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Previews

Soft-fiber-reinforced tough and fatigue resistant hydrogels

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Drawing inspiration from natural materials, a new practical strategy for fabricating strong, tough and fatigue resistant hydrogels is reported by compositing modulus-contrasting, but compositionally similar, hydrogel fibers and matrix together. The strategy is generalizable to various fabrication methods such as 3D printing, electrospinning, and molding.

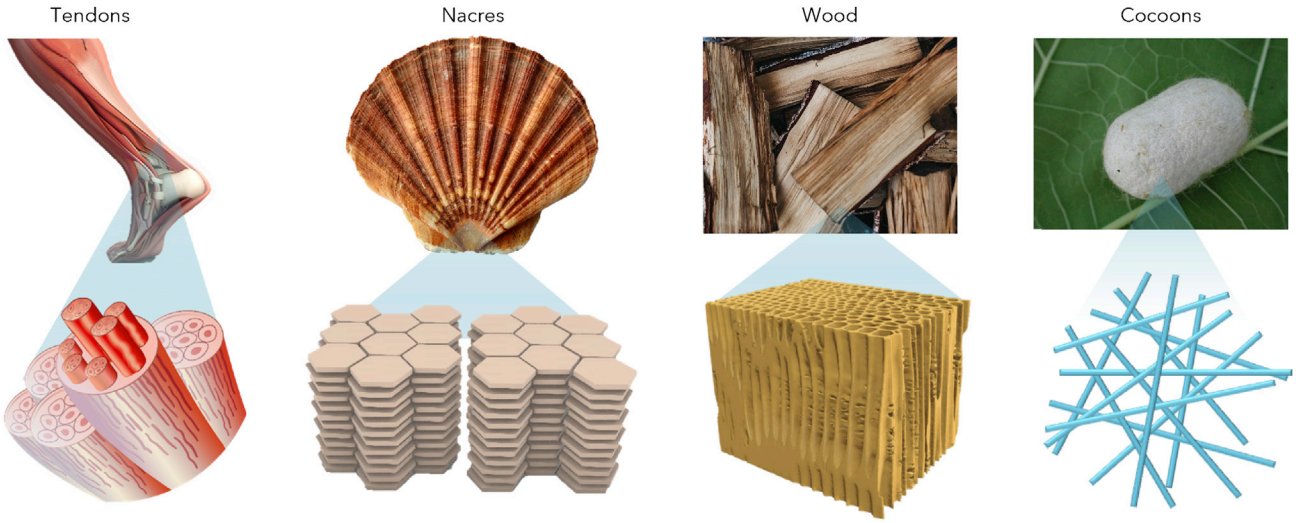

Figure 1. Natural materials with anisotropic and/or fibrous structures

From left to right: tendons exhibit aligned fibrous microstructures; nacres exhibit layered brick-and-mortar microstructure; wood exhibit aligned porous microstructure; cocoons exhibit random fibrous microstructure. The leg illustration was reproduced and adapted from illustration by Scientific Animations under CC BY-SA license.

Tough and fatigue-resistant hydrogels bring unique opportunities for biomedical and soft robotics field as a class of durable structural materials. Hydrogels, with their high water content and porous structures, are highly biocompatible and are seeing emerging applications in tissue scaffolding and replacements. Due to their high diffusivity and stretchability, hydrogels are also suitable candidates for bio-electronics[1] and soft actuators[2] applications. However, conventional hydrogels with homogeneous structures often failed to provide desirable mechanical robustness and longevity for these applications. Although hydrogels can be easily toughened by inducing a secondary network,[3] they suffer from fatigue at loadings much lower than their maximum tensile stress and strain. On the contrary, many natural materials such as tendons possess a combination of high strength, high toughness and high fatigue resistance with comparable water content and composition as hydrogels. Their high mechanical properties originate from the inherent fibrous and/or anisotropic microstructures, which could serve as mighty barriers to pin down cracks.[4] Such a structural design is prevalent in many species like trees, nacres, and insects, etc. (Figure 1), which holds special interest for guiding the design of man-made materials.

Fiber reinforcements and their accompanying toughening theories are widely adopted in the make of composite materials.[5] However, conventional fibrous composite hydrogels use rigid fibers, which significantly reduced the stretchability and water content of these originally stretchable and tissue-like hydrogel materials. In addition, rigid fibers may encounter interface compatibility issues with the soft matrix, due to the highly mis-matching moduli and bond-types.

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https://doi.org/10.1016/j.matt.2021.05.006

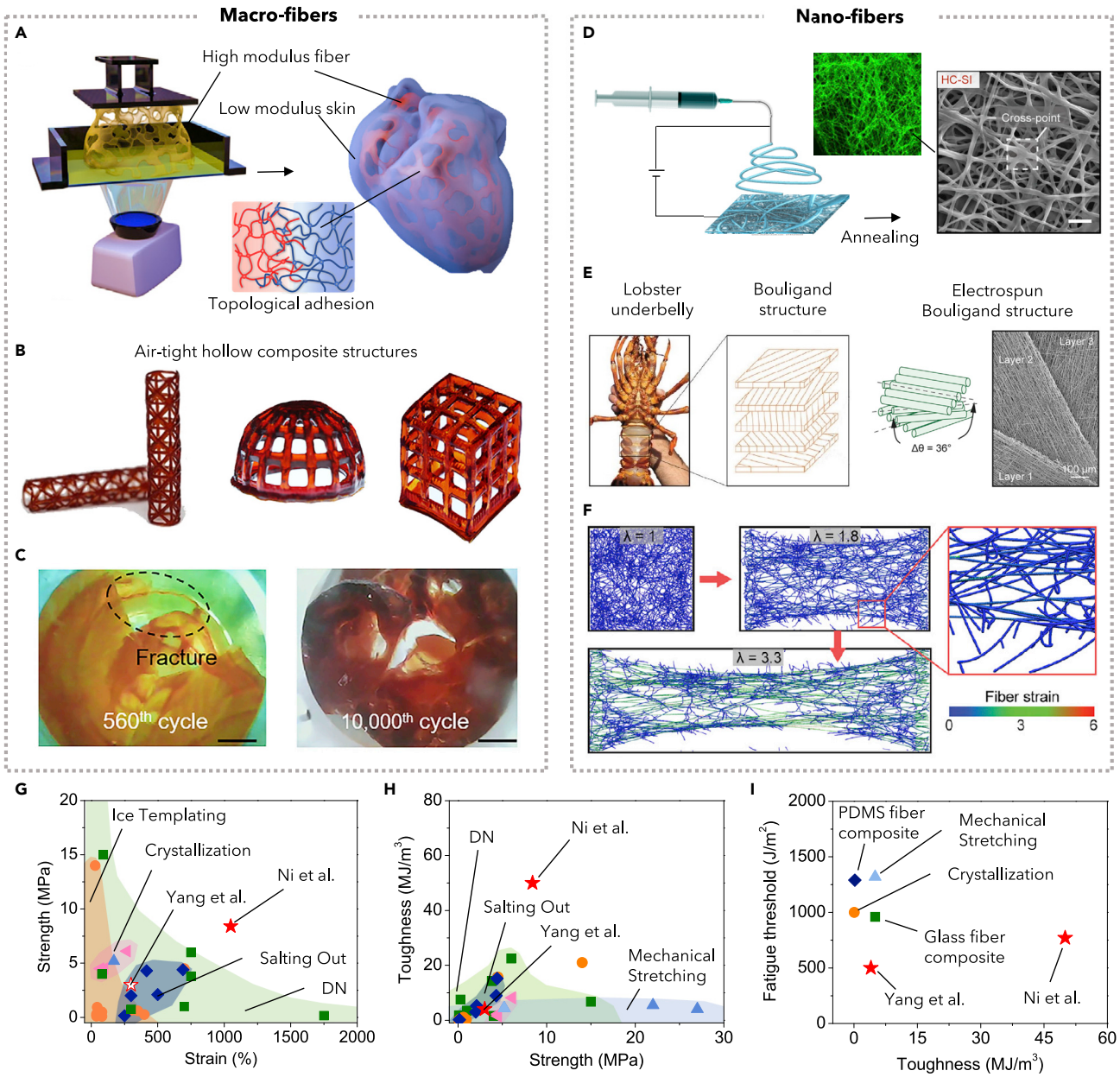

Figure 2. Recent reports of soft-fiber-reinforced hydrogels

(A) Illustration of the fabrication procedure of 3D printed macro-fiber-reinforced hydrogel.

(B) Fiber skeletons created by 3D printing and ferric ion crosslinking.

(C) The macro-fiber-reinforced heterogeneous heart valve compared with a homogeneous heart valve. Scale bar: 1 cm.

(D) Illustration of the fabrication procedure of electro-spun nano-fibrous hydrogel. Scale bar: 10 μm.

(E) Layer structure of lobster underbelly and Bouligand type electro-spun hydrogel.

(F) Simulation of the fracture of nano-fibrous hydrogel.

(G–I) Strength vs. strain plot (G), toughness vs. strength plot (H), and fatigue threshold vs. toughness plot (I) of the work by Ni et al. and Yang et al. compared to reported values of tough hydrogels made by other methods. DN is short for double-network.

(A)–(C) are reproduced and adapted from the paper by Yang et al.; (D)–(F) are reproduced and adapted from the paper by Ni et al.

To preserve the stretchability of hydrogel materials, recently, various soft fiber reinforced hydrogels are being developed.[6–9] The embedded soft fibers can range from macro-fibers at millimeter level to nano-fibers. Yang et al. developed hydrogels consisting of a 3D printed macro-fiber mesh and a soft skin casted on the mesh (Figure 2A).

The hydrogels can be fabricated into various shapes and form free-standing hollow structures due to the support of the relatively higher modulus fiber skeleton (Figure 2B). Ni et al. developed hydrogels composed of welded electro-spun nanofibers (Figure 2D). A biomimetic hydrogel with structure similar to lobster underbelly was fabricated by electro-spinning multi-layer structures with a certain inter-layer angle offset (Figure 2E). In these works, the fibers were made with hydrogels owning a relatively higher degree of polymer chain aggregation with high-density physical crosslinking, and thus showed higher modulus, strength and toughness compared to their less aggregated counterpart.

Incorporating fibers of similar composition has the benefit of facile formation of coherent interfacial bonding. In the work by Ni et al., thermal evaporation and thermal annealing was used to weld the fibers together. Due to the easy crystallization of poly (vinyl alcohol) (PVA), the PVA fibers were coherently connected to each other after the treatment and significantly improved the ultimate stress and strain of the hydrogel. Yang et al. ensured excellent adhesion between the tougher fiber and softer matrix through topological adhesion,[10] which is achieved by molecularly stitching the hydrogels together. Topological adhesion provides stretchable adhesion at the hydrogel interface and is applicable to various hydrogel materials, which provides the basis for the universality of soft-fiber-reinforced hydrogels.

Incorporating fibers of similar composition but of contrasting mechanical properties can bring about significant improvement in fatigue resistance. In the work by Yang et al., a high fatigue threshold of ~450 J/m^2 was achieved while maintaining moderate stretchability of 300% (Figure 2G-I). The authors demonstrated the printing of a hydrogel heart valve, which could sustain over 10,000 cycles of opening and closing, compared to only 560 cycles for a homogeneous tough hydrogel of the same composition (Figure 2C). In the work by Ni et al., a high fatigue threshold of 770 J/m^2, high strain of ~1,100% and high toughness of ~50 MJ/m^3 were simultaneously achieved. Compared to previously reported hydrogel composites, these new works demonstrated comparable fatigue thresholds while maintaining high stretchability and toughness. It should be noted that an extension of the classical Lake-Thomas theory was proposed by Ni et al., which provided a theoretical model for predicting the fatigue threshold of soft-fiber-reinforced hydrogel composites (Figure 2F).

In summary, the soft-fiber-reinforced hydrogels unveils a general strategy for fabricating hydrogels of simultaneous high strength, stretchability, toughness, and fatigue resistance. The higher modulus fibers can be formed by facile physical crosslinking of hydrogels. Due to the similar composition of fiber and matrix, stretchable and coherent bonding can form between the fibers and matrix by additional physical crosslinking or topological adhesion. With 3D printing, the heterogenous hydrogels can be made into various shapes and improve the lifetime of the shape morphing devices. The mechanical properties of these hydrogels can be further improved by combining layers into Bouligand structure.

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