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Shaping gels and gels mixture to create helices

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In cooking, food gels such as agar-agar or alginate are often prepared and presented in the form of spheres or spaghetti. While experimenting in our kitchen, we realized that it is quite difficult to make more advanced shapes. In this study, we sought to develop new methods to obtain more complex shapes. Our first challenge was to obtain helices. The best method we selected was to deposit the solutions before their gelation in a thread. The robustness of the method is tested by systematically changing the thread pitch, diameter and depth. From the deformation under its own weight, we propose to deduce the mechanical characteristics of the helix. These values are compared to those obtained in the laboratory using indentation testing. Finally, we experimented with mixed gels obtained by combining agar-agar and alginate.

I. INTRODUCTION

When the first lockdown started, we wanted to take this opportunity to finally get into molecular cooking which mixes culinary art and science. It was the ideal meeting place for science enthusiasts and cooking lovers. It was also an opportunity to exchange with colleagues and to explore the connections between fluid mechanics and the food industry. And perhaps most of all, it gave us the opportunity to keep the children busy while giving them a taste for research and science.

Gelation is one of the basic phenomena of molecular cooking¹. This method allows to control the texture and the flavours of the product and thus opens new possibilities of food manufacturing. In this article we will focus on the shaping of gels into complex shapes. Morphing of food is a common problem encountered by manufacturers²⁻⁴. The methods developed use physical and chemical phenomena like swelling or deswelling of material with anisotropic properties to create three dimensional shapes⁵. In this study, we explored the possibility to use gels and mixture of gels to create 3D shapes.

A quick search on the internet reveals that the most popular methods used to obtain gelatinous structure is by using agar-agar or sodium alginate. With kits bought on the internet and with components used in gastronomy, we quickly started trying to produce gels. We first used sodium alginate which is used in food as a thickener, stabilizer and gelling agent. Sodium

alginate, the sodium salt of alginic acid extracted from brown seaweed (Phaeophyta) is soluble in water and forms hydrogels in the presence of divalent cations, like Ca^{2+} , through cation binding⁶. In the field of molecular gastronomy, sodium alginate is used to create spheres. There are two methods which differ based on the calcium content in the product to be encapsulated in the gel. When the substance contains no calcium, sodium alginate is added and the substance is "cooked" in a bath of calcium. The reverse (we talk then of external spherification) is preferred when the substance contains calcium ions. In this case substance is cooked in a sodium alginate bath and the gelation reaction stops when the spheres are removed. Using sodium alginate is not the only way to obtain spheres with gels. They are also obtained with agar-agar, a product extracted from certain species of red seaweeds^{7,8}. This substance is used in very small quantities and has practically no taste nor color. It is a perfect vegetable binder and gelling agent to replace animal gelatin. There is a multitude of recipes in which agar-agar⁹ is used to produce jams, fruit jellies, flans or pastries... The gel is formed when the agar-agar diluted in water is heated to 90°C and then cooled to a temperature of about 40°C. To make spheres, drops of hot agar-agar solution are formed and left in a "cold" not water-miscible liquid, typically oil, forming gel spheres.

In cooking, sodium alginate or agar-agar gels are often employed to form spheres and straight fibers (spaghetti). In this study, we investigate whether it is possible to realize more complex shapes such as a helical filament with those gels using the tools in our kitchens. We have a set of utensils to make homemade pasta. To obtain fusilli which has a spindle shape similar to the one we want to make, the dough is extruded through a pasta die with ad-hoc perforations^{10,11}. Agar-agar and alginate before gelation are far too liquid compared to pasta dough to use the same technique. A second method that can be used at home is based on a combination of pasta paddles used to roll pasta, each giving a unique shape and texture. One of the paddles has a groove that looks like a screw channel. It appeared that placing a strand of alginate solution in the groove prior to immersing in a calcium bath was very promising solution. After a few hours, it was quite easy to peel off the gel. Based on this first observation, we present two new meth-

ods to generate flexible helices made of sodium alginate or a mixture of alginate with agar-agar. These methods consist in casting an alginate solution (eventually added with agar) in a helical mold prior to immersing it in a bath of calcium lactate. The first section details the methods to produce helices made of different hydrogels. Then, we present the helices resulting from these methods along with a characterization of their mechanical properties. In particular we measure the deformation of the helices when hanged vertically from which we deduced their Young’s modulus. Finally, we discuss how these results compare with previous measurements obtained with same hydrogels and give some perspectives to these methods.

II. EXPERIMENTAL METHODS

A. Mold fabrication

To reproduce and optimize the groove geometry, we 3D printed molds with helicoidals grooves (see Fig.1) using a polylactide filament, also known as PLA. The typical geometry of the molds is shown in Fig. 1. In this work, we used eleven molds with different geometric parameters which are detailed in table I.

In a second step, we improved the device by adding a removable sheath that can be placed around the first mold. The sheaths are also made in 3D printing and have a slightly larger diameter than the diameter D of the mold. This technique allows the use of the most liquid gels.

B. Protocol for the gels

In this work, we focused on two different types of gels: pure sodium alginate and a mixture of sodium alginate with agar-agar. As we have seen in the introduction, sodium alginate can form a gel either by immersing the solution in a calcium ion bath or by immersing a fluid rich in calcium ion in an alginate bath. Both methods were tested but we will present experiments performed with the first method (dipping sodium alginate in a calcium ion bath). The following sections describe the preparations of the different solutions and the method followed to obtain the helices.

1. Method used to obtain sodium alginate helices

Different concentrations of sodium alginate were used to prepared the solution. We used three concentrations: 20, 30 and 40 g/L. All products are food grade compounds and were obtained from QUIMICA M.G. The sodium alginate powder was first dissolved in water (pH 6) at ambient temperature until all lumps have disappeared. Drops of food coloring were then added to the solution. The colors are used to identify the

Mold	ℓ_m [mm]	D [mm]	R [mm]	p [mm]
1 H20-6	24	20	2.5	6
2 H15-7	30	15	2	7
3 H10-6	24	10	2	6
4 H11-7	30	11	2	7
5 H8-7	30	8	2	7
6 H10-5	30	10	2	5
7 H8-5	30	8	2	5
8 H15-5	30	15	2	5
9 H10-10	30	10	2	10
10 H8-10	30	8	2	10
11 H15-10	30	15	2	10

TABLE I. Geometric parameters of the molds used to make the helices. ℓ_m : length, D: diameter, R: depth of the groove, p: pitch.

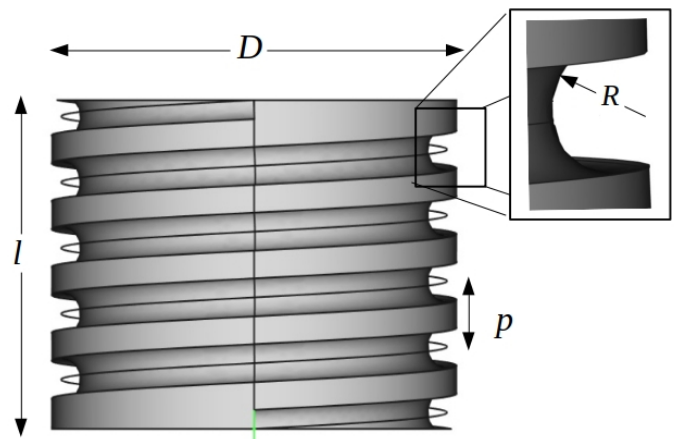


FIG. 1. Sketch of the molds. They were first drawn with autocad and then printed with a 3D printer. D: diameter of the mold, ℓ : height of the mold, R groove depth and p: pitch.

sodium alginate concentration used in the preparation: green, yellow and blue for respectively 20, 30 and 40 g/L.

For concentrations above 20 g/L, the solution is sufficiently viscous so that the groove can be filled without the liquid leaking out. A syringe is used to place the solution into the groove and once filled, the mold is immersed for 5 minutes into the calcium lactate bath (20 g/L). The mold is removed from the bath and washed with clean water. To prevent the drying of the gel, the mold is then placed in an air-tight box for 10 hours. This duration is chosen to ensure that the gelling process has occurred throughout the whole section of the helix.

For the 20g/L sodium alginate solution the process should be slightly modified, as the solution flows very easily and drains out of the mold before gelation begins. In these cases, the molds are immersed in the alginate solution and placed in the freezer for a time, in such a way as to allow the solution to begin to solidify, but not com-

pletely. Once the desired solidification point is reached, the excess sodium alginate is removed from the outside of the mold with the help of a spatula and immediately immersed in the calcium lactate bath.

2. Helices obtained by mixing agar-agar and sodium alginate

Two protocols can be used to obtain a mixture of agar-agar and alginate gels. For the first protocol, the sodium alginate solution has to be heated up to 90°C before adding the agar-agar. The solution is stirred until the agar-agar is completely dissolved. This phase takes typically no more than two minutes. When the solution cools down an agar-agar gel forms and embeds the alginate. For the second protocol, a hot agar-agar solution, with twice the desired final concentration, *i.e.* 20 g/L agar-agar, is mixed with the same volume of a 40 g/L alginate solution. In this way, a final solution of 10 g/L of agar-agar and 20 g/L of alginate is obtained. There are no significant differences between the gels obtained with both methods.

We carried out rheological measurements (rotational rheometer Anton Paar MCR 501 with a cone-plane geometry) to confirm that the sodium alginate molecules are not affected by the heat. Figure 2 shows the results for a solution of 20 g/L of sodium alginate, which is heated for 10 minutes at different temperatures and then cooled again. We see that the rheological property is not affected by the different heating conditions. The alginate solution shows, whatever the treatment, a rheofluidizing behavior for shear rates above 10 s⁻¹.

When this agar gel is immersed in a calcium bath, the alginate reacts and allows to fix the shape we set. We have used this property to make helices. For this, the still warm agar-agar alginate mixture is placed in a syringe. A tube is connected and the solution is injected into the tube. The tube is then placed under cold water or left on the table. After a few minutes, a gel forms in the tube. The syringe is then emptied and filled with air and the tube reconnected. The injection of air allows the agar gel to come out. The gel keeps the shape of the tube and is then deposited inside the groove. The mold is then immersed in the calcium lactate solution.

The helices that we will characterize in the following were made with an alginate concentration of 20 g/L and agar concentrations of 10 and 20 g/L.

3. Measurements of the elastic properties using indentation testing

The mechanical response of the sample is examined using nanoindentation testing (Anton-Paar). The method consists of driving a spherical tip of radius $R_i = 200\mu\text{m}$ into the sample with a controlled penetration depth, δ . The spherical tip assumed to be perfectly rigid is initially in contact with the surface of the gel. Then the

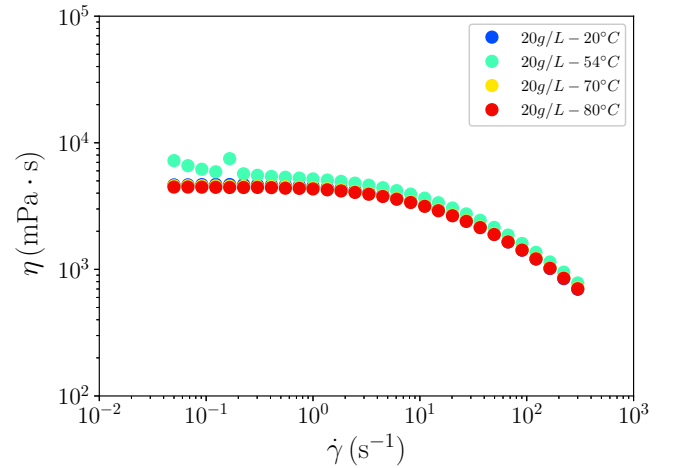


FIG. 2. Dynamic viscosity η as a function of the shear rate $\dot{\gamma}$ for sodium alginate solutions with a concentration of 20 g/L kept at different temperatures during 10 min.

tip is driven inside the sample with a controlled loading speed of 10 $\mu\text{m}/\text{min}$ until a maximum load is reached. The applied force, F , is measured as a function of the penetration depth, δ . Measurements are reported in figure 3 for several samples. The resulting loading curves are well fitted by the Hertz contact law revealing the elastic behaviour of the material:

$$F = \frac{4E\sqrt{R_i}}{3(1-\nu^2)}\delta^{3/2}, \quad (1)$$

where E is the Young's modulus of the sample and ν is the Poisson's ratio of the sample ($\nu = 0.4$ for alginate gels¹²). The fit of the indentation-force curve with a Hertz law provides an estimation of the Young's modulus of alginate gels.

III. EXPERIMENTAL RESULTS

Figure 4 presents three helices made with the same mold and pure alginate gels of increasing concentrations. We note that the alginate gel adopts a well-defined helical shape whatever the alginate concentration. A helix obtained with a mixture of alginate and agar-agar gels is shown in Fig. 5. Here again the gel filament is observed to be well-shaped as a helix. One of the main differences between the two methods is that the second produces filaments of circular cross section.

The helices are flexible and may experience large deformations when handled vertically. By assuming that they deformed like elastic springs, we will show that the Young's modulus of the gel can be estimated from the measurement of this deformation. This simple test will allow to compare the mechanical properties of different gels. We will first describe the procedure and the result

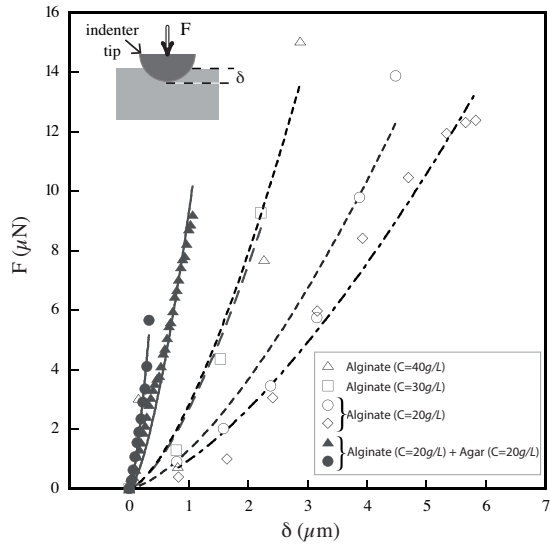


FIG. 3. Elastic behaviour of alginate gels using indentation testing. The load, F , applied to the materials is plotted as a function of the penetration depth, δ , of the indenter tip. Each series of dots was obtained on a specific sample. Lines: fit of the data by the Hertz contact law given by Eq.(1).



FIG. 5. Helix made of alginate (20 g/L) and agar-agar (10 g/L) suspended under its own weight. The white bar represents 5 mm.

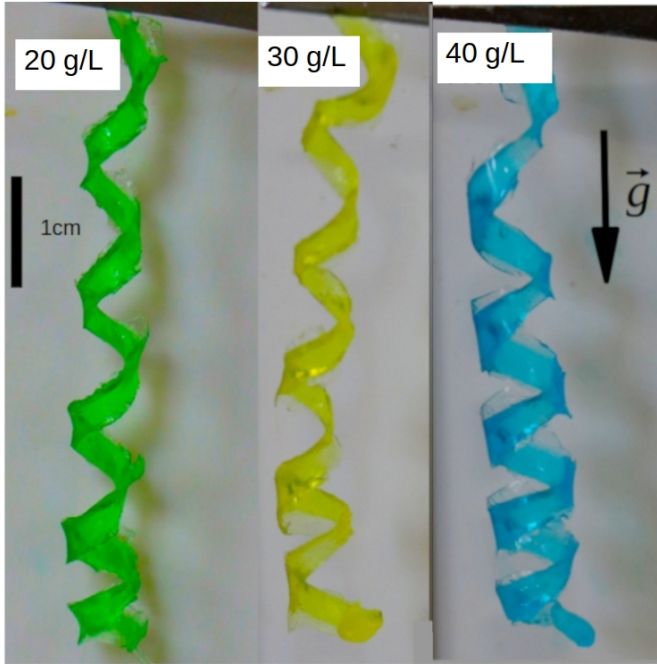


FIG. 4. Three alginate helices suspended under their own weight. The alginate concentration is respectively from left to right 20, 30, 40 g/L. The length of the vertical bar is 1 cm.

for alginate gels. The method will be finally extended to gel obtained by mixing agar-agar and alginate.

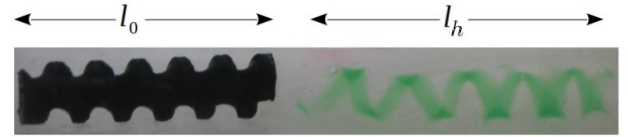


FIG. 6. Helical shaped gel corresponding to a 20 g/L sodium alginate concentration immersed in water. The black mold used to shape the helical filament stands at the left. The mold length is $\ell_m = 30$ mm and corresponds to mold 5 in Tab.I.

A. Measurement of ℓ_0

In order to measure the length of the helical filament in the absence of stress, the helices were left to sediment slowly in a container filled with water. In this way, contact forces with a solid substrate or stresses due to gravity are reduced and ℓ_0 can be estimated with a better precision. Figure 6 shows the picture of one helix made of alginate along with its mold. We see that the helix matches quite well the groove of the mold: the pitch, the length and the diameter are very close. Figure 7 displays ℓ_0 normalized by the length ℓ_m of the mold used to fabricate the helix. In the case of pure alginate, the rest length of the helix is slightly larger than the mold length whatever the concentration in alginate. The inset of Fig. 7 show the same measurements for helices made of alginate ($c = 20$ g/L) and agar-agar gels with two concentrations. Despite the fact that results are more dispersed with gel

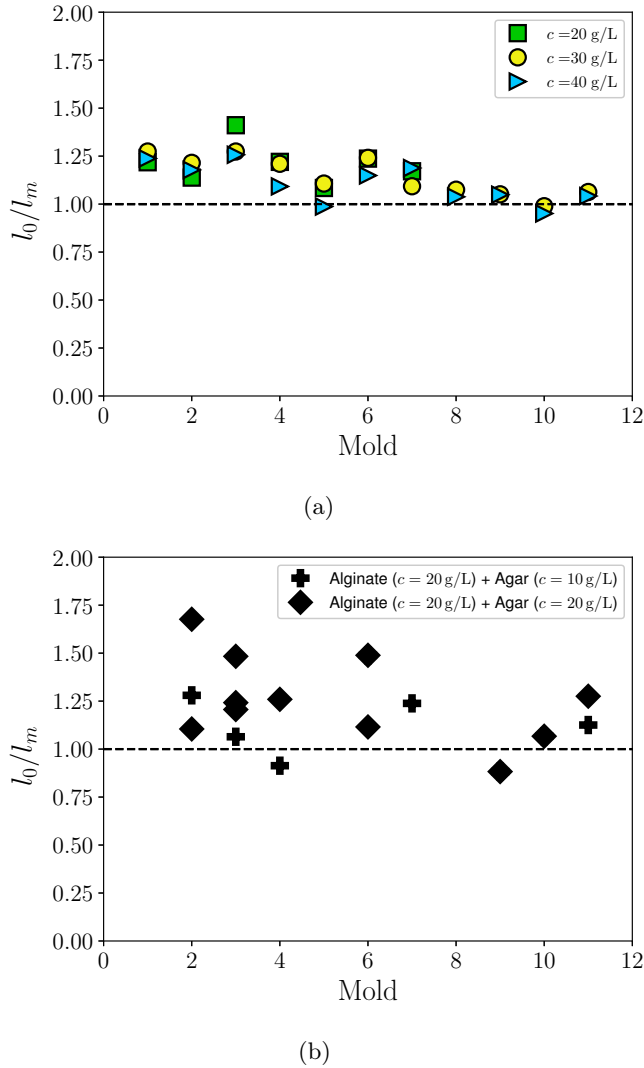


FIG. 7. (a) Estimated length ℓ_0 of pure alginate helices after sedimentation in a water normalized by the length ℓ_m of the mold. Green squares, yellow circles and blue triangles correspond to helices obtained with respectively a concentration of 20, 30 and 40 g/L in alginate. The indices of the x-axis refer to mold reference given in Table I. (b) Same results for helices obtained with a mixture of alginate at 20 g/L and agar-agar gels. Crosses and diamonds represent measurements made for agar-agar concentrations of 10 and 20 g/L respectively.

mixtures, the ratio ℓ_0/ℓ_m is also generally larger than one in this case.

B. Measurement of ℓ

The helices were hung by one end and pictures were taken. The new length ℓ of the helices deformed by their own weight was then estimated. Figure 8 shows the vertical deformation of hanging helix $(\ell - \ell_0)/\ell_0$ made of pure alginate as a function of the helix diameter D and

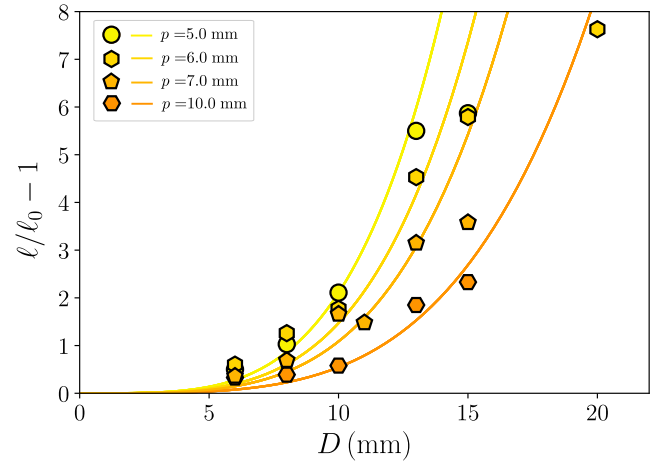


FIG. 8. Normalized vertical deformation of the helix hanging on its own weight as a function of the helix diameter D for different pitches p . The helices are made with a concentration $c = 30$ g/L in alginate. Solid lines correspond to the predictions of Eq.(4) for $E = 40$ kPa.

for different pitches p . Note that the length of the helix trapped by the clamp was subtracted from ℓ_0 . We observe that for a given concentration in alginate and a given filament radius, the normalized deformation of the helix increases with its diameter and reduces with its pitch. Thus, diameter and pitch appear to be critical parameters for the mechanical properties of these flexible helices.

C. Model

In order to rationalize our observations, we develop a mechanical description of the helix deformation under its own weight. The helix is assumed to be made of a filament with a cylindrical cross section (diameter d), an elastic material of density ρ and Young modulus E . At rest, the diameter, pitch and length of the helix are respectively D , p and ℓ_0 . The stiffness k of the helix is given by the relation¹³

$$k = \frac{Ed^4p}{8D^3\ell_0}, \quad (2)$$

and the total mass M of the helical filament writes

$$M = \rho \frac{\pi d^2 \ell_0}{4} \sqrt{1 + \left(\frac{\pi D}{p}\right)^2}. \quad (3)$$

When the helix is submitted to its own weight, it extends by a length $\Delta\ell = \ell - \ell_0$ which expresses $\Delta\ell = \frac{Mg}{2k}$. Combining these equations, we get a prediction for the normalized vertical length $\ell/\ell_0 = (\ell_0 + \Delta\ell)/\ell_0$

$$\frac{\ell}{\ell_0} = 1 + \frac{\pi \rho g \ell_0 D^3 \sqrt{1 + \left(\frac{\pi D}{p}\right)^2}}{E d^2 p}. \quad (4)$$

In order to compare this prediction with our measurements, we can plot the vertical deformation $(\ell - \ell_0)/\ell_0$ as a function of the quantity $\mathcal{P} = \pi \rho g \ell_0 D^3 \sqrt{1 + \left(\frac{\pi D}{p}\right)^2} / d^2 p$. A linear variation of the data will indicate an elastic regime. We can then get the elastic modulus as the inverse of the slope of the data.

D. Estimations of Young's modulus

We first present the estimation of the Young's modulus from the vertical deformation of gel helices. Figure 9 shows all the data for the vertical deformation of alginate helices as a function of the parameter \mathcal{P} . For pure alginate helices, we observe that the vertical deformation increases with \mathcal{P} . When $\mathcal{P} < 150$ kPa, the increase is linear and it becomes sub-linear for larger values of \mathcal{P} . The solid line shows the best fit of the experiments for $\mathcal{P} < 150$ kPa with a linear law. The inverse of the slope of the linear fit provides an estimation for the Young's modulus of the alginate $E = 36 \pm 4$ kPa. These data do not reveal any clear dependency of E with the alginate concentration. Results for helices made of a mixture of alginate and agar-agar gels are shown in the inset of Fig.9. The dispersion of these results reflects the greater difficulty to fabricate these helices. Indeed, the wrapping of a soft and fragile gel filament into a helical mold is a difficult step. Nevertheless, we observe a linear variation of the helices deformation as a function of the parameter \mathcal{P} and no strong impact of the agar-agar concentration. We also observe that the elastic limit is reached for higher stresses than before. The best fit of these data with a linear law gives an estimation of the Young's modulus for mixed gels $E = 270 \pm 20$ kPa. The double gelation process produces stiffer helices.

On the other hand, we wanted to see if the Young's modulus value obtained by a macroscopic deformation measurement and based on the assumption that the helices behave mechanically like springs are close to the values that can be measured by local measurements. In this way, indentation testing was performed on a fragment of a pure alginate helix. The fit of the indentation-force curve with a Hertz law (see Fig. 3) provides an estimation of the Young modulus of the alginate gels as: $E = 92 \pm 40$ kPa, and no clear dependencies with the concentration in alginate can be observed. In addition, the Young modulus estimated from indentation-force curve on a fragment of alginate and agar-agar helix gives $E = 873 \pm 301$ kPa. These local measurements performed on different samples are

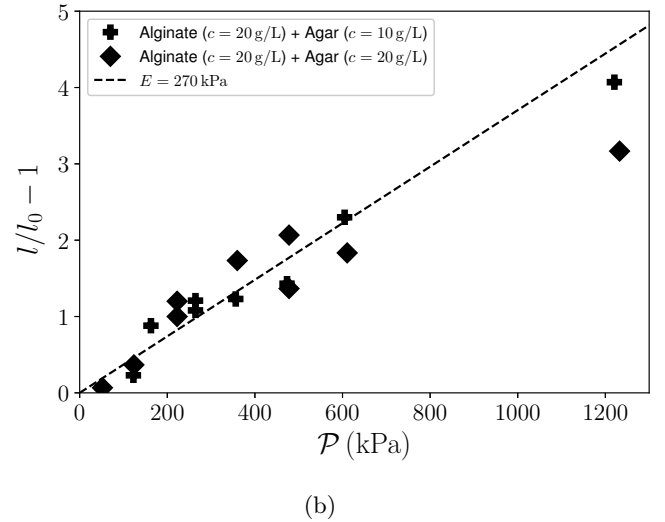
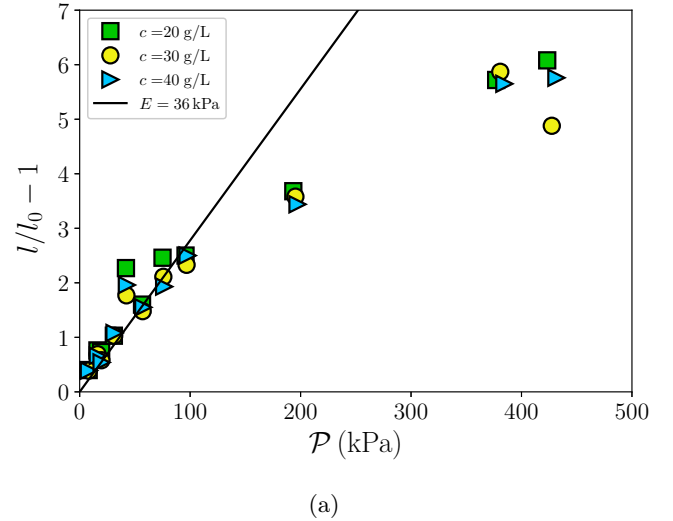


FIG. 9. (a) Normalized vertical deformation of alginate helices hanging on their own weight $(\ell - \ell_0)/\ell_0$ as a function of the parameter $\mathcal{P} = \pi \rho g \ell_0 D^3 \sqrt{1 + \left(\frac{\pi D}{p}\right)^2} / d^2 p$ for different concentration c in alginate. (b) Same results for helices made of alginate ($c = 20$ g/L) and agar-agar ($c = 10$ g/L for crosses and $c = 20$ g/L for diamonds).

in good agreement with the measurements based on material indentation and the vertical deformation of the helical filament. This proves that this inexpensive and easy to implement method is valid for characterising soft gels. Note that the significant uncertainty in the measurements is due to the low stiffness of the gel and therefore the low value of the Young's modulus obtained at the resolution limit of the instrument.

IV. DISCUSSION

The mechanical properties of alginate hydrogels determined here above can be compared with previous measurements. Compression experiments realized on alginate beads prepared in the same range of concentration provide a Young's modulus between 5 to 300 kPa, in relative agreement with our observations^{14,15}. However, these experiments show a slight increase of E with the alginate and the cation concentrations in contrast with our experiments where the impact of the gel concentration is not significant. Other studies show that the mechanical properties of alginate hydrogels also depend on the ionic strength of the solutions and the storage environment^{16,17}. Thus, it would be interesting to explore in further detail how these parameters impact the mechanical characteristics of our hydrogels helices.

The second method allows to obtain helices with a regular section and a very clean shape. The difficulty we have encountered with this method concerns the wrapping phase around the mold. In order not to break the agar filament, it is necessary that this operation be done slowly and carefully, especially for the smaller diameter molds. We have not quantitatively characterized the bending strength of the agar-agar alginate mixture but this appears to be a point of improvement of our method.

As noted in the introduction, it is also possible to create a gel by dipping a solution containing calcium ions in an alginate bath. We then talk of external spherification. We also test the possibility of using this method to stiffen agar-agar and make it take a new shape. First, calcium lactate (30g/L) is dissolved in a warm liquid solution containing 10 g/L of agar-agar. We then use the same method as before. After cooling, the agar-agar is rolled onto a mold and then dipped into solution containing 5g/L of sodium alginate (instead of a calcium lactate bath as previously). With these conditions, we do not obtain a gel strong enough to keep the desired shape. However, we believe that this approach is promising but requires further study to optimize the different concentrations to be used.

V. CONCLUSION AND PERSPECTIVES

In this study, we propose two "recipes" allowing to shape filaments made of hydrogels into helices, the first with pure alginate and the second with a combination of alginate and agar-agar gels. These methods enable the creation of helices with a wide range of length, pitch and diameter and different gel concentrations. We also propose a simple test to characterize the mechanical properties of these helices: measuring their vertical deformation when they hang under their own weight. Assuming that the helix behaves as an elastic spring, we estimate the Young's modulus of these objects and we find estimations in good agreement with independent indentation tests as well as the estimations given in the

literature. Finally, this work proves that it is possible to impose a natural curvature to gels which have very low rigidity. This opens new avenues to fabricate complex shapes with soft gels, a fact that might be of interest for soft robotics, bio-encapsulation and 3D printing techniques.

Indeed, soft robotics are now looking for new manufacturing methods in order to shape biocompatible and biodegradable materials and reduce its environmental footprint¹⁸. On the other end, alginate encapsulation of molecules of biological significance, such as enzymes, drugs, macromolecule, microorganism or stem cells is a well-established method^{19,20}. Our study shows that more complex shapes can be obtained from the mixture of two different gels which could have applications in this field by increasing for example the surface to volume ratio and increasing the exchanges between the capsule and the environment. An interesting perspective of this work would be to transfer these methods to 3D printing. The idea would be to extrude a filament made of alginate and agar gels directly in a removable and porous matrix immersed in a calcium lactate bath. This possibility of shaping the flexible filament into the desired shape will be considered in future work.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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