Anti-fatigue-fracture hydrogels

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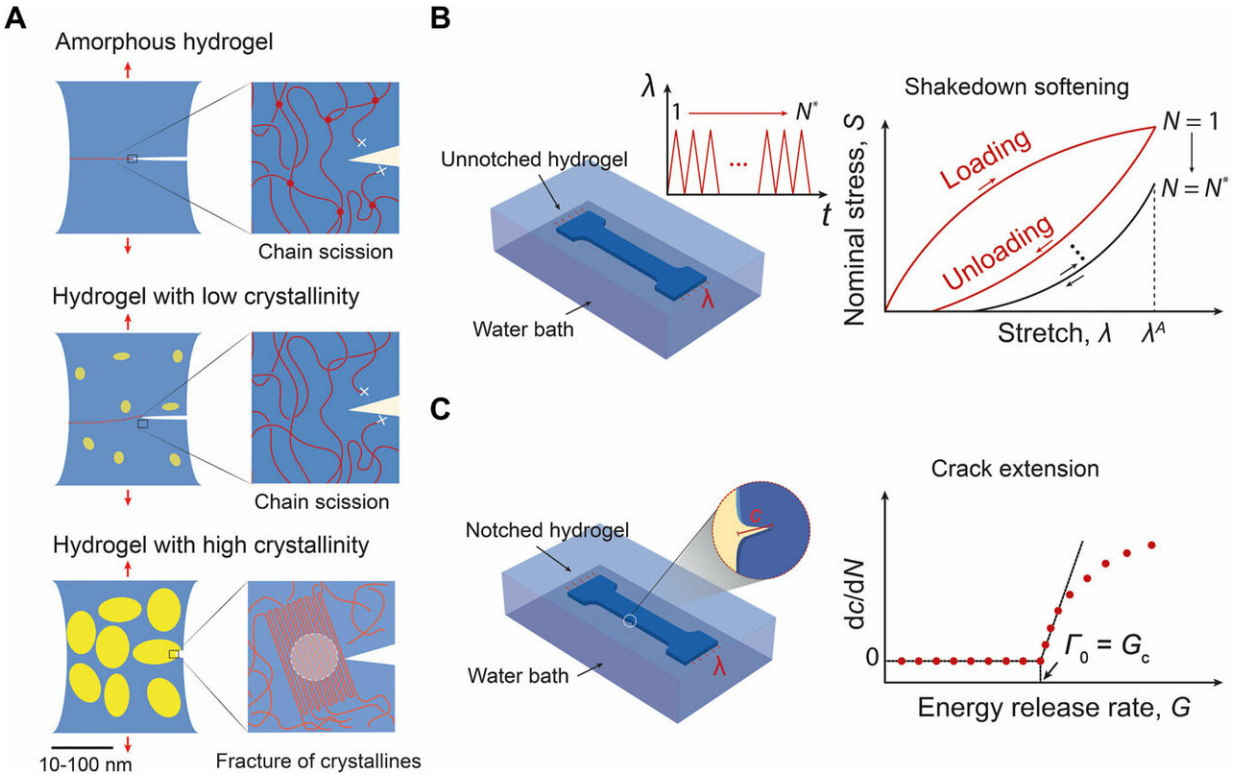


Design principle for anti-fatigue-fracture hydrogels. (A) Illustration of fatigue crack propagation in an amorphous hydrogel and in hydrogels with low and high crystallinities under cyclic loads. The yellow areas represent crystalline domains, and the blue areas denote amorphous domains. In the amorphous hydrogel and the hydrogel with low crystallinity, the fatigue threshold can be attributed to the energy required to fracture a single layer of polymer chains per unit area. In the hydrogel with high crystallinity, the fatigue crack propagation requires fracture of crystalline domains. (B) Illustration of measuring nominal stress S versus stretch λ curves over N cycles of the applied stretch λA. The stress-stretch curve reaches steady state as N reaches a critical value N*. (C) Illustration of measuring crack extension per cycle dc/dN versus energy release rate G curves.

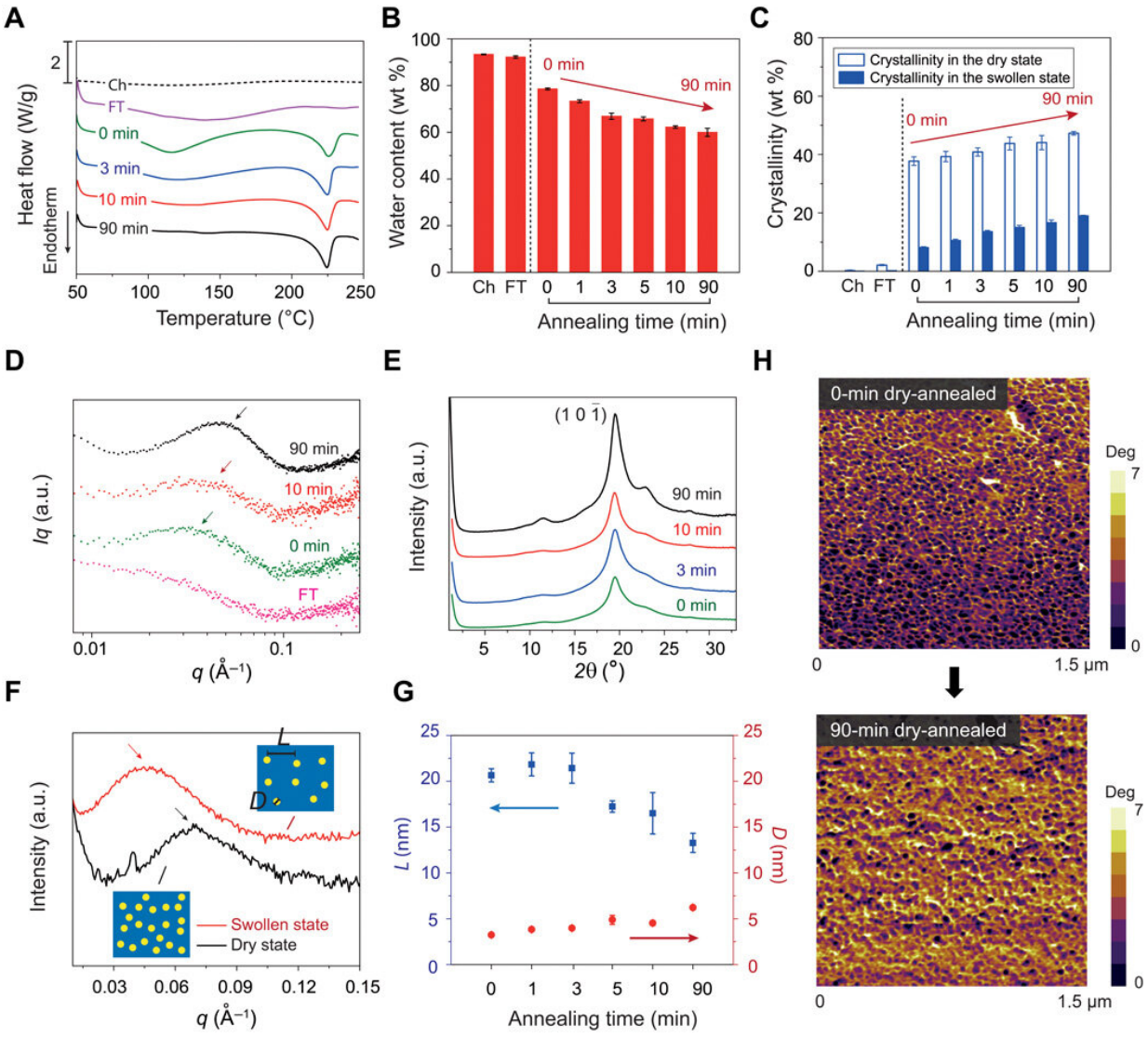
By linearly extrapolating the curve to intercept with the abscissa, we can approximately obtain the critical energy release rate Gc, below which the fatigue crack will not propagate under infinite cycles of loads. By definition, the fatigue threshold Γ0 is equal to the critical energy release rate Gc. Credit: *Science Advances*. Doi: 10.1126/sciadv.aau8528

Hydrogels are polymer networks infiltrated with water, widely used for tissue engineering vehicles of drug delivery and novel platforms for biomedical engineering. Emerging applications for new hydrogel materials call for robustness under cyclic mechanical loads. Materials scientists have developed tough hydrogels that resist fracture under a single cycle of mechanical load, yet these toughened gels still suffer from fatigue fracture under multiple cycles of loads. The present fatigue threshold for synthetic hydrogels is reported in the order of 1 to 100 J/m^2.

In a recent study, Shaoting Lin and a team of materials scientists at the Massachusetts Institute of Technology (MIT) proposed the design of an anti-fatigue-fracture hydrogel. To develop the proposed hydrogel, the scientists needed the materials to have energies per unit area at a much higher value than that required to fracture a single layer of polymer chains. To accomplish this, they controlled the introduction of crystallinity in to hydrogels to substantially enhance their anti-fatigue-fracture properties. In this work, Lin et al. disclosed the fatigue threshold of polyvinyl alcohol (PVA) with a crystallinity of 18.9 weight percent (18.9 wt%) in the swollen state to exceed 1000 J/m^2. The results are now published in *Science Advances*.

The pioneering work of Gong et al has inspired materials scientists to engineer hydrogels that are increasingly tough to resist crack propagation in a single cycle of mechanical load for industrial and biomedical

applications. Hydrogels are toughened via mechanisms to dissipate mechanical energy, such as the fracture of short polymer chains and reversible crosslinks into stretchy polymer networks. Yet, the existing tough hydrogels suffer from fatigue fracture under multiple cycles of mechanical loads. The highest fatigue threshold on record so far is 418 J/m^2 for a double network hydrogel, poly (2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS)-PAAm. The outcome is credited to the high intrinsic fracture energy of the PAAm network with very long polymer chains.



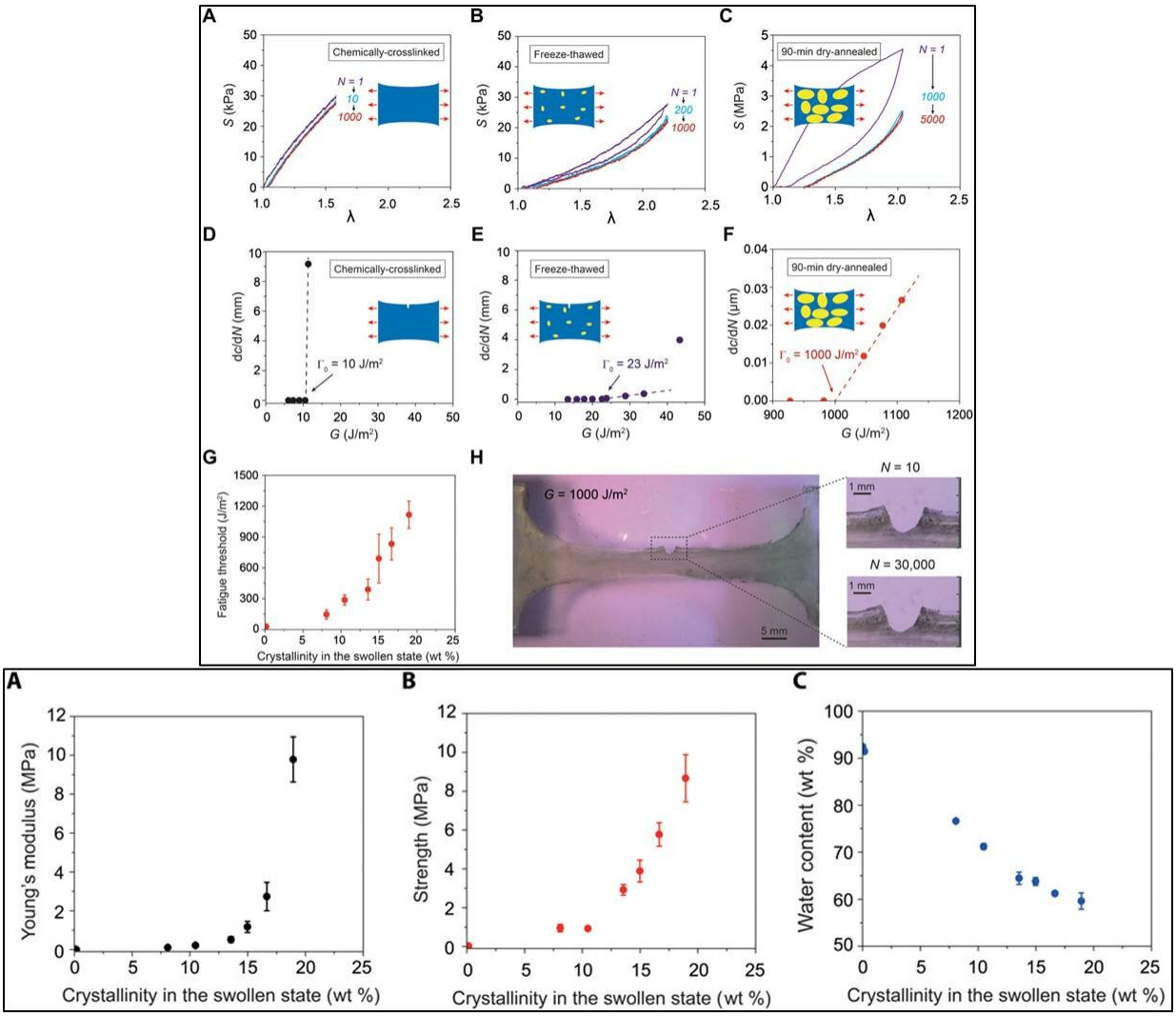
Characterization of crystalline domains in PVA hydrogels. (A) Representative DSC thermographs of chemically cross-linked (Ch), freeze-thawed (FT), and dry-annealed PVA with annealing times of 0, 3, 10, and 90 min. (B) Water contents of chemically cross-linked, freeze-thawed, and dry-annealed PVA with annealing times of 0, 1, 3, 5, 10, and 90 min. (C) Measured crystallinities in the dry and swollen states of chemically cross-linked, freeze-thawed, and dry-annealed PVA with annealing times of 0, 1, 3, 5, 10, and 90 min. (D) Representative SAXS profiles of freeze-thawed and dry-annealed PVA, with annealing times of 0, 10, and 90 min. (E) Representative WAXS profiles of dry-annealed PVA with dry-annealing times of 0, 3, 10, and 90 min. a.u., arbitrary units. (F) SAXS profiles of 90-min dry-annealed PVA in the dry state and swollen state. The insets illustrate the increase of the distance between adjacent crystalline domains due to swelling of amorphous polymer chains. (G) Estimated average distance between adjacent crystalline domains L and average crystalline domain size D of dry-annealed PVA with annealing times of 0, 1, 3, 5, 10, and 90 min. (H) AFM phase images of dry-annealed PVA with annealing times of 0 and 90 min. Credit: *Science Advances*. Doi: 10.1126/sciadv.aau8528

Biological tissues such as cartilage, tendons, muscles and heart valves with extraordinary anti-fatigue properties are comparatively superior to synthetic hydrogels. For instance, the biomechanics of fracture energy in the knee joint after prolonged cycles of loads is above 1000 J/m^2. This is due to the inherent, anti-fatigue properties of biological tissues based on highly ordered and partially crystalline collagen fiber structures. Lin et al. were inspired to develop biomimetic hydrogels centered on such anti-fatigue properties of biological tissues. Their hypothesis was that increased crystallinity in synthetic hydrogels could increase the fatigue threshold of the material, therefore the fatigue threshold in such biomimetic materials will be higher since crystalline domains had to be fractured for crack propagation.

To test the hypothesis, Lin et al. used PVA in the study as a model

hydrogel with tunable crystallinity. They increased the annealing time of the PVA hydrogel to confer higher crystallinity, larger crystalline domain size and smaller average distance between the adjacent domains. The increased crystallinity greatly enhanced the PVA hydrogel fatigue thresholds (for a crystallinity of 18.9 weight percent, the fatigue threshold exceeded 1000 J/m^2.)

The scientists then created kirigami hydrogel sheets that were highly stretchable and resistant to fatigue fracture. They based the hydrogel models on a strategy to maintain high water content and low moduli, while rendering the hydrogels resistant to fatigue fracture. The new work revealed a new anti-fatigue-fracture mechanism in hydrogel development, as well as a practical method to design such hydrogels for diverse practical applications.



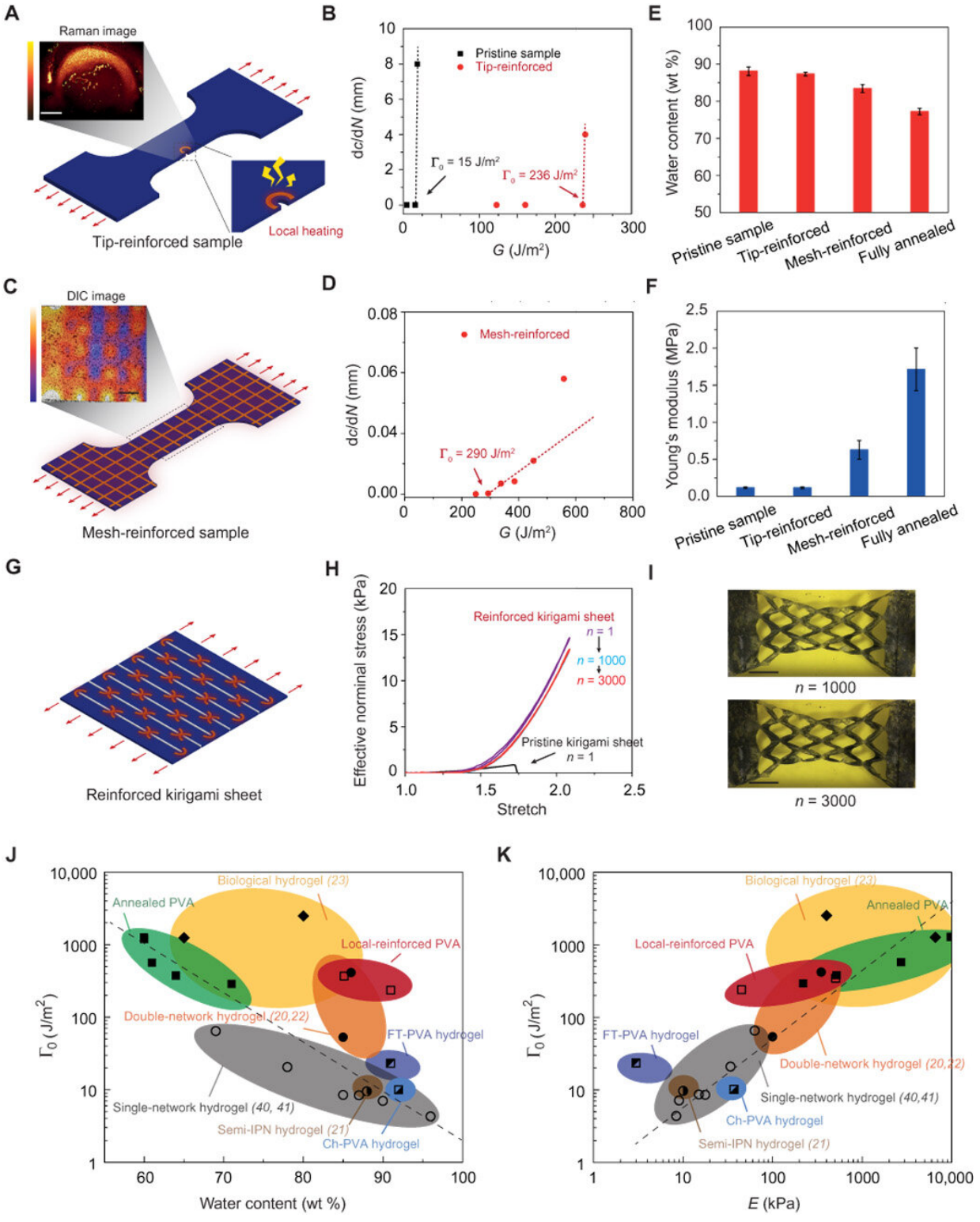
Top panel: Measurement of fatigue thresholds of PVA hydrogels. Nominal stress S versus stretch λ curves over cyclic loads for (A) chemically cross-linked hydrogel at an applied stretch of λA = 1.6, (B) freeze-thawed hydrogel at an applied stretch of λA = 2.2, and (C) 90-min dry-annealed hydrogel at an applied stretch of λA = 2.0. Crack extension per cycle dc/dN versus applied energy release rate G for (D) chemically cross-linked hydrogel, (E) freeze-thawed hydrogel, and (F) dry-annealed hydrogel with annealing time of 90 min. (G) The fatigue threshold increases with the crystallinity of the hydrogel in the swollen state. (H) Validation of fatigue threshold as high as 1000 J/m2 in 90-min dry-annealed hydrogel using the single-notch test. Lower panel: Young's moduli, tensile strengths, and water contents of PVA hydrogels. (A) Young's modulus versus crystallinity in the swollen state. (B) Tensile strength versus crystallinity in

the swollen state. (C) Water content versus crystallinity in the swollen state. Credit: *Science Advances*. Doi: 10.1126/sciadv.aau8528

To form hydrogels crosslinked by crystal domains during materials development, the scientists first froze a solution of uncrosslinked PVA at -20 degrees C for 8 hours and thawed it at 25 degrees C for 3 hours. This was followed by further drying in an incubator at 37 degrees C and annealing at 100 degrees C for a variety of time ranges from zero to 90 minutes. As a control, the scientists also fabricated a chemically crosslinked PVA without crystal domains (amorphous polymer network). To measure the crystallinities of the resultant PVA hydrogels in their dry state, Lin et al. used differential scanning calorimetry (DSC).

The crystallinity of the PVA samples increased in the dry state and further evolved with increased annealing time. To quantify evolving crystalline morphology of the samples, the scientists used small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS). To validate tuning of the crystalline domains in the PVA hydrogel with increased annealing time with phase images, the scientists used atomic force microscopy (AFM). The resulting images showed bright areas of relatively high modulus (corresponding to the crystalline domain) and dark areas of relatively low modulus (corresponding to the amorphous polymer).

To perform all fatigue tests in the study, Lin et al. used fully swollen hydrogels immersed in a water bath to prevent dehydration-induced cracks. Using dog bone-shaped material samples, the scientists performed cyclic tensile tests and systematically varied the applied stretch. As the stretch increased, the crystalline domains transformed into aligned fibrils along the loading direction.

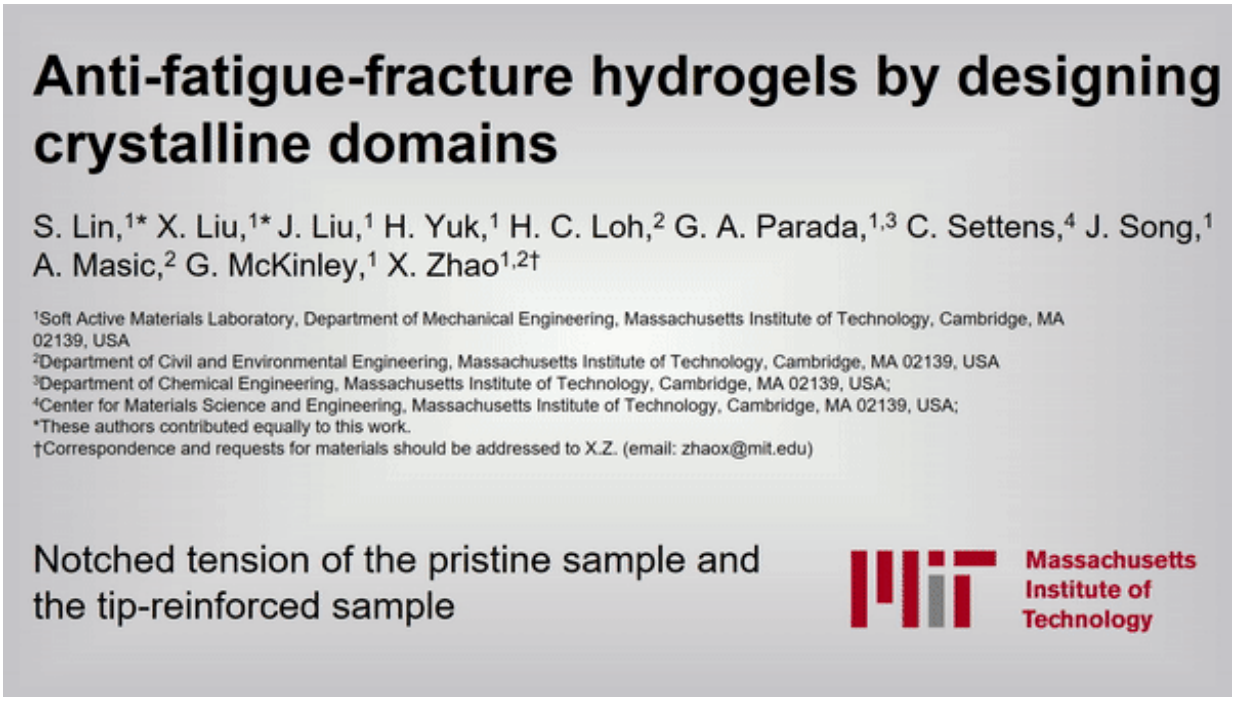


Patterning highly crystalline regions in PVA hydrogels. (A) Illustration of

introducing a highly crystalline region around crack tip. Inset: Raman spectroscopy with bright color representing low water content and dark color representing high water content. (B) Comparison of crack extension per cycle dc/dN versus applied energy release rate G between the pristine sample and the tip-reinforced sample. The fatigue thresholds of the pristine sample and the tip-reinforced sample are 15 and 236 J/m2, respectively. (C) Illustration of introducing mesh-like highly crystalline regions. Inset: Digital image correlation (DIC) method shows large deformation in low-crystallinity regions and small deformation in high-crystallinity regions. (D) Crack extension per cycle dc/dN versus applied energy release rate G of the mesh-reinforced sample. The fatigue threshold of the mesh-reinforced sample is 290 J/m2. (E) Water contents of the pristine sample, the tip-reinforced sample, the mesh-reinforced sample, and the fully annealed sample. (F) Young's moduli of the pristine sample, the tip-reinforced sample, the mesh-reinforced sample, and the fully annealed sample. (G) Illustration of introducing highly crystalline regions around cut tips in a pristine kirigami sheet. (H) Effective nominal stress versus stretch curves of the reinforced kirigami sheet under cyclic loads. Effective nominal stress versus stretch curve of the pristine kirigami sheet under a single cycle of load. (I) Images of the reinforced kirigami sheet under 1000th cycle and under 3000th cycle. (J) Comparison of fatigue thresholds and water contents among reported synthetic hydrogels PVA hydrogels with patterned highly crystalline regions, and biological tissues. (K) Comparison of fatigue thresholds and Young's moduli among reported synthetic hydrogels, PVA hydrogels with patterned highly crystalline regions, and biological tissues. IPN in (J) and (K) represents interpenetrating polymer network. Credit: *Science Advances*. Doi: 10.1126/sciadv.aau8528

The energy required to damage the crystalline domains and fibrils was much higher than that required to fracture a single layer of the same polymer in its amorphous state. The scientists quantified the dependence of the fatigue threshold on the crystallinity. Both Young's modulus and the tensile strength of the hydrogels increased with crystallinity.

Lin et al. then proposed another strategy to introduce specifically programmed, highly crystalline regions in the hydrogels. For this, they used computer-aided design of electric circuits to induce localized heat treatment to anneal selected regions of the hydrogels. As examples of the procedure, Lin et al. locally introduced a highly crystalline ring-shaped region around a crack tip. Despite the small area, the alteration caused a fatigue threshold of more than 236 J/m^2 to delay crack propagation. As a second example, the scientists patterned mesh-like highly crystalline regions on the pristine hydrogel. The alternation conferred a fatigue threshold of 290 J/m^2, relatively low Young's modulus (627 kPa) and high water content (83 weight percent), compared with the pristine unmodified hydrogel.



Tension of the pristine notched sample and the tip-reinforced sample. The pristine sample fractures at the stretch of 1.2 with the fracture energy of 22 J/m2 . The tip reinforced sample can be stretched to 1.5 without rupture and reaches the fracture energy of 300 J/m2. Credit: *Science Advances*. Doi:

10.1126/sciadv.aau8528

Lin et al. then compared the fatigue thresholds, water contents and Young's modulus of hydrogels reported in literature. They showed that by patterning highly crystalline regions, tip- and mesh-reinforced PVA hydrogels could outperform the existing synthetic hydrogels. The materials can also maintain relatively high water content and low Young's moduli. The scientists aim to apply this strategy of patterning to highly crystalline regions of various structures of hydrogels to improve anti-fatigue performance.

In this way, enhancing the anti-fatigue-fracture performance of hydrogels can contribute to a number of applications and research directions in advanced materials. In biomedical engineering, anti-fatigue hydrogels can be used for hydrogel-based, implantable tissue replacements of the meniscus, invertebral disc and cartilage. These medical translations require mechanical robustness for long-term interactions with the human body. The newly developed anti-fatigue-fracture hydrogels can offer a novel materials platform for biomedical and industrial applications.

More information: Shaoting Lin et al. Anti-fatigue-fracture hydrogels, *Science Advances* (2019). DOI: 10.1126/sciadv.aau8528

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