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Cation-induced folding of alginate-bearing bilayer gels: an unusual example of spontaneous folding along the long axis

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The spontaneous folding of flat gel films into tubes is an interesting example of self-assembly. Typically, a rectangular film folds along its short axis when forming a tube; folding along the long axis has been seen only in rare instances when the film is constrained. Here, we report a case where the same free-swelling gel film folds along either its long or short axis depending on the concentration of a solute. Our gels are sandwiches (bilayers) of two layers: a passive layer of cross-linked *N*,*N*′-dimethylacrylamide (DMAA) and an active layer of cross-linked DMAA that also contains chains of the biopolymer alginate. Multivalent cations like Ca^{2+} and Cu^{2+} induce these bilayer gels to fold into tubes. The folding occurs instantly when a flat film of the gel is introduced into a solution of these cations. The likely cause for folding is that the active layer stiffens and shrinks (because the alginate chains in it get cross-linked by the cations) whereas the passive layer is unaffected. The resulting mismatch in swelling degree between the two layers creates internal stresses that drive folding. Cations that are incapable of cross-linking alginate, such as Na^+ and Mg^{2+}, do not induce gel folding. Moreover, the striking aspect is the direction of folding. When the Ca^{2+} concentration is high (100 mM or higher), the gels fold along their long axis, whereas when the Ca^{2+} concentration is low (40 to 80 mM), the gels fold along their short axis. We hypothesize that the folding axis is dictated by the inhomogeneous nature of alginate-cation cross-linking, *i.e.*, that the edges get cross-linked before the faces of the gel. At high Ca^{2+} concentration, the stiffer edges constrain the folding; in turn, the gel folds such that the longer edges are deformed less, which explains the folding along the long axis. At low Ca^{2+} concentration, the edges and the faces of the gel are more similar in their degree of cross-linking; therefore, the gel folds along its short axis. An analogy can be made to natural structures (such as leaves and seed pods) where stiff elements provide the directionality for folding.

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Introduction

Polymer hydrogels that undergo changes in their shape have been of great interest to many laboratories,[1–3] including our own.[4,5] One such change in shape is where a rectangular film or strip of a gel folds, *i.e.*, rolls up, to form an open tube. Such folding of gels has been induced in response to external stimuli such as temperature,[4,6,7] pH,[8] or light,[9] or in response to specific aqueous solutes such as enzymes.[5] Gels that fold usually have a hybrid design, such as two different layers combined in a simple sandwich or bilayer, or a more complex pattern of one gel in another created by photolithography or 3-D printing.[1–3] In all cases, the individual gels in the hybrid are made by the polymerization of monomers and cross-linkers into a network held by covalent bonds. The natural inspiration for the study of shape-changing gels comes from plant-based structures such as seed pods, awns, and leaves, all of which exhibit the ability to change their shape in specific scenarios.[10–12]

Folding of gel strips can occur in two ways, as shown in Fig. 1. Initially, the gel is a rectangular strip with a length (long edge) ℓ, a width (short edge) w and a thickness t. "Short-side" folding occurs along the short axis, as shown in Fig. 1a (Panels a2–a5). Here, the two short edges approach each other and eventually meet, or one edge wraps under the other (Panels a4 and a5). The final tube has a width equal to the strip width w. The alternative is "long-side" folding, where the gel folds along its long axis, as shown in Fig. 1b (Panels b2–b5). In this case, the two long edges approach each other until one goes under

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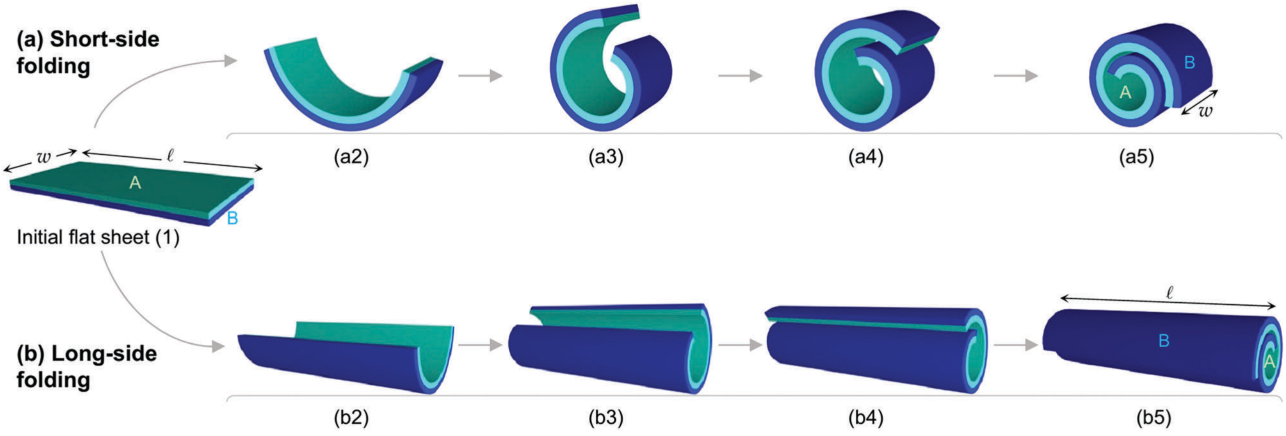


Fig. 1 Two modes for folding of a flat rectangular sheet. Initially, the sheet has a length ℓ and a width w. The schematics in (a) depict short-side folding, where the folding occurs along the short axis of the sheet. Ultimately, the sheet rolls up into a tube with a final width w. The schematics in (b) depict long-side folding, where the folding takes place along the long axis of the sheet. Here, the sheet rolls up into a tube with a final length ℓ. The sheets in this study are bilayer gels, composed of two gel layers A and B. The A layer forms the inner surface of the folded tubes in all cases.

the other (Panels b4 and b5). The final tube has a length equal to the strip length ℓ. The radii of the final tubes in the two cases will depend on the number of folds, but generally the short-side tube will have a larger radius than the long-side tube. To our knowledge, most previous reports of gel folding,[1–3] including our own,[4,5] have all been instances of short-side folding. This is explained as follows. A gel, being a solid object with finite stiffness, requires energy to bend and fold.[7,13] This bending energy increases with curvature, *i.e.*, it takes more energy to form a tighter fold. Since long-side folding implies tighter folds (higher curvature), it requires more bending energy than short-side folding. For this reason, short-side folding has always been the preferred mode for gels that were allowed to freely swell in water. The only reports of long-side folding[14–17] are for gels or inorganic membranes that were constrained in some way prior to folding, *e.g.*, by placing on a substrate or by clamping on one end. Such constraints introduce a bias into the folding direction – *e.g.*, the substrate restricts diffusion of water into the gel in one direction.[17] In such cases, once folding is initiated along a certain axis, the behavior continues even when the constraint is removed.

In this paper, we describe free-swelling gels that can exhibit both long-side and short-side folding depending on variables including the composition of the gel and the external conditions. To our knowledge, this is one of the first detailed studies on gels that spontaneously fold in solution along their long side. Moreover, we demonstrate instances where the same gel shows long-side folding under one condition (*i.e.*, one concentration of a solute) and short-side folding at a different condition (*i.e.*, a different concentration of the same solute). Our gels are sandwiches (bilayers) of two layers, each of which is a cross-linked polymer. The active layer additionally contains an uncross-linked biopolymer (alginate) solubilized in it. Alginate is an anionic polysaccharide[18] that has been extensively studied by various scientists,[19–26] including our lab.[27–30] Solutions of alginate are known to get gelled upon addition of certain divalent cations. In the present case, when a strip of our alginate-bearing hybrid gel is placed in a solution of multivalent cations like Ca^{2+}, Fe^{3+}, or Cu^{2+} (all of which are known to cross-link alginate chains[18,22]), the gel strip undergoes folding. Cations that do not cross-link alginate, such as Na^{+} and Mg^{2+}, do not induce gel folding. Such specific-ion-induced folding has not been reported previously, to our knowledge, and is one of the significant aspects of this study. Why do the gels fold in response to the ions, and why does folding occur along the long-side? These are the two key questions from this study, and we put forward a mechanism that addresses each of them. The present study is likely to inspire the design of new folding gels with control over the folding direction. This in turn will provide the underpinnings for the design of sophisticated soft robots and machines.

Results and discussion

The hybrid gels here are bilayers (sandwiches) of two different gels, designated A and B in Fig. 2, each of 0.15 mm thickness. *N*,*N*′-Dimethylacrylamide (DMAA) was used as the monomer and *N*,*N*′-methylene bis(acrylamide) (BIS) as the cross-linker for both gels. First the liquid precursor to Gel B, consisting of 10 wt% DMAA and BIS at 1.3 mol% relative to DMAA, was spread between two glass slides (see Experimental section for details) and cross-linked by exposure to ultraviolet (UV) light. Thereafter, the precursor to Gel A was introduced above Gel B. The Gel A precursor had the same concentrations of DMAA and BIS and additionally had dissolved sodium alginate (Alg). The Alg used here was of medium molecular weight (∼100 kDa) and was at a concentration of 2 wt%. Upon UV cross-linking, the hybrid gel strip was formed, with final dimensions of 25 mm (ℓ) × 9 mm (w) × 0.3 mm (t). The structure of the A/B hybrid gel is shown in Fig. 2: note that Gel B (demarcated as DMAA) is the passive layer and Gel A (denoted as DMAA/Alg) is the active layer. Alginate chains in Gel A are not physically or chemically cross-linked; however, these linear chains are trapped within the chemically cross-linked DMAA network.

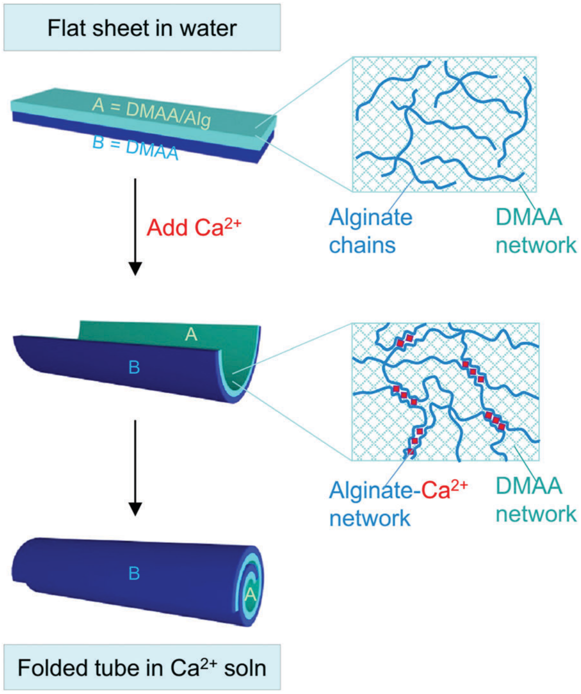


Fig. 2 Schematics of the composition and nanostructure of our folding bilayer gels. Gel B (bottom layer, dark blue) is a network of DMAA. Gel A (top layer, cyan) is a DMAA network in which alginate (Alg) chains are solubilized as discrete entities, as shown by the inset. The A/B sheet is flat in water. When multivalent cations like Ca^{2+} are added, the sheet folds into a tube, typically along the long-side. The Ca^{2+} ions cross-link the Alg chains in Gel A, making it a double network (DMAA + Alg/Ca^{2+}), as shown by the inset. In the folded tube, Gel A is always on the inside and Gel B on the outside.

The A/B hybrid gels are flat sheets initially and remain so when added to water containing salt (NaCl). However, a shape change occurs when the same gel is introduced into an aqueous solution containing a multivalent cation like Ca^{2+} (Fig. 2). Such cations are known to cross-link linear alginate chains into three-dimensional networks.[18] Thus, when the A/B gel comes into contact with Ca^{2+}, the B layer (DMAA) will be unaffected, but the A layer (DMAA/Alg) will become a ''double-network'' gel, *i.e.*, one having two different interpenetrating networks: a chemically cross-linked DMAA network and a physical network of alginate chains cross-linked by Ca^{2+} cations. This additional cross-linking in the A and not the B layer causes the hybrid gel sheet to roll up into a tube (Fig. 2). The precise mechanism for this shape change will be discussed later. As depicted in Fig. 2, the A layer is always on the inside of the tube while the B layer is on the outside.

We now show results for a range of Ca^{2+} concentrations in solution. For these experiments, identical hybrid gels were placed in solutions containing different concentrations of $CaCl_2$. Each gel was an A/B hybrid with 2 wt% of alginate included in Gel A. Folding occurred at both low and high Ca^{2+}, but with distinct differences, as shown by the photos in Fig. 3. At 40 and 80 mM Ca^{2+}, the gel folds along its short side (Fig. 3a and b) as indicated by the schematics. The end result in each case is a tube with an inner diameter ∼3 mm, an outer diameter ∼7 mm, and a width of 9 mm (which was the width w of the initial flat strip). In contrast, at 100 and 200 mM Ca^{2+} (and at all higher Ca^{2+} concentrations), the gel folds along its long side (Fig. 3c and d). The final tube in these cases has a length of 20 mm (which was the length ℓ of the initial gel strip), an inner diameter ∼2 mm, and an outer diameter ∼4 mm. Thus, the diameters of the long-side tube are much smaller than that of the short-side tube. In all the tubes, the B layer is on the outside. Regarding the kinetics of the shape change, both long- and short-side folding occurred rapidly and were completed within 10 to 30 s after the flat gel was introduced into a given solution. All the photos shown in this paper were taken after the folded structure had reached a steady state, *i.e.*, showed no further changes. In many cases, for the sake of clarity, the photo of the folded gel was taken after it was carefully removed from solution and placed on a flat sheet of paper.

Next, we varied the concentration of alginate (Alg) in Gel A. All other parameters of the gel were identical to those used above, and folding was studied in 500 mM of Ca^{2+}. The results are shown by the photos in Fig. 4. At low Alg concentrations (0.25 and 0.5 wt%), the gel does not fold completely, but it partially curls. The curl is along the short-side at 0.25 wt% Alg

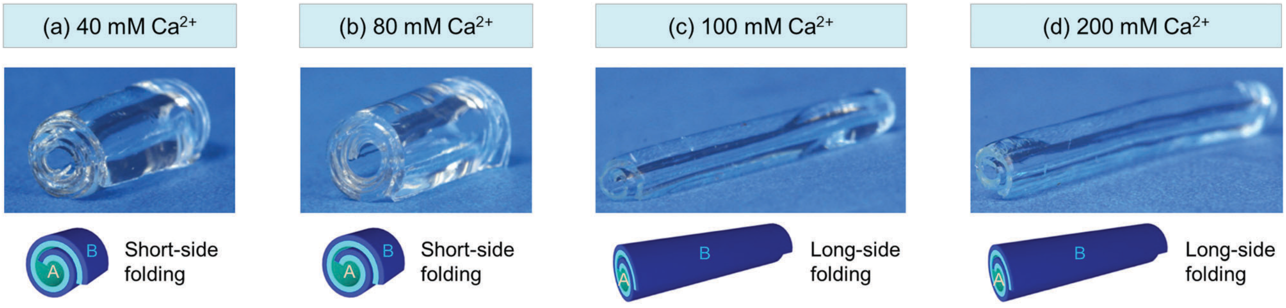


Fig. 3 Folding of gel sheets at various Ca^{2+} concentrations. Each sheet is an A/B hybrid (A = DMAA + 2 wt% Alg; B = DMAA). The sheets show short-side folding at low Ca^{2+}, as indicated by the photos for (a) 40 mM and (b) 80 mM Ca^{2+}, with the folded tubes having an inner diameter (ID) ∼ 3 mm, and an outer diameter (OD) ∼ 7 mm. On the other hand, the sheets show long-side folding at high Ca^{2+}, as indicated by the photos for (c) 100 mM and (d) 200 mM Ca^{2+}, with the folded tubes having an ID ∼ 2 mm, and an OD ∼ 4 mm.

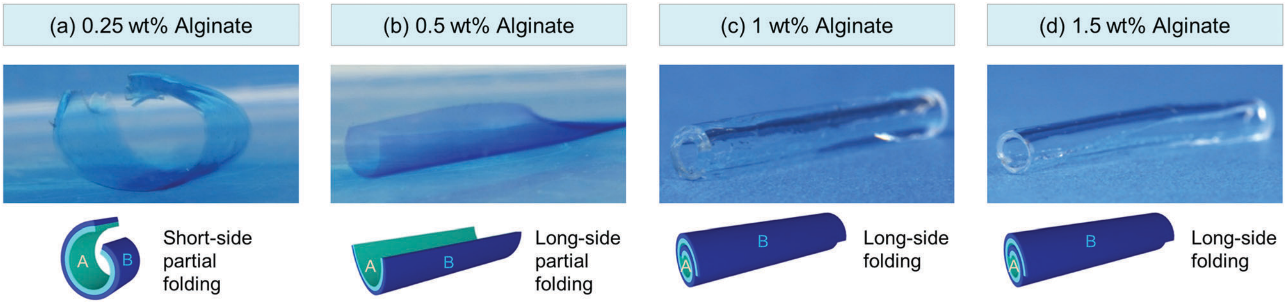


Fig. 4 Folding of gel sheets at various alginate (Alg) concentrations. The sheets are A/B hybrids (A = DMAA + varying Alg; B = DMAA) and are studied in 500 mM Ca^{2+}. (a) For 0.25 wt% Alg, the sheet shows partial short-side folding. (b) For 0.5 wt% Alg, the sheet shows partial long-side folding. For higher Alg, *i.e.*, (c) 1 wt% and (d) 1.5 wt%, the sheets completely fold long-side into tubes having an ID ∼ 2 mm, and an OD ∼ 4 mm.

(Fig. 4a) and along the long side at 0.5 wt% Alg (Fig. 4b). At 1 wt% Alg and higher, the curling of the gel is complete (along the long-side) and it forms a closed tube (Fig. 4c and d). Thus, the results show that sufficient Alg is needed in Gel A to induce folding. We also examined a different alginate with a higher molecular weight (∼500 kDa). Hybrid gels were made with the above alginate at 1 wt% in Gel A and with an identical Gel B. These gels were tested in 500 mM Ca^{2+} and they also folded long-side, much like the gels in Fig. 4c. This suggests that our folding results have broad applicability to any kind of alginates.

We then varied the type of cation in solution. In all cases, the chloride salt of the cation was added to a solution containing an A/B hybrid gel strip that had 2 wt% Alg in Gel A. We found folding to occur only in the case of multivalent cations that are known to cross-link Alg,[18–22] including Ca^{2+}, Sr^{2+}, Cu^{2+}, and Fe^{3+} (Fig. 5). In contrast, with cations that are known to have no effect on Alg,[18] including monovalent ones like Na^+ and K^+ as well as the divalent Mg^{2+}, no folding was observed regardless of the cation concentration. In other words, any cation that converts Alg sols into gels, also induces folding of our Alg-bearing hybrid gels. Fig. 5 also shows that the tightness of the fold, *i.e.*, the inner diameter of the tube varies with cation type. The results are for 500 mM of the respective salt, and at this concentration, all the gels exhibit long-side folding into tubes. For each cation, photos of the overall folded tube as well as optical micrographs of the tube's cross-section are shown. The inner diameter of the tube is largest at 1.9 mm in Ca^{2+} whereas it is the smallest at 0.9 mm in Fe^{3+}. The outer diameter of the tube remains constant at around 4 mm regardless of the cation. Smaller inner diameters arise when the tube makes multiple tight folds, *i.e.*, it indicates a greater propensity of the flat strip to curl inwards.

To gain insight into the folding of our hy brid gels with different cations, we conducted rheological experiments. For this, we focused on Gel A (DMAA + 2 wt% Alg) and studied its rheology before and after ionic cross-linking. First, we placed a disc of Gel A in water, allowed it to equilibrate for 24 h, and then measured its dynamic moduli as a function of frequency. As expected, the dynamic rheological response is characteristic of a gel (Fig. 6a), with the elastic modulus G' being much greater than the viscous modulus G'', and both G' and G'' being independent of frequency.[5,28] The value of G' is the gel modulus, and it is a measure of the gel's stiffness. For Gel A

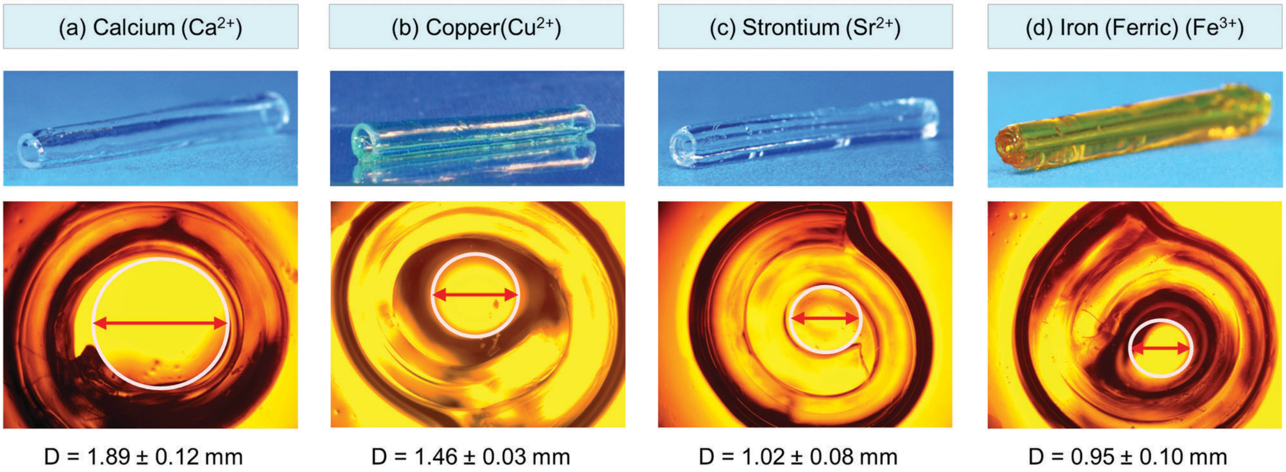


Fig. 5 Folding of gel sheets in various multivalent cations. The sheets are A/B hybrids (A = DMAA + 2% Alg; B = DMAA) and are studied in 500 mM of (a) Ca^{2+}; (b) Cu^{2+}; (c) Sr^{2+}; and (d) Fe^{3+}. In all cases, the tubes fold long-side, as shown by the photos on top. The optical micrographs on the bottom show the tube cross-sections, allowing the ID (arrows) of each tube to be resolved. The ID decreases from (a) to (d) as can be seen from the values.

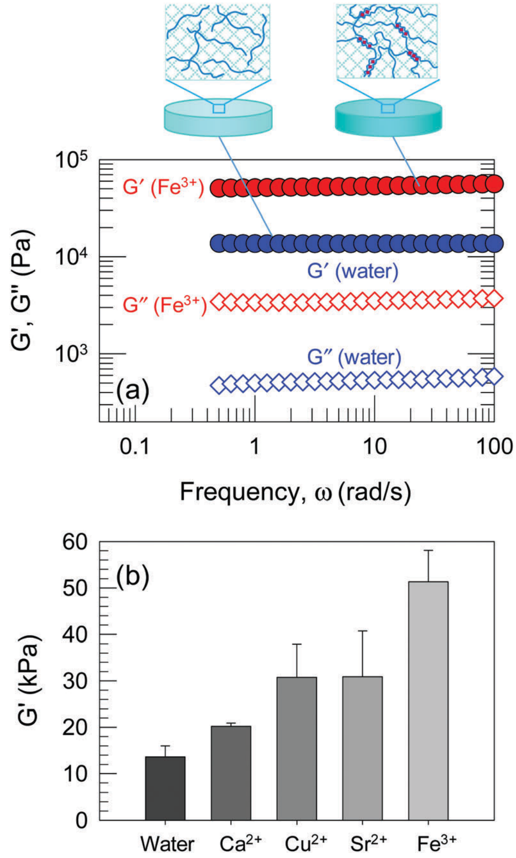


Fig. 6 Rheology of Gel A before and after cross-linking by multivalent cations. (a) Plot of the elastic modulus G' and the viscous modulus G'' as functions of frequency are shown for Gel A (DMAA + 2 wt% Alg) in water (blue symbols) and in 500 mM Fe^{3+} (red symbols). The moduli are independent of frequency for both cases, but the values are higher when the Alg is cross-linked by the cations, as indicated by the schematics. (b) The value of the gel modulus G' is plotted against the type of cation (all studied at 500 mM). Error bars represent the standard deviations across multiple measurements.

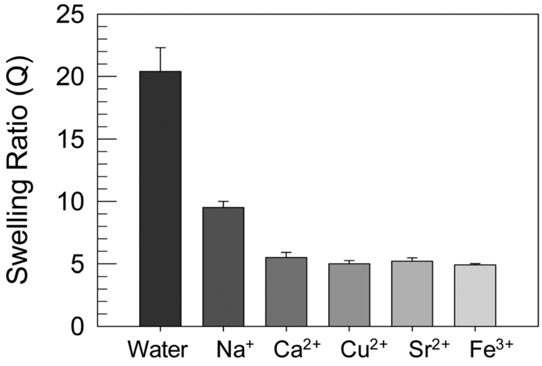


Fig. 7 Extent of swelling of Gel A in the presence of various multivalent cations. The swelling ratio Q (*i.e.*, mass of swollen gel divided by mass of dry gel) is plotted (each cation is at 500 mM). Error bars represent the standard deviations across multiple measurements.

in water (*i.e.*, when the Alg in the gel is not ionically cross-linked), G' is ∼14 kPa, and this is similar for a gel of DMAA alone that does not contain Alg. Next, we placed discs of Gel A in solutions of different cations (each at 500 mM), allowed the gels to equilibrate for 24 h, and then conducted the same rheological experiment. The dynamic rheology is qualitatively the same (Fig. 6a), but both moduli are higher when the Alg chains are cross-linked by the cations. Note that, the gel is now a double network, *i.e.*, with co-existing networks of DMAA and Alg. Thus, the increase in gel modulus G' correlates with the increase in cross-link density, which is as expected. Fig. 6b shows that cross-linking with Ca^{2+} increases G' to ∼20 kPa, while Sr^{2+} and Cu^{2+} give G' ∼30 kPa, and Fe^{3+} causes G' to rise to ∼50 kPa. Thus, the gel modulus (stiffness) follows the order: $Fe^{3+} > Sr^{2+} \sim Cu^{2+} > Ca^{2+}$. Similar trends are seen for the modulus of bulk alginate gels crosslinked by such cations.[20,21] The same order in reverse is seen for the inner radius of the folded tube in Fig. 5, *i.e.*, the stiffer the gel, the tighter the tube.

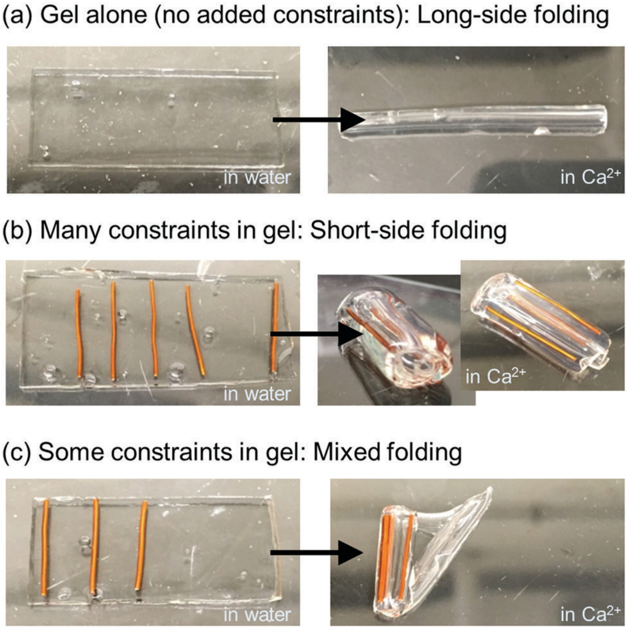
Next, we studied the extent of gel swelling since this parameter is expected to correlate inversely with the cross-link density.[24] For this, discs of Gel A (DMAA + 2 wt% Alg) were placed in different solutions and weighed at steady state. The weight of the swollen gel was then divided by the weight of the dry gel to give the swelling ratio Q. Fig. 7 shows that the highest Q (∼20) is for the gel in deionized water. When the same gel is placed in 500 mM Na^+, it swells less ($Q \sim 9$). This is because the ions screen the electrostatic repulsions between the anionic Alg chains in the gel and thereby reduce the osmotic driving force for swelling. Finally, when the gel is in solutions of multivalent cations (each at 500 mM concentration), the swelling is further reduced by about 40% ($Q \sim 5$). This reduction in gel volume can be attributed to the cross-linking of Alg by the cations. However, we did not find any significant differences in Q for the different cations. Also, for comparison, we also studied the swelling of Gel B (DMAA only). In this case, the Q in Na^+ and Ca^{2+} are about the same ($Q \sim 9$). This confirms that in Ca^{2+}, Gel B is much more swollen than Gel A.

Now, we turn to the crucial questions from this study, which are: (1) why does folding occur at all; and (2) why does it typically occur along the long-side. With regard to the first question, our empirical finding is that folding requires the presence of multivalent cations like Ca^{2+} and Fe^{3+} that cross-link the Alg chains in Gel A. The extra cross-links in Gel A make this layer 2–3 fold stiffer relative to its initial level (Fig. 6), and concomitantly, the denser network of Gel A shrinks by about 40% (Fig. 7). Gel B is unaffected by the same cations. Such selective stiffening and shrinking of one layer in the A/B gel, creates internal stresses that drive the rectangular strip to curl and fold.[4,5] In all cases, the shrunken layer of Gel A forms the interior of the folded tube while the unperturbed layer of Gel B forms the exterior of the tube. In previous studies on the folding of anisotropic gels (*e.g.*, induced by stimuli such as temperature), the same aspects are observed.[1–5] That is, folding occurs when one layer of a gel shrinks relative to the other, and the more swollen layer forms the exterior of the folded structure. We therefore conclude that the mechanism for folding here is analogous to those in previous studies. The key difference in our case is the cause for the swelling mismatch, which is by ionic cross-linking of one layer. Such use of specific ions to trigger gel folding has not been reported before.

Next comes the question regarding the axis of folding. As noted, here we have the unusual case of long-side folding in freely-swelling gel sheets. This result is observed regardless of the aspect ratio of the sheet. That is, we made A/B gel strips with different length ℓ and width w dimensions (the thickness t was kept the same at 0.15 mm) and tested these strips in 500 mM Ca^{2+} solutions. Folding occurred along the long side in all cases, as expected from Fig. 3. Overall, our experiments reveal that long-side folding requires sufficiently high concentrations of Alg in the gel (at least 1 wt%) as well as of the crosslinking cations outside the gel (at least 100 mM). These are important observations, which imply that strong and rapid binding of the Alg chains to the cations (and in turn, their cross-linking) is necessary for long-side folding of the gel.

We hypothesize that the cation-induced cross-linking of the Gel A layer is not homogeneous; rather, we expect the cations to bind preferentially along the edges of the rectangular sheet (Fig. 8a). That is, as the cations diffuse into Gel A through both the edges and the faces, they will contact the edges from both above and from the side, whereas they will only contact the face of the gel from above. This point is valid for any diffusing solute and has been made by Ionov *et al.*[17] in the context of gel folding. Due to these "edge effects", the edges of the Gel A layer will become more cross-linked and hence more stiff compared to the face and interior of this layer (Fig. 8b). If so, we postulate that the edges will act as constraints during the onset of folding.[16] In other words, either the longer or the shorter edges of the sheet must bend to permit folding of the sheet. The longer edges will pose a more stringent constraint due to their greater length, and so it is the shorter edges that will bend and curl. This favors long-side folding (Fig. 8c). On the whole, we explain long-side folding as arising due to "edge effects", *i.e.*, a preferential stiffening of the edges of the gel sheet.

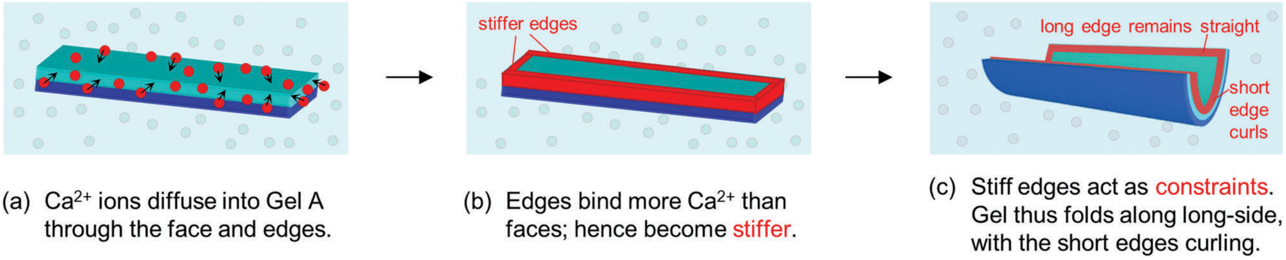
Support for this folding mechanism comes from two ancillary experiments. First, we worked with an A/B gel sheet (composition as in Fig. 3) that shows long-side folding in 500 mM Ca^{2+} (Fig. 9a). Then, in an identical gel sheet, we embedded pieces of copper wire (0.5 mm in diameter) parallel to the short edges. In 500 mM Ca^{2+}, this sheet folds along its short side (Fig. 9b) because the copper wires act as additional constraints that hinder bending along the long side. The implications from this result are that the folding direction is dictated by the presence (or absence) of constraints. Indeed, such constraints can permit the gel to overcome its typical (chemically driven) tendency. An analogy can be drawn to natural materials like leaves and seed pods, where stiff elements (*e.g.*, made from cellulose or chitin) act as mechanical


(a) Gel alone (no added constraints): Long-side folding

(b) Many constraints in gel: Short-side folding

(c) Some constraints in gel: Mixed folding

Fig. 9 Mechanical constraints can dictate the direction for gel folding. The gels are A/B hybrids (A = DMAA + 2% Alg; B = DMAA) and are flat sheets in water while they are folded in 500 mM of Ca^{2+}. (a) The gel by itself shows long-side folding. (b) Copper wires (orange) are placed in the gel parallel to the short-side. The gel then displays short-side folding. (c) Copper wires are placed parallel to the short-side over half of the gel. In this case, the part of the gel with the wires folds short-side, while the rest of the gel tries to fold long-side.



(a) Ca^{2+} ions diffuse into Gel A through the face and edges.

(b) Edges bind more Ca^{2+} than faces; hence become stiffer.

(c) Stiff edges act as constraints. Gel thus folds along long-side, with the short edges curling.

Fig. 8 Proposed mechanism for long-side folding of A/B hybrid gels in solutions of cations like Ca^{2+}. The Gel B (DMAA) layer is shown in dark blue and the Gel A (DMAA + Alg) layer in cyan, as in Fig. 2. (a) When the flat gel sheet is placed in the Ca^{2+} solution, the cations diffuse into Gel A and bind to the Alg chains, which results in the Alg getting cross-linked. The ions will enter the gel through the top face as well as the edges, as shown by the arrows. Ions adjacent to the gel are shown in red and the rest of the ions in grey. Due to the multiple contacts, the edges of Gel A will preferentially bind more Ca^{2+}. (b) This will result in the edges becoming stiffer compared to the faces, as shown by the red color. (c) The stiff edges will act as constraints that oppose gel folding. Folding is favored because Gel B is more swollen than Gel A, but for folding to occur, either the long or short edges will have to bend and curl. Due to their smaller length, it will be the short edges that curl, resulting in long-side folding.

constraints that dictate the directionality of the shape change.[10–12] Interestingly, if we altered the placement of copper wires such that the wires only covered one part of the sheet (Fig. 9c), the gel shows a more complex folding behavior: it tries to fold along its short side for the part with the wires and along its long side over the remainder of the gel.

In a second experiment, we incubated our A/B gel in a solution containing a chelated form of calcium (Ca-EDTA) and a slow-releasing acid, D-glucono-δ-lactone (GdL). GdL is gradually hydrolyzed into acid over a few hours, and as this acid contacts the chelator, free Ca^{2+} is released into solution. We chose our conditions such that the total Ca^{2+} released would be 500 mM. Over a period of several hours, the A/B gel did fold, but this folding occurred along the short side, despite the high Ca^{2+}. This experiment shows how the kinetics of Alg/Ca^{2+} binding are important in regards to the folding direction. Our hypothesis is that rapid kinetics are necessary to induce the stiffening of edges relative to the faces of the Gel A layer. Slow kinetics, on the other hand, will lead to more homogeneous crosslinking of Gel A, and if so, the A/B sheet will fold along its short side, as is typically the case for gel folding. This also explains the effects of Alg and Ca^{2+} concentrations: when these are low, the kinetics of Alg/Ca^{2+} binding is slowed down, and this leads to short-side folding.

Conclusions

Regarding the design of shape-changing gels

In this study, we have put forward a new design for shape-changing A/B bilayer gels. One layer (Gel A) contains the biopolymer alginate (Alg). The two layers are otherwise identical, being made from the same monomer. In the presence of multivalent ions like Ca^{2+}, the Alg chains in Gel A get cross-linked and so this layer stiffens and shrinks. The resulting mismatch in swelling degree between the two layers creates internal stresses that induce the bilayer gel to transform from a flat sheet to a folded tube. The above design for a folding gel is very simple and unique. Most existing designs use chemically distinct monomers to form the layers of a bilayer (or similarly patterned) gel. Also, the trigger that induces folding of our gels is the concentration of multivalent cations, and this trigger is also quite unconventional, as compared to oft-studied triggers like pH and temperature. We speculate that the above design and concept can be generalized. That is, a folding gel can be made by incorporating a different uncross-linked polymer, instead of Alg, in one layer of a bilayer gel. Then, if a chemical moiety was to cross-link this polymer, we predict that this moiety would cause the overall gel to fold. Many new kinds of folding gels can be created using the above design template.

Regarding the folding direction

The other interesting finding from this study is the spontaneous folding of gels along their long side, which happens when there is sufficient Alg in Gel A and sufficient multivalent cations in solution. To our knowledge, this is one of the first examples of gels spontaneously exhibiting long-side folding in solution. In other cases of folding involving free-swelling gels, including our own previous studies, the gels folded along their short side. To explain long-side folding, we have hypothesized a mechanism in which the edges of Gel A become cross-linked before the faces. This inhomogeneous cross-linking creates stiff edges, which act as constraints that hinder folding. The gel then folds in such a way that the longer edges remain straight while the shorter edges bend and curl. This explains the folding along the long axis. If the Alg and Ca^{2+} concentrations are reduced, the cross-linking of Gel A becomes more homogeneous, and folding then occurs along the short side. Also, if we deliberately introduce mechanical constraints, we can induce the gel to fold in a direction different from its natural tendency. In this regard, an analogy can be made to natural structures (such as leaves and seed pods) where stiff elements provide the directionality for folding.

Materials and methods

Materials

The monomer dimethylacrylamide (DMAA) and the crosslinker *N*,*N*′-methylene bis(acrylamide) (BIS), were purchased from Sigma-Aldrich. Two sodium alginates were purchased: one of medium molecular weight (∼100 kDa) from Sigma-Aldrich,[30] and the other from Carbomer with a molecular weight ∼500 kDa.[28,29] The UV initiator Irgacure 2959 was obtained from BASF. All gels were prepared using deionized (DI) water. Ethylene-diamine-tetraacetic acid, disodium salt (EDTA), strontium chloride hexahydrate, calcium chloride dihydrate, iron(III) chloride, copper(II) chloride, and D-glucono-δ-lactone (GdL) were purchased from Sigma Aldrich.

Preparation of hybrid gels

All monomers were dissolved in DI water, which had been degassed for 30 min to remove dissolved oxygen. The precursor to Gel A was prepared by mixing 10 wt% DMAA, BIS at a concentration of 1.3 mol% relative to DMAA, the required concentration of alginate, and 0.5 wt% Irgacure 2959 (photoinitiator). The Gel B precursor was prepared by mixing all the above except for the alginate. The hybrid gel was prepared using a reaction cell consisting of two glass slides (75 mm × 50 mm) separated by a spacer.[5] Gel B precursor was first introduced into the reaction cell with two sides of double sided tape used as a spacer. The cell was then exposed to UV light at 365 nm from a MelodySusie 36W UV lamp. Within about 10 min of UV exposure, Gel B was formed. The cell was then disassembled and the spacer height was increased by using two additional pieces of double sided tape. Gel A precursor was then introduced into the reaction cell and polymerized by UV light, as above, to form Gel A. The overall A/B hybrid was then peeled off and cut into strips. All strips had a thickness (t) of 0.3 mm. Typical strips had dimensions of 25 mm (ℓ) × 9 mm (w). Strips with other dimensions were also tested, including 50 × 16, 30 × 10, 30 × 15, 25 × 12, and 25 × 25 (all in mm). For the experiments in Fig. 9, pieces of copper wire (24 gauge, 0.5 mm in diameter) were cut and placed in the Gel A precursor (parallel to the short side) prior to UV exposure.

Rheological studies

Experiments were performed at 25 °C on an AR2000 stress-controlled rheometer (TA Instruments). Gel samples were cut into discs of diameter 20 mm and thickness 1 mm, and were studied using 20 mm parallel plates. A solvent trap was used to minimize drying of the samples. Dynamic stress-sweeps were first performed to identify the linear viscoelastic (LVE) region of the sample. Dynamic frequency sweeps were then conducted at a constant strain amplitude within the LVE of the sample.

Swelling measurements

For these experiments, gels were cut into discs of diameter 20 mm and thickness 1 mm. The discs were immersed in a given solution and allowed to swell for 24 h. Next, the discs were blotted dry using a Kimwipe and weighed. Afterwards, the discs were freeze-dried and weighed again. The swelling ratio Q was calculated as the ratio between the swollen and dry weights.

Conflicts of interest

There are no conflicts to declare.

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