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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 interpenetrating-network 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.

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 3×10^9 cycles over their lifetime [3], generally can achieve both high resilience (>80%) [2,4] and high toughness (>1200 J/m^2) [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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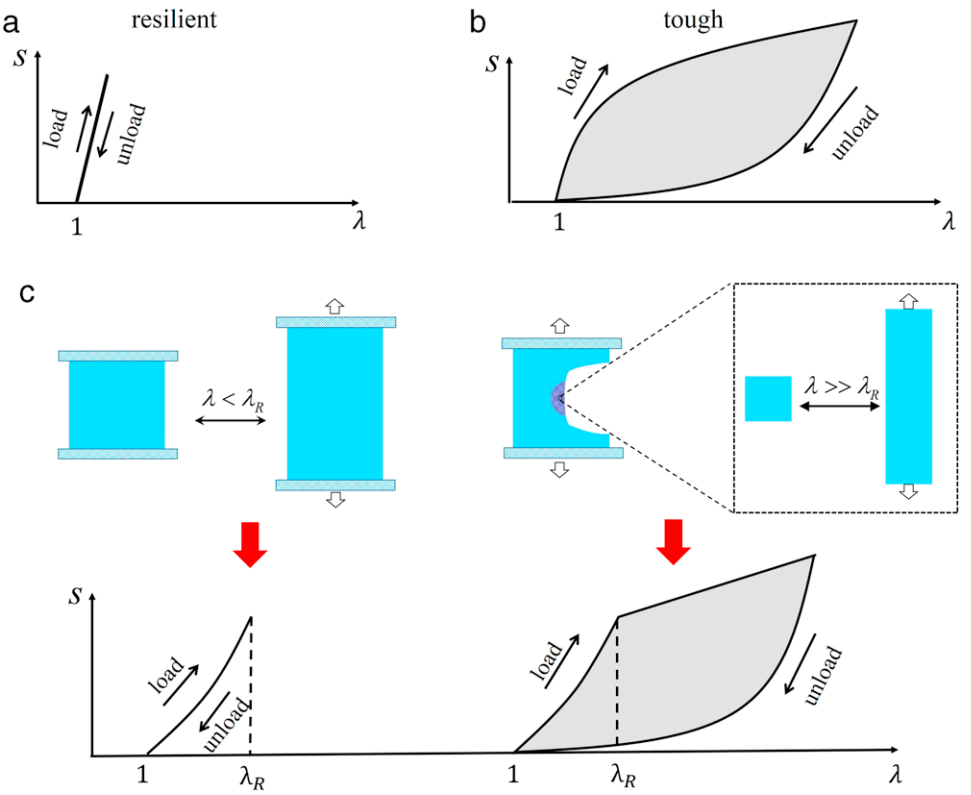

Fig. 1. Schematics of the design principle for tough and resilient hydrogels: (a) Resilience material requires low mechanical dissipation under deformation, indicated by small hysteresis in the stress–strain curve. (b) Tough material requires high dissipation during crack propagation in it, indicated 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 λ_R, but significantly dissipative when deformed beyond λ_R. Hydrogel around a crack tip will be deformed beyond λ_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^2 (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*, Λ_R, in tough hydrogels, so that

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

where Λ_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 $\Lambda_{\max}$ 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, λ, 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 λ_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 λ_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