

Highly stretchable and tough hydrogels

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Hydrogels are used as scaffolds for tissue engineering¹, vehicles for drug delivery², actuators for optics and fluidics³, and model extracellular matrices for biological studies⁴. The scope of hydrogel applications, however, is often severely limited by their mechanical behaviour⁵. Most hydrogels do not exhibit high stretchability; for example, an alginate hydrogel ruptures when stretched to about 1.2 times its original length. Some synthetic elastic hydrogels^{6,7} have achieved stretches in the range 10–20, but these values are markedly reduced in samples containing notches. Most hydrogels are brittle, with fracture energies of about 10 J m^{-2} (ref. 8), as compared with $\sim 1,000 \text{ J m}^{-2}$ for cartilage⁹ and $\sim 10,000 \text{ J m}^{-2}$ for natural rubbers¹⁰. Intense efforts are devoted to synthesizing hydrogels with improved mechanical properties^{11–18}; certain synthetic gels have reached fracture energies of 100–1,000 J m^{-2} (refs 11, 14, 17). Here we report the synthesis of hydrogels from polymers forming ionically and covalently crosslinked networks. Although such gels contain $\sim 90\%$ water, they can be stretched beyond 20 times their initial length, and have fracture energies of $\sim 9,000 \text{ J m}^{-2}$. Even for samples containing notches, a stretch of 17 is demonstrated. We attribute the gels' toughness to the synergy of two mechanisms: crack bridging by the network of covalent crosslinks, and hysteresis by unzipping the network of ionic crosslinks. Furthermore, the network of covalent crosslinks preserves the memory of the initial state, so that much of the large deformation is removed on unloading. The unzipped ionic crosslinks cause internal damage, which heals by re-zipping. These gels may serve as model systems to explore mechanisms of deformation and energy dissipation, and expand the scope of hydrogel applications.

Certain synthetic hydrogels exhibit exceptional mechanical behaviour. A hydrogel containing slide-ring polymers can be stretched to more than 10 times its initial length⁶; a tetra-poly(ethylene glycol) gel has a strength of $\sim 2.6 \text{ MPa}$ (ref. 7). These gels deform elastically. An elastic gel is known to be brittle and notch-sensitive; that is, the stretchability and strength decrease markedly when samples contain notches, or any other features that cause inhomogeneous deformation¹⁹. A gel can be made tough and notch-insensitive by introducing energy-dissipating mechanisms. For example, a fracture energy of $\sim 1,000 \text{ J m}^{-2}$ is achieved with a double-network gel, in which two networks—one with short chains, and the other with long chains—are separately crosslinked by covalent bonds¹¹. When the gel is stretched, the short-chain network ruptures and dissipates energy²⁰. But the rupture of the short-chain network causes permanent damage. After the first loading, the gel does not recover from this damage; thus, on subsequent loadings, the fracture energy is much reduced²¹. To enable recoverable energy-dissipating mechanisms, several recent works have replaced the sacrificial covalent bonds with non-covalent bonds. In a gel with a copolymer of triblock chains, for example, the end blocks of different chains form glassy domains, and the midblocks of different chains form ionic crosslinks²². When the gel is stretched, the glassy domains remain intact, while the ionic crosslinks break and dissipate energy. The ionic crosslinks then re-form during a time

interval after the first loading²². Recoverable energy dissipation can also be effected by hydrophobic associations^{17,18}. When a gel made with hydrophobic bilayers in a hydrophilic polymer network is stretched, the bilayers dissociate and dissipate energy; on unloading, the bilayers re-assemble, leading to recovery¹⁷. However, previous studies along these lines have demonstrated fracture energy comparable to, or lower than, that of the double-network gels.

We have synthesized extremely stretchable and tough hydrogels by mixing two types of crosslinked polymer: ionically crosslinked alginate, and covalently crosslinked polyacrylamide (Fig. 1). An alginate chain comprises mannuronic acid (M unit) and guluronic acid (G unit), arranged in blocks rich in G units, blocks rich in M units, and blocks of alternating G and M units. In an aqueous solution, the G blocks in different alginate chains form ionic crosslinks through divalent cations (for example, Ca^{2+}), resulting in a network in water—an alginate hydrogel. By contrast, in a polyacrylamide hydrogel, the polyacrylamide chains form a network by covalent crosslinks. We dissolved powders of alginate and acrylamide in deionized water. (Unless otherwise stated, the water content was fixed at 86 wt %.) We added ammonium persulphate as a photo-initiator for polyacrylamide, and N,N-methylenebisacrylamide as the crosslinker for polyacrylamide. After degassing the solution in a vacuum chamber, we added N,N,N',N'-tetramethylethylenediamine, at 0.0025 the weight of acrylamide, as the crosslinking accelerator for polyacrylamide, and calcium sulphate slurry ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as the ionic crosslinker for alginate. We poured the solution into a glass mould measuring $75.0 \times 150.0 \times 3.0 \text{ mm}^3$, covered with a 3-mm-thick glass plate. The gel was cured in one step with ultraviolet light for 1 hour (with 8 W power and 254 nm wavelength at 50 °C), and was then left in a humid box for 1 day to stabilize the reactions. After the curing step, we took the gel out of the humid box, and removed water on its surfaces using N_2 gas for 1 minute.

The gel was glued to two polystyrene clamps, resulting in specimens measuring $75.0 \times 5.0 \times 3.0 \text{ mm}^3$. All mechanical tests were performed in air, at room temperature, using a tensile machine with a 500-N load cell. In both loading and unloading, the rate of stretch was kept constant at 2 min^{-1} . We stretched an alginate–polyacrylamide hybrid gel to >20 times its original length without rupture (Fig. 2a,b). The hybrid gel was also extremely notch-insensitive. When we cut a notch into the gel (Fig. 2c) and then pulled it to a stretch of 17, the notch was dramatically blunted and remained stable (Fig. 2d). At a critical applied stretch, a crack initiated at the front of the notch, and ran rapidly through the entire sample (Supplementary Movie 1). Large, recoverable deformation is demonstrated by dropping a metal ball on a membrane of the gel fixed by circular clamps (Supplementary Movie 2). On hitting the membrane, the ball stretched the membrane greatly and then bounced back. The membrane remained intact, vibrated, and recovered its initial flat configuration after the vibration was damped out. A ball with greater kinetic energy, however, caused the membrane to rupture after large deformation (Supplementary Movie 3).

The extremely stretchable hybrid gels are even more remarkable when compared with their parents, the alginate and polyacrylamide

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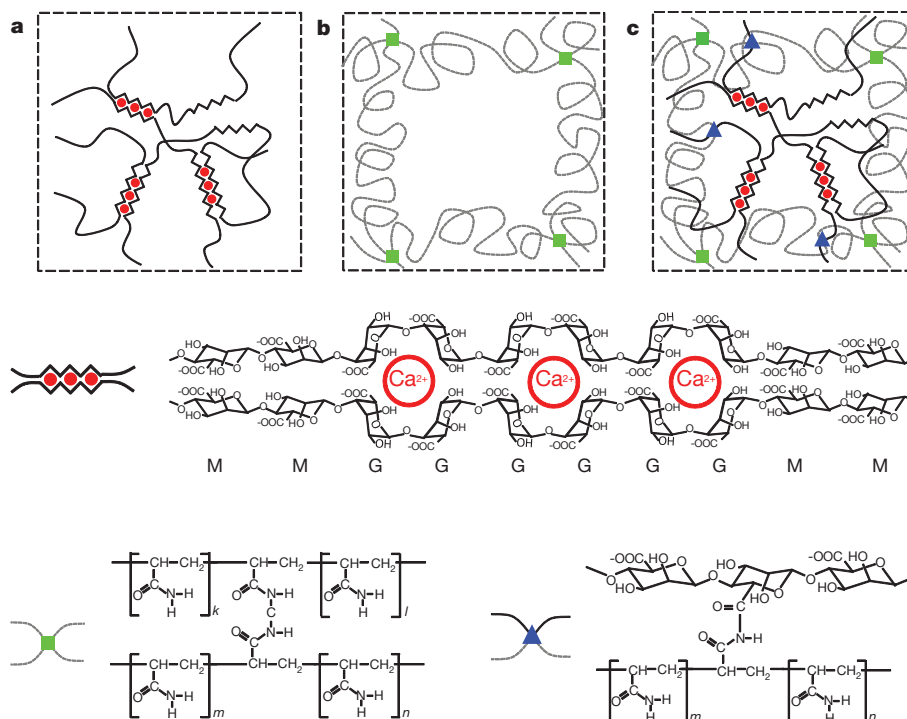
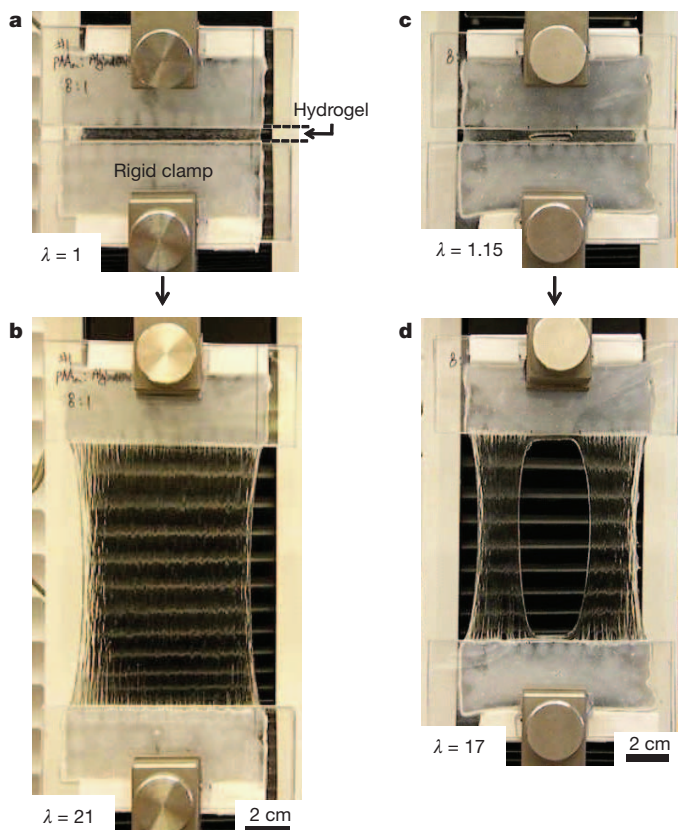


Figure 1 | Schematics of three types of hydrogel. **a**, In an alginate gel, the G blocks on different polymer chains form ionic crosslinks through Ca^{2+} (red circles). **b**, In a polyacrylamide gel, the polymer chains form covalent crosslinks through N,N-methylenebisacrylamide (MBAA; green squares). **c**, In an alginate-polyacrylamide hybrid gel, the two types of polymer network are intertwined, and joined by covalent crosslinks (blue triangles) between amine

groups on polyacrylamide chains and carboxyl groups on alginate chains. Materials used were as follows: alginate (FMC Biopolymer, LF 20/40); acrylamide (Sigma, A8887); ammonium persulphate (Sigma, A9164); MBAA (Sigma, M7279); N,N,N',N'-tetramethylethylenediamine (Sigma, T7024); $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma, 31221); ultraviolet lamp (Hoefer, UVC 500).



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hybrid gel was 29 kPa, which is close to the sum of the elastic moduli of the alginate and polyacrylamide gels (17 kPa and 8 kPa, respectively). The stress and stretch at rupture were, respectively, 156 kPa and 23 for the hybrid gel, 3.7 kPa and 1.2 for the alginate gel, and 11 kPa and 6.6 for the polyacrylamide gel. Thus, the properties at rupture of the hybrid gel far exceeded those of either of its parents.

Hybrid gels dissipate energy effectively, as shown by pronounced hysteresis. The area between the loading and unloading curves of a gel gives the energy dissipated per unit volume (Fig. 3b). The alginate gel exhibited pronounced hysteresis and retained significant permanent deformation after unloading. In contrast, the polyacrylamide gel showed negligible hysteresis, and the sample fully recovered its original length after unloading. The hybrid gel also showed pronounced hysteresis, but the permanent deformation after unloading was significantly smaller than that of the alginate gel. The pronounced hysteresis and relatively small permanent deformation of the hybrid gel were further demonstrated by loading several samples to large values of stretch before unloading (Fig. 3c).

After the first loading and unloading, the hybrid gel was much weaker if the second loading was applied immediately, and recovered somewhat if the second loading was applied 1 day later (Fig. 3d and Supplementary Fig. 1). We loaded a sample of the hybrid gel to a stretch of 7, and then unloaded the gel to zero force. The sample was

Figure 2 | The hybrid gel is highly stretchable and notch-insensitive. **a**, A strip of the undeformed gel was glued to two rigid clamps. **b**, The gel was stretched to 21 times its initial length in a tensile machine (Instron model 3342). The stretch, λ , is defined by the distance between the two clamps when the gel is deformed, divided by the distance when the gel is undeformed. **c**, A notch was cut into the gel, using a razor blade; a small stretch of 1.15 was used to make the notch clearly visible. **d**, The gel containing the notch was stretched to 17 times its initial length. The alginate/acrylamide ratio was 1:8. The weight of the covalent crosslinker, MBAA, was fixed at 0.0006 that of acrylamide; the weight of the ionic crosslinker, CaSO_4 , was fixed at 0.1328 that of alginate.

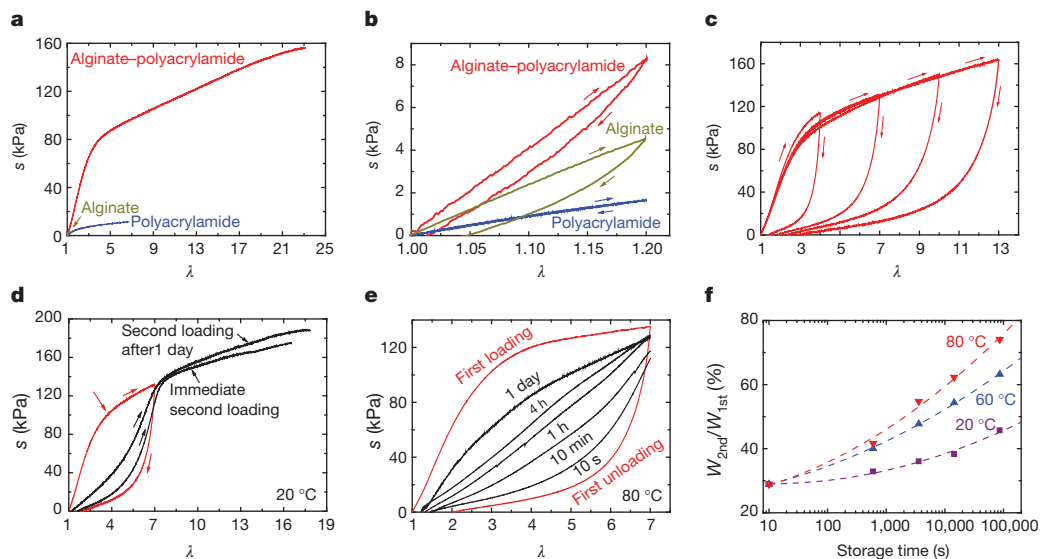


Figure 3 | Mechanical tests under various conditions. **a**, Stress–stretch curves of the three types of gel, each stretched to rupture. The nominal stress, s , is defined as the force applied on the deformed gel, divided by the cross-sectional area of the undeformed gel. **b**, The gels were each loaded to a stretch of 1.2, just below the value that would rupture the alginate gel, and were then unloaded. **c**, Samples of the hybrid gel were subjected to a cycle of loading and unloading of varying maximum stretch. **d**, After the first cycle of loading and

unloading (red curve), one sample was reloaded immediately, and the other sample was reloaded after 1 day (black curves, as labelled). **e**, Recovery of samples stored at 80 °C for different durations, as labelled. **f**, The work of the second loading, W_{2nd} , normalized by that of the first loading, W_{1st} , measured for samples stored for different durations at different temperatures. The alginate/acrylamide ratio was 1:8 for **a** and **b**, and 1:6 for **c–f**. Weights of crosslinkers were fixed as described in Fig. 2 legend.

then sealed in a polyethylene bag and submerged in mineral oil to prevent water from evaporating, and stored in a fixed-temperature bath for a prescribed time. The sample was then taken out of storage and its stress–stretch curve was measured again at room temperature. The internal damage was much better healed by storing the gel at an elevated temperature for some time before reloading (Fig. 3e and Supplementary Fig. 2). After storing at 80 °C for 1 day, the work on reloading was recovered to 74% of that of the first loading (Fig. 3f).

We prepared gels containing various proportions of alginate and acrylamide to study why the hybrids were much more stretchable and stronger than either of their parents. When the proportion of acrylamide was increased, the elastic modulus of the hybrid gel decreased (Fig. 4a). However, the critical stretch at rupture reached a maximum at 89 wt % acrylamide. A similar trend was observed for samples with notches (Fig. 4c). The fracture energy reached a maximum value of 8,700 J m⁻² at 86 wt % acrylamide (Fig. 4d). The densities of ionic and covalent crosslinks also strongly affect the mechanical behaviour of the hybrid gels (Supplementary Figs 3, 4), as well as that of pure alginate gels (Supplementary Fig. 5) and pure polyacrylamide gels (Supplementary Fig. 6).

Our experimental findings provide insight into the mechanisms of deformation and energy dissipation in these gels. When an unnotched hybrid gel is subjected to a small stretch, the elastic modulus of the hybrid gel is nearly the sum of those of the alginate and polyacrylamide gels. This behaviour is also suggested by viscoelastic moduli determined for the hybrid and pure gels (Supplementary Fig. 7). Thus, in the hybrid gel the alginate and polyacrylamide chains both bear loads. Moreover, alginate is finely and homogeneously dispersed in the hybrid gel, as demonstrated by using fluorescent alginate and by measuring local elastic modulus with atomic force microscopy (Supplementary Fig. 8). The load sharing of the two networks may be achieved by entanglements of the polymers, and by possible covalent crosslinks formed between the amine groups on polyacrylamide chains and the carboxyl groups on alginate chains (Fig. 1, Supplementary Figs 9, 10). As the stretch increases, the alginate network unzips progressively²³, while the polyacrylamide network remains intact, so that the hybrid gel exhibits pronounced hysteresis and little permanent deformation. As only the ionic crosslinks are broken, and

the alginate chains themselves remain intact, the ionic crosslinks can re-form, leading to the healing of the internal damage.

The giant fracture energy of the hybrid gel is remarkable, considering that its parents—the alginate and polyacrylamide gels—have fracture energies of 10–250 J m⁻² (Supplementary Figs 5, 6). The relatively low fracture energy of a hydrogel comprising a single network with covalent crosslinks is understood in terms of the Lake–Thomas model⁸. When the gel contains a notch and is stretched, the deformation is inhomogeneous; the network directly ahead of the notch is stretched more than elsewhere (Supplementary Fig. 11). For the notch

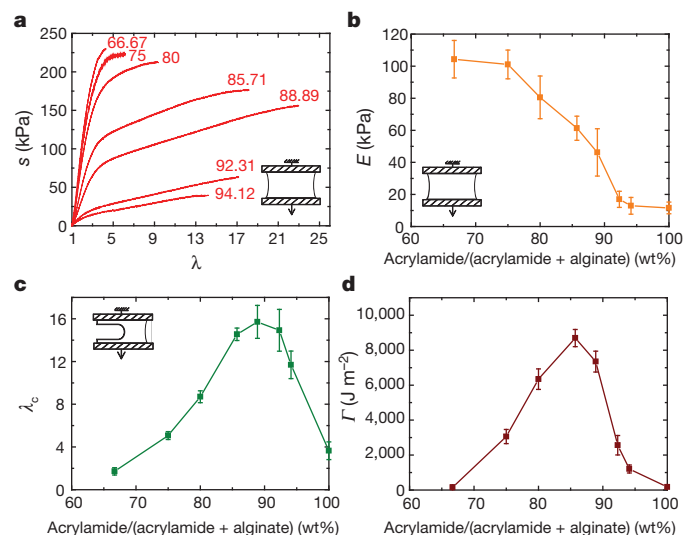


Figure 4 | Composition greatly affects behaviour of the hybrid gel. **a**, Stress–strain curves of gels of various weight ratios of acrylamide to (acrylamide plus alginate), as labelled. Each test was conducted by pulling an unnotched sample to rupture. **b**, Elastic moduli calculated from stress–strain curves, plotted against weight ratio. **c**, Critical stretch, λ_c , for notched gels of various weight ratios, measured by pulling the gels to rupture. **d**, Fracture energy, Γ , as a function of weight ratio. Weights of crosslinkers were fixed as described in Fig. 2 legend. Error bars show standard deviation; sample size $n = 4$.

to turn into a running crack, only the chains directly ahead of the notch need to break. Once a chain breaks, the energy stored in the entire chain is dissipated. In the ionically crosslinked alginate, fracture proceeds by unzipping ionic crosslinks and pulling out chains²⁴. After one pair of G blocks unzip, the high stress shifts to the neighbouring pair of G blocks and causes them to unzip also (Supplementary Fig. 11). For the notch in the alginate gel to turn into a running crack, only the alginate chains crossing the crack plane need to unzip, leaving the network elsewhere intact. In both polyacrylamide gel and alginate gel, rupture results from localized damage, leading to small fracture energies.

That a tough material can be made of brittle constituents is reminiscent of transformation-toughening ceramics, and of composites made of ceramic fibres and ceramic matrices. The toughness of the hybrid gel can be understood by adapting a model well studied for toughened ceramics²⁵ and for gels of double networks of covalent crosslinks^{26,27}. When a notched hybrid gel is stretched, the polyacrylamide network bridges the crack and stabilizes deformation, enabling the alginate network to unzip over a large region of the gel (Supplementary Fig. 11). The unzipping of the alginate network, in its turn, reduces the stress concentration of the polyacrylamide network ahead of the notch. The model highlights the synergy of the two toughening mechanisms: crack bridging and background hysteresis.

The idea that gels can be toughened by mixing weak and strong bonds has been exploited in several ways, including hydrophobic associations¹⁸, particle-filled gels^{7,15} and supramolecular chemistry^{17,22}. The fracture energy of the alginate–polyacrylamide hybrid gel, however, is much larger than previously reported values^{14,17,20,28} for tough synthetic gels (100–1,000 J m⁻²), a finding that we attribute to how the alginate network unzips. Each alginate chain contains a large number of G blocks, many of which form ionic crosslinks with G blocks on other chains when enough Ca²⁺ ions are present¹. When the hybrid gel is stretched, the polyacrylamide network remains intact and stabilizes the deformation, while the alginate network unzips progressively, with closely spaced ionic crosslinks unzipping at a small stretch, followed by more and more widely spaced ionic crosslinks unzipping as the stretch increases.

Because of the large magnitude of the fracture energy and the pronounced blunting of the notches, we ran a large number of experiments to determine the fracture energy, using three types of specimen, as well as changing the size of the specimens (Supplementary Figs 12–16). The experiments showed that the measured fracture energy is independent of the shape and size of the specimens.

Our data suggest that the fracture energy of hydrogels can be greatly increased by combining weak and strong crosslinks. The combination of relatively high stiffness, high toughness and recoverability of stiffness and toughness, along with an easy method of synthesis, make these materials ideal candidates for further investigation. Further development is needed to relate macroscopically observed mechanical behaviour to microscopic parameters. Many types of weak and strong molecular integrations can be used, making hybrid gels of various kinds a fertile area of research. In many applications, the use of hydrogels is often severely limited by their mechanical properties. For example, the poor mechanical stability of hydrogels used for cell encapsulation often leads to unintended cell release and death²⁹, and low toughness limits the durability of contact lenses³⁰. Hydrogels of superior stiffness, toughness, stretchability and recoverability will improve the performance in these applications, and will probably open up new areas of application for this class of materials.

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Supplementary Information is available in the online version of the paper.

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Author Contributions J.-Y.S., X.Z., W.R.K.I., D.J.M., J.J.V. and Z.S. designed the study and interpreted the results. X.Z. developed the protocol for fabrication of the gels and prepared initial samples. J.-Y.S. and W.R.K.I. improved the protocol, and performed mechanical tests and recovery tests. J.-Y.S. obtained Fourier transform infrared spectra and performed thermogravimetric analysis. O.C. and J.-Y.S. conducted the experiment with fluorescent alginate and that using the atomic force microscope. K.H.O. contributed to the discussion of results. J.-Y.S., W.R.K.I. and Z.S. wrote the manuscript. All authors commented on the manuscript.

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