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# Designing extremely resilient and tough hydrogels via delayed dissipation

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# ABSTRACT

While high resilience of a material requires low mechanical dissipation of the material under deformation, high toughness requires significant mechanical dissipation during crack propagation. Here we reconcile this pair of seemingly contradictory properties to design extremely tough and resilient hydrogels. We propose a resilient domain for hydrogels' deformation, below which hydrogels are deformed with low mechanical dissipation, but above which the deformation is highly dissipative. Therefore, hydrogels will appear resilient under moderate deformation within the resilient domain, but materials around crack tips will be deformed beyond the resilient domain and thus dissipate significantly to toughen the hydrogels. We implement the resilient domain by pre-stretching an interpenetratingnetwork hydrogel to damage the short-chain network to a controlled degree. The resultant hydrogel is highly resilient if deformed within the pre-stretched range (i.e., resilient domain), but highly dissipative if deformed beyond the resilient domain because of further damage of the short-chain network-achieving both high resilience of 95% and high toughness of 1900  $J/m^2$ . To quantitatively explain the experimental results, we further adopt an interpenetrating-network model with network alteration, which can guide the design of future resilient and tough hydrogels.

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# 1. Introduction

High resilience of a material requires low mechanical dissipation of the material under deformation, which is indicated by small hysteresis loops in the stress-strain curves of the material being deformed and undeformed (e.g., Fig. 1(a)). On the other hand, high toughness requires significant mechanical dissipation during crack propagation in a material, and thus large hysteresis loops in the corresponding stress-strain curves of the material (e.g.,

Fig. 1(b)). While resilience and toughness seem to be a pair of intrinsically contradictory properties for a material, many biological tissues or hydrogels are indeed both resilient and tough. For example, heart valves [1–3], which need to deform more than  $3 \times 10^9$  cycles over their lifetime [3], generally can achieve both high resilience (>80%)[2,4] and high toughness (>1200 J/m<sup>2</sup>) [1] in order to be both energy-efficient and robust. Designing synthetic hydrogels that are both tough and resilient will not only help the replacement and regeneration of relevant tissues such as heart valves, but also advance fundamental knowledge in mechanics and materials science. Despite the successes in developing hydrogels with high toughness [5-11]or high resilience [12,13], recent efforts on designing both tough and resilient hydrogels mostly focus on one property (e.g. reporting resilience without toughness) [14–16]. In







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**Fig. 1.** Schematics of the design principle for tough and resilient hydrogels: (a) Resilience material requires low mechanical dissipation under deformation, indicated by small hysteresis in the stress–strain curve. (b) Tough material requires high dissipation during crack propagation in it, indicated by large hysteresis in the stress–strain curve. (c) Resilient and tough hydrogel can be designed with delayed dissipation. The hydrogel is resilient when deformed within a resilient domain  $\lambda_R$ , but significantly dissipative when deformed beyond  $\lambda_R$ . Hydrogel around a crack tip will be deformed beyond  $\lambda_R$  and therefore significantly dissipates mechanical energy to toughen the hydrogel.

addition, existing works in the field mostly rely on specific materials [14–16]. However, a general principle together with practical methods that can guide the design of resilient and tough hydrogels using different materials will be particularly valuable.

Here, we report a general principle to design resilient and tough hydrogels via delayed dissipation (Fig. 1), as well as a practical method to implement the principle by controlling the damage in interpenetrating-network hydrogels (Fig. 2). We validate the design principle and method with interpenetrating-network hydrogels including Polyacrylamide–alginate (PAAm–alginate) and Polyacrylamide–Polyethylene glycol (PAAm–PEG) hydrogels. We show that the resultant hydrogels can indeed achieve both high resilience up to 95% and high toughness up to 1900 J/m<sup>2</sup> (Figs. 3 and 4). We further adopt a theoretical model to fit the current results, which may be used to guide the design of future resilient and tough hydrogels.

#### 2. Design principle and method

While toughening of hydrogels generally relies on a combination of mechanisms for dissipating mechanical energy and maintaining high elasticity of the hydrogels [10], we further propose to design a *resilient domain*,  $\Lambda_R$ , in tough hydrogels, so that

- (1) When  $\Lambda_{\max} \leq \Lambda_R$ , the hydrogel is resilient;
- (2) When  $\Lambda_{\text{max}} > \Lambda_R$ , deformation of the hydrogel significantly dissipate mechanical energy

where  $\Lambda_R$  is a measurement of deformation, such as principal stretches, the first invariant of Green deformation tensor [17], and effective stretch of polymer chains [18], and  $\Lambda_{\text{max}}$  the same measurement of the maximum deformation of the hydrogel in one loading–unloading cycle.

Since the hydrogel samples in the current study will all undergo pure-shear tension (Fig. 3(a)), different measurements of deformation will lead to equivalent results. To focus on the essential idea, we will choose the principal stretch along the applied force direction,  $\lambda$ , as the measurement of deformation (Fig. 3(a)). Therefore, the hydrogel is resilient when the maximum principal stretch of the hydrogel along the applied force direction  $\lambda_{max} \leq \lambda_R$ , and highly dissipative when  $\lambda_{max} > \lambda_R$  (Fig. 1(c)). In particular, the hydrogel around crack tips can be highly stretched over  $\lambda_R$ , and therefore significantly dissipate mechanical energy to toughen the hydrogel (Fig. 1(c)).

To implement the design principle, we pre-stretch interpenetrating-network hydrogels with distinctly different chain lengths to  $\lambda_R$  (Fig. 2) [5,6]. The pre-stretch will damage the short-chain network in the hydrogels to controlled degrees, which tend to increase with the pre-stretch. As a result, if the pre-stretched hydrogel is further



**Fig. 2.** Schematics of a practical method to implement the design principle by controlling damage of interpenetrating-network hydrogels. The pre-stretch will damage the short-chain network in the hydrogels to controlled degrees. If the pre-stretched hydrogel is further deformed within the range of  $\lambda_R$ , it will be resilient. If the sequent deformation is beyond the range of  $\lambda_R$ , more chains in the short-chain network can be fractured to further dissipate mechanical energy.



**Fig. 3.** Experimental validation of the design principle and method with PAAm–alginate hydrogel. (a) Schematics of the pre-stretch and further deformation of the hydrogel sample; (b) Stress vs. stretch curves of the sample pre-stretched to  $\lambda_R = 5$  and further stretched to  $\lambda_{max} = 5$  and 8, respectively. (c) Stress vs. stretch curves of the sample with  $\lambda_R = 5$  stretched to  $\lambda_{max} = 2$ , 3 and 4, at different rates.

deformed within the range of  $\lambda_R$ , it will be highly resilient; since the available sacrificial chains or bonds within the range of  $\lambda_R$  have been mostly consumed. On the other hand, if the subsequent deformation is beyond the range of  $\lambda_R$ , more chains in the short-chain network can be fractured to further dissipate mechanical energy. Therefore, the pre-stretched hydrogel can maintain high toughness, due to large deformation (over  $\lambda_R$ ) of materials around crack tips (Fig. 1(c)). It should be noted that the pre-stretch should be much lower than that ultimate stretch of the hydrogel, in order to avoid depletion of the short chains and damage of long chains.

# 3. Experimental validation and results

To validate the design principle, we first choose interpenetrating networks of PAAm-alginate to form the hydrogel. The de-crosslinking and fracture of the alginate short-chain network can dissipate mechanical energy, and the PAAm long-chain network maintains high elasticity of the hydrogel-leading to the high toughness of the resultant hydrogel [5]. A pre-gel solution was prepared by mixing 4.1 mL 4.8 wt% alginate (Sigma, A2033) and 5.5 mL 18.7 wt% acrylamide (Sigma, A8887). We added 377 µL 0.2 g/100 ml N, N-methylenebisacrylamide (Sigma, 146072) as the crosslinker for polyacrylamide and 102  $\mu$ L 0.2 M ammonium persulphate (Sigma, 248614) as a photo initiator for polyacrylamide. After degassing the pre-gel solution in a vacuum chamber, we added 200  $\mu$ L 1 M calcium sulfate (Sigma, C3771) as the crosslinker for alginate and 8.2  $\mu$ L N, N, N', N'-tetramethylethylenediamine (Sigma, T7024-50M) as the crosslinking accelerator for polyacrylamide. Thereafter, the pre-gel solution was infused into a



**Fig. 4.** Tunable resilience and fracture toughness of tough and resilient PAAm–alginate hydrogels. (a) Resilience *R* as a function of maximum stretch  $\lambda_{max}$  for samples with  $\lambda_R = 4, 5$  and 6, respectively. (b) Fracture energy  $\Gamma$  vs. resilient domain  $\lambda_R$  of the hydrogels, error bar denotes STD, n = 3; (c) Distribution of the maximum principal stretch around the crack tip of a hydrogel with  $\lambda_R = 5$  under pure-shear test before crack propagation. (d) Maximum principal stretch along the central line of the sample.

glass mold measuring  $80 \times 60 \times 2 \text{ mm}^3$  and was subjected to ultraviolet light for 60 min with 8 W power and 254 nm wavelength to cure the hydrogel. The resultant hydrogel was soaked in DMEM for 15 h to swell to equilibrium, approximating the physiological conditions *in vivo* [19].

The hydrogel was cut into specimens measuring 40  $\times$  $6 \times 2$  mm<sup>3</sup>. Pure-shear tension was applied on the samples with Micro-Strain Analyzer (MSA) tensile tester at room temperature (Fig. 3(a)). The principal stretch of the sample along the applied force direction,  $\lambda$ , can be measured as the current length of the sample over the initial length (Fig. 3(a)). We first loaded the sample to  $\lambda_R = 5$  and then unloaded for 5 cycles to deplete the sacrificial bonds and chains (see Fig. 3(b)). Thereafter, the pre-stretched hydrogel sample was further stretched to maximum principal stretches of  $\lambda_{max} = 2, 3, 4, 5$  and 8 with a rate of  $0.02 \text{ s}^{-1}$  and then unloaded (Fig. 3(b) and (c)). It can be seen that when  $\lambda_{max} \leq \lambda_R$ , the hysteresis loop in the loading-unloading curves are almost negligible, indicating negligible mechanical dissipation and high resilience. Furthermore, we increased the loading rate on the pre-stretched sample to  $0.1 \text{ s}^{-1}$ , and found that the small hysteresis loops were unaffected. On the other hand, when the pre-stretched sample is deformed to  $\lambda_{max} = 8$ (i.e., beyond resilient domain), an apparent hysteresis loop appeared, indicating significant mechanical dissipation.

Moreover, the resilient domain of the hydrogel can also be tuned by changing the value of the pre-stretch  $\lambda_R$ . We next pre-stretched hydrogel samples to  $\lambda_R = 4$ , 5 and 6, respectively; and then measured the resilience of the samples under various deformations (Fig. 4). The resilience of samples in the pure-shear tests (Fig. 3(a)) can be calculated as

$$R = 1 - \frac{\oint sd\lambda}{\int_{1}^{\lambda_{\max}} sd\lambda} \tag{1}$$

where  $\oint sd\lambda$  is the area of hysteresis loop in the loading-unloading cycle,  $\int_{1}^{\lambda_{\text{max}}} sd\lambda$  the area under the load-ing curve, *s* the nominal stress in the sample, and  $\lambda_{\text{max}}$ the maximum nominal stretch in the cycle. As shown in Fig. 4(a), for various values of  $\lambda_R$ , when  $\lambda_{max} \leq \lambda_R$ , the resilience of the hydrogels is consistently high, over 90%; when  $\lambda_{\text{max}} > \lambda_R$ , the resilience decreases drastically in some cases (e.g., R = 35%, when  $\lambda_R = 4$  and  $\lambda_{max} = 8$ ), indicating significant mechanical dissipation. We further used pure-shear tests to measure the fracture toughness of hydrogels pre-stretched to various resilient domains (i.e.,  $\lambda_R = 1-5$ ). From Fig. 4(b), it can be seen that the fracture toughness can indeed maintain a relatively high level, over  $1800 \text{ J/m}^2$ . To validate that the high toughness is due to the deformation of hydrogels around crack tip above  $\lambda_R$ , we used digital image correlation technique [20,21] to obtain the distribution of maximum principal stretches around the notch of a tough and resilient hydrogel with  $\lambda_R = 5$ . From Fig. 4(c) and (d), it can be seen that the maximum principal stretch in the region around the notch tip can indeed reach values much higher than  $\lambda_R$  before crack propagation to dissipate mechanical energy and therefore toughen the hydrogel.

While the dissociated ionic crosslinkings in alginate network can reform after pre-stretching the PAAm-alginate hydrogels to decrease the resilience of the hydrogel [5], it seems swelling the hydrogels in media can significantly reduce this effect (Fig. S5(a)). For example, a hydrogel pre-stretched to  $\lambda_R = 3$  can maintain high resilience of 77% over 67 h. In addition, we also demonstrated the same design principle and method with PAAm–PEG hydrogels, which can maintain high resilience ~90% over time, since the fractured short PEG chains during pre-stretch cannot re-heal (Figs. S1–S4, S5(b)). In addition, the resilient PAAm–PEG hydrogels can also maintain relatively high toughness over 400 Jm<sup>-2</sup> (Fig. S3).

# 4. Theoretical model

We next use the interpenetrating-network model with network alteration to predict the loading–unloading behavior and the tunable resilience of our tough and resilient hydrogel [22]. For details of the model, please refer to Ref. [22]. In brief, the model assumes each network is swollen in the solution of water and other networks, so that the effective stretch of polymer chains in the long-chain network  $\Lambda_l$  and the short-chain network  $\Lambda_s$  can be expressed respectively as

$$\Lambda_{l} = C_{l}^{-1/3} \sqrt{\frac{\lambda_{1}^{2} + \lambda_{2}^{2} + \lambda_{3}^{2}}{3}},$$

$$\Lambda_{s} = C_{s}^{-1/3} \sqrt{\frac{\lambda_{1}^{2} + \lambda_{2}^{2} + \lambda_{3}^{2}}{3}}$$
(2)

where  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are principal stretches of the hydrogel, and  $C_l$  and  $C_s$  the volume concentrations of the longchain network and the short-chain network, respectively. Here, we set  $C_l = 0.083$  and  $C_s = 0.017$ , which is approximated by the recipe of the PAAm-alginate gel (4.1 mL 4.8 wt% alginate and 5.5 mL 18.7 wt% acrylamide). For a hydrogel sample under pure-shear deformation (Fig. 3(a)), we have  $\Lambda_l = C_l^{-1/3} \sqrt{(\lambda^2 + \lambda^{-2} + 1)/3}$  and  $\Lambda_s =$  $C_s^{-1/3} \sqrt{(\lambda^2 + \lambda^{-2} + 1)/3}$ . Assuming Langevin chains, the nominal stress along the applied force direction on the hydrogel sample under pure-shear deformation (Fig. 2(a)) can be expressed as [22]

$$s = kT \left( \frac{C_s^{1/3} \beta_s N_s \sqrt{n_s}}{3\Lambda_s} + \frac{C_l^{1/3} \beta_l N_l \sqrt{n_l}}{3\Lambda_l} \right) \left( \lambda - \frac{1}{\lambda^3} \right)$$
(3)

where  $N_l$  and  $N_s$  are the numbers of chains per unit volume of the long-chain and short-chain networks without water or other networks, respectively,  $n_l$  and  $n_s$  are the numbers of freely joint links on a chain of the long-chain and shortchain networks, respectively,  $\beta_s = L^{-1} \left( \Lambda_s / \sqrt{n_s} \right)$ ,  $\beta_l = L^{-1} \left( \Lambda_l / \sqrt{n_l} \right)$ , and  $L^{-1}$  is the inverse Langevin function defined by  $L(x) = \operatorname{coth}(x) - 1/x$ .

While the long-chain network (i.e.,  $N_l$  and  $n_l$ ) does not vary with the deformation of the hydrogel, the shortchain network alters significantly due to its damage during deformation [10]. By adopting the network alteration theory [23], we assume

$$N_{s} = N_{s0} \exp\left[-p \cdot \left(\Lambda_{s}^{\max} - C_{s}^{-1/3}\right)\right]$$
(4)

$$n_{\rm s} = n_{\rm s0} \exp\left[q \cdot \left(\Lambda_{\rm s}^{\rm max} - C_{\rm s}^{-1/3}\right)\right] \tag{5}$$



Fig. 5. Comparison of fracture toughness and resilience of various synthetic and biological hydrogels.

where *p* and *q* are the network-alteration parameters which satisfies  $p \ge q \ge 0$ , and  $\Lambda_s^{\text{max}}$  is the maximum value of  $\Lambda_s$  throughout the deformation process including the pre-stretch. In the pure-shear deformation,  $\Lambda_s^{\text{max}} = C_s^{-1/3} \sqrt{\left(\lambda_{\text{max}}^2 + \lambda_{\text{max}}^{-2} + 1\right)/3}$ . In addition, assuming all chains in both networks are effective at un-deformed state of the hydrogel, we have  $n_{s0}N_{s0}v = 1$  and  $n_lN_lv = 1$ , where *v* is the volume of a freely-joint link in both networks. Further assuming  $n_B$  is much larger than  $n_{A0}$  (i.e.,  $n_B = 100n_{A0}$ ), the constitutive behavior of the hydrogel can be characterized by a set of four parameters:  $n_{A0}$ , v, *p* and *q*. By selecting physically reasonable values of these parameters,  $v = 9 \times 10^{-28}$  m<sup>-3</sup>,  $n_{A0} = 132$ , p = 0.19and q = 0.079, the model can consistently predict the resilient-dissipative transition of the hydrogels with resilient domains (Fig. S6).

## 5. Conclusion

We report a general principle for the design of resilient and tough hydrogels via delayed dissipation. Based on the principle, a resilient domain is defined for the deformation of tough hydrogels. We further implement the delayed dissipation and resilient domain by prestretching interpenetrating-network hydrogels to damage the short-chain network within controlled ranges, achieving extremely high resilience ( $\sim$ 95%) and high toughness  $(\sim 1900 \text{ J/m}^2)$  (see Fig. 5 for comparison with counterpart biological and synthetic hydrogels [1,2,4,12]). Since the design principle and method reported here are materialindependent, we expect they can be used to make existing tough hydrogels resilient and to design future tough and resilient hydrogels. In addition, it is noted that natural rubbers indeed achieve high resilience and high toughness via delayed dissipation at large deformation, when polymer chains begin to detach from reinforcing particles, giving the Mullins effect [24]. It is expected the design principle and method proposed here can be used to design new tough and resilient elastomers such as triple-network tough elastomers recently developed [25].

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.eml.2014.11. 002.

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