Design Strategies and Perspectives on the Toughening of Hydrogels via Fully Physical Crosslinking

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Abstract

Conventional hydrogels are inherently brittle and mechanically weak, limiting their application in load-bearing or dynamic environments. Although extensive development has been made in hydrogel toughening, the most dominant techniques rely upon chemical crosslinking, which restrains their adaptability and functionality because of the permanence of covalent bonds. While dynamic covalent bonds have been introduced to enhance reversibility in covalently crosslinked systems, they often require harsher conditions, display delayed responsiveness, and involve more

complex chemistry. Given these challenges, physical crosslinking methods —such as metal-ligand coordination crosslinks, crystalline region formation, electrostatic interactions, hydrophobic association, polymer chain entanglement, host–guest interaction, and hydrogen bonding— have been considered promising strategies to enhance both toughness and dynamic features. These characteristics provide high versatility and practicality, enabling advanced applications in areas such as soft robotics and tissue engineering. This review presents a comprehensive analysis of strategies and perspectives for toughening hydrogels via fully physical crosslinking and highlights emerging applications that exploit the unique advantages of reversible physical networks.

1. Introduction

Due to their high water content and soft-tissue-like characteristics, hydrogels have gained attention as a promising way to replicate natural tissues [1-3]. However, their inherent softness poses a significant limitation for mechanically demanding practical applications. To address this issue, several strategies have been reported to increase the mechanical toughness of hydrogels, including the inclusion of functionalized nanofillers [4-6], construction of interpenetrating networks [7, 8], double networks [9-11], hybrid nanocomposite formulations [12, 13], and the use of multi-arm or novel chemical crosslinkers [14-16]. Despite these advances, most of these methods are still based on covalent crosslinking, which is permanent and irreversible and often limits the dynamic or reconfigurable capabilities of the resulting hydrogel system.

On the other hand, physically crosslinked hydrogels that are stabilized through reversible non-covalent interactions have appeared as a viable option to enhance hydrogel toughness [17-19]. These systems show improved mechanical performance and display adaptive behaviors, such

as self-healing [20-22], shape memory [23], architectural reconfigurability [24], and responsiveness to external stimuli [25, 26]. Although the mechanical robustness of physically crosslinked hydrogels is lower than their covalently crosslinked counterparts, these reversible forces enable better adaptability and tunability of functionality. These properties are particularly desirable to advanced soft robotics applications [27] and biomedical devices [28], where both mechanical resilience and responsiveness are crucial.

In addition, various dynamic covalent bonds have been developed to endow chemically crosslinked hydrogels with responsiveness in recent years [25–28]. These systems tend to demand harsh conditions to initiate reversibility, deliver delayed response times, and take on more complicated architectures. Therefore, there remains a pressing need to develop tough and functional hydrogels based on physical crosslinking strategies that simultaneously enhance mechanical integrity and dynamic functionality, offering rapid and easily triggerable responsiveness—thus facilitating broader practical applications. Although several hybrid chemical–physical crosslinking systems have been explored and demonstrate high mechanical performance [29-33], the partial incorporation of covalent bonds can still limit dynamic behavior and introduce brittleness. This arises from the reduced capacity for network rearrangement, as the presence of permanent covalent bonds restricts the reversible interactions necessary for energy dissipation and structural adaptability. In contrast, recent studies have shown that fully physically crosslinked hydrogels can achieve both high mechanical toughness and dynamic responsiveness simultaneously [34-38], offering distinctive properties with significant potential for advanced applications such as fast and reversible soft actuators, injectable drug delivery systems, and reprocessable three-dimensional (3D) printed devices.

This review presents a concise and thorough overview of the latest developments in hydrogel toughening using fully physical crosslinking strategies, different from earlier reviews which focused on the covalent or hybrid crosslinking routes. These physically crosslinked hydrogels are classified into two primary classes: (1) physical single-network hydrogels and (2) physical multi-network hydrogels. Physical single-network hydrogels comprise a single physically crosslinked polymer network, whose enhanced toughness stems from physical interactions within the network [39]. In contrast, physical multi-network hydrogels—such as double-network hydrogels—contain two or more polymer networks, where more than one can be physically crosslinked, enabling enhanced energy dissipation and mechanical robustness [40]. The review discusses key design principles, elucidates the underlying toughening mechanisms and associated functionalities, and presents the applications of these hydrogels. Additionally, it highlights emerging trends and outlines future research directions for developing the next generation of tough and functional hydrogels via physical crosslinking.

2. Physical Interactions within Hydrogels

Physical interactions are fundamental in constructing and reinforcing physical hydrogel networks, enabling the design of systems that are not only robust but also exhibit dynamic responses such as self-healing, stretchability, and shape memory [41, 42]. Table 1 and Figure 1 illustrate the major non-covalent physical interactions in hydrogel systems that synergistically contribute to their mechanical strength and dynamic functionalities. Among them, metal–ligand coordination stands out for its ability to form strong yet reversible crosslinks, providing high energy dissipation and durability under stress [43]. Hydrogen bonding, although weaker in bond strength, provides abundant and tunable connections, supporting structural flexibility, particularly in networks with

carboxyl and amide functionalities [44]. Crystalline domains, often formed via freeze–thaw cycles, impart rigidity and fatigue resistance by introducing ordered structures stabilized by hydrogen bonding or π–π stacking [45-47]. Electrostatic interactions—ranging from permanent ionic crosslinks to reversible sacrificial bonds—enhance both mechanical integrity and functional attributes such as conductivity [48, 49].

Table 1. Summary of Common Physical Interactions within Hydrogel Systems.

Physical Interaction	Estimated bond energy (kJ/mol)	Common hydrogel systems	Contribution to Toughening
Metal-ligand coordination	80 – 440 [50, 51]	Poly(acrylic acid)–Fe^{3+}	Reversible coordination bonds that dissipate energy under stress and resist fracture.
Hydrogen bonding	8 – 184 [50, 52, 53]	Polyacrylamide Polyacrylic acid	Dynamic, reversible bonds that break and reform to absorb mechanical energy.
Crystalline domain formation	10 – 88 [53, 54]	Poly(vinyl alcohol)	Rigid crystalline regions that hinder crack propagation and enhance fatigue resistance.
Electrostatic interactions	100 – 350 [55]	Poly(acrylic acid)–Chitosan	Ionic bonds dissipate mechanical energy and reinforce the network.
Polymer chain entanglement	Not defined	Various polymers (non-specific)	Entangled chains restrict crack propagation and absorb mechanical stress.
Hydrophobic associations	Not defined	Poly(acrylamide–stearyl methacrylate) + SDS micelles	Reversible aggregation of hydrophobic domains that dissipate energy under deformation.
Host–guest interaction	25 – 36 [56]	β-Cyclodextrin–adamantane-modified polymer	Supramolecular inclusion complexes that act as sacrificial bonds to delay fracture.

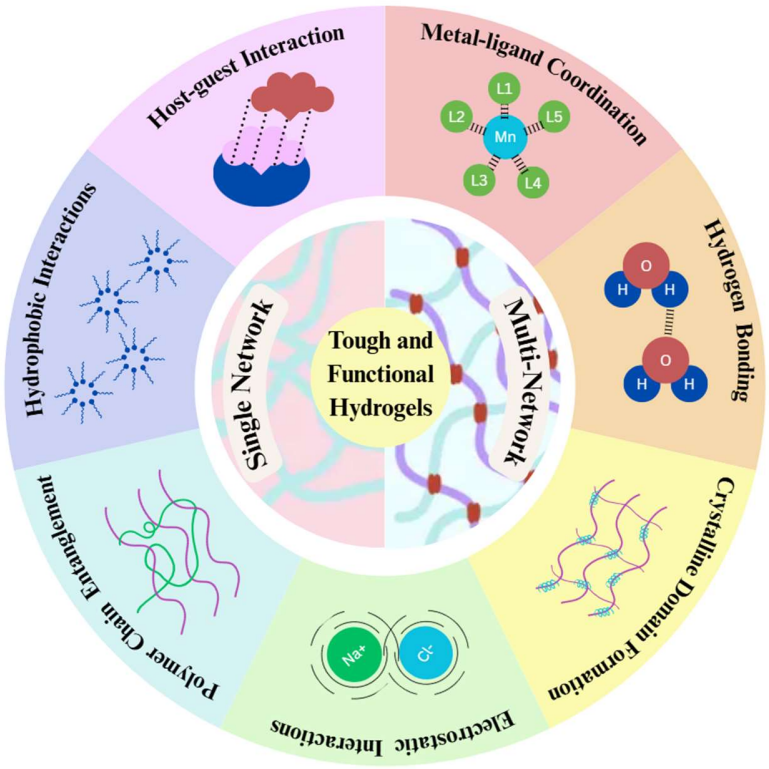

Figure 1. Overview of Common Physical Interactions within Hydrogel Systems.

Beyond well-defined physical interactions, polymer chain entanglement and hydrophobic associations offer mechanical reinforcement through physical interlocking or aggregation of non-polar groups [57-59]. These interactions are especially effective in energy dissipation and preventing fracture propagation during deformation. Furthermore, host–guest interactions, driven by precise molecular recognition, function as dynamic and reversible linkages that delay failure, encode mechanical memory, and enable shape-memory behavior [60-62]. Some physical processes, such as phase separation and self-assembly [63], and salting out [64-66], have also been used to facilitate the formation of physical crosslinking domains that reinforce the hydrogel network. Other physical interactions, such as van der Waals forces and dipole–dipole interactions,

are also considered physical crosslinks but generally play a minor or supportive role in network formation and seldom dominate the toughening mechanism on their own. Together, these physical interactions create a versatile design toolbox for tailoring hydrogel properties to meet diverse application needs—from biomedical scaffolds to soft robotics. Strategically combining these interactions offers great potential for developing the next generation of adaptive and multifunctional hydrogel materials.

3. Tough and Functional Hydrogel System

3.1. Physical Single-Network Hydrogels

3.1.1 Design Strategies

Physical single-network hydrogels are an ideal platform for achieving highly reversible crosslinks. The stability of their network is governed by physical interactions, typically involving multiple types of interaction to ensure adequate mechanical integrity. These physical interactions are reversible and may demonstrate self-healing and self-recovery properties within the hydrogel network. However, the absence of stable covalent bonds is restrictive to their mechanical stability, making them generally less durable. To give them additional strength, other gelation agents (e.g., macromolecules or functional nanoparticles) can be incorporated to enhance intermolecular interactions and achieve stronger physical crosslinking. Relative to multi-network hydrogels, single-network hydrogels usually exhibit greater reversibility and functional flexibility because their structure is only dependent on dynamic physical crosslinks within the single network allowing for quick responses to the external stimulus, cyclic deformation, and reversible structural

adjustment. Several physical single-network hydrogels have been developed to harness these properties across diverse applications (Table 2).

Table 2. Summary of Physical Single Network Hydrogels

No	Polymer	Additive	Physical cross-linking interactions	Tensile strength (MPa)	Elongation at break (%)	Toughness (kJ/m^3)	Key functional property	Reference
S1	Poly(acrylic acid)	Liquid metal cellulose nanocrystals	Electrostatic interactions Hydrogen bonding Polymer chain entanglement	1.8	2,000	1,800	High ionic conductivity and piezoionic	[67]
S2	Polyampholytes	-	Electrostatic interactions	1.8	750	4000 $J/m^{2\#}$	Self-recovery and self-healing	[68]
S3	Polyampholytes	-	Electrostatic interactions Polymer chain entanglement	1.9	~850	-	Self-healing	[69]
S4	Poly(vinyl alcohol)	Tannic acid	Crystalline domain formation Polymer chain entanglement	16	~1,000	98,000	Shape memory	[70]
S5	Poly(vinyl alcohol)	Tannic acid and cellulose nanocrystals	Crystalline domain formation Hydrogen bonding	8.7	1,108	58,200	Self-recovery	[34]
S6	Poly(vinyl alcohol)	-	Crystalline domain formation Hydrogen bonding	23.5	~1,500	210,000	-	[66]
S7	N-hydroxyethyl acrylamide and methyl acrylate	Tween 80 micelles	Hydrophobic associations Hydrogen bonding	0.7	1,687	508	Self-recovery	[35]
S8	Poly(acrylamide-co-stearyl methacrylate)	SDS micelles and vinyl hybrid silica nanoparticles	Hydrophobic associations Hydrogen bonding	0.3	2,800	1,920	Self-healing	[71]
S9	Poly(acrylamide-lauryl - methacrylate)	Latex particles	Hydrophobic associations	0.8	~ 2400	6,900	Self-recovery and puncture resistant	[72]
S10	Polyacrylamide	Clay nanosheet, graphene oxide nanosheet, surfactant	Hydrophobic associations Hydrogen bonding	0.2	2,500	1,120 $J/m^{2\#}$	Self-Healing	[73]
S11	Polyacrylamide	Graphene oxide nanosheet	Electrostatic interactions Hydrogen bonding	0.4	3,435	4,740	-	[74]
S12	β-cyclodextrin and adamantane acrylamide	Host and guest molecules Ferric citrate	Host-guest interaction Metal-ligand coordination Hydrogen bonding	2.6	1,770	19,000	Shape memory	[36]

$^{\#}$ Fracture toughness in the unit of J/m^2

One key interaction used to form tough physical hydrogels is electrostatic bonding, which leverages the relatively strong ionic bonds to enable dynamic responses to environmental changes. One of the most effective examples of this is the utilization of electrostatic interactions among liquid metal-cellulose nanocrystals (LM-CNCs) and the polymer backbone, as proven by Rahmani et al. [67] (Figure 2a). In the study, liquid metal (LM) nanoparticles are coated with cellulose nanocrystals (CNCs), which leave hydroxyl functional groups on the oxide surface of the LM nanoparticles. These hydroxyl moieties serve as regions for physical crosslinking with poly(acrylic acid) (PAA) polymer backbones. The hydrogel is formed through polymerization of acrylic acid (AA) using these LM-CNC particles, which results in a robust hydrogel with piezoionic properties. Its superior mechanical strength results from ionic interaction between the negatively charged carboxyl groups of PAA and positively charged areas on the surface of LM oxide, hydrogen bonding between hydroxyl groups of CNCs and PAA carboxyl groups and PAA chain entanglement. These combined interactions synergistically reinforce the hydrogel network. As a result, the optimized PAA hydrogel containing 1% LM and 0.5% CNC exhibits a high toughness of up to 1.8 MJ/m^3 and an elongation at break of approximately 2,000% (Figure 2b). Soaking the hydrogel in a NaCl solution for one hour increases its electrical conductivity to 3.8 S/m, as Na^+ and Cl^- ions diffuse into the network. After being cut and self-healed, the hydrogel demonstrates high mechanical self-healing efficiency, retaining nearly full performance in the original NaCl-soaked state (Figure 2c). The incorporation of LM-CNC particles provides robust physical crosslinking and enables piezoionic behavior. This highlights its potential for durable applications in wearable sensors and self-powered touch-sensitive devices.

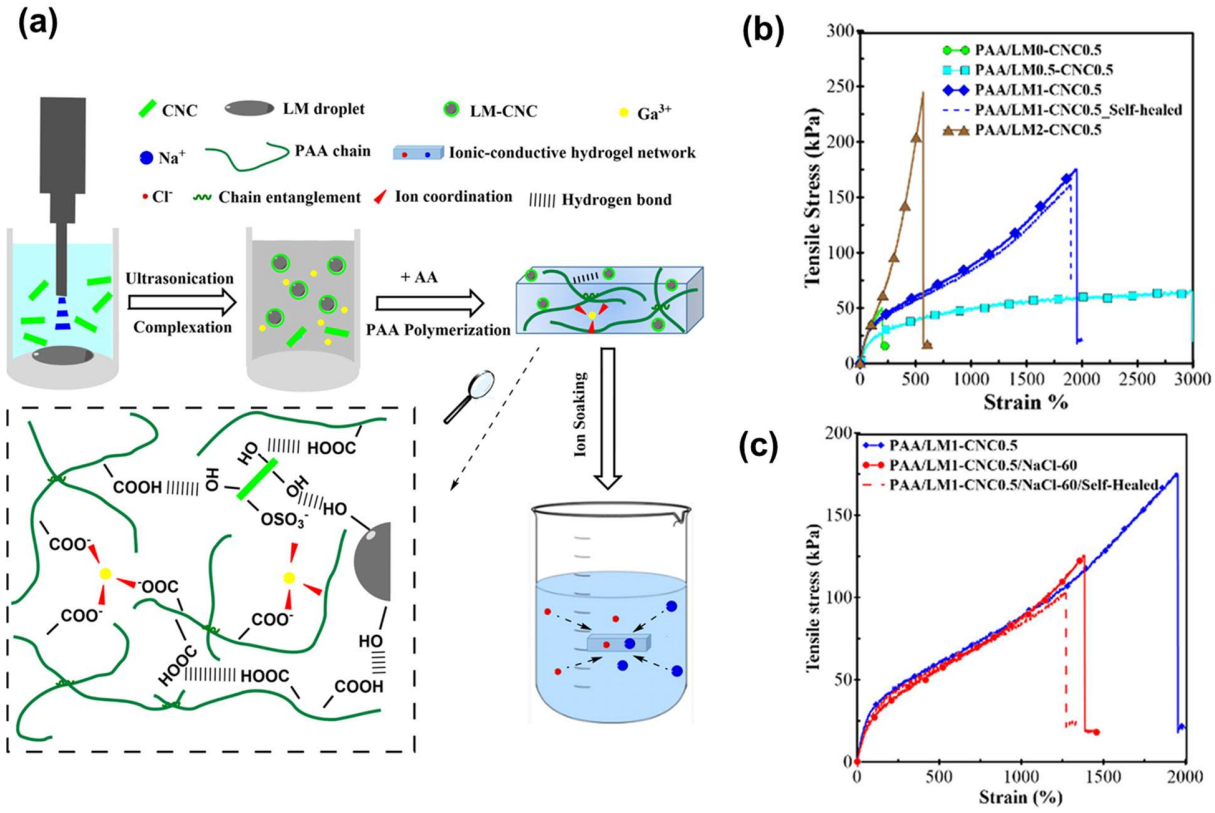

Figure 2. Tough Polyacrylic Acid (PAA)-based Hydrogel Incorporating Cellulose Nanocrystals (CNC)-functionalized Liquid Metal (LM) Particles. (a) Schematic illustration of the synthetic process and the resulting hydrogel network. (b) Tensile stress-strain curves of PAA hydrogels with varying LM and CNC concentrations. The notation PAA/LM_x-CNC_y represents hydrogels with different weight percentages of LM (x) and CNC (y). The self-healed sample was shown for comparison. (c) Tensile stress-strain curves of the PAA/LM_1-$CNC_{0.5}$ hydrogel at the as-prepared state, after soaking in NaCl for 60 minutes (NaCl-60), and after self-healing following NaCl soaking (NaCl-60/Self-Healed). Modified and reproduced with permission from [67].

Another strategy to enhance hydrogel toughness through electrostatic interactions involves the use of polyampholyte networks—polymers that contain randomly distributed cationic and anionic repeat units. Sun et al. developed physically crosslinked single-network hydrogels based

on polyampholytes, which exhibited excellent toughness, stretchability, self-recovery, and biocompatibility [68]. These hydrogels were synthesized via one-step random copolymerization of the anionic monomer sodium p-styrenesulphonate (NaSS) and a cationic monomer, either 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC) or methyl chloride quaternized N,N-dimethylaminoethyl acrylate (DMAEA-Q). Electrostatic interactions between the monomers enabled polymer chain crosslinking. The ionic bonds exhibit a broad strength distribution—strong bonds act as permanent crosslinks, imparting elasticity, while weaker bonds reversibly break and reform to dissipate energy. The mechanical properties of the hydrogels can be tuned by varying the ionic combinations. Among these, the poly(NaSS-co-MPTC) hydrogel with a total concentration of 2.1 M exhibited the highest tensile strength (up to 1.8 MPa), elongation at break (up to 750%), and fracture toughness (up to 4000 J/m²). Additionally, this system demonstrated a high self-healing efficiency, retaining up to 94% of its original tensile strength. Furthremore, relatively high self-heal efficiency is observed in this system with up to 94% maintaining original tensile strength. With excellent mechanical properties in physiological solutions, these materials show significant potential as structural biomaterials. This system provides a distinctive example of tough hydrogels predominantly relying on electrostatic interactions.

In a subsequent study, Sun et al. from the same research group further explored the formation mechanism and structural characteristics of polyampholyte hydrogels [69]. A tough, self-healing hydrogel was created by copolymerizing equimolar amounts of oppositely charged monomers at high concentrations (approximately 40–50 wt%) (Figure 3a) with comparable mechanical properties as their previous work. In the as-prepared state, the hydrogel is very soft and weak at low monomer concentration (C_m = 1.3 M), but becomes noticeably tougher as the concentration increases (Figure 3b). After water equilibration, the hydrogels exhibit high tensile strength but limited elongation at break, due to the formation of strong inter-chain ionic bonds that

restrict their extensibility (Figure 3c). To elucidate the dynamic molecular structure, they employed a viscoelastic analysis of the tensile behavior, focusing on the effects of dialysis, monomer concentration, and observation time. By fitting the tensile data using a combined upper-convected maxwell model and Gent strain hardening model, they quantitatively distinguished the roles of strong (elastic) inter-chain ionic bonds and weak (viscoelastic) intra- and inter-chain ionic bonds within the hydrogel network.

Furthermore, a recent study by Li et al. also examined polyampholyte hydrogels with hierarchical structures comprising ionic interactions, transient and permanent chemical networks, and bicontinuous hard/soft-phase domains [75]. Their findings revealed that the mesoscale hard/soft-phase architecture plays a dominant role in governing the long-term mechanical memory of self-healing hydrogels subjected to cyclic stretching. Regarding electrostatic interactions, the incorporation of ionic liquids had also emerged as a promising strategy to physically toughen hydrogels by facilitating reversible crosslinking and efficient energy dissipation [76, 77]. In addition, this approach imparts long-term stability, ionic conductivity, and tunable network dynamics to the physically crosslinked network [78, 79].

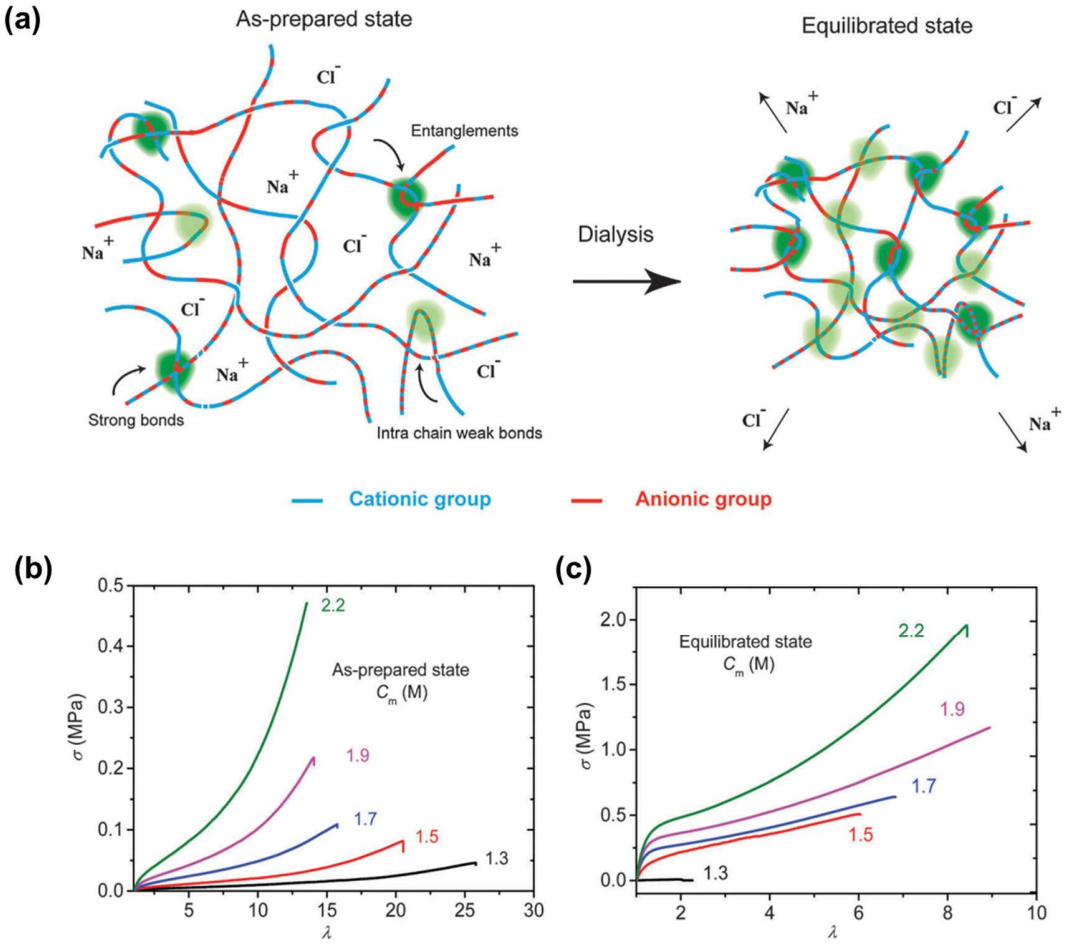

Figure 3. Physical Polyampholyte Hydrogel. (a) Schematic illustration of the crosslinking network in polyampholyte hydrogels, showing multiple ionic bonds with a wide strength distribution in both the as-prepared and water-equilibrated states. (b, c) Tensile stress–strain curves of polyampholyte hydrogels in the as-prepared and water-equilibrated states at varying monomer concentrations (C_m = 1.3, 1.5, 1.7, 1.9, 2.2). σ: tensile stress; ε: elongation. Modified and reproduced with permission from [69].

In addition to electrostatic forces, the formation of crystalline domains serves as another important physical crosslinking mechanism and has been widely utilized in poly(vinyl alcohol) (PVA) hydrogels. These crystalline domains within the polymer network are typically induced

through a freeze-thaw process [80]. For instance, Wei et al. employed freeze-thaw cycles in PVA chains to induce crystalline domain formation, while incorporating tannic acid (TA) multifunctional macromolecules to facilitate strong hydrogen bonding (Figure 4a) [70]. Through this approach, they developed a fully physically crosslinked single-network hydrogel that exhibits both high toughness and shape memory properties. The PVA-TA hydrogels were prepared using a conventional freezing/thawing method, involving freezing below 0 °C followed by thawing at ambient temperature. In addition to crystalline domain formation, soaking the hydrogel in saline solutions such as NaCl induced chain entanglements, triggering a salting-out effect. The NaCl-treated hydrogel exhibited a high tensile strength of up to 16 MPa, 22 times greater than that of the untreated hydrogel, and an exceptional toughness of 98 MJ/m^3, despite being a single-network system without covalent bonding (Figure 4b and c). These outstanding mechanical properties arise from the crystalline domains, which enhance network density and resist crack propagation, while the saline-induced physical interactions act as sacrificial bonds that break under stress to dissipate mechanical energy. Furthermore, the hydrogel exhibits shape memory behavior due to the formation of physical interactions that stabilize temporary shapes and facilitate reversible deformation. Its excellent biocompatibility and cytocompatibility further position it as a promising candidate for biomedical applications, such as surgical sutures.

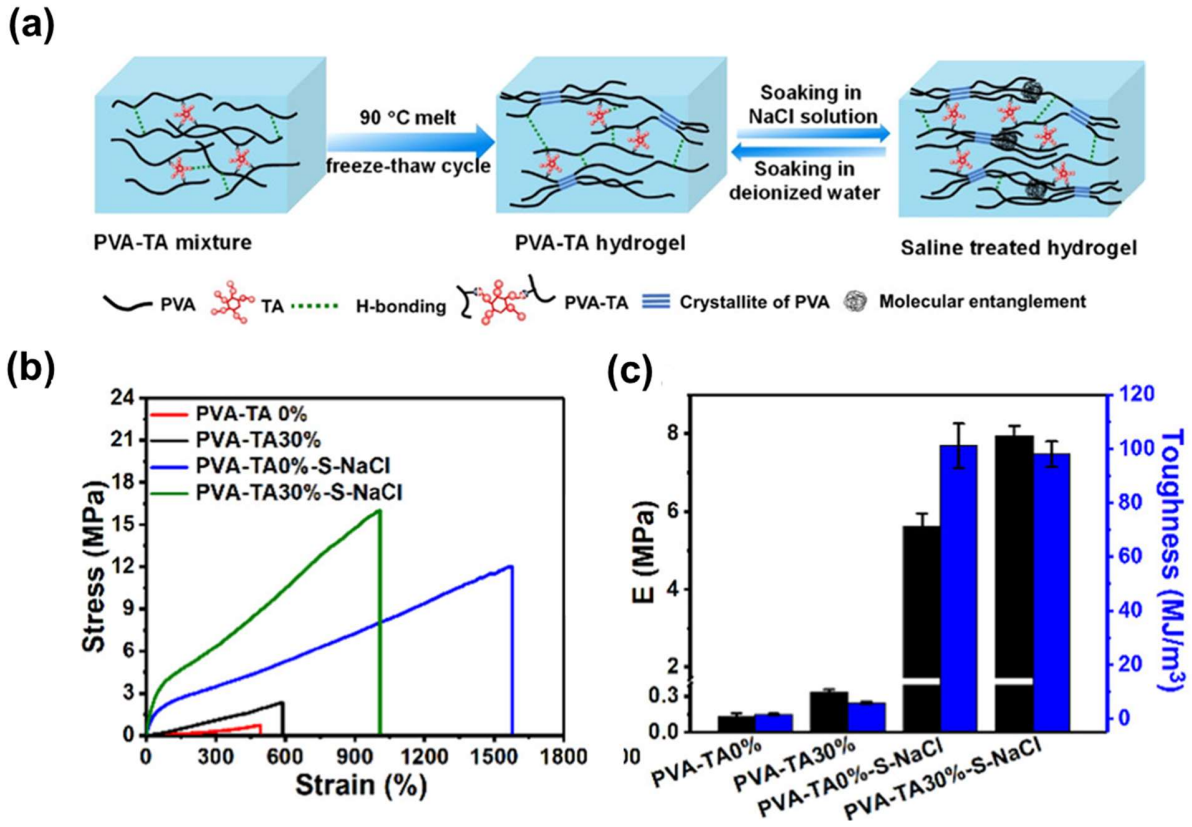

Figure 4. Poly(vinyl alcohol) (PVA)–Tannic Acid (TA) Hydrogel with Molecular Alignment. (a) Schematic illustration of the synthesis procedure for saline-treated PVA–TA hydrogels. (b, c) Tensile stress–strain curves, elastic moduli (*E*) and toughness values of PVA–TA hydrogels containing 0 and 30 wt.% TA powder, with and without saturated NaCl treatment (S-NaCl). Modified and reproduced with permission from [70].

Another study by Lin et al. utilized a freeze-thawed PVA hydrogel to construct a tough, multifunctional physically crosslinked hydrogel, mainly strengthened through crystalline domain formation and supplemented by hydrogen bonding [34]. They incorporated TA and CNC to further enhance physical crosslinking via multiple hydrogen bonding interactions. The PVA hydrogel containing 20% TA and 20% CNC was the strongest sample synthesized, achieving a tensile

strength of 8.7 MPa, toughness of 58.2 MJ/m³, and elongation at break of 1,108%. The healing process was evaluated by adding a Fe^{3+} solution, which accelerated healing by promoting rapid formation of dynamic metal–phenolic coordination bonds between Fe^{3+} and the catechol groups of TA, thereby reinforcing network reformation at the damaged interface. The toughening mechanism was attributed to the role of the rigid CNCs, which were uniformly dispersed throughout the hydrogel matrix. These CNCs helped maintain structural integrity under stress, reduced stress concentrations, and enabled energy transfer from the flexible PVA chains to the stiff nanocrystals. This process helped prevent crack propagation and contributed to the hydrogel's high toughness. Additionally, the hydrogel exhibited adhesive properties attributed to the numerous catechol groups in the TA molecules, mimicking the mussel adhesion mechanism. This study demonstrates a biomimetic strategy for developing tough hydrogels for biomedical applications.

In a similar study, Hua et al. employed PVA with physical processing, including freeze-casting and salting out, to achieve exceptionally high mechanical properties—a tensile strength of 23.5 MPa and toughness of 210 MJ/m³ [66]. During the process, pre-concentrated PVA chains strongly self-coalesced and phase-separated from the original homogeneous solution, resulting in a mesh-like nanofibril network on the surface of micrometre-scale aligned pore walls. Mechanistically, directional freezing concentrated the PVA, forming the aligned pore walls and raising the local polymer concentration well above the nominal value, while salting out induced phase separation that promoted aggregation and crystallization of PVA into nanofibrils. The toughening mechanism arises from structural densification via hydrogen bonding and crystalline domain formation, combined with fibril pull-out, bridging, and energy dissipation. These multiscale structural interactions resulted in simultaneous enhancements in strength, stretchability, and toughness. This process significantly enhanced the mechanical properties and offers a versatile strategy that can be extended to other polymers.

Hydrophobic association is another important physical interaction for forming crosslinked hydrogels, where non-polar molecules or regions aggregate in an aqueous environment, facilitating the self-assembly of hydrophobic domains that serve as physical crosslinking points [81-83]. Several hydrogel systems utilize hydrophobic association as a primary interaction, often in combination with other physical interactions, to achieve enhanced mechanical toughness. Leveraging this mechanism, Yang et al. synthesized hydrophobically modified hydrogels through the copolymerization of hydrophilic N-hydroxyethyl acrylamide (HEAM) and hydrophobic methyl acrylate (MA) in the presence of Tween 80 micelles via emulsion polymerization, resulting in highly stretchable and mechanically robust physically crosslinked hydrogels [35]. The water-insoluble MA monomers were solubilized and polymerized in Tween 80 micelles, while the hydrophilic HEAM monomers polymerized outside the micelles. Tween 80 micelles enabled the integration of hydrophobic poly(MA) and hydrophilic poly(N-hydroxyethyl acrylamide (HEAA)) chains into a physically crosslinked network stabilized by hydrophobic interaction and hydrogen bonding. This synergy contributed to a tensile strength of up to 0.7 MPa and toughness of 508 kJ/m^3. Higher HEAM content provided more hydroxyl and amide groups for hydrogen bonding with Tween 80, which enhanced network crosslinking and mechanical strength. The hydrogel also exhibited rapid self-recovery with approximately 60% recovery in stiffness and 33% recovery in toughness since it contained reversible crosslinking interactions. Micelle-assisted hydrophobic association was also demonstrated by Shi et al., who developed a tough, stretchable, and self-healing single-network hydrogel [71]. The poly(acrylamide (AM)-stearyl methacrylate) (P(AM-SMA)) was physically crosslinked through hydrophobic associations within sodium dodecyl sulfate (SDS) micelles, hydrogen bonding between AM chains, and pseudo-covalent interactions mediated by vinyl silica nanoparticles. Their self-healing ability can be enhanced by increasing the treatment temperature, allowing recovery of up to ~72% of the original tensile strength. This

improvement is attributed to the diffusion of grafted polymer chains and the formation of hydrophobic interactions at the cut interfaces. This work highlights the potential of hierarchical physical crosslinking driven by micelle-mediated hydrophobic associations for designing robust single-network hydrogels.

Similarly, Lv et al. reported a tough hydrogel system that also relied heavily on hydrophobic association interactions, but employed hybrid particles instead of micelles [72]. They enhanced the mechanical toughness and energy dissipation of the hydrogels by incorporating inorganic–organic hybrid latex particles (Figure 5a). A series of hydrogels was synthesized via copolymerization of AM with one of four hydrophobic monomers (HM) of varying alkyl chain lengths. Corresponding silica-grafted latex particles bearing hydrophobic polymer shells—poly(butyl acrylate) (PBA), poly(lauryl methacrylate) (PLA), or poly(stearyl methacrylate) (PSA)—were introduced to establish dynamic physical crosslinking within the network. Hydrophobic interactions between the hydrophobic side chains of the polymer network and the hydrophobic shells of silica-grafted latex particles induced their self-assembly into physically crosslinked domains, forming a dynamic network that enhanced energy dissipation. These reversible, non-covalent interactions enabled effective stress dissipation under deformation, significantly enhancing the toughness of the hydrogel. Among the formulations studied, the hydrogel composed of poly(AM-lauryl methacrylate (LA)) and silica-grafted PLA exhibited the most favorable mechanical properties, achieving a tensile strength of 0.8 MPa, toughness of 6.9 MJ/m^3, and an elongation at break of approximately 2,400% (Figure 5b). In contrast, hydrogels prepared without hydrophobic monomers lacked efficient interactions with the hybrid particles, resulting in inferior mechanical performance. The incorporation of dynamic and reversible physical crosslinking enabled by the hybrid particles endowed the hydrogel with rapid self-recovery, enhanced puncture resistance, and tunable mechanical behavior.

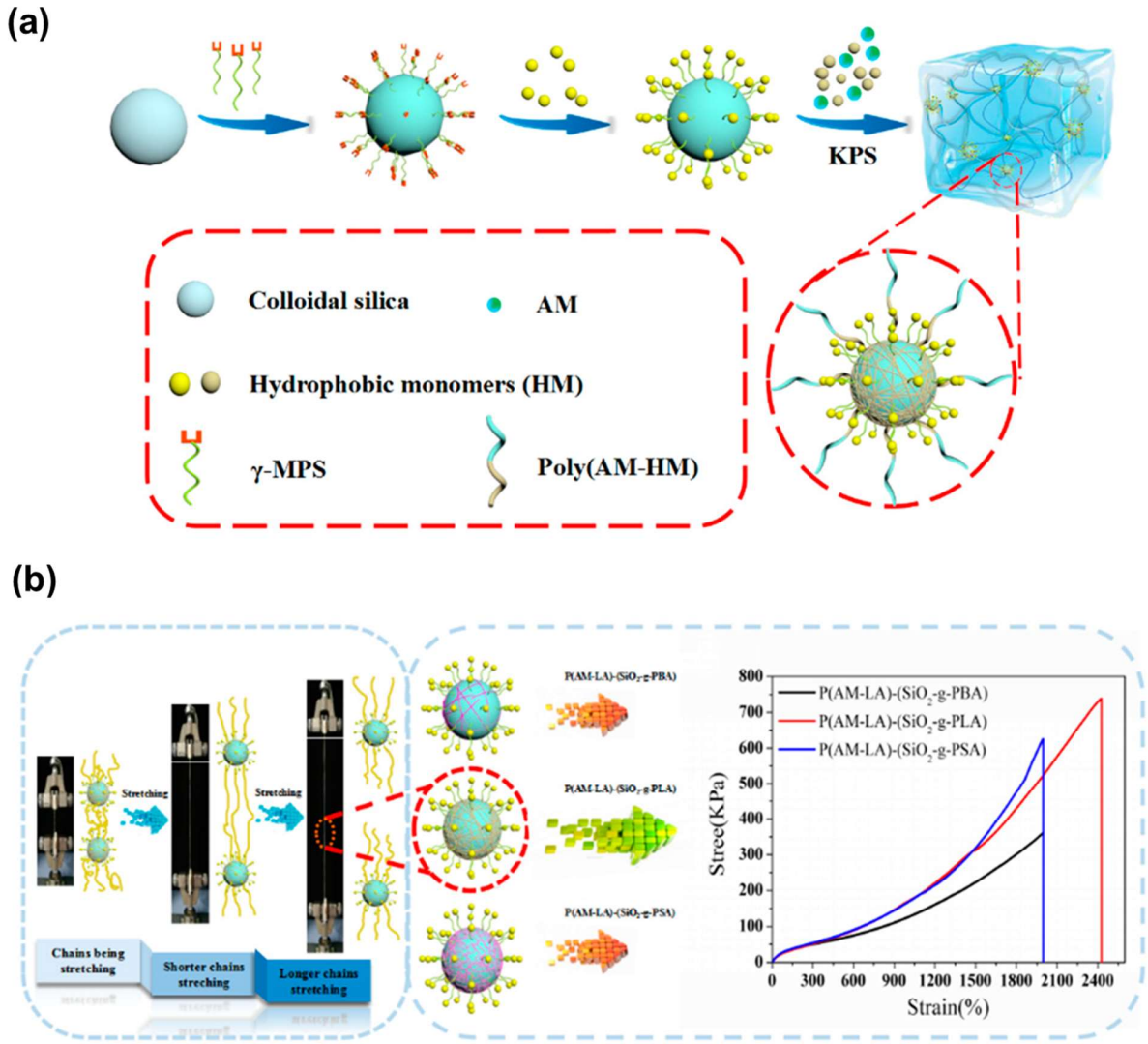

Figure 5. Hydrophobic Hydrogels with Inorganic-organic Hybrid Latex Particles. (a) Schematic illustration of the synthesis process for poly(acrylamide (AM)-hydrophobic monomer (HM)) hydrogels incorporating colloidal hybrid particles. The hydroxyl groups on the silica surface were modified to vinyl groups via a condensation reaction with 3-methacryloxypropyltrimethoxysilane (γ-MPS). (b) Tensile stress–strain curves of poly(AM–lauryl

methacrylate (LA)) hydrogels containing different hybrid particles: SiO_2-grafted poly(butyl acrylate) (SiO_2-g-PBA), SiO_2-grafted poly(lauryl methacrylate) (SiO_2-g-PLA), and SiO_2-grafted poly(stearyl methacrylate) (SiO_2-g-PSA), along with a schematic illustration of the energy dissipation mechanism in the hybrid hydrogels. Modified and reproduced with permission from [72].

Hydrophobic association was also incorporated into a multimechanism physically crosslinked hydrogel by Cui et al. [73], who combined it with hydrogen bonding facilitated by clay and graphene oxide nanosheets. The resulting hydrogel exhibited high tensile strength, excellent toughness, and remarkable stretchability, along with shape-memory behavior and self-healing efficiency of up to 86% of the original tensile strength. Its strain-sensitive conductivity, attributed to the presence of graphene oxide, and selective dye adsorption, resulting from the negatively charged clay and graphene oxide, enable potential applications in biosensing and wastewater treatment. Graphene oxide nanosheet is also used by Liu et al. as a crosslinker to improve the mechanical characteristics of poly(acrylamide) (PAM) hydrogels [74]. In this system, strong electrostatic interactions and hydrogen bonding between PAM chains and graphene oxide nanosheets led to the formation of a densely crosslinked organic–inorganic nanocomposite hydrogel with significantly improved mechanical strength. These studies highlight the potential of graphene oxide as a physical multifunctional crosslinker for hydrogel toughening, owing to its rich surface chemistry, and excellent mechanical properties.

A physical tough hydrogel was also achieved through host–guest interactions, such as those between multivalent poly-cyclodextrins (Poly-CD) and adamantane units, which served as robust crosslinking sites to enhance network stability in the work of Rahmani et al. [36]. This approach enabled the development of an all-physically crosslinked, mechanically robust, room-temperature

shape self-adjustable hydrogel with programmable deformation and shape self-fixation capabilities. The hydrogel was synthesized via copolymerization of acrylic acid, N-(2-hydroxyethyl) acrylamide, and an inclusion complex monomer composed of β-cyclodextrin (host) and adamantane acrylamide (guest), forming a network reinforced by three types of non-covalent interactions: host–guest inclusion, hydrogen bonding, and Fe^{3+}-carboxylate coordination introduced through ferric citrate. These synergistic interactions contributed to the enhanced mechanical performance and stability of the hydrogel (Figure 6a). The resulting hydrogel demonstrated high mechanical properties, including a tensile strength of up to 2.6 MPa, an elongation at break of 1770%, and a toughness of 19 MJ/m^3. Its shape adjustability was enabled by the reversible reconstruction of Fe^{3+}-carboxylate coordination interactions, allowing the hydrogel to lock itself into a new shape while storing elastic energy, thereby facilitating its shape memory function (Figure 6b). The toughening mechanism in this system relies on a combination of strong host–guest interactions and multiple sacrificial bonds—including hydrogen bonding and coordination interactions between COO^- and Fe^{3+}—which dissipate energy during deformation. Despite the typically weak nature of host–guest interactions, the high association constant between β-cyclodextrin and adamantane, combined with interchain hydrogen bonding and metal–ligand coordination, endowed the network with robust physical crosslinking and enhanced mechanical integrity.

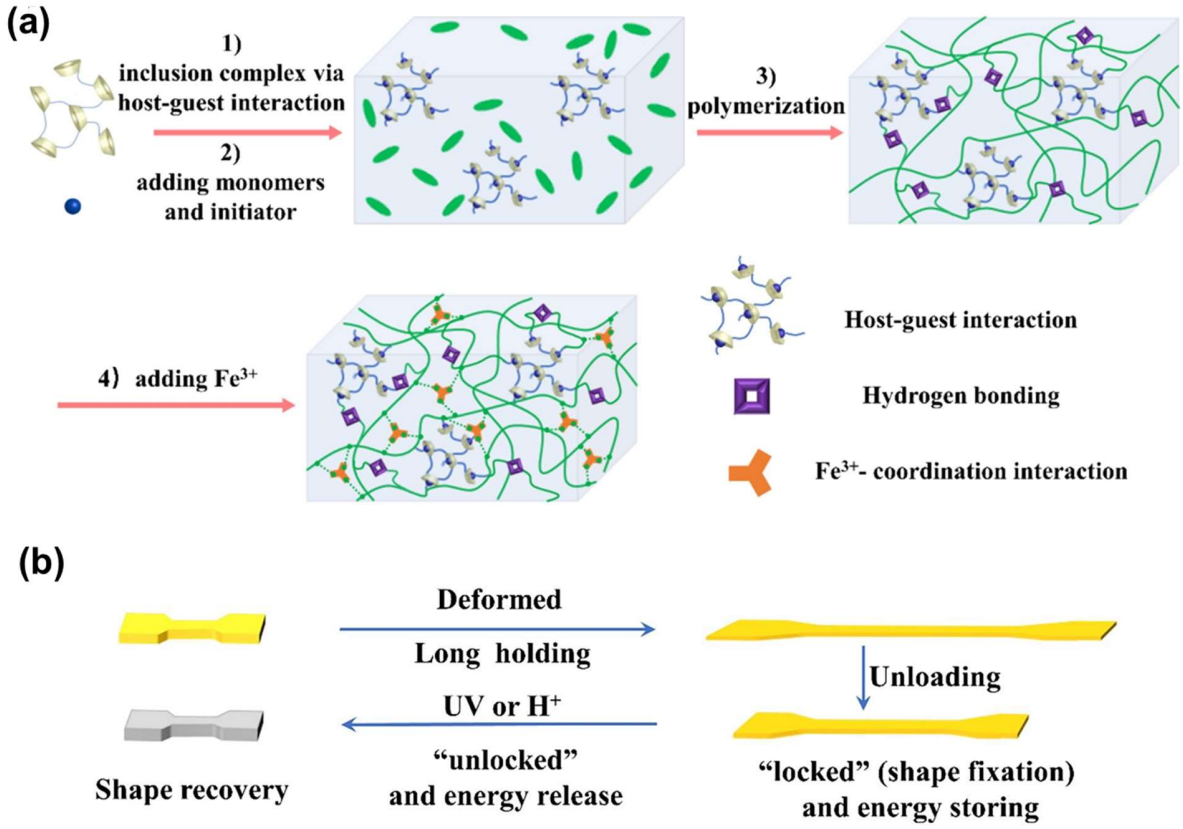

Figure 6. Room Temperature Shape Self-adjustable Tough Hydrogel. (a) Schematic illustration of the synthesis process of the tough hydrogel featuring multiple non-covalent crosslinking for room-temperature shape self-adjustability. (b) Schematic illustration of the energy storage and release mechanism associated with shape fixation at room temperature within the hydrogel. Modified and reproduced with permission from [36].

3.1.2 Perspectives

Various systems have demonstrated that even without covalent crosslinking, single-network hydrogels can achieve robust physical crosslinking with mechanical strengths reaching the MPa range. Figure 7 summarizes their mechanical performance across different systems for comparison. Most physically crosslinked single-network hydrogels exhibit good elasticity due to

the reversible and weaker nature of their physical bonds compared to covalent crosslinks. This elasticity helps prevent brittleness by enabling the network to dissipate energy through reversible bond breakage and reformation. Effective physical toughening of these hydrogels is typically achieved by employing a range of strategic design approaches including:

- *Additive utilization:* As physical crosslinking is relatively weak, in most cases, additives such as nanoparticles (cellulose nanocrystals, silica nanoparticles, clay nanosheets, graphene oxide nanosheets), micelles, macromolecules (tannic acid), or host–guest molecules are added to physically reinforce the network by serving as physical crosslinking nodes or sites of interaction strengthening to compensate for the absence of covalent bonds. Stronger physical interactions, such as electrostatic interactions, may be sufficient to build the network without such additives.
- *Self-Assembly and Phase Separation:* Certain physical interactions—such as hydrophobic association and hydrogen bonding—can drive self-assembly into organized structures or induce phase separation into disordered domains [84-89]. These processes lead to molecular clustering, segregation, or ordering, resulting in networks or domains that have been shown to effectively reinforce hydrogels across various systems [90-92]. The degree of toughening depends on several factors, such as the molecular weight of monomers, monomer concentration, and processing conditions.
- *Multimodal Physical Interactions:* High-performance hydrogels typically employ multiple modes of physical interactions (e.g., crystalline domain formation and hydrogen bonding) in order to achieve synergistic mechanical reinforcement.
- *Network Homogeneity and Connectivity:* A well-connected and homogeneous network structure generated by multiple physical crosslinking is essential in preventing brittle failure and maintaining elasticity under mechanical loads.

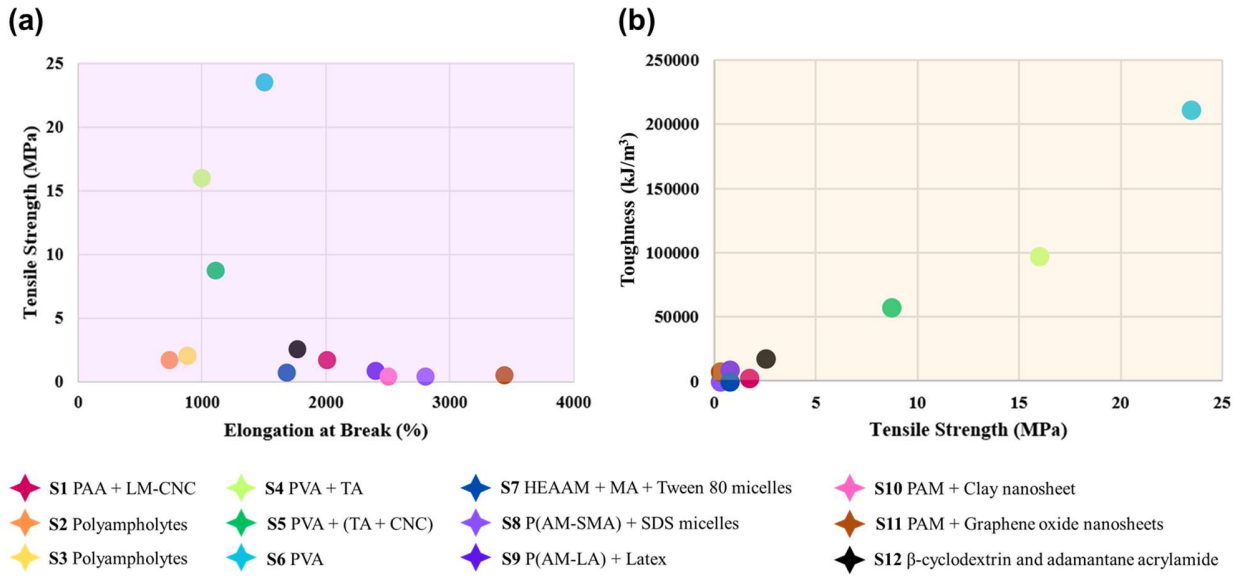

Figure 7. Comparison of the Mechanical Properties of Various Physical Single-network Hydrogels. (a) Tensile strength and elongation at break. (b) Toughness and tensile strength.

Although considerable mechanical performance has been achieved, there remain great challenges in creating single-network physical crosslinking hydrogels that are tough and functional. These networks can fail prematurely under repeated mechanical stress, making it difficult to maintain mechanical integrity during cyclic loading or long-term use. In particular, many physically crosslinked hydrogels show diminished mechanical performance after undergoing self-recovery or self-healing. Additionally, certain types of physical crosslinking (such as those involving crystalline domains or particle-based reinforcement) have a tendency to create heterogeneous network structures with regions of varying crosslink density, resulting in stress concentration points and potential of brittle failure occurring. Furthermore, the relatively loose

network structure of physically crosslinked hydrogels often leads to high swelling ratios, which must be carefully evaluated when considering their practical use.

Moving forward, beyond addressing the existing challenges, future research is expected to focus on expanding the functional capabilities of physically crosslinked hydrogels. This includes integrating advanced features beyond conventional self-recovery or self-healing, such as reversible adhesion and detachment, and structural reconfigurability. Moreover, the development of predictive design frameworks that strategically combine multiple physical interactions is anticipated to play a pivotal role. Tools such as molecular dynamics (MD) simulations [93, 94] and machine learning [95, 96] are likely to become increasingly important in guiding the rational design and optimization of physical crosslinking networks. Beyond fully physically crosslinked systems, certain hybrid double-network hydrogels that combine both physical and chemical crosslinking have demonstrated exceptional toughness together with high recoverability [31, 97, 98]. This is enabled by an optimal balance between the reversible physical network and the robust covalent network.

Recent advances also highlight the importance of polymer chain entanglements facilitated by ultra-long chains, which enable fine-tuning of chain dynamics and interaction strength [99]. Physically entangled hydrogels based on acrylamide and methylenebisacrylamide (MBAA) chemical crosslinkers have also been introduced, exhibiting high toughness and stretchability due to the free-sliding dynamics of entanglement-cluster crosslinking interactions [100]. Furthermore, microscale process-induced mechanisms for physical toughening—such as phase separation [87] and thermal treatment [101]—are emerging as promising approaches that can be combined synergistically with larger-scale toughening methods to further enhance hydrogel durability and functionality.

3.2. Physical Multi-Network Hydrogels

3.2.1 Design Strategies

While single-network hydrogels offer advantages such as structural simplicity, high reversibility, and the ability to achieve impressive mechanical properties, their relatively low crosslinking density and limited number of crosslinking points can restrict energy dissipation, potentially compromising long-term durability under repeated mechanical stress. To overcome this, multi-network hydrogels are typically constructed to enhance toughness and energy dissipation through more design-flexible mechanisms enabled by combining multiple networks [102-104]. In common design strategies for tough and robust double-network hydrogels, the first network is engineered to be rigid and brittle, serving as a sacrificial bond network to dissipate energy [105-107]. The second network is flexible and stretchable, ensuring the hydrogel's integrity during deformation. Additionally, multimodal physical interactions act synergistically or complementarily between networks to reinforce mechanical performance without requiring intentional bond breakage [108]. Incorporating an additional physically crosslinked network substantially improves mechanical robustness and broadens the scope of functional applications. While multi-network hydrogels traditionally rely on at least one chemically crosslinked network, there is growing interest in fully physically crosslinked double-network systems as a promising alternative for achieving enhanced toughness and functional performance (Table 3).

Table 3. Summary of Physical Multi-Network Hydrogels

No	1st network polymer	2nd network polymer	Physical cross-linking interactions	Tensile strength (MPa)	Elongation at break (%)	Toughness (kJ/m^3)	Key functional property	Reference
M1	Poly(acrylic acid) with ferric ions	Chitosan	Metal-ligand coordination Polymer chain entanglement Electrostatic interactions	3.7	1,200	2.8 kJ/m$^{2\#}$	Self-healing	[37]
M2	Polyacrylic acid with ferric ions	2-hydroxypropyltrimethyl ammonium chloride chitosan	Metal-ligand coordination Electrostatic interactions	~10	300	-	Self-recovery	[109]
M3	Polyacrylamide with ferric ions	Polyanionic cellulose with iron (III) chloride	Metal-ligand coordination Hydrogen bonding	0.4	500	1,500	-	[110]
M4	Poly(vinyl alcohol)	Chitosan with trisodium citrate	Crystalline domain formation Electrostatic interactions Hydrogen bonding	12.7	302	22,000	Self-recovery Antifatigue	[111]
M5	Poly(vinyl alcohol)	Alginate	Crystalline domain formation Electrostatic interactions Hydrogen bonding	15	765	56,000	High ionic conductivity	[112]
M6	Poly(vinyl alcohol)	Poly(acrylamide-acrylic acid)	Crystalline domain formation Hydrogen bonding Polymer chain entanglement	1.2	550	1,250	Self-healing	[113]
M7	Debranched corn starch	Poly(vinyl alcohol)	Crystalline domain formation Hydrogen bonding	0.2	797	579	Self-recovery	[38]
M8	Agar	Poly(N-hydroxyethyl acrylamide)-acrylic acid with iron ions	Electrostatic interactions Hydrogen bonding	~1	1,100	6,280	Self-healing	[114]
M9	Low-methoxyl pectin	Poly(acrylamide)	Host-guest interaction Electrostatic interactions Hydrophobic associations Hydrogen bonding	~0.3	~1,500	-	Self-recovery, shape memory	[115]
M10	Poly(N-vinylpyrrolidone)	Poly(acrylamide)	Hydrogen bonding	1.2	~2,700	-	Shape recoverability	[116]

$^{\#}$ Fracture toughness in the unit of J/m²

A notable example of a physically crosslinked double-network hydrogel was reported by Wang et al., who developed a system comprising a PAA network interpenetrated by a chitosan (CS) network, with ferric ions (Fe^{3+}) incorporated to enhance crosslinking (Figure 8a) [37]. This hydrogel exhibits excellent mechanical strength, toughness, and self-healing capabilities, enabled by the synergistic effect of multiple physical interactions. The primary network, formed by PAA, is crosslinked via metal–ligand coordination with Fe^{3+} ions. The secondary network consists of long-chain chitosan, which is physically entangled through immersion in a saturated sodium chloride (NaCl) solution. Additionally, electrostatic interactions arise between the negatively charged carboxyl groups of PAA and the positively charged amine groups of chitosan. They investigated the effects of immersion time (Figure 8b) and Fe^{3+} concentration (Figure 8c) on mechanical performance, reporting a tensile strength of up to 3.7 MPa, elongation at break reaching 1,200%, and fracture toughness up to 2.8 kJ/m². These mechanical properties are attributed to the combined effects of strong metal–ligand coordination, physical entanglement of chitosan chains, and inter-network electrostatic interactions. Owing to the dynamic and reversible nature of its physical crosslinks, the hydrogel exhibits excellent self-healing capability while maintaining high mechanical strength and toughness, rendering it a strong candidate for high-load-bearing applications.

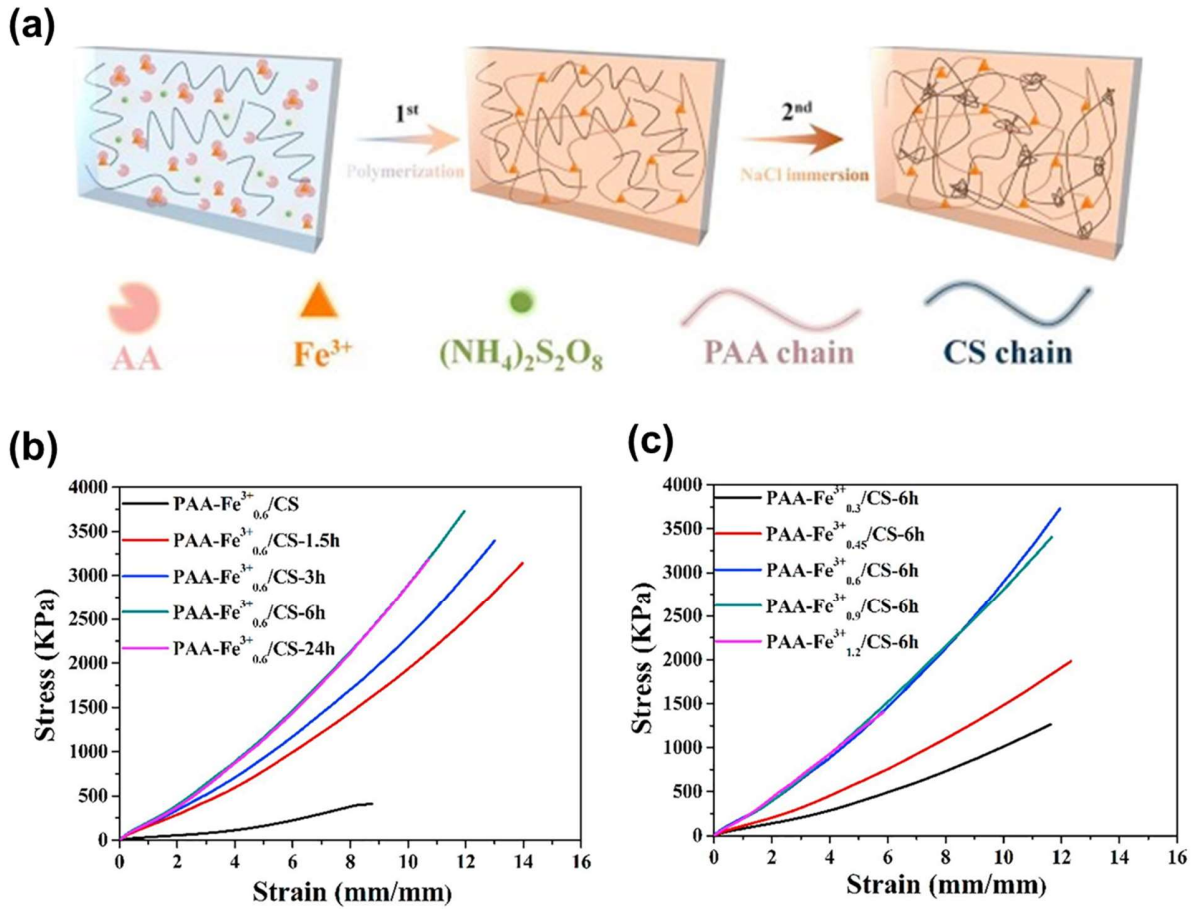

Figure 8. Physically Crosslinked Double Network Hydrogels of Chitosan (CS) and Poly(acrylic acid) (PAA) Incorporating Ferric Ions (Fe^{3+}). (a) Schematic illustration of the construction of PAA–Fe^{3+}/CS double network hydrogels. (b) Tensile stress–strain curves of PAA–$Fe^{3+}_{0.6}$/CS hydrogels after immersion in saturated NaCl solution for different durations (0 to 24 hours), with 0.6 mmol of Fe^{3+} added to the precursor solution. (c) Tensile stress–strain curves of PAA–Fe^{3+}_{x}/CS hydrogels after 6 hours of immersion in saturated NaCl solution, with varying Fe^{3+} molar concentrations (*x* indicates the amount of Fe^{3+} in mmol added to the precursor solution). Modified and reproduced with permission from [37].

A similar physical hydrogel system was developed by Xu et al., who designed a physically crosslinked double-network hydrogel using PAA and 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) with ferric ions [109]. In this design, electrostatic interactions occurred between the cationic quaternary ammonium (R_4N^+) groups of HACC and the anionic carboxylate (COO^-) groups of PAA, while metal–ligand coordination formed between Fe^{3+} ions and the COO^- groups. This architecture established a dual-network structure entirely based on ionic physical interactions. The resulting hydrogel was tough, transparent, and self-healable, offering a promising approach to robust and multifunctional soft materials. Another tough physical double-network hydrogel that relies on metal–ligand coordination is the PAM/polyanionic cellulose (PAC) hydrogel mediated by ferric ions [110]. In this design, PAM is physically crosslinked with PAC via hydrogen bonding, while PAC also forms metal–ligand complexes through its carboxylate (COO^-) groups and Fe^{3+} ions introduced from an $FeCl_3$ solution. The hydrogel was optimized by varying the PAC content while maintaining a constant $FeCl_3$ concentration. The study further suggested that self-healing properties could be introduced by incorporating PAA, increasing the $FeCl_3$ concentration, or avoiding equilibration in water. These studies demonstrate the strong bond energy of metal–ligand interactions and their potential to toughen hydrogels formed from a variety of different monomers.

In addition to metal–ligand interactions, which are known for their high bond energy, another promising physical interaction involves the formation of crystalline domains, particularly within PVA networks. Jiang et al. employed crystalline domain formation in PVA through cyclic freezing–thawing and subsequent soaking in a trisodium citrate (Na_3Cit) solution to construct the first physical network, while the second physical network was established through ionic interactions between the amino and carboxyl groups of chitosan (Figure 9a) [111]. Additional

hydrogen bonding occurs between PVA and chitosan, as well as within individual PVA and chitosan networks and crystallized PVA domains. The hydrogel was optimized by systematically evaluating the effects of freeze-thaw cycles and trisodium citrate concentration on its mechanical properties (Figure 9b and c). The stiff chitosan-based ionic network effectively dissipated mechanical energy and inhibited crack propagation, thereby enhancing toughness. Due to its reversible ionic interactions and hydrogen bonding, the hydrogel demonstrates outstanding self-recovery and antifatigue performance below the yield strain.

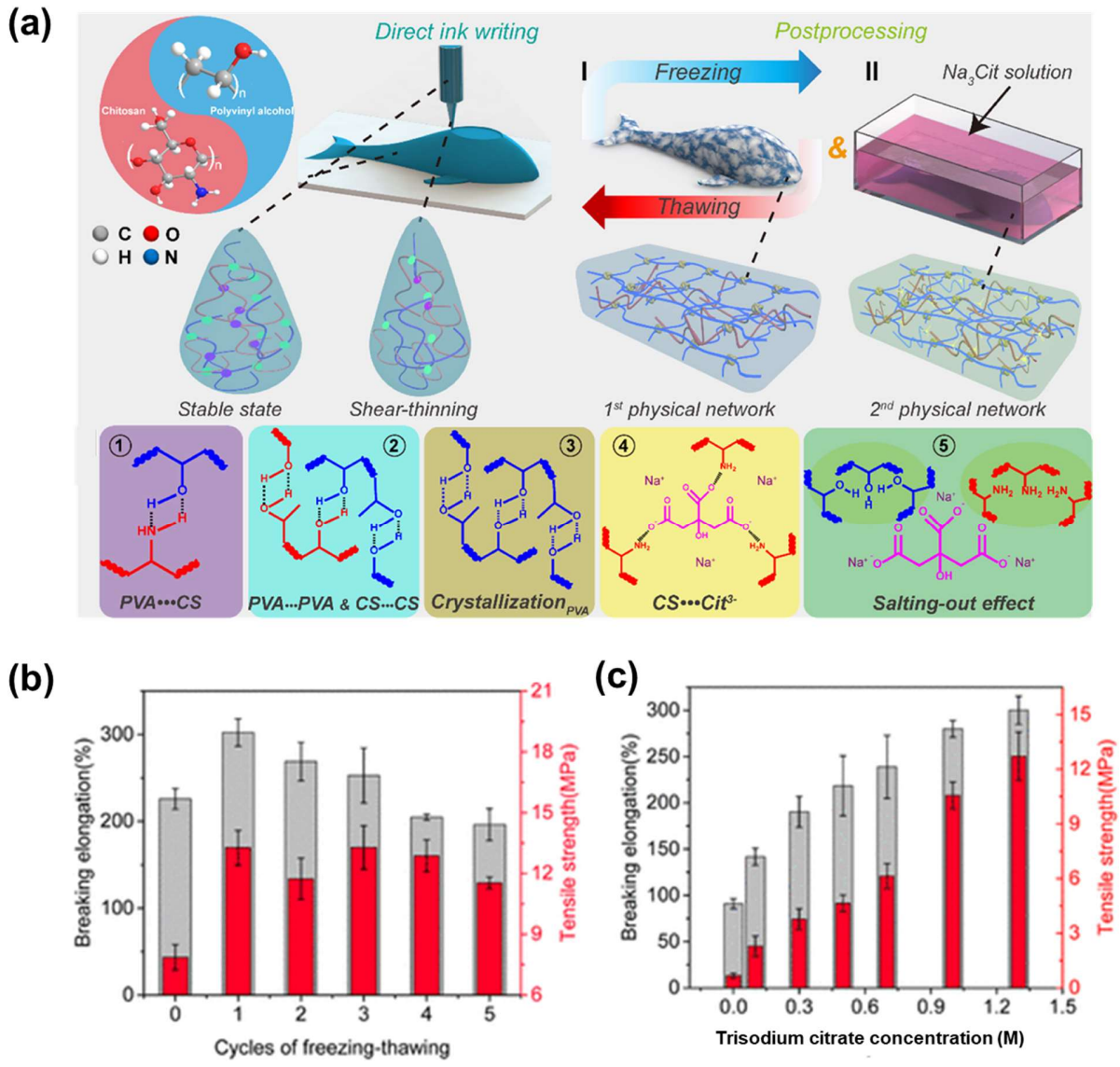

Figure 9. 3D-printed Hybrid Chitosan (CS)/Poly(vinyl alcohol) (PVA) Hydrogel Crosslinked via Ionic Crystallization. (a) Schematic illustration of the hybrid CS/PVA hydrogel ink and its dual-step postprocessing: cyclic freezing–thawing followed by soaking in trisodium citrate (Na_3Cit) solution, along with the major molecular interactions involved. (b) Tensile strength and elongation at break of CS/PVA hydrogels after different numbers of freezing–thawing cycles (all samples soaked in 1.3 M Na_3Cit solution). (c) Tensile strength and elongation at break of CS/PVA

hydrogels treated with one freezing–thawing cycle and soaked in Na_3Cit solutions of varying concentrations. Modified and reproduced with permission from [111].

Cui et al. also developed a double-network hydrogel primarily based on PVA crystallization, which is complemented by ionic interactions and hydrogen bonding [112]. In their system, alginate forms the first network, physically crosslinked by multivalent cations (e.g., Ca^{2+}, Zn^{2+}), while PVA forms the second network. Interactions between PVA chains were enhanced by the salting-out effect of kosmotropic anions when the hydrogel was soaked in salt solutions, which also improved ionic conductivity. The effects of different salt solutions on the as-prepared alginate/PVA hydrogel were evaluated, with $ZnSO_4$ demonstrating the most significant enhancement in toughness. Further investigation into the concentration of $ZnSO_4$ (0.5 M, 1 M, and 2 M) revealed that the hydrogel equilibrated in 2 M $ZnSO_4$ exhibited optimal mechanical performance, achieving a tensile strength of up to 14.95 MPa, toughness of 55.98 MJ/m^3, elongation at break of 765%, and conductivity of 1.5 S/m. These properties suggest that the alginate/PVA hydrogel holds great promise as a reliable solid electrolyte for soft electronic applications and represents one of the strongest physically crosslinked hydrogel systems.

A similar physically crosslinked double-network design was reported by Gong et al., in which PVA forms crystalline domains in the first network, while the second network consists of a poly(AM-AA) copolymer stabilized by hydrogen bonding and polymer chain entanglement [113]. These relatively weak and reversible interactions impart dynamic properties such as rapid recovery and anti-fatigue behavior. However, the self-healing efficiency of the double-network hydrogel remains limited, reaching only up to 37%. Their results showed that both tensile strength and elongation at break increased with higher poly(AM-AA) content and freeze–thaw cycles.

Shang et al. also utilized PVA, but as the second network, in combination with debranched starch (DBS) as the first network to construct physically crosslinked double-network hydrogels (Figure 10a) [38]. These hydrogels were fabricated via *in situ* self-assembly and a freeze–thaw cycle, where DBS formed a hydrogen-bonded gel network and PVA developed crystalline domains that reinforced the structure. In this system, self-assembled starch nanoparticles act as physical crosslinking domains that stabilize the network without covalent bonding. The absence of chemical crosslinkers allowed the resulting hydrogels to achieve excellent fatigue resistance through the synergistic effects of reversible hydrogen bonding and nanoscale DBS crosslinkers. Increasing the debranching time of starch using pullulanase from 4 to 12 hours led to more elastic hydrogels with reduced tensile strength (Figure 10b and c). Notably, the hydrogels retained over 85% of the dissipated energy at the 20^{th} cycle of compression loading–unloading compared to the first cycle.

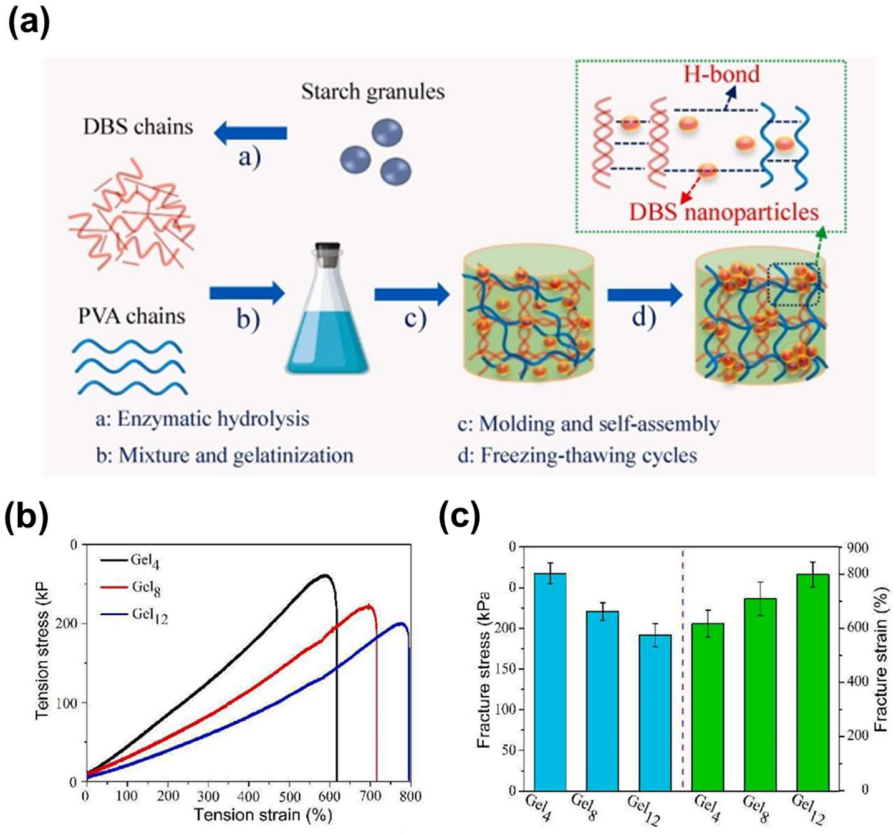

Figure 10. Physical Double-network Starch-based Hydrogel. (a) (a) Schematic illustration of the fabrication process of debranched corn starch/polyvinyl alcohol (PVA) double-network hydrogels via *in situ* self-assembly followed by freeze–thaw cycling. (b) Tensile stress–strain curves, and (c) fracture stress and strain of hydrogels prepared with different pullulanase treatment times (4, 8, and 12 hours, corresponding to Gel_4, Gel_8, and Gel_{12}, respectively). Modified and reproduced with permission from [38].

In addition to polysaccharides such as alginate, chitosan, and starch, agar has also been used to fabricate physical hydrogels, as demonstrated by Zhang et al. [114]. They developed a physically crosslinked double-network hydrogel that is tough, adhesive, and self-healing. Agar

formed the first network, while poly(HEAM)-PAA copolymer was used for the second network, along with Fe^{3+} ions. Physical crosslinking primarily occurred through hydrogen bonds within the agar double-helix structure, within the copolymer chains, and between the two networks. Additionally, electrostatic interactions were present between Fe^{3+} ions and the COO^- groups in the second network's copolymer chains. This hydrogel not only exhibited high toughness of up to 6.28 MJ/m^3 but also demonstrated strong surface adhesion to various untreated materials—including wood, glass, aluminum, paper, and pig skin. Their toughening mechanism primarily arises from reversible sacrificial Fe^{3+}–PAA ionic interactions within the second network, which effectively dissipate energy under stress. Additionally, the local pH generated by Fe^{3+}–carboxyl group interactions enhances the stability of metal coordination bonds, leading to stronger binding and improved mechanical performance. The hydrogel also exhibits high self-recovery and self-healing capabilities, with enhanced efficiency at elevated temperatures. Notably, the agar-based double-network hydrogel containing Fe^{3+} ions achieved up to 75% mechanical recovery in toughness.

Although most physical hydrogels utilize multiple types of physical interactions, Song et al. developed a physical double-network hydrogel that is tough, stretchable, and relies exclusively on hydrogen bonding [116]. This work presents an approach for fabricating fully physical hydrogels, achieved through cooperative hydrogen bonding between a pre-existing polymer and an *in situ* polymerized polymer. In this system, poly(N-vinylpyrrolidone) (PVP) formed the first network, while PAM constituted the second (Figure 11a). The two networks were interconnected solely through hydrogen bonds between their polymer chains. The mass ratio of the in *situ*-formed polymer (PAM) to the pre-existing polymer (PVP) plays a crucial role in determining the final mechanical properties of the hydrogels. Tough hydrogels are obtained only when the mass ratio exceeds 10, corresponding to a high AM concentration. At the optimal mass ratio, the hydrogels

exhibited a tensile strength of up to 1.20 MPa and an elongation at break of more than 2,500% (Figure 11b and c). The wide choice of polymers and monomers that can form stable interpolymer complexes through hydrogen bonding makes this method versatile and applicable to prepare many kinds of hydrogels. They demonstrate that the strong cooperative hydrogen bonding between pre-existing PVP chains and *in situ* formed PAM chains results in evenly distributed, flexible cross-linking sites, which, along with the long polymer chains, enable efficient load distribution and significantly contribute to the hydrogels' exceptional mechanical properties.

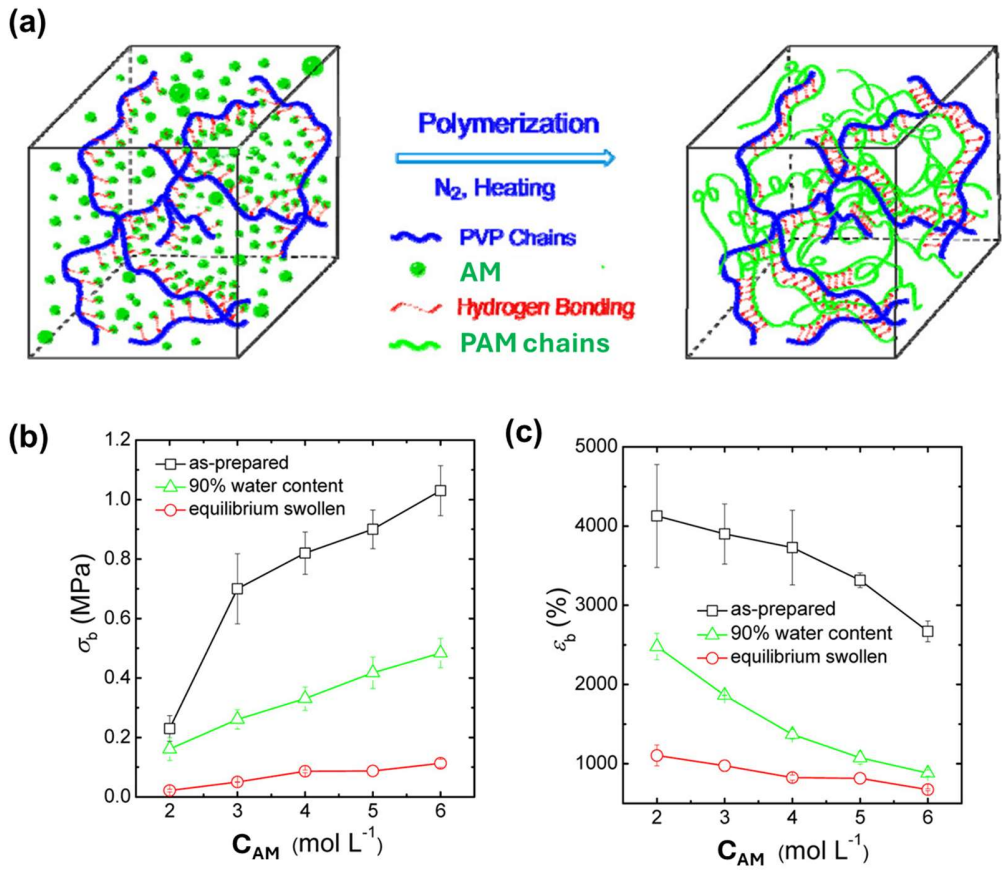

Figure 11. Physically Cross-Linked Hydrogel via Strong Cooperative Hydrogen Bonding. (a) Schematic illustration of the formation mechanism and microstructure of poly(N-

vinylpyrrolidone) (PVP)–in situ–polyacrylamide (PAM) hydrogels. (b) Tensile strength and (c) elongation at break of the hydrogels as a function of monomer concentration (C_{AM}) in their as-prepared state (water content = 86.3%, 81.3%, 76.9%, 72.9%, 69.3% for C_{AM} = 2, 3, 4, 5, and 6 mol L^{-1}, respectively), at 90% water content, and in the equilibrium swollen state (water content = 99.0%, 98.1%, 97.2%, 96.6%, 95.5% for C_{AM} = 2, 3, 4, 5, and 6 mol L^{-1}, respectively). Modified and reproduced with permission from [116].

3.2.2 Perspectives

Fully physically crosslinked multi-network hydrogels combine high mechanical robustness with reversible crosslinks, preserving functionality such as self-recovery. Their performance across various systems is summarized in Figure 12. Toughness typically arises from the sacrificial breaking and dynamic reformation of physical crosslinks, which dissipate energy under stress without permanent damage. A common design strategy in physical multi-network hydrogels involves combining a synthetic polymer, which provides a robust framework, with a natural polymer that contributes unique physical crosslinking mechanisms—such as electrostatic interactions (chitosan, alginate, and pectin) and hydrogen bonding (agar, chitosan, alginate, and pectin). In many cases, the incorporation of multivalent ions to induce metal–ligand coordination significantly enhances the mechanical performance of these hydrogels. Fully synthetic multi-network hydrogels are also employed, but strong inter-network interactions are essential for achieving high toughness and long-term stability. Unlike chemically crosslinked systems, these hydrogels demonstrate exceptional fatigue resistance and recovery owing to the reversible and dynamic nature of their physical crosslinks, which enables repeated energy dissipation and structural restoration. Compared to physical single-network hydrogels, physical multi-network

systems achieve enhanced toughness by effectively decoupling energy dissipation from structural support across distinct networks. Key design strategies include:

- *Mechanical decoupling between networks:* Utilizing multiple polymer networks with distinct mechanical roles enables the separation of energy dissipation and load-bearing functions — for example, by synergistically integrating a soft natural polymer network that dissipates energy with a rigid synthetic polymer network that bears mechanical loads.
- *Sequential network formation:* Controlled, stepwise polymerization of individual networks allows precise tuning of each network's structural properties, ensuring a balance between the hydrogel's mechanical performance and functionality.
- *Enhanced multi-responsiveness:* Incorporating diverse physical crosslink types within different polymer networks enables the hydrogel to exhibit multiple physical responses across a broader range of stimuli, providing greater versatility than chemically crosslinked or physical single-network hydrogels.
- *Highly tunable properties:* The independent adjustability of each network's composition, together with the reversible nature of physical crosslinks, enables precise control not only over mechanical performance but also over other attributes such as swelling behavior, recoverability, and degradability.

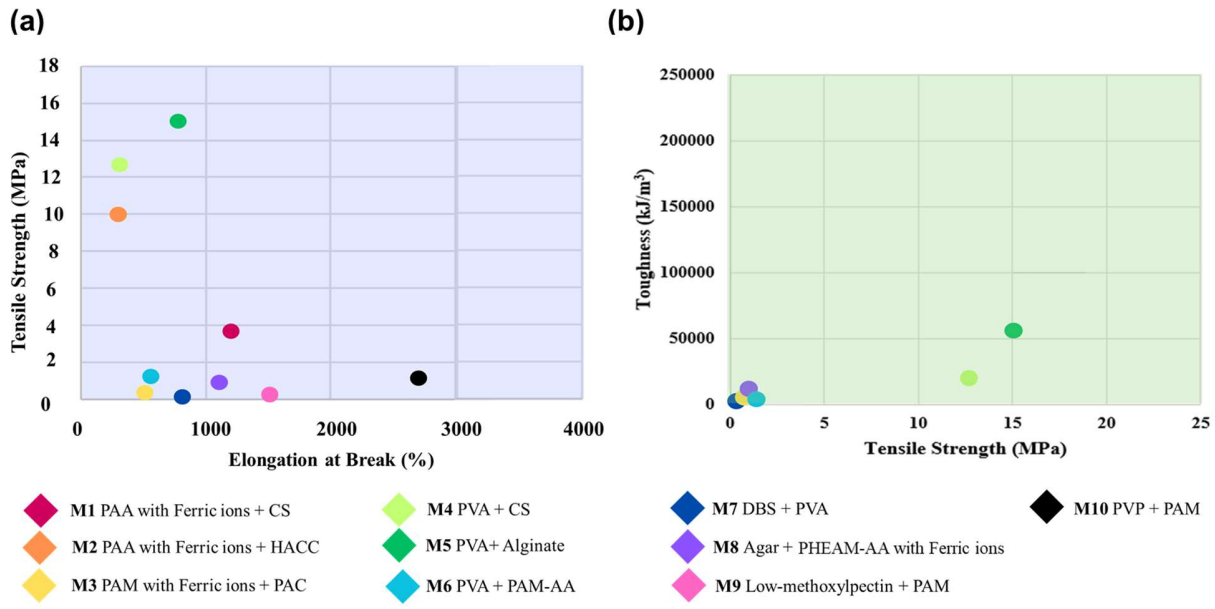

Figure 12. Comparison of the Mechanical Properties of Various Physical Multi-network Hydrogels. (a) Tensile strength and elongation at break. (b) Toughness and tensile strength.

The fabrication of physical multi-network hydrogels is more complex than that of physical single-network. Therefore, careful design and synthesis are crucial, and optimizing the resulting properties is challenging. MD simulations may have limitations in precisely capturing the full mechanical and dynamic behavior of physical double-network hydrogels due to their multiscale complexity and dynamic reversible bonding. To address this, alternative and complementary approaches such as coarse-grained MD [117] and mesoscale simulations [118] may be employed. Furthermore, the mechanical integrity of self-healed hydrogels remains limited, as several studies have reported a reduction in mechanical properties after healing.

In advancing fully physically crosslinked multi-network hydrogels, energy dissipation remains a key factor governing their mechanical performance. A promising approach involves

implementing hierarchical and multiscale design strategies [119-121], where distinct polymer networks contribute to energy dissipation across multiple length scales—from the nanoscale to the macroscale—drawing inspiration from natural structural materials. Such hierarchical architectures create continuous or discrete gradients in structure and properties spanning from molecular to macroscale levels, leading to complex mechanical, swelling, and functional behaviors that exceed those achievable by chemical or hybrid hydrogels, which are generally limited to molecular-to-microscale structuring. Some involvement of covalent crosslinking can also significantly enhance mechanical performance by integrating weak, temporary bonds with strong, permanent ones [122]. Furthermore, fully physically crosslinked hydrogels closely mimic the mechanics of natural tissues through reversible, non-covalent interactions combined with multilayered structural organization which resembles the complexity found in biological systems. As a result, these hydrogels offer a promising platform for developing next-generation materials that replicate the dynamic and resilient behavior of living tissues.

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Conflict of Interest

The authors declare that they have no conflict of interest.

Author Contributions

S.P. and FK. W. conceived the idea and developed the outline. S.P., Y.S.Y.L., and D.K.F.L. collected and analyzed data and drafted the manuscript. S.P., Y.T.C. and FK. W. compiled all sections and reorganized the writing with contributions from all authors.

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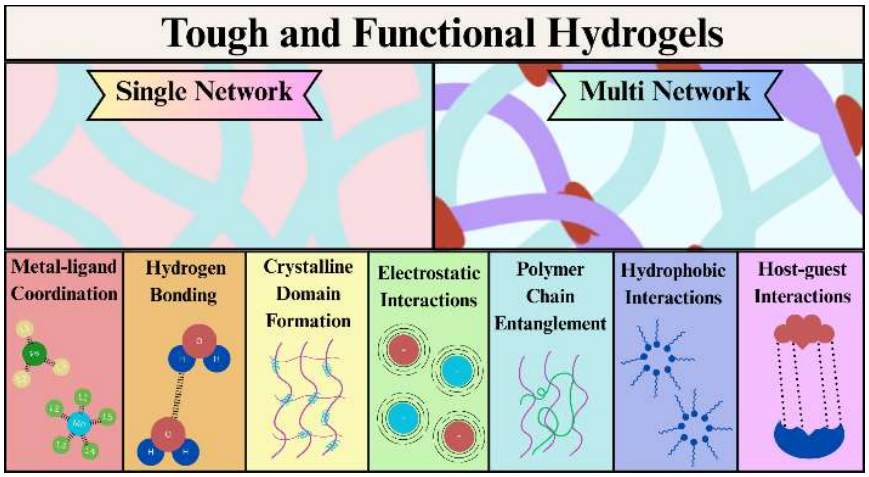

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