storage, and distribution systems, *Ceram. Trans.* 256 (2016) 187–200.
- [6] C. Ohl, M. Kappa, V. Wilker, F. Scheffler, M. Scheffler, Novel open-cellular glass foams for optical applications, *J. Am. Ceram. Soc.* 94 (2011) 436–441.
- [7] S.T. Schwab, C.R. Blanchard, R.C. Graef, The influence of preceramic binders on the microstructural development of silicon nitride, *J. Mater. Sci.* 29 (1994) 6320–6328.
- [8] A. Zocca, H. Elsayed, E. Bernardo, C.M. Gomes, M.A. Lopez-Heredia, C. Knabe, P. Colombo, J. Günster, 3D-printed silicate porous bioceramics using a non-sacrificial preceramic polymer binder, *Biofabrication* 7 (2) (2015) 02500822.
- [9] H. Elsayed, H. Javed, A.G. Sabato, F. Smeacetto, E. Bernardo, Novel glass-ceramic SOFC sealants from glass powders and a reactive silicone binder, *J. Eur. Ceram. Soc.* 38 (2018) 4245–4251.
- [10] J.S. Fernandes, P. Gentile, R. Moorehead, A. Crawford, C.A. Miller, R.A. Pires, P.V. Hatton, R.L. Reis, Design and properties of novel substituted borosilicate bioactive glasses and their glass-ceramic derivatives, *Cryst. Growth Des.* 16 (2016) 3731–3740.
- [11] S. Eqtasadi, A. Motealleh, P. Miranda, A. Lemos, A. Rebelo, J.M.F. Ferreira, A simple recipe for direct writing complex 45S5 Bioglass 3D scaffolds, *Mater. Lett.* 93 (2013) 68–71.
- [12] S. Eqtasadi, A. Motealleh, P. Miranda, A. Pajares, A. Lemos, J.M.F. Ferreira, Robocasting of 45S5 bioactive glass scaffolds for bone tissue engineering, *J. Eur. Ceram. Soc.* 34 (2014) 107–118.
- [13] S. Eqtasadi, A. Motealleh, A. Pajares, P. Miranda, Effect of milling media on processing and performance of 13-93 bioactive glass scaffolds fabricated by robocasting, *Ceram. Int.* 41 (2015) 1379–1389.
- [14] S. Hillier, Accurate quantitative analysis of clay and other minerals in sandstones by XRD: comparison of a Rietveld and a reference intensity ratio (RIR) method and the importance of sample preparation, *Clay Miner.* 35 (2000) 291–302.
- [15] P.N. De Aza, Z.B. Luklinska, M. Anseau, F. Guitian, S. De Aza, Morphological studies of pseudowollastonite for biomedical application, *J. Microsc.* 182 (1996) 24–31.
- [16] P.N. De Aza, Z.B. Luklinska, M.R. Anseau, F. Guitian, S. De Aza, Bioactivity of pseudowollastonite in human saliva, *J. Dent.* 27 (1999) 107–111.
- [17] A. Ray, A.N. Tiwari, Compaction and sintering behaviour of glass-alumina composites, *Mater. Chem. Phys.* 67 (2001) 220–225.
- [18] T. Uchino, A. Aboshi, S. Kohara, Y. Ohishi, M. Sakashita, K. Aoki, Microscopic structure of nanometer-sized silica particles, *Phys. Rev. B* 69 (2004) 155409.
- [19] P. Colombo, E. Bernardo, Macro- and micro-cellular porous ceramics from preceramic polymers, *Compos. Sci. Technol.* 63 (2003) 2353–2359.
- [20] H. Elsayed, F. Carraro, S. Agnoli, D. Bellucci, V. Cannillo, L. Ferroni, C. Gardin, B. Zavan, E. Bernardo, Direct ink writing of silica-carbon-calcite composite scaffolds from a silicone resin and fillers, *J. Eur. Ceram. Soc.* 38 (2018) 5200–5207.
- [21] L. Fiocco, H. Elsayed, L. Ferroni, C. Gardin, B. Zavan, E. Bernardo, Bioactive wollastonite-diopside foams from preceramic polymers and reactive oxide fillers, *Materials* 8 (2015) 2480–2494.