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A simple graphite-based support material for robocasting of ceramic parts

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Abstract

A simple graphite-based recipe is proposed for use as secondary fugitive ink for robocasting. The ink exhibits excellent rheological performance and physico-chemical compatibility with other ceramic inks and can be completely burned-out by a heat treatment at 800 °C for 2h. The simplicity of the preparation process, together with its low cost, make it an optimal choice for this task. The development of such an ink will greatly facilitate the manufacture of complex ceramic parts requiring the use of a support structure during assembly by direct ink writing.

Keywords

Robocasting; direct ink writing; fugitive ink; support material; graphite

Introduction

The fabrication of complex three dimensional parts is crucial for a wide variety of technological applications in multiple industries such as aerospace, automotive, or biomedical devices, to name a few. Over the last decades, bottom-up strategies for the fabrication of such parts, globally referred to as additive manufacturing (AM)—or, more colloquially, 3D printing —techniques, have gained increased attention [1]. Among the wide variety of AM technologies (stereolithography, selective laser sintering, etc.), direct-write techniques offer the greater versatility and a particular suitability for the fabrication of ceramic parts [2]. In particular, robocasting, also referred as direct ink writing [3], has already been successfully used for the commercialization of certain ceramic products [4] and is receiving increasing attention by ceramic research groups all over the world [4–8]. This technique comprises the use of inks with controlled rheological behaviour capable of retaining their shape during the layerwise extrusion-based assembly process.

The self-supporting capacity of the robocasting inks allows the fabrication of porous structures and some very complex shapes without requiring the use of molds or sacrificial support materials. However, as also occurs in other AM techniques, under certain circumstances (e.g. when spanning large gaps or creating large overhanging features) it is unavoidable to use a secondary support structure to warrantee the proper assembly of a specific design. In these cases, algorithms for calculating the

support structure pattern and a system allowing for the alternate printing of the two materials now comprising the model are needed. And, most importantly, a suitable secondary ink of a fugitive material is required.

The ink of support material must, obviously, meet the typical requirements for a robocasting ink, namely: it must maintain its shape even under the load of overlaying layers and, under higher shear stresses, be able to flow through fine deposition nozzles without clogging. Additionally, this ink must be chemically compatible with the colloidal ink of the main material, and easily removable in the post-processing steps, leaving no byproducts after decomposition. A suitable method for the elimination of the support structure would be to burn it out along with any binder present in the deposited inks. In the case of robocast ceramics parts, the selection of a suitable material for this fugitive ink is facilitated by the high sintering temperatures required for consolidation of the printed structures. However, the intrinsic fragility of ceramics and the extreme weakness of the green structure impose the additional requirement that such secondary ink must exhibit a degree of shrinkage similar to that of the main one. This is necessary to avoid the generation of (micro)cracks during the drying process, which would likely propagate during sintering. Finally, since these inks are intended to be removed, it is preferable to formulate them from inexpensive materials and they should be easy to prepare. Therefore, simple recipes, avoiding the use of too many additives, should be sought in order to reduce the preparation time.

The literature on the development of such support inks is still scarce. Wax-based inks have been reported to be suitable as fugitive support materials for building

microvascular networks and other polymer-based structures [9,10]. However, this is not an ideal solution for the fabrication of ceramic parts by robocasting since elimination of such supports involves melting, and the forces associated to this process may affect the structural integrity of the weak ceramic green part. Also, this and other polymer-based supports may exhibit significantly different levels of contraction compared to the main ceramic-based ink during drying, which might also produce cracking in the ceramic green body. A more suitable solution has been proposed by Smay and col. [11] consisting on the use of a concentrated aqueous gel of carbon black as a combustible support material [12]. Although the feasibility of such procedure was evidenced in those work by optical images, the details of the preparation and debinding procedure for such ink has not yet been published, to the best of our knowledge. Consequently, it is not possible for other authors to replicate that route. For that reason, this work seeks to provide the first detailed recipe for a fugitive carbon-based ink for robocasting, as a solution for building complex ceramic parts that require a support material, and to give details on the ink rheological properties and the appropriate debinding procedure.

Experimental method

Materials and ink preparation

Aqueous suspensions of graphite powder (282863 Sigma Aldrich, particle size <20 µm, as provided by supplier) were prepared using carboxymethyl cellulose (CMC) (CMC-35, Mw=35,000, Lamberti Iberia S.A.U., Castellón, Spain) as the single

multifunctional (dispersant, binder...) additive [4]. An aqueous solution (4 wt.%) of CMC was prepared and then graphite powder was added to create a suspension. Solid (graphite) content was varied from 35 to 50 wt.% in order to determine the optimal composition of the ink. The powder was added in a single batch and, subsequently, the ink was homogenized for 7 min at 700 revolutions per minute in a planetary mixer (ARE 250, Thinky Corp., Japan).

The rheological properties of the colloidal inks prepared were evaluated using a rheometer (DHR-2, TA Instruments) and a plate-plate geometry (40 mm diameter, 550 µm gap). Storage modulus was measured in oscillatory mode at 10 Hz, within the oscillatory stress range of 0.1–100 Pa. This enabled also the estimation of the ink yield stress as the critical oscillatory stress at which the initially linear response (linear viscoelastic regime) ends [13].

In order to demonstrate the suitability of the optimized graphite ink as fugitive support for brittle ceramic parts, an alumina (SPA-0.5, Ceralox, Sasol North America Inc., USA; particle size distribution: D90 = 0.8 µm, D50 = 0.4 µm, D10 = 0.2 µm, as provided by supplier) ink (45 vol.%) was prepared. Briefly, a concentrated stable suspension of the alumina powder in distilled water was prepared by using Darvan® C (R.T. Vanderbilt, Norwalk, CT) as a dispersant (2.5 wt.% of dispersant relative to the weight of alumina). Then hydroxypropyl methylcellulose (Methocel F4M, Dow Chemical Company, Midland, MI) was added to the mixture to increase viscosity and the ink was finally gellified by adding 4 vol.% of polyethylenimine (PEI), relative to the total liquid content.

Robocasting, thermal treatment and characterization

The developed inks were transferred into separate dispensable cartridges and, after removing any trapped bubbles by repeated vigorous tapping, placed in a computer-controlled robocasting system (Aerotech A3200, supplied by 3D Inks, Stillwater, OK, USA). The inks were sequentially extruded through conical nozzles ($d \geq$ 250 μm) in order to fabricate a sphere, as a good example of a three-dimensional structure requiring the use of supports. The 3D model for this part and its support structure was generated using an appropriate control software (Robocad 4.2, 3D Inks, Stillwater, OK, USA). Deposition was carried out in air, rather than within an oil bath, which seems to provide better mechanical performance in the case of solid ceramic parts [15]. After assembly, the 3D bicomponent structure was dried out for 24 h at room temperature. No humidity control was required to avoid crack formation for the materials tested in this work, which does not mean such control may not be required in other systems or parts.

Thermogravimetric analysis (TGA) was carried out (heating ramp of 10 °C min^{-1}) as a first step in determining the optimal thermal treatment to remove the fugitive material. The results of the graphite ink TGA were corroborated by putting a bulk graphite parallelepiped structure of 7×10×20 mm in a tubular furnace and optically evaluating the volatilization process. For this purpose, photographs of this structure were taken during a heating ramp (10 °C min^{-1}) at different temperatures through a suitable observation window, and the variation in its cross-sectional area was determined.

The bicomponent 3D assembly was subsequently thermally treated in air to remove the graphite and all ink binders using a heating rate of 3 °C min^{-1} up to the optimal temperature, where the part was kept for 2 h. Later, a heating ramp of 3 °C min^{-1} was set up to 1550 °C where sample was hold for 2 h to ensure the sintering of the alumina structure.

The microstructure of the support material struts in as-dried state was analyzed through Scanning Electron Microscopy (SEM) observations (S-3600N, Hitachi, Japan), while the quality of the fabricated part was assessed by optical means.

Three-point bending tests were performed on graphite filaments (extruded through nozzles with a diameter of 584 μm) using a universal testing machine (AG-IS10kN, Shimadzu Corp., Kyoto, Japan). Tests were performed in air, at a constant cross-head speed of 0.6 mm min^{-1}. The flexural strength of the filaments was estimated as the maximum stress applied in each test. A total of 25 samples were tested in order to obtain statistically reliable values. Weibull statistics were used for the analysis of the resulting strength data.

Results and Discussion

As a first step, ink performance was evaluated in terms of extrudability. Inks rich in graphite (50 wt. % and over) were difficult to extrude through deposition nozzles with a diameter of 250 μm and, thus, were rejected. Inks with lower graphite contents exhibited excellent flowing behavior, attesting to the aptness of the binder selected in this study. Due to the apolar nature of graphite, CMC becomes a more appropriate choice over other

options like ionic polyelectrolites. The lower charge of this multifunctional binder facilitates greater adsorption [16] onto the graphite surface. This, in turn, enhances its effectiveness as dispersant—enabling the incorporation of a great amount of powder into the suspension—as well as a network forming (i.e. gelling) agent.

Rheological measurements provide a quantification of the inks mechanical properties, enabling the identification of the optimal ink composition. Figure 1a shows the shear elastic (storage) modulus, G', versus oscillation stress amplitude, τ, for graphite suspensions with solid contents of 35 wt.%, 40 wt.% and 47 wt.%. For all of them, linear viscoelastic plateaus are noticeable, preceding an accentuated fall of G' at a given oscillatory yield stress, τ_y, when the gel network starts to collapse. Although the plateau is less defined for more concentrated slurries, with G' decreasing more significantly with the shear stress, ink modulus monotonously increased with graphite content at any given shear stress, and the yield stress was also greater in the more concentrated inks. This is more clearly appreciated in Figure 1b which shows the evolution of the static elastic modulus G'_0 (estimated as the value of the storage modulus G' at τ = 0.1 Pa) and the oscillatory yield stress τ_y with the graphite content. A dramatic increase of both properties is observed with increasing graphite content. The ink stiffness increased by almost 4 orders of magnitude from $3.8 \cdot 10^3$ Pa at 35 wt.% to $1.3 \cdot 10^7$ Pa at 47 wt.%, and similarly τ_y increased by a factor of 6.3, from 0.91 Pa to 5.74 Pa. Since maximum values from both magnitudes are desirable features for robocasting inks—as they represent the ability of the ink to sustain load and retain shape—it is evident that the optimal ink is that with

47 wt.% of graphite. This ink exhibited the highest G' and τ_y values while still maintaining excellent extrudability.

Those values are indeed high enough to warranty the ability of this ink to sustain the load of any overlayers even when deposited in the form of an open porous support scaffold. The structural quality of the ink can be assessed also on the SEM micrograph of Figure 2, showing one such a porous robocast structure made from the graphite ink, in as-dried condition. The rods show a good circular shape in the transversal section of the rods—i.e. they are not deformed into an elliptical shape by the weight of the overlaying material— and they remain straight, without sagging into a catenary shape, when spanning underlaying gaps. Regarding the microstructural features, the graphite platelets have been evidently aligned parallel to the rod axis during the extrusion of the ink. As a consequence, the microporosity, which is nonetheless high as correspond to a green body, is somewhat lower close to the rod surface. This is deemed to be beneficial to the strength and mechanical integrity of the support structures, especially, after drying. In fact, the flexural strength of the green graphite filaments—estimated as the central value of the corresponding Weibull distribution— was measured to be 1.04 ± 0.04 MPa, which is remarkably high for unsintered struts.

Concerning the optimal temperature for burning out the graphite ink, Figure 3 shows both the TGA data (left Y axis) and the evolution of the cross sectional area (normalized to its initial value, right Y axis) for a given graphite scaffold with temperature. In spite of the fact that the structure was dried for 24 h at room temperature before initiating the thermal treatment, the first weight (and area) loss (200-500 ºC) is due to the

evaporation of residual, adsorbed water, plus the elimination of the carboxymethyl cellulose (autoignition temperature is 370 ºC, according to MSDS). Thereafter, a significant increase in material loss is produced upon the onset of graphite oxidation (~ 500 ºC) into gaseous species, mainly CO_2. It can be seen that both the weight and the area loss rates reached a maximum value at around 600 °C. However, an incomplete oxidation takes place at times up to 2h at this temperature producing local discoloration in the adjacent ceramic part during the sintering stage. To avoid this undesired interaction, a somewhat higher temperature of 800 ºC ensured the complete elimination of the graphite structures in 2 h or less, without discoloration of adjacent ceramic parts. Thus, a heat treatment at 800 ºC for 2h was selected as optimal for the removal of the graphite supports fabricated using the ink composition proposed in this work. Optimal heating ramp will depend of the robocasting ink composition used for the ceramic part.

Figure 4 illustrates the fabrication of a sphere using the developed support inks. Figure 4a shows the as-dried alumina green part fabricated using the ink with 47 wt.% graphite content as support material. There is no evidence of cracking in the brittle alumina sample due to shrinkage mismatch. Measured linear shrinkage during drying was low for both materials: 3.7 ± 0.8 % for the alumina part and 4 ± 1 % for the graphite support. If the ceramic part had a larger shrinkage, typical for example in inks involving ceramic nanopowders—e.g. a 26 vol.% hydroxyapatite ink fabricated by our group from nano-sized powders (Captal R, Plasma Biotal Ltd., UK) has a shrinkage of 10.1± 0.7 %—, it is possible to adjust the shrinkage of the graphite ink by reducing also its solid content from the optimal value indicated in this work. In that case, in order to preserve the

rheological properties of the fugitive ink it is necessary to increase the CMC content. For example, an ink with 35 wt.% of graphite and suitable printability was fabricated by increasing the CMC content from 4 wt.% to 10 wt.%. Such an ink exhibited a shrinkage of 9 ± 1 %, which matches within the errors the shrinkage of the aforementioned nano-hydroxylapatite ink. Nonetheless, the authors would like to point out that a high level of shrinkage in both the ceramic part and its support structure during drying should be avoided whenever possible—by maximizing the solid content in the robocasting inks—, not only to minimize the possibility of cracking during drying, but also to increase shape retention. In any case, it is evident that the proposed graphite ink can indeed be used to match the shrinkage of any ceramic part.

Moreover, as evidenced in Fig. 4b, showing the same part after the burn-out and sintering heat treatment, the graphite ink was completely removed after the heat treatment, leaving either no signal of discoloration or deformation of the ceramic part. Thus, the graphite ink was demonstrated to be an adequate candidate as support material for complex 3D models that require the use of such scaffolds during assembly.

Conclusion

The graphite ink proposed in this work fulfils all the necessary requirements for use as secondary fugitive ink for robocasting of ceramic parts. The excellent rheological performance and the simplicity of the preparation process, the possibility of matching its shrinkage to that of the primary ink, together with its low cost and physico-chemical

compatibility with other ceramic inks make it an optimal choice for this task. The development of such a simple support ink will greatly facilitate the manufacture of complex ceramic parts by direct ink writing.

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Figures

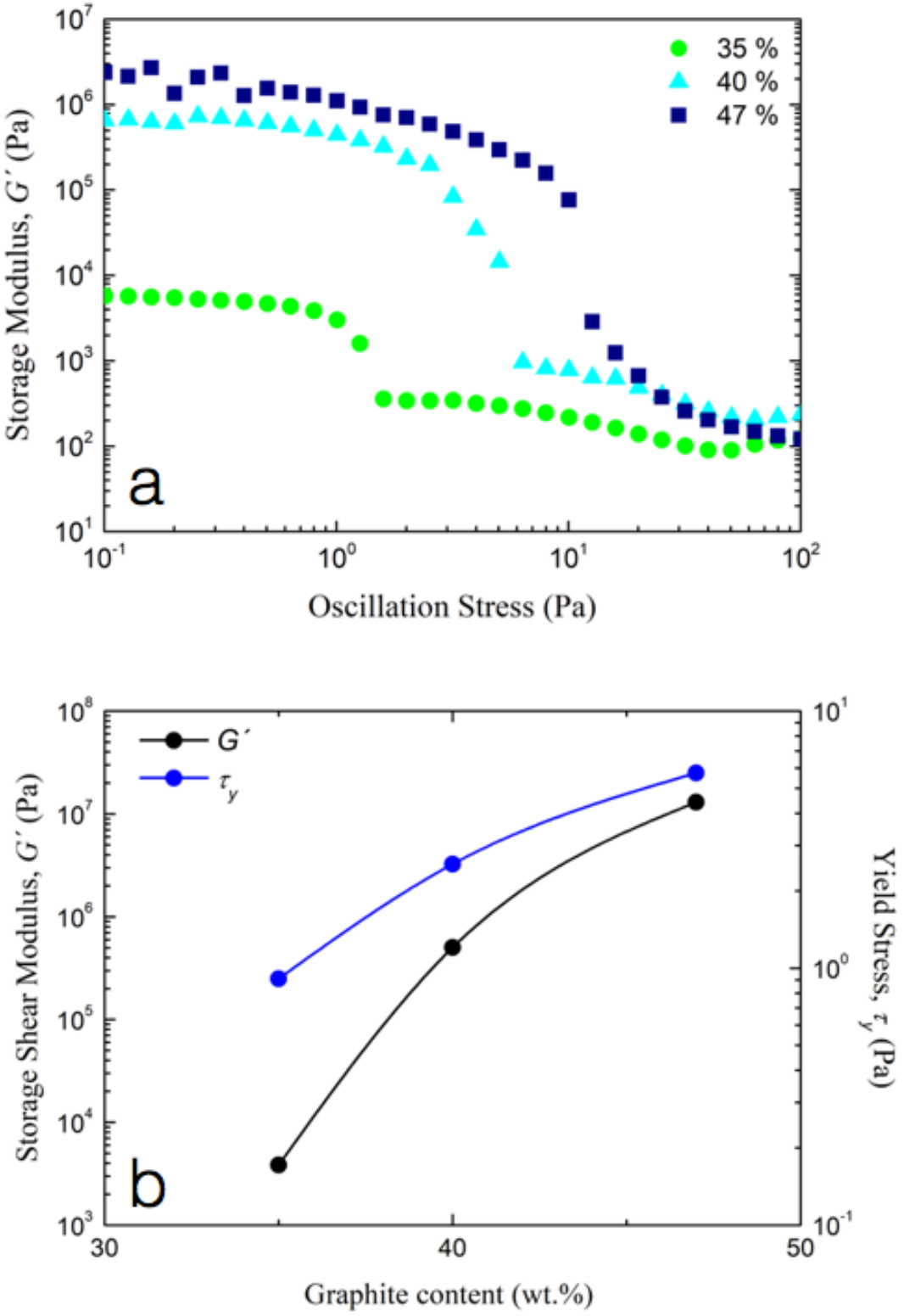


Figure 1

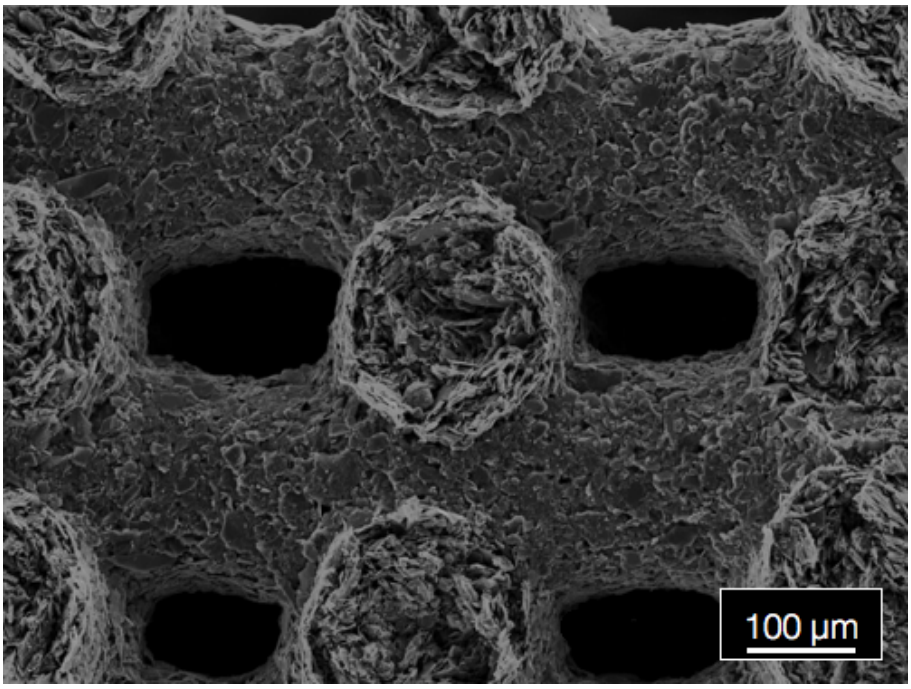
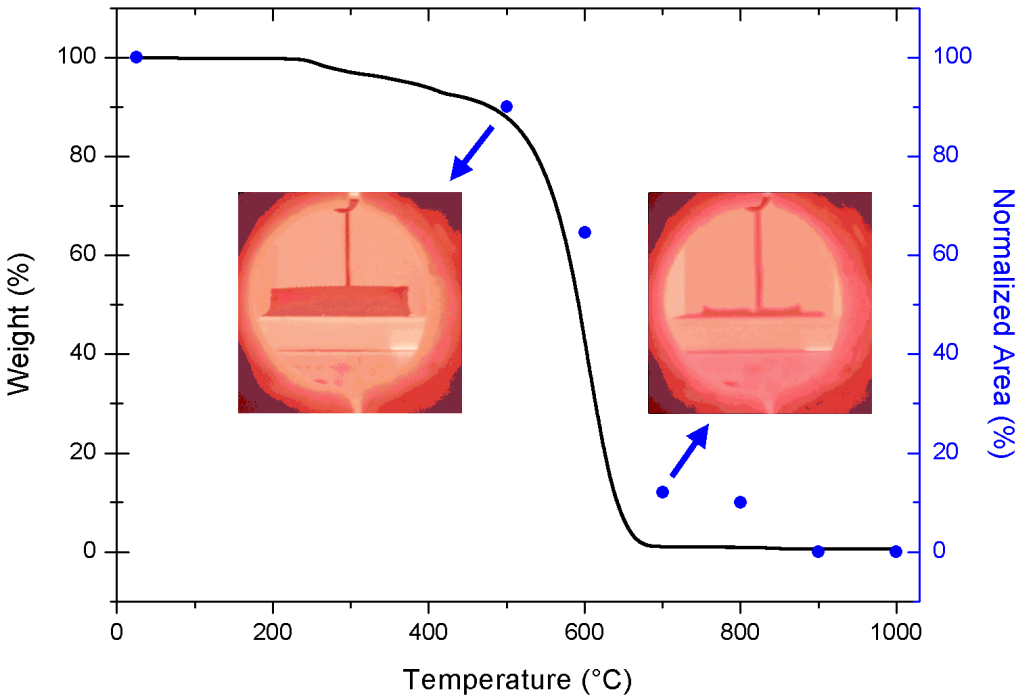


Figure 2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Normalized Area (%)
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20
40
60
80
100
0
200
400
600
800
1000

Figure 3

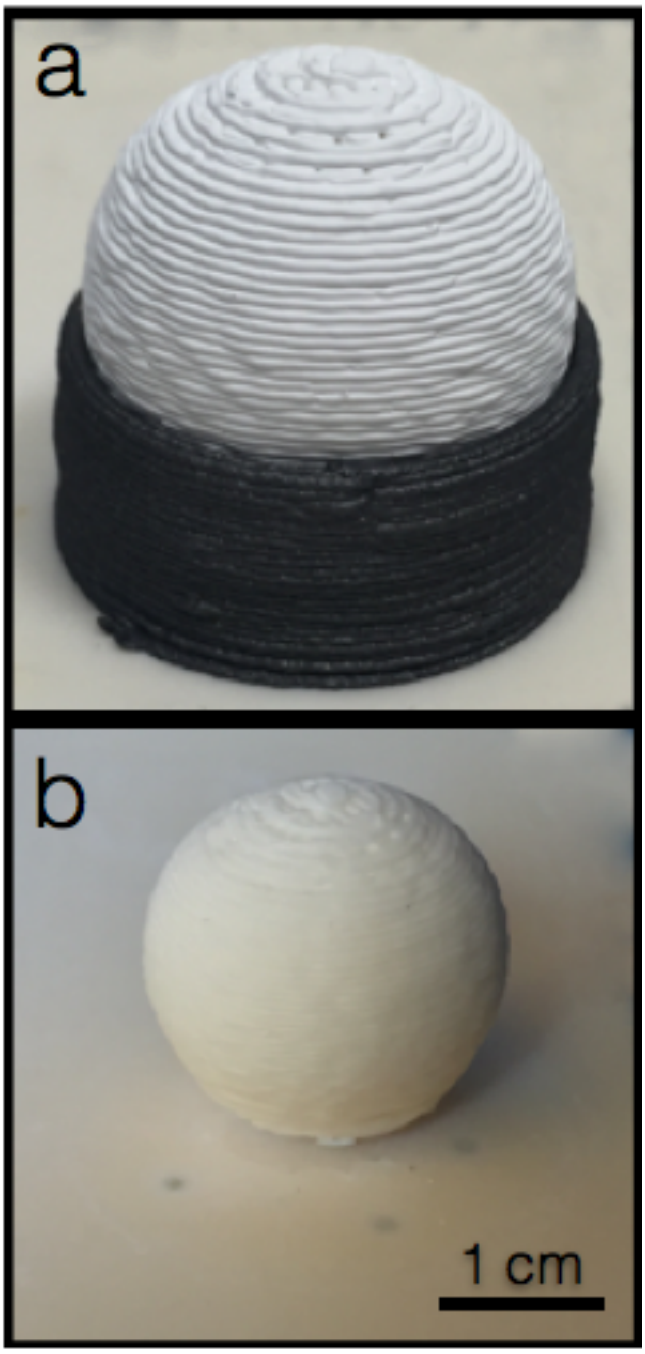

Figure 4

Figure Captions

Figure 1. a) Storage shear modulus, *G'*, as a function of oscillation stress for graphite inks with different contents (35, 40, and 47 wt.%). b) plateau storage modulus at low shear (left Y axis) and yield stress (right Y axis) of graphite inks as a function of solid content.

Figure 2. SEM image of a cross-sectional cut through a 3D graphite robocast structure fabricated using an ink with a solid-loading of 47 wt.%.

Figure 3. Weight variation from TGA measurements on a graphite ink (left Y axis) and evolution of the cross-sectional normalized area of a graphite sample with temperature. In situ optical images of the sample are provided at temperatures corresponding to the indicated points.

Figure 4. Optical images of an alumina sphere assembled by robocasting using graphite ink as a fugitive support: a) as-printed; b) after burn-out and sintering.