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Clément Perrinet, Edwin-Joffrey Courtial, Arthur Colly, Christophe Marquette, René Fulchiron. Enhancing the Yield Stress in Liquid Polydimethylsiloxane to Allow Its 3D Printing: Hydrogels as Removable Fillers. *Macromolecular Materials and Engineering*, 2021, 306 (2), pp.2000553. 10.1002/mame.202000553 . hal-03113976

HAL Id: hal-03113976

<https://hal.science/hal-03113976>

Submitted on 14 Dec 2022

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Enhancing the Yield Stress in Liquid PDMS to Allow its 3D Printing: Hydrogels as Removable Fillers

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Abstract:

For manufacturing parts of very soft materials by liquid deposition modeling (e.g., to mimic living soft tissues), formulations of 3D-printable polydimethylsiloxane have been developed, with the aim of increasing the yield stress of the liquid and reducing the final mechanical modulus. In the present work, suspensions of solid-like hydrogel particles, which are easily 3D-printable, are prepared in order to generate yield stress, and the suspended phase is removed after manufacturing by taking advantage of the thermo-reversibility of the hydrogel behavior, resulting in porosity, which reduces the final rigidity. The reported approach is even more efficient than a previous approach based on emulsion formulations.

1. Introduction:

Silicone 3D printing has, for several years, been a major challenge in 3D printing technology in the medical devices industry ^[1]. For decades, silicone (composed largely of polydimethylsiloxane, PDMS) has been widely used in the medical devices industry, owing to its biocompatibility due to high chemical stability which prevents interactions with living cells ^[2]–^[4], and for its softness, due to its flexible backbone structure composed of alternating silicon and oxygen atoms. This softness is essential for engineering objects which reproduce the mechanical behavior of human tissues ^{[5]–[9]}. The Young's modulus of all human tissues ranges from 10 kPa to 10 MPa ^[10], with cartilaginous tissues (trachea, esophagus, muscles) above 1 MPa, and very soft tissues below 100 kPa ^[11]. PDMS formulations are often presented as liquid materials which require curing to get a solid and constant shape. Once cured, the silicone is infusible, i.e. un-printable, thus, the process of shaping needs to occur before the curing.

3D printing processing is subject to dynamic innovations, and established categories such as fused deposition modeling (FDM), selective laser sintering and UV curing are becoming less relevant. The printings in this work are conducted with a liquid deposition modeling (LDM) system, derived from FDM. LDM involves a driven syringe depositing the viscous formulation on a tray, without any heating system.

Innovation in processes and material formulations have been recently developed in order to target sophisticated parts made of soft tissues. For example, by dip-coating and leaching techniques, soft materials mimicking soft vascular tissues have been obtained ^[12]; however, the process is an indirect 3D printing process, since a rigid template must be previously formed.

The printing of liquid PDMS of low viscosity (typically from 0.5–5 Pa s) with LDM technology is a paradoxical challenge – liquid PDMS requires high viscosity to keep a given shape, and the cured PDMS needs to be as soft as possible to mimic living tissues. Usually, fillers are added in order to make a liquid more viscous. However, these fillers also confer a high Young's modulus to the cured material ^[13].

As described in a previous report ^[14], the main challenge to countering this paradox is enhancing the yield stress behavior of the liquid silicone. Yield stress fluids are characteristic of a biphasic or a bi-component fluid. Examples of yield stress materials include concentrated emulsions, such as cosmetic creams, toothpastes, foams, polymer gels, slurries, and some composites ^{[15]–[18]}. The elastic or solid-like behavior under weak stress is related to interactions between these inclusions in a main phase. The yield stress corresponds to the breakage or modification of such interactions. This may be the breaking of a percolation network continuity or the elastic deformation of a droplet in an emulsion. The viscosity under a sufficient stress decreases, and the system becomes flowable. In addition, for most of these systems, at rest, the microstructure reforms or evolves spontaneously in order to rebuild the network. If the microstructure re-establishes at rest, an increase of apparent yield stress with time is observed ^[19], revealing the thixotropic character of the material.

For silica/PDMS formulations, adding polyethylene glycol (PEG) ^[14] creates a weak network which changes the behavior of the system at rest. For a low-filled PDMS, it has been proposed that an emulsion can be made which will enhance the yield stress of the system, and allow the printing of such formulations ^[20]. It should be mentioned that emulsion formulations have already been used for 3D printing, but with rigid materials, such as photocurable

polycaprolactone^{[[21]]} or acrylate polymer^{[[22]]}^{[[23]]}. The aim was essentially to obtain a very porous final rigid scaffold.

In this work, which deals with nearly-unfilled PDMS, it is proposed to synthesize suspensions of soft, hydrosoluble inclusions in PDMS, in order to enhance the yield stress before curing and wash off the fillers after curing, creating a porous system with a low Young's modulus, comparable to soft human tissues.

The existence of yield stress in filled polymers is a well-known phenomenon, described in several systems^{[[13]]}^{[[24]]}^{[[26]]}. It arises due to the generation of a percolated network of fillers in the polymer matrix. This network is characterized by the attractive forces between fillers, which impact the magnitude of the yield stress. This yield stress is highly dependent on the volume fraction of inclusions^{[[26]]}, up to a maximum close packing which represents the maximum possible fraction that can be inserted in the continuous matrix. This maximum packing value can vary between 0.52 and 0.70, depending on the system^{[[27]]}. The percolation threshold is another characteristic value whose magnitude is highly dependent on the shape of the inclusions and their interactions. For microscopic inclusions, it is usually around 20% v/v, and it can be as low as 1% v/v for nanometric inclusions^{[[13]]}. The percolation threshold may be described as the lowest volume fraction of inclusions at which every inclusion is in contact with at least two other inclusions, creating a continuous network of inclusions in the polymeric matrix. In this work, the fillers are thermo-reversible hydrogels which are very soft solids that are easily breakable or deformable, and which cannot be considered as hard spheres. Thermo-reversible hydrogels can be turned into a liquid when the temperature is increased, or decreased, to a characteristic temperature^{[[28]]}. These hydrogels are not stabilized by crosslinking^{[[29]]}. Only the polymeric

conformation in water, arising from soft interactions such as hydrogen bonding, sustains the shape of the system. Thus, the material is a very breakable solid which is also hydrosoluble.

2. Results and discussion

2.1. Hydrogel

Hydrogels are polymers with hydrophilic functions which enable the trapping of water molecules in their network ^[28]. Hydrogels can be divided into two categories, based on the chemical or physical nature of the cross-link junctions. Permanent bonds are obtained by chemical cross-linking, while temporary bonds constitute physical networks. These bonds can result from polymer chain entanglements, ionic interactions, hydrogen bonds, or hydrophobic interactions ^[28].

In this work, only physical hydrogels are of interest, as these gels require solvation with a hydrophilic solvent after processing. The first physical chosen hydrogel was Pluronic F127, provided by BASF, which is of the poloxamer family. Poloxamers are copolymers which combine polyethylene oxide (PEO) and polypropylene oxide (PPO). In water, poloxamers are present as unimers, however, with increasing concentration, a transition to micelle conformation can occur. Moreover, this transition may also occur by increasing temperature. In this work, poloxamer gels were formed by adding 20 wt. % poloxamer to water. This is above the critical micelle concentration (CMC) (18 wt. %). The unimer—micelle transition occurs near 18 °C ^[30]. ^[31]. Accordingly, above 18 °C, poloxamer are in micelle conformation ^[30], with the hydrophilic parts of polymer structures spread toward the outside, allowing interactions between micelles, leading to gelation ^[29]. Below 18 °C, the gel is destroyed and becomes liquid. Above

70 °C, the poloxamer gel again turns into a liquid. Thus, the gelation of poloxamer in water is possible in a temperature window from 18 °C to 70 °C

The second physical hydrogel used is constituted of agar, a well-known natural polymer, usually sold as a pork gelatin substitute. It is a natural polymer of galactane, which has the property to solubilize in hot water and form a gel after cooling. The gel is formed from interactions between polymer chains, owing to helical portions which lead to associations by double-helices. This association is lost at high temperatures, where the agar molecules adopt a random coil conformation, with the transition temperature being approximately 40 °C ^[32]. This type of conformation is predominant in the sol, but can also exist as connecting lengths in the gel structure, imparting some elasticity. Agar gels represent an important hysteresis in the cooling-heating process, and the transitional temperature window between the liquid and gel states is large. An applied temperature of 90 °C may be needed to liquefy the system from the gel state, though it must be cooled to 30 °C in order to recover gel consistency.

2.2. Rheological behavior

2.2.1. Rheological experiments

The characterization of yield stress could be performed using several methods ^[33]. To get a quantitative measure, the stress growth experiment is a simple method, as it gives an absolute value of the yield stress and measures the impact of the inclusion volume fraction. A more qualitative way is to perform a frequency sweep, which will show a plateau at low frequencies, signifying a percolated network in the system. Figure 1 shows the rheological characterization of the different formulations. It is important to mention that, for these experiments, only one part of the PDMS was used to avoid cross-linking, which would have made experiments impossible due to the relatively short pot-life (20 min) of the RTV 3503 (in the present work, although part B

was used, the results are considered similar to those which would have been obtained if part A was used). From these results, it is clear that the higher the amount of hydrogel, the higher the yield stress value. Nevertheless, it should be remembered that the PDMS phase must remain continuous in order to ensure the integrity of the final object – furthermore, the blend of hydrogel/PDMS must form a co-continuous phase structure. Hence, for the agar gel/PDMS system, a maximum volume fraction of 65 % v/v was obtained. This value is the expected one for most filled formulations ^[27], ^[34], ^[35]. This maximum packing value is linked to the maximum yield stress value, which is approximately 240 Pa. In comparison, for the poloxamer gel/PDMS system, a maximum packing value of only 52 % v/v was obtained, which is quite low, according to the literature, but has been previously observed ^[27]. Its maximum yield stress value is 220 Pa, close to the value obtained for agar gel/PDMS. The quality of the percolated network is seen in the frequency sweep test results, which shows that the plateau at low frequency appears at around 20 % v/v for poloxamer gel/PDMS systems, and at 30 % v/v for agar gel/PDMS systems. The important increase of the yield stress value, owing to the creation of a percolated network, should enable the 3D printing of such filled PDMS formulations.

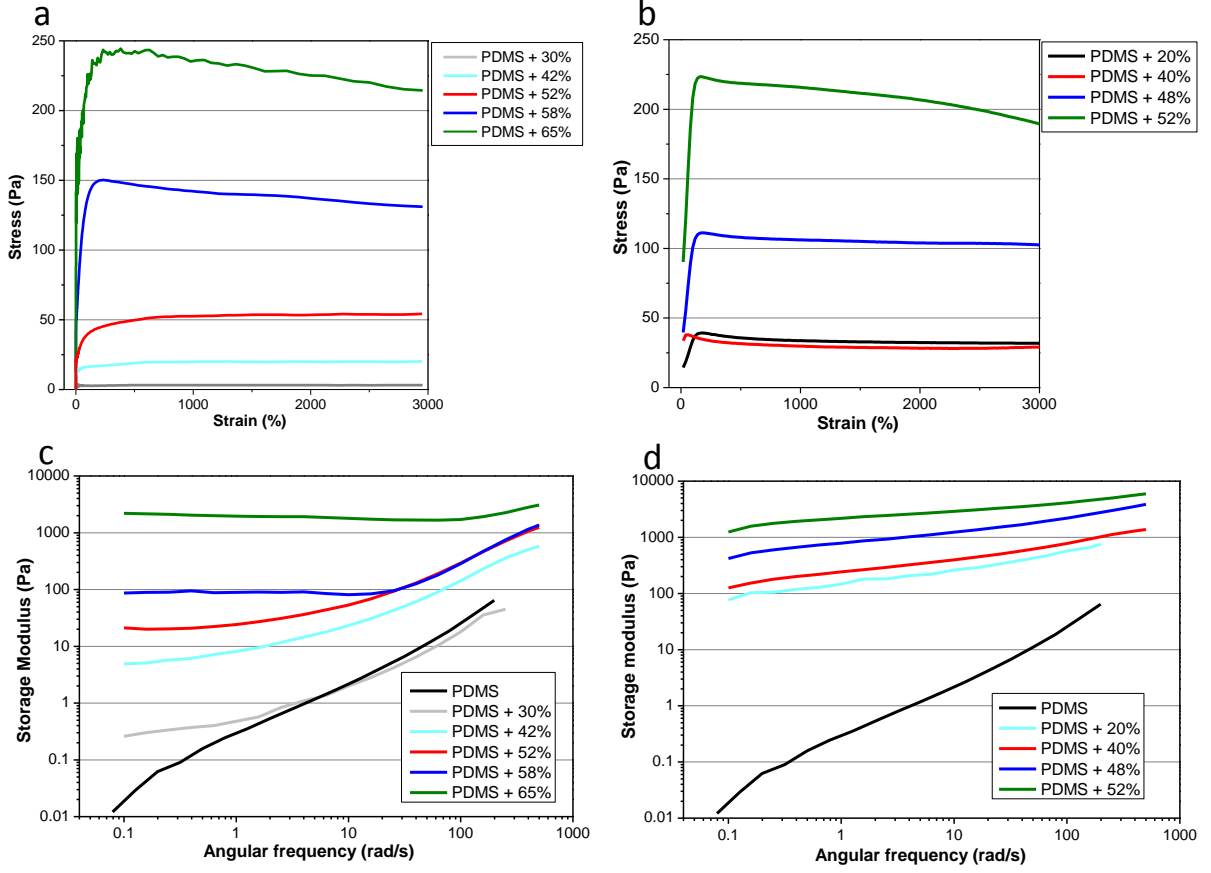


Figure 1: Rheological Characterization: a) Stress growth experiments at 1 s⁻¹ for agar gel/PDMS systems, b) Stress growth experiments at 1 s⁻¹ for poloxamer gel/PDMS systems, c) Frequency sweep experiments for agar gel/PDMS systems, d) Frequency sweep experiments for poloxamer gel/PDMS systems. For all experiments, only part B of PDMS was used.

2.2.2. Rheological modeling

The evolution of a suspension's rheological parameters, including the yield stress, often follows a power law of the difference between the inclusion volume fraction (Φ) and the volume fraction at the percolation threshold (Φ_p) [13]–[35]–[39], as shown in Equation (1):

$$\sigma_c = m * (\Phi - \Phi_p)^a \quad (1)$$

For hard filler suspensions, the exponent a is reported to be highly dependent on the interactions between the particles and the suspending liquid. For example, for fumed silica suspensions in PDMS, Paquien et al. observed a decrease in a from 7.2 to 2.8 with increasing number of hydrophobic silica surface treatments [16]. Using a similar approach, Auscher et al. [40] have shown that, for zirconia particles dispersed in a polyethylene matrix, a hydrophobic treatment of zirconia with stearic acid leads to reducing both the percolation threshold and the exponent a (from 3.6 to 2.1, for the percolation law applied to the yield stress). This variation of the exponent has been explained by considering the weakening of the interactions between particles by the presence of molecules at their surface, which favors interactions with the suspending liquid. Thus, the contacts between particles become softer, and the global rigidity of the network increases at a lower rate with the contact number (i.e., with the volume fraction of fillers).

The measured yield stress as a function of the inclusion volume fraction was analyzed, with consideration to Equation (1). The first crucial parameter in this equation is the inclusion volume fraction at the percolation threshold (Φ_p). This parameter is usually not easy to determine accurately, and its value can affect determination of the other parameters. In this work, it was simply considered that Φ_p was reached when the yield stress was detectable. In addition, it was verified that the value was consistent with the storage modulus curves, where a marked plateau in the low frequency range is obtained for volume fractions above the threshold Φ_p . The other parameters (m and a) were determined by simple regression.

Figure 2 shows the suitable prediction of the experimental yield stress values by the calculated curves fit to the data. The obtained parameters are given in Table 1, together with the maximum possible hydrogel fractions and the corresponding yield stresses.

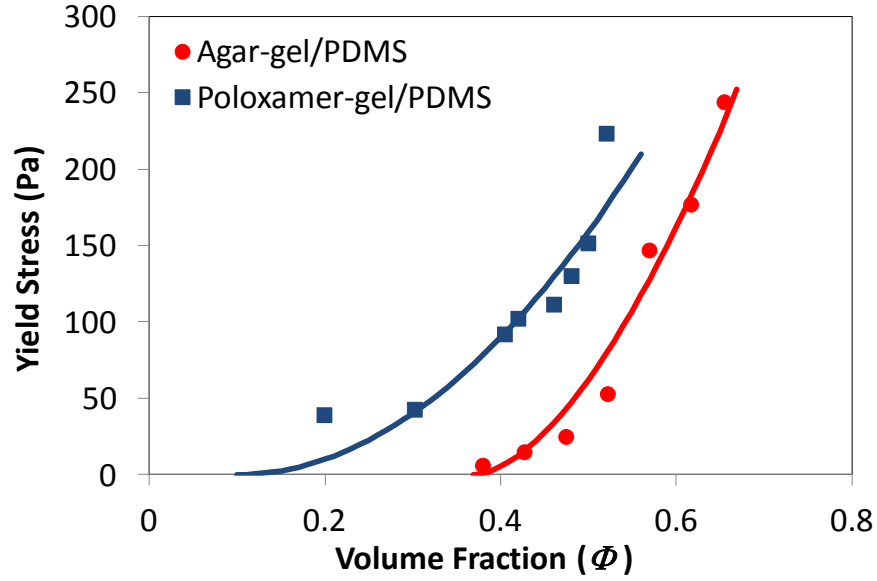


Figure 2: Yield stress as a function of the inclusion volume fraction. Symbols: experimental values, solid lines: Percolation laws (Eq. 1)

Table 1: Fitted parameters of Eq. 1 (maximum hydrogel fractions and corresponding yield stresses), for poloxamer gel/PDMS and agar gel/PDMS.

Suspension	Φ_p	a	m	$\sigma_{c \max}$	Φ_{\max}
Poloxamer-gel/PDMS	0.10	1.99	981	223	0.52
Agar-gel/ PDMS	0.37	1.68	1920	244	0.65

The relatively low values (<2) obtained for the exponent a compared to those obtained for hard filler suspensions may be explained by the fact that the suspended hydrogels are highly soft, so that the contacts between particles are not punctual and rigid but rather allow the particles to be deformed, leading to a “soft” percolated network.

2.3. 3D Printing

For the following 3D printing tests, the most interesting formulations (i.e. those with the highest yield stresses) from each system were chosen, namely PDMS + 52% v/v of poloxamer gel (PDMS+52%Plu) and PDMS + 65% v/v of agar gel (PDMS+65%Ag). Figure 3 shows the 3D

printing results obtained for the hexagonal shape selected to test the material's properties, with a low surface area sustaining the object and an increasing over-hanging of the hexagon's walls. It must be pointed out that the printed objects shown in Figure 3c and Figure 3d have been washed to remove the hydrogel. This last step will be detailed in the next section.

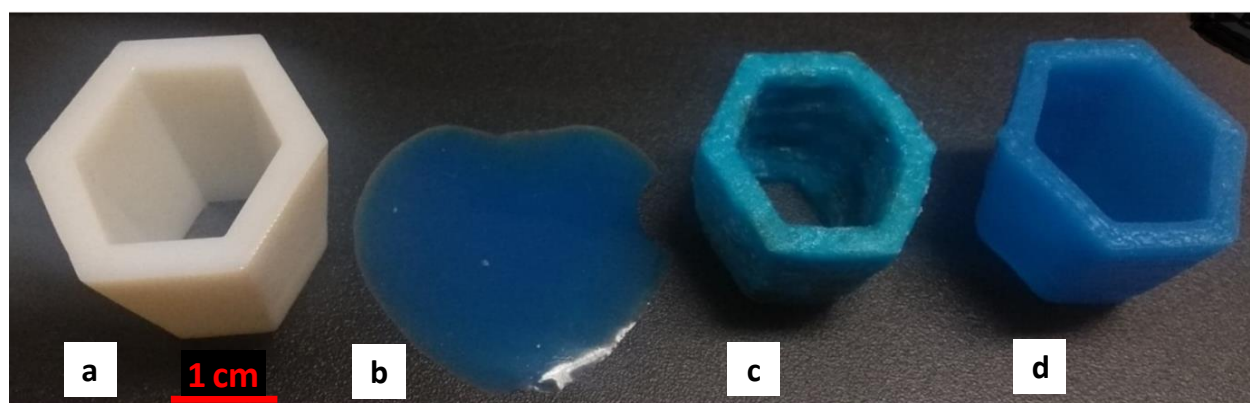


Figure 3: Printing results: a) control object, b) unmodified PDMS object, after curing, c) PDMS+65%Ag) object, after curing and washing, d) PDMS+52%Plu, after curing and washing.

The unmodified PDMS formulation is clearly unsuitable for 3D printing (see Figure 3b), as the liquid PDMS behaves like a low-viscosity liquid with no yield stress, and, consequently, no 3D shape was obtained. For modified formulations with yield stresses of 240 Pa (Figure 3c) and 220 Pa (Figure 3d), objects with height 2.5 cm and medium complexity were printed, with satisfactory fidelity (>92%). Details of the measurements are reported in **Supporting Information 1**. As discussed in a previous report ^[14], increasing yield stress enables the printing of more complex structures. The first layers can be printed and withstand the weight of upper layers without collapsing ^[41]. Basically, the higher is the yield stress, the easier is the 3D printing process because it makes the under construction object stronger to support the successive added layers. In the present work, 3D printing tests have not been systematically carried out with different amounts of hydrogels so that it is difficult to determine the minimum yield stress needed for the printing (obviously this can depend on the printed object complexity). However, the yield

stress measurement as a function of the hydrogel amount (and its modeling by Equation 1) may evidently be a guide to choose the appropriate formulation and explore the printing possibilities following the criterions that the yield stress, and thus the hydrogel amount, must be high enough. However, the maximum possible amount of hydrogel must not be exceeded otherwise the phase inversion will ruin the process (the PDMS must remain a continuous phase). Moreover, the evolution of the yield stress and the maximum amount of hydrogel are dependent on the hydrogel nature (see Figure 2). In that regard, the rheological measurements are an essential tool to characterize the suspension.

Moreover, it can be added that the overall appearance still varies with the formulation. The object made from PDMS+65%Ag has a rugged surface aspect, whereas the object made from PDMS+52%Plu appears smoother. This comes from the difference in the amount of inclusions removed after cleaning and from differences between inclusion sizes, which will be discussed later.

2.4. Solvent extraction

A selective extraction was conducted in order to wash the printed objects of their hydrogels. Solvent selection depends on the hydrogel property – hydrogels have to be brought to the liquid phase (both gels are thermally reversible), and inclusions need to be accessible to the solvent. A PDMS swelling solvent could therefore be useful.

For poloxamer gel/PDMS systems, the maximum volume ratio is quite low (52% v/v). Although the interconnectivity of hydrogel particles is desired, it must be considered that a (small) fraction of the particles are isolated from the global network (leading to some closed porosity after extraction). Ethanol is a well-known solvent for swelling PDMS, and water is the best solvent for

solvating the poloxamer. Thus, a 50:50 mix of both solvents was heated to ebullition, poloxamer gel/PDMS objects were immersed in the co-solvent, and a reflux system was installed. For agar gel/PDMS objects, the agar volume fraction is relatively high, so that the swelling of PDMS by the solvent is less necessary than for poloxamer gel/PDMS objects. Moreover, the agar gel flows at a higher temperature than the poloxamer gel, and the water/ethanol refluxing mix does not reach 90 °C. Thus, boiling water is preferred for agar gel/PDMS objects. The specific extraction solvents applied to both systems each succeeded in extracting gel inclusions from the cured PDMS, verified by thermogravimetric analysis (TGA). These TGA experimental data are available in **Supporting Information 2**, and show the quasi-total extraction of the hydrogel inclusions (the curves for PDMS and PDMS+Gel washed off are superimposed up to 400°C), apart from 3–4 % of agar molecules, which may remain in the PDMS after washing.

Figure 4 shows SEM pictures obtained for both formulations (PDMS+65%Ag and PDMS+52%Plu), revealing the porosity after solvent extraction. The pores are clearly much larger for the sample formulated with agar gel (typically 200–400 µm in diameter) than for the sample formulated with the poloxamer (typically 10–20 µm in diameter). From these pictures, it can be concluded that, although the material prepared with the poloxamer shows less porosity due to less hydrogel being incorporated, it may still be of interest due to its very fine porosity. In that respect, it must be pointed out that the porosity structure is governed by first the total amount of hydrogel but also, and above all, by the initial quality of the suspension and the aptitude of the hydrogel to be thinly fragmented during the mixing. It arises that the formulation with the poloxamer leads to much finer dispersion than with the Agar (so fine that a lot of pores may even not be visible by SEM). The material prepared with the agar gel shows much larger pores, likely to the detriment of the mechanical resistance of the material at high deformation.

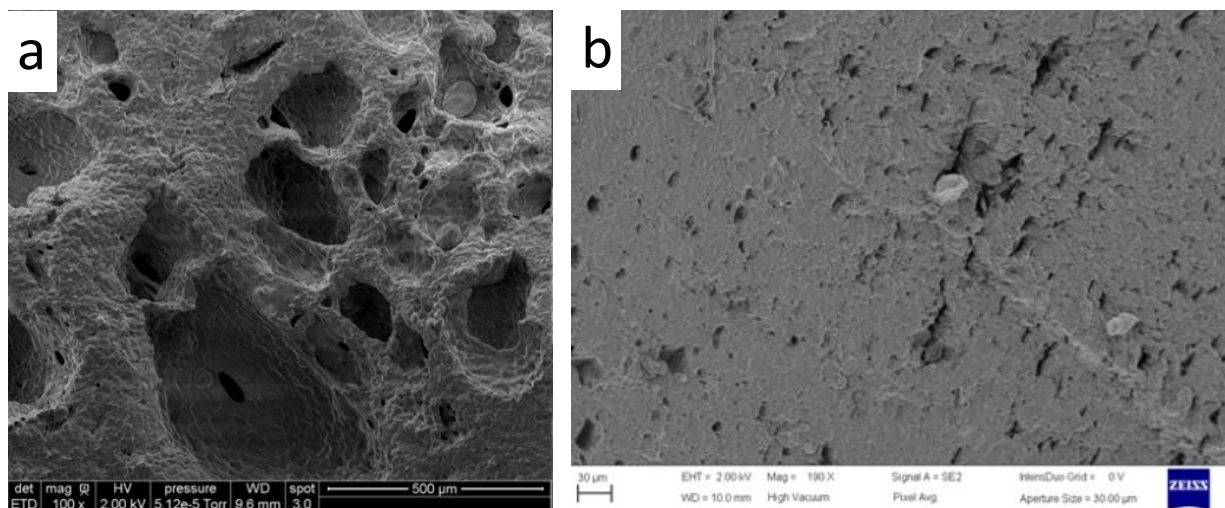


Figure 4: SEM observations: a) sample PDMS+65%Ag after extraction of the Agar, b) PDMS+52%Plu, after extraction of the Poloxamer.

2.5. Young's modulus

As previously mentioned, one of the main goals in this work was to obtain a PDMS material with a very low Young's modulus, in order to mimic soft human tissues under 100 kPa. The mechanical measurement, shown in Figure 5, shows a large decrease in Young's modulus from the initial value of the PDMS material, owing to the protocols used in this work. It is possible to decrease Young's modulus from 250 kPa (PDMS) to 50 kPa for the PDMS+52%Plu washed system, and further to 25 kPa for the PDMS+65%Ag washed system, the porosity in the latter being a more contributing factor. **Incidentally, this strong decrease in stiffness clearly indicates that the possible shrinkage of the material after extraction is not very important; otherwise the porosity would have been reduced, thus preventing the stiffness reduction.**

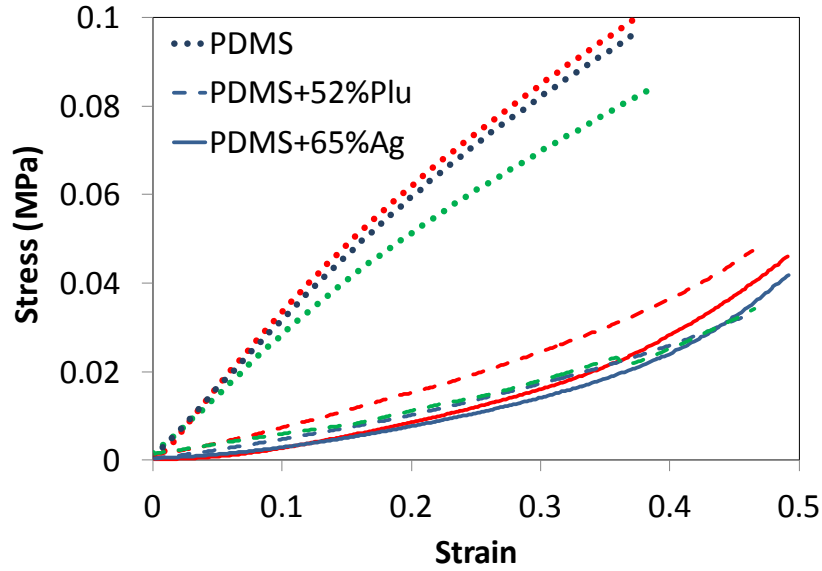


Figure 5: Compression measurements (repeated 3 times) of unmodified PDMS silicone (dotted lines), PDMS+52%Plu after extraction of the poloxamer (dashed lines) and PDMS+65%Ag after extraction of the agar (solid lines).

3. Conclusion

The 3D printing of soft PDMS is a challenge for the medical devices industry. The liquid deposition modeling 3D printing system is a cheap, accurate and simple technology which can meet this challenge. It requires an appropriate understanding of the printed materials' rheological properties. With this considered, the yield stress turns out to be a key parameter with which to enlarge the scope of printability of new materials via liquid deposition modeling technology. Here, a new approach to enhance this yield stress fluid behavior by adding soft hydrogel fillers like poloxamer and agar gels, without hardening the final material, was described. Furthermore, the removal of these fillers after curing of the printed PDMS creates a porous matrix, which is significantly softer than the initial PDMS, contributing to the successful printing of non-trivial sharpened PDMS objects with Young's modulus below 50 kPa. Each technical solution which further enhances the yield stress of the initial liquid PDMS will contribute to the printing of even more complex shapes.

4. Methods

4.1 Materials:

The PDMS used was Bluesil RTV 3503 from Elkem Silicones. It is provided in two liquid parts: Part A containing vinyl groups, and part B containing Si-H groups. Equal volumes of each part require mixing for the hydrosilylation reaction to occur, leading to a cross-linked material. The pot-life of the blend at ambient temperature is approximately 20 min. It should be noted that a small amount of silica (4.5% v/v) is included in this PDMS formulation. Hydrogels were synthesized by adding corresponding amounts of polymer powder, poloxamer (20 wt. %) (Pluronic F127, Sigma Aldrich) or agar (5 wt. %) (Sigma Aldrich), and mixing in a measured amount of boiling water, under stirring and reflux of water vapor.

4.2 Suspensions preparation:

Suspensions of poloxamer gel/PDMS were prepared by adding a corresponding amount of both materials, premixing by hand with an iron stick followed by high shearing in an Ultra-Turrax T50 Homogenizer (IKA) at 7000 tr min^{-1} , until the formulation obtains a gel consistency, or otherwise for 5 min, for the lowest levels of hydrogels. Agar gel/PDMS suspensions are, in a liquid state, first placed in an oven at 90°C in a closed recipient, followed by mixing at this temperature as for the poloxamer gel suspensions. Being much harder than the Poloxamer gel, the agar gel's dispersion in the solid state was not possible with an Ultra-Turrax mixer. Hydrogel content values have been selected empirically so that, on the one hand, an obvious effect was detected on the rheological behavior and, on the other hand, the value did not overpass the maximum possible, which would lead to loss of the PDMS phase continuity (leading to a friable final material). The obtained suspensions were stable for at least several days, despite no emulsifier being used.

4.3 Rheological tests:

Rheological measurements were conducted using an ARES G2 rheometer (TA Instruments, USA) with a cone-plate geometry of 25 mm diameter and a cone angle of 0.1002 rad. The yield stress measurements were performed in transient mode, carrying out a stress growth experiment at a constant strain rate of 1 s^{-1} . The stress/strain curve presented a maximum of stress which was taken as the static yield stress value.

4.4 3D Printing process:

A liquid deposition modeling (LDM) device with a COSMED 333 Cartesian 3D printer (Tobeca, France) of 10 μm movement precision was used to print the suspensions. Bi-component cartridges of 50 mL (Nordson EFD, USA) were filled with PDMS parts A and B, each being previously blended with the desired amount of hydrogel. **It can be mentioned that because of the very low viscosity of the liquid PDMS, no degassing was required; no bubbles were trapped in the blend.** The blending of the two parts is ensured at the exit of the cartridge, owing to a static mixer positioned upstream of a 200 μm diameter conical nozzle (Nordson EFD, USA). Extrusion was ensured using a pneumatic system, Equalizer and Ultimius V (Nordson EFD, USA). Dispensing pressure was adapted for each suspension. 3D printing was controlled via the Repetier Host software (Repetier, V2.0.1, Germany) at a printing speed of 10 mm s^{-1} . The STL file was a homemade hexagonal model of medium complexity ^[6], which can be printed without any non-print travel and has a small overhang of 5° (0 being vertical). The file was sliced with the Slic3r software (Slic3r, V3, Italia) using adapted printing parameters. The control sample was printed with Verowhite resin using the Object30 Pro 3D printer (Stratasys, USA). This rigid sample was used as a reference to evaluate the dimensional fidelity of the PDMS samples.

4.5 Solvent extraction:

The cross-linked silicone containing the hydrophilic gel was immersed in boiling solvent for 12 h, then dried at 80 °C for 12 h and then at 100 °C for a further 12 h. The solvent was water (b.p. 100 °C) for PDMS+65%Ag sample, and a water/ethanol mixture (50/50) (b.p. approximately 85°C) for PDMS+52%Plu. The sample was previously shaped using a small laboratory press equipped with a cylindrical mold (13 mm diameter, 7 mm thickness), also used for mechanical characterization.

4.6 Purification measurements:

The first analysis was conducted by measuring the mass loss after purification. TGA tests were conducted using a Q500 TGA (TA Instruments), with a temperature ramp of 5 °C min⁻¹, up to 600 °C.

4.7 Mechanical characterization:

Compression tests were carried out to determine Young's modulus. Samples of 13 mm diameter and 7 mm thickness were prepared in a small laboratory press (as for solvent extraction experiments). To characterize mechanical behavior, each sample was squeezed between plates (25 mm diameter) on an ARES G2 Rheometer, at 0.01 mm s⁻¹ for 600 s. Nominal stress was calculated by dividing the measured force by the sample section (132.7 mm²). The nominal strain was calculated by dividing the plate displacement by the initial sample thickness. Then, Young's modulus was obtained from the slope of the stress/strain plot for the first 0.1 of strain (the given values are the average of 3 measurements).

SEM observations: The cured systems were observed after hydrogel extraction by SEM. A Merlin electron microscope (from Zeiss) was used to characterize the sample PDMS+52%Plu,

using a 2 kV electron beam and a magnification of 190×. For the sample PDMS+65%Ag, a Quanta 250 microscope (FEI) was used, using a 2 kV electron beam and a magnification of 100×.

Acknowledgments:

This work was supported by the French government through FASSIL project, selected by FUI (Fonds Unique Interministériel) and by the region Auvergne-Rhône-Alpes. The authors especially thank Jean-Marc Francès and Damien Djian from Elkem Silicones for materials supply and very helpful discussions. The authors also acknowledge the ‘Centre Technologique des Microstructures (CTμ)’ of University Lyon 1 for the SEM experiments and especially Pierre Alcouffe of IMP, UMR5223 laboratory.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Additive Manufacturing, Silicone, Hydrogel, Suspensions, Yield Stress Fluid

References

- [1] F. Liravi, E. Toyserkani, *Addit. Manuf.* **2018**, 24, 232.
- [2] B. Arkles, *Chem. Tech.* **1983**, 13, 542.
- [3] F. Mahyudin, H. Hermawan, *Biomaterials and Medical Devices: A Perspective From an Emerging Country*, Springer, Cham, **2016**.
- [4] M.C. Tai, C. B. Cosar, E. J. Cohen, C. J. Rapuano, P. R. Laibson, *Cornea*, **2002**, 21, 135.
- [5] L. William Luria, *Oper. Tech. Plast. Reconstr. Surg.* **2002**, 9, 67.
- [6] D. W. Good, A. Khan, S. Hammer, P. Scanlan, W. Shu, S. Phipps, S. H. Parson, G. D. Stewart, R. Reuben, S. A. McNeill, *PLoS ONE* **2014**, 9, 112.
- [7] G. A. Holzapfel, *The Handbook of Materials Behavior Models*, Academic Press, New York, **2001**, 3, 1049.
- [8] J. D. Humphrey, *Proc. Math. Phys. Eng. Sci.* **2003**, 459, 3.
- [9] M. Zhang, P. Nigwekar, B. Castaneda, K. Hoyt, J. V. Joseph, A. di Sant'Agnese, E. M. Messing, J. G. Strang, D. J. Rubens, K. J. Parker, *Ultrasound Med. Biol.* **2008**, 34, 1033.
- [10] S. V. Murphy, A. Atala, *Nat. Biotechnol.* **2014**, 32, 773.

- [11] T. A. Krouskop, T. M. Wheeler, F. Kallel, B. S. Garra, T. Hall, *Ultrason. Imaging* **1998**, 20, 260.
- [12] J. E. Lee, S. J. Park, Y. Yoon, Y. Son, S.-H. Park, *J. Mech. Behav. Biomed. Mater.* **2019**, 91, 193.
- [13] M. M. Rueda, M.-C. Auscher, R. Fulchiron, T. Périé, G. Martin, P. Sonntag, P. Cassagnau, *Prog. Polym. Sci.* **2017**, 66, 22.
- [14] E.-J. Courtial, C. Perrinet, A. Colly, D. Mariot, J.-M. Frances, R. Fulchiron, C. Marquette, *Addit.Manuf.* **2019**, 28, 50.
- [15] M. I. Aranguren, E. Mora, J. V. DeGroot Jr., C. W. Macosko, *J. Rheol.* **1992**, 36, 1165.
- [16] J.-N. Paquien, J. Galy, J.-F. Gérard, A. Pouchelon, *Colloids Surf. A* **2005**, 260, 165.
- [17] G. Ovarlez, S. Cohen-Addad, K. Krishan, J. Goyon, P. Coussot, *J. Non-Newton. Fluid Mech.* **2013s**, 193, 68.
- [18] P. Coussot, in *Soft and Biological Matter*, Springer, Cham, **2014**.
- [19] N. J. Alderman, G. H. Meeten, J. D. Sherwood, *J. Non-Newton. Fluid Mech.* **1991**, 39, 291.
- [20] C. Perrinet, E.-J. Courtial, A. Colly, C. Marquette, R. Fulchiron, *Adv. Mater. Technol.*, **2020**, 5, 1901080.
- [21] B. A. Dikici, G. C. Reilly, F. Claeysens, *ACS Appl. Mater. Interfaces* **2020**, 12, 12510.
- [22] N. A. Sears , P. S. Dhavalikar, E. M. Cosgriff-Hernandez, *Macromol. Rapid Commun.* **2016**, 37, 1369.
- [23] A. Malayeri, C. Sherborne, T. Paterson, S. Mittar, I. Ortega Asencio, P. V. Hatton, F. Claeysens, *Int. J. Bioprint.* **2016**, 2, 67.
- [24] P. Coussot, in *Rheophysics: Matter in all its States*, Springer International Publishing, **2014**.
- [25] A. Fall, H. de Cagny, D. Bonn, G. Ovarlez, E. Wandersman, J. A. Dijksman, M. van Hecke, *J. Rheol.* **2013**, 57, 1237.
- [26] I. M. Krieger, T. J. Dougherty, *Trans. Soc. Rheol.* **1959**, 3, 137.
- [27] S. Gallier, E. Lemaire, F. Peters, L. Lobry, *J. Fluid Mech.* **2014**, 757, 514.
- [28] E. M. Ahmed, *J. Adv. Res.* **2015**, 6, 105.
- [29] F. Ullah, M. B. H. Othman, F. Javed, Z. Ahmad, H. M. Akil, *Mater. Sci. Eng. C Mater. Biol. Appl.* **2015**, 57, 414.
- [30] M. Vadnere, G. Amidon, S. Lindenbaum, J. L. Haslam, *Int. J. Pharm.* **1984**, 22, 207.
- [31] P. Alexandridis, T. Alan Hatton, *Colloids Surf. A* **1995**, 96, 1.
- [32] K. C. Labropoulos, S. Rangarajan, D. E. Niesz, S. C. Danforth, *J. Am. Ceram. Soc.* **2001**, 84, 1217.
- [33] P. C. Møller, J. Mewis, D. Bonn, *Soft Matter* **2006**, 2, 274.
- [34] R. J. Flatt, P. Bowen, *J. Am. Ceram. Soc.* **2006**, 89, 1244.
- [35] P. J. Carreau, P. A. Lavoie, F. Yziquel, in *Rheology Series*, Vol. 8 , Elsevier, New York **1999**.
- [36] G. Heinrich, M. Klüppel, in *Filled Elastomers Drug Delivery Systems*, Springer Berlin Heidelberg, **2002**, 1.
- [37] Z. Zhou, M. J. Solomon, P. J. Scales, D. V. Boger, *J. Rheol.* **1999**, 43, 651.
- [38] G. M. Channell, C. F. Zukoski, *AIChE J.* **1997**, 43, 1700.
- [39] H. J. Choi, M. S. Cho, J. W. Kim, C. A. Kim, M. S. Jhon, *Appl. Phys. Lett.* **2001**, 78, 3806.
- [40] M.-C. Auscher, R. Fulchiron, T. Perie, and P. Cassagnau, *Polymer* **2017**, 132, 174.
- [41] A. Lopez, C. A. Marquette, E.-J. Courtial, *Prog. Addit. Manuf.* **2020**, DOI: <https://doi.org/10.1007/s40964-020-00143-5>.

Supporting Information.

Enhancing the Yield Stress in Liquid PDMS to Allow its 3D Printing: Hydrogels as Removable Fillers

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Supporting Information 1:

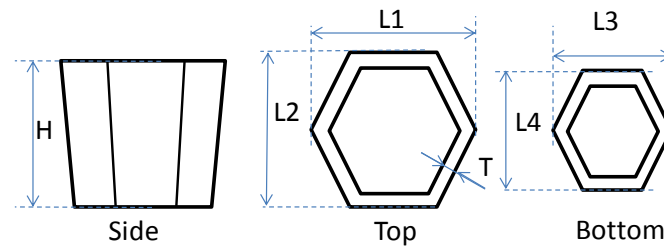


Figure S1: Measured dimensions of the printed objects

Table S1: Measured values of objects dimensions

	Control	PDMS+52% Plu	Difference (%)	PDMS+65% Ag	Difference (%)
H (mm)	25.3	23.30	-7.91	21.00	-17.00
L1 (mm)	33.20	32.80	-1.20	32.80	-1.20
L2 (mm)	33.30	30.00	-9.91	30.50	-8.41
L3 (mm)	24.40	25.10	2.87	22.00	-9.84
L4 (mm)	24.40	21.50	-11.89	24.80	1.64
T (mm)	4.40	3.60	-18.18	3.90	-11.36
Average difference (%)			-7.70		-7.69

Supporting Information 2:

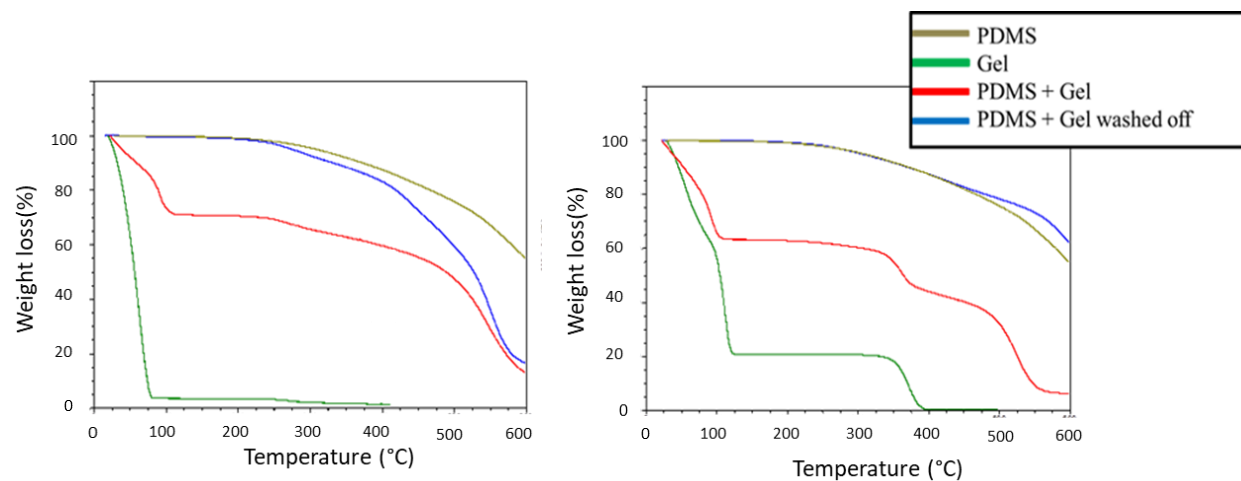


Figure S2. TGA analyses of PDMS+65%Ag (left) and PDMS+52%Plu (right) at different steps of the process, and comparison with the raw hydrophilic liquid.