

Ink Formulation in Direct Ink Writing of Ceramics: A Meta-Analysis

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Abstract

Direct ink writing (DIW), or robocasting, is emerging as a key additive manufacturing technique for ceramic materials. Nevertheless, controlling ink rheology, finding optimal ink properties for printability, and optimising final mechanical properties have consistently posed major challenges. This review addresses these critical aspects of ceramic DIW through a meta-analysis. It encompasses rheological data from various ceramic inks and reviews methods for tuning ink properties to improve printability. The collected rheological properties are integrated into various printability criteria and models, leading to the proposal of an empirical criterion based on two key rheological parameters. Furthermore, the mechanical properties of both dense and porous ceramic components are discussed, revealing their correlations with rheology and processing defects. This comprehensive work serves as a valuable toolkit and guideline, providing researchers with the necessary insights to develop superior ink formulations and enhance the mechanical performance of robocasted ceramic components.

1. Introduction

Additive manufacturing (AM) of ceramics represents a resource and energy-efficient approach to material design and production. Traditional methods of ceramic processing, based on subtractive manufacturing, lead to substantial material wastage and involve the design of complex moulding and casting processes that are time-consuming and offer limited design possibilities. On the other hand, AM is a net-shape technology offering unparalleled material efficiency by creating intricate ceramic structures layer-by-layer from computer-generated models. An important advantage of AM is its ability to produce complex ceramic components, providing greater design freedom and enabling the creation of engineering hardware with improved functionality [1-4]. Moreover, it enables the cost-effective manufacturing of small quantities or tailor-made components, making it valuable in the aerospace and medical sectors [5]. For instance, the high design freedom enabled by AM allows for the fabrication of customised ceramic implants, such as orthopaedic and dental implants, tailored to fit patients' unique anatomies, promoting better regeneration and integration [6, 7]. In the aerospace sector, it allows for weight reduction by designing detailed internal structures, such as lattice geometries, reducing weight while maintaining structural integrity, contributing to better fuel efficiency and overall performance [8, 9]. However, despite their enormous potential, the commercialisation of ceramic additive manufacturing faces practical challenges including materials limitations, equipment complexity, post-processing requirements, cost concerns, scalability, and lack of standards [4, 5]. Overcoming these challenges through ongoing research and development is crucial for enabling wider adoption of ceramic additive manufacturing across industries.

Over the last 30 years, various AM methods have been developed for producing complex ceramic parts. These techniques are categorised by feedstock types: (1) powder feedstock-based methods, including selective laser melting/sintering [10] and binder jetting [11]; (2) slurry-based methods, including direct ink writing (DIW)/robocasting [12, 13], stereolithography [14, 15], digital light processing [16], and inkjet printing [17, 18], and (3) solid feedstock-based methods such as fused deposition modelling [19] and laminated object manufacturing [20]. These approaches have their strengths and weaknesses. For instance, powder-based AM techniques are suitable for porous ceramics because they employ coarse particles to ensure flowability during printing, but this limits sinterability and produces porous preforms that require post-sintering infiltration for high density. Solid feedstock additive manufacturing (AM) methods can produce dense ceramics. However, these methods use plies/filaments that could be expensive and require long debinding cycles to burn out a high quantity of polymer binder. This polymer binder is responsible for significant shrinkage and restricts part size. Stereolithography and direct light processing offer high printing resolution and surface finish, but their use of photopolymer resin limits the range of materials and part dimensions. In addition, the mismatch in refractive index between the ceramic powders and photocurable resins limits their applicability for the fabrication of large parts with non-oxide ceramics. DIW emerges as a promising technology for the additive manufacturing of intricate

ceramic structures. It employs high solid loading with submicron powders facilitating high sintered densities and low shrinkage with no material limitations and offers multi-material printing capability. DIW has provided cost-effective manufacturing solutions across a range of industries applications, including filters for metal casting, catalyst supports, TGA/DTA crucibles, functionally graded materials, extreme environment heat exchangers and micro-reactors, and lab wares [21]. However, improving printing resolution and green strength can further extend its market. Overcoming these challenges requires a comprehensive understanding of the technology to guide the design of novel ink formulations.

Over the past five years, several reviews regarding ceramic DIW have been published. Peng et al. summarised the accomplishments and potential of the DIW process for single and multi-ceramic printing, as well as the creation of shapeable and self-shapeable geometrically complex ceramic structures [22]. Daguana et al. discussed the challenges of making porous and dense bioceramics using DIW, as well as the ink formulations and biofunctionality of robocasted scaffolds [23]. Balani et al. reviewed different techniques and challenges of DIW [12]. Barbara and Ginebra provided an overview of the rheological tests used to assess the printability of DIW inks [13]. Laminin et al. summarised the important ink formulations for DIW ceramics, and explained how processing parameters affect printability and ink rheology [24]. As noted in these reviews, it is essential to have a printable ink for successful DIW of ceramics with desirable functional and structural properties. Since the late 90s, various ink formulations have been reported in the literature. However, many of them are developed through trial and error, making it difficult to select a suitable formulation for a particular application. This thorough review aims to fill this gap by offering a comprehensive overview of the essential ink properties and their impacts on printability and mechanical properties of robocasted ceramics. The objective of this review is to assist researchers in academia and industries in developing suitable ink formulations for the DIW of functional and structural ceramics with desirable properties.

2. Background

The DIW process has been illustrated in **Figure 1A**. A ceramic ink/paste is extruded through a nozzle, whose movement is pre-programmed by a computer, to print complex 3D structures. The printed structure is first left to dry in the ambient or humidified environments to prevent crack formation and warping from rapid drying [25]. The dried part is debinded to eliminate organic components and sintered. Throughout the drying and sintering processes, the printed structure typically shrinks, these dimensional changes should be considered during the initial design phase.

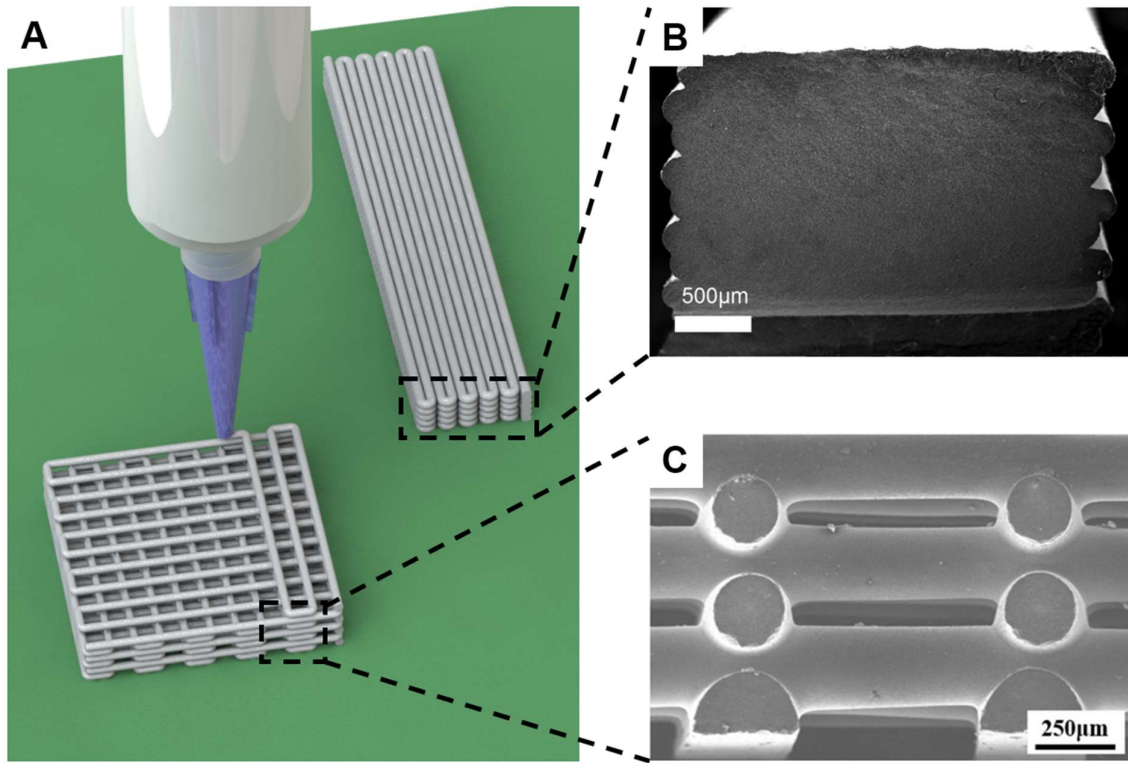


Fig. 1. (A) Schematic showing direct ink writing of ceramics. SEM micrograph showing the (B) cross-section of a sintered dense alumina bar, reprinted from Feilden et al. with permission [59] and (C) cross-section of a SiC scaffold with log-pile structure, reprinted from Sun et al. with permission [140].

2.1. Overall design criteria for DIW inks

The important characteristics of a DIW ink are: (1) extrudability, (2) shape fidelity, and (3) fusibility of printed filaments. It is ideal for DIW inks to exhibit a non-Newtonian, shear thinning fluid behaviour and their flow characteristics are usually described by the Herschel-Bulkley model [26]:

$$\tau = \tau_y + K\dot{\gamma}^n$$

Equation 1

where τ is the shear stress, τ_y is the yield stress, K is the viscosity parameter, $\dot{\gamma}$ is the shear rate, and n is the shear thinning parameter. τ_y can be considered as the point where the viscosity shows a very rapid decrease with an increase in shear [27]. For DIW, an optimal τ_y is necessary for the printed part to support its own weight and prevent shape distortion caused by both surface tension and weight of the printed part [28]. However, an overly high yield stress should be avoided to reduce extrusion pressure and facilitate easy fusion of the filaments [29]. For example, Figure 1B shows the cross-section of a DIW alumina bar with well-fused filaments without residue porosity; this indicates an optimal yield

stress. A smaller value of K indicates lower viscosity, which is preferred to prevent nozzle clogging and print uniform filaments [30]. An n value between 0 to 1 indicates a shear thinning behaviour and is preferred to maintain a uniform ink flow and print consistent filaments. As illustrated in **Figure 1**, shear thinning behaviour is characterised by a decrease in viscosity as the shear rate increases. On the contrary, a shear thickening ink demonstrates an increase in viscosity as the shear rate rises, resulting in particle jamming that disrupts uniform flow and leads to nozzle clogs [31].

The viscoelastic behaviour of DIW inks is usually characterised by dynamic rheological measurements/parallel plate oscillatory measurements [28, 32]. A complex shear modulus (G^*) is obtained:

$$G^* = G' + iG''$$

Equation 2

where G' is the storage modulus/elastic modulus, and G'' is the loss/viscous modulus. G' represents the solid-like/elastic behaviour, while G'' describes the liquid-like/viscous behaviour of a material [20]. As illustrated in **Figure 1B**, at low stresses, $G' > G''$, which indicates more energy is stored, and the ink behaves more like a solid. As the shear rate increases, G' and G'' intersect, representing a transition from a solid-like to a liquid-like behaviour. After the intersection point, G'' is above G' , indicating that the viscosity, instead of elasticity, becomes dominant, and the ink can flow like a liquid [33]. At low stresses, G' is equivalent to the elastic modulus of the material and defined as equilibrium storage modulus, G'_{eq} . Inks with high G'_{eq} are desirable since high stiffness means less shape change and better structural integrity [34]. A high G'_{eq} is also desirable to avoid elastic bending of filaments in scaffolds (**Figure 1C**). Apart from the rheological parameters, it is important to avoid agglomeration and air entrapment during ink preparation through optimal mixing and degassing cycles. Also, depending up on the applications, some additional ink design criteria may be needed. For example, DIW has been extensively studied to fabricate bioceramic and bioactive glass scaffolds for tissue engineering [35-38]. For such applications, polymeric additives used in the process and the post-printing treatments should be easily removable by high-temperature sintering and should not compromise the biocompatibility of the material [39, 40].

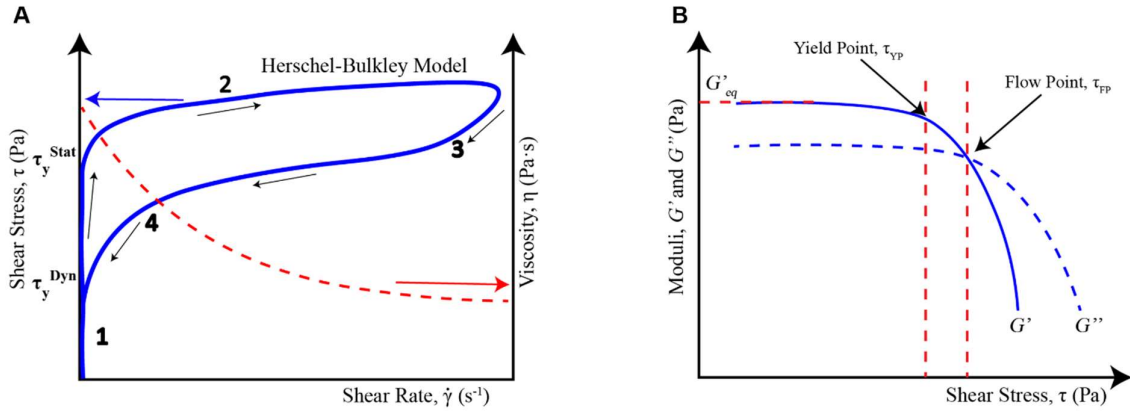


Figure 1. (A) Hysteresis flow curve of a DIW ink showing different stages of extrusion, figure recreated under the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>) from M'Barki et al. [28]. (B) Plot showing the viscoelastic behaviour of DIW inks, where G' is the storage modulus and G'' is the loss modulus.

2.2. Definition of yield stress

Three methods have been reported to determine the yield stress of inks. One way is to fit shear stress and shear strain data to the Herschel-Bulkley model (**Equation 1**) and the value of yield stress is given by the y-intercept of the plot, as shown in **Figure 1A**. Many researchers also interpret the crossover of G' and G'' as the yield stress (**Figure 1B**) [41-43] due to the difficulties and uncertainties in determining the greatest applied shear stress before flow happens in the flow ramp [27]. This intersection point represents the onset of the flow behaviour or a solid-to-liquid transition. In the third method, as shown in **Figure 1B**, the initial drop of G' has also been considered as the onset of yield behaviour due to the change of linearity of G' , indicating a structural breakdown of the material [44]. To avoid ambiguity, in this article, the value obtained from the Herschel-Bulkley model is defined as the yield stress (τ_y), the crossover of G' and G'' is defined as the flow point, τ_{FP} and shear stress corresponding to 10% drop in G'_{eq} value is defined as the yield point, τ_{YP} . In addition, when talking about general yield behaviours, yield parameters will be used as a general term to describe the changes in yield stresses, flow points, and yield points.

The yield stress, obtained from the Herschel-Bulkley model, can be further divided into static (τ_y^{Stat}) and dynamic (τ_y^{Dyn}) yield stresses. A typical hysteresis stress measurement is shown in **Figure 1A**. τ_y^{Stat} and τ_y^{Dyn} are the yield stresses that are obtained from increasing and decreasing shear rate respectively. During the test, the stress is first applied (stage 1), and the ink is extruded through the nozzle (stage 2). The onset of the slope change is then determined as τ_y^{Stat} . The shear rate is then decreased (stage 3), resulting in stress relaxation (stage 4). In simple terms, τ_y^{Stat} measures the minimum stress required to extrude the ink from the nozzle from a rest state, and in order for the ink to

continue to flow, a stress larger than τ_y^{Dyn} is needed; τ_y^{Dyn} can be calculated by fitting the data collected while decreasing the shear rate to the Herschel-Bulkley model [28, 44].

2.3. Families of inks

Cesarano et al., the inventors of DIW, developed the first ceramic ink by adding less than 2% organic additives to highly-loaded colloidal slurries (up to 65 vol%) [1, 2]. Since then, the development of various inks has been the focus of ceramic DIW research.

In this article, the inks have been divided into four categories: colloidal, polymeric, emulsion and foam inks, as well as organogel inks. These categories have been established based on different formulations, as shown in Figure 2. Colloidal inks are achieved through a fluid-to-gel transition by tuning interparticle forces, which also contribute to their rheological properties. In the case of polymeric inks, despite also being water-based formulations, their strength is derived from the three-dimensional network structure formed among ceramic particles, polymeric additives, and water. In other words, the polymeric matrix, rather than direct interparticle interactions, plays a more crucial role in determining the rheological properties of polymeric inks. Emulsion/foam inks, on the other hand, include an additional phase (oil for emulsion inks and air for foam inks) to create the DIW ink. Finally, organogel inks are non-aqueous and based on organic solvents. In this subsection, methods to formulate these types of DIW inks will be reviewed.

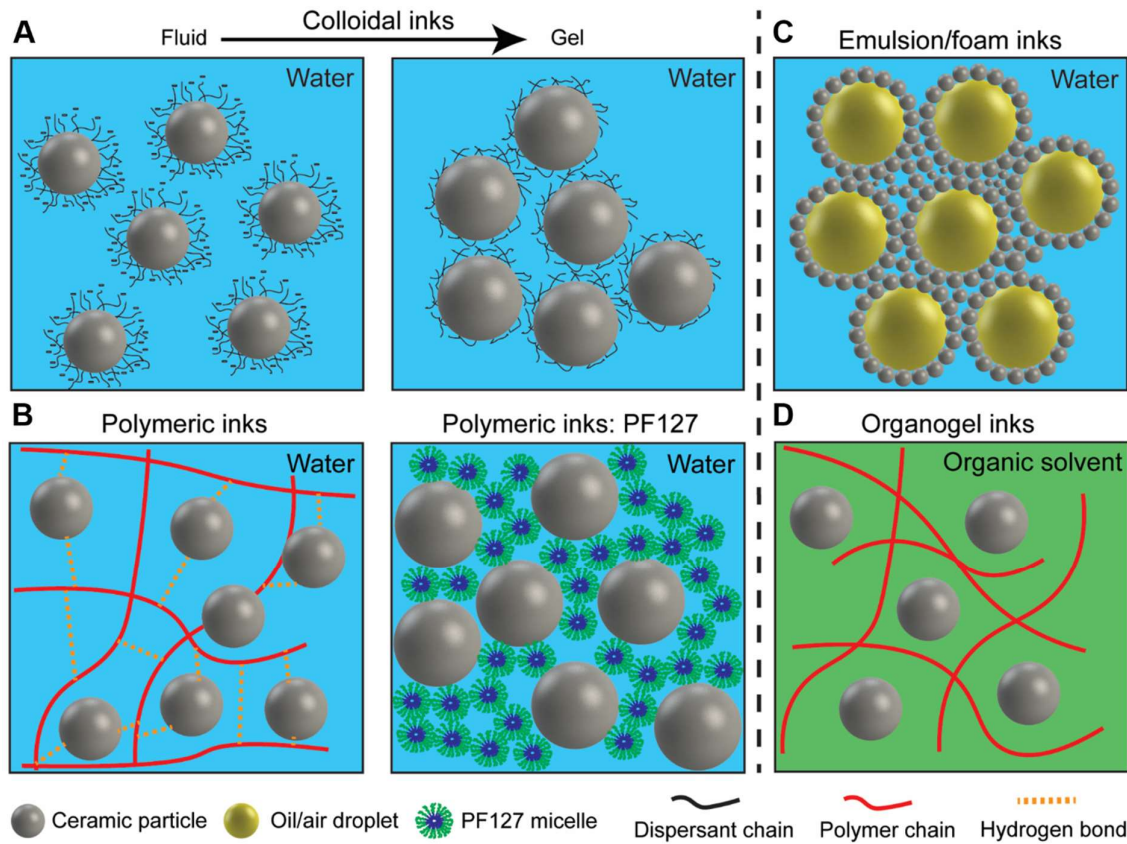


Figure 2. Schematic diagram of different types of ceramic DIW inks and their characteristics: (A) colloidal inks, (B) polymeric inks, (C) emulsion/foam inks, and (D) organogel inks. Recreated and adapted with permission from del-Mazo-Barbara and Ginebra [13] and Li et al. [157].

2.3.1. Colloidal inks

The design of colloidal inks relies on a fluid-to-gel transition achieved by tuning the interparticle interactions. As shown in **Figure 2A**, firstly, a highly-loaded suspension with low viscosity is prepared by dispersing ceramic particles in water with the help of a dispersant such as DARVAN® 821A, an ammonium salt of poly(acrylic acid)(PAA). By absorbing readily onto the surface of ceramic particles, the dispersant helps the particles to achieve a negatively-charged surface, leading to electrostatic repulsion and a well-dispersed suspension [22]. Then, the gelation is achieved through controlled flocculation by changing the system environment that results in a change of balance between van der Waals, electrostatic, and steric forces [45].

Several methods have been reported to achieve gelation in colloidal inks. One method involves tuning the pH. In many cases, the stable ceramic suspension in the previous step is prepared under a relatively high pH value that is greater than the isoelectric point (IEP), and the addition of anionic dispersant lowers the IEP, leading to a well-dispersed and homogenised suspension [46]. Gelation can be induced by lowering the pH value, which brings the pH closer to IEP, increasing the attractive interaction between particles [45]. Another way to obtain printable gels is by adding salt species that screen the charges between ceramic particles and inside the polymer layers formed in the previous dispersion stage

[46]. Finally, the addition of polyelectrolytes is another common method to achieve gelation; for instance, poly(ethylenimine)(PEI) can form a second cationic layer on top of the first anionic layer, and can act as a bridging flocculant [46]. It is worth mentioning that in some cases, high molecular-weight PEI can also be used as a cationic dispersant to stabilise the suspension, especially when PEI can generate high electrostatic potential with another ceramic species, such as boron carbide and silicon carbide [47, 48].

Sometimes, on top of the flocculants, other **polymeric** additives are included in the formulation to tailor the properties of the ink. For example, cellulose derivatives, such as ethyl cellulose and methyl cellulose, are used as a binder to assist the shape retention of the green body or as a thickening agent to tailor the rheology and prevent phase separation during extrusion [47, 49, 50]. For colloidal inks, the shear thinning behaviour mainly comes from the breaking of particle networks under shear and understanding interparticle interactions is important for tailoring the properties of the ink. **Colloidal** inks that meet the rheological requirements for printing can achieve relatively high solid loadings (~ 60 vol%) [51]. However, they are extremely sensitive to surface modifications and thus require careful control [45].

2.3.2. **Polymeric** inks

In polymeric inks, the desired viscoelastic properties predominantly arise from a polymeric matrix (Figure 3B). This differs from colloidal inks, where such properties mainly depend on the inter-particle network. For these inks, multifunctional (dispersant, binder, gelation agent) polymeric additives, such as cellulose derivatives [52-55], sodium alginate [54, 56], polyvinyl alcohol (PVA) [57, 58], and Pluronic F-127 (PF127) [35, 36, 59], are used to make a pre-mixed aqueous solution, followed by the addition and mixing of ceramic particles. These additives form a polymeric network that tailors the rheological properties of the DIW ink to achieve ideal printability. An important class of polymeric ink is based on hydrogels. Hydrogels consist of a porous polymeric network filled with water, where water-absorbing capability arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains [Ahmad_JAR2015]. A wide range of natural and synthetic hydrogels have been investigated for DIW, primarily in the field of tissue engineering, soft robotics, and wearable device applications [Baniasadi et al._ACIS2024]. An important hydrogel-based ink that is attracting much attention in DIW of ceramics uses **pluronic hydrogels** [35, 59, 62-72]. For these inks, complicated manipulation of interparticle forces is not required; instead, the hydrogel acts as a carrier for ceramic powders [59]. Thanks to the gel matrix that provides the strength of the ink, this type of ink can be used to print a wide range of materials with different compositions [35]. **Pluronic hydrogels exhibit a reversible thermal gelation.** At low temperature (around 0°C), the copolymer blocks of polyethylene oxide (PEO) and polypropylene oxide (PPO) dissolve in water, and the PF127 solution is liquid-like; mixing of ceramic particles and homogenisation can be carried out at this stage. Upon raising the temperature to around room temperature (20°C), due to the reduction in the degree of hydrogen bonding between PPO and water,

polymers rearrange to form micelle aggregates, leading to the formation of a gel, and a printable ink with a suitable viscoelasticity [35, 73]. During printing, the shear force exerted by the printer leads to a reversible breakdown of the hydrogel network. This causes polymer micelles to roll over each other, facilitating easier ink flow through the nozzle. Subsequently, the extruded ink filament retains its shape due to the restoration of the gel network in the absence of shear stress.

2.3.3. Emulsion and foam inks

By definition, an emulsion is a mixture that consists of two or more immiscible liquids. The difference between emulsion and foam inks is that emulsion inks have oil-water interfaces, while foam inks possess liquid-gas interfaces [74]; both inks can potentially be used to create highly-porous ceramic parts. Emulsion/foam gels were first developed for gel-casting of ceramics [75, 76]. However, these gels did not have the required rheological properties for DIW. Later, Minas et al. developed an ink that has the desired properties to print porous alumina scaffolds with poly(vinyl alcohol) (PVA) as the interface-active molecule [74]. Machado showed that by using branched copolymer surfactant (BCS), an amphiphilic copolymer of methacrylic acid (MAA), polyethyleneglycol methacrylate (PEGMA), ethyleneglycol dimethacrylate (EGDMA), and 1-dodecanethiol (DDT), to stabilise emulsions it was possible to tailor the microstructure of the printed bioceramics, hydroxyapatite (HA) and β -tricalcium phosphate (β -TCP) [77]. In this case, BCS acts as both a surfactant and a dispersant. At high pH values, BCS is attached to the surface of ceramic particles, and the steric and electrostatic effects make it function as a dispersant, allowing a higher solid loading. Upon the addition of chemicals, such as HCl [78] and Glucono- δ -lactone (G δ L) [79], that lower the pH of the suspension, the attractive interaction between the functionalised ceramic particles increases due to the formation of hydrogen bonding [77]; this leads to the assembly of a 3D network with a higher modulus.

The origin of the shear thinning behaviour of emulsion inks comes from the relatively weak attraction between ceramic particle-covered oil droplets. Upon applying a shear force, the network held by the attractive force is disrupted, accompanied by the deformation of droplets [80, 81]. Plus, at higher shear rates, it becomes increasingly difficult for the network to reform [80]; the ink, therefore, exhibits a shear thinning behaviour. This type of ink has been used by different groups to fabricate ceramic scaffolds with both open macroporosity between struts and internal microporosity inside individual struts, and the total porosity achievable can be as high as $\sim 94\%$, compared with $\sim 60\%$ using colloidal and polymeric inks [35, 74, 82]. Recently, through the DIW of emulsion inks, Cai successfully printed porous bulk alumina parts with mechanical properties similar to those made via other techniques such as gel casting and hot pressing [29]; this proves the potential of using emulsion inks to fabricate ceramic parts with high porosity.

2.3.4. *Organogel inks*

While the vast majority of the studies focus on water-based formulations, some recent papers have reported to use pure organic solvents for dispersing ceramic particles. These **organogel** ink systems possess some unique advantages over the more universal colloidal and **polymeric** inks. For instance, when dispersed in tetraethylene glycol dimethyl ether (tetraglyme), fumed silica nanoparticles can form a strong network even with low solid contents due to the low hydrogen-bonding ability of such organic solvent [83]. Zhang et al. also showed that with diethylene glycol (DEG), Poly(ethylene glycol) diglycidyl ether (PEGDE) and EpoThin 2 Hardener (ETH), a universal self-curable ink for printing ceramic materials was achieved [84, 85]. After printing, the shape of the green body could be further modified via simple mould casting [84]. The shape-forming capability of the ceramic green body was also demonstrated by Elizarova et al. with a dispersing medium of novolac phenolic resin dissolved in methyl ethyl ketone [86]. In some cases, using a high-boiling point organic solvent can also prevent the constant drying of the ink in the ambient environment [87-89].

2.3.5. *Other types of inks*

Apart from the categories of inks discussed above, another frequently reported class of ink is the **preceramic polymers-based ink**, which rely on the pyrolysis of organosilicon polymers to produce ceramic materials [90-95]. Compared with inks containing organic additives, the advantage of using preceramic polymers is the low decomposition mass loss and low sintering shrinkage [91].

DIW has also been combined with different techniques to fabricate ceramic parts. For instance, by using a thermoplastic binder, fused deposition modelling (FDM) can be integrated with DIW. In this method, the feedstock is heated, transforming it into an extrudable paste. The extruded filament cools upon contact with the ambient air and solidifies, giving shape fidelity to the extruded filament. UV-assisted DIW of ceramics has also been investigated [97, 98]. This method utilizes a UV-curable ink that is instantaneously hardened upon UV irradiation, preserving the structural integrity. Another emerging method is embedded DIW, in which the structural integrity of printed part is maintained by a 3D supporting medium. In this method, the ceramic ink is dispensed into a 3D supporting medium instead of being deposited onto a flat substrate, [99-102]. Embedded printing has dramatically enhanced the capability of DIW, making it possible to print complex 3D free-form geometries without the need for support [100].

Although the aforesaid techniques possess significant potential for advancing the DIW of ceramics, this review specifically focuses on ceramic particulate-based systems whose printability depends solely on the ink's viscoelastic properties. Consequently, studies involving the inks mentioned above were excluded during the screening process.

3. Methods

This systematic review focuses on the DIW of ceramic materials. The studies included were selected based on the recommended process by Preferred Reporting Items for Systematic Reviews and Meta-Analyses extension for Scoping Reviews [103]. Peer-reviewed articles from the Web of Science online database (www.webofscience.com) were systematically selected, beginning from the start date of the database until 13 March 2024. The search strategy and the screening process are depicted in the supplementary information (Table S1 and Figure S1). Three authors (ZL, RM, and SZ) independently conducted the study screening and data collection. In cases of discrepancies, the authors discussed the full-text manuscript and reached a consensus. This meta-analysis covered a variety of robocasted ceramic-based materials, including alumina [28, 42, 43, 49, 50, 53, 56, 59, 63-65, 70, 71, 74, 82, 84, 86, 104-125], zirconia [33, 45, 51, 65, 69, 72, 84, 126-135], silicon carbide [47, 59, 64, 86, 109, 136-145], silicon oxynitride and silicon nitride [25, 34, 60, 89, 146-150], boron carbide [48, 68, 137, 140, 151, 152], calcium phosphate [35, 57, 88, 153-155], barium titanate [41, 46, 55, 156, 157], lead zirconate titanate [3, 158-160], clay [161-166], silica [58, 87, 167], ceria [168, 169], titania [54, 170], zirconium diboride [171, 172], barium calcium zirconate titanate [173], chromium aluminium carbide [174], commercial dental feldspathic porcelain [175], hafnium diboride [66], lithium lanthanum zirconium tantalum oxide [176], lithium manganese oxide [177], lithium aluminosilicate [178], lithium disilicate [179], nickel zinc ferrite [180], potassium-sodium niobate [181], titanium aluminium carbide [182], and yttrium barium copper oxide [183]. Glass materials [36, 37, 39, 52, 62, 67, 83, 184-187] and different minerals, such as cordierite [188, 189], gypsum [190] and mullite [191], were also included.

Information regarding different parameters that affect the ink properties and the mechanical properties of final parts was manually collected from the above-mentioned sources. Data listed in tables or throughout the text were directly noted, and data points presented in the form of plots were digitised by using OriginPro. More specifically, the equilibrium storage modulus, G'_{eq} , was determined from the value of the initial plateau of the G' curve that was obtained from oscillatory measurements. Three methods were used to describe the yield behaviour of the ink. Yield stresses, τ_y , which are commonly obtained from fitting the experimental data to the Herschel-Bulkley model, could be directly collected, or calculated by fitting the shear stress-shear rate plot with the Herschel-Bulkley model. Flow points, τ_{FP} , were determined by manually selecting the crossover of G' and G'' , and the displayed stress value on the x-axis of the oscillatory measurements plot was taken as τ_{FP} . In some cases, only the G' curve was reported; the yield point, τ_{YP} , was then evaluated at the point where the slope of the G' curve started to change (at $G' = 0.9 G'_{eq}$) [3]. In this study, many of these properties are plotted against the solid loading in ceramic ink suspensions. Although the solid loading may not be the perfect parameter to capture the variations in ink properties due to differences in particle properties such as particle shapes and size distributions, it is a commonly reported variable in the ink formulation process, and since the

influences of solid loading on suspension properties have been well-studied, changes in ink properties caused by other factors can be better analysed [192].

Printability was determined by collecting information from individual papers. An ink was considered nonprintable if the authors claimed that the ink was too weak to retain the printed shape (slumped) or the pressure needed for extrusion was too large (clogged). In some cases, photos of printed samples from the article or supplement materials were used to help distinguish the printability of the ink; if the printed shape did not show any slumping and the features designed were clearly visible, the ink used to print that part was marked as printable. Three printability models are included in this paper. For the Smay and M'Barki printability models, densities of the inks were estimated using the following equations (**Equation 3** for colloidal and **polymeric** inks, and **Equation 4** for emulsion/foam inks):

$$\rho_{ink} = \rho_{ceramics} \cdot V_f^{ceramics} + \rho_{water} \cdot V_f^{water}$$

Equation 3

$$\rho_{ink} = \rho_{oil/air} \cdot V_f^{oil/air} + (\rho_{ceramics} \cdot V_f^{ceramics} + \rho_{water} \cdot V_f^{water}) \cdot V_f^{suspension}$$

Equation 4

where ρ_{ink} , $\rho_{ceramics}$, ρ_{water} and $\rho_{oil/air}$ are the densities of the DIW ink, the ceramic content, water, and the dispersed phase in emulsion/foam inks (oil or air), and $V_f^{ceramics}$, V_f^{water} and $V_f^{oil/air}$ are the volume fraction of the ceramic content, water and the dispersed phase in emulsion/foam inks (oil or air). For studies reporting ink compositions in weight fractions, the volume fraction of each component was converted based on different densities. The density of water was taken as 1 g/cm³, and the densities of the ceramic content and the oil phase were either collected from the materials section of the article or the manufacturer website. For samples with spans, most authors stated the designed span length in the methods section. However, for papers that did not clearly indicate the design, the span length was determined digitally by looking at the centre-to-centre distance between the adjacent struts on the green samples. A similar method was used to determine the sample height for the M'Barki printability model.

When collecting data for mechanical properties, the relative density of dense ceramics is usually reported, and if not, it was calculated by dividing the reported density by the theoretical density of the ceramic materials [82]. When calculating the critical defect sizes, fracture toughness values of ceramics were collected for alumina (3.12 MPa·m^{1/2}) [193], zirconia (6–13 MPa·m^{1/2}) [194, 195], silicon carbide (3.30 MPa·m^{1/2}) [196] and hafnium diboride (7.50 MPa·m^{1/2}) [197]. Since the data collected for this section cover a wide range of ceramic materials, a direct comparison of strength values may lead to misleading results, considering the fact that mechanical properties are highly material-dependent. In order to obtain useful information that can be applied on both stronger and weaker materials, both the bending strength of dense ceramics and the bending and compressive strength of ceramic

scaffolds/porous ceramics have been normalised by the bending strength (modulus of rupture) of the corresponding dense materials [198]: alumina (500 MPa) [199], zirconia (960 – 1500 MPa) [195, 200, 201], silicon carbide (450 MPa) [202], calcium phosphate (119 – 250 MPa) [203, 204], titania (140 MPa) [205], titanium aluminium carbide (430 MPa) [206], hafnium diboride (568 MPa) [197], and 45S5 Bioglass® (103 MPa) [207]; the variation in modulus of rupture values originates from different compositions, and the source that best matches each composition was selected for normalisation. These sources include brochures of commercial products and publications covering relevant ceramic materials. Products or samples with a relative density greater than 99% were selected, and their moduli of rupture were used to normalise the collected data. As discussed by Deville et al. in a similarly styled meta-analysis study, the method of normalisation can be questioned. This is particularly true for low-porosity materials where the primary fracture mode is not bending. However, in porous ceramics under compression, local stresses are predominantly in the bending state, leading to failure due to local bending [198, 208, 209]. This normalisation process enables a fair overview of the mechanical properties of various ceramic materials.

In this work, the majority of the figures were plotted to demonstrate data collected from the literature. Due to the large number of data sets involved, it is difficult to differentiate each set of data based on both colours and shapes to make the plots colour-blind friendly. As a result, a colour-blind safe palette was chosen. The RGB colour codes for the four colours selected are: (0, 0, 0), (86, 180, 233), (230, 159, 0) and (0, 158, 115).

4. Results and discussion

4.1. Ink rheology

Controlling the rheology of DIW inks is the key to successfully print ceramic parts with ideal properties. Herein, different factors that influence the crucial rheological properties, namely different yield parameters (τ_y , τ_{FP} , and τ_{YP}), equilibrium storage modulus (G'_{eq}), shear thinning coefficient (n) and viscosity parameter (K), will be discussed by analysing reported data from the literature. Among the three yield parameters, since yield stress and flow point both represent the stress needed for the ink to “flow”, these two parameters will be included in the same plot. On the other hand, the yield point, which indicates a structural breakdown of the DIW ink, will be addressed separately [29].

4.1.1. Yield parameters and equilibrium storage modulus

As shown in Figure 3, the yield parameters (τ_y , τ_{FP} , and τ_{YP}) are positively correlated with the equilibrium storage modulus (G'_{eq}). This is expected, as these properties are determined by the strength of the network forming across the ink, regardless of the ink type. The stronger the network, the greater resistance to (1) elastic deformation, implying a high storage modulus, and (2) viscous flow, implying high yield parameters. [210]. This figure includes both printable and non-printable inks; therefore, some data points have relatively high G'_{eq} but low yield parameters (red boxes). Although this may be ideal,

as a high G'_{eq} represents high stiffness and better shape retention for the printed structure, while a low yield parameter indicates better extrudability, it does not necessarily guarantee printable inks. As will be discussed in **Section 4.2**, for an ideal DIW ink, there should be a range of G'_{eq} and yield parameter values that ensure structural integrity after printing while maintaining good extrudability.

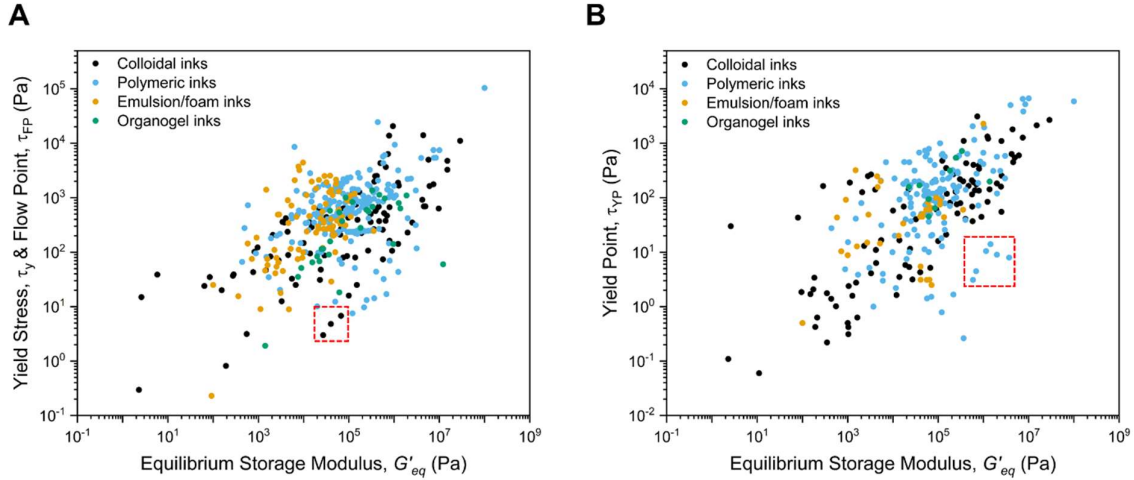


Figure 3. Relationship between the equilibrium storage modulus and (A) yield stress/flow point and (B) yield point.

The relationship between yield parameters, G'_{eq} , and the solid loading of ceramic content is depicted in **Figure 4**. A high solid loading is desirable to minimise post printing drying- and sintering-shrinkages [46]. According to the figure, colloidal inks are typically formulated with solid loadings ranging from 40 to 65 vol%, whereas other types of inks are usually formulated with loadings below 60 vol%. Relatively high solid loadings are achievable with colloidal ink because their pseudoplastic properties rely on the fluid-to-gel transition by tuning interparticle interactions. In contrast, **polymeric** inks require various polymeric binders to attain desirable pseudoplasticity, limiting the maximum solid content that can be incorporated. Indeed, the increased difficulty in preparing inks with high solid loadings is a significant drawback for **polymeric** inks that employ a simple formulation process, such as those based on PF127 hydrogel [67]. However, the maximum solid loading is also influenced by particle properties. For instance, a printable **polymeric** ink with Pluronic P-123 as the binder, along with LiMn_2O_4 and carbon as solid content, has been reported to reach a solid loading of 75 vol% [177]. The high solid content achievable may be attributed to the mixture of solid materials with different particle sizes, resulting in more effective packing and, consequently, a smaller apparent volume of the powder compact and a higher solid loading [211].

In the following subsections, based on different ink types, factors influencing the ink rheology will be reviewed and discussed.

The effect of various processing parameters on rheological properties of inks can be described by [46, 212]:

$$P = k \left(\frac{\Phi}{\Phi_{gel}} - 1 \right)^x$$

Equation 5

where P is the property of interest, k is a pre-factor, Φ is the solid loading, Φ_{gel} is the gel point, and x is a scaling exponent. In Figure 4A, yield parameters and G'_{eq} increase with solid loadings (Φ), which is consistent with Equation 5. Adding more ceramic content reduces the distance between individual particles, resulting in a smaller interaction volume [121]; it is, therefore, more difficult for the particle to flow through the surrounding network due to electrostatic repulsive forces [120, 213]. For the same reason, as the solid loading reaches a certain value, the viscosity of the ink rises dramatically with a slight increase in the solid content [192].

Referring to Equation 5, another important factor influencing the rheological properties is the gel point (Φ_{gel}), which represents the minimum loading required for a fluid-to-gel transition to occur. In a ceramic ink, Φ directly affects the bond density, while Φ_{gel} is inversely proportional to the strength of attraction between particles [3]. If ceramic particles are modified to be more attractive to each other, the value of Φ_{gel} will drop, indicating a lower solid volume fraction needed for gelation; at the same solid loading, this means higher values of yield parameters and G'_{eq} . This phenomenon can also be supported with the boxed data points in Figure 4A. Li et al. showed that, with the same SiC solid loading, the G'_{eq} values could vary by nearly two orders of magnitude, depending on the amount of PEI flocculant used [138]. Furthermore, Φ_{gel} can be tuned using various flocculants, dispersants, and by altering pH and particle-size distribution. The following paragraphs detail the effect of these factors.

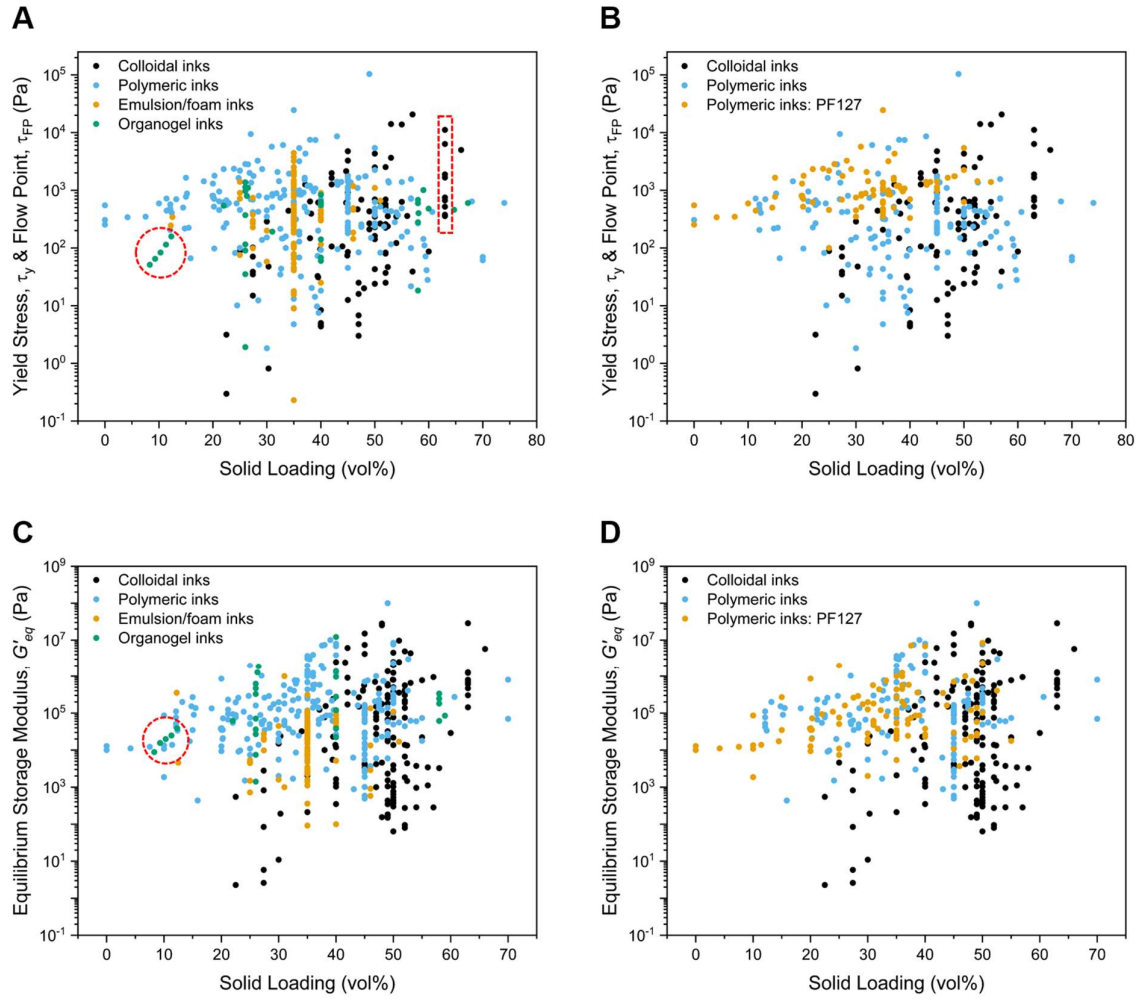


Figure 4. (A), (B) yield stress/flow point and (C), (D) equilibrium storage modulus versus solid loading, with data from PF127 hydrogel inks separated and shown in (C) and (D).

Flocculants are used to induce the fluid-to-gel transition in colloidal ink. The rheological properties of the gel are influenced by the type, amount, and molecular weight of the flocculant. A study on BaTiO₃-based ink using poly(acrylic acid) (PAA) dispersant showed that the addition of more PEI (poly(ethylenimine)) flocculant of the same molecular weight resulted in higher G'_{eq} [46]. PEI is used to form a second polymer layer that enables one ceramic particle to bridge with another particle nearby, achieving flocculation. During this process, PEI molecules form complexes with the dispersant polymer, and a higher amount of PEI molecules can, therefore, lead to more complex formation and bridging between particles [46, 49]. Similarly, the study concluded that when the same amount of PEI was added, using a polymer with a higher molecular weight led to a higher modulus [46]. In this case, the molecular weight of PEI polymers can play a significant role. Polymers with higher molecular weight tend to have a larger molecule size, which enables more complexes to form, enhancing the bridging efficiency [46]. Furthermore, when using PAA-PEI complex to formulate DIW inks, several studies based on alumina and SiC inks showed that the [COOH]:[NH_x] ratio played a significant role in determining the rheology

[49, 120, 138]. When the ratio is low, the excessive PEI chains can attach both to the PAA chains and the negatively charged sites of the ceramic particles, leading to particle aggregation and ink flocculation. Therefore, more PEI leads to a lower $[\text{COOH}]:[\text{NH}_x]$ ratio and a higher yield stress [138]. However, an excessive PEI may also lead to lower G'_{eq} and viscosity due to the excessive polymer chains presented [49]. Additionally, the amount of dispersant added can also influence ink rheology. The balance between the steric repulsive force induced by the dispersant layer and the attractive interaction between ceramic particles needs to be delicately controlled. Liao et al. proposed that the excessive dispersant added could form a thick steric barrier that weakened the flocculation, resulting in lower yield parameters and G'_{eq} , despite the increased additive concentration [45].

Salts, such as NaCl or BaCl_2 , can also be used as flocculants. The type of salt selected will influence the resulting ink properties. Compared with monovalent salt species, divalent salts are significantly more efficient in aiding the flocculation and raising the storage modulus of the ink. For monovalent salt species, the salt added solely acts as a tool to screen the charges from the dispersant polymer; this reduces the repulsive electrostatic force between ceramic particles. On the other hand, for divalent salts, apart from a more effective screen mechanism due to higher valence, cations can form complexes with the anionic groups on the polymer dispersant from two separate ceramic particles (ion-bridging effect) [46, 157]. Due to this additional bridging effect, a more rapid escalation of G'_{eq} can be observed.

Yield parameters and G'_{eq} of colloidal inks are shown to be sensitive to pH changes [3]. Since in most cases, the addition dispersant substantially alters the zeta potential-pH behaviour of the ceramic ink, a slight change in pH may significantly affect the interparticle interactions, leading to widely divergent ink properties [214]. Studies have also shown that the polymeric thickening agent/viscosifier/binder, such as methylcellulose, can affect the rheological properties of the ceramic ink. Under the same solid loading, adding more such additives tends to enhance the above-mentioned properties of the ink; using polymeric binders with higher molecular weight also has a similar effect [48, 120].

Finally, particle size and particle size distribution also affect the yield parameters and G'_{eq} . For inks with unimodal particle size distribution, finer particles possess higher surface energy and tend to agglomerate, leading to higher viscosity. In addition, due to the formation of a highly linked network of particles and interparticle friction between finer particles, the flow of the ink is hindered, and yield stress and G'_{eq} will be higher [138, 167]. Upon the addition of coarser particles, yield stress, G'_{eq} and viscosity of the DIW inks are shown to be lowered [138, 167, 215]. For particles with a broad size distribution, smaller particles can fit into spaces between larger particles; this leads to more free space for individual ceramic particles to move around, making the flow easier and hence, a lower viscosity [192, 216] and a smaller force/yield stress needed for the ink to flow [215, 217].

Polymeric inks

Polymeric inks, unlike colloidal inks, do not require careful manipulations of interparticle forces to achieve the gelation/flocculation of DIW inks. Instead, ceramic powders are added to a pre-mixed aqueous solution with various rheology modifiers added. After mechanical mixing, a printable DIW ink is obtained. Cellulose derivatives [52-55], sodium alginate [54, 56], polyvinyl alcohol (PVA) [57, 58], and PF127 [35, 36, 59] are commonly used processing additives to formulate inks with desirable rheological properties. Similar to colloidal inks, **polymeric** inks also exhibit higher yield parameters and G'_{eq} with increasing solid loading due to the reduced mean interparticle spacing and interaction volume upon the addition of solid content [53] (**Figure 4**). Apart from the solid loading, studies have shown that with the addition of more **polymeric** binder (sodium alginate, carboxymethyl cellulose, and PVA), yield parameters and G'_{eq} tend to increase [52, 54, 150]. This phenomenon can be attributed to the increased bonding between the particles and **polymeric additives**, as well as the increased number of chain entanglements of the molecules either adsorbed at the particle surface or in the dispersing liquid, increasing the intrinsic viscosity of the dispersing medium [37, 58, 187]. In addition, Eqtesadi et al. proposed that at low concentrations (<1 wt%), a high molecular weight multifunctional binder such as carboxymethyl cellulose was able to induce bridging flocculation. However, at higher concentrations, if an excessive amount of binder was added, the adsorbed molecules led to a dense polymer outer layer, reducing the probability of one polymeric chain bridging between more than one particle; this hindrance of bridging flocculation resulted in reduced yield stress and G'_{eq} [37].

PF127 is a popular and convenient additive to formulate DIW inks. Unlike the binder systems discussed above, PF127 solutions form thermoresponsive hydrogels that can act as a carrier medium for ceramic particles. Due to the straightforward formulation of such inks, only a few factors can influence the ink rheology. The first factor is the hydrogel concentration. Increasing the PF127 concentration leads to higher viscosity, flow point, and G'_{eq} due to the stronger intrinsic hydrogel network [68]. **Figure 4B and D** shows that hydrogel inks exhibit higher yield stress and G'_{eq} with increasing solid loading, and apart from the reduced interaction volume of ceramic particles [121], this trend **is** attributed to the smaller space for the movement of hydrogel molecules upon the addition of solid content. With more ceramic powders, it is more difficult for individual hydrogel micelles to flow past each other due to the close contact between ceramic particles; hence a larger force is required for the ink to flow [59]. Compared with other types of inks, the increment of the yield stress for hydrogel inks tends to be more gradual and the range of yield stress across various solid loadings is much narrower (**Figure 4B and D**). This can be explained by their nature. Here, the fluid-to-gel transition is achieved by changing the temperature and forming a hydrogel network. The hydrogel added plays the role of a carrier to push the ceramic particles forward, and a significant part of the yield stress/flow points of the ink comes from the strength of this hydrogel network [59].

The relationship between G'_{eq} and solid loading is particularly intriguing. Feilden's work showed that at low solid loadings (< 20 vol%), the rise in G'_{eq} was minimal, while upon the addition of more ceramic particles, a rapid increase in the modulus values was observed [59]. When the solid volume fraction is low, only a few particles are in close contact with each other, and the relatively small number of contact points is not enough to form a stiff network. Below 20 vol%, the increase in solid loading only contributes to the increasing number of particles in contact, but the formation of a network is still difficult; this explains the slow and steady increase in G'_{eq} values at low ceramic loadings. The situation changes following the addition of more ceramic powder. The number of particles that are touching each other is high enough for rigid networks to form. Beyond this point, adding more solid content further increases the number of contact points and the stiffness of the ceramic ink [59].

For hydrogel inks, the dispersants affect the ink stiffness but show insignificant effect on the yield stress/flow point of the ink [59]. One possibility is that with the addition of dispersant, the attraction between ceramic particles reduces, making it more challenging for them to come close enough to form a strong network; the stiffness G'_{eq} of the ink is, therefore, lower. On the other hand, no matter whether a rigid network is formed between ceramic particles, the hydrogel carriers can still flow and push the solid content even though the space of movement may reduce in the presence of a particle network. Because of this, the addition of dispersant has a minimal influence on the yield behaviour but can strongly affect G'_{eq} . Another speculation to explain this phenomenon is that in the absence of a dispersant, ceramic particles are not well-dispersed and form agglomerates with water trapped between them. This trapped water, or "dead water", does not contribute to the dispersion of particles, leading to the "actual" solid content being much higher. This might also explain the decreased G'_{eq} observed upon adding a dispersant. Additionally, the impact of adding a dispersant on the PF127 hydrogel itself remains unclear, which may further elucidate the observed trends. The material-dependent behaviour of the stiffness of hydrogel inks is a result of the different interparticle interactions for different powders and can be affected by many factors such as average particle size, particle size distribution, particle geometry, surface roughness and different IEP [192, 218, 219]. Once more, this variation in interaction forces will affect the formation of the particle network, which affects the G'_{eq} but not as much the flow and yield behaviour of the DIW ink [59].

Emulsion/foam inks

Several studies have shown that for emulsion and foam inks, values of viscosity, yield stress and G'_{eq} increase with higher solid loadings, with other factors kept constant [29, 74]. This is unsurprising as this trend is common for a particulate system [220]. However, this trend is not demonstrated in **Figure 4A and C**, partly due to the scarcity of data resulting from limited research on direct ink writing (DIW) of emulsions and foam inks [29, 108]. What is more interesting, as shown in Figures 5A and 5C, is that values for yield stress and G'_{eq} vary considerably at the same solid loading, depending on the dispersed

phase type, amount, and droplet size, as well as the ceramic particle size distribution and surfactants, which are discussed in the following paragraphs.

The desirable viscoelastic properties of emulsion and foam inks result from bridging among the particle-covered oil droplets, originating either from attractive interactions or interfacial tension and elasticity of the interface [80, 81]. Increased bridging strength, which scales with the amount and decrease in surface area/size of the dispersed phase droplets, translates to increased G'_{eq} and yield stress. For example, research on DIW of oil-in-water-stabilized emulsion inks demonstrated that yield stress and G'_{eq} increased with increasing oil amount and stirring speed due to an increased number of particle-covered oil droplets [108], making the 3D network stiffer [221]. Similarly, for foam inks, a higher mixing intensity led to smaller bubble size, higher bubble volume fraction and a higher G'_{eq} [42]. It is noteworthy that stirring speed and time have a significant effect on droplet size, as increased speed imparts energy to the system, breaking larger drops into smaller ones, and an optimum time allows for obtaining equilibrium droplet size, where a balance between interface generation, stabilization, and coalescence occurs [Donmez 2019] [29].

Another important factor governing droplet size is the surfactant. It has been demonstrated that surfactants increase the hydrophobicity of ceramic particles, thereby enhancing the adhesion of ceramic particles to the oil-water interface and improving droplet stability [76]. The increased droplet stability prevents relatively small droplets from disappearing, lowering the average droplet size in the emulsion and escalating the yield stress and G'_{eq} of the ink due to the increased contact area [108]. It has also been proposed that when an excess amount of surfactant is added, the dissolved surfactant in the ink may cause a higher viscosity [29].

Furthermore, the ceramic particle size is crucial in achieving stable emulsion/foam ink. A particle size significantly smaller than the droplet size facilitates covering the entire droplet surface, forming a smooth layer [222]. If the particle size is comparable to that of the droplet; the local flow fluctuation and direct droplet-particle interactions may cause the deformation and break-up of the droplets [223]. Similar to the packing of ceramic particles, in emulsion/foam inks, droplet size distribution affects the packing and ink rheology; a broader distribution of droplet sizes leads to a more effective packing, resulting in lower viscosity, yield stress, and G'_{eq} [224].

Organogel inks

Due to the straightforward formulation process of non-aqueous inks based on organic solvents, the factors influencing ink rheology are not as complicated as those discussed above for other types of inks. Like other inks, the rheological properties of organogel inks depend on the solid loading. Dudukovic et al. demonstrated that the tetraglyme-based inks exhibited higher G'_{eq} and yield stress (circled data points in **Figure 4A and C**) when the solid loading was gradually increased from 8.3 to 12.3 vol%. [83]. The strength of the dispersing matrix also has an impact on the overall properties of organogel inks. An et

al. showed that increasing the amount of polystyrene-polyisoprene-polystyrene (SIS) powder, which was mixed with n-methyl-2-pyrrolidone (NMP) solvent to make the dispersing medium, significantly improved the stiffness and yield stress of the NiZn-ferrite ink [180]. Finally, despite not being systematically studied, the rheology of organogel inks is likely to be dependent on ceramic powder properties, such as particle size and particle size distribution, as discussed previously [138, 167, 192, 215-217].

4.1.2. Shear thinning coefficient (n) and viscosity parameter (K) (Herschel-Bulkley model)

The shear thinning coefficient (n) and viscosity parameter (K) are also important rheological properties for DIW inks. All inks reported exhibit a shear thinning behaviour, with a shear thinning coefficient smaller than one (Figure 5A). There is a positive correlation between the viscosity parameter K and yield stress/flow point (Figure 6B). Yield stress is a distinctive property of viscoelastic materials, measuring the minimum stress necessary to permanently deform ink and determine its ability to retain shape. In contrast, viscosity measures the resistance to the viscous flow of ink and determines the stress required to extrude it. [210]. In the case of DIW inks, given that the yield stress and viscosity both originated from the strength of interparticle/polymeric networks, this trend is expected.

Interestingly, in Figure 6C, there appears to be an inverse relationship between the viscosity parameter and shear thinning coefficient. Viscosity, which measures resistance to flow, originates from the gel network and inter-particle friction. Shear thinning arises from the gel-to-fluid transition in inks under shear loading due to the gradual breaking up of the gel network. One possible explanation for the low shear thinning coefficient at high viscosities is a strong gel network, which exhibits a more pronounced decrease in viscosity upon network breakup. Conversely, there is a gradual decrease in viscosity under shear loading for a weaker gel network. While this explanation might account for the observed correlation, it is also possible that these observations stem from the limitations of simple rheological models, such as the Herschel-Bulkley model employed here. Particularly at high ink yield stresses, a more complex analysis could be beneficial to fully characterize and capture the behavior of the complex fluids used in DIW. [225].

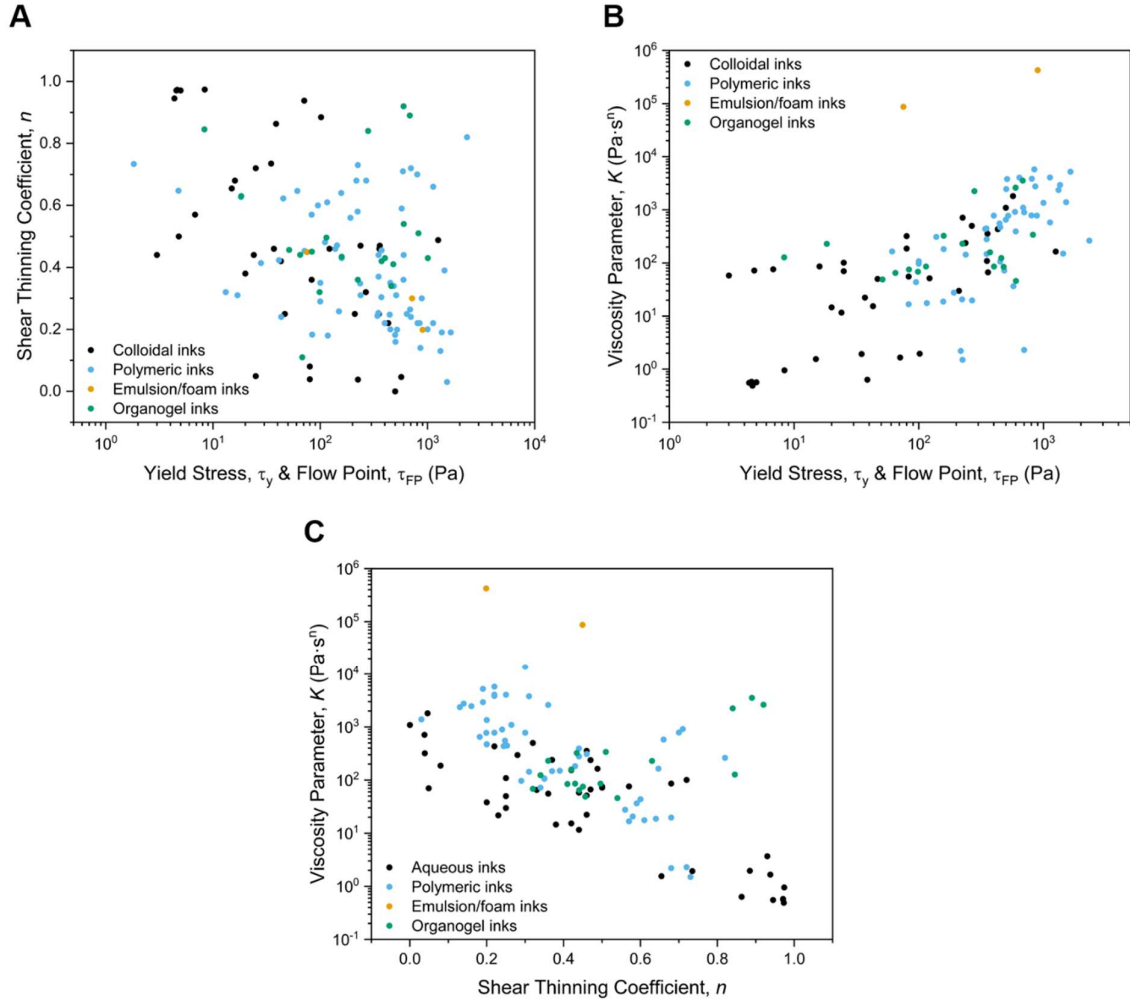


Figure 5. Relationship between (A) yield stress/flow point and n , (B) yield stress/flow point and K , and (C) n and K .

4.2. Printability

A DIW ink is deemed printable if it exhibits easy extrudability, shape fidelity and filament fusibility. These desirable traits come from a combination of rheological properties that can vary depending on the printed geometry and filament shape [3, 119]. Various methods have been introduced to predict printability, some of which are purely empirical, while others, like Smay's and M'Barki models, are based on the force balance on the printed filaments [3, 28, 108, 163]. The following paragraphs examine these models and discuss their advantages and disadvantages.

4.2.1. Rheology-based criteria

In this approach, different ranges of rheological properties/parameters, such as G'_{eq} , τ_y or τ_{FP} , τ_{YP} , flow transition index (FTI), and Φ , have been proposed as parameters to predict the printability of DIW inks, as shown in **Table 1**. FTI and Φ are defined as τ_{FP}/τ_{YP} and G'_{eq}/τ_{FP} , respectively [226]. FTI indicates the ink's ability to yield, break and rebuild during printing [227]. An FTI value approaching 1 indicates that the ink starts to flow immediately after deformation within a short range of strain [228,

229]; this suggests a soft material with a brittle network, making it suitable for DIW [227]. Conversely, an ink with a high FTI value (> 20) implies a large yield zone between the yield point and flow point [230]. In this case, the particle network is weak and not ideal for printing [227]. On the other hand, Φ should be higher than 20 for a printable ink, based on a minimal deformation of overhanging structures while maintaining the ink extrudability [226].

Table 1. Range of rheological properties/parameters proposed for printable inks [183].

Rheological properties/parameters	Proposed range for printable inks
Equilibrium storage modulus, G'_{eq}	10^4 to 10^6 Pa
Yield stress or flow point, $\tau_{y/FP}$	100 to 2000 Pa
Yield point, τ_{YP}	100 to 2500 Pa
FTI (τ_{FP}/τ_{YP})	0-20
Φ (G'_{eq}/τ_{FP})	>20

Figure 6 shows the reported values of G'_{eq} , τ_y or τ_{FP} , τ_{YP} , FTI, and Φ for various DIW ink formulations and the ranges of proposed printable parameters/properties (**Table 1**) are marked with dashed lines. Examples of a printable and a non-printable/slumping ink are shown in **Figure 6A** and their rheological properties are also included in **Figure 6B to F**. It is evident that these criteria can provide a relatively accurate prediction of printable inks. However, it struggles to predict unprintable inks that slump, which is indicated by a large number of hollow circles within the defined printable region (**Figure 6B, C, E and F**). One potential reason for the inaccuracy is the lack of consideration of the printed geometry. For instance, an ink strong enough to print small overhanging features may struggle to maintain the structural integrity as the overhanging length increases.

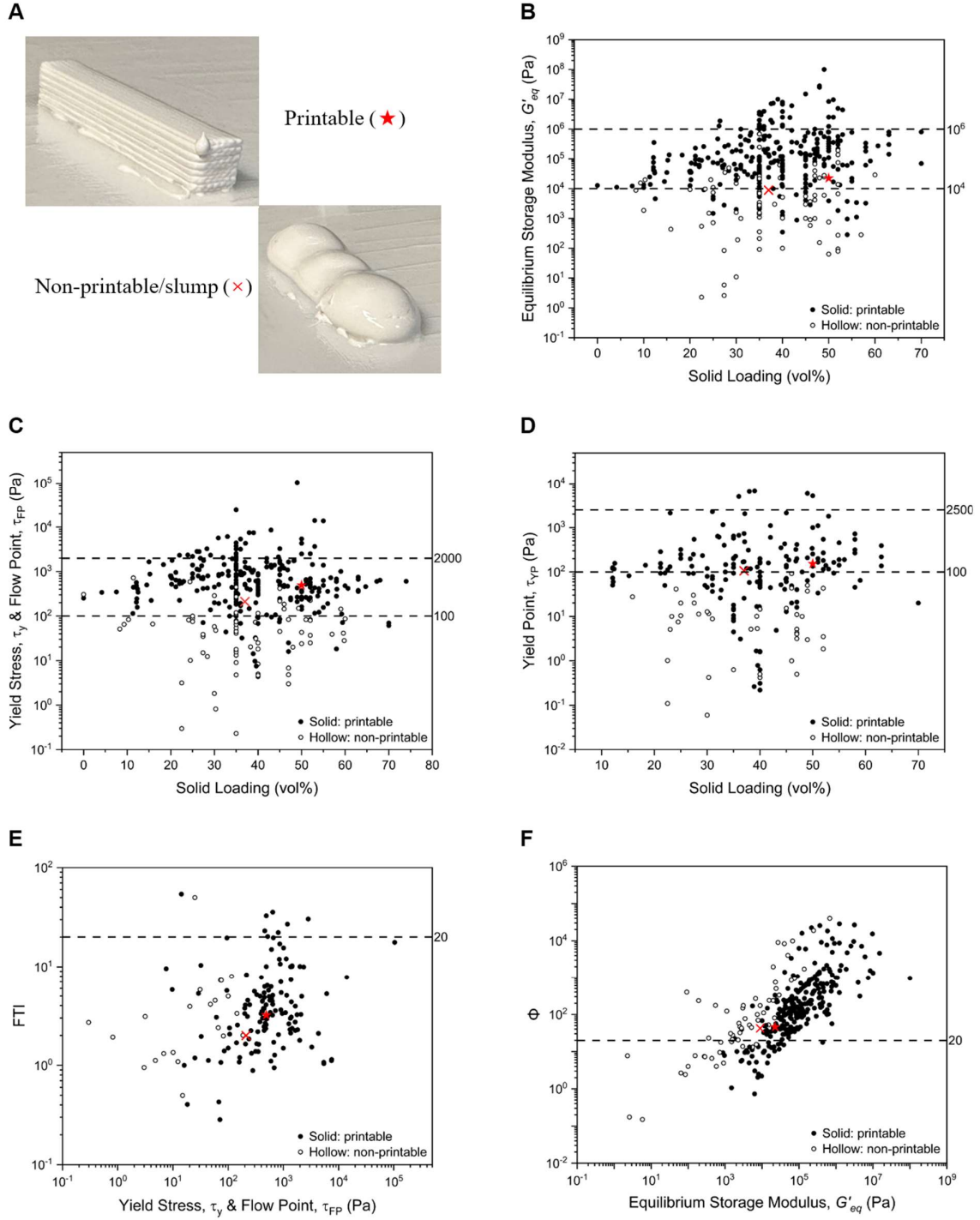


Figure 6. Comparison of published ink properties against proposed range of rheological properties/parameters for printable inks. Photos in (A) illustrate two example inks (37 vol% and 50 vol% alumina inks with 20 wt% PF127) that result in good shape fidelity (printable) and slumped structure (non-printable), and their rheological properties are included in (B) to (F) as ★ and × respectively.

4.2.2. Smay model for structures with spanning features

DIW has been used widely to print scaffolds with 3D periodic structures [3, 105, 107]. These structures contain spanning features between two points of contact, and due to the lack of support in the middle,

these spans are susceptible to shape change and slumping. Therefore, a criterion is needed to design an ink that minimises the midspan deflection. Smay et al. proposed the first model to predict the printability of DIW inks to print structures with spans [3, 231]. In this model, the stiffness of the ink, G'_{eq} , is considered to define the structural integrity of printed scaffolds. According to this model, the deformation of filament is assumed to be elastic and the printed ink should be stiff enough to support itself against the gravitational force to minimise the mid-span deflection (acceptable midspan deflection being smaller than 5% of the nozzle diameter) [3]. This model is expressed by the following equation:

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

Equation 6

where ρ is the density of the ink, g is the gravitational acceleration ($\sim 9.81 \text{ m/s}^2$), L is the span length, and D is the nozzle diameter. In this case, 1.4 is a shape factor for circular filaments. Different shape factors should be used if filaments with different cross-sectional shapes (2.94 for square filaments and 1.66 for hexagonal filaments) [119]. After rearranging **Equation 6**, a dimensionless number S can be obtained:

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

Equation 7

According to this model, a value of S greater than 1 indicates that the ink is printable with no significant midspan deflection. By fitting the experimental data collected into the model (**Figure 7**), it can be seen that although almost all printable points are above the $S = 1$ line, however, most of the non-printable points can also be seen in the “printable” region. These observations align with multiple reports. For instance, Chan et al. reported the limitation of the Smay model in predicting the printability of emulsion inks that slumped, regardless of the nozzle sizes or the fraction of oil content [108]. Goddam et al. also showed that the predicted G'_{eq} value given by the Smay model was at least 6 orders of magnitude lower than the actual modulus of the inks required for printing [127]. The model's limited applicability suggests that G'_{eq} may not be the sole factor controlling printability. Additionally, the model only considers the weight of the printed filament as the cause of slumping, while other forces also affect shape change, as discussed in the following model.

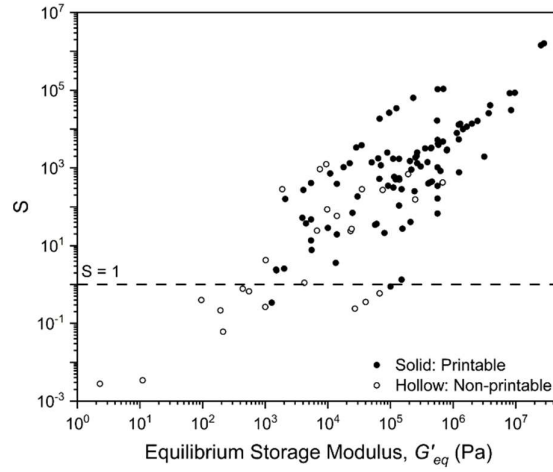


Figure 7. Comparison of published experimental data against the Smay printability model.

4.2.3. M'Barki model for monolithic structures

M'Barki et al. proposed a model for monolithic ceramics considering the shape fidelity as a printability criterion [28]. According to this model, an optimal yield stress is required to retain the shape of printed parts to counter the slumping/deformation caused by gravity and surface tension. By studying the shape retention of boehmite gels, whose rheological properties can be controlled by ageing time, M'Barki et al. showed that the capillary force trying to minimise surface energy played a significant part in the slumping of the printed structure. As shown in **Figure 8**, the shape fidelity is achievable if the yield stress (red arrows) of the ink is large enough to overcome the combined effect of the object's weight (black arrow) and surface tension (blue arrows).

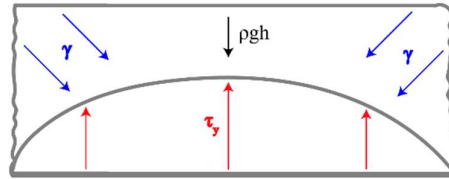


Figure 8. Schematic diagram showing the factors that contribute to the shape retention/slumping of the printed part. Figure recreated under the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>) from M'Barki et al. [28].

In this model, a dimensionless number Ξ was proposed to predict printability:

$$\Xi = \frac{\tau_{y/FP}}{\gamma D^{-1} + \rho gh}$$

Equation 8

where γ is the surface tension of the ink. Here, γ is approximated as the surface tension of water, which is around 72.8 mN/m. In this M'Barki model, if Ξ is greater than one, the ink is predicted to be printable. Results collected from published studies are compared with the M'Barki model in **Figure 9**. As evident,

this model can provide a fairly accurate prediction, with almost all hollow points (non-printable) below the standard line. However, there are several factors that can potentially affect its accuracy. First, in the original model, the authors used dynamic yield stress, τ_y^{dyn} , rather than static yield stress, τ_y^{stat} . τ_y^{dyn} defines the minimum stress needed to maintain the continuous flow (**Figure 1A**). It was suggested that during printing, the yield stress of the ink should be high enough to overcome the factors that force the ink to continue to flow, which leads to slumping [28]. Thus, it is reasonable to consider τ_y^{dyn} as the true yield stress of the ink when considering shape retention. However, most authors have reported τ_y^{stat} , which could hamper the comparison of the published data with the model. In general $\tau_y^{stat} \geq \tau_y^{dyn}$, Cai demonstrated that the value of τ_y^{stat} for the same emulsion ink could be twice as high as that of τ_y^{dyn} [29]. In addition, the exclusion of G'_{eq} may be responsible for the discrepancy between experimental data and the model as it governs the elastic deflection of printed filaments.

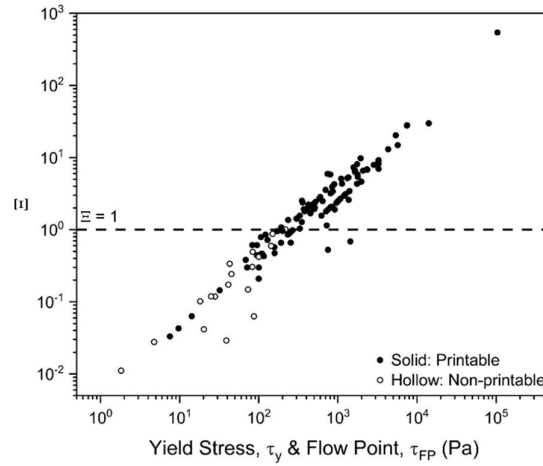


Figure 9. Comparison of published experimental data against the M'Barki printability model.

4.2.4. Chan model

Chan et al. proposed that the printability is related to the yield stress and G'_{eq} , and can be predicted by the following equation [108]:

$$G'_{eq} = \frac{P}{\tau_{y/FP}}$$

Equation 9

where P is a constant that represents the product of the equilibrium storage modulus, G'_{eq} , and the yield stress/flow point, $\tau_{y/FP}$. According to this model, G'_{eq} and $\tau_{y/FP}$ data for printable (solid points) and non-printable/slump (hollow points) inks were plotted in **Figure 10A**. After adding the restrictions based on the empirical criteria (**Table 1**) for G'_{eq} (10^4 to 10^6 Pa) and $\tau_{y/FP}$ (100 to 2000 Pa), it can be observed that most of the printable points lie within the central boxed region. However, some non-

printable points are still present within this region, which is consistent with findings in **Figure 6B** and **C** when one single rheological property is used to predict printability. In order to further narrow down the printable region to exclude all non-printable points, **Figure 10B**, which involves the product of $\tau_{y/FP}$ and $G'_{eq}(P)$, is created. From this figure, the lowest P value to ensure printable inks is 10^7 Pa^2 ; all non-printable hollow points are below this threshold. Therefore, if an ink can simultaneously meet all three conditions in **Table 2**, it is likely to be printable (the green shaded region in **Figure 10A**).

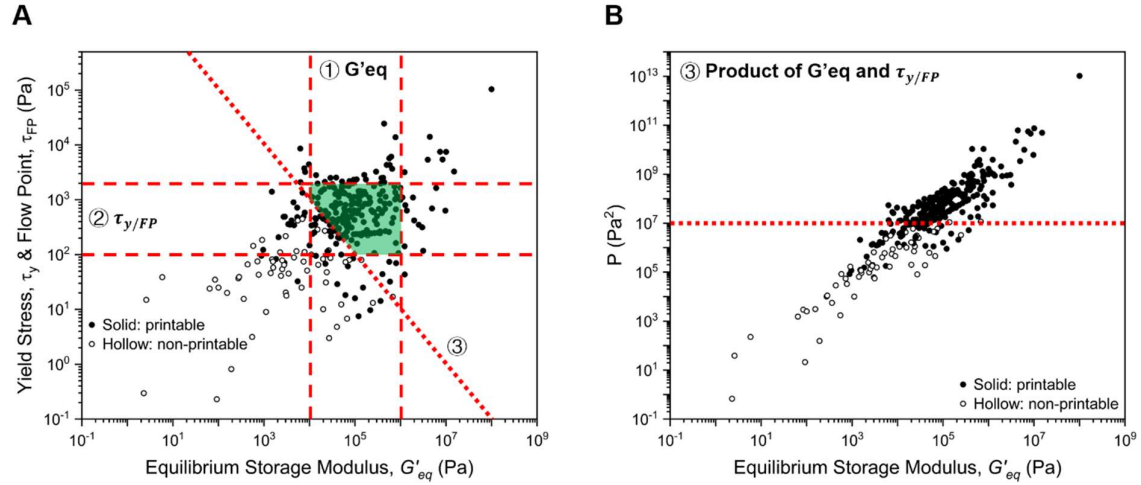


Figure 10. Plots of the Chan printability model: (A) $\tau_{y/FP}$ versus G'_{eq} , with solid and hollow shapes showing the printability of the ink and (B) the product (P) of G'_{eq} and $\tau_{y/FP}$. The green shaded area represents the predicted printable region.

Table 2. a new printability criterion based on two rheological properties ($\tau_{y/FP}$ and G'_{eq}) and their product (Chan model).

Rheological properties	Proposed range for printable inks
Equilibrium storage modulus, G'_{eq}	10^4 to 10^6 Pa
Yield stress or flow point, $\tau_{y/FP}$	100 to 2000 Pa
Product of G'_{eq} and $\tau_{y/FP}$, P	$>10^7 \text{ Pa}^2$

This approach is a blend of Smay's perspective [3], which assumes that the distortion in scaffold spans is elastic and that ink stiffness is crucial, and M'Barki's [28] viewpoint that ink for bulk parts should have a high yield stress to prevent flow induced slumping. Thus, the method should be suitable for both scaffolds with spanning features and dense monolithic parts. In addition, when printing dense structures, the need to fuse the printed filaments and eliminate trapped porosity may indicate that it is desirable for the yield stress of DIW inks to lie within the lower part of the shaded printable region (**Figure 10A**). Although the Chan model does not take the sample geometry into consideration, the data collected here

covers a wide range of nozzle diameters (100 to 2000 μm) and span length (200 to 2500 μm). Therefore, the criterion proposed here should be suitable for most feature sizes used in DIW printing of ceramics.

4.3. Mechanical properties of final ceramic parts

This section discusses the mechanical properties of DIW ceramics reported in the literature [25, 28, 33-38, 42, 43, 51-54, 56, 59, 65-67, 69, 71, 74, 82, 107, 109-111, 113, 115, 117, 121, 122, 124, 127-133, 135, 136, 141, 142, 146, 148-151, 154, 161, 162, 168, 170-172, 174, 182, 185-187, 191, 232-234]. Although there are limited reports on the mechanical properties, this section aims to identify factors influencing and strategies to improve the structural efficacy of DIW ceramics. Both dense and porous ceramics can be fabricated using DIW. In the case of porous ceramics, there are two reported types: scaffolds and monoliths (see **Figure 11**). The scaffolds can have porous and dense struts. In the case of porous struts, the total porosity comprises (1) the macroporosity (in millimetre range) from pre-designed spacings between filaments and (2) the microporosity of the strut. Porous monoliths solely comprise microporosity, which is henceforth referred to as bulk porosity. The microporosity is achieved by (1) the removal of organic content after printing, (2) using sacrificial template, (3) irregular particle packing, and (4) partial sintering [35, 53, 235].

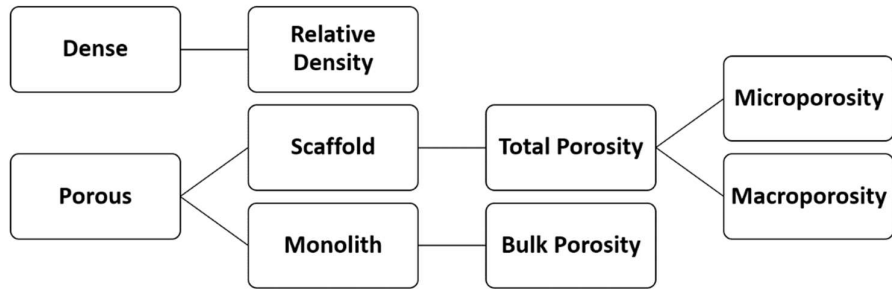


Figure 11. Different categories of ceramic objects made via DIW and their characteristic properties.

The colloidal and **polymeric** inks are used to produce dense ceramics. On the other hand, due to very low solid loadings (< 15 vol%), emulsion and foam inks cannot be used to create dense structures [74, 235]. All types of inks can potentially be used to produce porous ceramics. In particular, emulsion and foam inks are preferred for producing highly porous (> 90%) ceramics. The following sections discuss the mechanical properties of dense and porous ceramics separately.

4.3.1. Dense parts

The relationship between solid loading and relative density is shown in **Figure 12A**. It is evident that dense ceramics with relative density of >95% are easily achievable with **polymeric** and colloidal inks. A relative density of 96.4% has been reported for SiC, even at a low solid loading of 28.4 vol% [109]. However, a high solid loading is preferable to avoid long debinding cycles, excess shrinkage and enable production of large-sized ceramics [236]. On the contrary, Baltazar et al. reported a low relative density after sintering (~80%), and residual porosity between filaments on printed 3Y-TZP ceramics [128]. This

porosity was caused by the space created when aligning the filaments directly on top of each other. While reducing the nozzle diameter has been demonstrated to marginally decrease porosity, a more efficient approach for eliminating these defects involves depositing new filaments within the grooves formed by the underlying layer, as opposed to stacking them in alignment with the previously printed ones (see Figure 2B from Feilden et al. [64] as an example).

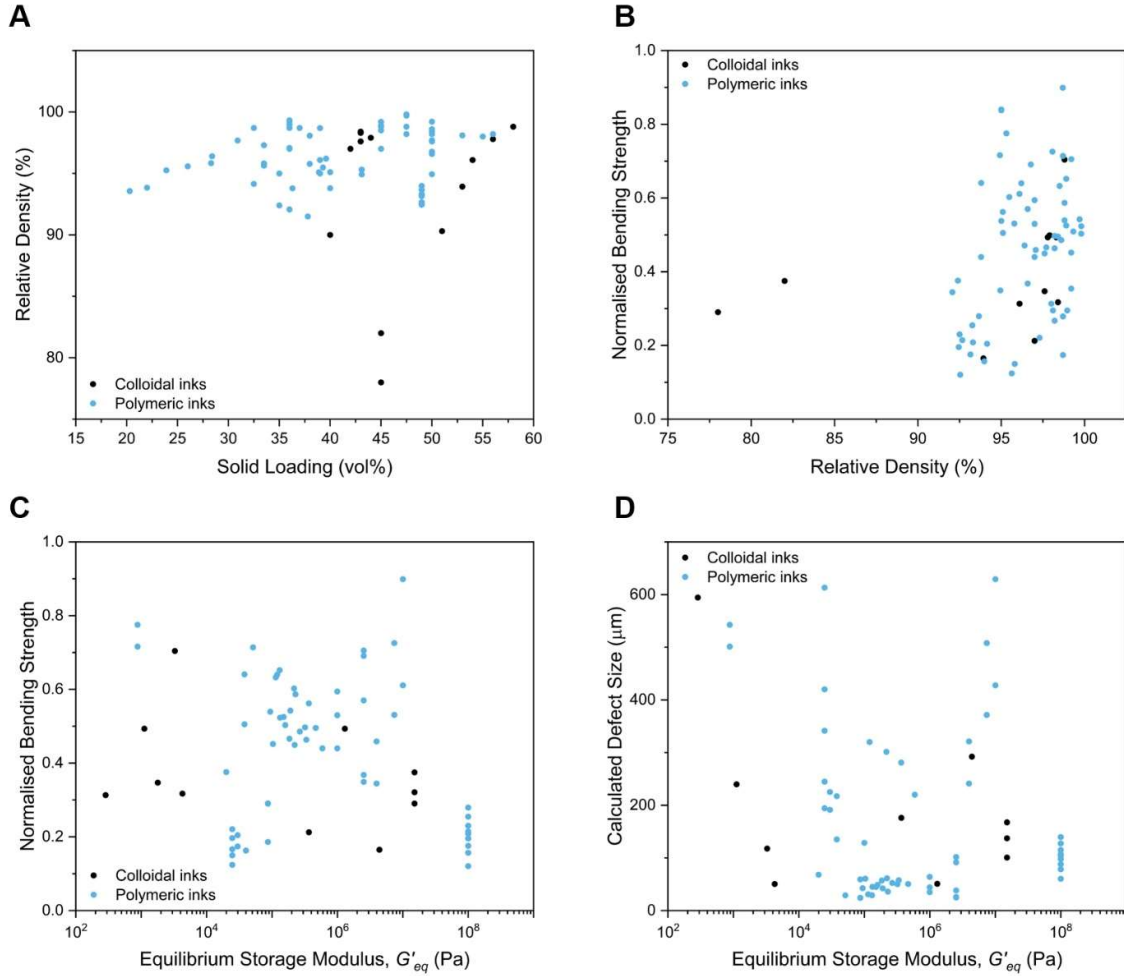


Figure 12. Plots for dense ceramic parts showing the relationship between (A) solid loading and relative density, (B) relative density and normalised bending strength, (C) G'_{eq} and normalised bending strength and (D) G'_{eq} and calculated defect size.

Figure 12B shows the plot of normalised bending strength versus relative density for DIW samples with **polymeric** and colloidal inks. The bending strength obtained with DIW are lower than the those reported for the conventionally processed ceramics. One major reason for such low strengths is the high surface roughness of the robocasted ceramics, which exhibits step-edges resulting from layer-by-layer deposition nature of the technique. The step size varies with the nozzle diameters, leading to different surface roughness and measured strength of the printed parts [59]. On the other hand, the bending strength of conventionally processes ceramics are usually measured using finely polished bending bars [237]. Studies have shown normalised strengths as low as 0.1 for DIW ceramics with a relative density

of > 95% [109, 132]. The possible reason for low strength is processing defects [132]. **Figure 12D** displays the critical defect sizes in printed ceramics, which are estimated using the following equation [238]:

$$K_C = Y\sigma\sqrt{\pi a_c}$$

Equation 10

where K_C is the fracture toughness, Y is a geometric factor (~ 1), σ is the strength of the material, and a_c is the critical defect size inside the sample. Consistent with the estimated critical defect sizes, defects up to several hundred microns have been reported in literature [132]. The defects are formed during ink preparation and printing. An improper ink preparation may lead to defects such as entrapped air bubbles and agglomerates. These defects can be removed by judicious design of inks with optimal combination of binders, dispersants, plasticisers, and flocculants followed by proper mixing and degassing [59]. The most deleterious defects ($\sim 500 \mu\text{m}$) are formed due to improper fusion of filaments during printing [132]. A high ink yield stress is preferred for shape fidelity, however, it also prevents proper fusion of filaments through capillary forces, causing interfacial cracking during sintering [28]. Improperly fused filaments also lead to anisotropy in mechanical properties. For instance, SiC and Al_2O_3 ceramics printed using hydrogel inks exhibited higher bending strength when the force line was applied perpendicular to the filament length. This issue can be solved by optimising the ink properties and isostatic pressing of samples post printing [132]. Cracks can also form in the green body during printing and subsequent drying because of rapid drying. Rapid drying causes improper fusion of the filaments and interfacial cracking, particularly when printing with fine nozzles due to the high surface area to volume ratio of the printed filaments. Furthermore, a rapid drying of green samples causes surfaces to dry and shrink at a faster rate compared to the bulk, leading to residual stresses and cracks. This issue can be resolved through a slow drying rate. For instance, for **polymeric** inks, crack-free green samples were obtained by printing and drying in humid conditions at room temperature [25].

Based on **Figure 12C**, a conclusion on the relationship between ink rheology and final mechanical properties cannot be drawn. This is because factors that increase the ink stiffness (G'_{eq}) may affect the sample strength positively or negatively. For instance, high solid loading leads to higher ink stiffness and a high green density, which ensures low sintering shrinkage and prevents matrix cracking, leading to higher strength [236]. On the other hand, as discussed in **Section 4.1**, yield strength and stiffness can be increased by adding additives, such as rheology modifiers and binders, however subsequent debinding could lead to high residual porosity leading to reduced relative density and strength [35].

4.3.2. Porous parts

Figure 13 shows the variation of normalised compressive strength with total porosity of porous scaffolds printed with colloidal, **polymeric**, and emulsion inks. The trendline were drawn based on

open-cell and closed-cell models proposed by Gibson and Ashby [239]. As evident from **Figure 13**, the variation of normalised compressive strength with total porosity is well-predicted by the open-cell model; this is expected as the grid structure inside a printed scaffold highly resembles that of the open-cell model. The deviation of data from the trendline may be due the fact that the models do not consider microstructural factors, pore size distribution, pore morphology, solid particle packing, and flaws [240]. The plot also reveals that the maximum achievable porosity with **polymeric** and colloidal inks is limited to 85%, whereas emulsion inks can achieve high porosities of $> 95\%$. For scaffolds created using emulsion inks, high total porosity is achieved by having both designed macropores between filaments and micropores within struts. From **Figure 13**, emulsion-ink scaffolds can achieve similar normalised compressive strengths at higher porosity. When comparing scaffolds with the same total porosity, the existence of micropores within struts in emulsion-ink scaffolds indicates a reduced interfilament porosity. Therefore, scaffolds made from colloidal and **polymeric** inks tend to have a higher proportion of macropores in the millimeter range. Considering a constant porosity, ceramic materials exhibit reduced strength as pore size increases [241], which explains the difference observed in **Figure 13**.

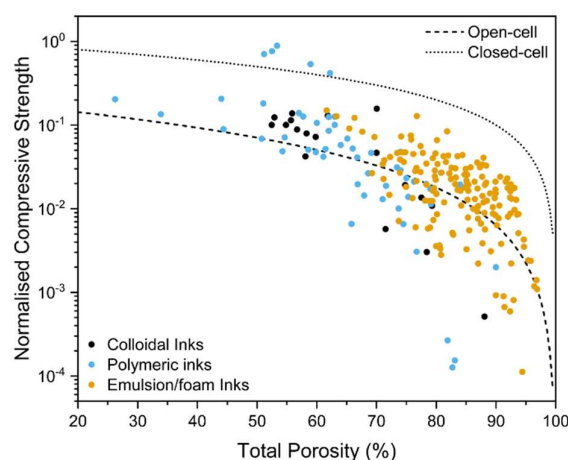


Figure 13. Plot for porous scaffolds showing the relationship between total porosity and normalised compressive strength. the upper and lower dashed lines correspond to the Gibson and Ashby closed-cell and open-cell models, respectively.

There are limited studies on the mechanical properties porous monoliths fabricated by DIW [29, 53, 82, 136]. As shown in **Figure 14**, bulk porosity of up to 90% has been achieved in porous monoliths using **polymeric** and emulsion inks. In case of **polymeric** inks, relatively high solid loading is required to ensure sufficient yield strength for shape fidelity, however, high solid loading limits the total porosity achievable. For instance, alumina ceramics printed with 2 wt% methylcellulose could not be printed at a solid loading of 46% due to insufficient ink strength. As highlighted in **Figure 14A**, the authors found 50% solid to be optimum for printability and was used to print porous alumina monoliths. The porosity was varied by changing the sintering time, a prolonged sintering time led to increased sintering shrinkage and lower bulk porosity [53]. On the contrary, emulsion inks with low solid content (15 vol%) were used to print porous monoliths with very high bulk porosities of 90% [242]. A lower solid loading

leads to a lower density of the emulsion and a higher bulk porosity in the final sample, resulting in reduced bending strength [29]. Additionally, the size of dispersed phase droplets, which eventually contribute to porosity, can be tuned by varying the stirrer speed during emulsification. For example, García-Tuñón et al. demonstrated that by increasing the stirring speed from 2000 rpm to 10,000 rpm, they were able to reduce the pore size from $33 \pm 13 \mu\text{m}$ to $4 \pm 1.5 \mu\text{m}$ [242].

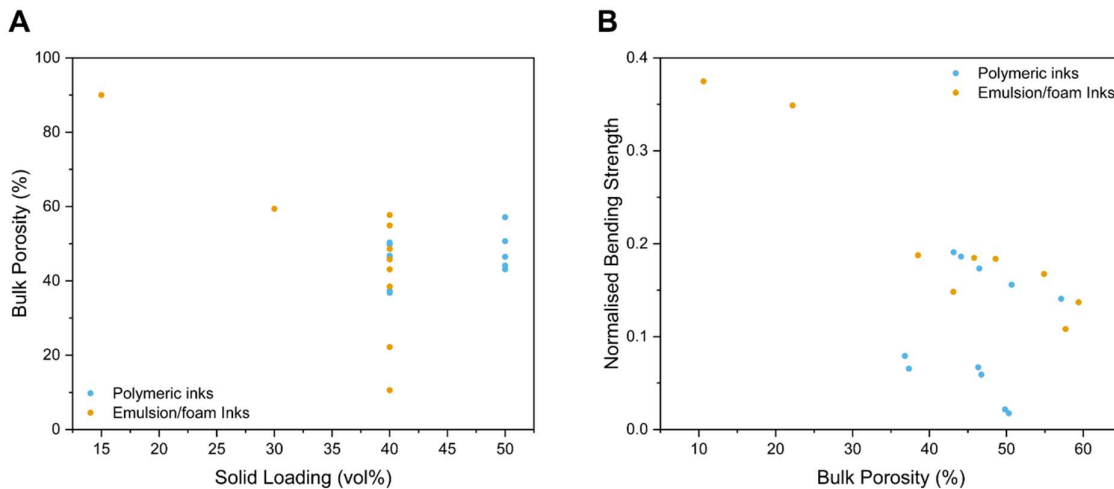


Figure 14. Plots for bulk porous parts showing the relationship between (A) solid loading and bulk porosity and (B) bulk porosity and normalised bending strength.

5. Conclusions and final considerations

In this paper we have compared the reported properties of a wide range of DIW inks used in the DIW of ceramic bodies. Our goal was to contrast a large amount of data in order to extract some general trends and assess the different approaches used to formulate inks with the adequate rheology. The use of many different data sources also enables a more systematic assessment of the different criteria proposed to assess the “printability” of an ink. It is clear from the outset that our use of solid content as the normalising criterion to plot the data can only provide a very partial picture. The inks are formulated with a very wide range of powders with different chemistries and particle size distributions that will play a key role on the rheology. As a result, key parameters can vary orders of magnitude for inks with the same solid content. However, many of the published papers lack detailed information on the powders used and the chemistry of the ink precluding the exploration of other dependences. This review shows that we may need more in-depth characterisation and more comprehensive reports on formulation to support a better understanding and the development of inks to print high-quality materials with improved spatial resolution.

Our comparison reveals some trends and points out areas for development. Most analyses of printing inks are based on the analysis of flow curves using the Herschel-Bulkley model and the use of oscillatory tests. The resulting values for key properties, such as the yield stress or the storage modulus, can vary by orders of magnitude in inks that are all reported as printable. The approaches used to

formulate the inks can be broadly classified into four different strategies: colloidal, **polymeric**, **organogel**, and emulsion/foam-based inks. Although there is a very large overlap in the properties of inks obtained using these different approaches, some general conclusions can be drawn. The colloidal approach tends to enable inks with larger solid contents that may be beneficial to achieve high green densities and reduce drying and sintering shrinkages. However, **polymeric** inks may enable more flexibility in formulation with a wide range of powder chemistries and powder size distributions. Emulsion and foam inks, with their low solid content in the suspension phase (<15 vol%), offer distinct advantages in producing highly porous ceramics with customisable pore sizes.

There are several “printability” models in the literature. Often the models are compared against one set of inks formulated with the same approach and chemicals and used to print a standard form (e.g., a dense bar or a log pile scaffold) under fixed printing conditions (nozzle design and printing speed). Consequently, these criteria provide only a partial view of the properties required for general printing. For example, the optimum rheology may vary depending on the type of structure being printed, ranging from dense bars to overhangs or log piles. Additionally, the “printability” criteria, which are based on parameters from oscillatory rheology and the Herschel-Bulkley models, may not fully capture the complex rheological behaviours of the inks and their relation to printing.

The data do not show a direct link between ink rheology and the mechanical properties of printed ceramics. The mechanical response is determined by processing defects such as residual pores, cracks, and surface roughness that often depend on the ink preparation and the printing conditions (e.g., printing speeds, filament overlapping, or nozzle design). Residual pores, primarily caused by entrapped air bubbles during ink preparation and inadequate filament fusion during printing, can be minimised through proper degassing of the inks and optimisation of rheology to eliminate interfilament pores using surface tension. To improve surface finish, using fine nozzles is recommended. Generally, designing nozzles to facilitate flow and eliminate dead zones is an important area of development. The post-printing process is also critical; isostatic pressing after printing can be a valuable technique for reducing residual pores and enhancing the mechanical properties. Appropriate drying and sintering schedules should be developed to control shrinkage and avoid crack formation. Finally, researching whether AI and machine learning approaches can guide the formulation of complex inks and the design of printing systems—with feedback loops capable of modifying printing conditions on the fly to respond to the printed features and ink variability—may be interesting. They could also be used to formulate inks specifically designed to print multimaterial structures using systems with multiple nozzles. This will require an in-depth characterisation of the inks to collect all the data that can be linked to printing performance. The final goal is to enhance the precision and reliability of the technique and to promote its further implementation as an industrial process.

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