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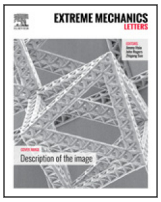

Fatigue-resistant adhesion I. Long-chain polymers as elastic dissipaters

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ABSTRACT

Tough adhesion is often achieved by using inelastic dissipaters. However, inelastic dissipaters fail to enhance adhesion under cyclic loads. Here we achieve fatigue-resistant adhesion by using a particularly simple kind of elastic dissipater: long-chain polymers. Each polymer chain is elastic before rupture. When a single covalent bond of the chain breaks, the elastic energy stored in the entire chain dissipates, amplifying the adhesion energy by the number of links on the chain. So far as the adherends provide the stiffness of an adhered sample, the adhesive can be made of polymer chains of extremely long length. As a proof of concept, we use polyacrylamide hydrogels to adhere two pieces of polyester cloth through topological entanglement. We find that both the adhesion energy and fatigue threshold increase with the polymer chain length and can reach 1400 J/m^2 and 300 J/m^2, respectively. The measured fatigue threshold of adhesion is linearly proportional to the square root of the chain length, in agreement with the Lake–Thomas model. This fatigue-resistant design can be extended to a variety of adhesion topologies for different adherends and adhesives.

1. Introduction

Adhesion between materials is widely used in nature and engineering. Adhesion of dry and hard materials, such as glasses, ceramics, metals, and plastics, has been used since antiquity [1,2]. Adhesion of wet and soft materials is important in bioengineering and surgery. Adhesion between tissue and hydrogel has been developed for tissue repair [3–7], drug delivery [8–11], bioelectronics [12–14] and wound dressing [3,15–18]. Tough adhesion of wet and soft materials is challenging and has attracted much attention in recent years [19].

Existing tough adhesions of wet surfaces are achieved by introducing inelastic dissipaters. When the adhered surfaces separate, energy dissipates not only through breaking bonds on the crack plane, but also through breaking sacrificial bonds in a large volume in the adherends. For example, in the adhesion of calcium alginate-polyacrylamide hydrogel with glass and with tissue, the adherends are connected by covalent bonds through bridging polymer chains. To break these interlinks, many ionic bonds formed by alginate and calcium ions in the hydrogel are broken to dissipate energy [3,20]. The adhesion energy is measured by the energy needed to advance the interfacial crack per unit area. The adhesion energy between hydrogels and various materials, such as glass, ceramic, metal and elastomers, has reached 1000 J/m^2 [20,21].

In many applications, the fatigue resistance of adhesion is important under cyclic loading condition. For example, a human heart pumps billions of times [22], which would require adhesives to sustain such cyclic loads. The fatigue resistance of adhesion is evaluated by fatigue threshold, below which the interfacial crack does not propagate under cyclic loads.

Inelastic dissipaters are effective to enhance the fracture toughness of hydrogels under a monotonic load, but are ineffective to enhance fatigue threshold [23]. For example, in sodium alginate-polyacrylamide hydrogel the sodium ions do not form ionic bonds between alginate chains. Its fracture toughness is 169 J/m and fatigue threshold is 17 J/m^2 [24]. In calcium alginate-polyacrylamide hydrogel, the calcium ions form ionic bonds, acting as inelastic dissipaters. The fracture toughness greatly increases to 3375 J/m^2, but the fatigue threshold increases only to 35 J/m^2. The inelastic dissipaters also fail to enhance the fatigue threshold in hydrogel adhesion. It is reported that the adhesion energy of calcium alginate-polyacrylamide hydrogel and porcine skin reaches 580 J/m^2, but the fatigue threshold of adhesion is only 24 J/m^2 [25].

Elastic dissipaters, however, can enhance both fracture toughness and fatigue threshold [26–29]. A good example of the concept of elastic dissipater is the microstructure of polymer network. When a polymer network is subject to a stretch, before the fracture of the chain, all the C–C links between two crosslinks

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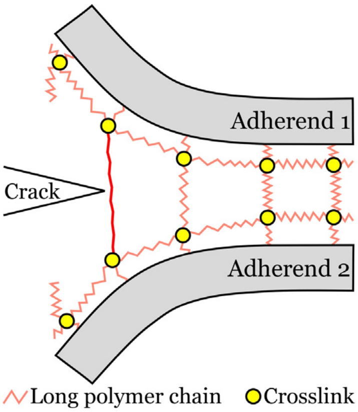

Fig. 1. A design of fatigue-resistant adhesion. Two adherends are connected by long polymer chains, which act as elastic dissipaters. Before the fracture of a polymer chain, all the C–C links on the chain are stretched to the fracture limit elastically. When a single C–C link breaks, the elastic energy stored in all the C–C links of the chain dissipates.

are stretched to the fracture limit elastically. When a single bond on the chain breaks, the elastic energy stored in the entire chain dissipates. The fracture energy and fatigue threshold are amplified by the number of C–C links on the individual polymer chains. However, simply increasing the chain length to enhance the fracture toughness and fatigue threshold decreases the stiffness of the material. One solution to resolve this conflict is to build double networks [30]. The long chain network provides fatigue threshold, and the short-chain network provides stiffness. With this solution, the fatigue threshold of a fully swollen double network hydrogel has reached 400 J/m^2 [30,31].

In this work, we introduce long polymer chains as an adhesive to adhere two adherends (Fig. 1). The polymer chains can interact with the two adherends through different chemical or physical mechanisms. The polymer chains between crosslinks act as elastic dissipaters. The polymer chains are made very long to dissipate more energy. While the long polymer chains have very low stiffness, the stiffness of the composite is provided by the adherends. Consequently, it is unnecessary to use a short-chain network to stiffen the adhesive. We demonstrate this concept using simple materials. The polymer chains are provided by a polyacrylamide (PAAm) hydrogel, as the chain length of PAAm hydrogel is easy to tune by changing the ratio of crosslinkers and monomers. The two adherends are both polyester cloth. We show that the adhesion energy can reach 1400 J/m^2 and the fatigue threshold can reach 300 J/m^2. We also show that the fatigue threshold of adhesion agrees with the Lake–Thomas model.

2. Experiments

2.1. Sample preparation

The chemical reagents were purchased from Aladdin, including acrylamide (AAm, monomer), N,N′-methylenebis acrylamide (MBAA, crosslinker), ammonium persulfate (APS, initiator), and N,N,N′,N′-tetramethylethylenediamine (TEMED, accelerator). We first dissolved 7 g AAm monomers in 18 g deionized water with MBAA crosslinkers, 0.0025 g APS initiators and 7.5 μL TEMED accelerators. The molar ratio of MBAA relative to AAm was varied from 0.0013 mol% to 0.1317 mol% with all other constituents of the solution being fixed. Two pieces of polyester cloth with the size of 100×15×0.15 mm^3 were overlapped. The as-prepared AAm solution was sprayed in the middle of the two cloth layers. The sample was placed between two glass plates covered by polyester films. A silicone rubber frame with the inner size of 100×15×0.3 mm^3 was also placed surrounding the sample between two glass plates to prevent the AAm solution flowing away before gelation. Then the sample was cured by an ultraviolent lamp of 15 W and 365 nm at 25 °C for 8 h in the environment full of nitrogen gas. The adhered sample was made of two pieces of cloth topologically bonded by the formed PAAm hydrogels. The average thickness, width and length of the sample is 0.3 mm, 15 mm and 100 mm. To maintain water content, the samples were stored in a sealed polyethylene bag before testing. The chain length of PAAm hydrogels is estimated by the number of monomers between two crosslinks $n = \frac{M_{AAm}}{2M_{MBAA}}$, where M_{AAm} is the moles of the AAm monomers and M_{MBAA} is the moles of the MBAA crosslinkers. We prepared four kinds of samples with different mole ratios of MBAA relative to AAm, 0.0013 mol%, 0.004 mol%, 0.0132 mol%, and 0.1317 mol%. The corresponding numbers of monomers between crosslinks n are calculated to be 37 957, 12 500, 3796, and 380.

2.2. Fracture test and fatigue test

To study adhesion energy and fatigue threshold, we adopt the 180-degree peel (Fig. 2a), which has been an established method for rubber [32,33] and adhesive [34,35]. The as-prepared adhesion samples were precut using a razor blade in the middle of the two pieces of cloth. The average length of precut is 20 mm. The width of precut is 15 mm, the same as that of samples. One leg of cloth separated by the precut was clamped on the fixed lower gripper. The other leg of cloth was clamped by the moving upper gripper of a tensile machine (SHIMADZU AGS-X). We used a load cell of 500 N to apply load.

For the 180-degree peel, the energy release rate takes the form [32]

$$G = 2F/w \qquad (1)$$

where F is the applied force of the tensile machine and w is the width of the sample. The elastic modulus of cloth is on the order of GPa, which is much larger than that of the hydrogel, so that the cloth is assumed to be inextensible.

We first applied monotonic loads at a displacement rate of 60 mm/min to the samples to measure the adhesion energy. The force–displacement curves were recorded by the tensile machine. Samples of each chain length were repeatedly tested for at least three times. The tests were carried out at 25 °C in the open air. The duration of each test is less than 100 s. The weights of adhesion samples before and after tests were measured to be the same, which means the water content remained unchanged during testing.

We next used 180-degree peel to study the fatigue of adhesion (Fig. 2a). We applied cyclic loads at a displacement rate of 60 mm/min to the samples. The period of each cycle is determined by the loading range from the minimum force $F_{MIN} = 0N$ to the maximum force F_{MAX} detected by the load cell. Fig. 2b shows the typical force–displacement curves over loading cycles under a given maximum energy release rate $G_{MAX} = 2F_{MAX}/w = 190$ J/m^2. The difference of displacement at the maximum force between cycles is twice of the crack growth, $\Delta d = 2\Delta c$, which was directly recorded by the tensile machine. The hysteresis loops in Fig. 2b indicates inelastic dissipation of adhesion. The first cycle has a litter larger hysteresis than subsequent cycles. When the crack propagates at steady state, the hysteresis loop is small but still varies between different cycles. These variations may be attributed to the irregularity of the adhesion interface. The fatigue tests were carried out at 25 °C in a homemade sealed acrylic chamber. During the fatigue tests, the vapor of deionized water was continuously sprayed on the inner surface of the chamber by a humidifier. The difference of weights of adhesion samples before and after tests was less than 8% of the initial weight.

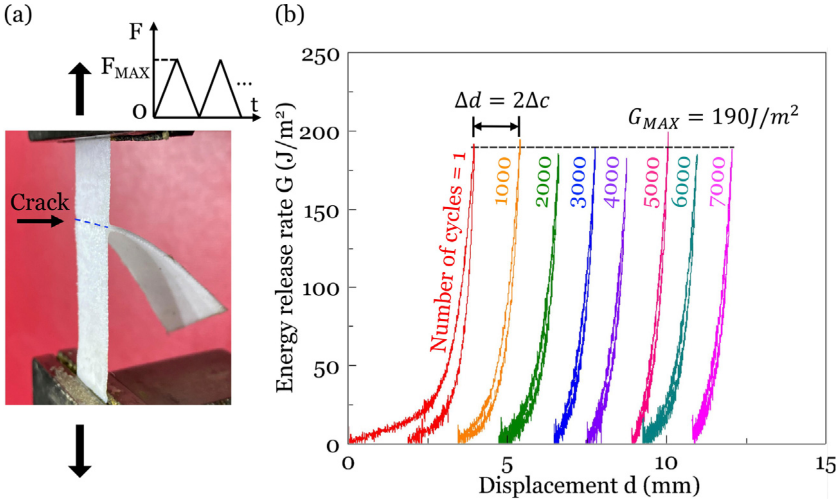

Fig. 2. Fatigue test. (a) The experimental setup of adhesion samples under cyclic loads from the minimum force $F_{MIN} = 0N$ to the maximum force F_{MAX} of a given value. (b) The force–displacement curves over loading cycles under the maximum energy release rate $G_{MAX} = 190$ J/m^2. The vertical axis transforms force into energy release rate by $G = 2F/w$. The difference of displacement at the maximum force between cycles is twice of the crack growth.

3. Results

3.1. Adhesion energy

Fig. 3a–d shows the recorded force–displacement curves of adhesion samples under monotonic loads. As the applied energy release rate increased, the precut crack first opened, blunted but did not extend. When the energy release rate reached the adhesion energy, the crack began to propagate and finally reached a steady state. The adhesion energy corresponds to the plateau of the energy release rate. The average adhesion energy of the four kinds of hydrogels with different chain lengths are 1404 J/m^2, 903 J/m^2, 849 J/m^2, and 184 J/m^2.

3.2. Fatigue threshold of adhesion

Fig. 3e–h shows the crack growth as a function of the number of cycles under different applied maximum energy release rates $G_{MAX} = F_{MAX}/w$. In the first few hundreds of cycles, the crack growth is oscillating, possibly due to the irregular shape of the precut made by razor blade. After hundreds of cycles, the crack propagates at a constant rate in the steady state. We obtain the crack growth per cycle in the steady state by a linear fit of this region. In the last few hundreds of cycles before final separation, the crack grows at an increasing rate. This change signifies that the steady crack growth is affected by the end boundary of the adhesion samples.

Fig. 3i–l plots the crack growth per cycle in the linear fitting region as a function of the applied energy release rate. When the applied energy release rate is larger, the crack grows faster. When the applied energy release rate is low, approaching the fatigue threshold, the crack does not grow. We adopt the following procedure to estimate the fatigue threshold [23,36]. We linearly extrapolate the data points in the plane of G and dc/dN (Fig. 3i-l). We use the data close to G axis and ignore the data far away. The intercept of the G axis gives the experimental fatigue threshold. The fatigue thresholds of adhesion for the four kinds of hydrogels with different chain lengths are 298 J/m^2, 140 J/m^2, 99 J/m^2, and 41 J/m^2. The minimum crack growth rates for the four sets of samples are on the orders of 10^{-7} m/cycle, 10^{-7} m/cycle, 10^{-8} m/cycle, and 10^{-9} m/cycle, respectively.

3.3. Lake–Thomas model

Under cyclic loads, Lake–Thomas model assumes that when the applied load approaches the fatigue threshold the crack growth only activates one dissipative process: breaking polymer chains ahead of the crack lying across the crack plane [37]. Therefore, the fatigue threshold is calculated as

$$\Gamma_0 = \alpha J l \sqrt{n}/V \qquad (2)$$

where J is the energy per covalent bond, l is the length per monomer, n is the number of monomers between two crosslinks, V is the volume per monomer and α is a numerical factor. For PAAm polymer chain, the parameters are $J = 3.3 \times 10^{-19} J$, $V = 8.93 \times 10^{-29}$ m^3 and $l = 0.447$ nm [37]. Considering the water content in PAAm hydrogels, the Lake–Thomas model is modified as $\Gamma_0 = \phi\alpha J l\sqrt{n}/V$, where ϕ is the volume fraction of polymer in hydrogels [26]. Our recipes give $\phi = 21.2\%$. Lake–Thomas model predicts that the fatigue threshold is linearly proportional to the square root of the chain length.

Fig. 4 plots the fatigue threshold and adhesion energy as a function of the square root of the chain length $\sqrt{n}$. Both fatigue threshold and adhesion energy increase as the chain length increases. Fig. 4(a) shows the linear dependence of the fatigue threshold on the square root of the chain length, as predicted by Lake–Thomas model. Inserting the material parameters in Eq. (2), the curve fitting gives the numerical factor $\alpha = 4.2$. The agreement with Lake–Thomas model further confirms our design strategy: increase the fatigue threshold of adhesion by simply increasing the chain length. The adhesion energy is the sum of the intrinsic fracture energy and the associated energy dissipation during crack propagation. It is easy to speculate that the adhesion energy also positively correlates with the chain length, as shown in Fig. 4(b).

4. Discussions

By simply increasing the chain length of PAAm polymer between two pieces of cloth, the adhesion energy reaches 1400 J/m^2 and the fatigue threshold of adhesion reaches about 300 J/m^2. These values are likely to meet the requirements for most potential biomedical applications. Tough adhesion enhanced by inelastic dissipaters shows a rapid degradation of fracture resistance under cyclic loads and significant loading-history dependent stress–stretch behavior [25]. By contrast, tough adhesion

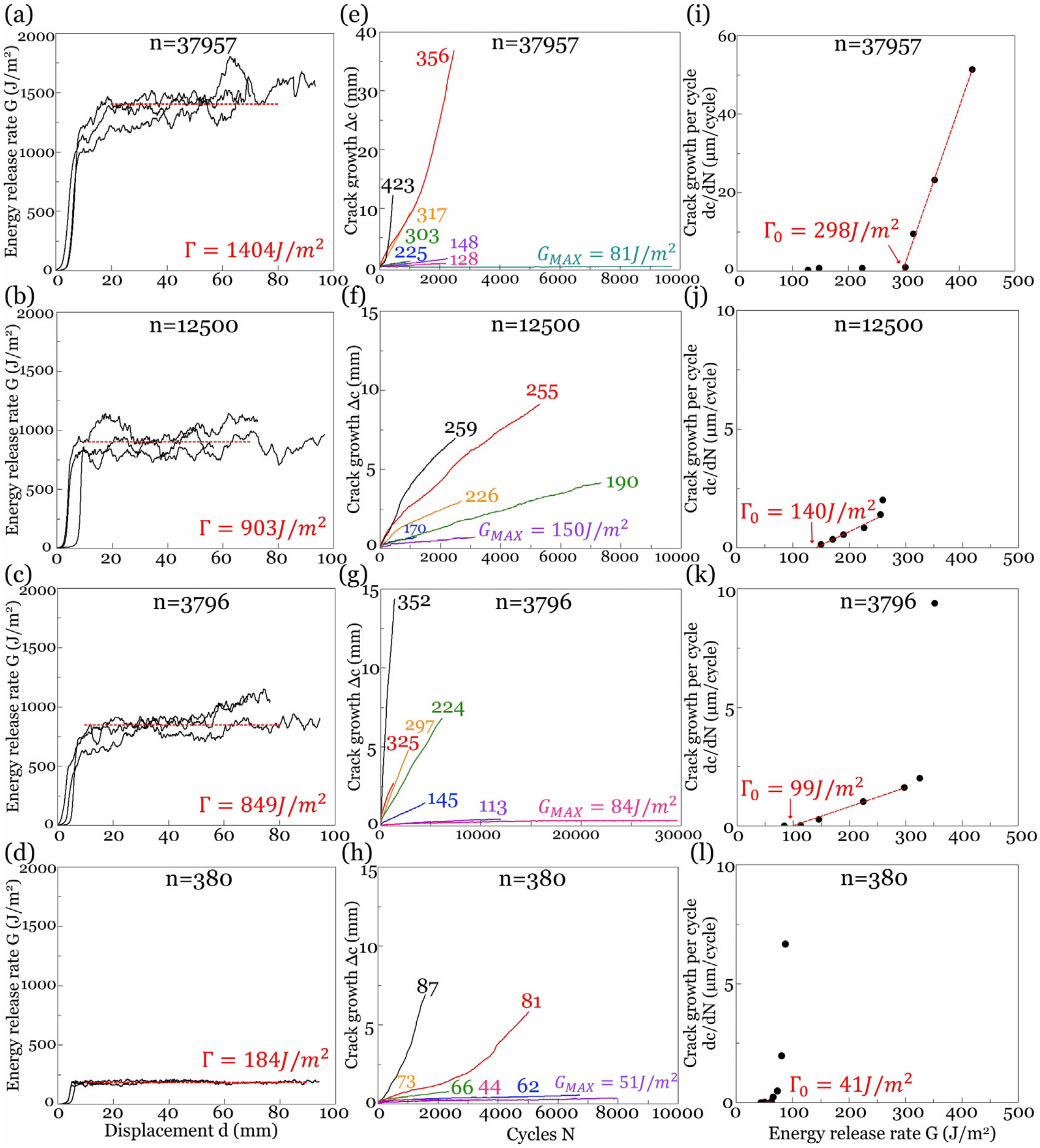

Fig. 3. Adhesion energy and fatigue threshold of cloth interface with four chain lengths of PAAm hydrogel adhesive $n = 37\,957, 12\,500, 3796, 380$. (a–d) The energy release rate G as a function of loading displacement of adhesion samples under monotonic loads. The plateau of G corresponds to the adhesion energy Γ. (e–h) The crack growth of adhesion samples over cycles with different applied maximum energy release rate G_{MAX}. (i–l) The crack growth per cycle as a function of G_{MAX}. The data points near the G axis are linearly extrapolated to obtain the fatigue threshold Γ_0.

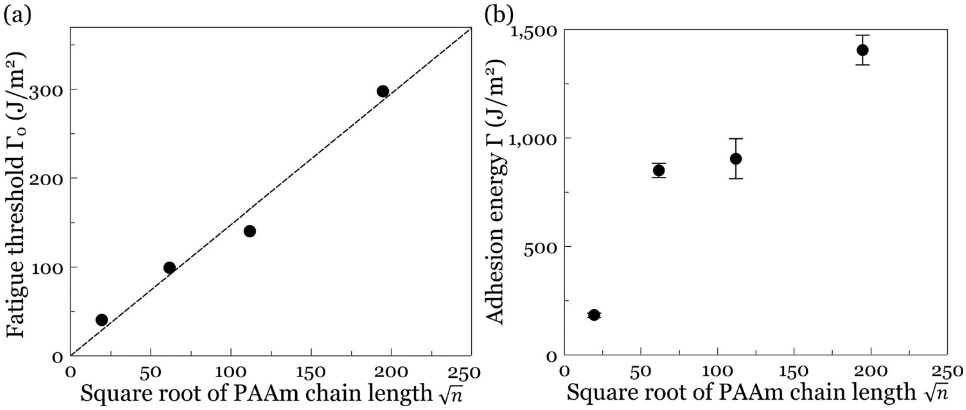

Fig. 4. The fatigue threshold of adhesion (a) and adhesion energy (b) as a function of the chain length of PAAm hydrogel adhesives between two adherends.

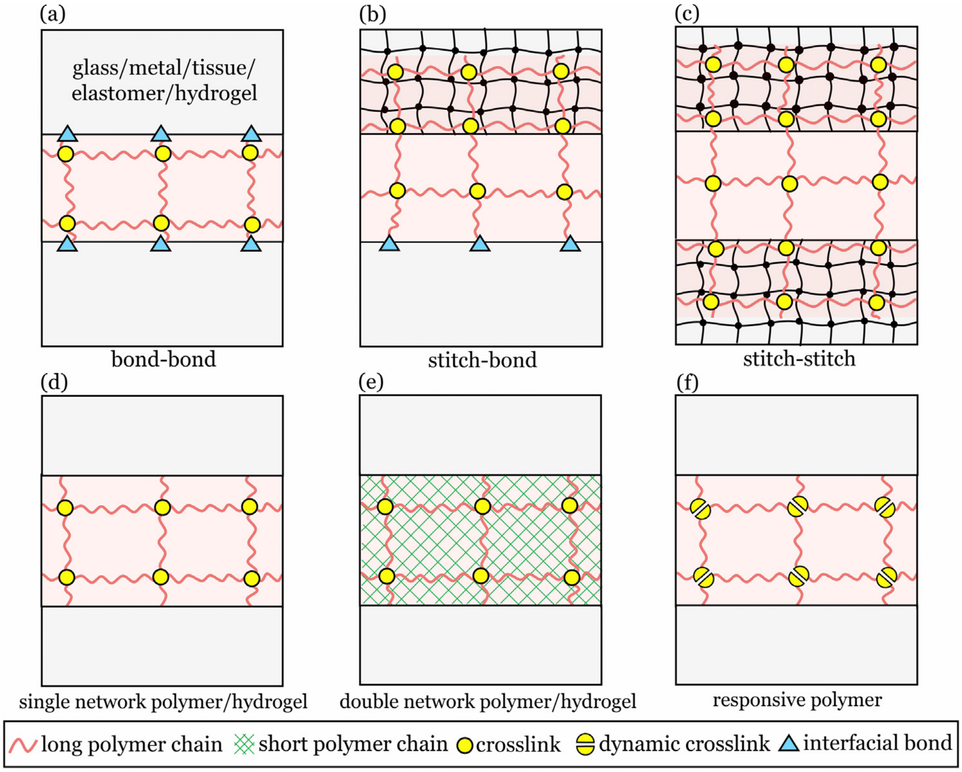

Fig. 5. Design of fatigure-resistant adhesion with different adhesion topologies. The adhesive of long polymer chains can adhere with the two adherends with (a) bond–bond topology (b) stitch-stitch topology (c) stitch-bond topology. The adhesive of long polymer chains has many choices. (d) single network polymers or hydrogels. (e) double network polymers or hydrogels (f) responsive polymers.

enhanced by elastic dissipaters maintains a very high capability to sustain cyclic loads. They behave elastically with slight fatigue symptoms, including residual stretch, stress relaxation and hysteresis under the fatigue threshold. With the elastic dissipation mechanism, tough adhesion achieved through elastic dissipater is also expected to have a good resistance of static fatigue.

The design strategy of using long-chain polymer to enhance fatigue threshold of adhesion is not limited to the cloth-PAAm demonstration in this work. This strategy can be generalized to a wide choice of topologies between adherend and adhesive. Fig. 5 describes some molecular topologies with the long-chain polymer strategy. The long-chain polymer of adhesive can adhere with the two adherends with chemical bonds (Fig. 5a). Either of the adherend can be glass, metal, tissue, elastomer, hydrogel, etc. If the adherend does not have complementary functional group on its surface, we can use surface modification [20], surface initiation [21], and bulk modification [38]. The long-chain polymer of adhesive can also adhere the two adherends by topological adhesion (Fig. 5b), as demonstrated in this work. In this topology, the adherend should have a strong and sparse polymer network to form the stitch. The long-polymer chains of adhesives diffuse into the polymer network of adherends and crosslink as a secondary network. Fig. 5c shows a combination of the above two topologies, with one adherend connected by chemical bond and the other adherend connected by topological adhesion.

The adhesive of long-chain polymer network has many choices to meet different requirements. The simplest choice is single network polymers such as commercial rubbers (PDMS, Ecoflex) or biocompatible polymers, and single network hydrogels such as PAAm hydrogels used in this work (Fig. 5d). One can also use double network polymers or double network hydrogels as the adhesive (Fig. 5e). While the long-chain primary network enhances the fatigue threshold of adhesion, the secondary network may provide other functions including high toughness, high stiffness, or anti-swelling property. One can even use responsive polymer networks with dynamic chemical crosslinks that can reversibly dissociate or reform in response to PH, heat, light, or redox condition [39–41] to achieve detachable fatigue-resistant adhesion.

Other than long-chain polymer network, architected structures can act as an elastic dissipater. It has been demonstrated that a composite with unidirectional hard fibers and a soft matrix shows high toughness and fatigue threshold [27–29]. When the crack extends, the soft matrix shears and delocalizes the high stretch of the hard fiber over a large area. When the bond near of the crack of the fiber fractures, all elastic energy stored in the fiber dissipates. Such architected structures can be used to design fatigue-resistant adhesion. Architected structures for adhesion deserve further attention [42,43].

5. Conclusion

We propose a strategy to design fatigue-resistant adhesion: use long-chain polymers as elastic dissipaters to adhere two solids. As a demonstration, we use PAAm hydrogels to topologically bond two pieces of polyester cloth. We prepared adhesion samples with four different chain lengths of the PAAm hydrogel adhesive. We use the 180-degree peel to measure the adhesion energy under monotonic loads and the fatigue threshold under cyclic loads. We find that both the adhesion energy and fatigue threshold increase with the chain length of PAAm hydrogel and can reach 1400 J/m^2 and 300 J/m^2 respectively. The fatigue threshold shows linear dependence on the square root of chain length, as predicted by the Lake–Thomas model. The design strategy of using long-chain polymers to enhance fatigue threshold of adhesion is not limited to the stitch-stitch topological adhesion, but applicable to a wide variety of molecule topologies. The adhesive can also be extended to elastomers, double network polymer/hydrogels and responsive polymers. Elastic dissipaters open a potent mechanism to create tough and fatigue-resistant adhesions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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