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Fracture Toughness and Fatigue Threshold of Tough Hydrogels

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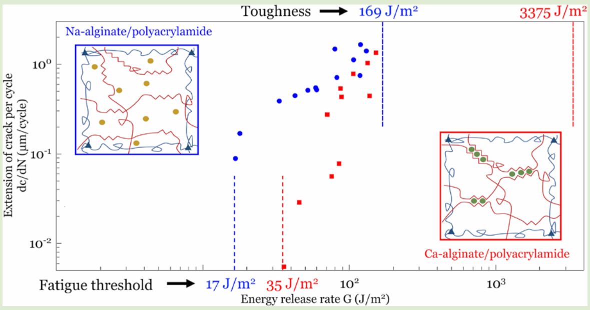
Supporting Information

ABSTRACT: Hydrogels of numerous chemical compositions have achieved high fracture toughness on the basis of one physical principle. As a crack advances in such a hydrogel, a polymer network of strong bonds ruptures at the front of the crack *and* elicits energy dissipation in the bulk of the hydrogel. The constituent that dissipates energy in the bulk of the hydrogel is called a *toughener*. A hypothesis has emerged recently that tougheners increase fracture toughness greatly but contribute little to fatigue threshold. Here we ascertain this hypothesis by studying hydrogels of two kinds, identical in all aspects except for tougheners. A Ca-alginate/polyacrylamide hydrogel has ionic bonds, which act as tougheners, resulting in a toughness of 3375 J/m^2 and a threshold of 35 J/m^2. A Na-alginate/polyacrylamide hydrogel has no ionic bonds, resulting in a toughness of 169 J/m^2 and a threshold of 17 J/m^2. These results motivate a discussion on the development of fatigue-resistant hydrogels.



A highly stretchable hydrogel may rupture at a small stretch when the hydrogel contains a crack-like flaw larger than a certain length. This flaw sensitivity originates from low fracture toughness.[1] The highly stretchable, but brittle, hydrogel typically aggregates a large amount of water and a polymer network of strong bonds. The water molecules in the hydrogel behave as a liquid of low viscosity, whereas the polymer network of strong bonds behaves as an entropic spring. When a crack advances in the hydrogel, the polymer network ruptures at the front of the crack, but the bulk of the hydrogel remains nearly elastic and dissipates little energy. Consequently, the fracture toughness of the hydrogel is low (1−100 J/m^2) and is about the energy of the strong bonds in a layer of polymer chains, in accordance with the Lake−Thomas model.[2] This picture holds true for gels of any strong-bond polymer network and any low-viscosity liquid.[3]

Hydrogels of numerous chemical compositions have been developed to achieve high toughness on the basis of one physical principle.[4−14] As a crack advances in such a hydrogel, the polymer network of strong bonds not only ruptures at the front of the crack but also transmits forces into the bulk of the hydrogel and elicits energy dissipation over a significant volume of the hydrogel. The constituent that dissipates energy in the bulk of the hydrogel is called a *toughener*. Tougheners dissipate energy through inelastic deformation (e.g., plasticity, viscosity, and distributed damage). For example, in a double network hydrogel, one network is highly stretchable, and the other network is less stretchable.[4,6] The two networks interpenetrate in topological entanglement. As a crack advances in the hydrogel, the interpenetrating networks not only rupture at the front of the crack but also transmit forces into the bulk of the hydrogel and rupture the less stretchable network over a significant volume of the hydrogel. That is, in the bulk of the hydrogel, the less stretchable network acts as a toughener through distributed damage, and the highly stretchable network acts as an entropic spring and remains intact. Since the discovery of this physical principle,[4] toughness above 10 000 J/m^2 has been demonstrated.[15] As another example, in a poly(vinyl alcohol)/polyacrylamide hydrogel, the PVA chains are not cross-linked through covalent bonds but interact with one another through hydrogen bonds. The PVA chains and the polyacrylamide network are in physical entanglement; the hydrogel is viscoelastic; and the PVA chains act as a toughener through high viscosity.[16]

For hydrogels of all kinds, fracture under cyclic stretch is much less studied than fracture under monotonic stretch. The paucity of work on fatigue fracture might be excusable before the discovery of tough hydrogels but has become disconcerting since.[17] Several recent studies have shown that all hydrogels tested so far are indeed susceptible to crack extension under cyclic stretch. The studies include nearly elastic polyacrylamide hydrogels,[17,18] double-network tough hydrogels,[19,20] and viscoelastic PVA/polyacrylamide hydrogels.[16] In particular,

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the nearly elastic polyacrylamide hydrogel and the viscoelastic PVA/polyacrylamide hydrogel have similar fatigue thresholds, even though their fracture toughnesses differ by an order of magnitude.[16] This finding leads to a somewhat disturbing hypothesis: tougheners increase fracture toughness but contribute little to fatigue threshold.

Here we ascertain this hypothesis for alginate/polyacrylamide hydrogels. We choose these hydrogels for three reasons. First, they exhibit extraordinarily high toughness.[6] Second, they have low fatigue threshold.[19] Third, the toughener in these hydrogels is alginate chains cross-linked through Ca^{2+}, and such a toughener can be readily removed by replacing Ca^{2+} with Na^+, while retaining all other constituents of the hydrogel.[21]

We prepare two kinds of hydrogels: Ca-alginate/polyacrylamide hydrogel and Na-alginate/polyacrylamide hydrogel (Figure 1). In order to make the comparison more evident, we choose a recipe so that the toughness of Ca-alginate/polyacrylamide hydrogel is much higher than that of Na-alginate/polyacrylamide hydrogel. In this paper we use the recipe in ref 21. To ensure a "fair" comparison, we design the synthesis such that the two hydrogels are identical in all aspects except for the Ca^{2+} and Na^+ ions. Both hydrogels contain a covalently cross-linked polyacrylamide network. In the Ca-alginate/polyacrylamide hydrogel, the alginate chains are cross-linked through the Ca^{2+} ions, which act as tougheners. In the Na-alginate/polyacrylamide hydrogel, the alginate chains are un-cross-linked, and the hydrogel is nearly elastic. For each kind of hydrogel, we measure the fracture toughness under monotonic stretch, the stress−stretch curves under cyclic stretch, and the crack extension under cyclic stretch.

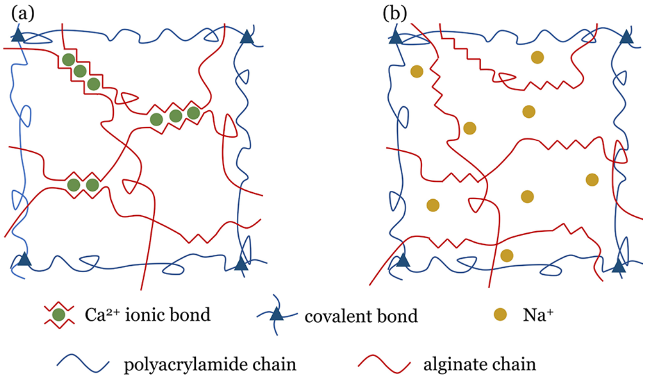

Figure 1. Two kinds of alginate/polyacrylamide hydrogels. (a) In a Ca-alginate/polyacrylamide hydrogel, the alginate chains cross-link into a network through Ca^{2+} ionic bonds. (b) In a Na-alginate/polyacrylamide hydrogel, the alginate chains are un-cross-linked. In either kind of hydrogel, the polyacrylamide chains cross-link into a network through covalent bonds.

As noted above, we prepared the two kinds of hydrogels identical in all aspects except for the Ca^{2+} and Na^+ ions.[21] We ensured this identity as follows (Figure 2). We first synthesized the Na-alginate/polyacrylamide hydrogel. We dissolved powders of sodium alginate chains and acrylamide monomers with mass ratio 1:8 in deionized water. Then, we added 0.028 mol % of *N,N*′-methylenebis(acrylamide) (MBAA, cross-linker), 0.152 mol % of ammonium persulfate (APS, initiator), and 0.031 mol % of *N,N,N*′,*N*′-tetramethylethylenediamine (TEMED, accelerator). All the above molar percentages were relative to acrylamide. We exposed the solution to the open air for several hours until all air bubbles in the solution went out. The solution was poured into an acrylic mold with the size of 150 × 150 × 0.8 mm^3 and placed in an oven at 25 °C for 24 h. The Na-alginate/polyacrylamide hydrogel formed, in which alginate chains were un-cross-linked and the polyacrylamide chains were covalently cross-linked, and water content was 86 wt %.

The as-prepared Na-alginate/polyacrylamide hydrogel was immersed in a 0.3 M $CaCl_2$ solution for 24 h to exchange ions and form Ca-alginate/polyacrylamide hydrogel.[21] Then the Ca-alginate/polyacrylamide hydrogel was immersed into deionized water for 24 h to remove the residual unreacted substance and reached a fully swollen state in equilibrium with

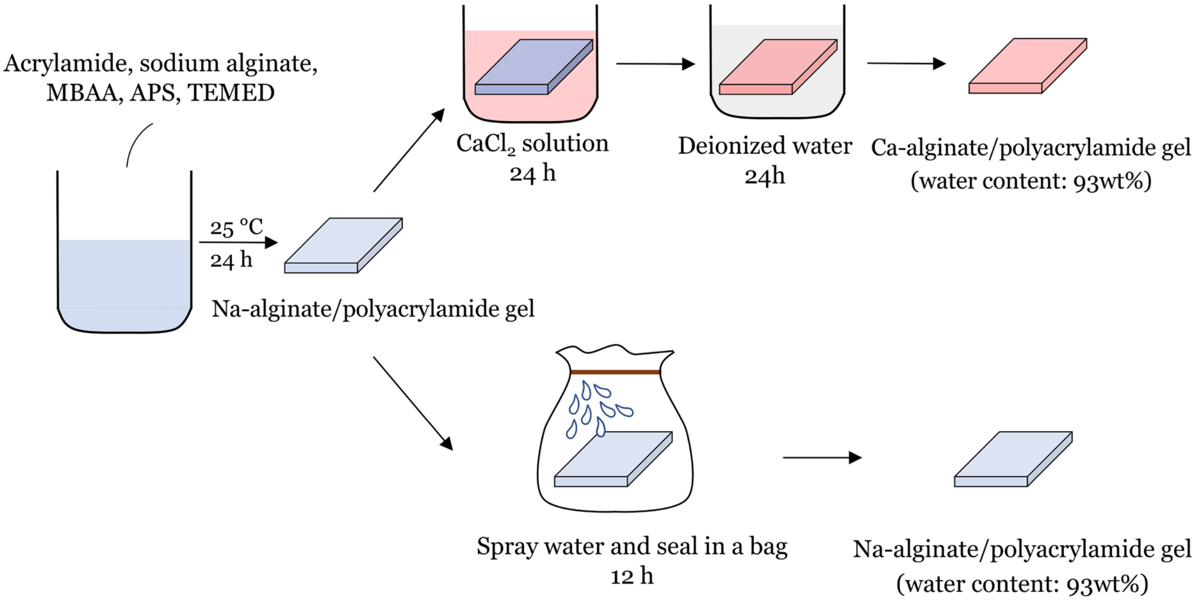

Figure 2. Procedures of synthesis ensure that the Ca-alginate/polyacrylamide hydrogel has the same concentrations of alginate, polyacrylamide, and water as the Na-alginate/polyacrylamide hydrogel.

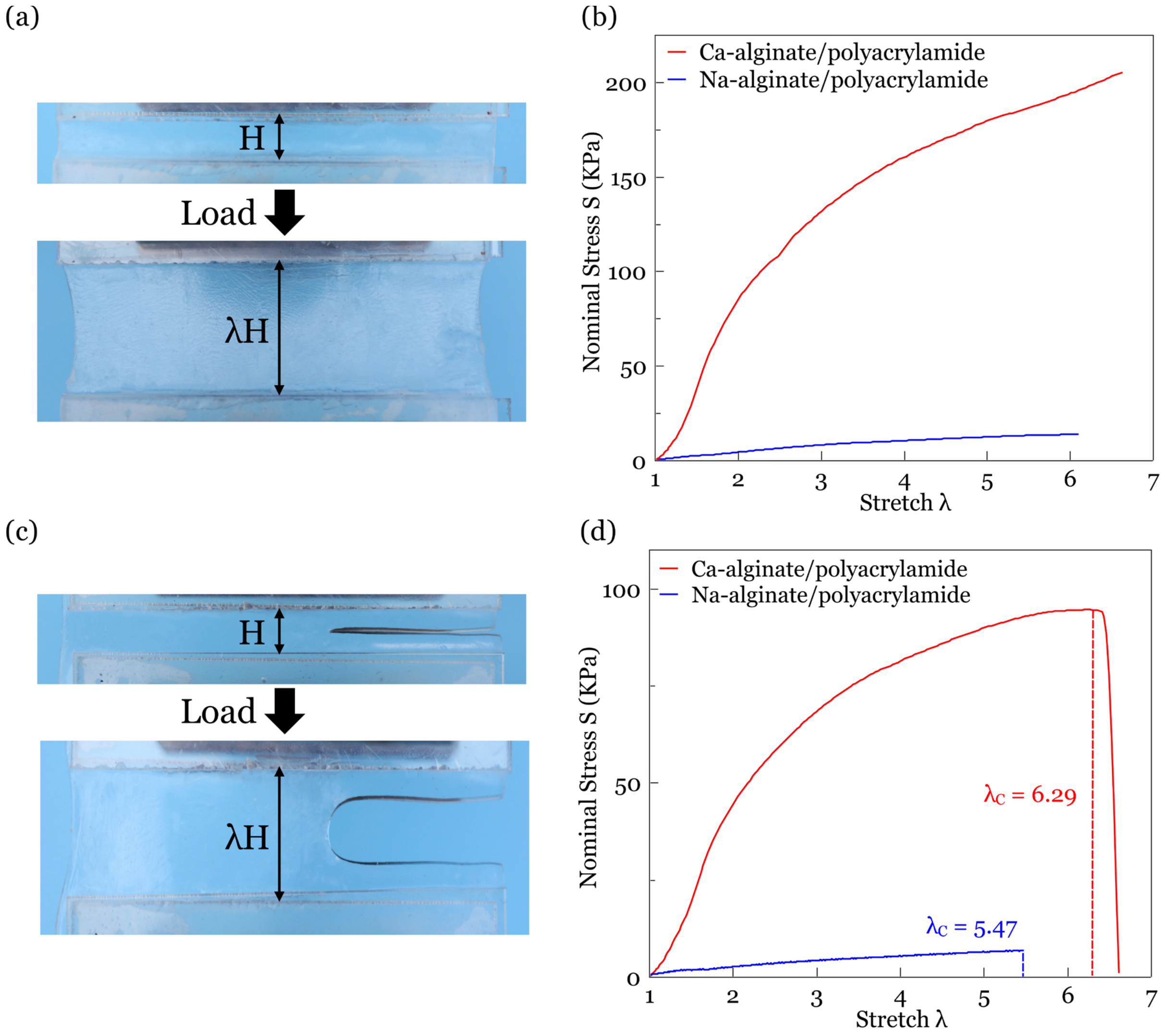

Figure 3. Fracture of the Ca-alginate/polyacrylamide hydrogels and the Na-alginate/polyacrylamide hydrogels under monotonic stretch. (a) An uncut sample is subject to monotonic stretch λ. (b) The stress−stretch curves of uncut samples for the two hydrogels. (c) A precut sample is subject to monotonic stretch λ. (d) The stress−stretch curves of precut samples for the two hydrogels. λ_C is the critical stretch when the crack begins to propagate noticeably.

the $CaCl_2$ solution. The average water content of the Ca-alginate/polyacrylamide hydrogel in the fully swollen state was 93 wt %.

We then increased water content in the as-prepared Na-alginate/polyacrylamide hydrogel as follows. We sealed the as-prepared Na-alginate/polyacrylamide hydrogel in a polyethylene bag, sprayed water onto it, and let the water diffuse into the hydrogel for 12 h. In this way, the water content of the Na-alginate/polyacrylamide hydrogel could be tuned to 93 wt %.

The average thickness of the final Na-alginate/polyacrylamide and Ca-alginate/polyacrylamide hydrogels was 1 ± 5% mm. The water content of the hydrogels was measured by a freeze-drying method. We measured the mass of the as-prepared alginate/polyacrylamide hydrogels, m_{gel}. We froze them in a refrigerator at −15 °C for 12 h and then placed the frozen samples in a freeze-drying machine (BIOCOOL FD-1A-80) for 24 h to sublimate all the water. We measured the dried mass of the dry polymer, $m_{polymer}$. The water content of hydrogels was calculated by $w_{water} = \frac{(m_{gel} - m_{polymer})}{m_{gel}}$.

We measured the toughness of the hydrogels using a method that involves two sets of samples.[6,22−25] We prepared the two sets of samples with the same geometry of a long rectangular sheet (50×5 mm^2). One set of samples was not cut with cracks. The other set of samples was precut with a 20 mm crack by a razor blade. To be consistent with the stretch rate of the fatigue test, we applied the monotonic displacement (SHIMADZU AGS-X tensile tester) at a rate of 15 mm/s on both the uncut and cut samples (Figure 3a, 3c). We plot stress−stretch curves of uncut (Figure 3b) and cut samples (Figure 3d) for the Ca-alginate/polyacrylamide hydrogel and the Na-alginate/polyacrylamide hydrogel. The nominal stress is the applied force divided by the cross-sectional area in the undeformed state. The stretch is the length of samples in the deformed state divided by that in the undeformed state.

For the pure shear test, the energy release rate G of the precut sample takes the form

$$G = HW(\lambda) \tag{1}$$

where H is the distance between the two grippers of the tensile tester when the precut sample is undeformed; $W(\lambda)$ is the

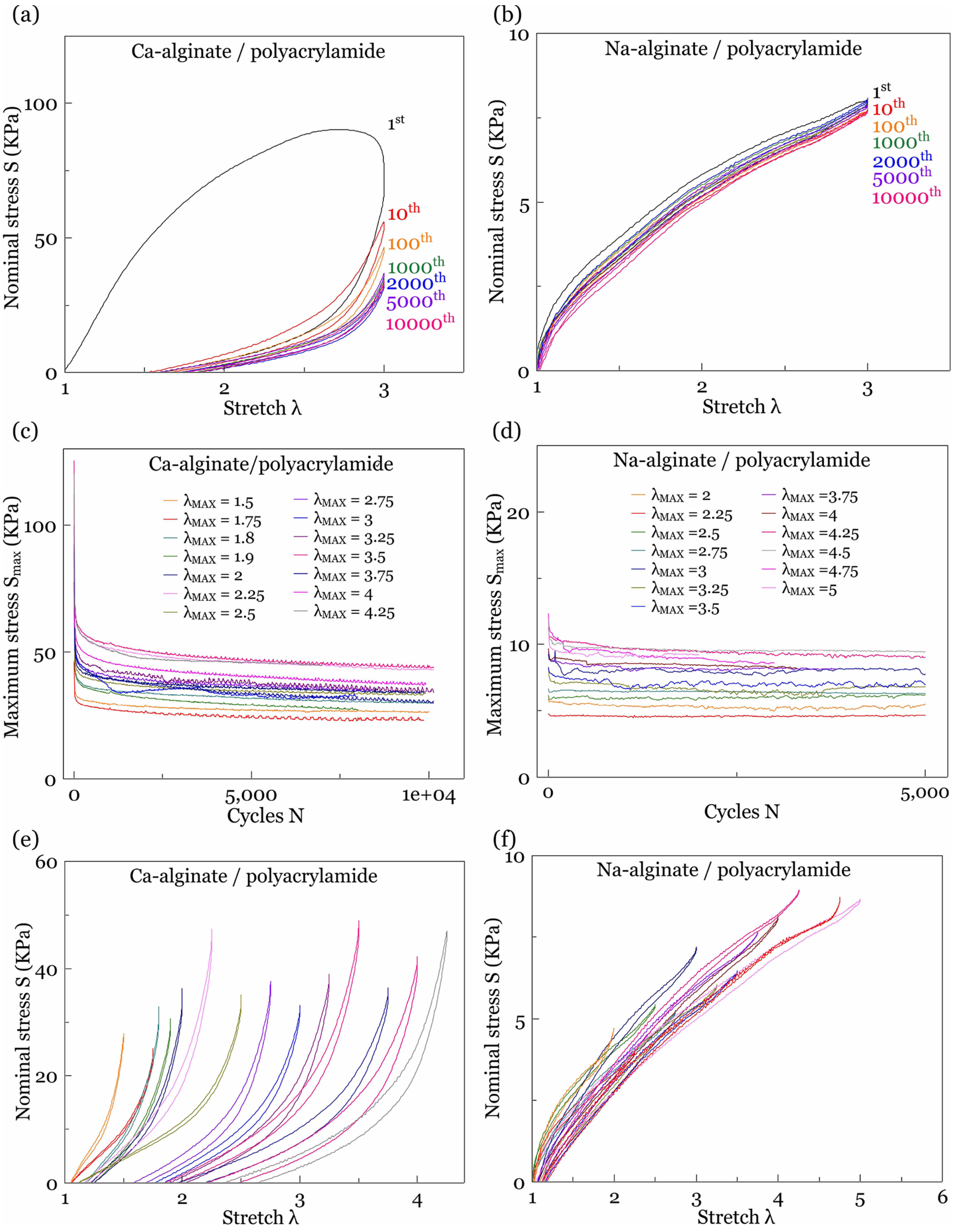

Figure 4. Fatigue damage of uncut samples under cyclic stretch. (a,b) The stress−stretch curves of the Ca-alginate/polyacrylamide hydrogel and Na-alginate/polyacrylamide hydrogel over cycles with $\lambda_{MAX} = 3$. (c,d) The maximum stress of the stress−stretch curves for the two kinds of hydrogels as a function of the number of cycles. (e,f) The stress−stretch curves of the 2000th cycle for the two kinds of hydrogels with different applied λ_{MAX}.

energy per volume of the uncut sample while stretched; and λ is the vertical stretch. The energy density $W(\lambda)$ is obtained by integrating the area below the stress−stretch curve of the uncut sample. The toughness is measured as the critical energy release rate

$$\Gamma = HW(\lambda_C) \tag{2}$$

The critical stretch λ_C is defined as the stretch just when the crack begins to propagate noticeably. For the Ca-alginate/polyacrylamide hydrogel, the crack grows greatly when $\lambda = \lambda_C$ and continues to grow with the decrease of the applied force (Figure 3d). For Na-alginate/polyacrylamide hydrogel, the whole sample ruptures into two pieces along the crack immediately when $\lambda = \lambda_C$.

The average toughness is 3375 J/m^2 for the Ca-alginate/polyacrylamide hydrogel and is 169 J/m^2 for the Na-alginate/polyacrylamide hydrogel. The toughness for the Ca-alginate/polyacrylamide hydrogels of other chemical compositions are

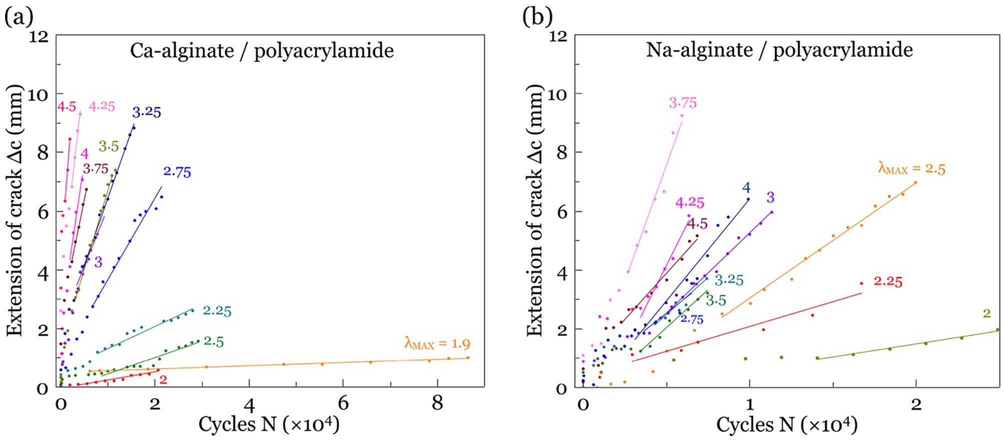

Figure 5. Crack extension under cyclic stretch. The crack extension as a function of the number of cycles with different applied λ_{MAX} for (a) the Ca-alginate/polyacrylamide hydrogel and (b) the Na-alginate/polyacrylamide hydrogel.

shown in the Supporting Information (Figure S1). The rate dependence of toughness is shown in the Supporting Information (Figure S2).

Next we prepared uncut samples with the geometry of a long rectangular sheet (50 × 5 mm^2) and applied cyclic displacement with a triangular profile at a rate of 15 mm/s. Following previous fatigue studies of hydrogels,[16−20] we set the stretch cycle between $\lambda_{\mathrm{MIN}} = 1$ and a given maximum λ_{MAX}. The tests for samples under cyclic stretch took several hours to several days. We sealed samples in an acrylic chamber and constantly sprayed water on the inner surface of the chamber during testing. The difference of the weight of samples before and after testing was less than 8% of the initial weight.

Figure 4a shows the stress−stretch curves of the uncut samples for the Ca-alginate/polyacrylamide hydrogels cycle by cycle with $\lambda_{\mathrm{MAX}} = 3$. The curve for the first cycle shows the biggest hysteresis and has the largest stress at the imposed stretch. Apparent residual stretch is observed when the stress is unloaded to zero. When we further unload samples to $\lambda_{\mathrm{MIN}} = 1$, samples suffer from compressive stress and often buckle. When the number of cycles increases, the hysteresis and maximum stress of each curve gradually decrease (Figure 4c). After almost 2000 cycles, the hysteresis becomes negligible, and the maximum stress almost does not change. At this time, the samples reach a steady state.

Figure 4b shows the stress−stretch curves for the Na-alginate/polyacrylamide hydrogels cycle by cycle. The residual stretch and hysteresis in each cycle are very small. The stress level decreases a little as the number of cycles increases (Figure 4d). These results of the two kinds of hydrogels are as expected. Under cyclic loads, the ionic bonds of the Ca-alginate/polyacrylamide hydrogels gradually dissociate and dissipate energy until the steady state is reached. The Na-alginate/polyacrylamide hydrogels have no ionic bonds and undergo little hysteresis. Figure 4e and 4f shows the stress−stretch curves of the 2000th cycle with different applied λ_{MAX} for the two hydrogels

We next applied cyclic stretch on the precut samples of the two kinds of hydrogels with the same loading profile. The precut samples were prepared with the same shape as the uncut samples. We used a razor blade to cut a 20 mm crack on samples for the Ca-alginate/polyacrylamide hydrogels. Following ref 18 to prepare a sharp crack for the Na-alginate/polyacrylamide hydrogel to propagate normally, we used a razor blade to cut a 10 mm crack on samples and then slightly stretched the precut samples by hand to let the razor-cut crack propagate for a few millimeters. The final crack for the Na-alginate/polyacrylamide hydrogel was around 20 mm. The extension of crack cycle by cycle was recorded by a digital camera (Nikon D5200). We plot the extension of crack Δc as a function of number of cycles N with different applied λ_{MAX} (Figure 5a and 5b). The crack of both of the hydrogels propagates rapidly in the beginning cycles and then reaches a steady state. In the steady state, the extension of the crack Δc is almost a linear function of the number of cycles N.

The steady-state extension of crack per cycle, dc/dN, is plotted as a function of the energy release rate G (Figure 6).

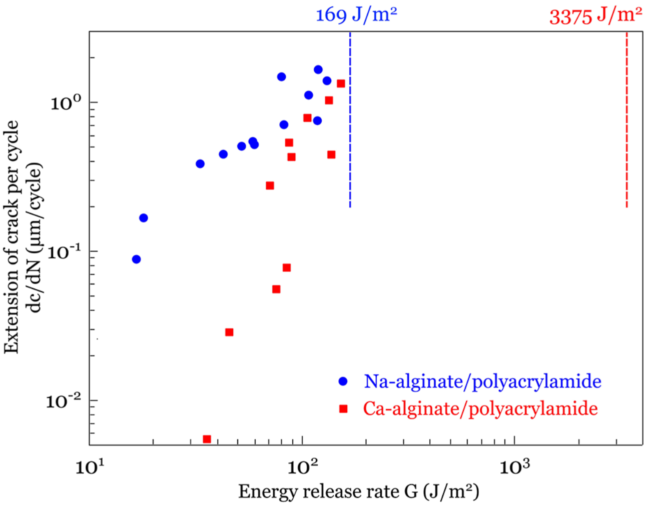

Figure 6. Extension of crack per cycle as a function of the energy release rate in the steady state. Also indicated are the values of toughness for the two kinds of hydrogels.

The energy release rate is calculated using the stress−stretch curve in steady state after 2000 cycles.[19] Also plotted are the two dashed lines indicating the toughnesses of the two kinds of hydrogels. With the same G, the crack growth per cycle of the Na-alginate/polyacrylamide hydrogel is higher than that of the Ca-alginate/polyacrylamide hydrogel. The rapid decrease of dc/dN shown on the logarithmic plane corresponds to the rapid increase of the number of cycles to failure. We simply define the fatigue threshold as the energy release rate at the

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lowest crack growth rate we obtained in our experiments. The crack of the Ca-alginate/polyacrylamide hydrogel extended by 0.47 mm after 80 300 cycles with the applied $\lambda_{\mathrm{MAX}} = 1.9$. The minimum crack growth per cycle is 0.0055 μm/cycle. The fatigue threshold of the Ca-alginate/polyacrylamide hydrogel is 35 J/m^2. The crack of the Na-alginate/polyacrylamide hydrogel extended by 0.96 mm after 10 800 cycles with the applied $\lambda_{\mathrm{MAX}} = 2$. The minimum crack growth per cycle is 0.088 μm/cycle. The fatigue threshold of the Na-alginate/polyacrylamide hydrogel is 17 J/m^2.

The fatigue threshold of elastomers has been commonly interpreted by the Lake–Thomas model.[2] The model assumes that when the applied load approaches the fatigue threshold the crack growth only activates one dissipative process: breaking polymer chains ahead of the crack lying across the crack plane. The fatigue threshold Γ_o adapted for hydrogels takes the form[17]

$$\Gamma_o = \phi_{\mathrm{PAAM}}^{2/3} bUl\sqrt{n} \tag{3}$$

where ϕ_{PAAM} is the volume fraction of the polyacrylamide network in the alginate/polyacrylamide hydrogels; b is the number of bonds per unit volume of the dry polymer; U is the C–C bond energy; l is the length of each monomer unit; and n is the number of monomer units in a polyacrylamide chain. The fatigue threshold predicted by the Lake–Thomas model is 9.1 J/m^2 for both hydrogels (see Supporting Information).

The model hypothesizes that the fatigue threshold only depends on the primary network, i.e., the polyacrylamide network of the two hydrogels. As an approximation, the model does not consider the entanglement effect or other effects of polymer interactions. The distributed damage in the bulk far away from the crack tip does not contribute to the threshold. Our experimental results show that the toughener (the Ca^{2+}-cross-linked alginate chains) increases the fracture toughness of the hydrogel by a factor of 20 but only increases the fatigue threshold of the hydrogel by a factor of 2. The experiments do show that the toughener lowers the crack extension rate when the applied stretch is above the threshold.

The mechanism of the modest increase in fatigue threshold due to the toughener is unclear to us at this writing. It is also unclear how one might design tougheners to significantly amplify the fatigue threshold. One way to increase the fatigue threshold is to increase the chain length of the polyacrylamide network. We have demonstrated previously that the threshold of the polyacrylamide/PAMPS hydrogel can reach 418 J/m^2 when we use a long chain with $n = 50\,000$. In particular, when we change the number of monomer units to be $n = 5000$ the measured threshold decreases to 220 J/m^2. Another possibility to increase the fatigue threshold is to introduce a self-healing primary network, so that the healing rate is faster than the crack extension rate per cycle.

In summary, our experimental data on the two kinds of hydrogels confirm the hypothesis: the toughener (Ca-cross-linked alginate) contributes greatly to fracture toughness but little to fatigue threshold. Whereas hydrogels of high fracture toughness have undergone substantial development, hydrogels of high fatigue threshold are still being explored.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00788.

> Additional experimental data, rate dependence of materials, and estimation of fatigue threshold (PDF)

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Notes

The authors declare no competing financial interest.

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