ACS Macro Letters
Letter
Cite This: ACS Macro Lett. 2018, 7, 312−317
pubs.acs.org/macroletters

Fatigue Fracture of Self-Recovery Hydrogels

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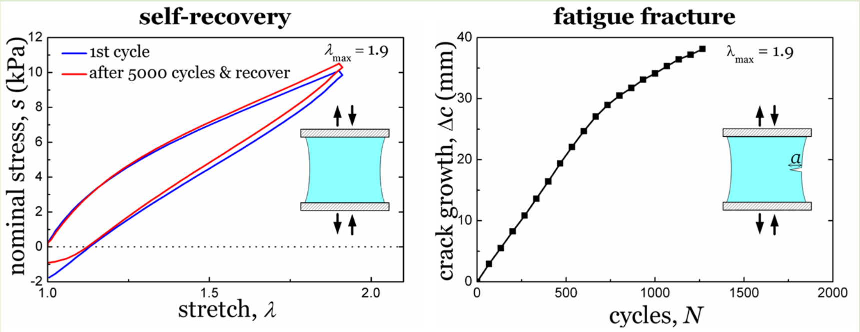
Supporting Information



ABSTRACT: Hydrogels of superior mechanical behavior are under intense development for many applications. Some of these hydrogels can recover their stress−stretch curves after many loading cycles. These hydrogels are called self-recovery hydrogels or even fatigue-free hydrogels. Such a hydrogel typically contains a covalent polymer network, together with some noncovalent, reversible interactions. Here we show that self-recovery hydrogels are still susceptible to fatigue fracture. We study a hydrogel containing both covalently cross-linked polyacrylamide and un-cross-linked poly(vinyl alcohol). For a sample without precut crack, the stress−stretch curve recovers after thousands of loading cycles. For a sample with a precut crack, however, the crack extends cycle by cycle. The threshold for fatigue fracture depends on the covalent network but negligibly on noncovalent interactions. Above the threshold, the noncovalent interactions slow down the extension of the crack under cyclic loads.

For several decades, hydrogels have been developed for biomedical applications such as tissue engineering,[1,2] wound dressing,[3] and drug delivery.[4] More recently, hydrogels are being developed for fire-retarding blankets,[5] muscle-like actuators,[6,7] skin-like sensors,[8−10] optical fibers,[11] transparent triboelectric generators,[12] and stretchable ionic devices.[13−18] Some of these applications require hydrogels to sustain cyclic mechanical loads. Fracture-resistant hydrogels have been developed.[19−25] It is urgent to learn if any of these hydrogels are also fatigue-resistant, i.e., durable under cyclic loads.

Fatigue is commonly studied in two types of tests using, respectively, uncut samples and precut samples.[26,27] When an uncut sample is subject to a cyclic load, any irreversible change in mechanical property, such as the elastic modulus, is called *fatigue damage* (Figure 1a). When a precut sample is subject to a cyclic load, the gradual extension of the crack is called *fatigue fracture* (Figure 1b). Both fatigue damage and fatigue fracture have been exhaustively studied in all materials whenever fatigue is "mission critical". Examples include metals, polymers, ceramics, and composites.[26−31]

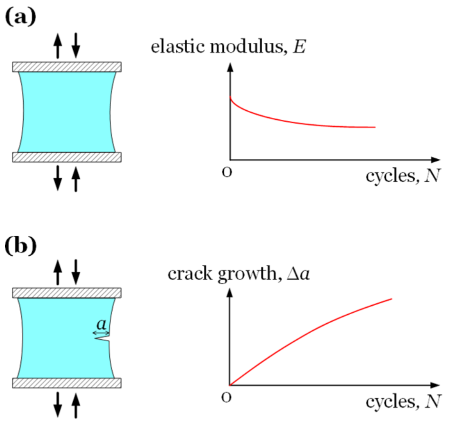


Figure 1. Two types of fatigue behavior: fatigue damage and fatigue fracture. (a) When an uncut sample is subject to a cyclic load, any irreversible change of a mechanical property is called fatigue damage. (b) When a precut sample is subject to a cyclic load, the gradual extension of the crack is called fatigue fracture.

The study of fatigue of hydrogels has started only recently. Measurements of fatigue damage include cycling-induced changes of elastic modulus,[32] stress−stretch hysteresis,[23,33−41] fracture stress,[42] swelling ratio,[43] and healing efficiency.[44] Noticeably, some hydrogels recover their material properties after many cycles of mechanical loads. These hydrogels have been called *self-recovery hydrogels* or even *fatigue-free hydrogels.* Such a hydrogel usually contains a network of covalently cross-

Received: January 16, 2018
Accepted: February 15, 2018

DOI: 10.1021/acsmacrolett.8b00045
ACS Macro Lett. 2018, 7, 312−317

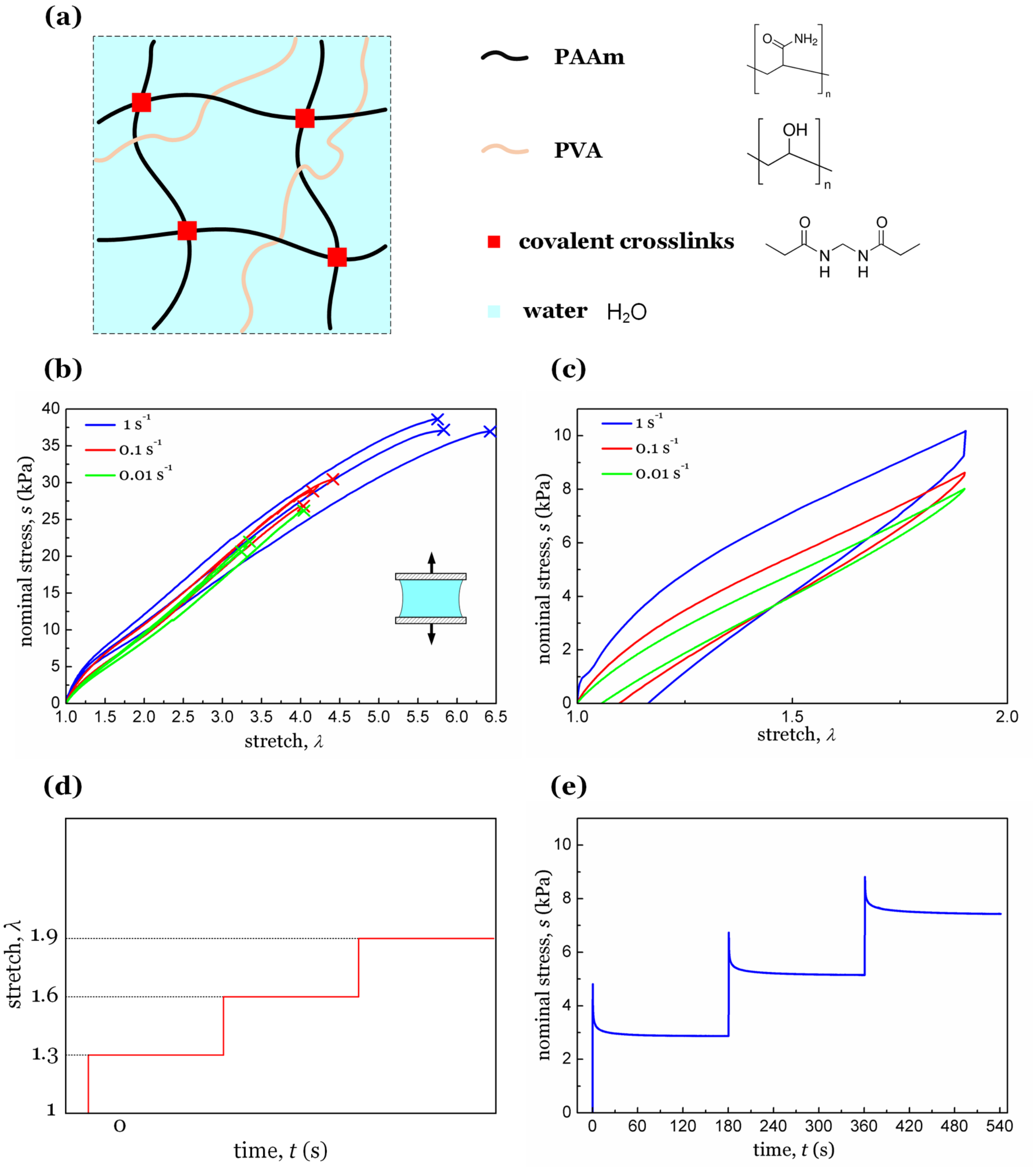


Figure 2. Viscoelasticity of the PAAm-PVA hydrogel. (a) The hydrogel consists of a covalently cross-linked PAAm network, along with un-cross-linked PVA chains. (b) Stress−stretch curves under different stretch rates. The cross represents the fracture of hydrogel. (c) Loading and unloading with different stretch rates. (d) Loading profile of the stress-relaxation test. (e) The nominal stress as a function of time following the loading curve in (d).

linked polymers, together with some noncovalent, reversible bonds, such as hydrogen bonds,[33,34,42] hydrophobic interaction,[35−37,45] polyion complexes,[23,39−41,44] and host−guest interaction.[46] The covalent network provides elasticity that motivates recovery. The reversible bonds break when the hydrogel deforms, induce energy dissipation, and toughen the material. The broken bonds can reform upon unloading and facilitate self-recovery of the material properties. Fatigue fracture, on the other hand, has only been studied in very few hydrogels: polyacrylamide,[47] alginate-polyacrylamide,[48] and poly(2-acrylamido-2-methylpropanesulfonic acid)-polyacrylamide.[49] These hydrogels do not contain significant reversible bonds and are not self-recovery hydrogels. A question remains: will a self-recovery hydrogel suffer fatigue fracture?

Here we show that self-recovery hydrogels do suffer fatigue fracture. In this sense, "fatigue-free" hydrogels do not exist. We synthesize a self-recovery hydrogel consisting of both a covalently cross-linked polyacrylamide (PAAm) network and un-cross-linked poly(vinyl alcohol) (PVA) (Figure 2a). Upon loading and unloading, the hydrogen bonds among the amide groups on PAAm chains and hydroxyl groups on PVA chains[50−55] readily break and reform, enabling self-recovery. For a sample without a precut crack, its stress−stretch behavior remains unchanged after thousands of loading cycles. For a sample with a precut crack, however, the crack extends with

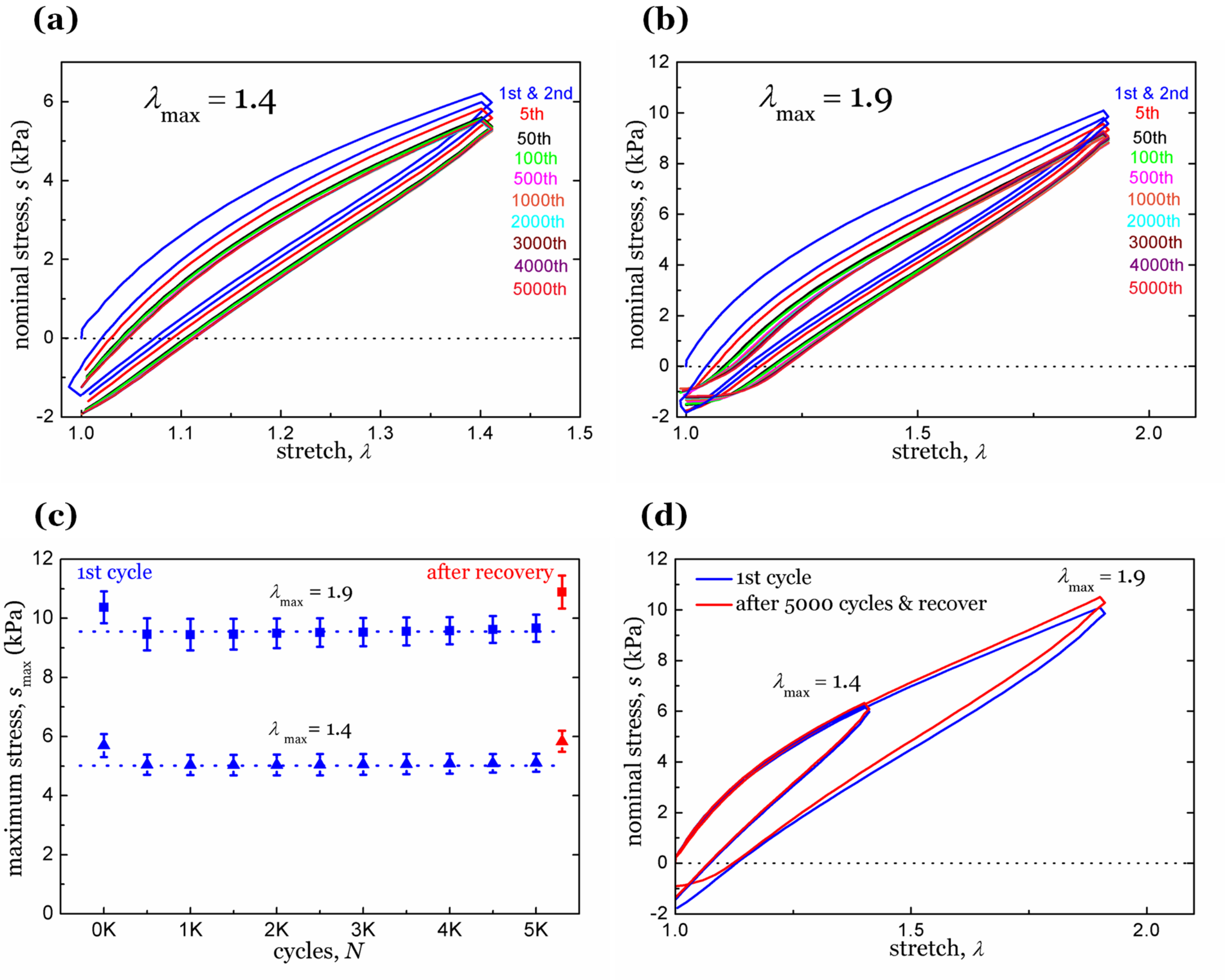


Figure 3. Self-recovery of the PAAm-PVA hydrogel. The hydrogel was loaded under stretch at (a) λ_{max} = 1.4 and (b) λ_{max} = 1.9, respectively, for 5000 cycles. Slight softening was observed in the first few cycles. After 100 cycles, the stress−stretch curves reach a steady state. (c) The maximum stress measured with cycles. The data represent the mean and standard deviation of three experimental results. (d) The stress−stretch curves before and after 5000 cycles are nearly identical.

cycles. We measure the crack extension per cycle as a function of energy release rate and determine the *threshold for fatigue fracture*, below which the crack does not propagate. We find that the threshold of the PAAm-PVA hydrogel is almost identical to the threshold of the hydrogel with the same PAAm network but with no PVA. We conclude that the threshold for fatigue fracture of a self-recovery hydrogel mainly depends on its covalent network but negligibly depends on the noncovalent interactions. When a sample is loaded above the threshold, the noncovalent interactions slow down the extension of the crack under cyclic loads.

We anticipate that the existence of PVA chains in the PAAm-PVA hydrogel enables both energy dissipation and self-recovery. The breaking and reforming of hydrogen bonds during a loading cycle can be reflected by the viscoelastic stress−stretch behavior of the hydrogel. Hence, we conducted the following mechanical tests to characterize the viscoelasticity.

We first stretched hydrogel samples to rupture with different stretch rates, 1 s^{-1}, 0.1 s^{-1}, and 0.01 s^{-1} (Figure 2b). No distinct rate dependency on the stress−stretch curves was found. However, samples under higher loading rate have higher stretchability. In the loading and unloading test with stretch between 1.9 and 1.0, the hysteresis area of the stress−stretch curve increases with the stretch rate (Figure 2c). The observed rate-dependent hysteresis and residual strains can be explained by the following molecular picture. During the stretch, the PAAm network is stretched, accompanied by continuous breaking and reforming of hydrogen bonds. The time scale for the rearrangement of polymer chains is longer than that of a loading cycle. Hence, as the hydrogel unloads, the PAAm-PVA hydrogel takes additional time to fully recover its initial configuration. A smaller stretch rate provides time for chain rearrangement and leads to smaller hysteresis and residual strain. After unloading, we observed that the residual strain kept decreasing with time, and all samples recovered their original geometry within a few minutes.

Viscoelasticity is further reflected in the stress relaxation of the hydrogel. We prescribed a loading profile as a step function of time (Figure 2d). The nominal stress was plotted as a function of time (Figure 2e). The hydrogel almost completely relaxed within 3 min, on the same order of the recovery time observed in the loading and unloading test.

We characterized the self-recovery of the PAAm-PVA hydrogel with the cyclic loading test using samples containing no precut crack. We placed a sample onto a humidity-controlled tensile machine and cyclically stretched it with a prescribed stretch λ_{max} ranging from 1.4 to 1.9 (Figure S1). We loaded the hydrogel for 5000 cycles without stop and recorded

DOI: 10.1021/acsmacrolett.8b00045
ACS Macro Lett. 2018, 7, 312−317

the evolution of stress−stretch curves over cycles (Figure 3a and b and Figure S2). Residual strain was observed at the end of each cycle. The tensile machine recorded negative forces due to slight buckling of the sample when it was unloaded to zero extension. Despite slight mechanical softening induced by viscoelasticity during the first several cycles (e.g., 1st, 2nd, 5th, and 50th cycles in Figure 3a and b), the stress−stretch curves in the following cycles are identical, indicating a steady state. Such a steady state is also reflected in the maximum stress reached in each cycle (Figure 3c). The cyclic softening is due to the incomplete reforming of noncovalent interactions within the short time scale of one loading cycle.[23,33−35,38−41,48] After 5000 cycles, the sample was settled for 3 min and loaded again for one more cycle. Comparing with the first cycle, we found that the hydrogel almost recovered its stress−stretch response (Figure 3d). The PAAm-PVA hydrogel is free from fatigue damage and is a self-recovery hydrogel.

Next, we study the fatigue fracture of the PAAm-PVA hydrogel. We cut a fresh sample with an initial crack of 2 cm and stretched it under the same cyclic loading conditions. The crack does not propagate under a small stretch of λ_{max} = 1.4 but gradually propagates by cycles when λ_{max} increases (Figure 4a, Figure S3). Larger λ_{max} leads to a faster cyclic crack growth. For a stretch of λ_{max} = 1.9, the crack propagates throughout the whole sample (7 cm) within 1500 cycles. Under further larger stretch, the hydrogel sample fails within hundreds down to several cycles (Figure 4b). We recall that, at the same stretch level, an uncut sample can still recover itself after 5000 cycles. The PAAm-PVA hydrogel is free from fatigue damage but suffers fatigue fracture.

Mechanical behavior of a soft material is generally sensitive to the presence of a crack.[56,57] Stress concentrates around the crack tip upon loading; that is, the stress at the crack tip is much higher than elsewhere in the material. The Lake−Thomas model[29] shows that the energy needed to break a covalent network and propagate the crack by unit area, commonly called the *intrinsic fracture toughness* or *threshold for fatigue fracture*, is on the order of 10 J/m^2. Below this threshold, a crack does not propagate with cycles. The Lake−Thomas model hypothesizes that the threshold only depends on the covalent network of a material but does not depend on the bulk energy dissipation from noncovalent interactions. To explore this picture in self-recovery hydrogels, we obtained the threshold for fatigue fracture through the fatigue fracture tests (see Supporting Information for detailed procedures). For each applied λ_{max}, we calculated the slope of crack growth Δc vs cycle number N and the energy release rate G from loading cycles in the steady state (eq S1 and Figure S4). We then plotted the slope dc/dN as a function of G (Figure 4b) and obtained the threshold as the intercept of the curve on the G axis through linear regression. The threshold of the current PAAm-PVA hydrogel is 9.5 J/m^2. We compared this value to the threshold value for the same PAAm hydrogel without PVA.[58] For consistency, the PAAm network and water content (∼88 wt %) were made identical in the two hydrogels. The measured threshold of the PAAm hydrogel is 8.4 J/m^2. We further estimated this number using the Lake−Thomas model for hydrogels[47] (see detailed derivation and eq S2 in the Supporting Information). The model only involves the covalent network and its volume fraction in the hydrogel. It predicts the threshold of 8.5 J/m^2. The three values agree well. The threshold of the PAAm-PVA hydrogel mainly depends on its covalent network but negligibly on the noncovalent interactions.

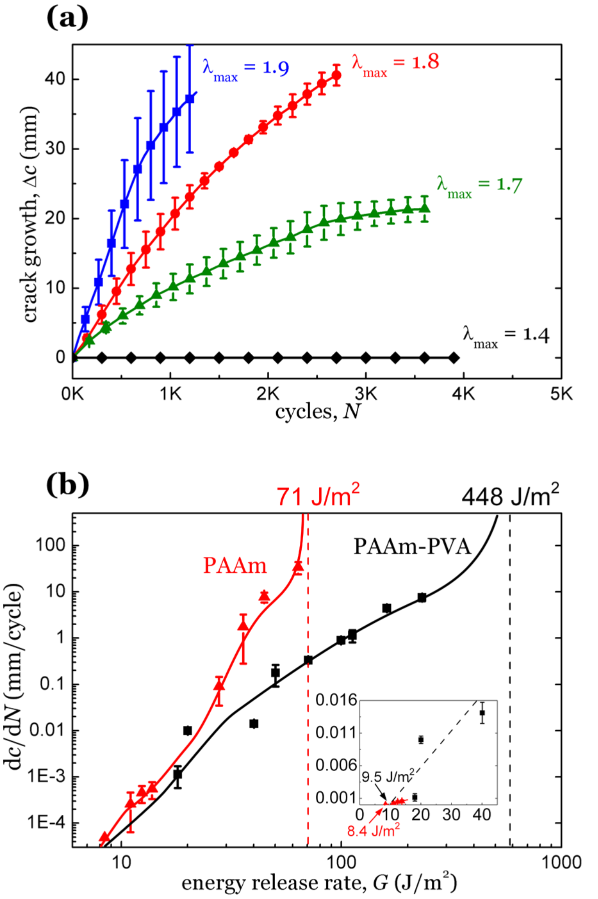


Figure 4. Fatigue fracture of the PAAm-PVA hydrogel. (a) The crack growth with cycles in a PAAm-PVA hydrogel under different applied stretch λ_{max}. (b) The crack growth per cycle dc/dN as a function of the energy release rate G for the PAAm hydrogel (data extracted from ref 58) and the PAAm-PVA hydrogel. Inset: linear regression of the first three points of experimental data. Vertical dashed lines: the experimentally measured bulk fracture toughness under the loading rate 0.4 s^{-1}. Solid curves: guiding lines of the data points. All the data represent the mean and standard deviation of three experimental results.

By contrast, the noncovalent interactions greatly amplify the *bulk* fracture toughness. We measured the bulk fracture toughness of the PAAm-PVA and PAAm hydrogels under 0.4 s^{-1}, upon which fast fracture occurs (dashed vertical lines in Figure 4b; see Supporting Information for detailed procedures). The bulk toughness of the PAAm-PVA hydrogel is 448 J/m^2, much larger than that of the PAAm hydrogel without PVA (71 J/m^2), due to the viscoelastic energy dissipation. Comparing the two curves in Figure 4b, we also see that, at a given value of the energy release rate above the threshold, the crack extension per cycle in the PAAm hydrogel is larger than that in the PAAm-PVA hydrogel. That is, noncovalent interactions do slow down the extension of a crack under cyclic loads.

The time scale of recovery of the PAAm-PVA hydrogel is on the scale of minutes. In contrast, the time scale of one loading cycle is about seconds. The cyclic loads do not allow complete recovery of the noncovalent interactions. The effective strain rate is even higher at the crack tip, due to the higher local stretch. Further increasing the strain rate in experiments is limited by the capability of the tensile machine. However, if the strain rate is extremely high and the noncovalent interactions do not recover at all, they are still anticipated to contribute negligibly to the threshold compared to the covalent network, for the following reason. In the steady state of fatigue fracture, the crack extends by fracturing the covalent network. The relatively weak noncovalent interactions around the crack tip have already broken through the thousands of cycles before reaching this steady state. As a result, the broken noncovalent interactions still contribute negligibly to the threshold.

In summary, we compared two types of fatigue in a self-recovery PAAm-PVA hydrogel: fatigue damage tested using samples without precut cracks and fatigue fracture tested using samples with precut cracks. While the hydrogel is nearly free from fatigue damage through 5000 cycles of loading, it suffers fatigue fracture. The threshold for fatigue fracture of the PAAm-PVA hydrogel is the same as that of the PAAm hydrogel without PVA. This experimental observation indicates that the threshold mainly depends on the covalent network but negligibly depends on the noncovalent interactions. When a sample is loaded above the threshold, the noncovalent interactions do slow down the extension of the crack under cyclic loads. The difference between the fracture of covalent network and the dissipation from noncovalent interactions is clearly made on fatigue of elastomers[59,60] but is rarely made in hydrogels. Self-recovery hydrogels are extensively studied nowadays and have been designated with many other names, including *self-healing*, *fatigue-free*, and *fatigue-resistant* hydrogels. Such a hydrogel typically contains a covalent network together with reversible, noncovalent interactions. The covalent network provides elasticity that motivates recovery. The recovery of noncovalent interactions makes the hydrogel free from fatigue damage. However, self-recovery hydrogels still suffer fatigue fracture. In developing hydrogels to sustain cyclic loads, one should characterize both fatigue damage and fatigue fracture.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00045.

> Material preparation, experimental methods, photos of mechanical testing, additional experimental data, and theoretical derivation (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by MRSEC (DMR-14-20570). X.P.M. was supported by the Cabeaux-Jacobs BAEF fellowship for one year at Harvard University.

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