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Direct ink writing of geopolymeric inks

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ABSTRACT

The development of geopolymeric inks with optimized rheological properties for DIW is presented; several inks with different water content and additives were compared to determine which parameters enable extrusion as well as shape retention. It is a challenging task, because the inks are subjected to ongoing poly-condensation reactions which continuously modify their rheological properties over time.

Highly porous ceramic lattices (porosity up to ~71 vol%) were fabricated with ~0.8 mm struts and unsupported features with very limited sagging. Their physical and mechanical properties were characterized and correlated. Our approach can be successfully extended to other formulations.

Geopolymeric foams have recently been proven as suitable for water filtration; the use of precisely designed, non stochastic printed structures could enhance the mechanical properties of the porous components, provide a better control of pressure drop and fluid dynamics inside the part and improve their performances consistently.

1. Introduction

Additive manufacturing (AM) of ceramics is a very attractive field of research that has the potential to disruptively change the way complex shaped bodies are fabricated [1].

The Direct Ink Writing (DIW) technique was originally named Robocasting after Cesarano's patent [2] and is a layer by layer fabrication technique which involves the robotic deposition of a viscoelastic ink extruded through a fine nozzle. Central to the approach is the creation of an ink that can be extruded in filamentary form and can undergo rapid solidification to maintain the shape of such filaments even as they span gaps in the underlying layer(s). Evaporation of solvent can be employed as mean of rapid solidification for pastes with high solid loading, but there are limitations in terms of nozzle size (typically >0.5 mm) in order to prevent clogging.

The ideal rheology for a DIW ink is that of a Bingham pseudoplastic fluid, i.e. a fluid who shows an initial yield stress and whose viscosity decreases with the increasing shear rate. In this way, the ink can be easily extruded at low pressure but is able to retain its shape once deposited, even in case of suspended struts. Such behavior is typical of a reversible gel and can be achieved in several ways, including flocculation of a ceramic suspension to form a gel (e.g. by a change in pH, ionic strength of the solvent, addition of polyelectrolytes), or the formulation of a ceramic ink containing a polymeric binder and plasticizer [3]. Another possibility is the use of gelling additives, which is favorable because it makes use of a very little amount of organic additives, therefore making a dedicated de-binding step unnecessary [4].

Geopolymers are inorganic materials with a chemical composition similar to that of zeolite and a variable microstructure (amorphous to semi-crystalline). Their synthesis involves the reaction between SiO_2 and Al_2O_3 species in a highly alkaline medium, leading to the formation of a continuous three-dimensional network. The exchange of silicon for aluminum in the network structure results in a net negative charge which is compensated by alkali cations. These materials can consolidate at low, even room temperature, leading to amorphous microstructures; heat treatment at temperatures >500 °C results in semi-crystalline structures resembling zeolites ones [5].

In a previous work, the network formation and consolidation was exploited for the fabrication of porous geopolymeric components through inverse replica of PLA 3D printed sacrificial templates [6]; in that case, the requirements in terms of rheological behavior for the infiltrating slurries were much less stringent in comparison to the strict control required for the fabrication of high-quality

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structures by direct printing. In a very recent publication, Xia and Sanjayan reported on the use of geopolymers associated with powder-based 3D printing; they were able to print samples with good accuracy, but densification is still an issue (which is typical of a powder-based approach) and it reflects on poor mechanical properties [7].

Few 3D printing companies and research groups started experimenting with large scale additive manufacturing of standard cement and concrete and are trying to progress to geopolymer based ones, but their focus is almost entirely on working time and mechanical resistance for the fabrication of simple shape buildings [8,9]. Little work has been so far conducted on direct ink writing of geopolymers, which would be less time consuming with respect to other AM technologies, would not produce any waste material and would allow to fabricate more complex shapes.

DIW of geopolymeric inks is a particularly challenging task, because the inks are subjected to ongoing (polycondensation/geopolymerization) reactions which continuously modified their rheological properties over time. Time has been involved as the 4th dimension in so-called 4D printing technologies with the aim of producing objects able to change their configuration or function depending on external stimuli [10–12]; geopolymeric slurries could be good candidates as smart materials for 4D printing once their reaction over time could be effectively controlled.

Here, the development of geopolymeric inks with optimized rheological properties for DIW is presented; several inks with different water content and different kinds and amounts of additives were compared in order to determine which parameters enable the optimal extrusion as well as the retention of the produced shape. Using these inks, highly porous ceramic components (porosity up to ~71 vol%) were fabricated. Such ceramic lattices could be suitable for many applications, including air and water filtration (as geopolymers are instrinsically meso-porous and their composition is close to that of zeolites) [13]. Indeed, geopolymeric foams have recently been proven as suitable for such applications [14]; the use of precisely designed, non stochastic printed structures could enhance the mechanical properties of the porous components, provide a better control of pressure drop and fluid dynamics inside the part and improve their performances consistently.

2. Materials and methods

2.1. Ink preparation

Four geopolymer mixtures were investigated, all comprising: metakaolin (Argical 1200S, Imerys S.A., Paris, FR) as source of alumino-silicate building blocks; a soluble sodium silicate solution (SS2942, Ingessil S.r.l., Montorio, IT); sodium hydroxide NaOH (Ika Werke GmbH & Co. KG, Staufen im Breisgau, DE); distilled water. The composition of the metakaolin and of the sodium silicate solution is summarized in Table 1.

First, a solution of sodium silicate, sodium hydroxide and water was prepared with the following molar ratios: $Na_2O/SiO_2 = 0.709$, $H_2O/Na_2O = 13$. The solution was prepared at least 24 h in advance and was stored at 4 °C; its composition in summarized in Table 2.

Table 1
Composition of the metakaolin and of the silicate solution in use.

Reagent	SiO_2 (wt%)	Al_2O_3 (wt%)	Na_2O (wt%)	H_2O (wt%)
Argical 1200 S	55	39	<1	/
SS 2942	28.35	/	9.77	61.88

Table 2
Chemical composition of the alkaline solution.

	SS 2942 (g)	NaOH (g)	H_2O (g)
Alkaline solution	400	56.64	53.56

All ink formulations had the following molar ratios: $Na_2O/SiO_2 = 0.263$; $SiO_2/Al_2O_3 = 3.8$; $Na_2O/Al_2O_3 = 1$. Concerning the content of water, the first ink had a molar ratio $H_2O/Na_2O = 13.78$. The second ink was derived from the first one with the addition of 7 wt% of poly(acylic acid) sodium salt with an average molecular weight of 5100 g/mol (PAA, Sigma-Aldrich, St. Louis, MO) as a rheology modifier. PAA is frequently used as a thickening agent in aqueous based systems as it creates an entanglement of polymer chains imparting a shear thinning behavior to the ink.

The third ink possessed a decreased water content, with a molar ratio $H_2O/Na_2O = 13$. The fourth ink derived from the third one with the addition of 5 wt% of poly(ethylenglycole) PEG with an average molecular weight of 1000 g/mol (Sigma-Aldrich, St. Louis, MO) with the same role as that of PAA. The four inks were labeled: GP 13.78, GP 13.78 PAA. GP 13 and GP 13 PAA respectively, and their formulations is summarized in Table 3. The density of the inks was calculated using the rule of mixture from the theoretical density of the individual raw materials.

For samples GP 13.78 PAA and GP 13 PEG, the additives were added to this solution under mechanical stirring at 500 rpm for 5 min at room temperature. Metakaolin powder was then added to the solution under mechanical stirring at 1000 rpm for 10 min at room temperature.

2.2. Rheological characterization

A rotational rheometer (MCR 302, Anton Paar, Graz, A) equipped with a 50 mm diameter plate–plate geometry was used, with a set temperature of 20 °C and a gap of 1 mm.

The rheology of the ink is the key factor for the DIW process, and is crucial for the fabrication of geometries with unsupported parts; in fact, the material has to bear its own weight with minimal deformation after being printed. The problem of determining the theoretical conditions for the stability of a spanning strut interested Smay et al. [15] and Schlordt et al. [16]. Based on a static beam bending model, Smay et al. demonstrated that in order to have a minimal deflection (<5% of the filament diameter) the following relation must be satisfied [15]:

$$G' \geq 0.35\gamma\left(\frac{L}{D}\right)^4 D \quad (1)$$

where G' is the shear storage modulus of the ink, γ is the specific weight of the ink in oil ($\gamma_{ink} - \gamma_{oil} = [\rho_{ink} - \rho_{oil}] \times g$; with g

Table 3
Formulations of the different inks.

	Argical1200S (g)	Alkalinesolution (g)	H_2O (g)	PAA (g)	PEG (g)	Density (g/cm^3)
GP 13.78	32.26	50	1.84	/	/	1.75
GP 13.78 PAA	32.26	50	1.84	5.89	/	1.53
GP 13	32.26	50	/	/	/	1.78
GP 13 PEG	32.26	50	/	/	4.11	1.73