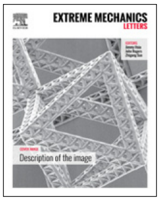
Contents lists available at ScienceDirect
Extreme Mechanics Letters
journal homepage: www.elsevier.com/locate/eml



Fatigue fracture of hydrogels

Jingda Tang [a,b], Jianyu Li [a], Joost J. Vlassak [a,*], Zhigang Suo [a,c,*]

[a] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA
[b] State Key Lab for Turbulence and Complex Systems, College of Engineering, Peking University, Beijing, 100871, China
[c] Kavli Institute of Bionano Science and Technology, Harvard University, Cambridge, MA 02138, USA

ARTICLE INFO

Article history:
Received 20 August 2016
Accepted 28 September 2016
Available online xxxx

Keywords:
Hydrogel
Delayed fracture
Fatigue fracture
Polyacrylamide

ABSTRACT

Rapid advances are taking place to develop hydrogels of high stretchability and toughness, but fatigue fracture has not been studied for any hydrogels. This negligence hinders the development of hydrogels and their applications. Here we initiate a study of fatigue fracture of hydrogels. We choose polyacrylamide hydrogel as a model material. To place fatigue fracture in context, we apply monotonic, static, and cyclic load, and observe three types of fracture behavior: fast fracture, delayed fracture, and fatigue fracture. Below the critical load for fast fracture, we find two distinct thresholds, one for delayed fracture, and the other for fatigue fracture. The fracture behavior of hydrogel is sensitive to both the amplitude of load and the concentration of water. We relate the experimental observations to the molecular picture of swollen polymer networks. Fatigue fracture of hydrogels is a topic ready for scientific studies and engineering advances.

1. Introduction

A rubber band can be stretched and released cyclically, but after many cycles, a crack nucleates, advances cycle by cycle, and cuts the rubber band. This fracture under cyclic load, commonly called fatigue fracture, has been studied exhaustively in hard materials of all types, including metals, plastics, ceramics, and composites [1,2]. Fatigue fracture has also been studied in soft materials, but the study has been limited to elastomers. [3–7].

We are unaware of any study of fatigue fracture of hydrogels. The lack of interest is itself interesting, considering that many aspects of the mechanical behavior of hydrogels are actively studied, including swelling [8], large deformation [9], and fracture [10–19]. One may speculate why fatigue fracture of hydrogels has not been studied. We note three likely reasons. First, synthetic hydrogels are a relatively new type of materials, and interest in their mechanical behavior started only after the commercialization of contact lenses in the 1960s and superabsorbent diapers in the 1980s. Second, fatigue fracture was not "mission-critical" in initial applications of hydrogels. Third, hydrogels in use may degrade or dehydrate before they rupture under cyclic load.

These reasons can no longer keep us complacent. In recent decades, the range of application of hydrogels has expanded enormously, in tissue regeneration [20], drug delivery [21,22], and soft machines [23–29]. Many of these applications require hydrogels to sustain cyclic stretch and release. Chemical degradation can be retarded by a suitable choice of polymer [30]. Dehydration can be mitigated by sealing hydrogels with low-permeability elastomers [25–31], and by dissolving humectants in hydrogels [32]. As research pushes the envelop of these life-limiting factors, the time is ripe to study fatigue fracture of hydrogels. Such a study will aid the development of fatigue-resistant hydrogels, and further broaden the applications of hydrogels. This paper initiates a study of fatigue fracture of hydrogels.

Incidentally, in the literature of hydrogels the word "fatigue" has been occasionally used to designate any change in hydrogels under cyclic load. Examples include change in elastic modulus [33], in hysteresis of stress–stretch curves [34,35], and in functional characteristics of devices [36]. Following the established usage in mechanics, we will use the word "fatigue" or the phrase "fatigue fracture" to designate the process of *rupture* under cyclic load.

2. The choice of material and principal observations

A hydrogel is an aggregate of water molecules and a polymer network. The polymer network can be either chemically or physically crosslinked, or a combination of both. For a hydrogel

---

* Corresponding authors.
E-mail addresses: vlassak@seas.harvard.edu (J.J. Vlassak), suo@seas.harvard.edu (Z. Suo).

http://dx.doi.org/10.1016/j.eml.2016.09.010

Please cite this article in press as: J. Tang, et al., Fatigue fracture of hydrogels, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.09.010

of a chemically crosslinked polymer network, a crack causes the hydrogel to rupture by breaking polymer chains across the plane of the crack [5]. For a hydrogel of a physically crosslinked polymer network, a crack causes the hydrogel to rupture by dissociating physical bonds and possibly pulling out polymer chains across the plane of the crack [37]. For a hydrogel with two interpenetrating networks, where a loose network is chemically crosslinked, and a tight network is either chemically or physically crosslinked, the synergy of the two networks greatly enhances the resistance to rupture [10,11,16–19].

In conversations among the developers of hydrogels, one hears the wish to create hydrogels of extraordinary fatigue resistance. But how does a hydrogel of “ordinary” fatigue resistance behave? The lack of facts on fatigue fracture in hydrogels of any kind hinders the development. To establish a baseline, this exploratory study, we choose covalently crosslinked polyacrylamide hydrogels. Polyacrylamide hydrogels are readily synthesized in laboratories worldwide, and are used in many applications, including water treatment, oil recovery, agriculture, and medicine [30]. Polyacrylamide is a key component in several recently developed tough hydrogels [16,17]. Many aspects of the mechanical behavior of polyacrylamide hydrogels have been characterized, including elasticity, viscoelasticity, and fracture [38]. Polyacrylamide may as well serve as a model material to study fracture of hydrogels, just as silica has long served as a model material to study fracture of hard materials, and copper has long served as a model material to study fatigue of metals.

To compare the fatigue resistance of two materials, or even to compare the fatigue resistance of “the same material” prepared under different conditions, we need to establish a common method of testing. We adopt a testing method established in fracture mechanics [4]. We make samples of the polyacrylamide hydrogel, cut a crack at the edge of each sample by using a razor blade, and observe the extension of the crack under load.

To place fatigue fracture in context, we apply load of three types: monotonic, static, as well as cyclic. We control the “load” by imposing stretch on a hydrogel, and report the “amplitude of load” by the energy release rate. As expected, the fracture behavior is sensitive to both the amplitude of load and the concentration of water. We use these two variables as the axes of a plane, and summarize our principal observations (Fig. 1).

Under monotonic load, during which the stretch increases at a constant rate, the crack remains stationary or grows slowly in the beginning, and then suddenly grows rapidly when the load reaches a certain level (Movie 1, see Appendix A). We call the rupture under monotonic load *fast fracture*, and call the load at which fast fracture occurs the *critical load for fast fracture*.

Under static load, where a stretch is rapidly applied and then held at a constant level below the critical load for fast fracture, we observe two types of behavior. When the level of the static load is high, the crack remains stationary or grows slowly in the beginning, and then suddenly grows rapidly after a time of delay (Movie 2, see Appendix A). When the level of the static load is low, the crack does not grow for the entire duration of the experiment. We call the rupture under static load *delayed fracture*, and call the load above which delayed fracture occurs the *threshold for delayed fracture*.

Under cyclic load, where the stretch is applied with the maximum load in each cycle below the threshold for delayed fracture, we also observe two types of behavior. When the maximum load in each cycle is large, the crack grows cycle by cycle (Movie 3, see Appendix A). When the maximum load in each cycle is small, the crack does not grow for the entire duration of the experiment. We call the rupture under cyclic load *fatigue fracture*, and call the load above which fatigue fracture occurs the *threshold for fatigue fracture*.

We further study the effect of the water content of the hydrogel on rupture. We make samples of the polyacrylamide hydrogel with the same polymer network, and then change the amount of water in each sample by equilibrating it with a moist environment, the humidity of which is set by an aqueous solution of a humectant (lithium chloride). We find that an increase in water content in the hydrogel reduces all three parameters: the critical load for fast fracture, the threshold for delayed fracture, and the threshold for fatigue fracture. In a plane with the water content of hydrogel and the amplitude of load as axes, we sketch the locations of the three types of fracture: fast fracture, delayed fracture, and fatigue fracture (Fig. 1).

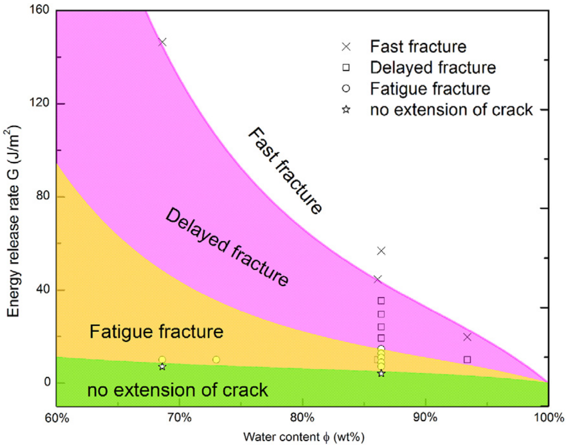


Fig. 1. In a plane with the axes of water content and energy release rate, we mark our experimental data, and schematically sketch the regions for various types of fracture behavior.

3. Experimental section

3.1. Preparation of samples

We purchased from Sigma Aldrich the following substances: acrylamide (AAm, monomer), N,N'-methylenebis(acrylamide) (MBAA, crosslinker), N,N,N',N'-tetramethylethylenediamine (TEMED, accelerator), ammonium persulfate (APS, initiator), and lithium chloride (LiCl, humectant).

We prepared the polyacrylamide hydrogel by free-radical polymerization [24]. We first prepared an aqueous solution of 2.2 M AAm, then added MBAA, TEMED and APS in quantities of 0.00156, 0.0046 and 0.0058 times the weight of AAm. This aqueous solution was injected into a $50 \times 40 \times 3$ mm^3 acrylic mold, sandwiched between two glass plates, and stored at room temperature for 24 h. The aqueous solution turned into a hydrogel. The as-synthesized sample was used in mechanical testing.

3.2. Control of water content

Lithium chloride (LiCl) has been used as a humectant to synthesize water-retaining hydrogels for stretchable, transparent, ionic devices [32]. As a secondary object, this work reports some data of LiCl-containing hydrogels. To prepare a polyacrylamide hydrogel containing LiCl, we first prepared an aqueous solution of 2.2 M AAm and 5.0 M LiCl, and then cured the hydrogel by following the same steps as above.

We then put the hydrogel into a closed container, in which we also placed an aqueous solution of 1 M, 3 M, or 6 M LiCl. In each case, the mass of the aqueous solution was over 100 times that of the hydrogel, so that the concentration was nearly fixed during the test. The hydrogel and the external solution were not in direct contact, but could exchange water molecules through the moisture in the chamber. We measured the mass of the hydrogel

Please cite this article in press as: J. Tang, et al., Fatigue fracture of hydrogels, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.09.010

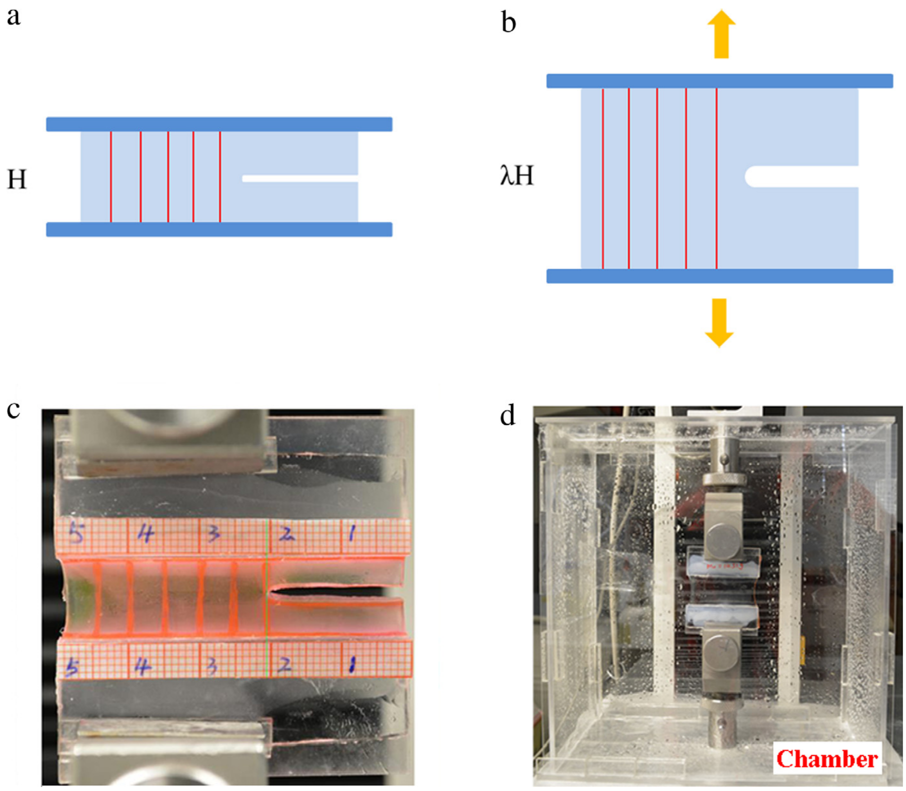


Fig. 2. Experimental setup to observe rupture of a hydrogel. (a) In the reference state, a sheet of hydrogel is clamped to two rigid grips. A crack is cut from the edge of the sample, while ruler lines are marked ahead the crack for measuring crack growth. (b) The two grips are pulled to stretch the sample. (c) A photo of a clamped hydrogel. (d) An acrylic chamber prevents the hydrogel from drying out.

once per day until the hydrogel and the solution equilibrated. This procedure enables us to synthesize samples of the same amounts of polymers and LiCl, but different amounts of water. The samples were then used in the test to observe fracture.

3.3. Observation of rupture

To apply load to the hydrogel, we used a setup known as the pure shear test (Fig. 2). A thin sheet of a sample, of a long rectangular shape ($10 \times 50 \times 3$ mm^3), was fixed to two rigid grips. A 20 mm long crack was cut from the edge of the sample using a razor blade. In the undeformed state, the height of the notched sample was $H = 10$ mm (Fig. 2(a)). The two grips were then pulled to deform the height of the sample to λH, where λ defines the applied stretch (Fig. 2(b)). To aid the determination of the extension of the crack, we marked ruler lines on the surface of the sample, and glued graph papers to the grips (Fig. 2(c)). The sample was mounted in a tensile tester (Instron model 3342) with a 1000 N load cell. To minimize dehydration during the test, we made an acrylic chamber and sealed it around the sample with petrolatum (Fig. 2(d)). As the tensile tester pulled the sample, a digital camera (Nikon D5200) filmed the tip of the crack and recorded the extension of the crack as a function of time.

To ensure that a sample did not dehydrate significantly during a test of a long time, we sprayed water on the inside wall of the acrylic chamber in testing a hydrogel without LiCl, and sprayed the aqueous solution of LiCl of the corresponding concentration on the inside wall of the acrylic chamber in testing a LiCl-containing hydrogel. In each test, we measured the mass of the sample before and after the test. The change of the mass of the hydrogel was within 2%.

4. Three types of fracture behavior

As noted before, we apply load by imposing the stretch λ, but this applied load does not allow a direct comparison of experimental data obtained from samples of different materials and geometries. Instead, following Rivlin and Thomas [3], we report the amplitude of load in terms of the energy release rate, G.

In the pure shear test, the energy release rate is determined by experimental measurement. The method is applicable for elastic materials of stress–stretch curves of any shape [17]. The experiment measures the stress–stretch curve of a sample with no crack, clamped to rigid grips, and under monotonic load (Fig. 3(a),(b)). Here we use the nominal stress (i.e., the applied force divided by the cross-sectional area in the undeformed swollen state). The area under the stress–stretch curve gives the strain energy density $W(\lambda)$. We emphasize that $W(\lambda)$ is the strain energy per unit volume in the sheet measured in the pure shear test. The energy release rate G takes the form [3]

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

This expression is a map that converts the applied stretch λ to the energy release rate G.

Even though the strain energy density $W(\lambda)$ is determined using a sample containing no crack, expression (1) indeed gives the energy release rate, i.e., the reduction in the elastic energy under constant applied displacement associated with the advance of a crack by unit area [3]. The polyacrylamide hydrogel is nearly elastic [38]; we adopt (1) as the driving force for the extension of the crack under monotonic, static, and cyclic load.

4.1. Fast fracture

The fracture energy Γ is the work required to advance a crack by unit area. We determined the fracture energy of the hydrogel

Please cite this article in press as: J. Tang, et al., Fatigue fracture of hydrogels, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.09.010

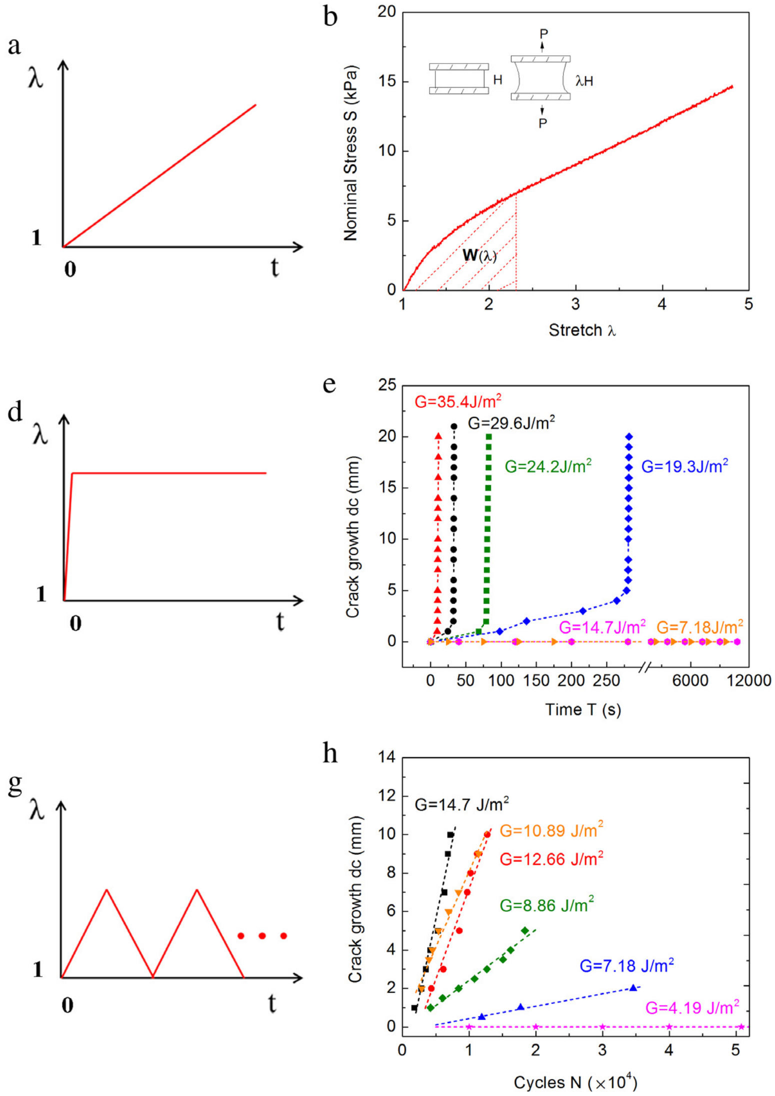


Fig. 3. Rupture under three types of load. (a) Monotonic load. (b) The stress–stretch curve of a sample without crack. (c) The stress–stretch curve of a sample with a crack. (d) Static load. (e) The extension of crack as a function of time. (f) The delay time as a function of energy release rate. (g) Cyclic load. (h) The extension of crack as a function of the number of cycles. (i) The extension per cycle as a function of energy release rate.

by stretching a sample containing a pre-cut crack under monotonic load, at a speed of 30 mm/min (Fig. 3(c)). The experiment measured the critical stretch λ_c, at which the pre-cut crack turned into a running crack. That is, at the critical stretch, λ_c, the sample underwent fast fracture, and the energy release rate G reached the fracture energy Γ. The expression

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

relates the fracture energy to the measured quantities. Our measurements gave the fracture energy of the hydrogel: $\Gamma = 56.8 \pm 3.8\ \mathrm{J/m^2}$, which is the critical load for fast fracture.

4.2. *Delayed fracture*

Hydrogels are susceptible to delayed fracture under static load [39–41]. When a sample containing a pre-cut crack is subject to a static load, below the critical load for fast fracture, the pre-crack initially remains stationary or grows slowly, and then suddenly runs rapidly. We stepped up the stretch at a rate of 30 mm/min, and then held the stretch at a constant level (Fig. 3(d)). Meanwhile we recorded the extension of the crack as a function of time (Fig. 3(e)). The observation was repeated for samples subject to several values of constant stretch λ, corresponding to several values of constant energy release rate G calculated from (1). When G was slightly below the fracture energy Γ, the crack ran rapidly after a small delay in time; for example, at $G = 35.4\ \mathrm{J/m^2}$, the crack ran rapidly after a delay of 8 ± 5.29 s. The delay time increased as G decreased (Fig. 3(f)). A threshold value of G existed, below which we did not observe rapid extension of the crack for the entire duration of the experiment. For example, at $G = 14.7\ \mathrm{J/m^2}$ and $G = 7.18\ \mathrm{J/m^2}$, the crack remained stationary after three hours.

4.3. *Fatigue fracture*

For a sample under a static load below the threshold for delayed fracture, the pre-cut crack remains stationary indefinitely. We next conducted experiment with cyclic load, with the maximum load in each cycle held at a value below the threshold for delayed fracture. We applied a cyclic stretch of triangular profile at a frequency of 1 Hz (Fig. 3(g)). The choice of this frequency is due to the limitation of the maximum loading speed of the tensile tester. The maximum stretch in each cycle λ corresponds to the maximum applied energy release rate according to expression (1). The crack advances cycle by cycle. We recorded the extension of the crack as a function

Please cite this article in press as: J. Tang, et al., Fatigue fracture of hydrogels, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.09.010

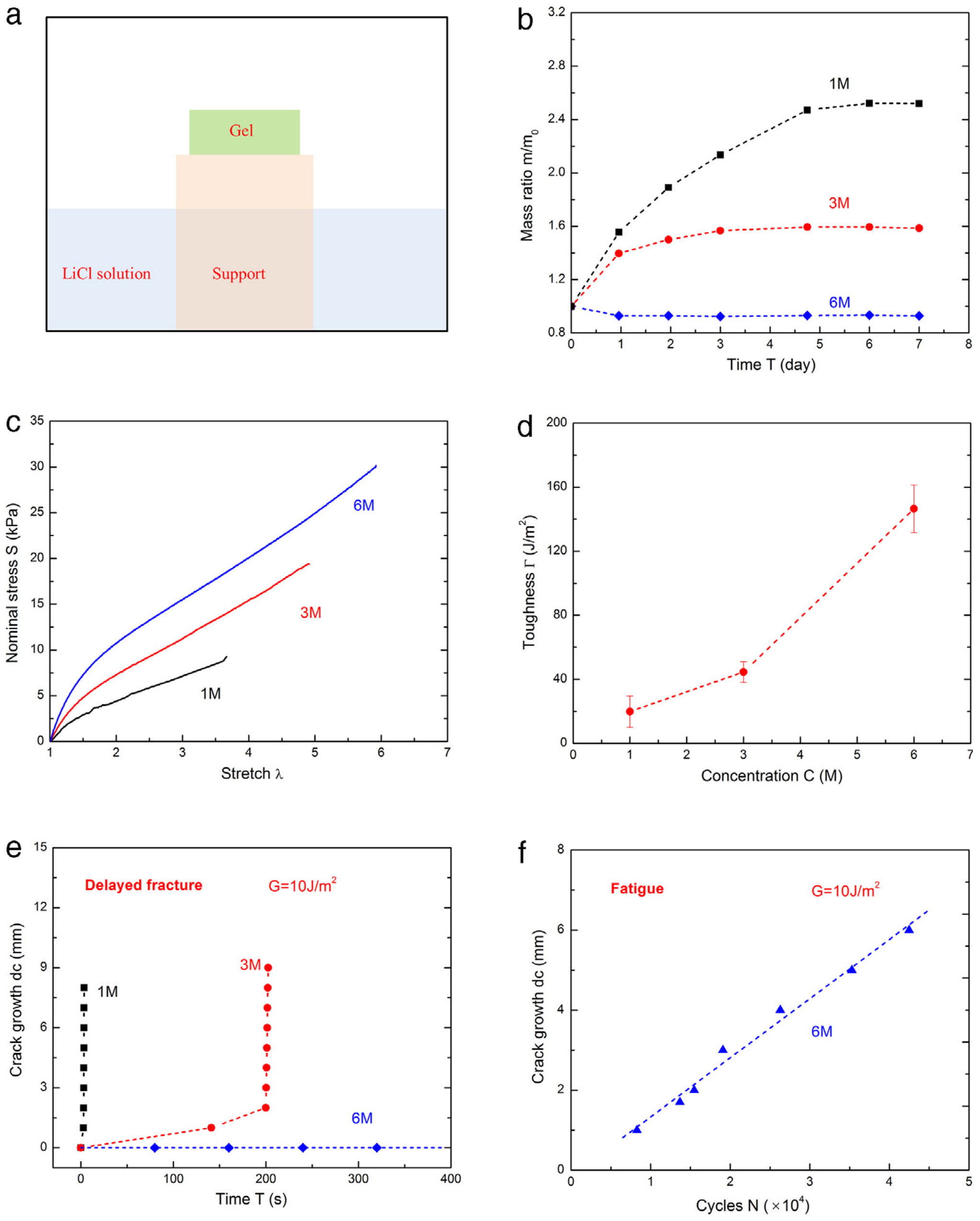


Fig. 4. Effects of water content on the fracture of a polyacrylamide hydrogel. (a) LiCl-containing hydrogel is put in a closed chamber, in vapor contact with an aqueous solution of LiCl. (b) The mass of the hydrogel in vapor contact with an aqueous solution of 1 M, 3 M, or 6 M LiCl. After a hydrogel is equilibrated with an aqueous solution of LiCl of a certain concentration, we measure (c) its stress–stretch curve, (d) its fracture energy and, (e) the extension of crack as a function of time under static load. (f) The extension of crack, under cyclic load, in a hydrogel equilibrated with an aqueous solution of 6 M LiCl. All concentrations in this figure refer to those in the external solution.

of the number of cycles (Fig. 3(h)). We then fit the data to a linear relation, and obtained the extension per cycle, dc/dN, as a function of G (Fig. 3(i)). The extension of the crack per cycle, dc/dN, varies almost linearly with G. This linear relation intercepts the G axis at a finite value of about 7.03 J/m^2. The intercept is called the threshold for fatigue fracture, and is denoted as Γ_0. The positive intercept on the G axis indicates that a threshold exists, below which the number of cycles to rupture increases rapidly [42]. To demonstrate this, we did a test of cyclic load with the maximum energy release rate $G = 4.19$ J/m^2 and found that the pre-cut crack remained stationary after 5.08×10^4 cycles (Fig. 3(h)). We will discuss the threshold for fatigue fracture in terms of the Lake–Thomas model (Section 6).

5. Effect of water content on fracture

Polymers can swell by absorbing solvents from the environment. Swelling, in turn, affects the mechanical behavior of the polymers [43–45]. For example, the fracture energy of a non-crystallizing elastomer decreases as the swollen polymer network reduces viscoelastic dissipation [44]. Hydrogels are known to change water content greatly. Here we study the effect of water content on the rupture of hydrogels.

As described in the Experimental section we prepared a hydrogel by starting with an aqueous solution of 2.2 M acrylamide and 5.0 M LiCl. We then put the hydrogel in a closed container with an aqueous solution of 1 M, 3 M, or 6 M LiCl. The hydrogel was not in direct contact with the aqueous solution, but was put on an acrylic support (Fig. 4(a)). Consequently, the hydrogel and the solution were in vapor contact—that is, they exchanged water molecules through the moisture in the container. We measured the mass of the hydrogel once a day, and found it to plateau after several days (Fig. 4(b)). When the concentration of LiCl in the solution is lower than that in the hydrogel, the gel swelled; otherwise the gel shrunk. In this way, we prepared samples of hydrogels containing the same amounts of polymers and LiCl, but different amounts of water. A sample of hydrogel equilibrated with the 6 M solution contains less water than that equilibrated with the 3 M solution, which contains less water than that equilibrated with the 1 M solution (Fig. 4(b)).

After a sample of hydrogel is equilibrated with the external solution, we measured its stress–stretch curve (Fig. 4(c)), and its fracture energy (Fig. 4(d)). As expected, the stiffness and fracture energy increase as the water content in the hydrogel decreases. We then applied a static load of $G = 10\ \mathrm{J/m^2}$, a value smaller than the fracture energy of all the samples. Delayed fracture happened to hydrogels equilibrated with the 1 M and 3 M solutions, but did not happen to the hydrogel equilibrated with the 6 M solution (Fig. 4(e)). The latter did suffer fatigue fracture with a crack growth rate of 1.48×10^{-4} mm/cycle at an energy release rate of $10\ \mathrm{J/m^2}$ (Fig. 4(f)).

6. Discussion

6.1. Map of fracture behavior

We have observed three types of fracture behavior: fast fracture, delayed fracture, and fatigue fracture. The fracture behavior of hydrogel is sensitive to both the amplitude of load and the concentration of water. We mark our experimental data on the plane spanned by the energy release rate and the water content (Fig. 1). We also schematically sketch the regions in which the three types of fracture behavior occur. A sample subject to monotonic load undergoes fast fracture when the energy release rate reaches the fracture energy, $G = \Gamma$. A sample subject to a static load, below the critical load for fast fracture but above the threshold for delayed fracture, the crack advances rapidly after a delay in time. A sample subject to a cyclic load, with the maximum load in each cycle below the threshold for delayed fracture and the threshold for fatigue fracture, the crack advances cycle by cycle. When the cyclic load is below the threshold for fatigue fracture, the crack remains stationary. An increase in the water content of hydrogel reduces all three critical parameters: the critical energy release rate for fast fracture, the threshold for delayed fracture, and the threshold for fatigue fracture.

These observations may be understood as follows. The less concentrated the external solution, the more swollen the equilibrated hydrogel, the more stretched the polymer chains in the hydrogel, and the lower the fracture energy. Under static load, below the critical load for fast fracture, the diffusion of water molecules to the region around the crack tip causes additional swelling. Thus the hydrogel of high water content is more vulnerable to delayed fracture. By contrast, the hydrogel of low water content has higher fracture energy; even though the local energy release rate increases with time, it equilibrates at a value lower than the fracture energy. We next relate these observations to the molecular picture of a swollen polymer network.

6.2. Molecular processes of delayed fracture

Delayed fracture in hydrogels may result from several molecular processes. First, common to all materials, any viscoelasticity can cause delayed fracture. Second, also common to all materials, any chemical reaction of the strained bonds at the crack tip and molecules in the surroundings can cause delayed fracture. Third, for a hydrogel of a physically crosslinked polymer network, delayed fracture can result from the time needed for polymer chains to dissociate physical crosslinks and possibly pull out across the plane of the crack [37,39–41].

A fourth mechanism, proposed in a recent theoretical paper, is specific to delayed fracture in chemically crosslinked gels [41]. When a sample containing a pre-cut crack is deformed, the deformation near the crack tip is larger than elsewhere in the sample. This concentrated deformation lowers the chemical potential of water near the crack tip, which drives water molecules to diffuse into the region around the crack tip, and further stretches the polymer chains there. Consequently, under a constant applied energy release rate, the local energy release rate increases with time. The crack propagates when the local energy release rate reaches the fracture energy of the hydrogel. The gradual increase of the local energy release rate takes time, which accounts for the delay to observe the rapid extension of crack. The theory also accounts for the other main experimental observations: the delay time increases as the applied energy release rate decreases, and a threshold applied energy release rate exists, below which the crack remains stationary indefinitely.

In our experiment, when we kept the sample at a low constant stretch, the crack remains stationary. Meanwhile we recorded the applied force as a function of time, and found negligible viscoelastic relaxation. This observation aside, we have not designed our experiment to ascertain the mechanism of delayed fracture. Rather, delayed fracture provides a context for the study of fatigue fracture.

6.3. Lake–Thomas model adapted to gels

The threshold for fatigue fracture of the hydrogel is reminiscent of that of elastomers, which has been extensively studied since 1958 [4,5,42]. Lake and Thomas [5] noted that the experimentally determined threshold for fatigue fracture in several elastomers is about $\Gamma_0 = 50\ \mathrm{J/m^2}$. As the amplitude of the applied energy release rate approaches the threshold for fatigue fracture, the extension of crack per cycle approaches zero. In this limit, Lake and Thomas hypothesized that the slow extension of the crack no longer activates the bulk of the elastomer to dissipate energy by processes like viscoelasticity and crystallization. Lake and Thomas further hypothesized that the slow extension of the crack activates a single energy-dissipating process: the crack extends by breaking the polymer chains lying across the crack plane. In this sense, the threshold Γ_0 is also called the *intrinsic fracture energy*. On the basis of the single-process hypothesis, Lake and Thomas derived a model that correctly predicted the experimentally determined threshold.

We now examine if the Lake–Thomas model predicts the threshold for fatigue fracture in the polyacrylamide hydrogel. To do so we need to adapt the Lake–Thomas model for gels. Such an adaptation has appeared in several papers, [15,46–48] but in different expressions. In what follows we present our adaptation of the Lake–Thomas model for gels.

We adopt the single-process hypothesis. At the front of a crack, the chains are stretched. Just before a polymer chain breaks, all C–C bonds along the chain are pulled to the state near the breaking point. Consequently, the mechanical energy needed to pull the chain to the breaking point equals the chemical energy of the entire chain. Following Lake and Thomas, we assume that only a single layer of polymer chains contributes to the intrinsic fracture energy Γ_0.

Let us estimate the chemical energy stored in the covalent bonds in the single layer of polymer chains. We can do this in the undeformed state. Consider a single-chain layer. The Lake–Thomas model assumes that the intrinsic fracture energy is the chemical energy stored in the unit area of the single-chain layer:

$$\Gamma_0 = eL, \tag{3}$$

where e is the chemical energy per unit volume of the gel, and L is the thickness of the single-chain layer in the undeformed state of the gel.

The chemical energy per unit volume of the gel is entirely due to the C–C bonds between monomers in the polymer chains:

$$e = \phi_p bU, \tag{4}$$

where ϕ_p is the volume fraction of the polymer in the gel, b is the number of C–C bonds per unit volume of the polymer, and U is the chemical energy of a C–C bond.

In the undeformed state, the thickness of the single-chain layer in a dry network is estimated by the distance between two ends of the chain, $l\sqrt{n}$, where l is the length of the monomer, and n is the number of monomers in the chain. This estimate assumes that the chain is modeled by a random walk. In a gel, due to swelling, the thickness of the single-chain layer is estimated by

$$L = \phi_p^{-1/3} l\sqrt{n}. \tag{5}$$

A combination of above expressions gives the intrinsic fracture energy of the gel:

$$\Gamma_0 = \phi_p^{2/3} bUl\sqrt{n}. \tag{6}$$

Observe that the expression $bUl\sqrt{n}$ is the intrinsic fracture energy of a dry elastomer, and is independent of the degree of swelling. The swelling reduces the intrinsic fracture energy according to the scaling relation $\Gamma_0 \propto \phi_p^{2/3}$. This scaling is expected. By definition, the fracture energy of a gel is the work needed to advance a crack divided by the cross-sectional area of the gel in the swollen and undeformed state. Swelling does not change the amount of polymers in the sample, but changes the cross-sectional area of the sample by a factor $\phi_p^{-2/3}$. The scaling $\Gamma_0 \propto \phi_p^{2/3}$ is the same as that in Refs. [46,47], but is different from those in Refs. [15,48].

In (6) the factor bUl is intrinsic to an individual monomer in a polymer chain, and has the unit of energy per unit area. The factor is the chemical energy of a C–C bond divided by the area of the monomer. The chemical energy per unit area has a magnitude about 1 J/m^2 for all types of materials (metals, ceramics, and polymers). For a polymer, we can estimate bUl as follows. The number of single bonds per unit volume of the polymer is estimated by the number of monomers per unit volume, $b = A\rho/M = 1.22 \times 10^{28}$ m^{-3}, where M is the molecular weight of acrylamide (71.08 g/mole), ρ is the density of acrylamide (1.443 g/cm^3), and A is the Avogadro number (6.022×10^{23}). The length per monomer is estimated as $l = b^{-1/3} = 0.434$ nm. The C–C bond energy is $U = 3.3 \times 10^{-19}$ J [5]. These values give an estimate $bUl = 1.8$ J/m^2.

The number of monomers between two crosslinks, n, relates to the number of chains per unit volume of polymer, N, by an identity:

$$n = b/N. \tag{7}$$

All three parameters, n, b, N, are independent of the degree of swelling. The number of chains per unit volume of polymer, N, can be estimated by shear modulus as follows.

6.4. Elasticity of a swollen polymer network

When the polymer chains in a gel are modeled by the Gaussian statistics, the stress–stretch relation takes the form [49].

$$\sigma_1 - \sigma_3 = \phi_p^{1/3} NkT\left(\lambda_1^2 - \lambda_3^2\right), \tag{8}$$

$$\sigma_2 - \sigma_3 = \phi_p^{1/3} NkT\left(\lambda_2^2 - \lambda_3^2\right), \tag{9}$$

where $\sigma_1, \sigma_2, \sigma_3$ are the true stresses in the three principal directions, $\lambda_1, \lambda_2, \lambda_3$ are the corresponding stretches, and kT are the absolute temperature in unit of energy. Here a true stress is the force divided by the cross-sectional area of a sample in the deformed state, and a stretch is defined by the length of the sample in the deformed state divided by the length of the sample in the undeformed swollen state. The gel is assumed to be incompressible, $\lambda_1\lambda_2\lambda_3 = 1$. These expressions generalize the neo-Hookean model of elastomers, and are applicable for gels of arbitrary free energy of mixing [50]. These expressions identify the shear modulus of the gel:

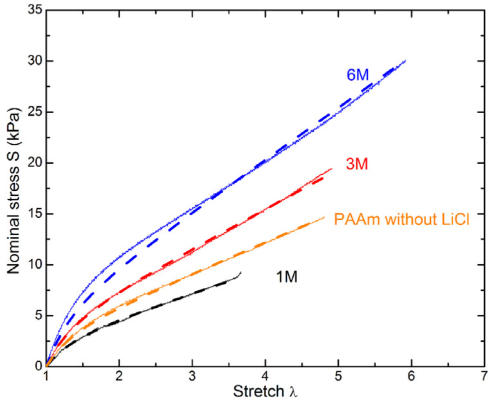


Fig. 5. The measured stress–stretch curves of four gels fit to the neo-Hookean model. Solid lines are experimental data and dashed lines are fitting curves.

$$G = \phi_p^{1/3} NkT. \tag{10}$$

Once the shear modulus G and volume fraction of polymer fraction ϕ_p are determined, (10) estimates the number of chains per unit volume of polymer, N.

In the pure shear test, $\sigma_3 = 0$, $\lambda_1 = 1$, $\lambda_2 = \lambda$, $\lambda_3 = 1/\lambda$. Eqs. (8) and (9) become

$$\sigma_1 = \phi_p^{1/3} NkT\left(1 - \lambda^{-2}\right), \tag{11}$$

$$\sigma_2 = \phi_p^{1/3} NkT\left(\lambda^2 - \lambda^{-2}\right). \tag{12}$$

The nominal stress in the direction of the applied force is given by $s = \sigma_2/\lambda$, namely,

$$s = \phi_p^{1/3} NkT\left(\lambda - \lambda^{-3}\right). \tag{13}$$

The prediction of the neo-Hookean model (13) fits well to the stress–strain curves determined in our experiments (Fig. 5). As noted before, we conducted mechanical tests using as-synthesized samples for gels without LiCl, but using pre-equilibrated samples for gels containing LiCl. In the case of gel pre-equilibrated with the external solution of 6 M LiCl, the difference between experimental data and the model is noticeable, possibly because the test at the large stretch is no longer a pure shear test, but is close to a uniaxial tensile test. The fitting gives the shear moduli for the four gels (Table 1). In determining the volume fraction of polymer ϕ_p in a LiCl-containing hydrogel, we took account of the volume of LiCl.

6.5. Does Lake–Thomas model predict the fatigue threshold of gel?

Inserting these values into (10), we obtain four estimates of the number of polymer chains per unit volume of polymer, N (Table 1). The number N should be independent of the degree of swelling, and should be the same in the four samples. The noticeable difference among various samples indicates that the experimental data deviate from the scaling relation (10). The cause of this deviation is undetermined. These estimates, along with (6) and (7), predict the intrinsic fracture energy Γ_0 of the four gels (Table 1). In experiments, we only measured the threshold for fatigue fracture in two gels: 7.03 J/m^2 for the gel containing no

Table 1
Properties of four polyacrylamide hydrogels.

Samples	Shear modulus G (kPa)	Polymer volume fraction ϕ_p (%)	Chain density N ($\times 10^{24}$ m^{-3})	Fatigue threshold theory Γ_0 (J m^{-2})	Fatigue threshold experiment Γ_0 (J m^{-2})
No LiCl	3.06	9.8	1.6	32.42	7.03
1 M	2.41	4.5	1.64	19.07	–
3 M	3.87	7.4	2.22	22.84	–
6 M	5.09	14.6	2.33	35.07	7–10

LiCl, and a range between 7–10 J/m^2 for the gel equilibrated with the external solution of 6 M LiCl.

The predictions of the Lake–Thomas model do not perfectly agree with our experimentally determined thresholds. Lake and Thomas themselves introduced several refinements to their basic model by considering the effects of the freedom of rotation about bonds, dangling chains, and the distribution of the chain length. We will not pursue these refinements here.

We note that none of their refinements consider an effect specific to gels: the migration of solvents in polymer networks. When a gel is subject to a static load, below the threshold for delayed fracture, the crack remains stationary, but water migrates to the crack tip. After the load is held constant for some time, the gel reaches a new state of equilibrium, with inhomogeneous concentration of water. However, when the applied load cycles, water will migrate again, to and from the crack tip. This molecular process of hysteresis is specific to gels. As such, the migration of water to and from the crack tip constitutes a new mechanism of fatigue. This mechanism is consistent a main finding of this work: two distinct thresholds exist, one for delayed fracture, and the other for fatigue fracture.

Even when the load is below the threshold for fatigue fracture, and the crack is stationary, the cyclic load still causes water to migrate to and from the crack tip. This process still dissipates energy. Its contribution to the threshold for fatigue fracture has not been studied.

7. Concluding remarks

Hydrogels have been developed for a myriad of applications, many of which require hydrogels to sustain cyclic stretch and release. The recent decade has witnessed the enormous effort to develop hydrogels of high stretchability and toughness, but fatigue fracture has not been studied in any hydrogels. This gap in our knowledge hampers the further development of hydrogels and their applications. This study uses a well-established and relatively simple hydrogel (polyacrylamide hydrogel) as a model material. To place fatigue fracture of hydrogels in context, we subject samples of the hydrogel to monotonic, static, and cyclic load. We observe three types of fracture behavior: fast fracture, delayed fracture, and fatigue fracture. We prepare samples of hydrogel with the same polymer network but different water content. The water content of the hydrogel, as well as the amplitude of load, significantly affects the fracture behavior. We sketch the conditions under which the types of fracture occur in the plane spanned by the water content and the energy release rate. Given the rapid development of hydrogels and their applications, fatigue fracture of hydrogels is a topic ready for scientific studies and engineering advances.

Acknowledgments

This work was supported by MRSEC (DMR-14-20570), and by NSF (CMMI-1404653). Tang was supported by China Scholarship Council (201306010164) as a visiting scholar for two years at Harvard University. We thank Professors David Mooney for the use of Instron tensile tester.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.eml.2016.09.010.

References

[1] S. Suresh, Fatigue of Materials, Cambridge University Press, 1998.
[2] R.O. Ritchie, Int. J. Fract. 100 (1999) 55–83.
[3] R. Rivlin, A.G. Thomas, J. Polym. Sci. 10 (1953) 291–318.
[4] A. Thomas, J. Polym. Sci. 31 (1958) 467–480.
[5] G. Lake, A. Thomas, Proc. R. Soc. Lond. Ser. A Math. Phys. Sci. 300 (1967) 108–119.
[6] W. Mars, A. Fatemi, Int. J. Fatigue 24 (2002) 949–961.
[7] W. Mars, A. Fatemi, J. Eng. Mater. Technol. 126 (2004) 19–28.
[8] W. Hong, Z. Liu, Z. Suo, Internat. J. Solids Structures 46 (2009) 3282–3289.
[9] W. Hong, X. Zhao, J. Zhou, Z. Suo, J. Mech. Phys. Solids 56 (2008) 1779–1793.
[10] J.P. Gong, Soft Matter 6 (2010) 2583–2590.
[11] X. Zhao, Soft Matter 10 (2014) 672–687.
[12] M.E. Seitz, D. Martina, T. Baumberger, V.R. Krishnan, C.-Y. Hui, K.R. Shull, Soft Matter 5 (2009) 447–456.
[13] J.A. Zimberlin, N. Sanabria-DeLong, G.N. Tew, A.J. Crosby, Soft Matter 3 (2007) 763–767.
[14] R. Long, C.-Y. Hui, Extreme Mech. Lett. 4 (2015) 131–155.
[15] C. Creton, M. Ciccotti, Rep. Progr. Phys. 79 (2016) 046601.
[16] J.P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, Adv. Mater. 15 (2003) 1155–1158.
[17] J.-Y. Sun, X. Zhao, W.R. Illeperuma, O. Chaudhuri, K.H. Oh, D.J. Mooney, J.J. Vlassak, Z. Suo, Nature 489 (2012) 133–136.
[18] H.R. Brown, Macromolecules 40 (2007) 3815–3818.
[19] Y. Tanaka, Europhys. Lett. 78 (2007) 56005.
[20] A.T. Neffe, B.F. Pierce, G. Tronci, N. Ma, E. Pittermann, T. Gebauer, O. Frank, M. Schossig, X. Xu, B.M. Willie, Adv. Mater. 27 (2015) 1738–1744.
[21] K.Y. Lee, D.J. Mooney, Chem. Rev. 101 (2001) 1869–1880.
[22] R. Langer, Nature 392 (1998) 5–10.
[23] D.J. Beebe, J.S. Moore, J.M. Bauer, Q. Yu, R.H. Liu, C. Devadoss, B.-H. Jo, Nature 404 (2000) 588–590.
[24] C. Keplinger, J.-Y. Sun, C.C. Foo, P. Rothemund, G.M. Whitesides, Z. Suo, Science 341 (2013) 984–987.
[25] J.Y. Sun, C. Keplinger, G.M. Whitesides, Z. Suo, Adv. Mater. 26 (2014) 7608–7614.
[26] C.H. Yang, B. Chen, J.J. Lu, J.H. Yang, J. Zhou, Y.M. Chen, Z. Suo, Extreme Mech. Lett. 3 (2015) 59–65.
[27] C.H. Yang, B.H. Chen, J.X. Zhou, Y.M. Chen, Z.G. Suo, Adv. Mater. 28 (2016) 4480-+.
[28] C. Larson, B. Peele, S. Li, S. Robinson, M. Totaro, L. Beccai, B. Mazzolai, R. Shepherd, Science 351 (2016) 1071–1074.
[29] D. Buenger, F. Topuz, J. Groll, Prog. Polym. Sci. 37 (2012) 1678–1719.
[30] M.J. Caulfield, G.G. Qiao, D.H. Solomon, Chem. Rev. 102 (2002) 3067–3084.
[31] H. Yuk, T. Zhang, G.A. Parada, X. Liu, X. Zhao, Nature Commun. 7 (2016).
[32] Y. Bai, B. Chen, F. Xiang, J. Zhou, H. Wang, Z. Suo, Appl. Phys. Lett. 105 (2014) 151903.
[33] A. Joshi, G. Fussell, J. Thomas, A. Hsuan, A. Lowman, A. Karduna, E. Vresilovic, M. Marcolongo, Biomaterials 27 (2006) 176–184.
[34] M.A. Haque, T. Kurokawa, G. Kamita, J.P. Gong, Macromolecules 44 (2011) 8916–8924.
[35] T. Bai, P. Zhang, Y. Han, Y. Liu, W. Liu, X. Zhao, W. Lu, Soft Matter 7 (2011) 2825–2831.
[36] Q. Yu, J.M. Bauer, J.S. Moore, D.J. Beebe, Appl. Phys. Lett. 78 (2001) 2589–2591.
[37] T. Baumberger, C. Caroli, D. Martina, Nat. Mater. 5 (2006) 552–555.
[38] J. Zhang, C.R. Daubert, E.A. Foegeding, Rheol. Acta 44 (2005) 622–630.
[39] D. Bonn, H. Kellay, M. Prochnow, K. Ben-Djemiaa, J. Meunier, Science 280 (1998) 265–267.
[40] S.B. Lindström, T.E. Kodger, J. Sprakel, D.A. Weitz, Soft Matter 8 (2012) 3657–3664.
[41] X. Wang, W. Hong, Soft Matter 8 (2012) 8171–8178.
[42] G. Lake, P. Lindley, J. Appl. Polym. Sci. 9 (1965) 1233–1251.
[43] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, 1953.
[44] K. Tsunoda, J. Busfield, C. Davies, A. Thomas, J. Mater. Sci. 35 (2000) 5187–5198.
[45] K.S. Anseth, C.N. Bowman, L. Brannon-Peppas, Biomaterials 17 (1996) 1647–1657.
[46] H. Mueller, W. Knauss, Trans. Soc. Rheol. (1957–1977) 15 (1971) 217–233.
[47] A. Ahagon, A. Gent, J. Polym. Sci.: Polym. Phys. Ed. 13 (1975) 1903–1911.
[48] Y. Akagi, H. Sakurai, J.P. Gong, U.-i. Chung, T. Sakai, J. Chem. Phys. 139 (2013) 144905.
[49] L.R.G. Treloar, The Physics of Rubber Elasticity, Oxford University Press, USA, 1975.
[50] S. Cai, Z. Suo, Europhys. Lett. 97 (2012) 34009.

Please cite this article in press as: J. Tang, et al., Fatigue fracture of hydrogels, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.09.010