Fatigue of Hydrogels

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Fatigue of Hydrogels

A dissertation presented
by

Ruobing Bai

to

John A. Paulson School of Engineering and Applied Sciences
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Engineering Sciences

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Fatigue of Hydrogels

Abstract

Hydrogels are actively studied and developed in both fundamental understanding and modern applications. Traditional hydrogels are soft and brittle. Hydrogels with toughness and stiffness comparable to natural rubber have been recently developed. However, all hydrogels suffer fatigue, i.e., any material failure under prolonged loads. A hydrogel sample can be uncut or precut with a macroscopic crack. The loading condition on the sample can be static or cyclic. Fatigue is observed in all combinations of sample types and loading conditions. This thesis explores fatigue of hydrogels under both static and cyclic loads. Hydrogels with different molecular structures show various fatigue behaviors, which are discussed in detail.

For cyclic fatigue of hydrogels, we study fatigue damage of uncut hydrogels and fatigue fracture of precut hydrogels. We study fatigue fracture of a nearly elastic, covalently crosslinked polyacrylamide hydrogels of various water contents. A polyacrylamide hydrogel is resistant to fatigue damage due to its near-elastic feature, but still suffers fatigue fracture. We also study fatigue of a polyacrylamide-calcium-alginate tough hydrogel with a covalently crosslinked polyacrylamide network and an ionically crosslinked calcium-alginate network. The tough hydrogel suffers both fatigue damage and fatigue fracture due to the continuous breaking of the weak calcium-alginate network and the relatively brittle covalent polyacrylamide network. We then study fatigue of a self-recovery hydrogel containing both covalently crosslinked polyacrylamide and uncrosslinked polyvinyl alcohol. A self-recovery hydrogel is able to recovery its property after many cycles of loads due to the reversible bonds, but is still susceptible to
fatigue fracture. With these studies, we find that the threshold for fatigue fracture depends on the covalent network of a hydrogel, but negligibly on any non-covalent interactions in the hydrogel. Above the threshold, the non-covalent interactions slow down the extension of the crack under cyclic loads.

For static fatigue of hydrogels, we focus on slow crack of polyacrylamide-calcium-alginate hydrogels. We measure the v-G curves of slow crack of hydrogel samples with the same polyacrylamide network. The v-G curve depends on the crack speed, sample size and amount of calcium ions added in the pre-gel solution. The threshold for slow crack does not depend on the sample thickness. We compare the measured thresholds for both fatigue fracture and slow crack. The threshold for fatigue fracture only depends on the primary network of polyacrylamide, but negligibly on the calcium-alginate toughener. In contrast, the threshold for slow crack depends on both the primary network of polyacrylamide and the solid-like toughener of calcium-alginate.

In addition to the fundamental study of fatigue of hydrogels, we present a new design principle of flaw-insensitive hydrogels under both static and cyclic loads. The design utilizes material anisotropy by aligning the polymer chains of the hydrogel in the molecular level to deflect a crack. Upon stretching, an initial flaw deflects, propagates along the loading direction, and peels off the material, leaving the hydrogel flawless again. The designed hydrogel is insensitive to any pre-existing flaw, even under more than ten thousand loading cycles.

Finally, we summarize some understanding of fatigue of hydrogels and future challenges for the topic. With the study in this thesis, it is hoped that the theoretical and experimental understanding can facilitate the development of hydrogels that resist both static and cyclic fatigue.
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Chapter 1 Introduction

1.1 Static and cyclic fatigue of hydrogels

A hydrogel is an aggregate of water molecules and a polymer network. Hydrogels were first reported in the landmark paper by Wichterle and Lim in 1960 for biological applications. Since then, synthetic hydrogels have developed into a class of materials of its own. Hydrogels have already been broadly used, and are still actively developed nowadays, for personal care and medical applications, such as contact lenses, superabsorbent diapers, tissue engineering, drug delivery, wound dressing, and artificial tissues. Hydrogels have also been used in recent years to develop nonmedical applications. Examples include artificial muscles, artificial skins, artificial axons, artificial eels, optical fibers, fire-retarding blankets, touchpads, triboelectric generators, liquid crystal devices, volatile vapor sensors, and ionotronic luminescent devices. Hydrogels can be made as highly stretchable, transparent, ionic conductors. Hydrogels can retain water in the open air when hydrogels dissolve hygroscopic salts and are coated with hydrophobic elastomers. Hydrogels containing salts can remain soft at temperatures below 0 °C. Hydrogels coated with elastomers can sustain temperatures above 100 °C without boiling. The property space further spans extensively when hydrogels are integrated with other materials to form water matrix composites (WMC). Also under development are methods to create strong adhesion between hydrophilic and hydrophobic polymer networks, and methods to fabricate integrated hydrogel devices through casting, coating, and printing.

The large-scale use of hydrogels is attractive for a number of reasons. Many kinds of polymers can form hydrogels. Such diversity enables suitable polymers to be selected to achieve specific functions. Hydrogels mostly consist of water. Many hydrogels are inexpensive and environmentally friendly. Hydrogels based on alginates are a case in point. Alginates are
extracted from seaweeds (e.g. rockweed and giant kelp) that are naturally abundant in the oceans throughout the world. The annual production of alginates is estimated to be less than 10% of that available in the algae crops. The sources of alginates are regarded as unlimited even for a steadily growing industry: it is conceivable that algae will be cultivated if large-scale applications emerge. In contrast, natural rubber is derived from a tree (Hevea Brasiliensis) that grows in tropical regions only.

Despite the low cost, examples of large scale use of hydrogels at the industrial level are still limited. One important reason is the poor mechanical property of hydrogels. Most traditional hydrogels are fragile, like tofu and Jell-O. A polyacrylamide hydrogel can be stretched several times its original length, but ruptures at a small stretch when the sample is pre-cut with a crack of length exceeding a few millimeters. This flaw sensitivity is common to all materials, but different materials are sensitive to flaws of different sizes. Flaw sensitivity is inversely related to a material property: fracture energy (also called toughness). The toughness is about 1-10 J/m² for tofu and Jell-O, about 100 J/m² for polyacrylamide hydrogels, about 1000 J/m² for cartilage, and above 10,000 J/m² for natural rubber. Hydrogels as tough as natural rubber have been developed. A tough hydrogel has a stretchable polymer network in topological entanglement with a network with sacrificial bonds. The hydrogel is tough when the stretchable polymer network is strong enough to break the sacrificial bonds in a large volume surrounding the front of a crack. That is, the sacrificial bonds act as tougheners. The discovery of this fundamental principle has instigated the worldwide search for hydrogels of various polymer networks and sacrificial bonds, and for applications of hydrogels previously unimagined.

Like all materials, as the property space spans and applications proliferate, hydrogels will be pushed into uses under extreme conditions. In particular, many applications will require hydrogels to sustain prolonged mechanical loads. For example, hydrogels will sustain prolonged deformation in artificial tissues, move repeatedly in soft robotic arms, stretch and relax in
artificial skins,\textsuperscript{21-27} and vibrate in transparent loudspeakers.\textsuperscript{11} Any failure of a material such as degradation of property and fracture of material, under prolonged loads, can be called fatigue. Here, we call the failure under prolonged static loads the static fatigue, while the failure under prolonged cyclic loads the cyclic fatigue. Both static fatigue and cyclic fatigue have been studied exhaustively in all established load-bearing materials, including metals, ceramics, plastics, elastomers, and composites.\textsuperscript{72-85} A glass, for example, may withstand a static load for a long time (days, weeks, or years) and then, without warning, breaks suddenly.\textsuperscript{81-85} As another example, a steel can survive an unlimited number of cycles of loads if the amplitude of load is below an endurance limit.\textsuperscript{80} However, if the steel contains a large enough crack, the crack will extend cycle by cycle. To enable new applications of hydrogels, as well as to aid further development of hydrogels, it is urgent to study fatigue of hydrogels.

This thesis studies fatigue of hydrogels under static and cyclic loads. Including fatigue, the mechanical behaviors of hydrogels are usually complex, and depend on the large variety of intrinsic tunable molecular variables of hydrogels, such as the bond type of crosslinks, polymer chain length and water content. Studies on hydrogels to relate their mechanical behaviors and molecular structures have been extensive in recent years.\textsuperscript{62,63} The mechanical behaviors under study include swelling,\textsuperscript{86} large deformation,\textsuperscript{87-94} instability,\textsuperscript{95-101} fracture,\textsuperscript{9,57,58,60,61,64,99,102-109} viscoelasticity,\textsuperscript{92,93,105-107,110,111} poroelasticity,\textsuperscript{86-89,106,109,110,112-115} Mullins effect,\textsuperscript{64,90-94,103,104,116} as well as fatigue.\textsuperscript{18,59,65-70,99,107,108,111,117-133} Several theoretical and computational models have been developed to generalize specific multi-dimensional, multi-axial mechanical behaviors of certain types of hydrogels. Examples include swelling and deformation of an elastic hydrogel,\textsuperscript{87} viscoelasticity and Mullins effect of a double-network hydrogel,\textsuperscript{93} and fracture of a double-network hydrogel.\textsuperscript{64} To quantitatively relate the microscopic molecular complexity to the macroscopic mechanical behavior of a hydrogel, these models usually require many fitting parameters even for a single material. Such large number of fitting parameters is potentially useful for practical applications where a specific material is focused on and firmly characterized
with sufficient experimental data. This case is not the focus of the current study. Beyond these specific models for certain types of hydrogels, there exists no theoretical model so far that can generalize and account for all the nonlinear, complex behaviors of a single hydrogel.

Along with the theoretical models for certain hydrogels, several simple mechanical tests have been used universally to study all hydrogels, probing their material properties and connecting them to the molecular structures. This bridge between the molecular interactions and macroscopic mechanics provides first-hand information for development of new hydrogels. Fatigue of hydrogels, without exception, is within the context of these simple tests, the resulting macroscopic observations, and their corresponding molecular behaviors.

Chapter 1 reviews fatigue of hydrogels based on these tests. In Section 1.2, we summarize the commonly used mechanical tests, and the information of materials reported from them so far. In Section 1.3, we discuss both static fatigue and cyclic fatigue of hydrogels with these tests, by focusing on five representative hydrogels. In Section 1.4, we provide the outline of the thesis.

1.2 Common mechanical tests of hydrogels

In this section, we summarize five commonly used mechanical tests, including monotonic stretch, constant stretch, constant stress, cyclic stretch, and self-recovery, together with the mechanical behaviors and material information that are usually reported (Table 1.1). The tests are conducted on two kinds of hydrogel samples, one without any precut crack, and the other with a macroscopic precut crack. Fatigue is observed in both samples under static and cyclic loads. In the rest of this chapter, we define stretch as the length of the sample in the deformed state divided by the length of the sample in the undeformed state. The difference between the stretch and 1 is commonly called the engineering strain.

1.2.1 Monotonic stretch

For any material, from glass, metals and ceramics, to plastics, elastomers and gels, whenever the mechanical property is studied, monotonic stretch is almost always the primary
test to conduct. In a representative loading profile of monotonic stretch, the applied stretch increases linearly with time under a constant rate. The applied stretch follows a constant direction, such as uniaxial tensile, uniaxial compressive, and simple shear.

The stress-stretch curve of a material is readily measured from the monotonic stretch test. The initial slope of the stress-stretch curve measures the elastic modulus of the material. A hydrogel with entropic elasticity is usually assumed as an incompressible material, if the characteristic time of the mechanical test is much smaller than the time scale of diffusion.\textsuperscript{87} Under uniaxial tensile or compressive monotonic stretch, the slope of the stress-stretch curve measures the Young’s modulus, which is three times the shear modulus of the incompressive hydrogel;\textsuperscript{87–89} under uniaxial pure shear, the slope of the stress-stretch curve is four times the shear modulus;\textsuperscript{61,119} under simple shear, the slope is the shear modulus itself as defined. Beyond the initial region of small deformation, which is usually several percent of strain, the stress-stretch curve behaves nonlinear, and may depend on the loading rate, due to the time-dependent dissociation or re-association of molecular interactions. The end of the stress-stretch curve corresponds to the complete failure of the material such as rupture throughout the sample. The stress and stretch levels at this point are defined as the strength and stretchability, respectively. The measured strength and stretchability qualitatively reflect the mechanical property of a material, but are usually not material constants. As an example, because of stress concentration, a sample usually fractures at one of its two ends in a uniaxial tensile test, and the strength and stretchability are reported accordingly. However, if such stress concentration is removed by tying knots instead of gripping at the two ends, the measured strength and stretchability can be greatly enhanced, but can still have large scatter among different samples due to the unknown imperfection pre-existing in a material.\textsuperscript{55,134} In some hydrogels, a yielding point can be observed from the stress-stretch curve where the stress reaches a local maximum, just like what is observed in ductile metals.\textsuperscript{57,58,70,135} A
hydrogel with two covalently crosslinked networks is such an example. Further detailed discussion of the yielding point will be given in Section 3.4.

For precut hydrogel samples, monotonic stretch is usually conducted to study the property of fracture. In many tough hydrogels with sacrificial bonds, the energy dissipation by breaking the sacrificial bonds usually depends on the loading rate. The stretchability of a precut hydrogel therefore also depends on the rate of monotonic stretch. For example, the poly(vinyl alcohol)-polyacrylamide (PVA-PAAm) hydrogel behaves viscoelastic due to the continuous breaking and reforming of hydrogen bonds between the PVA chains. The stress-stretch hysteresis is large at a high strain rate, but negligible at low rate. As a result, the stretchability of a precut PVA-PAAm hydrogel greatly increases with the strain rate. This rate-dependent fracture is generally observed in all hydrogels, due to effects such as poroelasticity, viscoelasticity and viscoplasticity.

Recall that under static prolonged loads, any failure of material is called static fatigue. One type of static fatigue, the slow crack, is reported by the monotonic stretch test. A slow-crack test is commonly conducted using peeling or tearing setups, and sometimes the pure shear setup. A slow-crack test characterizes the relationship between the speed of crack extension $v$ and the energy release rate, i.e., the energy it takes to extend a crack by unit area, denoted as $G$, in the unit of $J/m^2$. This $v$-$G$ curve has been studied in various hydrogel systems. Because no hydrogel is completely elastic, the measured fracture toughness or energy release rate for crack propagation in a hydrogel is never a material constant, but always depends on the speed of crack extension or loading rate. When a crack extends, new crack surface is generated, accompanied by the unloading of the material near the crack tip. For inelastic hydrogels with nonzero stress-stretch hysteresis, this unloading process induces additional energy dissipation, thus toughens the hydrogel. As the speed of crack extension decreases, the rate of loading and unloading of the material at the crack tip also decreases, leading to smaller hysteresis loop. The energy release rate required to extend the crack hence
becomes lower at small speed. As a result, the hydrogel suffers slow crack, as one kind of static fatigue. In a standard \(v-G\) curve, the energy release rate approaches a finite value when the crack speed approaches zero. This threshold for slow-crack reflects the resistance to fracture of the hydrogel after removing the rate-dependent dissipation in the material, and provides molecular information such as the bond type and strength of the hydrogel network at the crack tip.\(^{139}\) As an example of static fatigue by slow crack, a polyacrylamide-calcium-alginate hydrogel has a measured energy release rate on the order of 4000 J/m\(^2\) at a crack speed of 10 mm/s. However, with an energy release rate of about 200 J/m\(^2\), a crack can still propagate in the hydrogel with a speed below 1 \(\mu\)m/s.\(^{140}\)

### 1.2.2 Constant stretch and constant stress

The Constant stretch and constant stress tests have been standard methods to characterize the rate-dependent behavior of a hydrogel. The constant stretch test measures the stress-relaxation, and the constant stress test measures the creep of the material. Under constant stretch the change of stress is recorded with time. Under constant stress, the change of stretch is recorded with time instead.

Based on the capability to sustain finite stress of the network, we classify two types of hydrogel networks under constant stretch or constant stress. Take the constant stretch test as an example. In a hydrogel with a solid-like network, the stress decreases over time, but reaches a finite plateau after a long time. The network therefore can permanently sustain finite loads like a solid. The plateau corresponds to the relatively strong and rate-independent network, such as a long-chain, covalently crosslinked network. In a hydrogel with a liquid-like network, the stress approaches zero after a long time. The network is easy to flow and unable to carry any load, just like a liquid. Similar comparison can be observed in the two networks under constant stress. The solid-like network is able to sustain the finite load with a constant deformation over a long time, while the liquid-like network continuously flows and deforms even under a small load.
Static fatigue of hydrogels is reported under constant stretch and constant stress. An uncut hydrogel with a liquid-like network will keep flowing under a constant load. This continuous elongation leads to fracture of the whole sample after a prolonged loading time. This behavior, denoted as \textit{creep fracture}, results from the viscoplastic property of the liquid-like network.\textsuperscript{107} A precut hydrogel may sustain a constant stretch without any crack propagation for a while, and then quickly fracture all of a sudden.\textsuperscript{117-119} This behavior, denoted as \textit{delayed fracture}, was first reported experimentally in physical hydrogels by Bonn et. al,\textsuperscript{117} but its mechanism is still under study, possibly due to poroelasticity or viscoelasticity.\textsuperscript{109,114,115,117,118,141} Creep fracture and delayed fracture observed in different hydrogels will be further discussed in Section 3.

1.2.3 Cyclic stretch

Cyclic stretch is extensively used to measure the stress-stretch hysteresis of hydrogels. The hysteresis is small for nearly elastic hydrogels, such as polyacrylamide,\textsuperscript{126} but is large and usually rate-dependent for hydrogels with tougheners.\textsuperscript{9,57-71}

Cyclic stretch is also used to characterize cyclic fatigue of a hydrogel. All hydrogels suffer cyclic fatigue. When an uncut sample is subject to a cyclic load, any irreversible change in mechanical property over cycles, such as the stress-stretch relation, is called \textit{fatigue damage}. When a pre-cut sample is subject to a cyclic load, the gradual extension of the crack is called \textit{fatigue fracture}. Cyclic stress-stretch curves show the fatigue damage of a hydrogel. A steady state is commonly observed after many cycles, where the stress-stretch curve does not change anymore. This steady state may result from the complete damage of the irreversible sacrificial bonds,\textsuperscript{126,128} or the continuous breaking and reforming of reversible sacrificial bonds.\textsuperscript{127} In cyclic fatigue fracture of precut samples, the crack extension is recorded as a function of cycles under a constant stretch or energy release rate in each cycle. A steady state is also observed where the crack extends by a constant length in each cycle. The crack extension per cycle in the steady state is a function of the applied energy release rate. The curve approaches infinity when the
energy release rate approaches the bulk fracture toughness measured under monotonic stretch, and approaches a finite value, called the *threshold for fatigue fracture*, when the crack extension per cycle approaches zero. Below this threshold, the crack does not extend under cyclic loads.

Another cyclic testing result called the *s-N curve*, has been widely used in practical applications to characterize cyclic fatigue of materials. An *s-N* curve measures the life time of a material using the number of cycles (*N*) it can sustain before failure under a constant stress (*s*). The samples for *s-N* curves are uncut, and often do not represent the actual service conditions. A considerable amount of scatter of data is usually observed in experiments even they are very carefully done, due to the unknown distribution of flaws in the material from sample to sample. Nonetheless, *s-N* curves can still roughly reflect the lifetime of a material under cyclic loads. The currently available data of *s-N* curves of hydrogels is very preliminary.

### 1.2.4 Self-recovery test

Hydrogels with tougheners involve breaking of sacrificial bonds upon stretching. If such breaking is irreversible, e.g., the breaking of the short-chain covalent network in a double-network hydrogel, the material property of the hydrogel will irreversibly change after the initial loading, leading to fatigue damage. Some hydrogels, however, can recover their material properties after many cycles of mechanical loads. These hydrogels are free from fatigue damage, and have been called *self-recovery hydrogels*. A self-recovery hydrogel usually contains a solid-like network that provides elasticity and motivates recovery, together with reversible sacrificial bonds, such as hydrogen bonds, hydrophobic interaction, and poly-ion complexes. The reversible bonds break when the hydrogel deforms and dissipate energy, but reform after staying in the undeformed state for some time, thus facilitate self-recovery of the material properties. A self-recovery test to verify this process usually contains an additional loading, after a certain time following the initial loading. The material properties,
such as the elastic modulus, stress-stretch hysteresis, and fracture stress, are compared between the initial cycle and the recovered cycle to measure the degree of recovery.
<table>
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<tr>
<td><strong>Monotonic stretch</strong></td>
<td><strong>Stress-stretch</strong>: mechanical strength, rate-dependency, yield stress, stretchability, and elastic modulus.</td>
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<td><img src="image1" alt="Graph of Stress-stretch" /></td>
<td><img src="image2" alt="Graph of Stress-stretch" /></td>
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<tr>
<td><strong>Constant stretch</strong></td>
<td><strong>Relaxation</strong>: fast crack extension after stretched by a certain time</td>
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<td><img src="image3" alt="Graph of Relaxation" /></td>
<td><img src="image4" alt="Graph of Relaxation" /></td>
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<tr>
<td><strong>Constant stress</strong></td>
<td><strong>Creep</strong>: viscoelasticity, viscoplasticity, poroelasticity.</td>
</tr>
<tr>
<td><img src="image5" alt="Graph of Creep" /></td>
<td><img src="image6" alt="Graph of Creep" /></td>
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<tr>
<td><strong>Cyclic stretch</strong></td>
<td><strong>Fatigue damage</strong>: irreversible change of material property over cycles.</td>
</tr>
<tr>
<td><img src="image7" alt="Graph of Cyclic stretch" /></td>
<td><img src="image8" alt="Graph of Cyclic stretch" /></td>
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<tr>
<td><strong>Self-recovery</strong></td>
<td><strong>Self-recovery capability</strong>: reversibility of bonds formation.</td>
</tr>
<tr>
<td><img src="image9" alt="Graph of Self-recovery" /></td>
<td><img src="image10" alt="Graph of Self-recovery" /></td>
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- **Stress-stretch**: fracture stretch and its rate-dependency.
- **v-G**: crack speed as a function of the energy release rate.
- **s-N curve**: lifetime of a material under cyclic loads with a constant stress.
- **Fatigue fracture**: the crack growth per cycle as a function of the energy release rate.
1.3 Representative hydrogels and their behaviors

From the representative loading profiles, we summarize static and cyclic fatigue of hydrogels in both uncut and precut samples. Static fatigue of hydrogels include: creep fracture (Figure 1.1b),\textsuperscript{107} static damage (Figure 1.1c), delayed fracture (Figure 1.1e),\textsuperscript{117-119} and slow crack (Figure 1.1f).\textsuperscript{99,108,111,120-125} Among them, static damage corresponds to the internal damage of a material built up under prolonged static loads. We are unaware of any systematically study of this behavior, but still list it here as a potentially important material property. Cyclic fatigue of hydrogels include the s-N curve (Figure 1.2b),\textsuperscript{18} fatigue damage (Figure 1.2c)\textsuperscript{59,65-70,126-133,145} and fatigue fracture (Figure 1.2e&f).\textsuperscript{119,126-128,145} The s-N curve is rarely reported in hydrogels, and also has not been systematically studied so far.

To place static and cyclic fatigue into contexts for further discussion, in this section, we review some representative hydrogels and their mechanical behaviors, especially fatigue, under the summarized loading profiles. The representative hydrogels include: polyacrylamide (PAAm) hydrogels in which polyacrylamide is covalently crosslinked, calcium-alginate (Ca-alginate) hydrogels in which alginate is ionically crosslinked, polyacrylamide-calcium-alginate (PAAm-Ca-alginate) hydrogels in which the above two networks interpenetrate each other, polyacrylamide-poly(2-acrylamido-2-methylpropane sulfonic acid) (PAAm-PAMPS) hydrogels in which two covalently crosslinked networks interpenetrate each other, and polyampholyte hydrogels in which the network is completely ionically crosslinked.
Figure 1.1 Static fatigue of hydrogels. (a) The sample is uncut. (b) Creep fracture: under a constant stress, the material keeps deforming and finally fractures. (c) Static damage: under a static load, the material property changes with time. (d) The sample is precut with a crack. (e) Delayed fracture: under a constant stretch, the crack does not extend in the precut sample for a while, but then propagates in a sudden. (f) Slow crack: a precut sample fractures slowly under a constant load. The load is characterized by the energy release rate. The speed of crack extension is a function of the applied energy release rate.
Figure 1.2 Cyclic fatigue of hydrogels. (a) The sample is uncut. (b) s-N curve: under a constant stress $s$, the material fractures after a certain number of cycles $N$. (c) Fatigue damage: under cyclic loads, the material property changes with cycles of loading. (d) The sample is precut with a crack. (e) Fatigue fracture: under cyclic loads, the crack grows with the number of cycles. (f) Fatigue fracture: the crack growth per cycle is a function of the energy release rate.

1.3.1 Polyacrylamide

A polyacrylamide (PAAm) hydrogel contains a covalent network but no sacrificial bonds as tougheners (Figure 1.3a). As a result, PAAm hydrogels are nearly elastic, which makes the theory of entropic elasticity applicable. PAAm hydrogels are readily synthesized, and are being used in water treatment, oil recovery, agriculture, medicine, as well as in most recently developed hydrogel devices. Many of these devices directly benefit from high water content, high stretchability, elasticity, and transparency of PAAm. PAAm is the primary network in many tough hydrogels. Its property has been extensively characterized, including thermodynamics of mixing, large deformation and swelling, fracture, adhesion with elastomers, and phase separation. All these facts together make
PAAm an excellent model material for fundamental studies, just as silica for studying fracture of hard materials, and copper for studying fatigue of metals.

Although a PAAm hydrogel is usually described as brittle and soft, it is not always the case. The mechanical properties of a PAAm hydrogel such as modulus, stretchability and fracture toughness depend significantly on its intrinsic molecular variables. As an example, the crosslinkers N,N’-Methylenebis(acrylamide) (MBAA) added to the precursor solution of PAAm can greatly affect its property. For a PAAm hydrogel with 1.9 M of acrylamide, adding 0.2 wt% of MBAA makes the hydrogel soft and brittle. The hydrogel can only be stretched to four times its initial length. The fracture toughness measured under the pure shear setup is 38.2 ± 3.4 J/m². For comparison, with 0.06 wt% of MBAA, the hydrogel becomes softer but much more stretchable and tough. It can be readily stretched over 15 times without fracture (Figure 1.3b), with a fracture toughness of 449 ± 26 J/m² (Figure 1.3c), comparable to the toughness of some tough hydrogels. The more crosslinks shorten the average polymer chain length in the PAAm network and increase the elastic modulus, but reduce the stretchability and the fracture toughness.

Poroelasticity of PAAm hydrogels has been characterized using stress relaxation under the indentation test. During the test, a probe is applied to indent the hydrogel by a prescribed depth and then held with time. The force sensed by the probe decreases with time and reaches a plateau after a long time. Different indentation depths lead to different force-relaxation curves (Figure 1.3d). However, if the time-dependent force is normalized using its initial value and the plateau value, and the loading time is normalized by the square of indentation depth, all the curves collapse onto one curve. Since the time scale of viscoelastic relaxation is assumed to be independent of the indentation depth, while the time scale of poroelastic relaxation caused by diffusion is proportional to the square of the length, the relaxation of hydrogel under the indentation test is caused by poroelasticity, but not by viscoelasticity.
Figure 1.3 PAAm hydrogels: basic characterization. (a) The molecular structure of a PAAm hydrogel. (b) The stress-stretch curve of the hydrogel depends on the amount of crosslinkers MBAA added in the precursor solution. (c) The fracture toughness of the hydrogel depends on the amount of crosslinkers. (d) Relaxation of PAAm due to poroelasticity measured under the indentation test.\textsuperscript{113}

Despite the near-perfect elasticity of PAAm hydrogels, it still suffers both static and cyclic fatigue. PAAm hydrogels slightly suffer slow crack growth,\textsuperscript{125,139} even though there is no obvious toughener in the material. For PAAm hydrogels with 1.9 M PAAm and 0.06 wt% MBAA, the energy release rate in the hydrogel is about 350 J/m\textsuperscript{2} at high speed, and approaches about 200 J/m\textsuperscript{2} at low speed (Figure 1.4a).\textsuperscript{139} Precut samples of PAAm hydrogels suffer delayed fracture.\textsuperscript{119} The delay time, i.e. the time period between the start of loading and the final
occurrence of running fracture, is longer for samples under a higher energy release rate (Figure 1.4b). When the energy release rate is below a certain value, denoted as the *threshold for delayed fracture*, the hydrogel does not fracture at all within the observable period of the experiment. The slow crack and delayed fracture of PAAm may relate to the poroelasticity of the hydrogel.\textsuperscript{118} Several theoretical models have been developed to study the relation between poroelasticity and fracture of hydrogels.\textsuperscript{109,114,115,118,141} However, the comparison between these models and experimental results remains unclear.

![Figure 1.4 PAAm hydrogels: static fatigue. (a) PAAm hydrogels suffer slow crack slightly. (b) PAAm hydrogels suffer delayed fracture.](image)

For cyclic fatigue of PAAm, being near-elastic, uncut samples of PAAm do not suffer fatigue damage. The stress-stretch curves exhibit little hysteresis, and change negligibly after thousands of loading cycles (Figure 1.5a).\textsuperscript{126} However, a precut PAAm hydrogel still suffers fatigue fracture (Figure 1.5b).\textsuperscript{119,127} The threshold for fatigue fracture depends on the intrinsic material variables such as the polymer chain length and the water content, and has been analyzed by the Lake-Thomas model initially derived for elastomers.\textsuperscript{75,119} Both experiments and
the Lake-Thomas model show that lower water content enhances the threshold. The experimental data and theoretical prediction agree well for hydrogels with higher water content, but deviate for hydrogels with low water content. In addition, the Lake-Thomas model indicates that the threshold increases with the polymer chain length. Compared to the threshold for delayed fracture, the threshold for fatigue fracture is lower for the same PAAm hydrogel. The relation between the two thresholds is still unclear.

Both the static and cyclic fatigue of PAAm indicate that PAAm hydrogels are not elastic enough. Some toughening mechanisms must exist to account for the nontrivial difference between the bulk fracture toughness and the thresholds. Even for nearly elastic hydrogels like PAAm, the material behaviors depend greatly on the intrinsic variables, such as water content, crosslink density, and distribution of the polymer chain length. There are still many unsolved problems relating the chemistry and mechanics of materials. As a result, PAAm is considered as the model material to study the mechanical behaviors of hydrogels including fatigue.

Figure 1.5  PAAm hydrogels: cyclic fatigue. (a) Uncut PAAm hydrogels do not suffer fatigue damage and have almost no stress-stretch hysteresis. (b) PAAm hydrogels still suffer
fatigue fracture. The fatigue fracture depends on the intrinsic variables of the hydrogel, such as the water content.\textsuperscript{145}

1.3.2 Calcium-alginate

Alginate hydrogels have long been used in biomedical applications such as pharmaceutics, drug delivery, tissue engineering and cell transplantation.\textsuperscript{6,156-158} Of particular interest is the calcium-alginate (Ca-alginate) hydrogel, which has recently become an essential composition in forming tough hydrogels\textsuperscript{61,71,159} and enabling new, unprecedented applications.\textsuperscript{7,8,18,63} A Ca-alginate hydrogel consists of alginate polymer chains ionically crosslinked by Ca\textsuperscript{2+} ions (Figure 1.6a). Ca-alginate hydrogels are usually much stiffer (elastic modulus $\sim$ 10-100 kPa) than PAAm hydrogels (elastic modulus $\sim$ 1-10 kPa) (Figure 1.6b). Ca-alginate hydrogels are also quite brittle. It has fracture toughness only on the order of 10 J/m\textsuperscript{2} (Figure 1.6c).\textsuperscript{61}

In Ca-alginate hydrogels, the alginate chains and Ca\textsuperscript{2+} ions form “egg box”-like interactions, with the energy of ionic bonds on the order of $kT$, where $kT$ is the temperature in the unit of energy.\textsuperscript{160,161} Such ionic bond is two orders of magnitude weaker compared to the covalent bond between alginate monomers.\textsuperscript{75} As a result, Ca-alginate has been assumed as a liquid-like network, i.e. the stress will relax to zero under a finite strain over a long time. Zhao et. al. conducted experiments by placing the Ca-alginate hydrogel under constant compressive strain in the phosphate-buffered saline (PBS) solution, and recorded the stress relaxation.\textsuperscript{162} For comparison, an alginate hydrogel covalently crosslinked by adipic acid dihydrazide (AAD) and EDC chemistry was tested under the same condition. While the covalently crosslinked alginate hydrogel maintains a finite stress after about 3 hours, the ionically crosslinked Ca-alginate hydrogel carries almost no stress (Figure 1.6d). The study concluded that the covalently crosslinked alginate network is more solid-like, while the ionically crosslinked alginate network is more liquid-like. However, the conclusion might be affected by the known degradation of Ca-
alginate network in PBS due to ion exchange or bacteria, which may have damaged the network over the test and lead to zero stress. If an Ca-alginate hydrogel is completely sealed in silicone oil instead of PBS during relaxation, the stress level in the hydrogel drops greatly at the beginning, but remains finite even after 12 days (Figure 1.6e). Without being immersed in PBS solution, the Ca-alginate hydrogel behaves solid-like.
because the ionic bond of the Ca-alginate crosslink is much weaker compared to the covalent bond of the alginate chain, fracture of the Ca-alginate hydrogel results from the breaking of ionic bonds and pull-out of alginate chains, instead of scission of alginate chains themselves. This molecular process of fracture leads to slow crack of Ca-alginate hydrogels (Figure 1.7a). The threshold for the slow crack is only a few J/m² for Ca-alginate hydrogels, smaller compared to the thresholds of covalently crosslinked PAAm hydrogels or other tough hydrogels (10-100 J/m²), where fracture is due to polymer chain scission at the threshold.

Cyclic fatigue of Ca-alginate hydrogels has been rarely studied, possibly due to the weak mechanical property of the hydrogel even under the first loading. The ionic bonds of calcium readily break during one cycle of loading and unloading, leading to considerable stress-stretch hysteresis under a cyclic stretch up to only 1.2 (Figure 1.7b). It would be interesting to see more cyclic fatigue studies of Ca-alginate hydrogels, especially with respect to the existence of steady state in fatigue damage, and the threshold for fatigue fracture.
1.3.3 Polyacrylamide-calcium-alginate

A PAAm hydrogel has a fracture toughness of about 100 J/m². A calcium-alginate hydrogel has a fracture toughness of about 10 J/m². Both hydrogels are brittle compared to natural rubber, but combining them together creates a tough hydrogel, PAAm-Ca-alginate, with fracture toughness as high as 10,000 J/m². This general design principle of creating tough hydrogels, i.e., using a stretchable polymer network in topological entanglement with a network with sacrificial bonds, was initiated by Gong and co-workers, and has instigated the worldwide search for hydrogels of various polymer networks and sacrificial bonds.

The PAAm-Ca-alginate hydrogel is a representative of such tough hydrogels. It has a covalently crosslinked PAAm network topologically entangled by an ionically crosslinked Ca-alginate network (Figure 1.8a). Upon stretching, the long-chain PAAm network provides elasticity and enables large stretchability, while the short-chain Ca-alginate network unzips and dissipates energy. The tough hydrogel can be both as stretchable as a covalently crosslinked...
PAAm hydrogel, and as stiff as an ionically crosslinked Ca-alginate hydrogel (Figure 1.8b). When a precut PAAm-Ca-alginate hydrogel is stretched, the PAAm network bridges the crack at the crack tip, while the unzipping of the Ca-alginate network surrounding the crack tip dissipates a large amount of energy, leading to exceptional fracture toughness. The fracture toughness is smaller when the amount of alginate is either too high or too low, but reaches maximum when the amount of alginate is in the middle (Figure 1.8c). This highest fracture toughness corresponds to the largest energy dissipation in the crack processing zone near the crack tip.

Similar to the Ca-alginate hydrogel, the hybrid hydrogel is rate-dependent. When the hydrogel is loaded to a constant stretch under different strain rates, its reaches different stress levels. A higher strain rate leads to a higher stress level. Afterwards, all the stresses relax to the same equilibrium stress level after some time (Figure 1.8d). The rate-dependent stress level after the immediate stretch indicates the time-dependent unzipping of the Ca-alginate network. The identical stress level after relaxation indicates the long-term, solid-like PAAm network in the hybrid hydrogel.
The PAAm-Ca-alginate hydrogel suffers slow crack (Figure 1.9a) due to the rate-dependency. When the crack speed is high, the unzipping of Ca-alginate dissipates a large amount of energy and toughens the hydrogel. When the loading rate is low, the unzipping takes minimum energy and fails to toughen the hydrogel. Under the tearing test, the energy release rate is over 4000 J/m² at the crack speed of 0.01 m/s, but only about 200 J/m² at the crack speed of 1 µm/s. Nonetheless, the solid-like Ca-alginate network at low speed still contributes to the threshold for slow crack. This is shown by comparing the PAAm-alginate hydrogels with the same PAAm network and amount of alginate, but with no Ca²⁺ (0-Ca), 25 mM of Ca²⁺ (1-Ca) and with 50 mM of Ca²⁺ (2-Ca) added in the precursor solution. The threshold for slow crack is 59, 173, and 952 J/m², respectively.

PAAm-Ca-alginate hydrogels suffer cyclic fatigue. An uncut PAAm-Ca-alginate hydrogel suffers fatigue damage. The weak ionic crosslink of Ca-alginate is almost irreversible after breaking. The stress-stretch hysteresis decreases drastically in the second loading cycle even if the hydrogel stays undeformed after an initial loading for one day (Figure 1.9b). The stress-stretch hysteresis in the first cycle is rate-dependent, but is large over a range of strain rates (Figure 1.9c). This large hysteresis during the first cycle and the significantly reduced hysteresis in the following cycle indicate that the majority of sacrificial bonds already break after the initial loading. However, the hydrogel still keeps softening over thousands of cycles of loading, until reaching a steady state (Figure 1.9d). This phenomenon is denoted as shakedown,
and has been observed under various cyclic stretches and rates.\textsuperscript{126} The molecular origin of shakedown is still under study.

In addition to fatigue damage, a PAAm-Ca-alginate hydrogel suffers fatigue fracture if it is precut.\textsuperscript{126} Because of the shakedown, the energy release rate corresponding to a constant cyclic stretch is large at the beginning cycles of loading, but decreases with the loading cycles. Under a constant cyclic stretch, the crack extension per cycle in a PAAm-Ca-alginate hydrogel is steep at the beginning cycles, and becomes smaller when reaching the steady state after thousands of cycles (Figure 1.9e). The threshold for fatigue fracture is on the order of 10 J/m\textsuperscript{2}, higher but close to the threshold of the PAAm hydrogel itself (Figure 1.9f). It is concluded that the threshold only depends on the long-chain covalent PAAm network, but negligibly depends on the Ca-alginate network as toughener.\textsuperscript{126} This conclusion has been verified in other hydrogel systems, with more careful control of the hydrogel compositions.\textsuperscript{127,128}
Figure 1.9 PAAm-Ca-alginate hydrogels: fatigue. (a) The hydrogel suffers slow crack. The threshold for slow crack depends on the amount of Ca$^{2+}$ ions added in the precursor solution. (b) The hydrogel cannot self-recover after an initial loading, even if being in the...
undeformed state for one day. The stress-stretch hysteresis is rate-dependent, but is large over a range of strain rate. (d) The hydrogel suffers fatigue damage. The stress-stretch curve reaches a steady state after thousands of loading cycles. This phenomenon is denoted as shakedown. (e) Because of shakedown, in a precut hydrogel under cyclic loading of constant stretch, the crack growth per cycle is large at the initial cycles, and is smaller when reaching a steady state after thousands of cycles. (f) The hydrogel suffers fatigue fracture. The threshold for fatigue fracture is on the order of 10 J/m², higher but close to the threshold of the PAAm hydrogel itself.

1.3.4 Polyacrylamide-poly(2-acrylamido-2-methylpropane sulfonic acid)

The polyacrylamide-poly(2-acrylamido-2-methylpropane sulfonic acid), or PAAm-PAMPS hydrogel is the first double-network hydrogel developed by Gong and co-workers with the toughening mechanism of breaking sacrificial bonds. Different from the PAAm-Ca-alginate hydrogel, the sacrificial bonds in the PAAm-PAMPS hydrogel come from the short-chain, covalently crosslinked PAMPS network (Figure 1.10a). Because the covalent bonds of the PAMPS network are relatively strong, the PAAm-PAMPS hydrogel shows an evident yielding point in the uniaxial tensile stress-stretch curve, accompanied by a necking phenomenon observed in the test (Figure 1.10b). The yielding point is the result from the competition between the elasticity of the PAAm network and the softening of the PAMPS network due to bond breaking. On the left of the yielding point, the elasticity of the PAAm network dominates, and the stress increases with the stretch. On the right of the yielding point, the breaking of PAMPS network is more significant, leading to a slight decrease and a following plateau of the stress level under further extension, just like the yielding of some metals. When the majority of the PAMPS network already breaks, the elasticity of the PAAm network dominates and the stress starts to increase again. The fracture toughness of a PAAm-PAMPS hydrogel is higher when the crosslinking density of the PAAm network decreases, similar as observed in the
covalently crosslinked PAAm hydrogel. On the other hand, the crosslinking density cannot be too low for the hydrogel to have a homogeneous and solid-like network, which again reduces the fracture toughness (Figure 1.10c).\textsuperscript{58,167}

Figure 1.10  PAAm-PAMPS hydrogels: basic characterization. (a) The molecular structure of the PAAm-PAMPS hydrogel. (b) The stress-stretch curve shows a yielding point.\textsuperscript{166}  (c) The fracture toughness is a function of the crosslinking density of the PAAm network.\textsuperscript{167}

For static fatigue, the PAAm-PAMPS hydrogel suffers slow crack as the PAAm hydrogel itself,\textsuperscript{104} but not as significant as the PAAm-Ca-alginate hydrogel. The energy release rate is
about 600 J/m² at a crack speed of 10³ mm/min, and drops to approximately 200 J/m² at a crack speed of 10⁻¹ mm/min. Similar to the slow crack of nearly elastic PAAm hydrogel, the slow crack of the PAAm-PAMPS hydrogel indicates some unexplored rate-dependent toughening mechanism.

For cyclic fatigue, because the breaking of the covalent PAMPS network is completely irreversible, an uncut PAAm-PAMPS hydrogel suffers fatigue damage under cyclic loads severely. The stress-stretch curve has pronounced hysteresis during the first cycle of loading, but almost no hysteresis in the following loading cycles (Figure 1.11b&c). The hydrogel does not recover its mechanical property even after one week in the undeformed state (Figure 1.11b). The stress-stretch curve in the second loading cycle follows the unloading curve of the first cycle, but behaves as a fresh material once exceeding the maximum stretch in the first cycle, showing the Mullins effect. Shakedown is also observed under cyclic loads (Figure 1.11c), similar to that in PAAm-Ca-alginate hydrogels. The threshold for fatigue fracture of a precut PAAm-PAMPS hydrogel reaches over 400 J/m² (Figure 1.11d), if the PAAm chain is made long enough by reducing the amount of crosslinkers in the precursor of the hydrogel. This value of fatigue threshold is higher than any other hydrogels reported so far, but still much lower than the bulk fracture toughness of the hydrogel (~ 4000 J/m²).

Although the fracture toughness of a PAAm-Ca-alginate hydrogel can be higher than that of a PAAm-PAMPS hydrogel, the PAAm-PAMPS hydrogel has advantage in specific applications. Alginate is a bio-polymer. The Ca-alginate network is formed by ionic crosslinks. These together make the Ca-alginate network degrade over time, leading to limited lifetime of the PAAm-Ca-alginate hydrogel. By contrast, the PAMPS network is covalently crosslinked, and is hardly degradable even implanted in a living body. The balance of fracture toughness and bio-stability makes the PAAm-PAMPS hydrogel a good candidate for development of new biological applications of hydrogels.
Figure 1.11  PAAm-PAMPS hydrogels: static and cyclic fatigue. (a) The hydrogel suffers slow crack.\textsuperscript{104} (b) The hydrogel shows significant stress-stretch hysteresis during the first loading, but shows almost no hysteresis in the following loading.\textsuperscript{116} Mullins effect is observed in the hydrogel. The hydrogel cannot recover its material property at all, even after one week staying in the undeformed state. (c) Fatigue damage of the PAAm-PAMPS hydrogel. The hydrogel reaches a steady state with negligible hysteresis after thousands of cycles.\textsuperscript{128} (d) The threshold for fatigue fracture can reach over 400 J/m\textsuperscript{2}, higher than any other hydrogels reported so far, but still much lower than the bulk fracture toughness of the hydrogel (~ 4000 J/m\textsuperscript{2}).\textsuperscript{128}
1.3.5 Polyampholytes

Physical hydrogels composed of polyampholytes have been developed and studied since 2013. The hydrogel has purely ionically crosslinked networks, but consists of two types of ionic bonds of different strength (Figure 1.12a). Although forming together a single ionic network, the strong ionic bonds act as the solid-like network and provide elasticity, while the weak ionic bonds act as the toughener and provide energy dissipation. This combination gives the polyampholyte hydrogel high stiffness, strength, toughness, as well as self-recovery and self-healing. Also because of this combination, the mechanical behavior of a polyampholyte hydrogel is complex, which markedly reflects its molecular structures.

The ionic bonds in polyampholyte hydrogels are reversible. The hydrogel can completely recover its stress-stretch behavior after being cut to two pieces, attached again, and allowed for 24 hours of self-healing. The existence of the solid-like strong ionic bonds gives the hydrogel a high stress level on the order of MPa, while the easy breaking and reforming of weak ionic bonds makes the hydrogel rate-dependent (Figure 1.12b). The fracture toughness can reach as high as thousands of J/m², increasing with the fraction of polymers in the hydrogel (Figure 1.12c).
Figure 1.12  Polyampholyte hydrogels: basic characterization. (a) The molecular structure of the hydrogel. (b) The stress-stretch curve is rate-dependent. The stress level is on the order of MPa. (c) The fracture toughness can reach as high as thousands of J/m², increasing with the fraction of polymers in the hydrogel.

Polyampholytes suffer static fatigue including slow crack and creep fracture. The slow crack above the threshold is governed by the viscoplastic process, and can be theoretically analyzed using the time-temperature superposition principle for elastomers. The energy release rate is about 200 J/m² even at a crack speed as low as 10⁻⁸ m/s, which is still much larger than the threshold of most elastomers (~ 50 J/m²) (Figure 1.13a). This indicates that the bulk dissipation still exists in the hydrogel even at such a low speed. Under a constant stress on the order of 0.1-1 MPa, polyampholyte hydrogels creep, and fracture after several hours (Figure 1.13b). The failure time of such creep fracture inversely depends on the loading stress (Figure
1.13c). The high energy release rate at the small crack speed in slow crack indicates that the hydrogel network is strong to sustain a relatively high load. On the other hand, the creep fracture indicates that the ionic network is still not strong enough, which will fracture with time if the applied load is high. Relating the slow crack and creep fracture in polyampholytes is interesting, which remains further study.

Figure 1.13 Polyampholyte hydrogels: static fatigue. (a) The hydrogel suffers slow crack. Above the threshold, the slow crack is governed by the viscoplastic process.\textsuperscript{108} (b) Under a constant stress, the stretch in the hydrogel keeps increasing, and leads to fracture of the entire sample after some time.\textsuperscript{107} (c) The failure time of the creep fracture inversely depends on the loading stress.\textsuperscript{107}

Cyclic fatigue of polyampholytes has only been explored in its capability of self-recovery (Figure 1.14a).\textsuperscript{67} Similar to other self-recovery hydrogels, the stress-stretch hysteresis is large when the strain rate is high, and small as the strain rate is low (Figure 1.14b). The hydrogel can almost completely recover itself after 30 minutes following an initial loading cycle. In comparison, the hydrogel can only completely heal itself 24 hours after being cut to two pieces and attached again.\textsuperscript{144} The different time scales of self-recovery and self-healing is possibly due to the fact that most strong ionic bonds do not break during the one cycle of loading and still
provide elasticity and motivate the recovery, but they completely break after cutting, thus take a much longer time to heal back.

**Figure 1.14 Polyampholyte hydrogels: cyclic fatigue.** (a) The hydrogel is able to recover its material property after 30 minutes. (b) Like other self-recovery hydrogels, the cyclic stress-stretch hysteresis is rate-dependent.

The study of cyclic fatigue damage and fatigue fracture of polyampholyte hydrogels is interesting for the following reason. In fatigue damage of an uncut sample of polyampholytes, the strong ionic bonds may well behave as a solid-like network and lead to a steady state in the stress-stretch curve with a non-trivial stress level. If the cyclic mechanical load is high, however, the strong ionic bonds may still break after many cycles, just as how they behave in the creep fracture. In this case, a steady state may never be observed. For the threshold for fatigue fracture of polyampholyte hydrogels, because even the strong ionic bonds are not strong enough compared to covalent bonds, the threshold may be comparable or smaller than that of covalently crosslinked hydrogels, but may still be larger than that of traditional physical hydrogels such as Ca-alginate.
1.4 Outline of the thesis

This thesis explores fatigue of hydrogels under both static and cyclic loads. Hydrogels with different molecular structures show various fatigue behaviors, which are discussed in detail. In Chapter 2, we begin the study by focusing on fatigue fracture of a nearly elastic polyacrylamide hydrogels of various water contents under cyclic loads. The polyacrylamide hydrogel has a single covalently crosslinked polymer network. In Chapter 3, we further study cyclic fatigue of a polyacrylamide-calcium-alginate tough hydrogel, which has a covalently crosslinked polyacrylamide network in topological entanglement with an ionically crosslinked calcium-alginate network. In Chapter 4, we show that self-recovery hydrogels are still susceptible to fatigue fracture under cyclic loads. We study a hydrogel containing both covalently crosslinked polyacrylamide and uncrosslinked polyvinyl alcohol. For static fatigue of hydrogels, we further study slow crack of polyacrylamide-calcium-alginate hydrogels in Chapter 5, and discuss the relationship between the thresholds for fatigue fracture under cyclic loads and slow crack under static loads. In Chapter 6, we present a new design principle of flaw-insensitive hydrogels under both static and cyclic loads. Finally, we summarize some understanding of fatigue of hydrogels and future challenges for the topic in Chapter 7. Chapter 8 provides conclusion of this thesis.
Chapter 2  Fatigue fracture of nearly elastic hydrogels

2.1 Introduction

This chapter focuses on fatigue fracture of polyacrylamide (PAAm) hydrogels. A PAAm hydrogel contains a covalent network, but negligible tougheners. As a result, PAAm hydrogels are highly stretchable and nearly elastic.\textsuperscript{89,110,126,170} The stress-stretch curves exhibit little hysteresis, and change negligibly after thousands of cycles of loads.\textsuperscript{126} This near-perfect elasticity makes the theory of entropic elasticity applicable,\textsuperscript{87-89} and simplifies the analysis of the fatigue tests by excluding the inelastic effects in hydrogels of complex rheology. PAAm hydrogels are readily synthesized, and are being used in water treatment, oil recovery, agriculture, medicine,\textsuperscript{146} as well as in most recently developed hydrogel devices.\textsuperscript{11-15,17-19,21-26,28,29,32-35,38,40,41} Many of these devices directly benefit from high water content, high stretchability, nearly perfect elasticity, and transparency of PAAm. As noted above, PAAm is the primary network in many tough hydrogels.\textsuperscript{57-59,61,147,148} Its property has been extensively characterized, including thermodynamics of mixing,\textsuperscript{149,150} large deformation and swelling,\textsuperscript{89} fracture,\textsuperscript{57,61} adhesion with elastomers,\textsuperscript{151} and phase separation.\textsuperscript{152} All these facts together make PAAm an excellent model material for fundamental studies, just as silica for studying fracture of hard materials,\textsuperscript{84,85,153} and copper for studying fatigue of metals.\textsuperscript{142,154,155} A comprehensive knowledge of fatigue fracture of such a model material can aid the understanding of fatigue fracture in other hydrogels.

Despite near-perfect elasticity, PAAm hydrogels do suffer fatigue fracture.\textsuperscript{119,126,127,171} In our previous work, fatigue tests were conducted for PAAm hydrogels to support the studies of the effects of hygroscopic salts and tougheners. However, the effects of chain length and water content—two basic variables of a hydrogel of a covalent network—have not been systematically studied. This chapter is devoted to the effect of water content on fatigue fracture of PAAm hydrogels. In addition to being a basic variable in hydrogels, water content plays important roles
in applications, such as removing heat in fire-retarding blankets, transporting ions in ionotronic devices, dissolving drugs in drug-delivery systems, and maintaining softness and biocompatibility in artificial tissues.

In this study, we form the PAAm networks in all samples under the same conditions, and then modify the water content of each sample through solvent exchange. We study hydrogels of 96, 87, 78, and 69 wt% of water. We measure the crack extension under cyclic loads, and measure the fracture energy under monotonic loading. For the hydrogels of the four water contents, the fatigue thresholds are 4.3, 8.4, 20.5, and 64.5 J/m², and the fracture energies are 18.9, 71.2, 289 and 611 J/m². The measured thresholds agree well with the predictions of the Lake-Thomas model for hydrogels of high water content, but not in the case of low water content.

2.2 Experimental Section

2.2.1 Preparation of hydrogels

PAAm hydrogels with different water contents were prepared following the same process. We purchased from Sigma Aldrich the following substances: acrylamide (AAm, A8887), N,N'-methylenebis(acrylamide) (MBAA, M7279), N,N,N',N'-tetramethylethylenediamine (TEMED, T7024), ammonium persulfate (APS, A9164), and lithium chloride (LiCl, 746460). All chemicals were received and used without further purification. AAm powders of 4.69 g were dissolved in 30 mL deionized water to form an aqueous solution. MBAA, TEMED and APS were then added in quantities of 0.0015, 0.0022 and 0.0036 times the weight of AAm in sequence. To dilute the concentration of the APS initiator, we dissolved APS into 1.2 mL deionized water before adding it to the precursor solution. The prepared pre-gel solution was degassed and injected into acrylic molds with dimensions of 120×60×1.5 mm³ and covered with an acrylic plate. The samples were then stored at room temperature for more than 18 hours for complete polymerization.
2.2.2 Modification of water content

The total mass of water in the precursor solution is 31.2 g. The mass of AAm in the pre-gel solution is 4.69 g. We assume all the monomers are polymerized to form the as-prepared hydrogel, and there is no water evaporation during the polymerization. As a result, the water content of the as-prepared hydrogel is calculated as $\frac{31.2}{31.2+4.69} = 87$ wt%. The hydrogels were then modified through solvent exchange to 96, 78, and 69 wt% of water (Figure 2.1a). When a hydrogel underwent solvent exchange, its weight was recorded daily (Figure 2.1b). The corresponding weight of the hydrogel with 96, 78, and 69 wt% of water is 3.5, 0.59 and 0.42 times the weight of the as-prepared hydrogel.

To prepare a fully swollen hydrogel of 96 wt% of water, we soaked an as-prepared hydrogel in deionized water for 5 days until it reached equilibrium. To prepare hydrogels of 78 and 69 wt% of water, we placed an as-prepared hydrogel into a closed chamber equilibrated with 10 wt% LiCl aqueous solution (Figure 2.1a). To ensure that the concentration of LiCl keeps nearly constant before and after the solvent exchange, we prepared the LiCl solution with a weight at least 100 times the weight of the hydrogel. The hydrogel was kept without direct contact with the solution, but could exchange water molecules through the moisture in the chamber. Upon reaching the expected water content after a few days, the hydrogel was taken out and sealed in a plastic bag for another 5 days for homogenization. The time scale of reaching homogenization was estimated as $t \sim L^2/D$, where $L$ is the thickness of the hydrogel, and $D$ is the effective diffusivity of water in the hydrogel. Taking $L \sim 10^{-3}$ m and $D \sim 10^{-10}$ m$^2$/s, we estimated $t \sim 10^4$ s. The time period in the experiment hence ensures the homogenization of water inside the hydrogel.

Prior to solvent exchange, all samples of the hydrogels were prepared under the same condition. The PAAm network so prepared was assumed to remain unchanged after solvent exchange—that is, the water content was the only controlled variable for all samples of hydrogels. In contrast, the mechanical behavior of a hydrogel can be significantly different if its water
content is varied before the formation of network (Figure 2.1c). To highlight such difference, we prepared hydrogels of 96 wt% of water using two methods. In one method, we made an as-prepared hydrogel of 87 wt% of water, and then fully swelled the hydrogel in water after the polymerization (Figure 2.1c left). In the other method, we added the same amount of chemical reactants, but directly prescribed 96 wt% of water in the precursor (Figure 2.1c right). The two hydrogels show a significant difference in their mechanical responses. In particular, the hydrogel prepared from the precursor of 96 wt% of water is too soft and fragile to be solid-like. On the other hand, the hydrogel prepared from the precursor of 87 wt% of water and then swollen to 96 wt% of water results in a solid-like structure of the polymerized hydrogel. Such structural disparity between the hydrogels prepared in these two ways is perhaps also observed in other laboratories, but we are unable to identify any systematic study.
Figure 2.1 Modification of the water content in PAAm hydrogels. (a) Preparation of PAAm hydrogels with a specified water content: the fully swollen hydrogels (96 wt% water) were prepared by soaking the as-prepared samples in deionized water for 5 days; the drier hydrogels (78 wt% & 69 wt%) were prepared by introducing the as-prepared samples in a chamber. After a hydrogel reached its specified water content, it was stored in a sealed bag for another 5 days to reach homogeneity. (b) The weight change of hydrogels during solvent exchange to reach specified water contents. The actual weight \( w \) is normalized by the initial weight \( w_0 \). (c) The comparison between two hydrogels of 96 wt% water made in different ways. Left: a precursor of
87 wt% water was first polymerized and then fully swollen to reach 96 wt% water. Right: a precursor of 96 wt% water was directly polymerized.

2.2.3 Setup of mechanical testing

We conducted pure shear tests to characterize the fatigue fracture of the hydrogels. Before the test, we cut a piece of hydrogel and glued it with two pairs of acrylic grips using the Krazy glue. Each sample was of 70 mm width and 10 mm length between the grips. We notched the sample with a 20 mm long horizontal crack from the middle of its edge using a razor blade. The sample was then fixed in a tensile machine (Instron model 5966) with a 10 N load cell. The average thicknesses of the samples of 96, 87, 78, and 69 wt% of water were 2.35, 1.50, 1.25, and 1.10 mm.

To minimize dehydration during each test, we made an acrylic chamber to seal the tensile machine and sample (Figure 2.2a). Water droplets were sprayed on the inner surface of the chamber before the test. We weighed all the samples before and after testing, and found no more than 6% weight loss. In the case of hydrogels with 96 wt% water, consider an initial hydrogel of a unit weight, of which 0.96 is water, and 0.04 is polymer. After the hydrogel loses 0.06 units of its initial weight, the weight of hydrogel becomes 0.94, and the weight of water in the hydrogel becomes 0.94 – 0.04 = 0.90. The water content therefore becomes 0.90/0.94 = 95.7 wt%. Similarly, the water content of the 69 wt% hydrogel will become 67 wt% after the 6% weight loss. The maximum weight loss of 6 % observed during experiments only induces slight reduction of the water content in the hydrogel, which is within the experimental error.

Fatigue fracture was tested following a cyclic linear stretch-time profile (Figure 2.2b). In all tests, the stretch of the sample was cycled between 1 and $\lambda_{\text{max}}$. We fixed the strain rate of the test to be $0.4 \text{ s}^{-1}$. This strain rate ensures 20,000 cycles within 8-16 hours. The effect of strain rate on fatigue is not studied here. To record the crack extension, we took photos every 15 minutes (20 minutes for some tests) throughout the test with a digital camera (Canon EOS 70D).
The photos were post-processed to obtain the crack extension over the loading cycles. We controlled the applied \( \lambda_{\text{max}} \) between 1.3 and 1.6 in all tests, so that the crack extended on the order of 0.1-1 cm in 20,000 cycles. Under the fixed strain rate of 0.4 s\(^{-1}\), the period of one loading cycle ranged from 1.5 s to 3 s. A single fatigue fracture test typically took about 8-16 hours. The resolution of the recorded crack extension every 15 minutes was on the order of 0.1 mm.

![Diagram of fatigue tests of hydrogels](image)

**Figure 2.2 Fatigue tests of hydrogels.** (a) Samples were tested with a tensile machine inside a humidity chamber to prevent dehydration during the experiment. (b) The stretch-time profile of the fatigue fracture test. The stretch \( \lambda \) is defined as the distance between the displaced grips divided by the initial distance between the grips.

### 2.2.4 Sharpening of the crack tip

In initial cycles, the fatigue fracture was transient, and the rate of crack extension was hardly reproducible. After some cycles, the extension of the crack reached a steady state. The similar phenomenon has been reported for elastomers.\(^{172}\) In most experiments, the transient process took more than 20,000 cycles. One contributing factor to the transient process is likely that the razor blade did not prepare a consistent, sharp crack. To prepare a sharp crack, we slightly stretched the razor-notched sample by hand to let the initial crack propagate for a few millimeters before the fatigue test (Figure 2.3a). We compared the fatigue crack extension of
hydrogels with and without such pre-extension (Figure 2.3b). With this method, the steady state was reached after \( \sim 10000 \) cycles (Figure 2.3c).

![Image](image.png)

**Figure 2.3** Sharpening the crack tip reduces the period of transient process. (a) The crack tip initially cut by a razor blade was sharpened by slightly extending the crack before the fatigue test. The scale bar is 1 cm. (b) The fatigue crack growth of hydrogels with and without the sharpening process. (c) The representative raw experimental data of all the four hydrogels of different water content. The data typically contain transient growth, followed by steady growth.

### 2.2.5 Quantification of the applied load

We adopted the pure shear test of Rivlin and Thomas.\(^{136}\) To convert the amplitude of load to the energy release rate \( G \), we adopted the following procedure.\(^6\),\(^{119}\) We monotonically loaded an unnotched hydrogel sample of the same geometry, under a strain rate of 0.01 s\(^{-1}\) (Figure 2.4a). We plotted the nominal stress (i.e. the applied force divided by the initial cross-
sectional area) as a function of the stretch. The area under the curve gives the elastic energy per unit volume $W(\lambda)$ (Figure 2.4b). The energy release rate $G$ for a notched hydrogel under cyclic stretch of amplitude $\lambda_{\text{max}}$ is

$$G = HW(\lambda_{\text{max}}),$$

(2.1)

where $H$ is the distance of the sample between the grips in the undeformed state. We also adopted Equation (2.1) to quantify the bulk toughness of the hydrogel, with $\lambda_{\text{max}}$ replaced by the critical stretch when a crack ran in a notched sample under monotonic loading. As noted before, PAAm hydrogels are nearly elastic, the stress-stretch curve has little hysteresis, and changes negligibly over thousands of loading cycles.

Figure 2.4 Converting the applied load to the energy release rate. (a) The applied stretch as a function time. (b) The nominal stress as a function of stretch.

2.3 Results and discussions

In the steady state of fatigue fracture, the crack grows linearly with the number of cycles (Figure 2.5a-d). We converted each applied stretch $\lambda_{\text{max}}$ to the corresponding energy release rate by Equation (2.1) using the stress-stretch curves of unnotched hydrogels (Figure 2.5e). Hydrogels with more water are more susceptible to fatigue fracture under the same level of energy release rate $G$. For example, at $G = 8.0 \text{ J/m}^2$, a crack in the hydrogel of 96 wt% of water propagates by about 0.6 cm within 5,000 cycles (Figure 2.5a). In contrast, at a similar load $G = 8.4 \text{ J/m}^2$, a crack in the hydrogel of 87 wt% of water only propagates less than 0.1 cm over
15,000 cycles (Figure 2.5b). We recorded the crack extension of approximately 1 cm over 20,000 cycles. The mechanical loads required for such scale of crack extension per cycle are 4.0 – 8.0, 8.4 – 13.8, 19.1 – 34.8, and 44.4 – 87.0 J/m², corresponding to the hydrogels of 96, 87, 78 and 69 wt% of water, respectively.

We further compared the energy release rate for fatigue fracture in our experiments to the bulk toughness of the hydrogels. For the hydrogels of 96, 87, 78 and 69 wt% of water, the toughness was 18.9, 71.2, 289 and 611 J/m², respectively (Figure 2.5f). The energy release rate for fatigue fracture is much smaller than the toughness of the hydrogel. This large difference motivates us to obtain the threshold for fatigue fracture, below which a crack does not propagate under cyclic loads.
Figure 2.5 Experimental data of fatigue fracture of PAAm hydrogels with different water content. The fatigue crack extension was recorded over loading cycles, in hydrogels of (a) 96 wt%, (b) 87 wt%, (c) 78 wt%, and (d) 69 wt% of water. Each curve is the representative of 3 individual tests. (e) Stress-stretch curves of unnotched hydrogels under pure shear tests. (f)
The toughness decreases with the water content of the hydrogel. The data represent the mean and standard deviation of 3 experimental results.

We calculated the threshold for fatigue fracture by extrapolation of the experimental data. We performed linear regression to fit the steady-state crack growth $\Delta a$ as a function of the loading cycle $n$. The slope of the linear curve, $\Delta a/\Delta n$, is a function of the energy release rate $G$ (Figure 2.6). $\Delta a/\Delta n$ is $\sim 50$ nm/cycle when $G$ is very small, but varies almost linearly with $G$ when $G$ becomes larger. The fitted linear curve intercepts the $G$ axis at a finite value. This value, denoted as $\Gamma_0$, is the threshold for fatigue fracture. Hydrogels of fully swollen state (96 wt%) have the lowest threshold of $4.3 \text{ J/m}^2$. As the hydrogel becomes drier, the threshold increases dramatically (Figure 2.6 & Table 2.1). Hydrogels of 69 wt% of water have a threshold of 64.5 J/m$^2$, even higher than the previously reported threshold for the PAAm-alginate tough hydrogel (53 J/m$^2$). As the water content becomes lower, the slope of $\Delta a/\Delta n$ vs. $G$ decreases. That is, the crack extension in cyclic loads is slower in a drier hydrogel, compared to the same polymer network with more water. Hence, from the aspects of both the threshold and the speed of crack extension, we conclude that the resistance to fatigue fracture of a hydrogel improves when its water content is reduced.
Figure 2.6 (continued) The crack extension per cycle $\Delta a/\Delta n$ as a function of the energy release rate $G$. All the data represent the mean and standard deviation of 3 experimental results.

The threshold for fatigue fracture of elastomers was described by the Lake-Thomas model as the energy required to break the covalent network and propagate the crack by unit area.\textsuperscript{74} The Lake-Thomas model has been adapted for gels in several papers, but in different expressions.\textsuperscript{105,119,173-175} Here we choose one of the adaptions, and estimate the threshold as\textsuperscript{119}

$$
\Gamma_o = \phi_p^{2/3} bUl \sqrt{n_o} .
$$

(2.2)

Here $\phi_p$ is the volume fraction of the polymer in the hydrogel, and is related to the water content $\alpha$ through

$$
\phi_p = \frac{(1-\alpha)/\rho}{(1-\alpha)/\rho + \alpha/\rho_{H2O}} ,
$$

(2.3)

where $\rho$ is the density of acrylamide (1.13 g/cm$^3$), and $\rho_{H2O}$ is the density of water (1.0 g/cm$^3$). $b$ is the number of C-C bonds per unit volume of the dry polymer, $U$ is the energy of a C-C bond, $l$ is the length of the monomer, and $n_o$ is the average number of monomers per chain. $bUl\sqrt{n_o}$ only depends on the PAAm network, but does not depend on the water content of the hydrogel.

For polyacrylamide, $b$ is estimated by the number of monomers per unit volume of the dry polymer, $b = A \rho / M = 9.57 \times 10^{-7}$ m$^{-3}$, where $M$ is the molecular weight of acrylamide (71.08 g/mole), and $A$ is the Avogadro number (6.022 $\times 10^{23}$/mole). The length of the monomer is estimated as $l = b^{-1/3} = 0.471$ nm. The C-C bond energy is $U = 3.3 \times 10^{-9}$ J.\textsuperscript{75} All together, these parameters give a value of $bUl = 1.3$ J/m$^2$.

The number of monomers between two crosslinks, $n_o$, can be estimated by $n_o = b/N$, where $N$ is the number of chains per unit volume of the dry polymer. Because we assume that all
the hydrogels have the same PAAm network, \( n_0 \) and \( N \) are expected to be constants. To estimate \( N \), we adopted the Gaussian chain model to the hydrogel, which relates \( N \) to the shear modulus \( \mu \) through\(^{87-89}\)

\[
\mu = \phi_\mu^{1/3} N k T,
\]

(2.4)

where \( kT \) is the temperature in the unit of energy. At room temperature, we take \( kT = 4.1 \times 10^{-21} \text{J} \). Experimentally, the shear modulus \( \mu \) can be calculated as 1/4 of the initial slope of the stress-stretch curve under the pure shear test of unnotched samples (Figure 2.5e).\(^{119}\)

With these, we calculated the value of \( N \) for each water content (Table 2.1). The calculated \( N \) varies greatly with the water content. In the current analysis, we take the average value of \( N = 4.4 \times 10^{24} \text{m}^{-3} \) for all the hydrogels, and calculate the theoretical values of \( \Gamma_0 \) from Equation (2.2) accordingly.

**Table 2.1** Properties of PAAm hydrogels

<table>
<thead>
<tr>
<th>Water content ( \alpha ) (%)</th>
<th>Polymer volume fraction ( \phi_p ) (%)</th>
<th>Threshold ( \Gamma_0 ) (J/m(^2))</th>
<th>Toughness (J/m(^2))</th>
<th>Shear modulus ( \mu ) (kPa)</th>
<th>Chain density ( N ) (10(^{24}) m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>3.6</td>
<td>4.3</td>
<td>18.9</td>
<td>2.80±0.32</td>
<td>2.07</td>
</tr>
<tr>
<td>87</td>
<td>12</td>
<td>8.4</td>
<td>71.2</td>
<td>5.92±0.22</td>
<td>2.93</td>
</tr>
<tr>
<td>78</td>
<td>20</td>
<td>20.5</td>
<td>289</td>
<td>11.27±0.46</td>
<td>4.70</td>
</tr>
<tr>
<td>69</td>
<td>28</td>
<td>64.5</td>
<td>611</td>
<td>21.09±0.92</td>
<td>7.86</td>
</tr>
</tbody>
</table>
The prediction of the Lake-Thomas model agrees well with the experimental results for hydrogels with high water content (low \( \phi_p \)), but deviates at \( \phi_p = 28\% \), where the experimental value of \( \Gamma_0 \) is much larger than the theoretical result (Figure 2.7a). The same deviation occurs between the measured shear modulus \( \mu \) and its theoretical prediction from the Gaussian chain model in Equation (2.4) (Figure 2.7b). The suggested scaling of \( \phi_p \) in Equation (2.2) and (2.4) does not fit the experimental data properly. In particular, the Lake-Thomas model adapted here does not account for the fatigue threshold of relatively dry hydrogels. Theoretical models with different scaling have been extensively studied in polymer physics,\(^{176-178}\) and may shed light on resolving this discrepancy. For example, at a high polymer volume fraction \( \phi_p \), it is hypothesized that the presence of polymer chain entanglements may have non-trivial contribution to the threshold and shear modulus.\(^{178}\) To better understand this deviation, more experimental data and improved theoretical analysis are currently under study.
Figure 2.7  Comparison between the experimental results and the theoretical prediction. (a) Fatigue threshold, theoretically predicted by the Lake-Thomas model in Equation (2.2). (b) Shear modulus, theoretically predicted by the Gaussian chain model in Equation (2.4). The four data points correspond to the hydrogels of 96, 87, 78, and 69 wt% of water, from left to right. The data in (b) represent the mean and standard deviation of 3 experimental results.

Despite this deviation, both the experimental results and the Lake-Thomas model show that lower water content (or higher polymer volume fraction) enhances the threshold. In addition, the Lake-Thomas model indicates that the threshold increases with \( n_0 \), the average number of monomers per chain.
2.4 Summary

Polyacrylamide hydrogels are highly stretchable and nearly elastic. Despite this near-perfect elasticity, polyacrylamide hydrogels are susceptible to fatigue fracture. A sample without pre-cut crack can sustain thousands of loading cycles without appreciable degradation in stress-stretch curves. When a sample with a pre-cut crack is subject to a cyclic load, however, the crack will extend cycle by cycle if the amplitude of the load (measured by energy release rate) exceeds a threshold. Here, we have characterized the effect of water content on fatigue threshold and fracture energy. Both the fatigue threshold and the fracture energy reduce as the water content increases. For hydrogels of fixed water content, the fatigue threshold is well below the fracture energy. So far as fatigue fracture is concerned, polyacrylamide hydrogels are not elastic enough. Some toughening mechanisms must exist to account for the large difference between the fatigue threshold and fracture energy. For polyacrylamide hydrogels of low water content, the measured fatigue threshold is significantly higher than the prediction of the Lake-Thomas model. These findings await further study.
Chapter 3  Fatigue fracture of tough hydrogels

3.1 Introduction

Several strategies have been developed to synthesize tough hydrogels, including double network hydrogels,\textsuperscript{57,61} nano- and micro-composite hydrogels,\textsuperscript{94,179,180} as well as tri-block copolymers and hydrophobic associated hydrogels.\textsuperscript{181,182} The fracture toughness has been enhanced by orders of magnitude, from $10 \text{ J/m}^2$ to $10,000 \text{ J/m}^2$. The mechanical behavior of tough hydrogels has become a field of active research.\textsuperscript{58,60}

High toughness of these hydrogels is achieved by breaking sacrificial bonds, such as covalent bonds in a short-chain network,\textsuperscript{57} or ionic crosslinks.\textsuperscript{61,181} Consequently, tough hydrogels are prone to degradation under cyclic loads. Examples include changes in elastic modulus,\textsuperscript{129} in hysteresis of stress-stretch curves,\textsuperscript{65,66} and in functional characteristics of devices.\textsuperscript{183} Fatigue fracture of tough hydrogels, however, has remained unexplored. This lack of information on fatigue fracture of tough hydrogels hinders their further development, knowing that fatigue fracture is a critical mode of failure of all other tough materials, including metals, plastics, elastomers and composites.\textsuperscript{73-75,77,80,136,184-186}

In this chapter, we explore fatigue fracture of tough hydrogels, which commonly include two interpenetrating networks. We focus on a polyacrylamide-calcium-alginate tough hydrogel, where polyacrylamide forms a network of covalent crosslinks, and calcium-alginate forms a network of ionic crosslinks.\textsuperscript{61} We find that the tough hydrogel exhibits \textit{shakedown after prolonged cycling}: the stress-stretch curve changes cycle by cycle, and reaches a steady state after thousands of cycles. The threshold for fatigue fracture is much below the toughness under monotonic load, but the extension of crack per cycle in the polyacrylamide-calcium-alginate tough hydrogel is much smaller than that in a single-network polyacrylamide hydrogel.
3.2 Experimental section

3.2.1 Preparation of tough hydrogel 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 calcium chloride. We purchased from FMC Biopolymer the sodium alginate (Manugel GMB).

We prepared polyacrylamide-calcium-alginate tough hydrogels following the two-step method.\textsuperscript{71}

In the first step, a single-network polyacrylamide hydrogel with interpenetrating sodium alginate was prepared. 40.54 g AAm and 6.76 g sodium alginate were dissolved in 300 ml deionized water to form an aqueous solution. We then added MBAA, TEMED and APS in quantities of 0.0012, 0.0025 and 0.0042 times the weight of AAm. The pre-gel solution was then degassed and injected into a 50×50×1.65 mm\textsuperscript{3} plastic mold and covered with a glass plate. The sample was stored at room temperature for 24 hours to form the polyacrylamide network. The sodium-alginate chains are believed to interpenetrate the polyacrylamide network, but do not form a network.\textsuperscript{71}

In the second step, the prepared hydrogel was soaked in a 0.5M calcium chloride solution for at least 2 days. This allows sufficient time for the exchange of calcium sodium ions between the hydrogel and the external solution, so that an alginate network of calcium crosslinks forms. To ensure that the concentration of calcium ions in the external solution keeps nearly constant before and after soaking the hydrogel, we prepared the calcium chloride solution with a weight at least 10 times the weight of the hydrogel. After soaking, the hydrogel was taken out of the solution and tested. The average thickness of the samples after soaking was measured to be 2.1 mm.

We also prepared a single-network polyacrylamide hydrogel following the method in the first step, but without adding the sodium alginate.
3.2.2 Testing method

We studied the stress-stretch behavior and fatigue fracture using the pure shear test (Figure 3.1a). A thin sheet of sample, of a long rectangular shape (10×50×2.1 mm³), was fixed to two rigid grips, and mounted in a tensile tester (Instron model 5966) with a 500 N load cell.

To minimize dehydration during the test, we made an acrylic chamber and sealed it around the sample with petrolatum (Figure 3.1a & Figure 3.3a). Water droplets were sprayed on the inner surface of the chamber to maintain the humidity. All the samples were weighed before and after the test, and no more than 3% weight was lost.

During the test, the tensile tester pulled the distance between the two grips cyclically between \( H \) and \( \lambda H \), where \( \lambda \) defines the maximum applied stretch per unit cycle (Figure 3.1b & Figure 3.3b). We recorded the force-displacement curve of each unnotched sample over many cycles, calculated the nominal stress (i.e., the applied force divided by the cross-sectional area in the undeformed state), and plotted the nominal stress as a function of stretch (Figure 3.1c&d). For the fatigue fracture tests, we notched a sample with a 20 mm crack before each test. We marked ruler lines on the surface of the sample, and glued graph papers to the grips (Figure 3.3c). As the tensile tester pulled the sample cyclically, a digital camera (Nikon D5200) recorded the extension of the crack.
Figure 3.1 **Shakedown after prolonged cycling.** (a) A sample of tough hydrogel is cyclically stretched in the pure shear test. (b) The loading profile of the test. Shakedown of stress-stretch curves was observed in tests with different loading frequencies, and shows no significant rate dependence: The loading frequency is **(c) 0.25 Hz**, **(d) 0.125 Hz**.

### 3.3 Shakedown after prolonged cycling

The stress-stretch curve of a hydrogel or an elastomer often depends on loading history due to various inelastic processes such as the Mullins effect,\textsuperscript{168,169} viscoelasticity,\textsuperscript{105,106,110,162,187} poroelasticity\textsuperscript{87,106,110,112,113} and viscoplasticity\textsuperscript{122}. In particular, the Mullins effect has been considered as the major factor to explain the softening of double network hydrogels over consecutive loading cycles,\textsuperscript{64,90–92,103,104,116} and has been attributed to progressive damage of the
polymer networks.\textsuperscript{116,88} All these studies, however, have been focused on the initial several loading cycles. Here we focus on the evolution of the stress-stretch curve over many cycles, and show that the evolution markedly affects the fatigue fracture.

We observe \textit{shakedown after prolonged cycling} (Figure 3.1c&d). Most of the energy dissipation, material softening and residual strain occur in the first cycle. Afterwards, the stress-stretch curve keeps changing, but the changes become smaller and smaller with increasing cycles and become negligible after some large number of cycles. For example, the stress-stretch curves are almost identical for the 8000\textsuperscript{th} and 10,000\textsuperscript{th} cycle. When the stress-stretch curve stops changing, we say that the tough hydrogel has shaken down to a steady state. The maximum stress in the steady state is much lower than that in the first loading cycle (Figure 3.2a). A relatively large residual strain was observed after the test.

Shakedown has been extensively studied in ductile metals.\textsuperscript{80} During cycling, a metal deforms plastically, and gradually approaches a steady state, when the residual stress generated during the early cycles inhibits further plastic deformation. Further cycling causes reversible elastic response. For the tough hydrogel, we interpret the shakedown as a result of cumulative unzipping of the ionic crosslinks. The polyacrylamide-calcium-alginate tough hydrogel consists of interpenetrating polyacrylamide network of covalent crosslinks and alginate network of calcium crosslinks. Upon stretching during the first cycle, some of the calcium crosslinks unzip, leading to softening. The re-zipping of the calcium crosslinks takes hours to days,\textsuperscript{61} and does not occur within the time period of each cycle. As the sample undergoes more cycles, more calcium crosslinks progressively unzip during each cycle, leading to further softening and accumulated residual strain. The stress-stretch curve reaches a steady state when the cyclic stretch cannot further unzip calcium crosslinks.

The rate-dependent stress-stretch behavior of polyacrylamide-calcium-alginate tough hydrogels has been studied recently.\textsuperscript{92} However, the required change of loading rate to observe clear rate-dependency is much larger than the range of loading rate in all current experiments.
Therefore, within the range of testing period we applied, we anticipate the stress-stretch behavior to be almost independent of the loading rate. To show this, we conducted cyclic tests on samples with different cyclic frequencies. No significant differences were observed in the stress-stretch curves (Figure 3.1c&d). As a result, we use a constant loading frequency in all of our cyclic tests, and neglect the rate-dependent effects such as viscoelasticity and poroelasticity.

The changing stress-stretch curves make it hard to quantify fatigue fracture before the steady state. To simplify the problem, we focus on the steady-state fatigue fracture of tough hydrogels in the following discussion. We define the steady state after 2000 loading cycles, when the change of maximum stress becomes relatively small (Figure 3.2a). We then plot the associated stress-stretch curves for different maximum stretches in the steady state (Figure 3.2b). At 2000 cycles, the stress-stretch curves still exhibit hysteresis, but the hysteresis loops are much narrower than those in the beginning cycles.

![Figure 3.2](image)

**Figure 3.2** (a) The maximum stress in each cycle decreases and approaches a steady state. (b) The stress-stretch curves after 2000 cycles for different maximum stretches $\lambda$. 

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3.4 Fatigue fracture of tough hydrogels

As described in Section 3.2, fatigue fracture tests were conducted on samples pre-notched with a 20 mm crack (Figure 3.3a). Following the previous discussion, all tests were conducted using the same frequency of 0.25 Hz. The number of loading cycles \( N \) was determined from the recording time of the camera and the period of one cycle, 4 s in this case. The crack growth \( \Delta c \) is plotted as a function of the number of cycles \( N \) (Figure 3.4). In all tests, the crack grows rapidly at first, becomes progressively slower afterwards, and in the end reaches a steady state. In the steady state, \( \Delta c \) is approximately a linear function of \( N \).

The fatigue fracture behavior is related to shakedown. Before reaching the steady state, the stress-stretch curve changes, and the hydrogel softens cycle by cycle. Under the same maximum stretch per cycle, \( \lambda \), the maximum load applied to the sample becomes smaller and smaller. As a result, the crack grows fast in the beginning cycles, but gradually slows down. When the stress-stretch curve reaches the steady state, the crack grows linearly with the number of cycles.

(a) tensile machine notched gel humidity chamber

(b)  \[
\lambda \quad 0 \quad N = 1 \quad N = 2 \quad \cdots \\
\begin{array}{c}
0 \\
\end{array}
\]

(c) 

\( N = 0 \)

\( N = 30000 \)
Figure 3.3 (continued) Fatigue fracture. (a) A notched sample is cyclically stretched. The sample and the grips are enclosed in a chamber with water droplets on its inner surface to control the humidity of the environment. (b) The applied loading profile over cycles. (c) The crack propagates cycle by cycle, and the evolution is recorded by photos. The crack propagation can be measured from the metric papers on the grips.

Figure 3.4 Crack growth as a function of the number of cycles $N$, under different maximum stretches. The crack growth reaches the steady state after thousands of cycles, and becomes approximately a linear function of $N$.

3.5 Characterization of fatigue fracture

In the tests, we prescribed the maximum stretch $\lambda$ in each cycle. However, to compare experimental data obtained from samples of various materials and geometries, we report the amplitude of load in terms of the energy release rate $G$ calculated from\textsuperscript{36}

$$G = W(\lambda)H,$$

where $H$ is the distance between the two grips when the sample is undeformed, and $W(\lambda)$ is the elastic energy per unit volume in the undeformed state determined from an unnotched sample. The tough hydrogel is not elastic, and we determine $W(\lambda)$ as follows.
Because a sample shakes down after prolonged cycling, the stress-stretch curve will keep changing until it reaches the steady state. To characterize fatigue fracture in the steady state, we used the stress-stretch curve measured in the steady state, rather than that measured in the first cycle. This method has been previously applied in the study of fatigue fracture of rubbers.\textsuperscript{78,168} To calculate the energy release rate under different applied stretch $\lambda$, we paired the stress-stretch curves and the crack growth curves with the same $\lambda$. The area under the stress–stretch curve gives the strain energy density $W(\lambda)$ (Figure 3.5a).

Even after thousands of cycles, the stress-stretch curves still exhibit hysteresis. In the literature on fatigue fracture in elastomer, some authors calculated $W(\lambda)$ by integrating the loading part of the curve,\textsuperscript{73} while others calculated $W(\lambda)$ by integrating the unloading part of the curve.\textsuperscript{78,138} Following Thomas,\textsuperscript{73} here we use the loading part of the stress-stretch curve to calculate $W(\lambda)$. Whether the loading or the unloading part is more proper needs further discussion, and is out of the scope of the current study. In a steady state, the hysteresis loop becomes narrow, and the difference between the energy release rates calculated from the loading and the unloading curves is typically less than 30%.

We then fit the crack growth $\Delta c$ in the steady state as a linear function of $N$, and obtain the extension per cycle $dc/dN$ as a function of $G$ (Figure 3.5b). When $G$ is relatively small, the extension of crack per cycle $dc/dN$ varies almost linearly with $G$. As $G$ increases, $dc/dN$ increases steeply, becoming a higher order polynomial function of $G$. Such behavior is similar to the fatigue fracture of elastomers.\textsuperscript{73-75}

We fit the linear relation and find its intercept with the $G$ axis, at a finite value of about 53.2 J/m$^2$, which we define as the threshold for fatigue fracture, denoted by $\Gamma_0$. Below this value, no crack growth was observed in the steady state until the end of the experiment.

In the fatigue fracture of elastomers, it has been shown experimentally that different geometries of the specimens lead to the same curve of $dc/dN$ vs. $G$.\textsuperscript{73} We have not verified this
point experimentally for the tough hydrogel, but also anticipate the curve for the gel to be independent of specimen geometry. Furthermore, it was shown previously that fracture energy of the tough hydrogel measured under the monotonic stretch is insensitive to the size and shape of the specimens.\textsuperscript{61}

![Diagram](image)

**Figure 3.5** (a) The energy release rate is calculated by integrating the stress-stretch curve in the steady state of the material far ahead of the crack tip. (b) In the steady state, the extension of crack per cycle, \(\frac{dc}{dN}\), is plotted as a function of energy release rate \(G\). A threshold is found, below which no crack propagation in the steady state occurs. Close above the threshold, \(\frac{dc}{dN}\) is found as a linear function of \(G\). \(\frac{dc}{dN}\) then increases rapidly with \(G\).
3.6 Discussion

3.6.1 Polyacrylamide hydrogels show no “shakedown”

We now compare the polyacrylamide-calcium-alginate tough hydrogel with a polyacrylamide hydrogel. The polyacrylamide hydrogel has a single network of covalent crosslinks, and we do not expect shakedown over a large number of cycles. To demonstrate this, we made a polyacrylamide hydrogel of the same size and loaded it under the same condition as the tough hydrogel. To minimize the effect caused by the difference of chemical network between the two gels, we used the same concentration of acrylamide monomer solution and added the same amount of crosslinker. Over 4000 cycles, the stress-stretch curve of the polyacrylamide hydrogel remains almost unchanged (Figure 3.6a), and the maximum stress in each cycle is constant over the whole period (Figure 3.6b). The sample ruptured afterwards due to the brittleness of the hydrogel.

The observation that the polyacrylamide hydrogel maintains the same stress-stretch loop during cyclic loading again confirms that the shakedown in the tough hydrogel is caused by the unzipping of the ionic crosslinks. With no ionic crosslinks, the polyacrylamide hydrogel has stable stress-stretch curves.
**Figure 3.6 (continued)** (a) A polyacrylamide hydrogel maintains stable stress-stretch loops over thousands of cycles. (b) The maximum stress in each cycle remains nearly constant over cycles.

### 3.6.2 Comparison between polyacrylamide hydrogel and tough hydrogel in fatigue fracture

The fracture toughness of the tough hydrogel is several thousands of $\text{J/m}^2$, much higher than the fracture toughness of the polyacrylamide hydrogel, which is usually on the order of 100 $\text{J/m}^2$. Here we compare their fatigue behavior.

We use the data of fatigue fracture in the polyacrylamide hydrogel from our previous paper, and plot it with the data of the tough hydrogel of the current study. It is shown that even under larger cyclic stretch $\lambda$ and higher mechanical load $G$, after the same number of loading cycles, the crack growth in the tough hydrogel is much smaller than the crack growth in the polyacrylamide hydrogel (Figure 3.7a).

We quantify the fatigue fracture resistance of the two gels through two parameters: the threshold for fatigue fracture $\Gamma_0$, and the slope of $dc/dN$ as a function of $G$. The two parameters represent different measures of the fatigue fracture resistance of a material. The threshold $\Gamma_0$ defines the critical energy release rate above which fatigue fracture occurs. Thus, a material is more fatigue fracture resistant with a higher threshold $\Gamma_0$. When a hydrogel is loaded above the threshold, the slope of $dc/dN$ vs. $G$ determines how fast the crack grows over the loading cycles. The smaller the slope, the better the fatigue fracture resistance. Our preliminary data shows that the tough hydrogel has a better fatigue fracture resistance than the polyacrylamide hydrogel in terms of both parameters (Figure 3.7b).
Figure 3.7 **Comparison between a polyacrylamide hydrogel and a tough hydrogel in fatigue fracture.** (a) The crack growth of the polyacrylamide hydrogel is faster (steeper slope) than that of the tough hydrogel, even under a less critical condition (smaller $\lambda$ and $G$ per cycle). (b) The fatigue threshold of the tough hydrogel is higher than that of the polyacrylamide hydrogel. The slope of $dc/dN$ vs. $G$ in the tough hydrogel is much lower than that in the polyacrylamide hydrogel. Both factors show that tough hydrogels have better fatigue fracture resistance than polyacrylamide hydrogels.

### 3.7 Summary

The stress-stretch curve of the polyacrylamide-calcium-alginate tough hydrogel keeps changing during cyclic loading and reaches a steady state after thousands of cycles. We call this phenomenon shakedown after prolonged cycling. Cycling softens the gel markedly. We measured the crack growth per cycle as a function of the applied mechanical load, quantified by the energy release rate in the steady state. The fatigue threshold of the tough hydrogel is about 53 J/m$^2$, whereas the fracture toughness of the tough hydrogel under monotonic load easily reaches several thousands of J/m$^2$. Still, the fatigue crack growth in the tough hydrogel is much slower than that in the polyacrylamide hydrogel. We hope that fatigue fracture of other tough
hydrogels will soon be studied and compared. Such studies will aid the development of tough and fatigue-resistant hydrogels.
Chapter 4  Fatigue fracture of self-recovery hydrogels

4.1 Introduction

Cyclic fatigue is commonly studied in two types of tests using, respectively, uncut samples and pre-cut samples. 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 4.1a). When a pre-cut sample is subject to a cyclic load, the gradual extension of the crack is called fatigue fracture (Figure 4.1b). 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.

![Diagram](image)

Figure 4.1 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 pre-cut sample is subject to a cyclic load, the gradual extension of the crack is called fatigue fracture.
Measurements of fatigue damage include cycling-induced changes of elastic modulus,\textsuperscript{129} stress-stretch hysteresis,\textsuperscript{59,65-70,130-132} fracture stress,\textsuperscript{133} swelling ratio\textsuperscript{183} and healing efficiency.\textsuperscript{144} 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 crosslinked polymers, together with some non-covalent, reversible bonds, such as hydrogen bonds,\textsuperscript{70,130,133} hydrophobic interaction,\textsuperscript{59,65,131,143} poly-ion complexes\textsuperscript{67-69,132,144} and host-guest interaction.\textsuperscript{190} The covalent network provides elasticity that motivates recover. 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,\textsuperscript{119,145} alginate-polyacrylamide,\textsuperscript{126} and poly(2-acrylamido-2-methylpropane sulfonic acid)-polyacrylamide.\textsuperscript{171} 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?

In this chapter, 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 crosslinked polyacrylamide (PAAm) network and uncrosslinked polyvinyl alcohol (PVA) (Figure 4.2a). Upon loading and unloading, the hydrogen bonds among the amide groups on PAAm chains and hydroxyl groups on PVA chains\textsuperscript{147,191-195} readily break and reform, enabling self-recovery. For a sample without pre-cut crack, its stress-stretch behavior remains unchanged after thousands of loading cycles. For a sample with a pre-cut crack, however, the crack extends with 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 non-covalent interactions. When a sample is loaded above the threshold, the non-covalent interactions slow down the extension of the crack under cyclic loads.

4.2 Viscoelasticity of the self-recovery hydrogel

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 4.2b). 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 4.2c). 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 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 4.2d). The nominal stress was plotted as a function of time (Figure 4.2e). The hydrogel almost completely relaxed within 3 minutes, on the same order of the recovery time observed in the loading and unloading test.
Figure 4.2 Viscoelasticity of the PAAm-PVA hydrogel. (a) The hydrogel consists of a covalently crosslinked PAAm network, along with uncrosslinked 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).

### 4.3 Fatigue damage of the self-recovery hydrogel

We characterized the self-recovery of the PAAm-PVA hydrogel with the cyclic loading test using samples containing no pre-cut crack. We placed a sample onto a humidity-controlled tensile machine, and cyclically stretched it with a prescribed stretch $\lambda_{\text{max}}$ ranging from 1.4 to 1.9 (Figure A1). We loaded the hydrogel for 5000 cycles without stop, and recorded the evolution of stress-stretch curves over cycles (Figure 4.3a&b and Figure A2). 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 cycle in Figure 4.3a&b), the stress-stretch curves in the following cycles are identical, indicating a steady state. Such steady state is also reflected in the maximum stress reached in each cycle (Figure 4.3c). The cyclic softening is due to the incomplete reforming of non-covalent interactions within the short timescale of one loading cycle.\textsuperscript{65-70,126,130,132} After 5000 cycles, the sample was settled for 3 minutes, and loaded again for one more cycle. Comparing with the first cycle, we found that the hydrogel almost recovered its stress-stretch response (Figure 4.3d). The PAAm-PVA hydrogel is free from fatigue damage, and is a self-recovery hydrogel.
The hydrogel was loaded under stretch (a) $\lambda_{\text{max}} = 1.4$ and (b) $\lambda_{\text{max}} = 1.9$ 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 3 experimental results. (d) The stress-stretch curves before and after 5000 cycles are nearly identical.

4.4 Fatigue fracture of the 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 condition. The crack
does not propagate under a small stretch $\lambda_{\text{max}} = 1.4$, but gradually propagates by cycles when $\lambda_{\text{max}}$ increases (Figure 4.4a, Figure A3). Larger $\lambda_{\text{max}}$ leads to a faster cyclic crack growth. For a stretch of $\lambda_{\text{max}} = 1.9$, 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 4.4b). 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.

4.5 Discussion

Mechanical behavior of a soft material is generally sensitive to the presence of a crack. 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 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 non-covalent interactions. To explore this picture in self-recovery hydrogels, we obtained the threshold for fatigue fracture through the fatigue fracture tests (See Appendix A for detailed procedures). For each applied $\lambda_{\text{max}}$, we calculated the slope of crack growth $\Delta c$ vs. cycle number $N$ and the energy release rate $G$ from loading cycles in the steady state (Equation A1 & Figure A4). We then plotted the slope $dc/dN$ as a function of $G$ (Figure 4.4b), 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. 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 (See detailed derivation and Equation A2 in Appendix A). 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 non-covalent interactions.

By contrast, the non-covalent 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 4.4b; see Appendix A 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 4.4b, 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, non-covalent 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 non-covalent 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 non-covalent 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 non-covalent interactions around the crack tip have already broken through the thousands of cycles before reaching this steady state. As a result, the broken non-covalent interactions still contribute negligibly to the threshold.
Figure 4.4 Fatigue fracture of the PAAm-PVA hydrogel. (a) The crack growth with cycles in a PAAm-PVA hydrogel under different applied stretch $\lambda_{\text{max}}$. (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. 145) 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 3 experimental results.
4.6 Summary

In this chapter, we compared two types of fatigue in a self-recovery PAAm-PVA hydrogel: fatigue damage tested using samples without pre-cut cracks, and fatigue fracture tested using samples with pre-cut 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 non-covalent interactions. When a sample is loaded above the threshold, the non-covalent interactions do slow down the extension of the crack under cyclic loads. The difference between the fracture of covalent network and the dissipation from non-covalent interactions is clearly made on fatigue of elastomers, 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, non-covalent interactions. The covalent network provides elasticity that motivates recovery. The recovery of non-covalent 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.
Chapter 5 Slow crack of hydrogels with complex rheology

5.1 Introduction

In Chapter 2 – 4, we have discussed fatigue of hydrogels under cyclic loads. This chapter studies one type of static fatigue, slow crack, of hydrogels. In particular, we focus on the static fatigue of tough hydrogels.

A tough hydrogel has a stretchable polymer network in topological entanglement with a network with sacrificial bonds. The hydrogel is tough when the stretchable polymer network is strong enough to break the sacrificial bonds in a large volume surrounding the front of a crack. That is, the sacrificial bonds act as toughener. Inspired by this design principle, various tough hydrogels have been developed, together with unprecedented applications based on their robust mechanical property.7-9,18,63

The various choices of tougheners lead to complex rheology of hydrogels, which further induces complex mechanical behaviors. For example, a polyacrylamide-poly(2-acrylamido-2-methylpropane sulfonic acid) (PAAm-PAMPS) hydrogel has a long-chain, covalent PAAm network interpenetrated by a short-chain, covalent PAMPS network. Because the covalent bonds of PAMPS are relatively strong, the hydrogel shows an evident yielding point in its uniaxial stress-stretch curve, accompanied by a macroscopic necking observed in the sample.58,135,166 As another example, an irreversible toughener usually induces severe softening and brittleness of a hydrogel under cyclic loads.126,128 By contrast, tougheners with reversible bonds such as hydrogen bonds,70,148 hydrophobic interaction,59,131 and poly-ion complexes enables self-recovery of the material property after many loading cycles, and even self-stiffening and toughening along the loading direction due to the alignment of polymer chains.148

The complex rheology of tough hydrogels poses challenges to studying their behaviors of fracture. Traditional fracture mechanics is based on elasticity and small-scale yielding criterion,
and does not account for hydrogels with inelastic zones of large scale, usually time-dependent dissipation. The concept of intrinsic fracture toughness, initiated by Lake and Thomas,\textsuperscript{75} provides a way to study the fracture of elastomers by focusing on the scission of the network at the crack tip. The intrinsic fracture toughness is defined as the minimum energy cost to propagate the crack by unit area, without including any energy dissipation from the toughener. For an elastomer with a covalent network and toughener, Lake and Thomas hypothesizes that the intrinsic fracture toughness only depends on the covalent network, but depends negligibly on the bulk energy dissipation from the toughener. By focusing on the intrinsic fracture toughness, one can remove the effect of complex rheology from the bulk material, and compare hydrogels of different rheology with respect to their elastic networks.

Intrinsic fracture toughness is commonly measured using two tests: fatigue fracture and slow crack. The fatigue fracture test characterizes the intrinsic fracture toughness under cyclic loads.\textsuperscript{73,75} During the test of a pre-cut sample with an initial crack, the crack extension per cycle \( \frac{dc}{dN} \) is measured as a function of the energy release rate \( G \). The threshold for fatigue fracture corresponds to the energy release rate when \( \frac{dc}{dN} \) approaches zero, and is referred as the intrinsic fracture toughness of the material. The slow crack test characterizes the intrinsic fracture toughness under static loads.\textsuperscript{138} In a slow crack test, the speed of crack extension \( v \) is prescribed, and is plotted as a function of the measured energy release rate \( G \). The threshold for slow crack corresponds to the energy release rate when \( v \) approaches zero, and is also referred as the intrinsic fracture toughness of the material. There is no evidence that the two thresholds are identical, or corresponding to a single material constant. Despite this ambiguity, the concept of intrinsic fracture toughness is still exceedingly useful in the common discussion of designing tough hydrogels.\textsuperscript{60,62,64,105,106}

The study of intrinsic fracture toughness of hydrogels has only started recently. Zhang et al. measured the intrinsic fracture toughness of a double-network polyacrylamide-Ca-alginate (PAAm-Ca-alginate) hydrogel by pre-stretching it to large deformation and then testing its
toughness, in order to deplete the energy dissipation of the toughener - the Ca-alginate network.\textsuperscript{64} Fatigue fracture of hydrogels has been initiated recently, and used to measure the fatigue thresholds of hydrogels containing at least a covalent network of polyacrylamide, including polyacrylamide hydrogels,\textsuperscript{119} polyacrylamide-Ca-alginate hydrogels in which alginate is ionically crosslinked,\textsuperscript{126} polyacrylamide -poly(2-acrylamido-2-methylpropane sulfonic acid) (PAAm-PAMPS) hydrogels in which PAMPS forms a short-chain covalent network,\textsuperscript{171} and polyacrylamide-poly(vinyl alcohol) (PAAm-PVA) hydrogels in which PVA provides reversible, noncovalent interactions.\textsuperscript{127} The threshold for fatigue fracture measured so far is much lower than the bulk fracture toughness of the hydrogel. The threshold depends on the long-chain covalent networks (i.e., the polyacrylamide networks for hydrogels studied so far), but negligibly on the tougheners, consistent with the picture that Lake and Thomas initially described. In addition to fatigue fracture, slow crack has been studied in physical hydrogels such as gelatin and Ca-alginate.\textsuperscript{122,196} The threshold for slow crack in these physical hydrogels is on the order of 1 J/m\textsuperscript{2}, corresponding to the pull-out of polymer chains at the crack tip during fracture. Slow crack of hydrogels with long-chain, covalent networks, however, has been studied very little. Existing studies mainly focus on the toughening mechanism, or the accompanied crack extension above the threshold, but negligibly on the threshold itself.\textsuperscript{108,120,125} It is unclear whether the threshold for slow crack is a material constant of the hydrogel. It is further unclear if the two thresholds for fatigue fracture and slow crack are identical or not.

In this chapter, we study slow crack of hydrogels with an elastic network and inelastic toughener of complex rheology. For such a hydrogel, we classify the rheological model of the toughener into two types, solid-like and liquid-like. To choose a representative material, we focus on the slow crack of PAAm-Ca-alginate double-network hydrogels. We conduct the stress-relaxation test on the Ca-alginate network to find out its solid-like rheological behavior. We conduct slow crack tests on the hybrid hydrogel and measure the $\nu$-$G$ curve of the hydrogel. The $\nu$-$G$ curve depends on the sample thickness, as well as the toughener in the hydrogel. The energy
release rate is over thousands of J/m² at high crack speed, but only around hundreds of J/m² at low crack speed. The energy release rate increases with the sample thickness at high speed, but is almost independent of the sample thickness at low speed. We explain this phenomenon by the rate-dependent crack processing zone, and estimate the size of the crack processing zone based on the experimental data. The energy release rate also increases with the amount of toughener added to the hydrogel. We calculate the threshold for slow crack of hydrogel samples with different thickness and different amount of toughener. The threshold depends negligibly on the thickness for a hydrogel with fixed composition. The threshold increases significantly with the amount of toughener in the hydrogel, due to the solid-like property of the Ca-alginate network. Finally, we compare the thresholds for fatigue fracture and slow crack, for hydrogels with the same PAAm network. The threshold for slow crack is contributed by both the solid-like networks of PAAm and Ca-alginate, while the threshold for fatigue fracture is only contributed by the long-chain PAAm network.

5.2 Rheological models of tough hydrogels

To assist the understanding of slow crack, we summarize two types of rheological models of a tough hydrogel. A tough hydrogel usually has a long-chain elastic network and a network with sacrificial bonds. We call the elastic network the primary network, and the network of sacrificial bonds the toughener. We represent the primary network, such as a long-chain, covalent PAAm network, by a spring. We represent the toughener, such as the short-chain covalent PAMPS network or ionic Ca-alginate network, by a spring together with a dashpot (Figure 5.1a). The spring represents the elastic response and the dashpot represents the time-dependent energy dissipation of the toughener.

Under deformation, the total force is the sum of forces on the primary network and the toughener. According to its capability to sustain force over a long time, we classify a toughener as either liquid-like or solid like. We use stress-relaxation to differentiate the two types of
tougheners (Figure 5.1b). A liquid-like toughener is represented by an elastic spring in series with a dashpot. Under a constant strain, the network carries a finite force at the beginning due to the incomplete relaxation of the dashpot. As the dashpot completely relaxes after a long time, the network carries no force, behaving like a liquid. By contrast, a solid-like toughener is represented by an elastic spring in parallel with a dashpot. Under the same strain, the network sustains a higher force at the beginning, and still carries a finite force on the spring even after the complete relaxation of the dashpot. Consequently, the toughener behaves like a solid.

![Rheological models of a hydrogel with an elastic network](image)

**Figure 5.1** Rheological models of a hydrogel with an elastic network. (a) The elastic network is represented by an elastic spring. The inelastic toughener is represented by an elastic spring with a dashpot. The toughener is classified as either liquid-like or solid-like. (b) Stress relaxation of solid-like and liquid-like tougheners.
We hypothesize the slow crack of a tough hydrogel depends on its toughener in the following way, described by the v-G curve (Figure 5.2). As the energy release rate approaches the threshold, the crack speed $v$ becomes so small that any rate-dependent dissipation from the toughener is neglected. The threshold therefore depends on the energy released by chain scission of the elastic network localized at the crack tip. Hydrogels with the same primary network but different tougheners (liquid-like vs. solid-like) have different thresholds. The threshold of a hydrogel with liquid-like toughener only depends on the primary network, since the liquid-like network sustains no force over the long-term relaxation. The threshold of a hydrogel with solid-like toughener depends on both the primary network and the elastic network of the toughener, but does not depend on the time-dependent dissipation from the dashpot. Therefore, with the same primary network, the hydrogel with solid-like toughener has a higher threshold for slow crack. Above the threshold, the time-dependent dissipation from the toughener can greatly contribute to the energy release rate. The hydrogel with liquid-like toughener may show a higher energy release rate compared to that with solid-like toughener, at the same crack speed.

![Diagram of v-G curves](image)

**Figure 5.2** The representative v-G curves of hydrogels with the same primary network, but solid-like and liquid-like tougheners.
5.3 Experimental section

5.3.1 Preparation of hydrogels

We purchased from Sigma Aldrich the following substances: acrylamide (AAm, A8887), N,N’-methylenebis(acrylamide) (MBAA, M7279), N,N,N’,N’-tetramethylethylenediamine (TEMED, T7024), ammonium persulfate (APS, A9164), and calcium sulfate dihydrate (CaSO\(_4\)·2H\(_2\)O, C3771). We purchased sodium alginate (Manugel GMB) from FMC Biopolymer. All chemicals were received and used without further purification.

To prepare the ionically crosslinked Ca-alginate hydrogel, we dissolved sodium alginate powders of 6.76 g in 300 mL deionized water to form an aqueous solution. We then added 1.29 g calcium sulfate dihydrate, corresponding to a final concentration of 25 mM Ca\(^{2+}\) in the solution. The pre-gel solution was completely mixed, degassed and injected into cylindrical acrylic molds of 6 mm height and 3 cm diameter, and covered with an acrylic plate. The samples were stored at room temperature for more than 18 hours for complete polymerization.

To prepare the double-network PAAm-Ca-alginate hydrogel, we dissolved AAm powders of 40.54 g and sodium alginate powders of 6.76 g in 300 mL deionized water to form an aqueous solution. We then added MBAA, TEMED and APS in quantities of 0.0012, 0.0025 and 0.0042 times the weight of AAm in sequence, together with 1.29 g calcium sulfate dihydrate into the solution. The pre-gel solution was completely mixed, degassed and injected into acrylic molds with 40 mm width, 90 mm length and variable thickness, and covered with an acrylic plate. The samples were then stored at room temperature for more than 18 hours for complete polymerization. To study the effect of sample thickness, we prepared samples with thickness of 0.4 mm, 1.0 mm, 1.5 mm and 3.0 mm, measured after the polymerization.

To study the effect of the Ca-alginate toughener in the PAAm-Ca-alginate hydrogel, we modified the amount of calcium sulfate dihydrate in the pre-gel solution. We synthesized three types of PAAm-alginate hydrogels, and named them o-Ca, 1-Ca and 2-Ca. The 0-Ca hydrogel corresponds to no calcium sulfate dehydrate added to the pre-gel solution, the 1-Ca hydrogel
corresponds to 1.29 g calcium sulfate dehydrate (25 mM Ca\textsuperscript{2+}), and the 2-Ca hydrogel corresponds to 2.58 g calcium sulfate dehydrate (50 mM Ca\textsuperscript{2+}).

5.3.2 Stress relaxation test

The prepared Ca-alginate hydrogel cylinder was compressed with a force gauge (HF-50N, M&A Instrument, Inc.) at a fixed compressive strain of 20% in the perpendicular direction (Figure 5.3a). The hydrogel and the force gauge were mounted on a homemade acrylic mold to reduce disturbance on the measurement. The hydrogel and the attaching end of the force gauge were completely immersed in silicone oil to avoid dehydration. Negligible buoyance force was observed by the force gauge. The whole setup was kept undisturbed for 12 days, with the compressive force measured every day.

5.3.3 Tearing test

The PAAm-Ca-alginate hydrogel sample was 40 mm in width and 90 mm in length. We glued stiff polyester films (clear polyester film, McMaster-Carr) of thickness 100 μm, width 20 mm and length 90 mm on the top and bottom surfaces of the sample (grey area in Figure 5.3b) using the Krazy glue. The polyester films restrict deformation of the sample during the tearing test. Afterwards, we used razor blades to pre-cut the sample with a crack of 20 mm from the middle of its width, forming two arms of 20 mm width and 20 mm length. The two arms were then fixed by the grips of a tensile testing machine, Instron 5966, with a 10 N load cell. During the test, the machine recorded the force as a function of the displacement (Figure 5.3b). The speed of crack extension is calculated as half of the loading speed of the machine.

To prevent dehydration during the test with low loading speed (< 0.1 mm/s), a humidity chamber was made to cover the entire sample and the grips. The humidity chamber was homemade with acrylic sheets, equipped with a household cool mist humidifier and a humidity control system (Zoo med, HygroTherm Humidity and Temperature Controller). The relative humidity in the chamber was maintained at 92 %. All the samples were weighed before and after the test, and no more than 5% weight was lost.
Figure 5.3 Experimental setups of (a) the stress relaxation test and (b) the tearing test.

5.4 Stress relaxation of the Ca-alginate network

In a PAAm-Ca-alginate hydrogel, the primary network is the covalently crosslinked PAAm, while the toughener is the ionically crosslinked Ca-alginate (Figure 5.4). The alginate chains and calcium ions form “egg-box”-like interactions, with ionic bond energy on the order of $kT$, where $kT$ is the temperature in the unit of energy. Such ionic bond is two orders of magnitude weaker compared to the covalent bonds forming the alginate chains. As a result, fracture of the Ca-alginate hydrogel is owing to the breaking of ionic bonds and pull-out of alginate chains, instead of scission of alginate chains themselves. The weak bonding energy of the ionic crosslinks also makes the Ca-alginate network easy to unzip under an even small force over a long enough loading time. Because of this, the Ca-alginate hydrogel and the PAAm-Ca-alginate hydrogel behave viscoplastic. Zhao et al. hypothesize that the Ca-alginate network is therefore liquid-like, which carries no force under a finite strain over a long time. They
conduct stress relaxation on the Ca-alginate hydrogel, and also on the alginate hydrogel covalently crosslinked by Adipic acid dihydrazide for comparison. While the covalently crosslinked alginate hydrogel maintains a finite stress after 3 hours, the ionically crosslinked Ca-alginate hydrogel carries almost no stress by then. However, both hydrogels are placed in a phosphate-buffered saline (PBS) solution during the test. The experimental result is hence affected by the swelling of the hydrogel induced by diffusion and degradation of the Ca-alginate network due to ion exchange or other reasons in PBS,\textsuperscript{163,164} which may have readily damaged the network over the long-time test, and lead to zero stress.

Figure 5.4 Molecular picture of PAAm-Ca-alginate hydrogels.

To exclude the effect of the ambient solvent and further verify its liquid-like or solid-like behavior, we measured stress relaxation of the Ca-alginate hydrogel immersed in silicone oil. The measured stress level under a compressive strain of 20% was around 6.5 kPa at the beginning, gradually decreased to about 2 kPa, and reached a plateau after 12 days (Figure 5.5). This significant decrease of stress level indicates the slow unzipping of the Ca-alginate ionic bonds, as well as the time-dependent energy dissipation of the Ca-alginate network in the PAAm-Ca-alginate hybrid hydrogel. The finite plateau of stress over a long time shows the solid-like behavior of the Ca-alginate hydrogels. Although the energy of a single ionic bond is small compared to the covalent bond, the large number of ionic bonds in the hydrogel still provide non-trivial elasticity to the network.
5.5 Slow-crack of PAAm-Ca-alginate hydrogels

A PAAm hydrogel has a fracture toughness of about 100 J/m². A calcium-alginate hydrogel has a fracture toughness of about 10 J/m². Both hydrogels are brittle, compared to natural rubber, but combining them together creates a tough hydrogel, PAAm-Ca-alginate, with fracture toughness as high as 10,000 J/m². The hybrid hydrogel can be both as stretchable as the covalently crosslinked PAAm hydrogel, and as stiff as the ionically crosslinked Ca-alginate hydrogel.

With relatively easy accessibility of materials and simple synthetic process, the PAAm-Ca-alginate hydrogel has been actively studied since its creation, and has been developed to unprecedented applications based on its robust mechanical property, such as soft robots, tough adhesives, and drug delivery systems. However, PAAm-Ca-alginate hydrogels suffer fatigue under cyclic loads. The energy dissipation by unzipping the large amount of Ca-alginate ionic bonds is almost irreversible, leading to irreversible change of material property after cycles of loading. The PAAm network that bridges the crack tip in the pre-cut double-network hydrogel under cyclic loads is no different from the PAAm network in a single covalently crosslinked PAAm hydrogel. As a result, the double-network PAAm-Ca-alginate
hydrogel also suffers severe fatigue fracture under cyclic loads, as the PAAm hydrogel itself does.\textsuperscript{119}

The slow crack behavior of PAAm-Ca-alginate hydrogels itself is interesting, but has not been reported. It indicates the long-term property and behavior of the hydrogel under continuous monotonic loads. In other words, we call the slow crack static fatigue. Beyond this, the available data of threshold for fatigue fracture under cyclic loads\textsuperscript{126} will allow a direct comparison to the threshold for slow crack of the same PAAm-Ca-alginate hydrogel. Such comparison between the two thresholds of a hydrogel or elastomer with the same polymer network has never been conducted before. It will unveil the relationship between the two thresholds, as well as the intrinsic fracture toughness.

### 5.5.1 Thickness dependence

Because the theory of fracture mechanics based on elasticity fails on the inelastic tough hydrogel, the experimentally measured fracture toughness of a tough hydrogel is not a material constant. We demonstrate this here by first studying the thickness dependence of the $v$-$G$ curve. We prepared samples of 0.4, 0.7, 1.5 and 3.0 mm thickness. The composition of hydrogel is fixed to PAAm-alginate with 1-Ca (25 mM Ca\textsuperscript{2+} ions). Under the tearing test, the force $F$ is recorded as a function of displacement (Figure 5.6). The force-displacement curve has a transient state at the beginning that is poorly repeatable, followed by a steady state corresponding to a plateau of the curve. The deformation of the hydrogel is restricted by the almost rigid backing layer. As a result, we assume there is no elastic energy stored in the material far away from the crack tip. The energy release rate in the steady state is related to the force $F$ and sample thickness $h$ as\textsuperscript{138}

$$G = \frac{2F}{h}.$$  \hspace{1cm} (5.1)

We conducted slow crack over a large range of crack speed from 0.5 $\mu$m/s to 10 mm/s. In all cases of different thickness, the force at the steady state increases with the crack speed, consistent with the large rate-dependent hysteresis of the Ca-alginate network.
Figure 5.6  Force-displacement curves of the slow-crack test of samples with different thickness of (a) 0.4 mm, (b) 0.7 mm, (c) 1.5 mm and (d) 3.0 mm. The force-displacement curve has a transient state at the beginning that is poorly repeatable, followed by a steady state corresponding to a plateau of the curve. The composition of hydrogel is fixed to PAAm-alginate with 1-Ca (25 mM Ca$^{2+}$ ions).

We calculated the energy release rate $G$ from each force-displacement curve under different crack speed $v$, and plotted the $v$-$G$ curves with $v$ ranging from 0.5 $\mu$m/s to 10 mm/s, of sample thickness of 0.4, 0.7, 1.5 and 3.0 mm (Figure 5.7). At a high crack speed, the energy release rate greatly increases with the thickness from 0.4 mm, 0.7 mm to 1.5 mm, but keeps
almost identical between 1.5 mm and 3 mm. For example, at the crack speed of 10 mm/s, the energy release rate is about 1500 J/m\(^2\) for \(h = 0.4\) mm, 2000 J/m\(^2\) for \(h = 0.7\) mm, and 4000 J/m\(^2\) for \(h = 1.5\) mm and 3 mm. At low speed, however, all the four v-G curves with different thicknesses approach almost the same threshold for slow crack, around 200 J/m\(^2\). It is therefore concluded that the measured fracture toughness of the PAAm-Ca-alginate hydrogel depends on the crack speed and sample size. In contrast, the threshold for slow crack of the same hydrogel does not depend on the sample size.

The current experimental observation can be of great importance to the toughening of hydrogel thin films or coatings. Thin films of hydrogels with micro or sub-micro size have found their broad use in modern applications. Examples include soft robots,\(^{13,197}\) artificial skins,\(^{22,25}\) medical devices,\(^{198}\) living responsive devices\(^{199}\) and chemical sensors.\(^{39}\) Development of robust, hydrogel thin film-based devices relies on currently available tough hydrogels, such as the PAAm-Ca-alginate hydrogel. However, the slow crack of PAAm-Ca-alginate hydrogels shows that the measured fracture toughness (energy release rate), even measured at a relatively high crack speed such as 1 mm/s, decreases from \(\sim 2500\) J/m\(^2\) to \(\sim 700\) J/m\(^2\) if the hydrogel becomes thinner from 1.5 mm to 400 \(\mu\)m. The measured fracture toughness will further decrease with slower crack speed, or further reduction of the film thickness. The toughening mechanism of incorporating energy dissipation does not work efficiently for hydrogel samples with small size, due to the limited crack processing zone in the sample.
Figure 5.7  The v-G curve of the PAAm-Ca-alginate hydrogel with the same composition (1-Ca) greatly depends on the thickness of the hydrogel sample. The solid lines are guiding lines for the experimental data.

The v-G curve depends on the sample thickness from 0.4 mm, 0.7 mm to 1.5 mm, but negligibly on the thickness from 1.5 mm to 3 mm. We explain this observation by studying the crack processing zone in the hydrogel. The crack processing zone is defined as the region where the material behaves inelastic and dissipates energy due to scission of covalent polymer chains and breaking of sacrificial bonds around the crack tip. The size of the crack processing zone is estimated as $G/W^*$, where $G$ is the energy release rate, and $W^*$ is the energy density associated with the polymer chain scission in the hydrogel. Because the scission of the covalent PAAm chain depends negligibly on the loading rate, we assume $W^*$ as a constant. As a result, the size of the crack processing zone $G/W^*$ increases with the crack speed, as $G$ does, due to the rate-dependent unzipping of the Ca-alginate network. At a low crack speed of 0.5 μm/s, the crack processing zone is relatively small compared to the thickness of the hydrogel sample. The size of the crack processing zone is therefore almost identical in samples of different thickness. The resulting measured energy release rate shows no thickness dependence (Figure 5.8a). In contrast, at a high crack speed (e.g., 5 mm/s), the crack processing zone becomes larger and
constrained by the smaller thickness 0.4, 0.7 and 1 mm (Figure 5.8a, top left), but not constrained by the larger thickness 1.5 and 3 mm (Figure 5.8a, top right). The measured energy release rate hence increases with the thickness from 0.4 mm, 0.7 mm, 1 mm to 1.5 mm, but keeps almost identical from 1.5 mm to 3 mm.

With the above thickness dependence, we estimate the approximate size of the crack processing zone. The independence of $G$ on thickness at 0.5 $\mu$m/s indicates that the crack processing zone is smaller than 0.4 mm at this speed. Above 0.5 $\mu$m/s, the energy release rate increases with the thickness and reaches a plateau between 1.5 mm and 3 mm (Figure 5.8a), indicating that the crack processing zone is smaller than 1.5 mm, but larger than 1 mm.

Next, we apply the approximate size of crack processing zone to estimate whether the crack speed in the experiment is low enough for complete relaxation of the Ca-alginate network. In the steady state of a tearing test, a small piece of material initially stays far away in front of the crack, unstretched, then approaches close to the crack tip, becoming stretched, and finally moves far behind the crack, becoming unstretched again. This whole process of loading and unloading is equivalent to the imaginary process of moving a piece of material from point A far in front of the crack, through point B at the crack tip, and finally to point C far behind the crack (Figure 5.8b) during the test. The time scale of the complete loading profile $t$, is estimated as

$$t \sim \frac{a}{v},$$

(5.2)

where $a$ is the size of the crack processing zone and $v$ is the crack speed. For complete relaxation of the Ca-alginate network, $t$ should be comparable or larger than the relaxation time of the Ca-alginate network measured by the stress-relaxation test before. The relaxation time is on the order of 10 days. At the smallest crack speed in the experiment $v = 0.5$ $\mu$m/s, the size of the crack processing zone is $a < 0.4$ mm. Substituting them into Equation (5.2), we obtain $t < 800$ s, far smaller than the relaxation time of 10 days. As a result, even under a crack speed as low as
0.5 μm/s, the Ca-alginate network in the tearing test is not fully relaxed. The toughener will still dissipate energy and contribute to the energy release rate, behaving more solid-like.

**Figure 5.8 Thickness-dependent energy release rate at constant crack speeds due to the constraint of crack processing zone.** (a) The energy release rate negligibly depends on the thickness at a crack speed of 0.5 μm/s. The energy release rate increases with the thickness from 0.4 mm, 0.7 mm, 1 mm to 1.5 mm, but reaches a plateau from 1.5 mm to 3 mm, at higher crack speeds. Such thickness dependence is explained by the constraint of crack processing zone at high crack speeds (schematics). (b) The loading and unloading process of a piece of material in the steady state of a tearing test. The time scale of the complete process is estimated by $t \sim \frac{a}{v}$, where $a$ is the size of the crack processing zone and $v$ is the crack speed.

5.5.2 Toughenner dependence

To study the effect of Ca-alginate network on the slow crack of the hydrogel, we fixed the sample thickness to be 1.5 mm, and synthesized PAAm-alginate hydrogels with no Ca$^{2+}$, 25 mM Ca$^{2+}$, and 25 mM Ca$^{2+}$ added in the pre-gel solution. The resulting hydrogels are called by 0-Ca, 1-Ca and 2-Ca hydrogels, respectively.
For 0-Ca hydrogels, the alginate chains are not crosslinked, and contribute negligibly to the toughening of hydrogel. As a result, the energy release rate measured in slow crack is low, and shows little dependence on the crack speed (Figure 5.9a & Figure 5.10). For 1-Ca and 2-Ca hydrogels, the energy release rate increases dramatically with more Ca$^{2+}$ added (Figure 5.9b,c, Figure 5.10). At the crack speed of 0.01 m/s, the measured energy release rate is about 250 J/m$^2$ for the 0-Ca hydrogel, 4500 J/m$^2$ for the 1-Ca hydrogel, and 10,000 J/m$^2$ for the 2-Ca hydrogel, indicating the effect of the Ca-alginate toughener.

![Figure 5.9](image)

**Figure 5.9** Force-displacement curves of PAAm-alginate hydrogels with different amount of Ca$^{2+}$ added in the pre-gel solution. (a) 0-Ca: no Ca$^{2+}$. (b) 1-Ca: 25 mM Ca$^{2+}$. (c) 2-Ca: 50 mM Ca$^{2+}$.

To compare the thresholds for slow crack of the three hydrogels, we conducted linear regression to the lowest three data points of each v-G curve (Figure 5.10), and obtained the thresholds by extrapolation. The threshold is 59, 173 and 952 J/m$^2$ for the 0-Ca, 1-Ca and 2-Ca hydrogel, respectively. This large variety of thresholds by simply modifying the amount of Ca$^{2+}$ ions again implies the solid-like property of the Ca-alginate network and its finite contribution to the threshold. The extrapolated values of thresholds may be inaccurate due to the incomplete relaxation of the Ca-alginate network, but can still reflect the strength of the hydrogel networks at extremely low crack speed.
Figure 5.10 The v-G curve of the PAAm-alginate hydrogel with the same sample size greatly depends on the amount of toughener. The threshold is calculated by extrapolation, and is 59, 173 and 952 J/m² for the 0-Ca, 1-Ca and 2-Ca hydrogel, respectively.

5.6 Discussion

Finally, we compare the thresholds for fatigue fracture and slow crack using the experimental data from the current study and our previous study on fatigue fracture of PAAm-Ca-alginate hydrogels. The hydrogel used for fatigue fracture test has a slightly higher water content and amount of Ca²⁺, due to the 2-step soaking method in the synthesis. Otherwise, the two hydrogels have the same PAAm network (with identical crosslink density) and amount of alginate chains.

As discussed before, we assume the PAAm-Ca-alginate hydrogel as a primary network with a solid-like toughener network. The solid-like network of Ca-alginate is much weaker than the primary network of PAAm. Under the cyclic loading of fatigue fracture, the material at the crack tip continuously undergoes large stretch. The cyclic fatigue fracture reaches a steady state after thousands of loading cycles, when the crack extension per cycle becomes a constant. By
then, the many thousand cycles of large stretch at the crack tip have already completely broken all the weaker bonds, leaving only the primary network to bridge the crack. As a result, the threshold for fatigue fracture $\Gamma_0$, i.e. the minimum energy release rate to propagate the crack by unit area, only depends on the primary network of PAAm, but does not depend on the weaker network of Ca-alginate, even though it is solid-like (Figure 5.11 left). In the case of slow crack, however, the material is unloaded before approaching the crack processing zone (see Figure 5.8b). Therefore, at the threshold $G_0$, only the rate-dependent component (dashpot) of the toughener is removed, while the solid-like component (spring) still makes finite contribution to toughening the material. The threshold for slow crack $G_0$ hence depends on both the primary network of PAAm and the solid-like toughener of Ca-alginate (Figure 5.11 right).

The above hypothesis is verified by the experimentally measured thresholds in both tests for hydrogels with the same primary network (PAAm) but various amounts of toughener. The threshold for fatigue fracture measured before is $\Gamma_0 = 53 \text{ J/m}^2$. The threshold for slow crack of the 0-Ca hydrogel measured in the current study is $\Gamma_0 = 59 \text{ J/m}^2$. The liquid-like toughener of the 0-Ca hydrogel has no contribution to the threshold. Hence, the above two threshold values are nearly identical, and both refer to the primary network of PAAm itself. The slight difference between the two values is within the acceptable experimental error, and may also result from the slightly different water contents of the two hydrogels. Nevertheless, the measured $\Gamma_0$ of the primary network PAAm in both tests is much smaller than the threshold for slow crack of the 1-Ca hydrogel, $G_0 = \Gamma_0 + \Gamma_1 = 173 \text{ J/m}^2$. The finite contribution from the solid-like Ca-alginate toughener to the slow crack at the threshold is about $120 \text{ J/m}^2$.

Because the ionic bond energy of Ca-alginate is much smaller than the covalent bond energy of PAAm, even at the threshold for slow crack, the breaking of the ionic bonds can take place in a large area, and can therefore dissipate more energy compared to the scission of a single layer of PAAm at the crack tip. As a result, $\Gamma_1 \sim 120 \text{ J/m}^2$ cannot be described as the
threshold or intrinsic fracture toughness of the Ca-alginate network. The relatively large value of $\Gamma_1$, merely results from the finite energy dissipation of unzipping ionic bonds at the threshold for slow crack.

![Diagram of tough hydrogel and threshold for fatigue fracture and slow crack.](image)

**Figure 5.11** Comparison between the threshold for fatigue fracture and the threshold for slow crack of a hydrogel with a primary network and solid-like toughener. The threshold for fatigue fracture only depends on the primary network, while the threshold for slow crack depends on both the primary network and the solid-like network of the toughener. The threshold for fatigue fracture $\Gamma_0 = 53 \text{ J/m}^2$ is obtained from ref. 126.

### 5.7 Summary

The intrinsic fracture toughness has been a broadly used concept in the conversation and design principle of toughening hydrogels. However, it is unclear whether a material constant related to such concept exists, or can be clearly measured in experiments. In this chapter, we try to resolve this ambiguity in hydrogels with long-chain covalent network, by comparing two commonly measured results of intrinsic fracture toughness from fatigue fracture and slow crack.
With the already measured threshold for fatigue fracture from our previous work, here we focus on slow crack of the same hydrogel, PAAm-Ca-alginate. We model the hydrogel as a combination of an elastic network of long-chain polymers (PAAm, primary network) and a network of sacrificial bonds (Ca-alginate, toughener). Based on its capability of sustaining finite loads over a long time, we classify the toughener into either liquid-like or solid-like. The Ca-alginate network is demonstrated to be solid-like by the stress-relaxation test. The v-G curves of slow crack are measured for hydrogels with the same primary network, but different sample thickness and amount of Ca-alginate toughener. The energy release rate depends on the crack speed, sample size and amount of toughener. The threshold for slow crack does not depend on the thickness of sample. We compare the experimental results from both fatigue fracture and slow crack. The threshold for fatigue fracture only depends on the primary network of PAAm, but negligibly on the Ca-alginate toughener, even it is solid-like. In contrast, the threshold for slow crack depends on both the primary network of PAAm and the solid-like toughener of Ca-alginate. In this case, the energy dissipation from unzipping the Ca-alginate network is even larger than that from the chain scission of the PAAm network.
Chapter 6  Designing flaw-insensitive hydrogels under static and cyclic loads

6.1 Introduction

In the previous chapters, we have shown that hydrogels suffer fatigue under both static and cyclic loads. In particular, a hydrogel is usually susceptible to fracture due to the existence of flaws like cavities, cracks and impurities.\textsuperscript{55,56} This sensitivity to flaw can be estimated by a critical length scale $\Gamma/W_c$, where $\Gamma$ is the fracture toughness of the hydrogel, and $W_c$ is the work to rupture measured with no or negligible flaw.\textsuperscript{55,56,200} A hydrogel is not sensitive to a pre-existing flaw with size smaller than $\Gamma/W_c$. Tough hydrogels have been developed with $\Gamma$ over thousands of J/m$^2$ that enhances this critical length scale.\textsuperscript{57-61,63,64,130,132,147} For example, a polyacrylamide-alginate hydrogel has $\Gamma \sim 10^4$ J/m$^2$ and $W_c \sim 10^5$ J/m$^3$, leading a critical flaw-sensitivity length scale of $\Gamma/W_c \sim 0.1$ m. In contrast, a covalently crosslinked polyacrylamide hydrogel only has $\Gamma/W_c \sim 10^{-3} – 10^{-2}$ m.\textsuperscript{55,61} Two issues still remain in the current design of tough hydrogels. First, the relatively small $\Gamma/W_c \sim 0.1$ m hinders large-scale applications of hydrogels, where the initial imperfection can be far beyond 0.1 m and lead the hydrogel to be flaw sensitive. More importantly, most tough hydrogels involve additional energy dissipation through breaking internal sacrificial bonds during loading. Such energy dissipation toughens the hydrogel when it is loaded for the first time, but fails in the subsequent cycles of loading. As a result, all tough hydrogels suffer fatigue fracture, i.e. the gradual extension of crack from an initial flaw under cyclic loads.\textsuperscript{119,126,127,145,171} The highest threshold for fatigue fracture of a tough hydrogel is only $\sim 400$ J/m$^2$, 1/10 of its bulk fracture toughness.\textsuperscript{171}

In this chapter, we show a design principle of flaw-insensitive hydrogels under both static and cyclic loads, without introducing large energy dissipation. The design principle mimics the existing biological materials. Many biological materials including biological shells,
human skins, human bones and cartilage benefit excellent fracture-resistance from their micro-structures. The micro-structures generate mechanical anisotropy, which leads to crack deflection, i.e. kinking of a crack tip instead of straight propagation in an initial flaw under loading. The crack deflection shields the zone that needs protection in the biological materials. One example is the toughening of human bones. Under loading, the osteons and their brittle interfaces can divert the crack path from the plane of maximum stress of an initial flaw, and reduce the stress intensity at the crack tip. Designing crack deflection has been applied in many materials including metals, ceramics, elastomers and composites, but has not been explored in hydrogels. In particular, most current designs for crack deflection rely on composites, with directional fibers or aligned inclusions. In the current work, we propose a design principle to achieve crack deflection in hydrogels through the alignment of polymer chains in the molecular level. The aligned polymer chains induce anisotropy, making the hydrogel mechanically weaker between the chains due to the non-covalent inter-chain bonding, but stronger along the chains due to the covalent bonding. Therefore, when the hydrogel is loaded along the aligned direction, a pre-existing flaw deflects from its initial direction of propagation, runs along the loading direction, peels off the material, and protects the remaining hydrogel. The design concept is general and can be used in any hydrogel systems. To demonstrate this method, we synthesize a polyacrylamide (PAAm) hydrogel with crystalline polyvinyl alcohol (PVA). The PVA network forms directional, aligned crystallization through mechanical stretching, and the PAAm network provides elasticity and supports the stretching. The aligned crystallization is achieved with a facile one-step soaking method, followed by a prescribed mechanical stretch. The critical degree of anisotropy for crack deflection is experimentally quantified with fracture mechanics. The resulting hydrogel is insensitive to flaws under both static and prolonged cyclic loads. The simple and generic designing principle is readily applicable to the existing tough hydrogel systems and other soft materials.
6.2 Preparation of the flaw-insensitive hydrogel by aligning polymer chains

Previous methods to form crystalline PVA hydrogels include freeze-thaw\textsuperscript{192,207-209} and cast-dry.\textsuperscript{147,210,211} Both methods require large change of either temperature or water content of the hydrogel, and usually take several processing cycles for sufficient crystallization. Adding specific salt such as Na\textsubscript{2}SO\textsubscript{4} into the PVA solution can enhance the crystallization, due to the effect of the ions on the hydrogen bonding.\textsuperscript{209,210} Different from the previous methods, we crystallized the PAAm-PVA hydrogel through a one-step soaking method (Figure 6.1a). We first made a covalently crosslinked PAAm hydrogel with uncrosslinked PVA chains (PAAm-PVA hydrogel). The hydrogel has no crystalline domains of PVA, and is highly transparent (Figure 6.1b). We then soaked the PAAm-PVA hydrogel into Na\textsubscript{2}SO\textsubscript{4} solution of 0.6 M for 30 minutes. The resulting hydrogel (PAAm-PVA-S) became translucent (Figure 6.1c), indicating the crystallization of PVA. The PAAm-PVA-S hydrogel prepared in this way has the similar stress-stretch behavior compared to the hydrogel prepared by the traditional freeze-thaw method (Appendix B, Figure B1). In addition, good self-recovery of the stress-stretch curve was found within one hour after the hydrogel was loaded for the first time (Figure B2). To align the PVA chains, we fixed the hydrogel into a customized acrylic mold with a prescribed stretch $\lambda_{\text{fix}}$. The stretch is tunable, and allows the PVA chains to be mechanically aligned and grow in the stretching direction in a controlled manner (Figure 6.1d). To compare the flaw sensitivity between the unaligned PAAm-PVA-S hydrogel and the aligned hydrogel, we cut an initial flaw of $\sim$3 mm on the edge of each sample, and uniaxially stretched it. For the unaligned hydrogel, the flaw quickly fractured through the whole sample once it started being stretched (Figure 6.1e). In contrast, the flaw in the aligned hydrogel with $\lambda_{\text{fix}} = 2.5$ simply peeled off a small piece of material along the loading direction, leaving the hydrogel flawless again. No fracture occurred in the remaining hydrogel until the end of stretching (Figure 6.1f).
Figure 6.1 Preparation of the flaw-insensitive PAAm-PVA-S hydrogel with aligned PVA crystalline domains. (a) The PAAm-PVA hydrogel is soaked in Na$_2$SO$_4$ solution for 30 minutes, and then mechanically stretched with a prescribed stretch $\lambda_{fix}$. (b) The initial PAAm-PVA hydrogel has no crystalline domains and appears transparent. (c) After soaking, the
resulting PAAm-PVA-S hydrogel forms crystallization and becomes translucent. (d) The PVA chains in the hydrogel are mechanically stretched and form aligned crystallization. The scale bar in (b) – (d) is 1cm. (e) An initial flaw (~3 mm) in an unaligned PAAm-PVA-S hydrogel quickly propagates throughout the sample once the loading starts. (f) The same-size initial flaw in an aligned hydrogel does not propagate across the sample, but deflects along the loading direction and peels off a piece of material, leaving the hydrogel flawless again. The scale bar in (e) and (f) is 2cm.

6.3 Kinetics of the Na$_2$SO$_4$-induced PVA crystallization

The capability to align the PVA chains in the hydrogel after soaking is due to the slow kinetics of PVA crystallization induced by Na$_2$SO$_4$. Without soaking in Na$_2$SO$_4$, the stress-stretch curve of the PAAm-PVA hydrogel keeps the same for 7 days after the polymerization (Figure 6.2a), indicating no growth of crystallization. In contrast, the stress-stretch curve of a PAAm-PVA-S hydrogel keeps stiffening daily after the polymerization, until reaching saturation after 7 days (Figure 6.2b). The soaked hydrogel is much stiffer than the unsoaked one even on the 1st day after soaking. The daily stiffening of the stress-stretch curve indicates the gradual growth of crystallization. This effect allows us to build mechanical anisotropy in the PAAm-PVA-S hydrogel by mechanical stretching after the soaking. The PAAm-PVA-S hydrogel with $\lambda_{fix} = 2.5$ for 5 days shows clear difference in stress-stretch curves in the aligned and transverse directions. The hydrogel is stiffer in the aligned direction, but softer in the transverse direction (Figure 6.2c). Other stretching profiles were also adopted and resulted in a similar anisotropy (Figure B3&B4). To observe the different crystalline structures in the hydrogels microscopically, we linked the fluorescent dye 5-DTAF to the hydroxide groups on PVA (see Figure B5 for the corresponding chemical reaction). The resulting PVA-rich regions show a brighter color under confocal microscopy. The PAAm-PVA hydrogel without soaking shows a homogeneous PVA distribution (Figure 6.2d), indicating no formation of crystallization. The unaligned PAAm-PVA-
S hydrogel, in contrast, shows brighter PVA-rich crystalline domains surrounded by darker PVA-poor regions (Figure 6.2e). The aligned PAAm-PVA-S hydrogel further shows directional, coarsened crystalline domains, proving the effect of mechanical stretching (Figure 6.2f).

**Figure 6.2 Kinetics of the Na$_2$SO$_4$-induced PVA crystallization.** (a) Without Na$_2$SO$_4$, no crystallization forms in the hydrogel over 7 days. The stress-stretch curve remains the same. (b) With Na$_2$SO$_4$, the crystallization grows daily, and stiffens the stress-stretch curve. (c) The crystallization can be further aligned by a mechanical stretch of $\lambda_{\text{fix}} = 2.5$, leading to anisotropic stress-stretch behaviors. The confocal images (d) (e) and (f) exhibit the microscopic structures of the above corresponding hydrogels. Each curve in (a) – (c) represents 3-5 experimental results. The scale bar in (d) – (f) is 20 μm.
6.4 Tunable degree of anisotropy

The degree of anisotropy in the hydrogel is tunable by the applied stretch $\lambda_{\text{fix}}$. For all the hydrogels with different values of $\lambda_{\text{fix}}$, we observed stiffening of the stress-stretch curve in the aligned direction (Figure 6.3a), and softening in the transverse direction (Figure 6.3b). The elastic modulus increases with $\lambda_{\text{fix}}$ in the aligned direction, and decreases in the transverse direction (Figure 6.3c). We further measured the fracture toughness in both directions under different $\lambda_{\text{fix}}$. The chain alignment toughens the hydrogel in the aligned direction, and embrittles the hydrogel in the transverse direction (Figure 6.3d). In particular, the crack deflection was observed in hydrogels with $\lambda_{\text{fix}} > 1.2$. The critical condition for the crack deflection can be characterized by comparing the fracture toughness in the two directions. When a hydrogel with an initial crack is stretched, the fracture toughness of the hydrogel in the direction along the crack tip is $\Gamma_1$, and the fracture toughness perpendicular to the crack tip is $\Gamma_2$ (inset of Figure 6.3e). The dimensionless parameter, $\alpha = \Gamma_2/\Gamma_1$, quantifies the degree of anisotropy in terms of the fracture toughness. When $\alpha = 1$, the material is isotropic, and the crack will propagate along its initial direction under uniaxial loading. As $\alpha$ becomes smaller, the material becomes more brittle in the direction of $\Gamma_2$, and tougher in the direction of $\Gamma_1$. When $\alpha$ becomes further smaller to reach a critical value of $\alpha_{\text{cr}}$, the material becomes so brittle in the perpendicular direction, that the crack starts to deflect. Under the assumption of linear elastic fracture mechanics, the theoretical value of $\alpha_{\text{cr}}$ for a material with the isotropic constitutive law is 0.26.\textsuperscript{112} For the aligned PAAm-PVA-S hydrogel, we approach an upper bound of $\alpha_{\text{cr}}$ experimentally. We plotted $\alpha = \Gamma_2/\Gamma_1$ as a function of $\lambda_{\text{fix}}$ (Figure 6.3e), together with the path of crack in each case (see Figure B6 for the complete crack path). $\lambda_{\text{fix}} = 1.0$ corresponds to an isotropic hydrogel, and the crack propagates along its initial direction under loading. When $\lambda_{\text{fix}} = 1.1$ and $\alpha = 0.8$, the transverse direction becomes brittle, but not enough for crack deflection. When $\lambda_{\text{fix}} = 1.2$ and $\alpha = 0.3$, the transverse direction becomes further brittle, and the crack kinks to approximately 45°.
Following the propagation, the crack goes up and down through a serpentine path. When $\lambda_{fix} = 1.3$, the crack deflects. The fracture toughness in the aligned direction $\Gamma_1$ cannot be experimentally measured. The critical condition for crack deflection in the current hydrogel is thus $\alpha_{cr} < 0.3$, close to the theoretical value of $\alpha = 0.26$ predicted by linear elastic fracture mechanics.
Figure 6.3 (continued) The degree of anisotropy of the hydrogel is tunable by $\lambda_{\text{fix}}$.

The stress-stretch curves show that with increasing $\lambda_{\text{fix}}$, the hydrogel becomes (a) stiffer in the aligned direction and (b) softer in the transverse direction. (c) The corresponding shear modulus changes with $\lambda_{\text{fix}}$. (d) The hydrogel becomes tougher in the aligned direction, but more brittle in the transverse direction, as $\lambda_{\text{fix}}$ increases. (e) $\alpha = \Gamma_2 / \Gamma_1$ represents the degree of anisotropy in terms of the fracture toughness. $\alpha$ decreases with $\lambda_{\text{fix}}$, and reaches $\alpha < 0.3$ when crack deflection occurs at $\lambda_{\text{fix}} = 1.3$. Inset photos: the crack path in hydrogels with $\lambda_{\text{fix}} = 1.0$, 1.1, 1.2 and 1.3, from left to right. Each curve in (a) and (b) represents 3-5 experimental results. Each data point in (c) and (d) represents the mean and standard deviation of 3-5 experimental results. The scale bar in (e) is 1cm.

6.5 Flaw-insensitivity under cyclic loads

We next demonstrate the flaw-insensitivity of the anisotropic PAAm-PVA-S hydrogel under cyclic loads. In many real applications, the flaw size is relatively small, but can still lead to catastrophic failure if the material is loaded repeatedly for many cycles. As an example, we notched an isotropic PAAm-PVA-S hydrogel ($\lambda_{\text{fix}} = 1.0$) with an initial flaw of 3 mm length on its edge. We then cyclically loaded the hydrogel sample with a stretch $\lambda_{\text{max}} = 220\%$ (Figure 6.4a). The hydrogel did not fracture after the first loading cycle. However, the small flaw quickly propagated through the whole sample subsequently, within 100 cycles (Figure 6.4b). In comparison, the same flawed PAAm-PVA-S hydrogel with $\lambda_{\text{fix}} = 2.5$ sustained more than 10,000 cycles without any crack propagation in the horizontal direction. Instead, a slight crack deflection was observed in the vertical direction, which reduced the stress concentration at the crack tip. The aligned hydrogel is insensitive to pre-existing flaws under cyclic loads, and does not require energy dissipation in the material.
We further characterized the complete fatigue fracture of these hydrogels using long initial cracks (20 mm). For the PAAm-PVA-S hydrogel with $\lambda_{fix} = 2.5$, the threshold for fatigue fracture in the transverse direction is 44.0 J/m² (Figure B7), comparable to the threshold measured in other hydrogels with a PAAm network.\textsuperscript{119,126,127,171} Crack deflection was observed in the aligned direction, with the initial crack tip extending vertically to the end of the sample (Figure B8). In the unaligned isotropic PAAm-PVA-S hydrogel, crack deflection appeared when the hydrogel was loaded under large $\lambda_{max}$ for many cycles (Figure B9), but did not show up under small $\lambda_{max}$. We hypothesize that the PVA chains tend to align under cyclic large stretch and prompt the directional crystallization. This dynamic, spontaneous alignment deflects the crack and enhances the resistance to fatigue fracture.
Figure 6.4 Flaw-insensitivity under cyclic loads. (a) A hydrogel is notched with an initial flaw (~3 mm) and cyclically loaded. (b) An unaligned hydrogel is sensitive to the initial flaw under cyclic loads, and completely fractures within 100 loading cycles. (c) An aligned hydrogel with $\lambda_{\text{fix}} = 2.5$ is not sensitive to the initial flaw, and sustains over 10,000 loading cycles. The scale bar is 1 cm.
6.6 Discussion

The fracture toughness of a material is the sum of two parts: the intrinsic part $\Gamma_{in}$ and the extrinsic part $\Gamma_{ex}$. The intrinsic part depends on the local fracture zone ahead of the crack tip, and the extrinsic part relies on mechanisms behind the crack tip, such as the large area of energy dissipation and crack deflection. Most hydrogels are toughened through the extrinsic mechanism of large energy dissipation. While $\Gamma_{ex}$ can be easily over thousands of J/m$^2$ by breaking weak bonds behind the crack tip, $\Gamma_{in}$ is only on the order of 10-100 J/m$^2$, determined by the local bonds at the crack tip. As a result, toughening by energy dissipation fails for hydrogels under cyclic loads, because the threshold for fatigue fracture is only determined by the intrinsic part $\Gamma_{in}$.

Utilizing a different extrinsic mechanism by crack deflection is facile yet effective. Instead of enhancing $\Gamma_{ex}$ through energy dissipation, the crack deflection due to anisotropy directly shields the high stress field in front of the crack tip, and guides the crack away from its initial path. Aligning polymer chains to achieve anisotropy has been successfully applied in many commercial products of ultra-stiff, tough and fatigue-resistant fibers, such as isotactic polypropylene and polyethylene. In addition, the natural rubber is isotropic in the undeformed state, but becomes anisotropic due to the aligned inter-chain crystallization when subject to a stretch. Such stretch-induced crystallization also enables crack deflection and helps the natural rubber sustain cyclic loads. Introducing crack deflection to hydrogels for fracture resistance, especially under cyclic loads, has not been explored before. Many current tough hydrogels contain two or more polymer networks. One network provides elasticity, and the other network breaks upon loading and dissipates energy. Based on this, one can readily align one of the polymer networks and form anisotropic hydrogels. Various methods have been developed to align the polymer chains in hydrogels, including microfluidics, shear flow and mechanical stretching. We anticipate the designing mechanism demonstrated in the
current study is applicable in more hydrogel systems, to achieve crack deflection and flaw-insensitivity.

6.7 Summary

In this chapter, we present a design principle of flaw-insensitive hydrogels under both static and cyclic loads through crack deflection. In the polymerization of a double-network hydrogel, one network can be microscopically aligned, leading to an anisotropic hydrogel. The degree of anisotropy can be further quantified and tuned, to induce crack deflection. We demonstrate this mechanism by making a polyacrylamide hydrogel with aligned and crystalline polyvinyl alcohol. Under stretching, an initial flaw in the hydrogel deflects and peels off the small piece of material, leaving the hydrogel flawless again. This toughening mechanism by crack deflection does not require energy dissipation, and makes the hydrogel insensitive to pre-existing flaws. The anisotropic hydrogel is resistant to fatigue fracture, and can sustain more than ten thousand loading cycles without failure. The current design is readily generalized to other hydrogel systems, and benefit future applications that require hydrogels to sustain prolonged cyclic loads.
Chapter 7 Discussion and future challenges

In this chapter, we discuss some understanding on the fatigue of hydrogels, together with some future challenges in the subject.

7.1 Static fatigue of hydrogels

Static fatigue has been reported as slow crack,99,108,111,120-125,140 delayed fracture,117-119 and creep fracture107 in different hydrogel systems. The mechanism of static fatigue in some hydrogels has been well studied, such as the slow crack of polyampholyte hydrogels above the threshold due to viscoplastic dissipation.108 However, most mechanisms remain unclear, and lack direct comparison between experiments and theory. For instance, the PAAm hydrogel and the PAAm-PAMPS hydrogel consist of covalently crosslinked networks, and are expected to be independent of loading rate in their fracture. However, the threshold for slow crack of the two hydrogels is still much smaller than the energy release rate measured with a high crack speed. The slow crack and delayed fracture of a covalently crosslinked hydrogel have been hypothesized to result from poroelasticity,109,114,115,118,141 but there is no direct evidence of comparison between the experimental observations and simulation results. Creep fracture under constant stress has been observed in uncut polyampholyte hydrogels with no covalent network. It has not been reported but is expected that the similar phenomenon under constant stress can occur in uncut hydrogels with covalent network such as PAAm, given the already observed delayed fracture in precut samples under a small load. All these aspects remain unexplored and require further study from both experiment and theory.
7.2 Cyclic fatigue of hydrogels

Cyclic fatigue of uncut hydrogels, i.e., fatigue damage, has been extensively studied. Cyclic fatigue of precut hydrogels, i.e., fatigue fracture, has also been studied in various hydrogel systems. Beyond these, fatigue fracture of self-healing hydrogels has not been reported. A self-healing hydrogel has completely reversible polymer networks, which essentially differs itself from a self-recovery hydrogel with irreversible covalent networks. Self-healing hydrogels with rapid healing are generally weak in mechanical properties, due to the weak bonds forming the hydrogel network. Such hydrogels may or may not suffer fatigue fracture, under different loading conditions. For example, a plastic liquid, such as lithium grease, flows easily upon a small mechanical load, but can always heal and reform its property following the load like liquid. A polyampholyte hydrogel is able to completely heal itself after 24 hours when being cut into two pieces, but is still expected to suffer fatigue fracture if the time of each loading cycle is insufficient for the strong ionic bonds to reform. The thixotropy of most self-healing hydrogels will further complicate their fracture behaviors, and lead to interesting scientific observations as well as potential useful information for designing fatigue-resistant hydrogels.

In addition, more fundamental studies are required for cyclic fatigue. Fatigue damage of uncut hydrogels with tougheners, has been observed to be accompanied by the shakedown phenomenon. While the shakedown of self-recovery hydrogels such as the PAAm-PVA hydrogel is due to the balance between breaking and reforming of reversible bonds in each loading cycle, the shakedown of hydrogels with irreversible tougheners calls for more theoretical understanding. The reason for the thousands of continuous cycles before reaching the steady state is unclear. For precut samples under cyclic loads, fatigue fracture has been systematically quantified for PAAm hydrogels with the same polymer network but different water contents. The experimentally measured threshold agrees well with the theoretical prediction of the Lake-Thomas model for hydrogels with high water content, but deviates
significantly for the case of low water content (Figure 7.1). In addition to water content, the effect of polymer chain length has not been quantitatively compared between experiment and theory. All these problems deserve further investigation.

![Fatigue Fracture Threshold](image)

**Figure 7.1** The threshold for fatigue fracture of PAAm hydrogels with different water content. The threshold is theoretically predicted by the Lake-Thomas model. The four data points correspond to PAAm hydrogels of 96, 87, 78, and 69 wt% of water, from left to right.

### 7.3 Intrinsic fracture toughness of hydrogels

The concept of *intrinsic fracture toughness* was initiated by Lake and Thomas in their study of elastomers. The intrinsic fracture toughness is defined as the minimum energy required to propagate a crack by unit area, without including any energy dissipation from the bulk material (Figure 7.2a). In their model of elastomers with covalent networks, Lake and Thomas hypothesizes that the intrinsic fracture toughness only depends on the covalent network, but depends negligibly on the bulk energy dissipation from the toughener. By focusing on the intrinsic fracture toughness, one can remove the effect of complex rheology from the bulk material, and compare hydrogels of different rheology with respect to their elastic networks.
The intrinsic fracture toughness of elastomers has been measured using both cyclic fatigue fracture and slow crack tests, and has been referred as the thresholds measured in the two cases. However, there is no evidence that the two thresholds are identical or corresponding to a single material constant. Despite this ambiguity, the concept of intrinsic fracture toughness is still exceedingly useful in the common discussion of designing tough hydrogels.

The study of intrinsic fracture toughness of hydrogels has only started recently. Zhang et al. measured the intrinsic fracture toughness of a double-network polyacrylamide-Ca-alginate (PAAm-Ca-alginate) hydrogel by pre-stretching it to large deformation and testing the toughness afterwards, in order to deplete all the energy dissipation of the Ca-alginate toughener. Fatigue fracture of hydrogels under cyclic loads has been initiated recently and used to measure the fatigue thresholds of hydrogels including PAAm, PAAm-Ca-alginate, PAAm-PAMPS, and PAAm-PVA. It has been found that the threshold for fatigue fracture is identical for hydrogels with the same long-chain covalent network but different tougheners. Therefore, the threshold depends on the long-chain covalent network, but negligibly on the toughener (Figure 7.2b). This is consistent with the picture that Lake and Thomas initially described. Before reaching the steady state of fatigue fracture for the measurement of threshold, the many thousand cycles of large stretch at the crack tip have already completely broken all the weaker bonds of the toughener, leaving only the long-chain covalent network to bridge the crack. In contrast, the threshold for slow crack of a hydrogel with a long-chain covalent network and solid-like toughener, such as the PAAm-Ca-alginate hydrogel, depends on both the covalent network and the toughener (Figure 7.2c). The material is unloaded before approaching the crack processing zone. Therefore, at the threshold for slow crack, only the rate-dependent component of the toughener is removed, while the solid-like component still makes finite contribution to toughening the material. For hydrogels with long-chain covalent networks
and solid-like tougheners, the threshold for slow crack is larger than the threshold for fatigue fracture.

**Figure 7.2 The thresholds for fatigue fracture and slow crack.** (a) The molecular picture of the Lake-Thomas model of the intrinsic fracture toughness.75 (b) The threshold for fatigue fracture depends on the long-chain covalent network (PAAm), but negligibly on the toughener (PVA). Hydrogels with the same long-chain covalent network but different tougheners have the same threshold for fatigue fracture. Above the threshold, the toughener reduces the crack extension per cycle.127 (c) The threshold for slow crack depends on both the long-chain elastic network (PAAm) and the solid-like toughener (Ca-alginate).140

In addition to the thresholds for fatigue fracture and slow crack, Tang et al have shown that the threshold for delayed fracture is smaller than that for fatigue fracture of a PAAm hydrogel.119 The relation between the three thresholds measured under fatigue fracture, slow crack and delayed fracture is unclear.

### 7.4 Substantiating theoretical models with careful experiments

The complex rheology of hydrogels poses an essential challenge to substantiate various theoretical models with data from carefully designed experiments. The combination of well-
established theory and careful experiments is not common in the study of fatigue of hydrogels. Here we highlight one example of such study so far.

The slow crack of gelatin hydrogels has been systematically studied by Baumberger, Caroli and Martina from both theory and experiment. \(^{122}\) A gelatin hydrogel is crosslinked by the hydrogen bonds in the collagen triple helix (Figure 7.3a). \(^{222,223}\) The v-G curve of the hydrogel is measured under the pure shear test, for a constant gelatin content in water/glycerol solvents of various glycerol concentrations, in order to modify the viscosity of the hydrogel (Figure 7.3b). The threshold is identical in all cases, on the order of 2.5 J/m\(^2\). Above the threshold, the energy release rate is approximately a linear function of the crack speed, and greatly increases with the concentration of glycerol. A theoretical model is derived to describe the fracture process and capture the v-G curve both at the threshold and at the high speed region. The theory hypothesizes that the slow crack of gelatin hydrogels corresponds to the breaking of hydrogen bonds between the triple helix crosslinks and the pull-out of the stretched polymer chains from the hydrogel matrix, different from the chain scission of the polymer network described in the Lake-Thomas picture. \(^{75}\) To substantiate this, the model verifies that the energy it takes for the chain pull-out is two orders of magnitude smaller than that for the chain scission, and is consistent with the measured value of the threshold. Above the threshold, the energy release rate is derived as \(G(V) = G_0 + \alpha(l/\xi)^2\eta V\), where \(G_0\) is the threshold, \(\alpha\) on the order of unity is the slope of the crack tip profile, \(l\) is the length of a fully stretched chain, \(\xi\) is the average mesh size, \(\eta\) is the viscosity of the solvent, and \(V\) is the crack speed. The second term in the equation represents the viscoplastic dissipation during the process of chain pull-out, and is much larger than the threshold at a high crack speed. To further substantiate this theoretical picture of chain pull-out, the crack tip is wetted with solvents containing different amount of glycerol and water. By doing so, the two terms in the energy release rate can be independently modified, measured and predicted. The experimental results agree quantitatively well with the theoretical model, which together describe the molecular picture of slow crack of gelatin hydrogels.
Fatigue of other hydrogels with direct comparison between theory and experiment has been studied recently, including the cyclic fatigue fracture of PAAm hydrogels with various water contents, and the dissipation mechanism of slow crack of polyampholytes hydrogels above the threshold. Despite these recent progresses, the combination of theory and experiment in fatigue of hydrogels is preliminary.

7.5 Designing fatigue-resistant hydrogels

The ultimate goal of the study is to design hydrogels that resist static and cyclic fatigue in both uncut and precut samples. For cyclic fatigue, hydrogels can be designed to resist fatigue damage with reversible tougheners, or with no toughener. Hydrogels can be designed to better resist fatigue fracture with lower water content or longer polymer chains, to enhance its fatigue threshold. The dissipation from tougheners has negligible effect on the fatigue threshold, but
still reduces the crack extension per cycle above the threshold. For static fatigue, the designing principle is less clear. Hydrogels with long-chain, covalently crosslinked networks seem to be capable of resisting creep fracture if there is no flaw in the sample, but may still suffer delayed fracture if a flaw exists. Rate-independent tougheners composed of covalently crosslinked networks such as PAMPS can reduce the rate-dependent effect of slow crack, compared to tougheners like the Ca-alginate network, which is significantly rate-dependent. Beyond all these preliminary results, it remains to be a serious challenge to develop hydrogels that resist both static and cyclic fatigue.
Chapter 8 Conclusion

Hydrogels are actively studied and developed in both fundamental understanding and modern applications. Traditional hydrogels are soft and brittle. Hydrogels with toughness and stiffness comparable to natural rubber have been recently developed. However, all hydrogels suffer fatigue, i.e., any material failure under prolonged loads. This thesis studies fatigue of hydrogels under both static and cyclic loads. In Chapter 1, we discuss mechanical tests universally applicable for all hydrogels and the physical interpretations behind these tests. We review commonly used mechanical tests including monotonic stretch, constant stretch, constant stress, cyclic stretch, and self-recovery. We summarize experimental results that have been reported and their related physical interpretation. We select five representative hydrogels, and review their mechanical behaviors under those mechanical tests. The representative hydrogels include a single covalent network hydrogel, a single ionic network hydrogel, a double network hydrogel with both covalent and ionic networks, a double network hydrogel with two covalent networks, and a purely ionic network hydrogel with strong and weak ionic crosslinks. We discuss static fatigue including creep fracture and static damage for uncut samples, as well as delayed fracture and slow crack for precut samples. We discuss cyclic fatigue including s-N curve and fatigue damage for uncut samples, as well as fatigue fracture for precut samples.

We next study fatigue fracture of polyacrylamide hydrogels under cyclic loads. Polyacrylamide hydrogels are highly stretchable and nearly elastic. Their stress-stretch curves exhibit small hysteresis, and change negligibly after many loading cycles. Polyacrylamide is used extensively in applications, and is the primary network for many types of tough hydrogels. Recent experiments have shown that polyacrylamide hydrogels are susceptible to fatigue fracture, but available data are limited. In Chapter 2, we study fatigue fracture of polyacrylamide hydrogels of various water contents. We form polymer networks in all samples under the same
conditions, and then obtain hydrogels of 96, 87, 78, and 69 wt% of water by solvent exchange. We measure the crack extension under cyclic loads, and the fracture energy under monotonic loading. For the hydrogels of the four water contents, the fatigue thresholds are 4.3, 8.4, 20.5, and 64.5 J/m², and the fracture energies are 18.9, 71.2, 289, and 611 J/m². The measured thresholds agree well with the predictions of the Lake-Thomas model for hydrogels of high water content, but not in the case of low water content.

Tough hydrogels of many chemical compositions have been developed in recent years, but their fatigue fracture has not been studied before. The lack of study hinders further development of hydrogels for applications that require long lifetimes under cyclic loads. Examples include tissue engineering, soft robots, and stretchable electronics. In Chapter 3, we study the fatigue fracture of a polyacrylamide-calcium-alginate tough hydrogel. We find that the stress-stretch curve changes cycle by cycle, and reaches a steady state after thousands of cycles. The threshold for fatigue fracture is about 53 J/m², much below the fracture energy (~10,000 J/m²) measured under monotonic load. Nonetheless, the extension of crack per cycle in the polyacrylamide-calcium-alginate tough hydrogel is much smaller than that in a single-network polyacrylamide hydrogel.

Some 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 non-covalent, reversible interactions. In Chapter 4, we show that self-recovery hydrogels are still susceptible to fatigue fracture. We study a hydrogel containing both covalently crosslinked polyacrylamide and uncrosslinked polyvinyl alcohol. For a sample without pre-cut crack, the stress-stretch curve recovers after thousands of loading cycles. For a sample with a pre-cut crack, however, the crack extends cycle by cycle. The threshold for fatigue fracture depends on the covalent network, but negligibly on non-covalent interactions. Above the threshold, the non-covalent interactions slow down the extension of the crack under cyclic loads.
We further explore the intrinsic fracture toughness of hydrogels under static and cyclic fatigue. Traditional fracture mechanics based on elasticity fails in these hydrogels due to their complex rheology. The concept of intrinsic fracture toughness, initiated by Lake and Thomas, provides a way to study the fracture by focusing on the scission of polymer network at the crack tip and removing the energy dissipation from the toughener in the bulk material. However, it is unclear whether a material constant related to such concept exists, or can be clearly measured in experiments. In Chapter 5, we try to resolve this ambiguity in hydrogels with long-chain covalent network, by comparing two commonly measured results of intrinsic fracture toughness from fatigue fracture and slow crack. With the already measured threshold for fatigue fracture from Chapter 3, we focus on slow crack of the same polyacrylamide-calcium-alginate hydrogel. We demonstrate the long-term solid-like behavior of the calcium-alginate network by the stress-relaxation test. We measure the v-G curves of slow crack of hydrogel samples with the same polyacrylamide network. The v-G curve depends on the crack speed, sample size and amount of calcium ions added in the pre-gel solution. The threshold for slow crack does not depend on the sample thickness. We compare the measured thresholds for both fatigue fracture and slow crack. The threshold for fatigue fracture only depends on the primary network of polyacrylamide, but negligibly on the calcium-alginate toughener. In contrast, the threshold for slow crack depends on both the primary network of polyacrylamide and the solid-like toughener of calcium-alginate.

Most of the existing tough hydrogels are developed by incorporating large energy dissipation via breaking internal sacrificial bonds. However, from Chapter 2 to 5, we have shown that these hydrogels still fracture under prolonged static and cyclic loads with the presence of even small flaws. Motivated by this, we present a new design principle of flaw-insensitive hydrogels in Chapter 6. The design utilizes material anisotropy by aligning the polymer chains of the hydrogel in the molecular level to deflect a crack. To demonstrate this principle, a polyacrylamide-polyvinyl alcohol hydrogel with crystalline, microscopically aligned polyvinyl alcohol chains is prepared. Upon stretching, an initial flaw deflects, propagates along the
loading direction, and peels off the material, leaving the hydrogel flawless again. The designed hydrogel is insensitive to any pre-existing flaw, even under more than ten thousand loading cycles. The critical degree of anisotropy for crack deflection is quantified by experiments and fracture mechanics. The concept of design can be generalized to other hydrogel systems, and benefit applications that require hydrogels to sustain prolonged loads.

Finally, we summarize some understanding of fatigue of hydrogels and future challenges for the topic in Chapter 7. With the study in this thesis, it is hoped that the theoretical and experimental understanding can facilitate the development of hydrogels that resist both static and cyclic fatigue.
Appendix

Appendix A  Supporting information for Chapter 4

A.1 Preparation of samples

We purchased from Sigma Aldrich the following substances: acrylamide (AAm, A8887), N,N’-methylenebis(acrylamide) (MBAA, M7279), N,N,N’,N’-tetramethylethlenediamine (TEMED, T7024), ammonium persulfate (APS, A9164), and polyvinyl alcohol (PVA, 341584). All chemicals were received and used without further purification. The PAAm-PVA hydrogel was synthesized using the following protocol. PVA powder (Mw 89, 000–98, 000, hydrolysis >99%) of 4.69 g was first dissolved in 30 mL deionized water at 90 °C. The mixture was stirred overnight until the solution became homogeneous. The solution was then mixed with 4.69 g AAm to form a 1:1 weight ratio of PVA: AAm solution. After that, we added MBAA, TEMED and APS in quantities of 0.0015, 0.0022 and 0.0036 times the weight of AAm, in sequence. The prepared pre-gel solution was degassed and injected into 70×70×1.6 mm³ plastic molds and covered with an acrylic plate. The samples were stored at room temperature overnight for complete polymerization, and tested immediately afterwards.

A.2 Mechanical testing methods

All mechanical tests were conducted under the pure shear setup [61,126]. In all tests, a thin sheet of sample, of a long rectangular shape (10×70×1.6 mm³), was fixed to two rigid grips, and mounted in a tensile tester (Instron Model 5966) with a 10 N load cell. All the experimental data represent three individual measurements.

In the viscoelastic test in Figure 4.2b&c, the length of a sample was $H = 10$ mm in its undeformed state. The sample was then stretched to $\lambda H$, under various strain rates, 1 s⁻¹, 0.1 s⁻¹, and 0.01 s⁻¹, respectively. We calculated the nominal stress (i.e., the applied force divided by the
cross-sectional area in the undeformed state) and plotted it as a function of stretch $\lambda$. In the stress-relaxation test in Figure 4.2d&e, a sample was rapidly (1 s$^{-1}$) loaded to stretches 1.3, 1.6, and 1.9 in sequence. Between each step, the sample was held for 3 minutes. The nominal stress was recorded as a function of time $t$.

In the fatigue damage test in Figure 4.3, a sample was cyclically stretched between $H$ and $\lambda_{\text{max}}H$, where $\lambda_{\text{max}}$ defines the maximum applied stretch per unit cycle. We plotted the nominal stress as a function of stretch $\lambda$ in each loading cycle. Different values of $\lambda_{\text{max}}$ between 1.4 and 1.9 were applied in the test. We loaded the sample for 5000 cycles continuously for each $\lambda_{\text{max}}$, with a constant strain rate 0.4 s$^{-1}$. Afterwards, the sample was left in the undeformed state for 3 minutes, and then loaded again for one more cycle. The stress-stretch curves in the 1st cycle and the last cycle were compared.

In the fatigue fracture test in Figure 4.4, a hydrogel sample was mounted in the tensile tester after being notched with an initial crack of length 1.5 cm with a razor blade. To further sharpen the crack tip, we preloaded the sample to propagate the crack for about 0.5 cm more. The sample was then left in the undeformed state for 10 minutes for complete recovery from any residual deformation due to the pre-load. Afterwards, the sample was cyclically deformed following the same loading profile in the fatigue damage test. We applied the same strain rate 0.4 s$^{-1}$ in all tests. To record the gradual extension of the crack, we used a digital camera (Cannon 70D) to take pictures of the sample every 10 minutes. We post-processed the pictures to obtain the extension of crack as a function of the cycle number.

To minimize dehydration during the fatigue tests, we made an acrylic chamber and sealed it around the tensile grips with petrolatum. Water droplets were sprayed on the inner surface of the chamber before each test. A humidifier was connected into the chamber, with its switch controlled by a digital humidity sensor placed inside the chamber, to ensure the relative humidity maintained above 92% throughout the test. To measure the amount of dehydration, we weighed all samples before and after tests, and found less than 3% weight loss.
In our previous paper, the hydrogels were relatively rate-insensitive. Thus, choosing either a constant frequency or a constant strain rate was arbitrary. The current hydrogel system is rate-sensitive. For consistency, we chose a constant strain rate to report both the fatigue and the bulk fracture toughness.

Figure A1  Schematics of the experimental setup and photos of the mechanical test.

Figure A2  Fatigue damage of the hydrogel under (a) $\lambda_{\text{max}} = 1.7$ and (b) $\lambda_{\text{max}} = 1.8$ respectively for 5000 cycles.
Figure A3  Photos show that an initial crack gradually propagates during cyclic loading.

A.3 Quantifying the energy release rate and threshold for fatigue fracture

We obtained the crack growth per cycle, $d\lambda/dN$, by calculating the slope of the curve $\Delta\gamma$ vs. $N$ in the steady state, where the curve starts to be linear. For example, we chose the slope of the curve after $N = 1000$ for $\lambda_{\text{max}} = 1.9$, and $N = 2000$ for $\lambda_{\text{max}} = 1.8$ and $\lambda_{\text{max}} = 1.7$. We quantified the energy release rate $G$ corresponding to the applied stretch $\lambda_{\text{max}}$ following the method previously used for fatigue fracture of tough hydrogels[126],

$$G = W(\lambda_{\text{max}})H,$$  \hspace{1cm} (A.1)

where $W(\lambda)$ is the integral of the loading part of stress-stretch curve in the steady state of an uncut sample (Figure A4). We plotted $d\gamma/dN$ as a function of $G$, and conducted linear regression on the first three points of the curve. The linear regression intercepts the $G$ axis at a positive value $\Gamma_0 = 9.5 \text{ J/m}^2$, i.e. the threshold for fatigue fracture.
Figure A4  $W(\lambda)$ is the integral of the loading part of stress-stretch curve in the steady state of an uncut sample.

To measure the bulk fracture toughness of the PAAm-PVA hydrogel under the same strain rate $0.4$ s$^{-1}$, we applied Equation (A.1) again, with $W(\lambda)$ as the stress-stretch curve of an uncut sample under $0.4$ s$^{-1}$, and $\lambda_{\text{max}}$ as the stretch upon which fast fracture occurs in a pre-cut sample under $0.4$ s$^{-1}$.

A.4 Estimating the threshold using the Lake-Thomas model

We estimated the threshold $\Gamma_0$ using the Lake-Thomas model for hydrogels,

\[ \Gamma_0 = \phi_p^{2/3} b U l \sqrt{n_o}, \]  

(A.2)

where $\phi_p$ is the volume fraction of the PAAm polymer in the hydrogel, $b$ is the number of C-C bonds per unit volume of the dry polymer network, $U$ is the chemical energy of a C-C bond, $l$ is the length of the monomer, and $n_o$ is the average number of monomers per chain.

For the acrylamide monomer, the number of C-C bonds per unit volume of the dry polymer is estimated by the number of monomers per unit volume, $b = A \rho / M_{\text{Aam}} = 9.57 \times 10^{-27}$ m$^{-3}$, where $M_{\text{Aam}}$ is the molecular weight of acrylamide (71.08 g/mole), $\rho$ is the density of acrylamide (1.13 g/cm$^3$), and $A$ is the Avogadro number ($6.022 \times 10^{23}$ /mole).
The length of monomer is estimated as $l = b^{-2/3} = 0.471 \text{ nm}$. The C-C bond energy is $U = 3.3 \times 10^{-19} \text{ J}$. All together, these parameters give a value of $bUl = 1.3 \text{ J/m}^2$.

For both PAAm hydrogel and PAAm-PVA hydrogel, the volume fraction of PAAm in the hydrogel is approximately $\phi_p = 12\%$, for the fact that PVA takes little volume compared to the volume taken by water molecules. The number of monomers between two crosslinks, $n_0$, can be estimated by $n_0 = b / N$, where $N$ is the number of chains per unit volume of the dry polymer. We assume all the added crosslinkers take part in the reaction and form crosslinks, thus $N = 2n_{\text{MBAA}}$ since each crosslink connects two chains on average. The number of crosslinker MBAA per unit volume of the dry polymer, $n_{\text{MBAA}}$, is estimated by the prescribed ratio during the sample preparation, $n_{\text{MBAA}} = 0.0015 bM_{\text{Aam}} / M_{\text{MBAA}}$, where $M_{\text{MBAA}}$ is the molecular weight of MBAA (154.17 g/mole). With these, we get $n_0 = M_{\text{MBAA}} / (0.003 M_{\text{Aam}}) = 723$.

Substituting all these values into Equation (A.2), we obtain $\Gamma_0 = 8.5 \text{ J/m}^2$. 

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Appendix B  Supporting information for Chapter 6

B.1 Preparation of materials

We purchased from Sigma Aldrich the following substances: acrylamide (AAm, A8887), N,N’-methylenebis(acrylamide) (MBAA, M7279), N,N,N’,N’-tetramethylethlenediamine (TEMED, T7024), ammonium persulfate (APS, A9164), polyvinyl alcohol (PVA, 341584) and sodium sulfate (Na$_2$SO$_4$, anhydrous, 1614807). All chemicals were received and used without further purification.

The PAAm-PVA hydrogel was synthesized in the following way. PVA powder (Mw 89,000–98,000, hydrolysis >99%) of 4.69 g was first dissolved in 30 mL deionized water at 90 °C. The mixture was stirred overnight to ensure homogeneity. We then added 4.69 g AAm to the mixture to form a 1:1 weight ratio of PVA:AAm solution. Afterwards, we added MBAA as crosslinker, TEMED as accelerator and APS as initiator in quantities of 0.0006, 0.0022 and 0.0036 times the weight of AAm, in sequence. The prepared pre-gel solution was degassed and injected into plastic molds of 70×50×1.6 mm$^3$, and covered by an acrylic plate. The samples were stored for 24 hours for complete polymerization.

The PAAm-PVA-S hydrogel was synthesized after the polymerization of the PAAm-PVA hydrogel. We soaked the PAAm-PVA hydrogel in the 0.6 M aqueous solution of Na$_2$SO$_4$ for 30 minutes. To ensure that the concentration of Na$_2$SO$_4$ in the solution keeps nearly constant before and after soaking the hydrogel, we prepared the aqueous solution with a volume at least 10 times the volume of the hydrogel. After soaking, the hydrogel was taken out and stored in a sealed plastic bag for maintaining hydration. The average thickness of the samples after soaking was measured to be 1.7 mm.

B.2 Inducing anisotropy of PAAm-PVA-S hydrogels

To make PAAM-PVA-S hydrogels with tunable degrees of mechanical anisotropy, we took the PAAm-PVA-S hydrogel out immediately after its 30 minutes soaking in the Na$_2$SO$_4$
solution, and cut it into samples of 40 mm length and 70 mm width. The samples were then stretched and fixed to an acrylic frame with a prescribed stretch $\lambda_{\text{fix}}$. The frame and sample were stored in a sealed plastic bag for 120 hours, to allow further crystallization of aligned PVA chains. Afterwards, the samples were dismounted from the acrylic frame, and stored in the sealed bag for additional 24 hours before testing (see Figure B4e for the complete history of the process). The degree of anisotropy was controlled by different values of $\lambda_{\text{fix}}$. The anisotropic hydrogels were cut and tested in the direction parallel to $\lambda_{\text{fix}}$ (aligned) and the direction perpendicular to $\lambda_{\text{fix}}$ (transverse).

**B.3 Mechanical testing**

All mechanical tests were conducted with a tensile machine, Instron Model 5966 with a 500 N load cell. Unless otherwise specified, all the testing samples were prepared as a rectangular shape of 10mm length and 50 mm width, with thickness measured individually for different sample types (e.g. with or without Na$_2$SO$_4$ and under different $\lambda_{\text{fix}}$). The samples were fixed to two pairs of acrylic grips by glue and then mounted into the tensile machine before testing. All the samples were tested after 6 days of their storage in sealed bags, except for the daily measurement of stress-stretch curves in Figure 6.2a&b.

For the uniaxial tensile test, a sample of length $H$ was mounted in the tensile machine. During the test, the sample was stretched to $\lambda H$, under a constant strain rate 0.05 s$^{-1}$. The tensile machine recorded the force as a function of extension. We calculated the nominal stress $s$ (i.e., the force divided by the cross-sectional area of hydrogel in the undeformed state) and plotted it as a function of stretch $\lambda$. The shear modulus $\mu$ was obtained as 1/4 of the initial slope of the stress-stretch curve, under the pure shear setup.$^{119}$ As mentioned before, all the samples were 10mm length and 50mm width, except for the PAAm-PVA-S hydrogel samples in the transverse direction with $\lambda_{\text{fix}} = 1.1, 1.2$ and 1.3 (8 mm length and 40 mm width), because the initial sizes of the hydrogels under these conditions were smaller than 50 mm. For the measurement of daily
change in stress-stretch curves (Figure 6.2a&b), an untested sample was used in each measurement.

The fracture toughness of the hydrogels was measured following the pure shear setup. A sample was pre-cut by a razor blade with an initial crack of 0.4 times its width. The sample was then stretched under a strain rate of 0.05 s$^{-1}$. The fracture toughness $\Gamma$ was calculated as $\Gamma = W(\lambda_c)H$, where $W(\lambda_c)$ is the integral of stress-stretch curve of the uncut sample, and $\lambda_c$ is the critical stretch when fast fracture happens. In the test, we defined $\lambda_c$ as the stretch where the stress-stretch curve of the pre-cut sample reaches the peak.

For the cyclic loading test, a sample was cut with a pre-existing flaw of 3 mm length from the middle of its side edge, and then stretched following a linear cyclic loading profile (Figure 6.4a) under a stretch $\lambda_{\text{max}}$ and a strain rate of 0.5 s$^{-1}$. To minimize dehydration during the test, we made an acrylic chamber and sealed it around the tensile machine. Water droplets were sprayed on the inner surface of the chamber before the test. The sample was weighed before and after each test, and found no more than 3% weight loss.

We used a digital camera (Cannon 70D) to record the loading samples in the experiments. For short-term tests (~ minutes), we took videos of the complete tests. For long-time tests (~ hours), we took pictures of the samples every 15 minutes. The videos and pictures were post-processed for analysis.

**B.4 Confocal microscopy**

For confocal microscopy, we prepared PAAm-PVA hydrogels following the same procedure, but adjusted the PVA:AAm weight ratio to 0.5:1, for better control of linking the fluorescent dyes to PVA. We prepared three types of hydrogels, including the PAAm-PVA hydrogel without Na$_2$SO$_4$, the unaligned PAAm-PVA-S hydrogel with Na$_2$SO$_4$, and the aligned PAAm-PVA-S hydrogel with $\lambda_{\text{fix}} = 2.5$. After 6 days of storage in sealed bags, the samples were taken out and further stained with fluorescent labeling.
To label hydrogel samples with fluorescence, we purchased sodium bicarbonate (NaHCO$_3$, 792519) and sodium hydroxide (NaOH, 795429) from Sigma Aldrich. We purchased 5-(4,6-dichlorotriazinyl) aminofluorescein (5-DTAF, D16) from ThermoFisher Scientific as the fluorescent dye. We linked the fluorescent dye 5-DTAF to the hydroxide groups on PVA (see Figure B5 for the corresponding chemical reaction). We first prepared 0.1 M NaHCO$_3$ aqueous solution, with pH = 9.0 adjusted by dripping 0.1 M NaOH solution. Afterwards, we dissolved 5-DTAF powders into the solution to form a 0.2 mg·mL$^{-1}$ 5-DTAF solution. We prepared 3 individual containers with the same 5-DTAF solution, and incubated each type of the hydrogel sample into one container for 5 minutes at room temperature. The volume of 5-DTAF solution was made 10 times the volume of the hydrogel sample. After 5 minutes, we took out the hydrogel samples and rinsed them in deionized water for 2 hours to remove the unreacted fluorescent dyes. The samples were then stored in sealed tubes and avoided light in 5°C environment for 12 hours before the testing.

We used a confocal microscope (Leica tcs-sp5) to map the domains of hydrogen bonding in the hydrogel sample. We excited the dyes with an Argon laser of 488nm band, and recorded images of 520 nm band.

**B.5 Comparing the freeze-thaw method and the soaking method**

To make a crystalline PAAm-PVA hydrogel by the freeze-thaw method, we took the same PAAm-PVA hydrogel prepared in the current study, and followed a cycle of temperature change between the room temperature and -10°C. The hydrogel was kept in a sealed bag in each temperature for 12 hours. After 5 cycles, we cut samples of the freeze-thawed PAAm-PVA hydrogel and tested its stress-stretch curve. The stress-stretch behavior of the freeze-thawed PAAm-PVA hydrogel is similar to that of the PAAm-PVA-S hydrogel by the soaking method. Both hydrogels show much stiffer stress-stretch curves compared to the initial untreated PAAm-PVA hydrogel without crystallization (Figure B1).
Figure B1 Comparing the hydrogels prepared with the freeze-thaw method (red), the soaking method (blue) and the untreated one (black).

B.6 Self-recovery of the PAAm-PVA-S hydrogel

The unaligned PAAm-PVA-S hydrogel was prepared following the same method in the main text. We first loaded the hydrogel for one cycle with a maximum stretch of 2.0 and strain rate 0.5 s$^{-1}$. We then loaded the hydrogel for a second cycle after 40, 70 and 300 minutes, respectively. The hydrogel gradually recovered to its initial stress level, and even became stiffer in the cases of 70 minutes and 300 minutes. The self-recovery to self-stiffening effect is believed to be caused by the re-growth of crystallization in the loading direction.
**Figure B2 (continued) Self-recovery of the PAAm-PVA-S hydrogel.**

### B.7 Other stretching profiles induce aligned crystallization

We tested the effect of other mechanical stretching profiles on the aligned crystallization in the PAAm-PVA-S hydrogel. For example, we made a rectangular sample of PAAm-PVA-S hydrogel with 60mm width and 90mm length. We stretched the sample to $\lambda = 2$ for 5 days, with 20 cycles each day, following the loading profile in Figure B3a. The cyclic stress-stretch curves of the sample become stiffer every day (Figure B3b), with a daily increasing maximum stress per cycle (Figure B3c). This daily stiffening indicates the gradual growth of the aligned crystallization in the stretching direction.
**Figure B3 (continued)** Daily cyclic stretching induces aligned crystallization in the hydrogel. (a) The loading profile and the real sample. The scale bar is 1 cm. (b) The daily stress-stretch curves for 20 cycles. The curves represent 3-5 experimental results. (c) The maximum stress keeps increasing every day. Each data point represents the mean and standard deviation of 3-5 experimental results.

We then compared the stress-stretch curves of the aligned PAAm-PVA-S hydrogels prepared with three different loading profiles. All the samples were cut to a rectangular shape of 50 mm width and 10 mm length. The first sample (Figure B4a&b) was prepared following the same loading profile in Figure B3a. The second sample (Figure B4c&d) was prepared under 20 cycles of loading for 3 days with a maximum stretch of 2.5. The third sample (Figure B4e&f) was prepared following the same profile described in the main text. All the three samples showed anisotropy with similar stress-stretch curves. We adopted the third loading profile for experimental convenience.
Figure B4 Three loading profiles of mechanical stretching (a) (c) and (e) all lead to anisotropy in the hydrogel, reflected by the corresponding stress-stretch curves (b) (d) and (f). The scale bar in (a) (c) and (e) is 1 cm. The curves represent 3-5 experimental results.
B.8 The chemical reaction to link 5-DTAF to PVA chains

![Chemical reaction diagram]

Figure B5 The chemical reaction to link 5-DTAF to PVA chains.\textsuperscript{224}

B.9 The complete crack paths in hydrogels with different $\lambda_{\text{fix}}$
Figure B6  The complete crack path in hydrogels under different fixed stretch (a) $\lambda_{\text{fix}} = 1.0$, (b) $\lambda_{\text{fix}} = 1.1$, (c) $\lambda_{\text{fix}} = 1.2$ and (d) $\lambda_{\text{fix}} = 1.3$. The scale bar is 1 cm.

B.10 The complete fatigue fracture behaviors of the PAAm-PVA-S hydrogel

We first characterized the aligned hydrogel with $\lambda_{\text{fix}} = 2.5$ in the transverse direction. For the hydrogel sample with a rectangular shape of 50 mm width and 10 mm length, we cut the sample by a crack of 20mm, and loaded it cyclically with a prescribed stretch $\lambda_{\max}$ and strain rate
of 0.5 s⁻¹. We recorded the crack growth Δa as a function of the cycle N (Figure B7a&b). We adopted the same method previously developed for the fatigue fracture of tough hydrogels, to relate the applied λ_{max} to the energy release rate. For a specific λ_{max}, we measured the cyclic stress-stretch curves of an uncut sample under the same strain rate 0.5 s⁻¹, until the stress-stretch curves stop changing and reach a steady state after many cycles (2000 cycles in this case). We then calculated the integral of the loading part of the stress-stretch curve in this steady state as W(λ_{max}). The corresponding energy release rate in the steady state is G = W(λ_{max})H, with the length H = 10 mm. Afterwards, we conducted linear regression on the steady-state part of the curve Δa vs N (dashed lines in Figure B7b), and plotted the crack extension per cycle, da/dN, as a function of G (Figure B7c). The linear curve that fits the data da/dN vs G intercepts the G-axis at a positive value of 44.0 J/m², which is the threshold for fatigue fracture of the current PAAm-PVA-S hydrogel in the transverse direction.

In addition to the aligned hydrogel in the transverse direction, we also studied fatigue fracture of the aligned hydrogel (λ_{fix} = 2.5) in the aligned direction (Figure B8), as well as the isotropic hydrogel with λ_{fix} = 1.0 (Figure B9).
Figure B7  Fatigue fracture of the PAAm-PVA-S hydrogel in the transverse direction. (a) Photos of the crack propagation over cycles. The scale bar is 1cm. (b) The crack growth $\Delta a$ as a function of the number of cycles $N$, under different cyclic stretch $\lambda_{\text{max}}$ and the corresponding energy release rate $G$. (c) The crack extension per cycle, $da/dN$ as a function of the energy release rate $G$. The linear fitting curve intercepts the $G$-axis at the threshold for fatigue fracture, $\Gamma_{\text{in}} = 44.0 \text{ J/m}^2$.

Figure B8  More crack deflection in the aligned direction of an aligned PAAm-PVA-S hydrogel ($\lambda_{\text{fix}} = 2.5$). The scale bar is 1 cm.
\( \lambda_{\text{max}} = 1.75, \text{ isotropic} \)

Figure B9  Crack deflection in an isotropic PAAm-PVA-S hydrogel \((\lambda_{\text{fix}} = 1.0)\) under a large enough cyclic stretch \( \lambda_{\text{max}} = 1.75 \). The scale bar is 1 cm.
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