Easily applicable protocol to formulate inks for extrusion-based 3D printing

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Abstract

3D printing is a disruptive technology that is a key driver of the new industrial revolution. Among the various 3D printing methods, direct-ink-writing (DIW) takes a viscous ink material, extrudes it through a nozzle, and deposits it layer-by-layer to create 3D objects. DIW is a versatile method that can print ceramics, polymers, metals, living cells, etc. Yet, the ink formulation is critical for the success of printing. One major challenge to operate the transition to Industry 4.0 is to educate laypersons on 3D printing, without the need to master physics and chemistry. In this paper, we propose a protocol to familiarize laypersons with ink formulation for DIW. Using this protocol, a clay-based ink was optimized and the best ink composition containing 48 wt% clay and 2.4 wt% bamboo fibers was used for printing. The experimental set-ups and details used in the work are easily available, cheap, sustainable, and safe, enabling its implementation in various settings from classrooms to workshops, without the need for specialized equipment.

Keywords: education, 3D printing, clay, extrusion.

INTRODUCTION

3D printing or additive manufacturing (AM) is a field that is anticipated to have a tremendous impact on the future of manufacturing [1]. Indeed, it allows the fabrication of complex parts in an automated fashion using layer-by-layer deposition of material. It is therefore a technology that demands knowledge on multiple levels: automated actuation, coding and computing, and materials and chemistry. To better prepare the next generation, it is therefore important to provide students with practical and scientific knowledge on 3D printing. Furthermore, teaching the fundamentals of 3D printing is particularly important as it is also predicted to yield significant societal impact, to the disadvantage of developing countries that are likely to face increased unemployment and insecurities if they are not able to follow the transition to this new technology [2-4].

Among the various 3D printing methods, direct-ink-writing (DIW), also called robocasting or extrusion-based 3D printing, is a method where an ink is extruded through a nozzle and deposited layer-by-layer onto a substrate (Fig. 1a). DIW can be applied to all materials types, from biological materials [5], ceramics [6], polymers [7], metals [8], composites of those [9], and for small and large-scale objects. For example, using DIW, it is possible to print a house of several meters [10] and a medical stent of a few millimeters [11]. Given the large range of materials and dimensions, it is a promising 3D printing method that can also contribute to a more sustainable future [9]. However, one main difficulty in DIW is the development of inks that are printable. Indeed, for each new composition there is a need to optimize the ink so that it is extrudable, i.e., can flow through the nozzle, and buildable, i.e., can withstand the weight of other layers without deforming. This is achieved through the control of the rheological, flowing properties of the ink. Specifically, the ink needs to be shear-thinning and to exhibit shape-retention or thixotropy (Fig. 1b) [7].

Fundamentals of rheology are generally taught in science, technology, engineering, and mathematics (STEM) subjects at university, undergraduate level, when addressing polymer melts or colloidal suspensions, and requires notions of physics and chemistry along with specialized equipment such as a rheometer [12]. However, here we argue that to prepare the younger generation for 3D printing, simple yet appropriate methods have to be found to elaborate ink compositions without the need for extensive physics and chemical knowledge, and without the use of expensive equipment. A few papers propose to teach rheology using commonly-used foods [13], or green hydrogels [14], but still use specialized equipment or chemicals, and are not explored in the context of 3D printing. For the development of DIW inks, safe, systematic, and sustainable procedures should be developed.

Here, we use clay as a medium for ink preparation and optimization by co-mixing with different ingredients, namely water, chitosan, and bamboo fibers. All ingredients are safe and can be manipulated outside of a chemistry lab, in a more informal setting. We replaced the need for a rheometer with other simpler characterization methods that do not require specialized equipment. Using these

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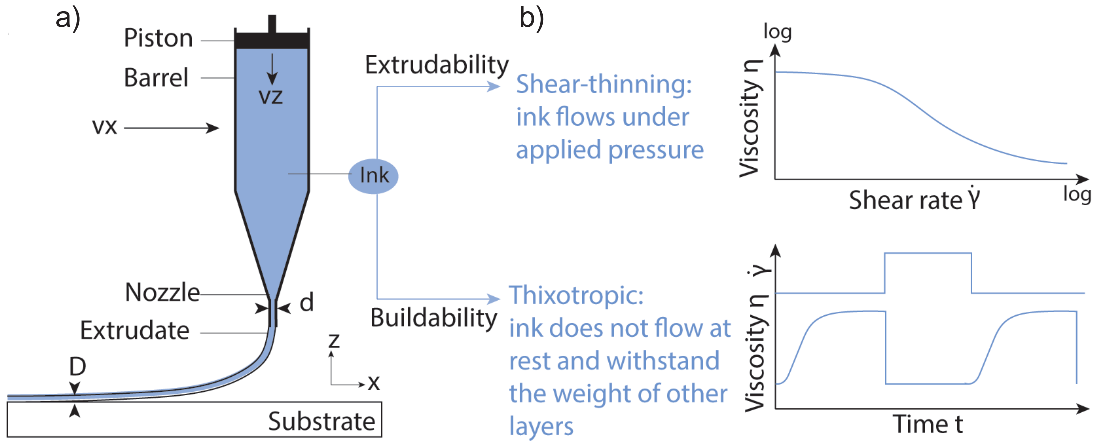

Figure 1: Schematic of direct-ink-writing (a): is the printing speed resulting from the lateral motion of the nozzle, is the flow speed resulting from the pressure applied by the piston to the barrel, is the nozzle diameter, and is the diameter of the extruded filament. Schematics representing the rheological requirements for the ink (b).

methods, an ink is developed and finally tested on a proper 3D printer. First, the system used is described as well as the theory behind the proposed protocol. Then, experiments are conducted to verify that the proposed protocol can yield an extrudable and buildable ink. Finally, the ink is tested using a 3D printer. The goal of the paper is to propose a simple method for ink optimization that is accessible to students of younger age, as well as to laypersons without access to specialized equipment. Optimization of the 3D printing process is however not within the scope of this paper.

INK SYSTEM AND CHARACTERIZATION METHODS

Ink system: for our demonstrations, we chose clay as a model medium because clay is: i) cheap and abundant, ii) safe and sustainable, and iii) has potential for concrete applications in several fields. Table I reviews the current progress in 3D printing of clay-based structures using DIW. Despite being one of the oldest materials used by mankind, 3D printing of clay is a nescient science with most papers published after 2014. Clay as a technological material has indeed renewed interest in green, sustainable structures in both the rich world and the developing countries. The use of clay as a raw ingredient for an ink composition is not always straightforward due to the large variety of clays and their difference in mineral and water content. The inks listed in Table I have all different water contents and additives. In the ink system studied in this paper, we explored the use of a hydrogel (chitosan) and bamboo fibers. Chitosan is an organic polysaccharide derived from crab shell, and is a waste from the food industry, whereas bamboo fibers is a natural material obtained from agricultural waste. These additives are therefore also easily available, cheap, and abundant, and do not present safety hazards in the scope of our experiments. Furthermore, organic hydrogels have been seldomly added to clay to form an ink for 3D printing. Combining organics and minerals in a composite matter has many potential interests for application, for example for the mechanical properties. Indeed, dried clay tends to be friable and brittle. Adding an organic network that can act as a glue between the minerals could potentially increase the strength and stiffness of the parts.

Determining extrudability: extrudability is the property by which a liquid or a semi-solid paste is flowing through a nozzle upon applied pressure. Extrudability requires thus the ability to flow. For viscous pastes, shear-thinning properties are required. One approach to characterizing the extrudability of inks with various compositions is to measure the swelling ratio D/d, where d is the diameter of the nozzle and D the diameter of the extrudate. Indeed, an ink without shear-thinning properties exhibits a die swell at the exit of the nozzle, also known as the Barus effect. The swelling results from radial stresses that develop in the nozzle due to a change from a parabolic flow profile to a straight flow profile (Fig. 2). Theoretically, die swell has been extensively studied in polymer melts under extrusion [26-28]. The swelling ratio at the exit of a circular nozzle is given by:

$$\frac{D}{d} \cong \sqrt{\frac{2}{3}\dot{\gamma}\left[\left(1+\frac{1}{\dot{\gamma}^2}\right)^{3/2}-\frac{1}{\dot{\gamma}^3}\right]} \tag{A}$$

with $\dot{\gamma}$ the shear rate. Given the definition of the viscosity (η) as the ratio of the stress (τ) over the shear rate:

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{B}$$

it is possible to approximate the die swell with:

$$\frac{D}{d} \cong \sqrt{\frac{2}{3}\frac{\tau}{\eta}\left[\left(1+\frac{\eta^2}{\tau^2}\right)^{3/2}-\frac{\eta^3}{\tau^3}\right]} \tag{C}$$

Based on Eq. C, we can deduce the following trends: i) for low viscosity liquids: $\eta\rightarrow 0$, so $D/d\rightarrow 2\tau/(3\eta)\rightarrow\infty$; and ii) for high viscosity liquids: $\eta\rightarrow\infty$, so $D/d\rightarrow[2\tau/(3\eta).(\eta^2/\tau^2)^{3/2}-(\eta^3/\tau^3)]^{1/2}\rightarrow 0$. These trends indicate that low viscosity liquids experience a large

Table I - Literature review data of clay-based inks used for direct-ink-writing and their applications.

Composition	Clay content* (wt%)	Additive	Print resolution (mm)	Application	Ref.
Columbia kaolinite clay	60-64	-	1-3	Construction	[15]
Fine white throwing clay	53	-	0.26-3	Artefacts	[16]
Clay	35-40	-	10	Casting molds	[17]
Lean clay soil	64	38.8% calcarenite sand, 0.48% straw fibers	1-12	-	[18]
Clay	68	20% salt	1-12	-	[18]
Clay	63	48.38% sand, 0.53% SHMP	-	-	[18]
Stoneware clay	77	-	6	Mechanical properties	[19]
Porcelain powder	73-77	-	-	Artefacts	[20]
Calcined clay	71	16.67% limestone, 5% fumed silica	-	Eco-efficiency	[21]
Laguna clay powder	67	-	0.5	Artefacts	[22]
Clay	50-56	0.2-0.8% sodium silicate	1.5-2.5	-	[23]
Clay	50-56	0.2-0.8% sodium polyacrylate	1.5-2.5	-	[23]
Clay	89	-	6-7	Bio-reef structures	[24]
Kaolinite clay powder	41	3% fly ash	5	-	[25]

**: with respect to water; SHMP: sodium hexametaphosphate.*

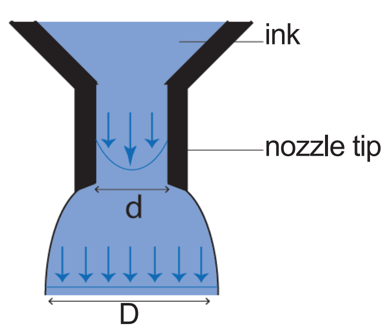

Figure 2: Schematic of the die swell at the nozzle tip.

die swell and that the diameters of the extrudates are larger than the nozzle diameter. For high viscosities, however, the die swell is reduced, with ultimately a swelling ratio of 0 indicating that the material is simply too viscous to get past through the nozzle. In the remainder of the paper, we refer to filaments for the extrudates. In an ideal scenario for 3D printing, the swelling ratio should be D/d=1. Based on this simple model, we thus propose to characterize the extrudability of ink mixtures by measuring the swelling ratio after extrusion. Being a consequence of the viscoelastic properties of the ink, clay and clay-chitosan mixtures, with and without bamboo fibers, are expected to experience some die swell as they are viscoelastic [29]. Although the swelling ratio might be influenced by the extrusion pressure, a handheld extrusion-mimicking method is sufficient to determine the extrudability for a sufficient number of tests and measurements. The results gathered showed good reproducibility of the method, despite the lack of control of the pressure (see results section).

Determining buildability: buildability is the property of materials to be deposited layer-by-layer on top of each other without collapse or deformation of the printed structure (Fig. 3). Buildability is also commonly referred to as shape-retention and is related to thixotropy and creep. Materials for 3D printing with good buildability are viscoelastic and possess a yield strength above which they flow. Also, they recover their stiffness and strength once the shear stress or shear rate is removed (Fig. 1b). Without rheology to observe the presence of yield strength or the viscosity as a function of time under constant stress, we propose to determine the buildability of inks by performing a quasi-static indentation-like test. The test consists in placing a solid stiff ball made of steel or ceramic on top of the ink and measuring the penetration depth of the ball. The penetration depth increases as the ink lacks buildability as is not able to withstand the weight of the small ball. The ideal penetration depth for 3D printing is therefore 0. This method is simple to put in place and is similar to the indentation and Pfefferkorn method used to measure the plasticity of clays [30].

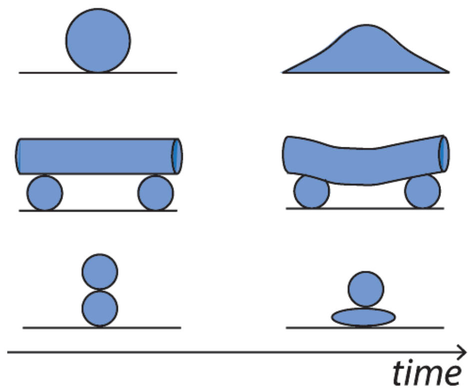

Figure 3: Schematics showing the cross-section of extruded filaments with poor buildability: with time, the shapes are deforming. From top to bottom: cross-section of a single filament collapsing under its own weight, a cross-section of a log-pile assembly sagging, and cross-section of a 2-layer stack with the bottom layer collapsing under the weight of the top layer.

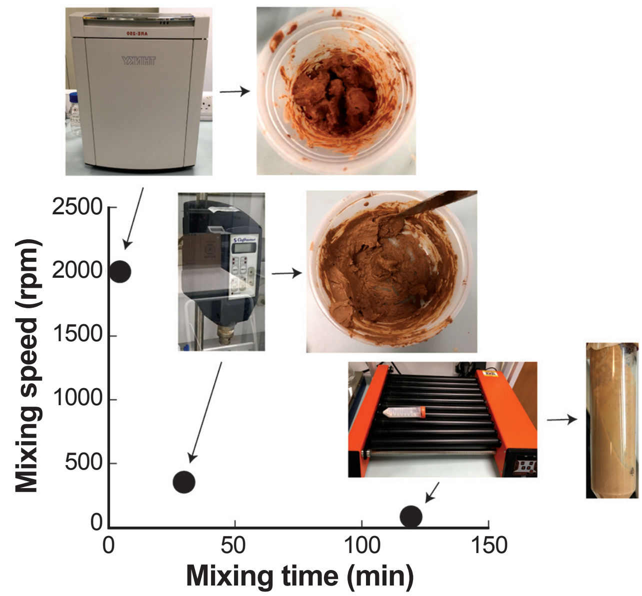

Figure 4: Mixing speed as a function of mixing time for three different types of equipment.

EXPERIMENTAL PROCEDURE

Materials: commercial pottery clay (natural clay, terracotta, Nara, Thailand), low molecular weight chitosan (Sigma-Aldrich), and short size bamboo microfibers of average length 200 µm and average diameter 30 µm (Indonesia) were used. Food grade vinegar with 5% acidity was used as acetic acid (Artificial Vinegar, Tai Hua, Singapore).

Ink preparation: first, chitosan solutions at 1 and 2 wt% were prepared using acetic acid and let to dissolve until homogeneous. Then, centimeter-sized balls of clay were manually taken from the block of clay. The bamboo microfibers were added with varying fiber to clay ratios, which are specified later in the text. The ingredients were placed in a plastic cup and mixed together using a mixer (ARE-250, Thinky, Japan) at a speed of 2000 rpm for 2.7 min to produce a homogeneous mixture. Degassing was performed using the same equipment at a speed of 2200 rpm for 3.5 min. Other tools can be used for this purpose, with the mixing speed and time, varying with the capabilities. Using a roller mixer, it took more than 10 times longer and it was only efficient for low viscosity mixtures, whereas using an overhead stirrer, similar to a blender, viscous pastes could be processed in an adequate amount of time (Fig. 4). This indicated that the mixing step can be optimized with common appliances. The ink compositions were varied while maintaining a constant volume of chitosan solution of 20 mL. The contents of clay (ϕ) and bamboo (ϕ_b) were calculated using the following equations, where chitosan refers to the aqueous chitosan hydrogel and therefore comprises the water content:

$$\phi = 100\,\frac{m_{clay}}{m_{clay} + m_{bamboo} + m_{chitosan}} \tag{D}$$

$$\phi_b = 100\,\frac{m_{bamboo}}{m_{clay} + m_{bamboo} + m_{chitosan}} \tag{E}$$

Extrudability and buildability experiments: extrudability experiments were carried out using handheld extrusion with syringes of nozzle diameters 2 to 10 mm and held vertically onto a plastic boat. The diameters of the extruded filaments were measured using a Vernier caliper. In this set of experiments, the total volume of chitosan was maintained at 20 mL, whereas the clay content was varied from 10 to 35 g with a constant 0.5 g of bamboo (experiment 1). Then, we also tuned the clay and bamboo contents so as to obtain the same total concentration of clay ϕ=43 wt% (experiment 2, see Table II for the detail). For varying bamboo content, the clay content was kept constant at 20 g and the bamboo content varied from 0 to 6 g (experiment 3). For the buildability test, an aluminum oxide ball of diameter 10.8 mm and of mass 2.73 g was placed onto the ink and its penetration depth was measured with a caliper. Each test was repeated more than 3 times and the values obtained averaged.

3D printing: it was carried out using 3D Potterbot Micro8 (3D Potter, USA) with an additional fixture placed inside to accommodate a smaller syringe loaded with the suspension (Fig. 5). Cut tapered nozzle tips from Nordson were placed at the exit of the syringes (in red in Fig. 5a). The substrate was a piece of filter paper taped onto the print bed and the printing was done at a flow rate of 1000% and a spacing of 1 mm. The flow rate value of 1000% was a setting on the equipment which corresponded to the piston of the extruder to move at a speed of 0.025 mm/s. The 3D

Table II - Composition detail for the experiment 2.

Chitosan (mL)	Clay (g)	Bamboo (g)	ϕ (wt%)	ϕ_b (wt%)
20	15	0	43	0
20	20	6	43	13

models were designed using computer-aided design software (Rhinoceros, Grasshopper, or AutoDesk Fusion 360) and Simplify3D or ideaMaker were used to translate the model to a g-code toolpath for the printing.

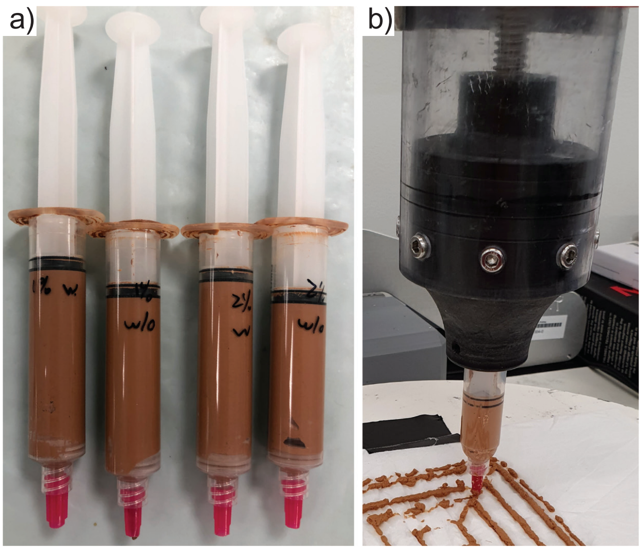

Figure 5: Picture of syringes loaded with the clay mixtures - the nozzles of the tips (in red) were cut to 4 mm diameter (a), and picture of the 3D printer with the nozzle fixed (b).

RESULTS AND DISCUSSION

Die swell measurement for ink's extrudability: to optimize ink composition, the extrudability was first explored by tuning the composition and measuring the die swell after extrusion through nozzles of 2 mm diameter (Fig. 6). In the ink system studied here, there were three components to be varied: chitosan solution, clay, and bamboo microfibers. Furthermore, the chitosan solution could be prepared at different concentrations. First, we varied the amount of clay maintaining a constant chitosan solution content of 20 mL and a constant bamboo fiber content of 0.5 g. We observed that for both 1 and 2 wt% concentrations of the chitosan solution, a higher amount of clay decreased the swelling ratio due to an increase in the viscosity (Fig. 6a). 40 wt% clay seemed to have more die swell than the 30 wt% but it could be caused by the high variation linked to the uncontrolled pressure applied to the piston of the syringe during extrusion [31]. It was also observed that at the lower clay concentrations (ϕ), the extruded filaments were not homogeneous in their cross-section (Fig. 6a, insert). It could be that the high fluidity of the ink led to sedimentation and agglomeration of the bamboo microfibers at the nozzle, requiring a higher force for extrusion and leading to larger extrudates. Once the bamboo fibers have been cleared from the nozzle, the ink could flow again with low pressure required and thin diameter, until the nozzle clogged again. At high concentrations, however, the filaments showed homogeneous dimensions. To achieve the ideal die swell of 1, clay concentrations at 60 and 65 wt% could be used for this amount of bamboo fibers. Varying the amount of bamboo fibers also tuned the extrudability due to an increase in viscosity. Adding more bamboo fibers while maintaining the total concentration of clay low at 43 wt%, the die swell could be significantly reduced down to an ideal ratio of 1 (Fig. 6b). To verify this effect, we used an ink containing originally 50 wt% of clay and 1 wt% of bamboo, corresponding to the 50 wt% clay in Fig. 6a, and added more bamboo to it. We could also observe that with higher bamboo content, the swelling ratio decreased to 1 (Fig. 6c).

Given that the origin of the die swell is due to the different flow profile between the fluid in the nozzle and at the exit, the nozzle diameter plays also a key role in the die swell [32]. The nozzle diameter is usually chosen depending on the intended applications (refer to Table I). In general, a smaller nozzle size is preferred for small objects or parts demanding high precision. For larger parts, for example in construction, a larger nozzle size is sufficient. In the following, the die swell was measured for various compositions using 2 and

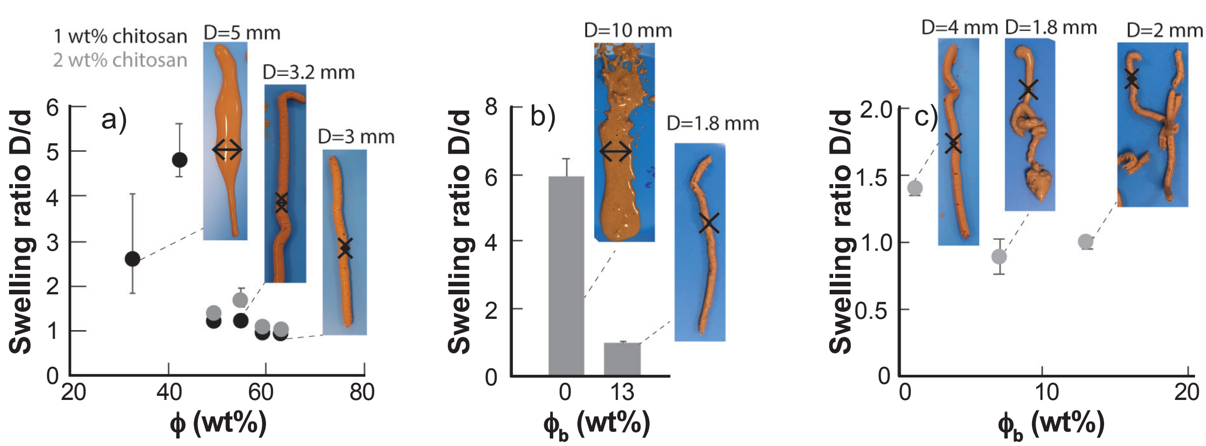

Figure 6: Effect of the composition on the swelling ratio after extrusion through a nozzle of 2 mm diameter: a) swelling ratio as a function of the concentration of clay (ϕ), for inks containing 20 mL chitosan at 1 and 2 wt% concentration (black and grey, respectively), constant content of bamboo fibers of 0.5 g, and increasing clay content; b) swelling ratio as a function of bamboo content (ϕ_b), with similar content of clay of 43 wt%; and c) with increasing bamboo content at a constant clay content of 20 g for 20 mL chitosan. Inserts are pictures of selected extrudates. The diameters D of the extrudates are indicated above each picture.

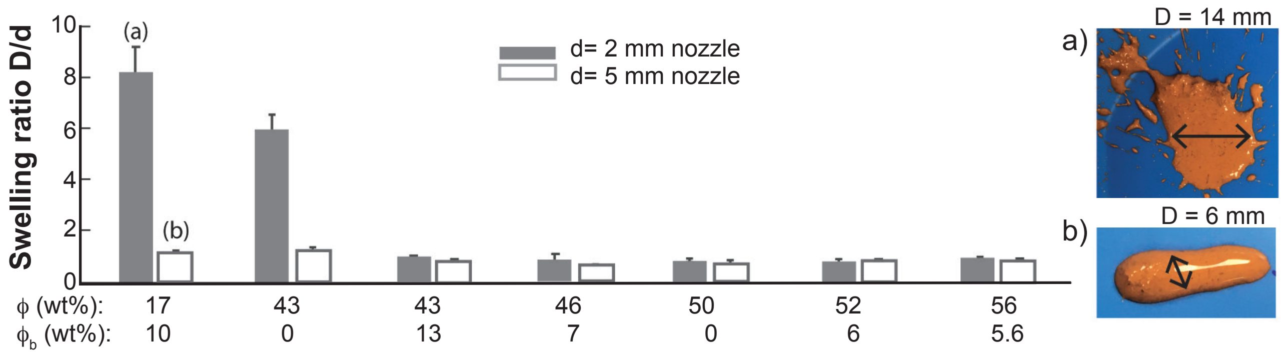

Figure 7: Effect of nozzle diameter (d) on the die swell: swelling ratio for different concentrations in clay (ϕ) and in bamboo (ϕ_b), using 2 wt% chitosan solution.

5 mm nozzle diameters (Fig. 7). For the very fluid inks exhibiting high die swell at 2 mm nozzle diameter, the ratio between the extrudate and the nozzle diameter was greatly reduced when using a larger nozzle. Indeed, for a thin nozzle, large back pressure developed at the nozzle, which led to splashing of the ink. For a larger nozzle, there was less backpressure and the ink could be extruded through the nozzle. From this series of experiments, several inks exhibited good extrudability with no die swell at a small nozzle diameter of 2 mm. Typically, inks with low bamboo content should contain around 60 wt% clay. A higher amount of bamboo could produce extrudable inks at lower content in clay. At the concentration tests, chitosan concentration had a negligible effect. Finally, inks that were not extrudable might be extrudable using larger nozzle diameters.

Penetration test for ink's buildability: after assessing the extrudability of inks using the proposed die swell method, the buildability was tested using the penetration test (Fig. 8a). When the inks were too liquid and the ball sank to the bottom of the vial, no penetration depth (d) could be measured and the ink was labeled 'too liquid'. Increasing the concentration in clay decreased the penetration depth and increased the buildability (Fig. 8b). Interestingly, the penetration depth is actually a measure of the viscosity of the ink (η_0), which is the viscosity at zero shear. Indeed, the relationship between the penetration depth and the clay content was found to follow a similar trend as for the Krieger-Dougherty relationship:

$$\eta_0 = C.\,(1-\frac{\phi}{\phi_{max}})^{\alpha} \qquad \text{(F)}$$

where C and α are constants, ϕ the concentration in solid, and ϕ_{max} the maximum concentration in clay. Usually, Eq. F is used for colloidal suspensions of concentration ϕ_p suspended in a liquid [33]. Clay, being composed of minerals such as aluminum oxide, silica, iron oxide, interacts with hydrogen bonds in presence of water to form a paste [34-36], the concentration ϕ of clay can be seen as a colloidal suspension with $\phi=\phi_p.w$ with w a diluting factor due to the water contained inside the clay. Therefore, in Eq. F, ϕ the concentration of clay can be used instead of ϕ_p. Then, taking the logarithm of the Eq. F, one obtains:

$$\ln(\eta_0) = C'+\alpha.\,\ln(1-\frac{\phi}{\phi_{max}}) \qquad \text{(G)}$$

with C' a constant. There is thus a linear relationship between $\ln(\eta_0)$ and $\ln(1-\phi/\phi_{max})$. From our experiments, we found that the logarithm of the penetration depth (p) had

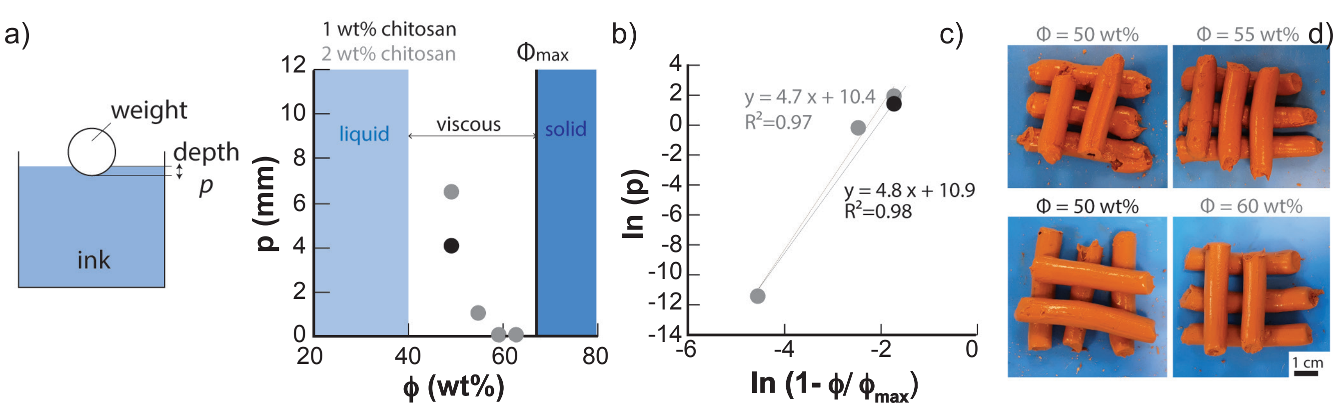

Figure 8: Data of the penetration test for the buildability: a) schematic of the principle of the measurement; b) penetration depth (p) as a function of clay content (ϕ); c) ln(p) as a function of $\ln(1-\phi/\phi_{max})$ and linear fit; and d) pictures showing top views of log pile structures extruded through a nozzle of 8.5 mm for different clay contents and chitosan concentrations. Dark writing refers to 1 wt% chitosan, grey writing to 2 wt% chitosan.

also a linear relationship with $\ln(1-\phi/\phi_{max})$, with a coefficient of correlation R_2 ~0.97-0.98 (Fig. 8c). Therefore, one can deduce that p is a measure of the viscosity η_0. For good buildability, a high η_0 is required to avoid the collapse of the structure. With ink containing 50 wt% clay or above, the penetration depth was low and log pile structures could be built. The shape could be preserved without visible deformation (Fig. 8d).

The methodology based on die swell and penetration depth to assess the extrudability and buildability of inks showed to be relevant and applicable to identify a good ink composition. The penetration test results might depend on the choice of the object placed on the ink. The weight of this object could be chosen according to the intended application and final product size. For example, a large printed part would require the first layers in the print to withstand the weight of a large amount of material. This weight could be estimated prior to the test and an object of similar weight could be used.

3D printing: to further verify that the inks optimized could be 3D printed using direct-ink-writing, we chose one ink composition that exhibited extrudability and buildability and tested it with the 3D printer (Fig. 9). 3D printing is a process that needs to be optimized on its own due to the multiple printing parameters, such as flow rate, infill density, printing pattern, nozzle speed, layer height. Here, a 1000% flow rate corresponding to a piston speed of 0.025 mm/s and height of 1 mm was able to extrude and deposit inks onto a substrate. Printing parameters optimization is generally conducted using a design of experiment procedures, which are outside the scope of this paper [37-40]. The choice of the substrate was determined prior to the test as a too smooth substrate does not allow the ink to adhere to the print bed, also a too soft or fragile substrate might be torn off during the printing or be too sensitive to the moisture emanating from the inks. As a result, a piece of filter paper as a substrate was used. The print shown in Fig. 9 contains several layers of an ink composed of 48 wt% clay and 2.4 wt% bamboo microfibers. Although the print was not perfect, it demonstrated that the ink chosen could be deposited using direct-ink-writing and that the protocol for the determination of extrudability and buildability was meaningful. Such a straightforward protocol could be applied to develop the 3D printing of sustainable materials and structures, such as those based on clay, by the laypeople, for a more sustainable world. Indeed, the proposed protocol could also enable the development of inks based on local materials at local places without further knowledge of chemistry. This capability has also applications for extra-terrestrial 3D printing, for example [41, 42]. Using the simple methods described in this paper, which do not require carrying heavy and costly characterizing equipment, astronauts could develop inks based on extra-terrestrial soil for future extra-terrestrial housing. No need for specialized equipment is an advantage because equipment tends to be heavy and demands space and electricity consumption, which are limited in spaceships. Also, a simple protocol reduces the amount of extra skills to be learned, which makes it adequate for any staff on the mission to participate.

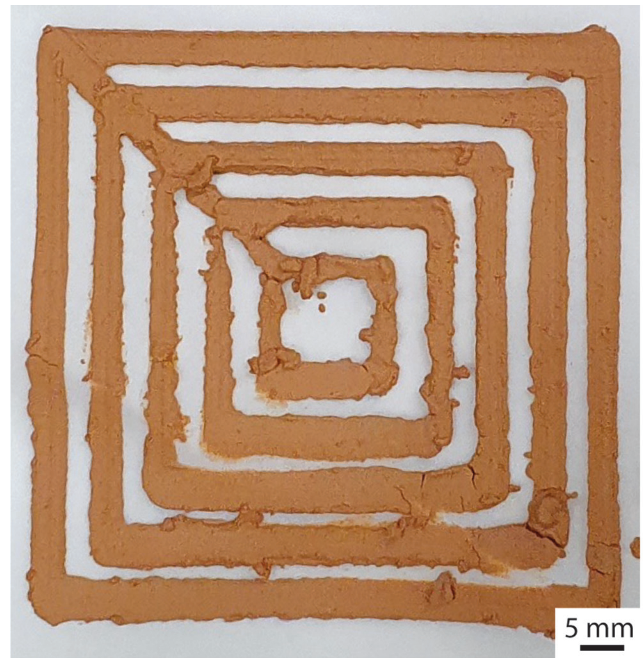

Figure 9: Direct-ink-writing: picture of a 3D printed pattern containing several printed layers, with ink composition containing 48 wt% clay and 2.4 wt% bamboo.

CONCLUSIONS

In this paper, a simple and easily applicable protocol for the optimization of the ink composition for 3D printing was developed and demonstrated using an ink based on organic fibers, clay, and a hydrogel, chitosan. The swelling ratio was found to be a good measurement of the extrudability for viscoelastic pastes, while the penetration depth provided an estimate of the viscosity and indicated the buildability. We found that the ink containing 48 wt% clay and 2.4 wt% bamboo fibers could be 3D printed nicely. The proposed strategy for ink development is simple to put in place and does not require extensive knowledge of physics and the rheological response of viscoelastic fluids. Furthermore, it does not require expensive or specialized equipment, making it easily accessible. Finally, the ingredients chosen in the composition are commonly available and do not present major hazards, making it safe as a simple protocol to instruct students of all ages and backgrounds to 3D printing using direct-ink-writing.

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