Strong and tough fibrous hydrogels reinforced by multiscale hierarchical structures with multimechanisms

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Abstract

Tough natural materials such as nacre, bone, and silk exhibit multiscale hierarchical structures where distinct toughening mechanisms occur at each level of the hierarchy, ranging from molecular uncoiling to microscale fibrillar sliding to macroscale crack deflection. An open question is whether and how the multiscale design motifs of natural materials can be translated to the development of next-generation biomimetic hydrogels. To address this challenge, we fabricate strong and tough hydrogel with architected multiscale hierarchical structures using a freeze-casting–assisted solution substitution strategy. The underlying multiscale multimechanisms are attributed to the gel's hierarchical structures, including microscale anisotropic honeycomb–structured fiber walls and matrix, with a modulus of 8.96 and 0.73 MPa, respectively; hydrogen bond–enhanced fibers with nanocrystalline domains; and cross-linked strong polyvinyl alcohol chains with chain-connecting ionic bonds. This study establishes a blueprint of structure-performance mechanisms in tough hierarchically structured hydrogels and can inspire advanced design strategies for other promising hierarchical materials.

1. Introduction

Hydrogels have excellent potential as advanced engineering materials for wearable electronics, tissue engineering, soft robotics, and biomedical engineering. However, conventional hydrogels are generally weak and fragile, which substantially limits their applications. In the last decade, many efforts have been devoted to developing enhanced hydrogels with excellent mechanical properties, such as topological hydrogels, nanocomposite hydrogels, double-network (DN) hydrogels, dual cross-linked hydrogels , and nanocrystalline hydrogels. However, these studies mainly focus on molecular engineering and composition, and the involved structural changes are limited to molecular scale or nanoscale. In contrast, natural hydrogels, which typically exhibit superior strength and toughness, are abundant in various plant and animal tissues, including xylems, phloems, muscles, and cartilages. This is attributed to their unique hierarchical structures, which range from microscopic anisotropic alignments to distinctive crystalline units at the molecular scale, resulting in synergistic strengthening and toughening of the overall materials. Inspired by nature, this paper reports a freeze-casting–assisted solution substitution approach to fabricate strong and tough fibrous hydrogels with hierarchical structures from molecular to micrometer scales. An integrated experiment-simulation approach is employed to systematically identify the underlying strengthening and toughening mechanisms at each length scale, providing general design strategies for other artificial hydrogel systems.

2. Results

Integrated experimental testing, characterization and theoretical simulation approach was employed to study the multimechanisms of fibrous hydrogels at each length scale:

a. A freeze-casting–assisted solution substitution approach to fabricate strong and tough fibrous hydrogels with hierarchical structures from molecular to micrometer scales by immersing the directional frozen polyvinyl alcohol (PVA) ice blocks into an ethanol solution with the addition of ferric chloride (Fig. 1).
b. The effects of ethanol substitution and Fe^{3+} on the mechanical properties of resulting hydrogels were investigated in experiments. It was shown that the ethanol substitution and Fe^{3+} can significantly increase the stiffness, strength, fracture toughness as well as the flaw-tolerant ability of the hydrogels.
c. At the microscopic level, representative volume element (RVE) analysis coupled with periodic boundary conditions (PBCs) was carried out to characterize the mechanical behavior and elastic properties of the

anisotropic fibrous hydrogel. It was shown that the ethanol substitution and Fe^{3+} can markedly increase the fiber wall stiffness, suggesting that the ion enhancement led to more polymer chains aggregated due to the formation of coordination bonds and resulted in high crystallinity.

d. Atomistic-level simulations were conducted using to explore the molecular mechanical behavior of PVA hydrogels and the effect of ethanol substitution and Fe^{3+} on intramolecular interactions between the PVA chains and water molecules. It was shown that the hydrogen bonds and multiple chain-connecting Fe bonds give rise to higher failure stress and strain, as well as the energy dissipation in fracture.

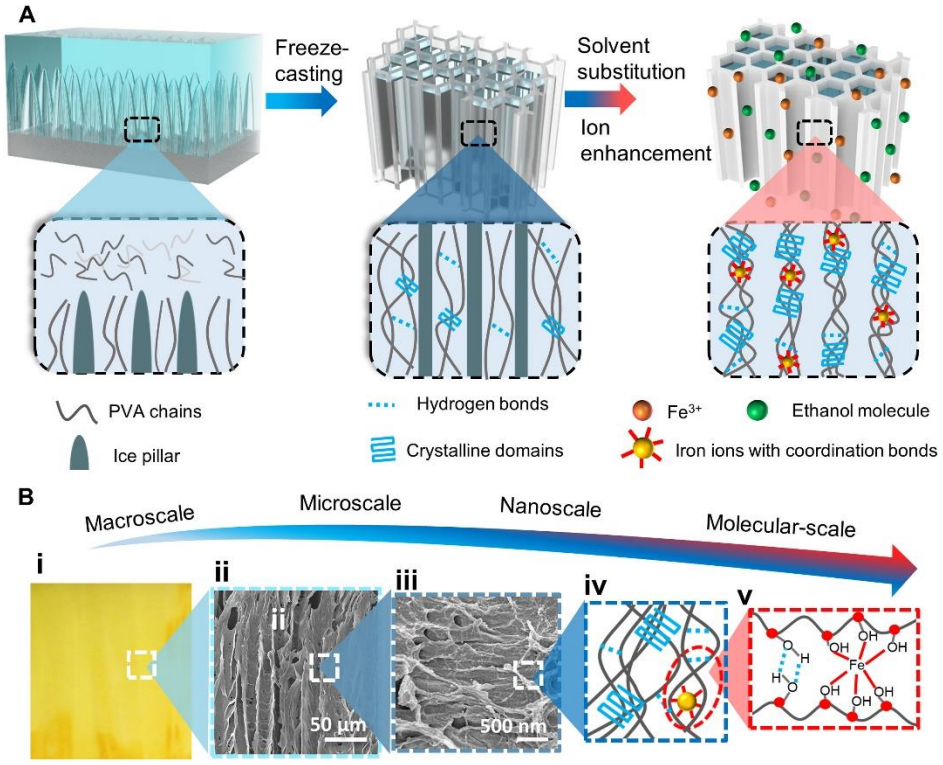

Fig.1 – Fabrication and hierarchical structures of tough fibrous hydrogels. (A) Schematic diagrams of the freeze-casting–assisted solution substitution strategy of the PVA hydrogel (FC-EtFe). (B) Hierarchical structures of the fabricated hydrogel. (i) Macroscopic view of FC-EtFe. (ii and iii) Scanning electron microscopy (SEM) image of the micro- and nanostructure. (iv) Aggregated polymer chains with nanocrystalline domains. (v) Illustration of the interactions of polymer chains.

3. Conclusions

This study proposes a nature-inspired synergistic strategy for the fabrication of strong and tough fibrous hydrogels with hierarchical structures across multiple length scales at micro-, nano-, and molecular levels, characterizes the multiscale multimechanisms of fibrous hydrogels in detail and establish the relationship between structure-performance mechanisms, which provide insight into the designing of hierarchical tough hydrogels. The systematic mechanistic analysis model can also be extended to other hierarchical material systems as a novel yet generic approach to the analysis of natural materials.

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