Viscoelastic Hydrogel Microfibers Exploiting Cucurbit[8]uril Host–Guest Chemistry and Microfluidics

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ABSTRACT: Fiber-shaped soft constructs are indispensable building blocks for various 3D functional objects such as hierarchical structures within the human body. The design and fabrication of such hierarchically structured soft materials, however, are often challenged by the trade-offs between stiffness, toughness, and continuous production. Here, we describe a microfluidic platform to continuously fabricate double network hydrogel microfibers with tunable structural, chemical, and mechanical features. Construction of the double network microfibers is accomplished through the incorporation of dynamic cucurbit[8]uril host–guest interactions, as energy dissipation moieties, within an agar-based brittle network. These microfibers exhibit an increase in fracture stress, stretchability, and toughness by 2–3 orders of magnitude compared to the pristine agar network, while simultaneously gaining recoverable hysteretic energy dissipation without sacrificing mechanical strength. This strategy of integrating a wide range of dynamic interactions with the breadth of natural resources could be used in the preparation of functional hydrogels, providing a versatile approach toward the continuous fabrication of soft materials with programmable functions.

KEYWORDS: microfluidic, hydrogel microfibers, supramolecular network, cucurbit[n]uril, self-healing

Hydrogels are essentially versatile building blocks in living materials, with live creatures as representative prototypes of hydrogel-embodied adaptive machines.1−6 The intricacy and vast diversity found in biological systems from soft molluscs to hybrid vertebrates, relies on the sophisticated merging of many biological modalities, including gels, tissues, fibers, muscles, tendons, and skeletal constructs.7−8 Such biological modalities are exceedingly complex and possess hierarchically assembled structures featuring a wide length scale, ranging from nano-, to micro-, to even macroscale, e.g., 3D fiber-shaped blood vessels, neural pathways, and muscle fibers.9−12 A high level of functionality can be achieved in artificial 3D structures through combination of tailor-made molecular engineering and structural complexity formulation.8 Although technologically incomparable to the high-level complexity of a natural system, these artificial counterparts have sparked the new generation of hierarchically structured functional materials exploited in advanced actuators, soft machines, flexible electronics, and artificial cellular constructs for tissue engineering, etc.5,4,13−22

Inspired by the 3D elongated structure of neural pathways and blood vessels, meter-long hydrogel microfibers have been successfully prepared through continuous microfluidic fabrication relying on the diffusion of Ca2+ into an alginate flow, as well as ionic cross-linking of alginate backbones.10,11,23−25 Unfortunately, alginate/Ca2+ systems exhibit low mechanical strength (fracture energies < 10 J m−2),2 which has posed challenges for their applications. Recently, significant progress has been made toward hydrogel networks with outstanding toughness, resilience, and elasticity, as well as stretchability. One example in particular exploits the formulation of double network (DN) constructs, pioneered by Gong and coworkers.5,26−27 DN hydrogels consist of two interpenetrating polymer networks with contrasting mechanical properties, where the first network is highly stretched and densely cross-linked (stiff and brittle) and the second is flexible and sparsely cross-linked (soft and stretchable).5,26

Herein, we report the design rationale for tough and highly stretchable hydrogel microfibers through microfluidics as outlined in Figure 1a (see Supporting Information (SI) Part I: Supplementary Experimental Details for the detailed fabrication process). The initial step involved the formation of hydrogel microfibers from a hot aqueous solution, consisting of agar and acrylamide-based monomer precursors. Prompt and effective cooling of the hot solution (inner tubular capillary, 700 mm) with ice water (external square capillary, 1000 mm) induced the rapid gelation of an agar phase, leading

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to the formation of the first network (SI Figure S1). Here, the sharp thermal transition induces agar network formation, enabling continuous fabrication of meter-long and transparent microfibers (Figure 1b), similar to the alginate/Ca\^{2+} system based on multiple laminar flow.\textsuperscript{10} However, different from the \textit{in situ} solidification of alginate flow relying on diffusion/penetration of Ca\textsuperscript{2+},\textsuperscript{10,11,23-25} which resulted in an inhomogeneous gradient, thermoinduced gelation of agar can be readily manipulated without any segregated microstructures. A subsequent UV-induced radical polymerization (365 nm, 8 W, 1 h, 0 °C) of acrylamide (AAm)-based monomer precursors is then carried out to generate the second hydrogel network (Figure 1c). The monomer precursors used here consist of a 95:5 mixture of hydrophilic acrylamide and 1-benzyl-3-vinylimidazolium bromide (BVIm), which serves as a supramolecular cross-linker upon complexation with cucurbit[8]uril (CB[8]) in a 2:1 manner ($K_{a1} = 4.21 \times 10^7$ $M^{-1}$; $K_{a2} = 4.25 \times 10^5$ $M^{-1}$),\textsuperscript{15,22} yielding a CB[8] supramolecular hydrogel network (Figure 1a). Homogeneous and transparent DN hydrogel microfibers are thus obtained (Figure 1d), other than the core–sheath structure as reported by Liu and co-workers.\textsuperscript{6} Moreover, our strategy here does not involve those multistep manipulations such as the monomer soaking and afterward polymerization.\textsuperscript{26} Our straightforward strategy represents a modular synthetic approach to a diverse range of DN microfibers with tunable polymer properties, by manipulating the monomer composition,\textsuperscript{28} which is not the theme of our current work.

As revealed in our previous works,\textsuperscript{29,30} incorporation of dynamic CB[8] host–guest complexes imparts the hydrogel networks with remarkable toughness and energy dissipation through reversible dissociation, while subsequent re-formation
of the ternary complexes leads to immediate recovery of mechanical properties and prompt self-healing at room temperature. In contrast, the agar network is constructed through the association and reorganization of coil-to-helix transitions, leading to a stiff and brittle network through helical bundles. Coupling these two disparate networks into one entity could generate a tough DN hydrogel. Tensile tests were conducted to probe the mechanical performance of DN microfibers, while hydrogel microfibers without CB[n] or alternatively with the smaller CB[7] macrocycle as well as pristine agar were used as controls. DN hydrogel microfibers exhibited excellent stretchability over 18x their original length (Figure 2a,d and SI Movie S1). In a sharp contrast, all controls were too brittle to stretch (Figure 2a and SI Movie S2), with a fracture strain below 40%. The extreme stretchability and outstanding toughness of the DN hydrogel microfiber could be directly attributed to force-induced dissociation of the CB[8] ternary complexes dissipating local stress, as well as...
spontaneous re-formation of the complexes, maintaining the tensile stress and strain.\textsuperscript{15,22}

It is important to note that all of the microfibers (including the three controls) exhibited comparable Young’s moduli (slope measured within 5% strain), which confirms that the material stiffness was dominated by the agar network (Figure 2b). However, the fracture stress of the Agar/CB[8] DN hydrogel microfibers was >4× that of the CB[7] control, >6× the control without any CB[n], and >20× that of pristine agar fibers (Figure 2a,c). The toughness of the agar/CB[8] DN hydrogel microfiber is estimated as 4.02 MJ m\textsuperscript{−3}, which is >470× that of the CB[7] control (8.49 × 10\textsuperscript{−3} MJ m\textsuperscript{−3}), and >530× the control without CB[n] (7.5 × 10\textsuperscript{−3} MJ m\textsuperscript{−3}) and >2800× that of pristine agar microfiber (1.43 × 10\textsuperscript{−3} MJ m\textsuperscript{−3}), corroborating a substantial increase in the toughness of the DN microfibers (Figure S3). On the other hand, the fracture strain (elongation at break) increased by over 2 orders of magnitude.

In light of its extreme stretchability, the cross-sectional area of the DN microfiber changed substantially during stretching; therefore, a further plot of true stress (σ\textsubscript{true} = σ\textsubscript{nominal}(1 + \lambda)) versus strain is more informative, assuming that the hydrogel is not compressible. As shown in Figure 2b, σ\textsubscript{true} at fracture reached as high as 8 MPa, >20× σ\textsubscript{nominal} and 2 orders of magnitude greater than σ\textsubscript{true} of the control fibers (Figure 2b and S1 Figure S2). Here we did not compare the mechanical properties between our hydrogel microfibers and the bulk hydrogel, due to their different polymerization conditions. Most reported double network hydrogels, for example, agar/PAAm DN hydrogel by Zheng and co-workers,\textsuperscript{31} were polymerized under inert conditions after rigorous removal of oxygen, thus yielding a much more regular network. In our case, fiber production was conducted in air and any interference of oxygen during polymerization was readily overcome by increasing the amount of initiator. This readily led to hydrogel microfibers with satisfactory mechanical performance and high efficiency with lower energy consumption.

While a few reports have exploited the generation of hydrogel microfibers using microfluidics,\textsuperscript{24} most of them focused on the generation of alginate/Ca\textsuperscript{2+} microfibers;\textsuperscript{10,11,23,25} our work here is the first report dedicated to tough and stretchable hydrogel microfibers through host–guest molecular engineering. Such methodology serves as a versatile toolbox, which can be readily extended to a wide variety of hydrogel microfibers with designed and programmable physical, chemical, and mechanical performance.

To ascertain the nonlinear and viscoelastic behavior of the DN hydrogel microfibers at large deformation, uniaxial stretching experiments were performed at various stretching rates (Figure 3a). The mechanical properties depend strongly on stretching rate and are typical for supramolecular hydrogel networks.\textsuperscript{2,5,15,22} A clear yielding phenomenon can be observed...
at a strain of ca. 70% with the yield stress increasing from 0.13 MPa (100 mm min\(^{-1}\)) to 0.25 MPa (600 mm min\(^{-1}\)). When the stretching rate increased, a slight decrease in the fracture strain was detected, however, accompanying with an increase in fracture stress and Young’s modulus (Figure 3b). This viscoelasticity profile is similar to that observed for the pure CB[8] supramolecular hydrogel network (without any agar),\(^{15,22}\) arising from time-dependent dynamic dissociation and reassociation of CB[8] host–guest complexes in the network.

Another distinctive and advantageous feature arising from supramolecular interactions in the network is their capability to undergo spontaneous dissociation/association, imparting both microstructural self-recovery and (macroscopic) bulk material self-healing. Stress–strain profiles under consecutive cyclic tensile tests (10–1500% strain, Figure 3c and SI Figures S4–S10) demonstrated appreciable hysteresis between each loading cycle. Notable increases in hysteresis energy (the energy consumed due to internal bond failure) reflect the amount of energy dissipation through force-induced dissociation of the ternary complexes. A substantial decrease in energy consumed due to internal bond failure) recombination after loading cycle. Notable increases in hysteresis energy (the energy consumed due to internal bond failure) reflect the amount of energy dissipation through force-induced dissociation of the ternary complexes. A substantial decrease in energy dissipation through force-induced dissociation of the ternary complexes serves to dramatically rearrange the ternary complexes.

While microscopic self-repair of the DN hydrogel microfibers is clearly evident (Figure 3c,d), further investigation into macroscopic self-healing was carried out through two different tests. A sample was cut with a blade (in approximately half of its original dimension, Figure 4a,b and SI Figure S11) and brought back into contact with itself to demonstrate direct self-healing (Figure 4d(i)), while another test took two different samples and “welded” them together through contact, displaying indirect self-healing or adhesion (Figure 4d(ii)). Previous reports have revealed that the self-healing performance of agar/polyacrylamide-based DN hydrogels could be only achieved favorably through exposure to elevated temperature, e.g., 95 °C, in order to activate melting, rearrangement, and re-formation of the agar network.\(^{31,32}\) Moreover, unfavorable self-healing at room temperature was reported by Gong and co-workers,\(^{33}\) since the presence of covalent cross-links dramatically inhibited polymer chain mobility.\(^{34}\) Surprisingly, in the case of agar/CB[8] DN hydrogel microfibers, substantial self-healing at room temperature was observed for both self-healed and adhered samples, sustaining stretching over 13× their original dimensions. As described in Figure 4c, self-healing and interfacial adhesion is promoted by the second CB[8] network within which the recomposition or rearrangement of the ternary complexes serves to dramatically accelerate reconstruction of the network,\(^{22}\) thus recovering the macroscopic mechanical properties. While complete self-healing/recovery was observed in the pure CB[8] hydrogel network,\(^{21}\) partial self-healing could be quantified with a healing efficiency (defined as the ratio of tensile work for the healed samples to that of the original samples) up to 70% in direct self-healing and 40% in adhesion, respectively. The difference in self-healing efficiency between the direct self-healing and adhesion here might be interpreted by the polymer chain state. Normally, the hydrogel surface possesses a lower water content than the inner part, due to the surface water loss, especially for hydrogel microfibers with a higher surface–volume ratio. Therefore, polymer chains within the hydrogel networks exhibit higher flexibility than those on the surfaces. That is why the new cut surface can self-heal faster than the adhesion between two hydrogel ends. A “scar” of the cut was still visible under microscopic observation after 12 h (Figure 4d(i-1),d(i-2)), which could be attributed to the limited chain mobility and rearrangement of the primary agar network. Undoubtedly, an increase in temperature would favor accelerating agar chain mobility, likely leading to a higher degree of self-healing, as demonstrated by Zheng and co-workers.\(^{21}\) In our case, considering the large surface to volume ratio of the microfiber, we did not exploit higher temperature-accelerated self-healing because it would lead to unavoidable water evaporation at elevated temperatures. Nevertheless, the room-temperature self-healing of the DN microfiber highlights the beauty of incorporating supramolecular recognition elements, e.g., CB[n] host–guest chemistry, into the system.

A major challenge in material design is the trade-off between stiffness and extensibility/toughness. Here, we circumvent this inherent trade-off by incorporating sacrificial, reversible CB[n] molecular recognition into a brittle agar hydrogel microfiber. Compared with pristine agar microfibers or previously reported alginate/Ca\(^{2+}\) microfibers, the DN microfibers produced here exhibit 2 orders of magnitude increase in fracture stress, stretchability, and toughness, while gaining recoverable hysteretic energy dissipation. Coexistence of such mechanical characteristics is rare for hydrogel microfibers. Fabrication of these DN hydrogel microfibers represents a powerful and facile method to produce anisotropic microscale supramolecular functional materials, holding great promise for myriad applications including artificial silks, tissue engineering, wearable electronic devices, and microactuators.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b21240.

Supplementary experimental details; supplementary results (Figures S1–S11) (PDF)

Movie S1 showing manual tensile test with the DN hydrogel microfibers (MP4)

Movie S2 showing manual tensile test with the DN hydrogel microfibers control in the presence of CB[7] (MP4)

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Notes
The authors declare no competing financial interest.

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