MS SHAREEN SHEUE LIAN CHAN (Orcid ID : 0000-0002-6677-2906)

DR GEORGE V FRANKS (Orcid ID : 0000-0002-5317-0981)

Article type : Special Issue Article

Direct Ink Writing (DIW) of hierarchical porous alumina stabilized emulsions: Rheology and printability

Shareen S.L. Chan ^a, Mitchell L. Sesso ^b, and George V. Franks ^{a,1}

^a Chemical Engineering, Melbourne School of Engineering, University of Melbourne, 3010 VIC, Australia

^b Engineering, La Trobe University, 3086 VIC, Australia

¹ Corresponding author.

Email address: gvfranks@unimelb.edu.au

1. Abstract

Bio-inspired multi-scaled (hierarchical) porous structures have remarkable strength and stiffness-to-density properties. Direct Ink Writing (DIW) or robocasting, an Additive Manufacturing (AM) (or also commonly known as 3D printing) material extrusion technique is able to create near-net-shaped complex geometries. A new approach of combining DIW, colloidal particle-stabilized emulsion paste inks and partial densification to create tailored architectures of hierarchical porosity on three scales has been demonstrated. The printed and sintered ceramic lattice structures possess relatively high overall porosity of 78.7% (on average), comprising mainly (64.7%) open porosity. The effects of formulation (surfactant and oil concentrations, solids particle size, and mixing speed) on rheology and pore size and morphology have been investigated. The rheological properties (storage modulus, yield stress and recovery of storage modulus) of the emulsions have been found to delineate the samples with good shape retention

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1111/JACE.17305](https://doi.org/10.1111/JACE.17305)

from those that slump. Additionally, the internal features of the sintered structures have been analyzed via X-ray tomography and SEM. The role of emulsion stability on printability and the internal structure of the prints has been investigated.

2. Introduction

Inspiration can be gained from remarkably efficient natural materials, such as bamboo, cork and bone (1). The essential design concept that results in their exceptional strength and stiffness-to-weight ratio lies in their hierarchical structural organization from nano- through meso- to macroscopic levels (2). In bone tissue engineering, both pore interconnectivity and pore size are critical (3). There is therefore a need to not only create different scales of porosity, but also to be able to tune them to the desired sizes. To synthetically mimic the multi-scaled porosity found in these natural systems, manufacturing processes have been developed, such as replica or sacrificial fillers that rely on the templating structure, e.g. preceramic polymers (4), coral (5), wood (6), and solid particles, e.g. salt (7), silk (8), as pore formers. Although seemingly straightforward, these methods are heavily reliant on the processing of the pore formers to tune the pore morphology. Other pore formation processes include induced phase separation; for instance, ice templating, in which the freezing process creates directional dendritic pore networks after sublimation (9). The prevalence of crack-like defects (10) however remains a challenge.

These processes are largely constrained to fabricating monoliths, with shape complexity a function of the mold design that may limit fabrication of certain materials. Where intricate geometries are not achievable, post-firing subtractive machining may be required to create complex shapes requiring costly tools made from diamond (11). Highly complex geometries with interconnected pore networks are impossible to be produced by conventional processing technologies (12). Therefore, there is motivation for Additive Manufacturing (AM) techniques which can fabricate near-net-shape, highly complex structures relatively simply with potential for industry-wide large-scale adoption. Recent publications have demonstrated that Direct Ink Writing (DIW) with ceramic particle stabilized foams and emulsions are able to fabricate multi-scale porous parts with unprecedented strength-to-weight ratios (13) and superior specific stiffness (14). These properties show promise for these materials' use in structural applications. Minas and co-workers (13) have also determined that open, interconnected pores offer the best performance under compression. Arango et. al. (15) demonstrated the printing of filaments containing both oil droplets and bubbles in TiO_2 suspensions. Little work has been conducted to understand how the paste formulation influences emulsion rheology or pore morphology.

By combining Direct Ink Writing (DIW), particle-stabilized emulsions and partial densification, we demonstrate a new approach of creating ceramic architectures of hierarchical porosity. Specifically, $> 100\ \mu\text{m}$ -scale porosity is created via the architected gaps between print filaments, while approximately 10 to 20 μm -diameter pores are templated by the oil droplets within filaments, and pores of less than 1 μm are created by partial sintering (see Figure 1). Through careful control of the formulations, suitable rheological properties for DIW can be obtained. By tuning both the formulation and printing parameters, a variety of pore morphologies can be obtained. The internal structures of the prints are analyzed, revealing features of interest. A surfactant is used to make the alumina particles weakly hydrophobic so that they stabilize Pickering emulsions that we use as paste inks for DIW. We use sodium 1-heptane sulfonate (C7), a surfactant we used previously (16,17) to produce macroscopic alumina particle stabilized foams via gel casting. In DIW, or material extrusion, it is recognized that a well-controlled shear-thinning viscoelastic response is essential for the feedstock to flow through the print nozzle when a stress is applied, then promptly retain its filament shape after deposition (18). Hence, developing an understanding and control of the rheological properties of the feedstock is invaluable to achieving successful prints.

3. Materials and methods

3.1 Particle sizing

The particle size distribution of the α -alumina powders (AKP-15, $d_{50} = 790\ \text{nm}$; AKP-30, $d_{50} = 350\ \text{nm}$; Sumitomo Chemicals, Japan) was measured using a laser diffraction particle size analyzer (Mastersizer 3000, Malvern, UK). A refractive index of 1.78 and absorption index of 0.01 were utilized. Alumina powders were dispersed in RO water until a laser obscuration of 10 to 15% was attained.

3.2 Ceramic suspension preparation

Polyvinyl alcohol (PVA) as the binder (1 wt% by solids weight) was dissolved in Reverse Osmosis (RO) water. Nitric acid was used to adjust the pH to 2.5 and rolled overnight. An aqueous colloidal suspension was created by stirring alumina powder at 35 vol% into the acidic PVA solution. The alumina suspension was adjusted to pH 3.5 with nitric acid. The alumina suspension was ultrasonicated with power 40 W for 2.5 min (Ultrasonic horn S-4000-010, Misonix Sonicators, USA). The acidic suspension was rolled overnight to achieve pH equilibrium and homogeneity. The required amount of surfactant, sodium 1-heptane sulfonate (C7), was added as a weight percentage of total solids, in the range of 0.04 to 0.10 wt%.

3.3 Preparation of particle-stabilized emulsions

The alumina suspension was re-adjusted to pH 4. The required volume of sunflower oil (Dhara sunflower oil, Parsram Foods Pty Ltd, Malaysia) was gradually introduced into the suspension, while the suspension was mixed with a flat-bottomed whisk attached to an overhead mixer (RZR 2020, Heidolph, Germany) at a speed of 300 or 400 rpm for 5 min. The amount of oil was measured as a volume percentage of total emulsion and varied from 40 to 70 vol%. The emulsions created (similar to whipped cream with stiff peaks) remained stable for a period of at least 2 weeks when stored in plastic air-tight containers.

3.4 3D printing of emulsions

Material extrusion (DIW or robocasting) was conducted using a commercially available pressure-controlled DIW system (3D-Bioplotter, EnvisionTEC, Germany). The pneumatic pressure was between 60 and 340 kPa, and print speeds were between 12 and 20 mm/s. The infill was a 90° log pile lattice structure. The lateral spacing between filaments investigated ranged from 0.8 to 1.5 mm. A layer height (vertical spacing of filaments) of 0.20 to 0.30 mm was investigated for a nozzle with inner diameter of 0.34 mm; 0.30 to 0.34 mm for 0.41 mm nozzles; and 0.34 mm for 0.51 mm nozzles. The nozzles are straight-walled stainless steel needles 12.7 mm long with a flat tip.

3.5 Rheology measurements

Rheological properties of the emulsions were characterized using a controlled shear rate and shear stress rheometer (MCR702 TwinDrive Rheometer, Anton Paar, Germany), using a four-bladed vane of 10 mm diameter and 20 mm length, and a cylinder of 30 mm diameter, at approximately 22°C. Oscillatory measurements for dynamic moduli were conducted at a constant angular frequency of 10 rad/s, and increasing shear strain from 0.01 to 1000%. Recovery of G' as a function of time after a strain-controlled shear of 500% for 20s was measured with an oscillatory three interval thixotropy test (3-ITT). Angular frequency was set at 13 rad/s, and a strain of 0.05% in the first and third intervals and 500% at the second interval.

3.6 Sintering

Samples were dried for a minimum of 24h under ambient conditions. No attempt was made to remove the oil phase before sintering to avoid warpage of the parts. Sintering was conducted in an electrical furnace (Model 1700, Tetlow Kilns & Furnaces Pty Ltd, Australia). The rate of temperature increase was set at 5°C/min and ramp down at 10°C/min. Additives were burnt out

at 350°C for 30 min. Sintering was carried out at 1400°C for 1h. The parts generally remained as right circular cylinders after sintering with no significant warpage.

3.7 Density measurements

The geometric bulk density (ρ_B) after sintering was determined by measuring the weight of the sample and the average of three measured values each of diameter and height. Measurement of the bulk density of the printed samples by Archimedes' method was considered less reliable since water can drip out of the mm-sized open pores between filaments. The total porosity of the sample is determined by the measured bulk density and the theoretical density (ρ_{TD}) of alumina 3970 kg/m³. The apparent density (ρ_A) is a measure of the parts where water cannot penetrate; as such it considers the volume of the solid and closed pores. It was measured by the Archimedes' principle from the dry and submerged weights.

Determination of the amount of open porosity between the printed filaments separately from the open porosity within the filaments is not possible using Archimedes' method. Instead, we estimate the amount of open porosity between the filaments using geometric analysis. Unit cells of the printed structure were established, in which the volumes of the unit cell and the filament within the cell were determined. The lattice parameters of the unit cell and the diameter of the filaments were determined from SEM images. Once the volume of open porosity between the filaments was known, one can determine the overall porosity in the filaments, as well as the fraction of porosity within filaments which is open or closed, using the measured bulk and apparent densities by volume balance. The principles for calculations are further discussed in section 4.6, and detailed steps presented in the supplementary materials.

3.8 Morphology characterization

Sintered samples were fractured and imaged with a Scanning Electron Microscope (SEM) (FlexSEM 1000, Hitachi, Japan). Pore size measurements were performed using image analysis software, Fiji (19), a distribution of ImageJ (20). Large-scale X-ray radiography was conducted at the Imaging and Medical Beamline (IMBL) at the Australian Synchrotron. Projection images were captured using the 'Ruby' beam monitor (21) with a 25 μ m terbium-doped gadolinium oxysulphide scintillator and a sCMOS detector (pco.edge; PCO Imaging, Michigan, USA) coupled via a Nikon 105 mm Macro zoom lens (Nikon). The beam energy was 35.0 keV, the sample-to-detector distance was (550 $\pm$ 5) mm, and the pixel size was approximately 5.8 μ m. The scanned samples were sintered cylindrical prints approximately 10 mm diameter and 10 mm height. Each CT scan acquired 1800 projections over 180°, i.e. a rotation of 0.1° between successive images. 99 images were captured per set of flat-field and dark-current images, before and after each scan.

The projection images were flat-field and dark-current corrected and reconstructed into slices using the X-TRACT software on the Australian Synchrotron's MASSIVE computing cluster. 3D volumes were rendered using the Drishti software (22).

3.9 Statistical analysis

Several variables are expected to have an influence on the printability or slumping of the structure including, storage modulus, yield stress and recovery of storage modulus as a function of time after printing. These results were analyzed using two-sided t -tests (not assuming equal variances) and discriminant analysis, utilizing the Minitab® Statistical Software (23) to determine the influence of these properties on printability. Additionally, a multivariate analysis of variance (MANOVA) was conducted to analyze the impact of variables on the rheological properties. Levels of $p < 0.05$ were considered to indicate the significance level.

4. Results

4.1 Visual appearance of emulsions

There are three classes of emulsions categorized by visual appearance and rheology. As shown in Figure 2, these are 1. Flow and levelling under gravity, 2. Stiff peaks and supporting its own weight, and 3. Granular. The emulsions of category 1 are generally low in either oil or surfactant content or both. The emulsions of category 2 have intermediate surfactant and oil content over the range investigated (typically about 50 to 60 vol% oil and 0.6 to 0.8 wt% C7). The emulsions found in categories 1 and 2 are oil-in-water emulsions. Emulsions of category 3 (high in either oil or surfactant or both) begin to invert partially to water-in-oil emulsions, consistent with the literature (24). The oil begins to coalesce and separate from the emulsion resulting in a granular appearance, similar to behaviour observed in particle-stabilized foams with the same powder and surfactant (16).

4.2 Effect of formulation on rheology

The dynamic moduli (storage modulus (G') and loss modulus (G'')) are the respective plateaus at low shear stresses (also known as the linear viscoelastic regime). The yield stress is defined as the shear stress at which the storage modulus (G') and loss modulus (G'') intersect, signifying the stress at which more energy is dissipated viscously than stored elastically.

As shown in Figure 3a, all compositions have a storage modulus of approximately an order of magnitude higher than its loss modulus. Their elastic response is stronger than their viscous

response, that is, at low applied shear stress, the energy stored in an elastic manner is greater than the energy dissipated by viscous flow. For visual clarity, only the storage modulus is presented in the following figures, although all samples demonstrated a higher storage modulus than loss modulus at low shear stresses.

An increase in the volume percent of the oil leads to an increase in both the dynamic moduli and yield stress, for category 2 emulsions (see Figure 3a). This behaviour is consistent with known emulsion rheological behaviour, where an increased dispersed phase increases rheological properties (25–28). Conversely, for phase-inverted category 3 emulsions, the opposite relation is observed – both dynamic moduli and yield stress decrease with increasing oil fraction (see Figure 3b).

By increasing the surfactant concentration, both the storage moduli and yield stress also increase, as seen in Figure 3c and d. The increase however becomes less pronounced at higher oil fractions. Phase separation is observed at higher surfactant concentrations and higher oil fractions.

By increasing the mixing speed during the emulsification process, the storage modulus and yield stress are increased (see Figure S1), consistent with higher mixing speeds producing smaller droplet sizes resulting in increased viscosity, storage modulus and yield stress (25,27). The increase is more significant at lower levels of surfactant.

4.3 Effect of rheology on printability

Emulsions with a low storage modulus and a low yield stress are found to be unable to retain their shape as a well-formed filament after deposition. They slump soon after printing and merge into adjacent filaments in the same layer and/or parallel filaments two layers above and below, losing the CAD-designed mm-scale porosity and the ability to print higher than a few mm (see Figure S2). These demonstrate poor fidelity to the 3D CAD model (29) and are from category 1 described above. These inks have poor printability and are represented by the hollow symbols in Figure 4a. On the other hand, emulsions with a high storage modulus and a high yield stress exhibit better shape retention, and therefore a better printability. These are indicated by solid symbols in Figure 4a. These are emulsions of categories 2 and 3 described above. Other details of the figure are described in the discussion section 5.2. A further quantification of slumping as the deflection of spanning filaments besides its time dependency on viscosity (30) could be investigated in future work.

The recovery of the ink from its shear-thinning flow under high shear stress during extrusion through the nozzle, to revert to its solid-like behaviour upon deposition, is believed to be essential for good printability (30–33). Therefore, a three interval thixotropy test (3ITT) was conducted to investigate the emulsions' recovery behaviour. After a relaxation time of 15 s, the G' recovered for a printable emulsion is higher than that for a slumping emulsion (see supplementary materials Figure S3). Several attempts were made to relate the recovery data to printability. The recovery time alone is not sufficient to delineate printability from slumping since the value of the recovered storage modulus varies for different emulsions by a few orders of magnitude. The value of the recovered modulus after a specific time was then considered. One such analysis considers the value of modulus recovered after 15 s and are plotted against the product of G' and τ_y in Figure 4b.

4.4 Optimization of print parameters

The layer height and print pressure were selected for optimization. The layer height was varied in increments of 0.02 mm (4 to 6% in terms of inner nozzle diameters). The optimal height is defined as the highest value that does not result in the filament losing adhesion with the previous layer during printing. The mean optimal layer height was determined as approximately (74 ± 15) % of the nozzle's inner diameter, consistent with previously published optimums of 70% (35). This was found not to vary much with different values of storage modulus and yield stress. There are also smaller layer heights which create acceptable prints that still have visible horizontal gaps between filaments, but these conditions result in less open porosity between filaments. We are aiming to maximize porosity, so the vertical gaps between parallel filaments should likewise be maximized. Details of layer heights chosen as optimum for further investigation for the respective nozzle sizes are presented in supplementary materials Table S1. For the DIW printer used in this work, typical print speeds range from 10 to 20 mm/s. Lower speeds result in prohibitively long print durations, while higher speeds cause the printer to vibrate unnecessarily due to the inertia in starting and stopping at high speeds. With print speed kept constant, print pressure is found to be highly dependent on the ink's yield stress. With an increasing yield stress, a higher print pressure is required to extrude the ink (see Figure S4).

4.5 Effect of formulation on pore morphology

The prints from category 2 emulsions had pores that were generally spherical with a unimodal size distribution of typically 5 to 20 μm in diameter (see Figure 5a). These small pores were also found in category 1 emulsions, but with additional large pores of 100 to 750 μm diameter (see Figure 5b). It is believed that these larger void spaces were created by the inadvertent inclusion of air bubbles into the emulsion. Category 3 emulsions did not reveal many spherical pores (see

Figure 5c). These emulsions did not print cylindrical filaments, but instead extruded granular and fractured filaments as shown in Figure 5d, as well as in Figure S5.

The various formulation and process variables influence the pore size within the filaments. The influence of these parameters on the average size of pores within filaments was determined by image analysis using Fiji (19). These were evaluated by two-sample two-sided *t*-tests and were all found to be statistically significant with $p < 0.05$. A greater oil volume fraction resulted in larger pore sizes. In Figure 6a, the mean diameter of pores in the filament cross-section is $(8 \pm 3) \mu\text{m}$. By increasing the oil by 10 vol%, the pore size increased to a mean of $(12 \pm 6) \mu\text{m}$ (see Figure 6b). The p -value is < 0.001 . One would think that increasing the oil content would also increase the pore content of the filament, but no significant difference in porosity of the filaments could be determined from the density data (presented in Figure S6 in the supplementary materials), due to the small number of samples. Increasing the surfactant concentration reduced the pore size. Figure 6c shows an emulsion at a lower surfactant concentration of 0.06 wt% C7 with mean pore size $(7 \pm 2) \mu\text{m}$, while Figure 6d is at a higher surfactant concentration of 0.08 wt% C7 with mean pore size $(5 \pm 3) \mu\text{m}$, reflecting a reduction in the pore size. The p -value is 0.001. This is consistent with the increase in surfactant increasing the contact angle of water on the alumina particles and thus encouraging the particles to adhere more strongly to the oil-water interface and producing smaller sized emulsion droplets. For emulsions made with a smaller particle size of 350 nm, the pores were observed to be smaller $(7 \pm 2 \mu\text{m})$, than those made with a larger particle size of 790 nm $(12 \pm 6 \mu\text{m})$ (see Figures 6e and f). The p -value is < 0.001 . This is not surprising as larger particles are not as effective in stabilizing emulsions as smaller particles. With a higher mixing speed of 400 rpm, the pores were generally smaller $(12 \pm 6 \mu\text{m})$ than the emulsions mixed at 300 rpm $(15 \pm 8 \mu\text{m})$ (see Figures 6g and h). The p -value is < 0.001 . The higher shear imparted by the increased mixing rate results in decreased oil droplet size.

4.6 Density and porosity

The porosity of the sintered prints was determined by solving for four unknown volume fractions of – 1. solids, 2. open porosity between filaments, 3. open porosity in filaments, and 4. closed porosity in filaments – using four equations. The first equation is based on volume balance, in which the sum of all four unknowns is unity. From the geometrically determined bulk density, the proportion of solids can be determined. As described in section 3.7, the unit cell analysis determines the open porosity between filaments. Lastly, the apparent density of the sample measured by Archimedes' method represents the solids content and closed porosity as a proportion of the filament volume. The detailed calculations are presented in the supplementary materials, and the data can be found in Table S2 in the supplementary materials.

The variation in density measurements between samples printed from the different formulations was not found to be significantly different from each other, so we only present the results from the average of all the samples. The individual densities are presented in Table S2 in the supplementary material. The overall porosity of the sintered prints was $(78.7 \pm 3.5)\%$, with a range of 73.1% to 84.4%, as determined from the geometrically determined bulk density. The solids occupy $(21.3 \pm 3.5)\%$ of the total volume. The largest scale of porosity that is created by the architected gaps between filaments accounted for $(41.0 \pm 8.6)\%$ of the total volume of the samples as determined from the unit cell analysis described in section 3.7. This mm-scale porosity between the filaments of $(41.0 \pm 8.6)\%$ measured via SEM imaging is less than that inferred from the CAD design and nozzle diameter which is $(72 \pm 7.5)\%$. This is likely due to shrinkage between filaments (approximately 23% linearly in both horizontal and vertical axes) during sintering.

There are also both open and closed pores located within the filaments, created by soft templating of oil droplets or from partial sintering. The open pores in the filaments accounted for $(23.7 \pm 9.3)\%$, while the closed pores occupied $(14.0 \pm 7.5)\%$ of the entire volume. Therefore, open porosity accounted for $(64.7 \pm 9.5)\%$ of the entire sample volume, which is a rather high level of pore network interconnectivity. The volume occupied by the filaments is $(59.0 \pm 8.6)\%$ of the total volume. As a percentage of filament volume, the combination of open and closed porosity was $(63.6 \pm 5.7)\%$. This value is close to the volume percentage of oil added to the emulsions. $(40.2 \pm 13.9)\%$ of the porosity within the filament was open pores. These average values are illustrated in Figure 7. The trends between porosity and the amount of surfactant and oil are inconclusive from the current set of data, due to a limited number of data points.

4.7 Internal structure of prints

The internal architectures of the sintered prints were investigated via computed tomography scans at the Australian Synchrotron, combined with Scanning Electron Microscopy of the fractured surfaces (see Figure 8). Most category 2 emulsion prints appeared similar to those presented in Figure 8a. Many, if not most, of the prints were not perfect. Regions within the printed samples occasionally had defects either due to nozzle clogging, bubbles in the paste, or poor adhesion between filaments. One example of such defects is highlighted in green in the top image of Figure 8b. An interesting feature found in some portion of some prints (primarily category 3 emulsions) was a hollow tubular “macaroni” shape that some filaments took on as shown in Figure 8b. Occasionally there was detachment of infill filaments from the filaments at the perimeter, which were seen as dark hollow gaps at the sides in Figure 8c. Another feature

primarily found in category 3 emulsions are “donuts” of material formed, which are especially prominent when viewed in a top-down topographic slice, as in the bottom image of Figure 8c.

5. Discussion

5.1 Effect of formulation on rheology and pore morphology

The influence of formulation and suspension preparation variables on the rheological properties was analyzed by statistical analysis of 27 different formulations, using two-sided t -tests (not assuming equal variances) and discriminant analysis. Also, a General Linear Model by multivariate analysis of variance (MANOVA) was fitted with the 4 formulation variables (particle size, surfactant concentration, oil fraction, mixing speed). All 4 variables were found to have a statistically significant effect on the storage modulus and yield stress as responses, so it can be concluded that changes in these 4 variables are associated with changes in the two rheological properties. It should also be noted that interaction effects may exist between oil fraction and mixing speed for storage modulus, as well as oil fraction and particle size for yield stress. When interpreting effects from variations in oil fraction, care should be taken to consider effects from the other interacting variable.

By increasing the proportion of oil as the dispersed phase in an oil-in-water emulsion, either the number of oil droplets increases, and/or the size of oil droplets increases. As observed in figure 6, there is evidence for the latter. As proposed by Princen (36), increasing volume fraction increases the storage modulus and yield stress, while increasing the droplet size decreases these rheological properties instead. When the droplet radius is increased, it should reduce G' accordingly. However, since volume fraction of oil is also increased, it likely has a larger influence on G' , resulting in a higher G' and G'' as seen in Figure 3a.

With an increase in the amount of surfactant, the hydrophobicity of surfactant-adsorbed alumina particles increases, such that the contact angle of water on alumina in air increases from about 30° (no surfactant) up to about 60° (16). A contact angle in this range promotes attachment of the particles to the oil-water interface and stabilizes oil-in-water emulsions (24). The improved stability of the emulsions should allow the dispersed oil phase to exist as smaller droplets. This effect can be seen in Figure 6b. The smaller oil droplets from an increased surfactant concentration (while the total amount of oil remains constant) results in greater G' and yield stress as observed in Figures 3c and d.

Larger particles can only stabilize larger oil droplets, as they can comfortably decorate around the oil droplets with a suitable contact angle (see Figure 9a). However, for smaller oil droplet

sizes (see Figure 9b), the large particles are unable to fit a sufficient number around the oil droplet resulting in a lack of capillary bridging between particles. Furthermore, the required contact angle increases to more than the particle's equilibrium contact angle. For successful stabilization, it is necessary for particles to be significantly smaller than the droplets, so that particles can be properly located around the droplets (37) (see Figure 9c). As the droplet size approaches the particle size, local flow fluctuations caused by the particles are more likely to induce droplet break-up (38). Therefore, larger particles tend to stabilize larger oil droplets.

By increasing the speed of mixing, more energy is introduced, thereby breaking up the oil into smaller droplets, producing smaller pore sizes as seen in Figure 6h. As derived by Princen (36), a smaller droplet radius translates to a greater G' and yield stress, consistent with our results in Figure S1.

In the current work, there do not appear to be conclusive trends between the various formulation parameters and the amount of porosity measured, as discussed in section 4.6 and the supplementary materials. There is no significant influence of the formulation or processing parameters on the porosity. An improvement in accuracy or reproducibility is probably required to study this effect in further detail.

5.2 Effect of rheology on printability

Previously published printability criteria are mainly about a minimum value for storage modulus or yield stress individually. In a review by Zocca et. al. (39), printable ceramic paste inks for DIW were claimed to have a storage modulus of 10^5 - 10^6 Pa and a yield stress in the range of 10^2 - 10^3 Pa, indicated by the smaller square (solid lines) in Figure 4a. Other teams report that the storage modulus needs to be more than 2 kPa (13) and the yield stress more than 200 Pa (13,40), shown as the dotted vertical and horizontal lines in the upper right region of Figure 4a. Neither of these criteria quite fit the data in Figure 4a. Smay and co-workers (41) proposed a minimum storage modulus for feedstocks able to print spanning structures, expressed as:

$$G' \geq 1.4\rho g \left(\frac{L}{D}\right)^4 D \quad (1)$$

where G' is the storage modulus, ρ is the density of the feedstock, L is the distance between the center of two adjacent filaments (i.e. span), and D is the filament diameter. M'Barki et. al. (29) accounted for the effects of gravity and capillary forces, and proposed a criterion for a minimum yield stress, written as:

$$\tau_y \geq \gamma D^{-1} + \rho gh \quad (2)$$

where τ_y is the shear yield stress, γ is the suspension's surface tension, D is the nozzle diameter, g is gravitational acceleration, and h is the height of the printed part. We compare our experimental results to these predictions. However, both criteria (29,41) struggled to correctly predict the paste inks that slumped (indicated by the red crosses $\times$ in Figure S7 in supplementary materials). The prediction based on storage modulus using equation (1) did not closely correspond to the observed results. The prediction based on yield stress, i.e. equation (2), fared slightly better, though it faced increasing difficulty in predicting printability for pastes with a higher density (i.e. lower oil volume fraction).

We hypothesize that the product of storage modulus and yield stress must exceed a critical value to avoid slumping as indicated by the diagonal dashed line in Figure 4a. In our earlier work on clay paste printing (34) we proposed that the relationship can be expressed as:

$$G' = \frac{C_1}{\tau_y} \quad (3)$$

where C_1 is a constant. In this work, we can further refine C_1 to be approximately 5×10^6 as per the linear discriminant function which placed 91.8% of observations in the right groups. Additionally, when compared with a different ceramic system – throwing clay composition with water (without oil and other additives) (34) – our printability criterion is also equally applicable. This shows its promise as a comprehensive criterion that is potentially applicable across many ceramic DIW paste systems.

Another criterion is based on the recovery of G' as a function of time after cessation of shear. Those pastes that do not recover to at least about 10000 Pa, within the first 15 s after deposition, will slump (see Figure 4b and Figure S3); although this criterion does not separate all the data correctly. Instead it appears that the required G' recovered has a dependence on the product of G' and τ_y . A delineation (indicated by the diagonal solid line in Figure 4b) that separates all the data into two groups has been found to be:

$$G'_{\text{recovered}} = \frac{C_2}{G' \times \tau_y} \quad (4)$$

where C_2 is a constant found to be approximately 6×10^{10} in this work. All three rheological parameters (storage modulus, yield stress and recovery of storage modulus) are therefore promising predictors for printability. Although this work is focused on porous lattice structures, equations 3 and 4 could be equally applicable for dense monoliths where more slumping could be desirable to eliminate voids, by selecting a slightly lower value of the constants.

5.3 Internal structure of prints

The emulsions that were better stabilized (category 2) had templated pores and more consistent rheology, resulting in straighter, more even filaments. With increasing oil and surfactant concentrations, the oil droplets were poorly stabilized. With a break-down in particle stabilization (category 3), oil separates out during printing. The oil no longer acts as pore templates, so the ceramic particles pack closely without a dispersed phase to template pores (see Figures 5c and d and Figure S5). Also, the filament surface has a fractured granular appearance rather than the smooth cylindrical surfaces produced from category 2 emulsions. This behaviour is consistent with other investigations of emulsion phase inversion (42–45), and could be caused by any one of a few possible mechanisms (16,24).

In some circumstances during drying or calcination, the fluid (oil and/or water) being drawn out from the center towards the outer surfaces of the filaments could have migrated the particles outwards with the fluid. This could have left behind an air pocket that coalesced with neighboring air pockets until a hollow tube was formed. If this occurred before or early in the sintering process the tubular structure would have been locked in during the sintering. An example is shown in **Error! Reference source not found.** It is not clear how the “donuts” observed in Figure 8a were formed although they tend to occur in the category 3 emulsions.

The separation of filaments from the sides and between layers were probably due to the infill or some of the layers shrinking more than the sides or other layers respectively. If the contour thickness (i.e. distance between the centers of the infill filament and the perimeter filament) or layer height were not sufficiently small, there would be poor adhesion between filaments. If the tensile force from shrinking was greater than the adhesive force, detachment would occur. Separation at the sides appears to be more common as the emulsions become more granulated. The uneven filaments of granulated emulsions trap more air between surfaces, so adhesion is reduced. This effect is more obvious at the sides than between layers, because in the latter, gravity assists to compress the filaments against the adjacent layers below thereby improving adhesion.

6. Conclusions

By Direct Ink Writing (DIW) of alumina particle-stabilized emulsions, we have created hierarchical ceramic architectures with multi-scaled porosity, and investigated the relationships between formulations, rheology, printability and pore morphology.

Particle size, surfactant concentration, oil fraction and mixing speed were found to have a statistically significant impact on the storage modulus and yield stress of the emulsions. An

This article is protected by copyright. All rights reserved

increase in any of these formulation parameters leads to a rise in both rheological properties. By varying the formulations, we have demonstrated that the pore microstructure within the printed filaments can be tailored to control the pore size. By increasing the surfactant concentration or mixing speed, or by reducing the oil fraction or particle size, smaller pores can be created within the print filaments.

At elevated oil or surfactant concentrations, the emulsions exhibit phase inversion resulting in clumps of agglomerated particles and coalesced oil regions. The phase-inverted emulsions did not produce microstructure with spherical pores, as the oil droplets could not be stabilized and were squeezed out during printing. These emulsions also presented a higher frequency of internal defects, as observed in the 3D reconstructions of their computed tomography X-ray scans.

Investigation of whether a printed object can retain its shape or slumps after printing, indicated that an emulsion's rheological properties are related to its printability. A sufficiently high product of the yield stress and the storage modulus, and a high storage modulus recovered shortly after experiencing a high shear stress (such as during extrusion through a print nozzle) are required to avoid slumping. We propose an improved criterion to predict an ink's printability from these three rheological properties.

7. Acknowledgments

This research is supported by an Australian Government Research Training Program (RTP) Scholarship, and ANSTO for beamtime at the Australian Synchrotron. We would like to thank Daniel Riley, Sam Pinches and Chris Hall for their help at the Australian Synchrotron. Thanks to David Dunstan and Dan Li for the technical discussions, and Cameron Patrick for statistical support provided via the Melbourne Statistical Consulting Platform.

8. References

1. Wegst UGK, Ashby MF. The mechanical efficiency of natural materials. *Philos Mag.* 2004 Jul 21;84(21):2167–81.
2. Wegst UGK. Bending efficiency through property gradients in bamboo, palm, and wood-based composites. *J Mech Behav Biomed Mater.* 2011 Jul 1;4(5):744–55.
3. Woodard JR, Hildore AJ, Lan SK, Park CJ, Morgan AW, Eurell JAC, et al. The mechanical properties and osteoconductivity of hydroxyapatite bone scaffolds with multi-scale porosity. *Biomaterials.* 2007;28(1):45–54.
4. Nangrejo MR, Bao X, Edirisinghe MJ. Processing of Ceramic Foams from Polymeric

- Precursor-Alumina Suspensions. *Cell Polym.* 2001 Jan 4;20(1):17–36.
5. White RA, Weber JN, White EW. Replamineform: a new process for preparing porous ceramic, metal, and polymer prosthetic materials. *Science.* 1972 May 26;176(4037):922–4.
 6. Mizutani M, Takase H, Adachi N, Ota T, Daimon K, Hikichi Y. Porous ceramics prepared by mimicking silicified wood. *Sci Technol Adv Mater.* 2005 Jan 12;6(1):76–83.
 7. Taboas JM, Maddox RD, Krebsbach PH, Hollister SJ. Indirect solid free form fabrication of local and global porous, biomimetic and composite 3D polymer-ceramic scaffolds. *Biomaterials.* 2003;24(1):181–94.
 8. McNamara SL, Rnjak-Kovacina J, Schmidt DF, Lo TJ, Kaplan DL. Silk as a biocohesive sacrificial binder in the fabrication of hydroxyapatite load bearing scaffolds. *Biomaterials.* 2014;35(25):6941–53.
 9. Deville S. Freeze-casting of porous ceramics: A review of current achievements and issues. *Adv Eng Mater.* 2008 Mar 1;10(3):155–69.
 10. Leo S, Jukes L, Pinches S, Tallon C, Franks G V. Freeze casting for near-net-shaping of dense zirconium diboride ceramics. *J Am Ceram Soc.* 2018 Jul 1;101(7):2770–85.
 11. Heimann RB. *Classic and Advanced Ceramics: From Fundamentals to Applications.* John Wiley & Sons, Ltd; 2010. 553 p.
 12. Chen Z, Li Z, Li J, Liu C, Lao C, Fu Y, et al. 3D printing of ceramics: A review. *J Eur Ceram Soc.* 2019;39(4):661–87.
 13. Minas C, Carnelli D, Tervoort E, Studart AR. 3D Printing of Emulsions and Foams into Hierarchical Porous Ceramics. *Adv Mater.* 2016 Dec;28(45):9993–9.
 14. Muth JT, Dixon PG, Woish L, Gibson LJ, Lewis JA. Architected cellular ceramics with tailored stiffness via direct foam writing. *Proc Natl Acad Sci.* 2017 Jul 24;114(8):1832–7.
 15. Torres Arango MA, Kwakye-Ackah D, Agarwal S, Gupta RK, Sierros KA. Environmentally Friendly Engineering and Three-Dimensional Printing of TiO₂ Hierarchical Mesoporous Cellular Architectures. *ACS Sustain Chem Eng.* 2017;5(11):10421–9.
 16. Chuanuwatanakul C, Tallon C, Dunstan DE, Franks G V. Controlling the microstructure of ceramic particle stabilized foams: Influence of contact angle and particle aggregation. *Soft Matter.* 2011 Nov;7(24):11464–74.
 17. Chuanuwatanakul C, Tallon C, Dunstan DE, Franks G V. Producing large complex-shaped ceramic particle stabilized foams. Gauckler L, editor. *J Am Ceram Soc.* 2013 May 1;96(5):1407–13.
 18. Lewis JA. Direct ink writing of 3D functional materials. *Adv Funct Mater.* 2006;16(17):2193–204.
 19. Schindelin J, Arganda-Carreras I, Frise E, Kaynig V, Longair M, Pietzsch T, et al. Fiji: An

- open-source platform for biological-image analysis. Vol. 9, Nature Methods. Nature Publishing Group; 2012. p. 676–82.
20. Rueden CT, Schindelin J, Hiner MC, DeZonia BE, Walter AE, Arena ET, et al. ImageJ2: ImageJ for the next generation of scientific image data. BMC Bioinformatics. 2017 Nov 29;18(1):529.
 21. Hall C, Hausermann D, Maksimenko A, Astolfo A, Siu K, Pearson J, et al. Detectors for the imaging and medical beam line at the Australian synchrotron. In: Journal of Instrumentation. 2013.
 22. Limaye A. Drishti: a volume exploration and presentation tool. In: Stock SR, editor. Developments in X-Ray Tomography VIII. 2012. p. 85060X.
 23. Minitab LLC. Minitab® 19 Statistical Software. 2019.
 24. Hunter TN, Pugh RJ, Franks G V., Jameson GJ. The role of particles in stabilising foams and emulsions. Adv Colloid Interface Sci. 2008 Mar;137(2):57–81.
 25. Princen HM, Kiss AD. Rheology of foams and highly concentrated emulsions. IV. An experimental study of the shear viscosity and yield stress of concentrated emulsions. J Colloid Interface Sci. 1989 Mar 1;128(1):176–87.
 26. Mason TG, Lacasse MD, Grest GS, Levine D, Bibette J, Weitz DA. Osmotic pressure and viscoelastic shear moduli of concentrated emulsions. Phys Rev E - Stat Physics, Plasmas, Fluids, Relat Interdiscip Top. 1997;56(3):3150–66.
 27. Princen HM, Kiss AD. Rheology of foams and highly concentrated emulsions. III. Static shear modulus. J Colloid Interface Sci. 1986 Aug 1;112(2):427–37.
 28. Eriksson R, Pajari H, Rosenholm JB. Shear modulus of colloidal suspensions: Comparing experiments with theory. J Colloid Interface Sci. 2009;332(1):104–12.
 29. M'Barki A, Bocquet L, Stevenson A. Linking Rheology and Printability for Dense and Strong Ceramics by Direct Ink Writing. Sci Rep. 2017;7(1):1–10.
 30. Schlördt T, Keppner F, Travitzky N, Greil P. Robocasting of alumina lattice truss structures. J Ceram Sci Technol. 2012;3(2):1–7.
 31. Sommer MR, Alison L, Minas C, Tervoort E, Rühs PA, Studart AR. 3D printing of concentrated emulsions into multiphase biocompatible soft materials. Soft Matter. 2017 Mar 1;13(9):1794–803.
 32. Lewis JA, Smay JE, Stuecker J, Cesarano JL. Direct ink writing of three-dimensional ceramic structures. J Am Ceram Soc. 2006 Dec 1;89(12):3599–609.
 33. Franchin G, Scanferla P, Zeffiro L, Elsayed H, Baliello A, Giacomello G, et al. Direct ink writing of geopolymeric inks. J Eur Ceram Soc. 2017;37(6):2481–9.
 34. Chan SSL, Pennings RM, Edwards L, Franks G V. 3D printing of clay for decorative architectural applications: Effect of solids volume fraction on rheology and printability.

- Addit Manuf (in Press. 2020 May 20;101335.
35. Tang S, Yang L, Li G, Liu X, Fan Z. 3D printing of highly-loaded slurries via layered extrusion forming: Parameters optimization and control. *Addit Manuf.* 2019 Aug;28:546–53.
 36. Princen HM. Rheology of Foams and Highly Concentrated Emulsions I. Elastic Properties and Yield Stress of a Cylindrical Model System. *J Colloid Interface Sci.* 1983;91(1):160–75.
 37. Tambe DE, Sharma MM. Factors controlling the stability of colloid-stabilized emulsions. I. An experimental investigation. *J Colloid Interface Sci.* 1993;157(1):244–53.
 38. Kaur S, Leal LG. Drop deformation and break-up in concentrated suspensions. *J Rheol (N Y N Y).* 2010;54(5):981–1008.
 39. Zocca A, Colombo P, Gomes CM, Günster J. Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities. *J Am Ceram Soc.* 2015 Jul 24;98(7):1983–2001.
 40. Peng E, Zhang D, Ding J. Ceramic Robocasting: Recent Achievements, Potential, and Future Developments. *Adv Mater.* 2018;30(47):1–14.
 41. Smay JE, Cesarano J, Lewis JA. Colloidal inks for directed assembly of 3-D periodic structures. *Langmuir.* 2002;18(14):5429–37.
 42. Dickinson E. Interpretation of emulsion phase inversion as a cusp catastrophe. *J Colloid Interface Sci.* 1981;84(1):284–7.
 43. Vaessen GEJ, Stein HN. The Applicability of Catastrophe Theory to Emulsion Phase Inversion. *Jounral Colloid Interface Sci.* 1995;176:378–87.
 44. Midmore BR. Synergy between silica and polyoxyethylene surfactants in the formation of O/W emulsions. *Colloids Surfaces A Physicochem Eng Asp.* 1998;145(1–3):133–43.
 45. Gosa KL, Uricanu V. Emulsions stabilized with PEO-PPO-PEO block copolymers and silica. *Colloids Surfaces A Physicochem Eng Asp.* 2002;197(1–3):257–69.

9. List of figures

Figure 1. Hierarchical porosity is created on three levels – a) $>100\ \mu\text{m}$ -scaled pores from architected gaps between print filaments, b) $\approx 20\ \mu\text{m}$ -diameter pores templated by the oil droplets within filaments, and c) sub-micron pores between solid particles from partial necking during sintering.

Figure 2. Appearance of emulsions which a) flow and level under gravity (category 1, AKP-15, 40 vol% oil, 0.04 wt% C7, 400 rpm), b) can support their own weight over at least a cm or so in height and maintain stiff peaks (category 2, AKP-15, 50 vol% oil, 0.08 wt% C7, 400 rpm), and c) appear granular (category 3, AKP-15, 40 vol% oil, 0.10 wt% C7, 400 rpm).

Figure 3. Increasing oil fraction leads to: a) an increase in dynamic moduli and yield stress in homogeneous O/W emulsions, but b) a decrease in dynamic moduli and yield stress in phase-inverted category 3 emulsions. Increasing surfactant concentration increases storage modulus and yield stress, the effect is c) more pronounced at lower oil fractions, and d) less pronounced at higher oil fractions. 0.10 wt% C7 at 50 vol% oil and 0.06-0.10 wt% C7 at 60 vol% oil showed phase inversion (category 3 emulsions).

Figure 4. a) Printability plot of storage modulus against yield stress. Solid symbols depict inks which could print lattices with distinguishable filaments and voids, while hollow symbols depict inks which printed filaments that slump and lose CAD-designed voids. Circles are data from this work on alumina emulsions, while squares are data on traditional throwing clay and water pastes (34). The diagonal dashed line indicates a possible printability boundary separating printable from unprintable inks, as per equation (3). b) G' recovered after 15s from the end of a high shear stress interval plotted against the product of G' and τ_y . A vertical dashed reference line is drawn at $G' \times \tau_y = 5 \times 10^6$, representative of the dashed line in Figure 4a. The diagonal solid line is a delineation expressed as per equation (4). The meanings of the equations are discussed in section 5.2.

Figure 5. SEM images of fractured cross-sections of sintered DIW-printed filaments, made with: a) a category 2 emulsion (AKP-15, 55 vol% oil, 0.06 wt% C7, 400 rpm) - generally spherical pores with a unimodal size distribution is observed; b) a category 1 emulsion that slumped after printing (AKP-15, 55 vol% oil, 0.07 wt% C7, 400 rpm) - a bimodal distribution is observed with larger pores; and c) a category 3 emulsion (AKP-15, 40 vol% oil, 0.10 wt% C7, 400 rpm) - no visible spherical pores. d) Granular appearance of the printed filaments of category 3 emulsions (AKP-15, 65 vol% oil, 0.08 wt% C7, 300 rpm).

Figure 6. SEM micrographs of sintered DIW-printed filaments demonstrating changes in pore size by varying: oil fraction (a-b) - smaller pore sizes are observed for a lower oil volume fraction in a) 55 vol% oil ($8 \pm 3 \mu\text{m}$), as compared to b) 65 vol% oil ($12 \pm 6 \mu\text{m}$) (AKP-15, 0.06 wt% C7, 400 rpm); surfactant concentration (c-d) - pore size decreases with an increasing surfactant concentration c) 0.06 wt% C7 ($7 \pm 2 \mu\text{m}$), d) 0.08 wt% C7 ($5 \pm 3 \mu\text{m}$) (AKP-30, 65 vol% oil, 400 rpm); particle size (e-f) - larger pore size is observed for the larger particle size e) 350 nm (AKP-30) ($7 \pm 2 \mu\text{m}$), f) 790 nm (AKP-15) ($12 \pm 6 \mu\text{m}$) (65 vol% oil, 0.06 wt% C7, 400 rpm); mixing speed (g-h) - smaller pore size was observed for the higher mixing speed g) 300 rpm ($15 \pm 8 \mu\text{m}$), h) 400 rpm ($12 \pm 6 \mu\text{m}$) (AKP-15, 65 vol% oil, 0.06 wt% C7). (a-f) are cross-sections of the fractured filaments, while (g-h) show the external surface of a filament.

Figure 7. Composition of average porosities in a sintered print. $(78.7 \pm 3.5)\%$ of the overall volume consists of pores. Open porosity accounts for approximately $(64.7 \pm 9.5)\%$ of the entire volume. $(63.6 \pm 5.7)\%$ of the filament is porosity.

Figure 8. All top images and the bottom image in c are 3D reconstruction of X-ray CT scan, while bottom images in a-b are SEM micrographs. a) (Top) Print from a category 2 emulsion showing relatively distinct filaments, which (bottom) have circular cross-sections but shows slight slumping across spans. (AKP-15, 0.06 wt% C7, 55 vol% oil, 400 rpm, 0.34 mm nozzle diameter, 1.0 mm infill distance, 0.28 mm layer height). b) (Top) Region of separation and a difference in density (difference in colors), with (bottom) hollow tubular "macaroni" shaped filament found typically near these regions. (AKP-30, 0.08 wt% C7, 65 vol% oil, 400 rpm, a category 3 emulsion, 0.34 mm nozzle diameter, 1.0 mm infill distance, 0.28 mm layer height). c) (Top) Gaps at the right and left show a separation of infill filaments from the sides and hollow slits running vertically through centers of stacked filaments. (Bottom) Top-down view exhibiting "donuts" of material where filament cores all around have been hollowed out. Gaps at the edges demonstrate a detachment of infill filaments from the perimeter. (AKP-15, 0.08 wt% C7, 60 vol% oil, 300 rpm, a category 3 emulsion, 0.34 mm nozzle diameter, 1.3 mm infill distance, 0.30 mm layer height).

Figure 9. Schematic of particle stabilization capability of large versus small particles. a) Particle-stabilized oil droplet in a Pickering oil-in-water emulsion. b) Same sized particles unable to stabilize smaller oil droplets due to larger optimal contact angle required. c) Smaller particles of similar hydrophobicity (similar contact angle) are able to stabilize smaller oil droplets.

jace_17305_f1.tif

jace_17305_f2.tif

jace_17305_f3.tif

jace_17305_f4.tif

jace_17305_f5.tif

jace_17305_f6.tif

jace_17305_f7.tiff

jace_17305_f8.tif

jace_17305_f9.tif

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Chan, SSL;Sesso, ML;Franks, GV

Title:

Direct ink writing of hierarchical porous alumina-stabilized emulsions: Rheology and printability

Date:

2020-10-01

Citation:

Chan, S. S. L., Sesso, M. L. & Franks, G. V. (2020). Direct ink writing of hierarchical porous alumina-stabilized emulsions: Rheology and printability. *Journal of the American Ceramic Society*, 103 (10), pp.5554-5566. <https://doi.org/10.1111/jace.17305>.

Persistent Link:

<http://hdl.handle.net/11343/275940>