Recent Strategies for Strengthening and Stiffening Tough Hydrogels

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Hydrogels are major components of the human body. To replace a damaged hydrogel in the body or support/monitor its normal operation, artificial hydrogels similar to those found in nature are required. As the development of morphologically adaptable soft yet tough hydrogels such as double-network (DN) and polyampholyte (PA) gels, they are applied to soft tissues such as the neural and epithelial tissues with elastic moduli ranging from a few pascals to several kilopascals. However, creating strong and stiff hydrogels emulating stiff load-bearing connective tissues with elastic moduli in the MPa-to-GPa range remains challenging. Herein, recent strategies and potential methods for strengthening and stiffening tough DN and PA gels (such as the reinforcement addition, polymer chain alignment, and solvent exchange) as well as the reinforcing and fracture mechanisms of the resulting hydrogels are summarized. The objective is to provide some insights into the optimal strategy and method for fabricating hydrogels with a combination of strength, stiffness, and toughness, which can emulate natural load-bearing tissues.

1. Introduction

Almost all components of the human body include hydrogels, which primarily consist of water molecules within polymer networks. Such natural hydrogels (biological tissues) are ionically conductive and adaptable to various morphologies in physiological environments, exhibiting a unique combination of mechanical properties, including variable strength, stiffness (elastic modulus), toughness (fracture energy), and fatigue resistance (fracture threshold). However, because these tissues usually demonstrate a limited ability to self-heal ability after damage, researchers have attempted to develop synthetic hydrogels with compositions resembling natural tissues.\(^{[1-5]}\) Furthermore, in bioelectronic applications, synthetic hydrogels are utilized as soft backbones that bridge rigid electronics and soft tissues.\(^{[6-8]}\)

The number of such applications has been gradually increasing since the development of tough hydrogels, such as double-network (DN) and polyampholyte (PA) gels.\(^{[9-13]}\) A typical DN gel is composed of two interpenetrating polymer networks: a rigid first-network serving as a sacrificial skeleton and a stretchable second-network serving as a deformable substance. These networks with contrasting mechanical properties synergistically interact to surpass the inferior mechanical characteristics of single-network hydrogels.\(^{[9,10]}\) In PA gels, the copolymerization of oppositely charged monomers produces supramolecules containing repetitive cationic and anionic groups.\(^{[11,12]}\) The resulting weak bonds are used for reversible sacrificial crosslinking, and strong bonds serve as permanent crosslinking that preserve the overall hydrogel structure. The presence of multiple ionic bonds with different strengths leads to the superior mechanical properties of PA gels. Accordingly, the unique polymeric structures of DN and PA gels are related to their characteristic fracture mechanisms involving effective energy dissipation and fracture resistance, which considerably expand the hydrogel application area. Such synthetic hydrogels have recently started emulating soft and tough tissues such as the neural, muscle, and epithelial tissues whose elastic moduli lie in the range of a few pascals to several kilopascals (Figure 1).\(^{[14-17]}\)

Despite these developments, the strength and stiffness of hydrogels remain significantly lower than those of load-bearing connective tissues organizing tendons, ligaments, cartilages, and blood vessels of which elastic moduli lie in the range of MPa-to-GPa, which are substantially stiffer than other tissues (Figure 1).\(^{[18-22]}\) To replace, fill, and support the damaged
stiff tissues with an artificial hydrogel or to apply bioelectronics with a bio-adaptable hydrogel interface for sensing/actuating the stiff tissues, the introduced hydrogel should possess high strength and stiffness. Such biomechanical match can minimize the implanted hydrogel deformation and mechanical/electrical decoupling between the hydrogel and the bioelectronics.\[14,16,23,24\] However, the development of highly strong and stiff hydrogels with mechanical properties similar to those of the load-bearing tissues still remains a challenge. Previous review articles described several strategies for developing mechanically robust (soft yet tough) hydrogels, which included topological networks, DNs, dual crosslinked networks, PA networks, supramolecular networks, and nanocomposites.\[24–30\] However, very few comprehensive reviews covering methods for strengthening and stiffening relatively tough hydrogels to fabricate hydrogels with the combination of strength, stiffness, and toughness have been published.

In this review, we summarize the recent approaches (strategies and methods) aimed at the strengthening and stiffening of tough DN and PA hydrogels as well as the reinforcement and fracture mechanisms of the resulting hydrogels. The mechanically enhanced DN and PA gels exhibit unique combinations of strength, stiffness, and toughness, which could allow them to emulate load-bearing tissues. We categorize strategies of the strengthened and stiffened DN and PA gels as “the addition of strong and stiff reinforcements to soft polymer matrices” and “polymer matrix manipulation” (Figure 2). The addition of reinforcements includes embedding inorganic particles (e.g., clay and silica), incorporating biominerals through mineralization (e.g., calcium phosphate), and impregnating macroscale fibers/fabrics (e.g., elastomer fibers and fiber-woven fabrics). From the perspective of polymer manipulation, a drawing method (stretching and fixation) for aligning polymer chains is described in detail. Moreover, other hydrogels whose fabrication methods may be applicable for enhancing DN and PA gel systems are discussed. Based on understanding of the reinforcing mechanism of each strategy and the hydrogel fracture mechanism, we outline several factors that should be considered for optimizing reinforcing effects and fabrication methods for mechanically robust hydrogels.

In the subsequent sections of this review, the following polymer abbreviations are used: poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS), poly(dimethylacrylamide) (PDMAAm), poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT), alginate (Alg), and polyacrylamide (PAAm). The rigid PAMPS, PDMAAm, PBDT, and Alg networks usually serve as a sacrificial first network, and the soft PAAm network generally serves as a stretchable second network.

### 2. Strong and Stiff Reinforcements for Composite Hydrogels

To improve the mechanical properties of materials, strong and stiff inorganic fillers, such as microsized or nanosized silica (\(\text{SiO}_2\)), glass, clay, alumina (\(\text{Al}_2\text{O}_3\)), calcium carbonate
Silica particles have been commonly used as a reinforcement, because silica surfaces have abundant –OH groups and can be easily modified by converting –OH groups into other functional groups such as –COOH and –NH2. Xu et al. fabricated a silica microparticle-reinforced Alg-PAAm DN composite gel with enhanced mechanical properties as compared with those of the pure polymer gel. After reinforcement, its tensile strength and elastic modulus increased by a factor of 2.8 from 94 to 264 kPa and by a factor of 5.6 from ≈25 to 140 kPa, respectively. The authors demonstrated that the silica/Alg bonds broke before the fracture of Alg networks due to weak interfacial adhesion between silica/Alg (Figure 3a). Despite the weak interfaces and their early rupture, interestingly, the composite gel exhibited improved extensibility. Meanwhile, Choi et al. utilized mesoporous silica microrods with ordered mesopores as a reinforcement for a tough Alg-PAAm DN gel (Figure 4a,b). As mesoporous silica particles have a high surface area, they can serve as inorganic fillers that more strongly interact with polymer chains than bare silica particles. The tensile strength and elastic modulus of the resulting composite gel were ≈140 and 25 kPa, which exceeded those of the pure polymer gel by 3.0 and 1.4 times, respectively (Figure 4c). The composite gel was also more stable in a physiological environment than the pure polymer gel, and its elastic modulus was independent of the functional groups on the silica surface. However, these functional groups strongly affected the extensibility of the composite gel.

The fracture strain was unexpectedly increased by silica particles and further affected by the functional groups on the silica surface. Because several previous studies demonstrated that PAAm is not adsorbed on the silica particles, one can expect that the enhancement of composite mechanical properties (including the elastic modulus and tensile yield strength) occurs at low strain due to the easier fracture of silica/Alg bonds than that of the Alg network (Figure 3a). However, the increase in the composite fracture strain implies that silica particles may be able to strongly interact with the PAAm network even after yielding (the fracture of silica/Alg bonds and Alg network) in contrast to the finding of previous studies, and that the micro-agglomerations consisting of a fragmented Alg

Figure 2. Schematic overview of recent approaches aimed at the strengthening and stiffening of tough hydrogels.

2.1. Embedding Strong and Stiff Particles

Various types of reinforcing fillers (reinforcements) are used for improving the mechanical properties of hydrogels. These include silica (SiO₂), graphite, and polymeric fillers, such as rubbers, elastomers, and engineering plastics, are commonly added to a soft polymer matrix. The composite materials partially exhibit the mechanical properties of their constituents, and, in some cases, they possess superior mechanical properties to those of the individual components. In essence, an applied force is transferred from the polymer matrix to the stiffer fillers, which bear a fraction of the load, thus increasing the overall material mechanical properties. In this mechanism, the interfacial adhesion (interfacial bonding strength) between the matrix and the fillers determines the improvement degrees of the composite strength (yield and fracture strengths), stiffness, and toughness (Figure 3). When interfacial bonds are broken first before polymer network yielding (Figure 3a), the fillers usually only contribute to the enhancement of stiffness (elastic modulus). If the interfacial adhesion is too weak to transfer load from the matrix to the fillers, the stiffness enhancement can be very slight. On the contrary, the fillers with strong interfacial adhesion enhance yield strength as well as composite stiffness (Figure 3b). After the yielding point, the softened polymer network that is still bonded with the fillers can plastically flow and undergo strain hardening, resulting in significantly enhanced fracture strength and toughness. Thus, because the composite mechanical properties strongly depend on the reinforcing and fracture mechanisms, selecting an appropriate filler type is particularly important.

In hydrogel materials, reinforcements containing polar functional groups such as –OH and –COOH would effectively enhance their mechanical properties due to fundamental characteristics of these hydrogels (such as softness and hydrophilicity). In particular, reinforcing tough DN and PA gels with strong and stiff fillers can produce adequately integrated strength, stiffness, and toughness; therefore, the resulting composite hydrogel is expected to demonstrate a high potential for emulating the load-bearing tissues.
network and silica particles may actively participate in energy dissipation. The described fracture behavior requires a more detailed investigation.

Wang et al. fabricated a silica nanoparticle-reinforced PAMPS-PAAm DN composite gel in which silica nanoparticles with the diameters of 150–300 nm acted.\cite{37} The authors used silica nanoparticles as pure mechanical reinforcements, or both the reinforcements and chemical crosslinkers (prepared by modifying their surfaces with vinyl groups) for copolymerization with AMPS yielding silica-grafted PAMPS species. Bare silica particles acted as the pure reinforcement in silica-filled PAMPS-PAAm composite gel, whereas vinyl-modified silica particles additionally served as the chemical crosslinker for PAMPS networks in silica-grafted PAMPS-PAAm composite gel. Both silica particles produced denser polymer networks with smaller pores, leading to significantly enhanced composite mechanical properties as compared with those of the pure polymer gel (Figure 4d). However, the enhancement degrees of the material strength and elastic modulus significantly differed depending on the selected silica particles (Figure 4e). The composite gel reinforced by bare silica (1 wt% silica-filled PAMPS-PAAm) exhibited a compressive strength of 10.9 MPa at a strain of 0.9 and a compressive modulus of 0.29 at a strain of 0-0.1, both of which were 2.2 larger than the corresponding parameters of the pure polymer gel. Furthermore, the composite gel reinforced by vinyl-modified silica particles exhibited a better enhancement in mechanical properties than those of the bare silica-reinforced composite gel. In particular, the compressive strength and compressive modulus of the composite gel (1 wt% silica-grafted PAMPS-PAAm) amounted to 16.5 and 0.33 MPa, which were 3.7 and 2.5 times larger than those of the pure polymer gel, respectively.

Clay minerals represent typical inorganic particles that have been widely used in various fields, such as catalysis, biology, optics, gas barriers, fire shields, and mechanical reinforcements.\cite{80–86} As Haraguchi et al. demonstrated that laponite clay nanosheets formed crosslinking junctions between polymer chains (acting as physical crosslinkers) due to the presence of Al–OH and –Si–OH groups in the clay structure and produced physical networks (i.e., nanocomposite hydrogel),\cite{40,41,77,85,86} researchers started using clay particles as physical crosslinkers to produce hydrogels and/or mechanical reinforcements to enhance the hydrogel mechanical properties. The physical crosslinker binds with polymer chains physically to form a 3D polymer network (hydrogel), whereas the mechanical reinforcement contributes to purely enhancing composite mechanical properties, rather than inducing gelation. Although many researchers experimentally confirmed the specific roles of clay particles in the hydrogel, only a few studies focused on the mechanical reinforcing effect of the clay particles in tough DN or PA gels.\cite{46–51}

Gao et al. fabricated an ATP clay nanorod-reinforced PAMPS-PAAm DN composite gel\cite{46} in which clay nanorods are with the

Figure 3. Reinforcing and fracture mechanisms of composite hydrogels. a) In the composite hydrogel containing reinforcements with weak interfacial adhesion, interfacial bonds, rigid sacrificial networks, and strong stretchable networks are ruptured in the specified order. b) In the composite hydrogel containing reinforcements with strong interfacial adhesion, rigid sacrificial networks are ruptured first, representing the yield point. Thereafter, interfacial bonds or stretchable networks are ruptured.
diameters of 20–30 nm and the lengths of 200–1000 nm. Using the concept applied to the abovementioned silica/PAMPS-PAAm composite gel,\textsuperscript{[37]} the authors prepared ATP-filled PAMPS-PAAm and ATP-grafted PAMPS-PAAm composite gels. Because PAAm chains strongly physisorbed on the ATP surface, in addition to acting as the mechanical reinforcement, pristine ATP nanorods acted as physical crosslinkers for a PAAm network (in the ATP-filled PAMPS-PAAm composite gel). Meanwhile, vinyl-modified ATP nanorods acted as both the physical crosslinkers for the PAAm network and chemical crosslinkers for the PAMPS (in the ATP-grafted PAMPS-PAAm composite gel). The incorporation of ATP nanorods densified the polymer networks resulting in smaller pores than those of the pure polymer gel. The composite gel reinforced by pristine ATP (2 wt% ATP-filled PAMPS-PAAm) exhibited the compressive strength of 7.7 MPa at a strain of 0.9 and a compressive modulus of 0.43 MPa at the strain of 0.05–0.1, which were 1.6 and 2.3 times higher than the corresponding values obtained for the pure polymer gel, respectively (Figure 4f). The composite gel reinforced by the vinyl-modified ATP (2 wt% ATP-grafted PAMPS-PAAm) possessed a compressive strength of 10.6 MPa and a modulus of 0.3 MPa, which exceeded those of the pure polymer gel by the factors of 2.2 and 2.8, respectively (Figure 4f).

Furthermore, some researchers studied the toughening effect of LDH particles whose physical and chemical properties closely resembled those of clay minerals.\textsuperscript{[52–54,85]} Hu and Chen reported that LDH nanoparticles could significantly enhance the mechanical properties of a PAAm hydrogel via a mechanism similar to that of typical clay particles.\textsuperscript{[52]} Therefore, such particles would be also able to serve as a reinforcement for enhancing the mechanical properties of DN and PA gels.

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**Figure 4.** Composite hydrogels embedded with strong and stiff particles. a) A photograph of pure polymer (Alg-PAAm) and mesoporous silica microrod-reinforced composite (silica/Alg-PAAm) gels. b) Fluorescent microscope image of the composite gel containing fluorescently labeled silica microrods. c) Stress–strain curves for the pure polymer and reinforced composite gels. Adapted with permission.\textsuperscript{[36]} Copyright 2017, Wiley-VCH. d) Cross-sectional scanning electron microscope (SEM) images of pure polymer (PAMPS-PAAm) and silica nanoparticle-reinforced composite (silica/PAMPS-PAAm) gels. Adapted with permission.\textsuperscript{[37]} Copyright 2012, The Royal Society of Chemistry. e) Different compressive strengths of the composite gel depending on the selected silica nanoparticles. Reproduced with permission.\textsuperscript{[37]} Copyright 2012, The Royal Society of Chemistry. f) Different compressive strength of the composite gel depending on the selected ATP nanorods. Reproduced with permission.\textsuperscript{[46]} Copyright 2014, The Royal Society of Chemistry. g) Schematic of a GO-reinforced Alg-PAAm composite gel. h) The difference in mechanical robustness between a pure PAAm gel and a GO/Alg-PAAm composite gel. Adapted with permission.\textsuperscript{[56]} Copyright 2013, The Royal Society of Chemistry. i,j) Cross-sectional SEM images and stress–strain curves of the pure polymer (Alg-PAAm) and functionalized GO-reinforced composite (A-aGO/Alg-PAAm) gels. Adapted with permission.\textsuperscript{[57]} Copyright 2017, American Chemical Society.
Because the interfacial bonding strength affects the reinforcing mechanism and consequent fracture strength and toughness of the material, the reinforcing mechanism of the composite hydrogels discussed earlier is different depending on the type of fillers used. The typical mechanical reinforcements with weak interfacial adhesion to polymer matrices (e.g., bare silica particles\textsuperscript{35}) have a limited ability to enhance the mechanical properties. As weak interfacial bonds of the reinforcement/matrix are first ruptured before the yielding of rigid networks and plastic deformation of stretchable networks, such reinforcements usually limitedly contribute to the increase in strength and toughness. (Figure 3a). On the contrary, composite materials containing reinforcements that are strongly chemical crosslinked with a rigid network (e.g., chemically cross-linkable silica\textsuperscript{37} and clay\textsuperscript{46}) nanoparticles) demonstrate different fracture behaviors. In such composites under tension, the rigid network is gradually stretched and broken first while the most load is transferred to the reinforcements, which is represented as the increased yielding stress; subsequently, the load is transferred to clusters of chemically crosslinked reinforcement and fragmented network (Figure 3b).

In the case of the reinforcements that are additionally physically crosslinked with a stretchable network (e.g., vinyl-modified clay nanoparticles in PAAm network\textsuperscript{46}), the clusters of the chemically crosslinked reinforcement and fragmented network may act as micro-crosslinkers for the stretchable network. These micro-crosslinkers can further contribute to energy dissipation until a complete rupture of the reinforcement/stretchable-network physical crosslinking or the stretchable network itself. In other words, it could be inferred that strong interfacial interactions between the reinforcements and the polymer matrices, originating from the chemical crosslinking with the rigid network and physical crosslinking with the stretchable network, substantially increase the load transfer and energy dissipation. Meanwhile, several previous studies demonstrated that silica nanoparticles also act as physical crosslinkers to form a polymeric network (hydrogel) except for the PAAm network\textsuperscript{31–34,37,79} therefore, one should consider the reinforcing mechanism of each filler (i.e., the role of each reinforcement in a specified polymer matrix) to achieve optimal reinforcing effects.

GO is considered a strong candidate for reinforcing fillers due to its excellent intrinsic mechanical properties. Unlike graphite, the polar functional groups (e.g., –OH and –COOH) and large specific surface area of GO permit various interactions, such as hydrogen bonds and electrostatic interactions, with polymer chains and allow their homogeneous dispersion in hydrogel matrices. The nanosized GO can also serve as a physical crosslinker forming polymer networks.\textsuperscript{56,57} Accordingly, the GO-reinforced composite hydrogels demonstrate significantly better mechanical properties than those of the pure polymer hydrogels.

Fan et al. fabricated a GO-reinforced Alg-PAAm (GO/Alg-PAAm) DN composite gel (Figure 4g,h) with a tensile strength and an elastic modulus of 202 and 30.8 kPa, respectively.\textsuperscript{56} These values were 1.8 and 1.5 times higher than those of the pure polymer gel. Liu et al. conducted the amination and alginate functionalization of the GO surface (A-aGO) to enhance its interfacial bonding and fabricated an A-aGO-reinforced Alg-PAAm (A-aGO/Alg-PAAm) DN composite gel.\textsuperscript{57} A-aGO formed hydrogen bonds with polymer chains and electrostatic interactions with Alg chains (–NH\textsubscript{3} on A-aGO and –COO\textsuperscript{–} on Alg). Compared with the pure polymer gel structure, the enhanced interactions between the composite constituents produced a dense polymer micronetwork with smaller pores and thinner pore walls denoted by the red circle in Figure 4i. As a result, A-aGO acted as both the mechanical reinforcement and the physical crosslinker for PAAm networks (Figure 3b), which significantly enhanced composite mechanical properties corresponding to a tensile strength above 1200 kPa and an elastic modulus of 280 kPa, which were 5.6 and 4.8 times higher than those of the pure polymer gel, respectively (Figure 4j).

2.2. Incorporating Bioiminerals through Mineralization within Hydrogel

Bioiminerals (bioceramics) such as calcium carbonate and calcium phosphate, including HA, have been applied for fabricating composite hydrogels that possess osteoconduction properties for osseointegration (i.e., bone regeneration) as well as mechanical robustness.\textsuperscript{97–97} Such composite hydrogels are generally obtained by two methods: physical mixing of bioiminerals in polymer matrices and in situ bioimineralization in polymer matrices.

As an example of a composite gel containing bioiminerals, Zhang et al. fabricated a nanohydroxyapatite (nHA) particle-reinforced Alg-PAAm DN composite gel scaffold by simply dispersing the nHA in the polymer matrix.\textsuperscript{64} These particles formed hydrogen bonds with polymer chains and produced more closely interconnected structures than those of the pure polymer gel. While the microporous Alg-PAAm gel scaffolds were relatively weak and brittle, the nHA/Alg-PAAm composite gel scaffolds consisting of 40 wt% nHA and 60 wt% polymers (except for water) exhibited significantly better mechanical properties.

Composite hydrogels reinforced by the in situ nucleated bioiminerals have also been developed.\textsuperscript{100–102} Rauner et al. found that calcium carbonate was mineralized on and within a polymeric hydrogel matrix containing urease (enzyme)\textsuperscript{91} and subsequently fabricated ultrastiff polymer composite gels by inducing calcium phosphate (CaP) mineralization within several hydrogel matrices containing alkaline phosphatase enzyme (Figure 5a,b).\textsuperscript{92} In the resulting mineralized CaP-reinforced Alg composite gel, the CaP content was 5–15 vol% depending on the mineralization time (1–7 d). The composite gel with a CaP content of 15 vol% possessed a tensile strength of \(\approx1.3\) MPa and an elastic modulus of 155 MPa (Figure 5c), which were remarkably higher than those of the pure PAAm hydrogel. (The tensile strength and elastic modulus of a typical PAAm gel were 0.010–0.025 and 0.005–0.015 MPa, respectively.)\textsuperscript{109} Figure 5c also shows that the strengthening and stiffening degrees of mineralized CaP strongly depend on the matrix polymer type, PAAm, PDMAAm, or poly(2-hydroxyethyl acrylate) (PHEA).

Fukao et al. conducted HA mineralization within a hydrogel matrix by alternatingly immersing the hydrogel in dipotassium phosphate (K\textsubscript{2}HPO\textsubscript{4}) and calcium chloride (CaCl\textsubscript{2}) solutions to fabricate an HA particle-reinforced PDMAAm-PDMAAm DN composite gel (Figure 5d,e).\textsuperscript{93} The as-prepared HA/PDMAAm network, in which polymer chains were strongly entangled within the hollow and spiny spherical HA clusters with the diameters of \(\approx800\) nm (Figure 5f), served as the
rigid first network, and the subsequent additional PDMAAm polymerization was conducted to obtain the stretchable second network (Figure 5d). Although the HA content in the composite gel did not exceed 0.31–2.39 wt%, its tensile strength and elastic modulus were 440 and 290 kPa, which were 2.9 and 2.0 times higher than those of the pure PDMAAm-PDMAAm DN gel, respectively (Figure 5g).

Note that unlike the typical inorganic reinforcements, the HA particles produced in that study represented hollow spherical polycrystals, which allowed the composite gel to possess a unique reinforcing mechanism. The hollow HA particles, especially those containing amorphous regions, appeared to stretch under tension (Figure 5f), and an inverse relationship was observed between the HA crystallinity and the dissipated energy. From these results, it can be hypothesized that a larger load amount was transferred to the low crystalline HA (particularly amorphous regions) that was stretched together with the polymer network, thus promoting the considerable energy dissipation of the composite gel. In contrast, the composite gel containing highly crystalline HA particles was too strong to be stretched with the polymer network; thus, a smaller load amount was transferred to HA, because load transfer primarily occurred at the early stage before the interfacial bonding fracture. The latter case represents a typical fracture mechanism of the strong and stiff filler-reinforced composites without strong interfacial adhesion, which is generally ineffective for enhancing mechanical properties (especially toughness). In other words, flexible reinforcements can delay the interfacial bonding rupture by stretching along with the polymer network under tension, thus increasing the material toughness.

2.3. Impregnating Macroscale Fibers/Fabrics

Fiber mesh and fiber-woven fabric reinforcements, such as thermoplastic-elastomer polylactic acid (PLA)\(^{101}\) or polyurethane fiber mesh,\(^{102}\) polycrylonitrile (PAN) fibrous films,\(^{103}\) stainless steel wool,\(^{104}\) poly(ε-caprolactone) fibers/fabrics,\(^{105,106}\) and glass fiber-woven fabrics,\(^{107–109}\) have been impregnated in hydrogel matrices to improve their mechanical properties. Previously, fiber-woven fabrics were utilized to produce 3D porous hydrogel scaffolds for tissue engineering.\(^{110}\) This method for impregnating strong and stiff fibers/fabrics on the macroscale has been widely used since the development of tough DN and PA gels.

Lin et al. fabricated a PLA fiber mesh-reinforced Alg-PAAm DN composite gel by infusing a pre-gel Alg-PAAm solution into the 3D-printed fiber mesh (Figure 6a).\(^{101}\) The resultant gel exhibited enhanced mechanical performance indicated by the unique tensile stress–strain curves. The tensile yield strength and elastic modulus of the composite gel increased by 6.5 times from 115 to 753 kPa and by 9.7 times from 660 to 6370 kPa, respectively, as compared with those of the pure polymer gel.
In addition, a considerable load was transferred to the PLA fiber mesh (continuous fibers), which increased the elastic modulus of the composite gel. After reaching the yield stretch of the fiber (≈1.4), the continuous fibers began to fracture (Figure 6b). Thus, a combination of the fiber and fiber/matrix interface fractures with matrix stretching generated the characteristic tensile stress–strain curves shown in Figure 6c.

He et al. fabricated a PAN nanofiber-reinforced Alg-PAAm DN composite gel, and Illeperuma et al. synthesized a stainless-steel wool-reinforced Alg-PAAm DN composite gel (Figure 6d). Both gels demonstrated very similar fracture behaviors. A large amount of the load transfer to the highly stiff reinforcements dramatically increased the stress generated in the short elastic region, and the subsequent failure of the fiber/matrix interface abruptly decreased its value (Figure 6e). When the fibers slide in the matrix with very few interfacial interactions (almost broken), the stretchable tough matrix receives the most load (Figure 3a). The balance between the residual stress in the fibers and the stress transferred to the matrix resulted in a plastic flow corresponding to the plateau regions in the obtained stress–strain curves (Figure 6e). Simultaneously, the stress concentration at the cavities formed between the fibers and the matrix apparently leads to a relatively early fracture (shorter strain) of the composite gel than that of the pure polymer gel. The tensile yield strength and elastic modulus of the PAN-reinforced composite gel increased by 4.4 times from 95 to 420 kPa and 170 times from 20 to 3400 kPa, respectively, as compared with those of the pure polymer gel. In the case of the stainless-steel wool-reinforced composite gel, the tensile yield strength and elastic modulus were equal to ≈640 and 7500 kPa, respectively.

King et al. and Huang et al. fabricated a glass fiber-woven fabric-reinforced PA composite gel (Figure 6f). Their PA matrices firmly adhered to the charged surfaces (indicating a strong interfacial bonding between the constituents) and underwent deswelling along with a thickness reduction, which maximized the strengthening and stiffening effect (Figure 3b). Figure 6f shows the fully fabric-impregnated composite gels with the completely adhered interfaces and low water contents. Notably, the water content in the composite gel obtained after equilibration in water was 31.9 wt% (37.6 vol%). As a result, the fabric-impregnated composite gels exhibited exceptional mechanical performance closer to that of the glass fabric rather than the pure polymer gel (Figure 6g). The produced fabric-impregnated composite gels possessed a superior tensile strength of ≈17 MPa and an elastic modulus of 606 MPa, which were 3.3 and 6060 times higher than those of pure polymer gel, respectively. Therefore, the observed degree of enhancement of the gel mechanical properties was incomparable with those of the aforementioned PLA, PAN, and stainless-steel wool-reinforced composite gels exhibited weak interfacial interactions between different components.

### 3. Polymer Matrix Manipulation by Aligning Polymer Chains

Because hydrogels contain 3D polymeric networks, their mechanical properties are determined by the polymer morphologies from the nanolevel (molecular weight, polymer structure and conformation, and crystallinity) to the macrolevel (macroscopic anisotropy, hierarchical structure, and the final product...
shape). From this perspective, several strategies have been suggested to improve the hydrogel mechanical properties, such as increasing the polymer crystallinity,[111–113] synthesizing unique microstructures containing lamellar or fibril structures,[114–116] and aligning polymer chains into an anisotropic densified structure.[117–122] However, the previous two strategies have limitedly applicable to specific polymers, including those with controllable crystallinity and microstructure, whereas aligning polymer chains could have been easily used to DN and PA gels. Therefore, in this section, we describe a universal and effective drawing method for aligning polymer chains into the anisotropic densified structure, which were successfully applied to enhance the mechanical properties of DN and PA gels on a macroscopic scale.

Drawing is considered an essential process widely used in textile engineering for strengthening and stiffening fibers/fabrics. During the drawing process, polymer chains are aligned along the longitudinal direction of the stretched fiber, and the aligned chains become held and denser by interchain bonds (e.g., hydrogen bonds). In other words, the unidirectional stretching induces randomly coiled polymer chains to be oriented with close contact, which facilitates intermolecular interactions. The oriented and intermolecular-bonded polymer chains lead to increases in the tensile strength and stiffness of the material, and the degree of increase is often further augmented if crystalline and/or hierarchical fibrous structures are formed.

Owing to the simplicity of this method and its strong reinforcing effect on the mechanical properties, it could be quickly applied to a hydrogel system, especially hydrogels that are stretchable and tough. In the typical DN and PA gels, the unidirectional stretching of the polymer network induces its anisotropic (linearly oriented) deformation,[123,124] and the subsequent fixation step such as an additional crosslinking for interchain bonds fastens the stretched state.[117–122] Because hydrogels have high water content and are easily swollen, the fixation step to hold the aligned chains is usually needed. It is noteworthy that such anisotropy is observed for natural load-bearing tissues and strongly contributes to their superior mechanical properties. Although there are also other methods for orienting polymer chains in hydrogel matrices, such as directional ion diffusion[125–129] and shear-force orientation techniques,[114,130–133] they have been rarely applied to the DN and PA gels; a detailed explanation of these methods is available in another review.[134]

Choi and Kim fabricated highly strengthened stiffened Alg-PAAm DN gels through remodeling polymer networks followed by a secondary crosslinking (i.e., drawing process consisting of pre-stretching and fixation) (Figure 7a).[118] When the DN gel was unidirectionally stretched, the polymer network was deformed and linearly oriented. The subsequent secondary ionic crosslinking between the closely and linearly aligned Alg chains induced the fixation of the stretched state. The obtained linear orientation of the polymer chains was confirmed by mechanical anisotropy. When tension was perpendicularly applied to the stretching-induced aligned chains, only a slight change in the elastic modulus of the hydrogel was observed (Figure 7b). In contrast, the elastic modulus of the hydrogel was significantly increased under tension along the stretched chain direction (Figure 7c). Accordingly, the stretching degree and secondary crosslinking ion types (fixation strength) determined the orientation of the polymer chains, the distance between the chains in the final

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Figure 7. Hydrogels reinforced by aligning polymer chains. a) Schematic showing a drawing process consisting of pre-stretching and fixation for anisotropically aligning polymer chains. b,c) Anisotropic elastic moduli of drawn Alg-PAAm gels with different pre-stretch ratios. d) Stress–strain curves for a non-pre-stretched hydrogel and pre-stretched/fixed (drawn) hydrogels. e) Elastic moduli of drawn hydrogels obtained after the fixation in different ionic solutions. Adapted with permission.[118] Copyright 2015, The Royal Society of Chemistry. f) Stress–strain curves for a non-drawn PBDT-PAAm gel and drawn gels with different pre-stretch ratios. Reproduced with permission.[120] Copyright 2020, American Chemical Society. g) Preparation of a PA gel containing repetitive cationic and anionic groups. h) Stress–strain curves for a non-drawn PA gel and drawn PA gels with different pre-stretch ratios. Adapted with permission.[140] Copyright 2016, The Royal Society of Chemistry.
hydrogel, and consequently the strength and stiffness increments (Figure 7d). As a result, the elastic modulus of the drawn Alg-PAAm hydrogel (pre-stretch ratio of 3 and subsequent Ba crosslinking) increased by 5.5 times from 200 to 1100 kPa as compared with that of the nonstretched gel (Figure 7d, green and blue lines). The ions with a stronger binding affinity to Alg chains, such as Al\(^{3+}\) and Fe\(^{3+}\), generated even stiffer hydrogels with elastic moduli as high as 5.3 MPa (Figure 7e), which were visually contrasted with the softer hydrogel (Figure 7e, the inset photographs).

Takahashi et al. recently developed a hybrid physically/chemically crosslinked PBDT-PAAm DN gel that was similar to the Alg-PAAm DN gel using a physically crosslinked PBDT network as the rigid first network\(^{[135]}\) and conducted the abovementioned pre-stretching and fixation procedures to obtain strong and stiff PBDT-PAAm DN gels.\(^{[120]}\) The stretching-induced linearly oriented PBDT was crosslinked and fixed in ZrCl\(_4\)O solution to produce a strengthened and stiffened DN gel. Because an octavalent tetramer complex [Zr(OH)\(_4\)]\(^{4+}\)4H\(_2\)O\(_{26}\) is generated in the ZrCl\(_4\)O solution and the PBDT sulfonate groups consequently form a [Zr(OH)\(_4\)]\(^{4+}\)4H\(_2\)O\(_{26}\)-PBDT coordination complex,\(^{[135–137]}\) the stretched PBDT chains can be fixed due to the formation of strong bonding by the octavalent Zr cluster. As a result, the tensile strength and elastic modulus increased by 1.8 times from 1.2 to 2.2 MPa and by 1.3 times from 1.0 to 1.3 MPa, respectively (Figure 7f, dark green and dark brown lines). Also, the resulting hydrogel exhibited mechanical anisotropy (Figure 7f).

In addition to the macroscopic stretching process for aligning polymer chains, other techniques inducing shear-force orientation, such as a 3D printing technique,\(^{[132,133]}\) could be potentially introduced to produce DN gels having intrinsically anisotropic aligned polymer chains. However, the typical radical polymerization with initiators usually demands a long UV irradiation or a high-temperature heating, which often hinders the effective quick fabrication through the 3D printing technique. Very recently, a new method has been developed to form a PAAm network under visible light with via rapid orthogonal photochemistry of ruthenium complex in a few seconds,\(^{[138,139]}\) which can be potentially applied to fabricate DN gels with the anisotropic structure.

Meanwhile, Cui et al. demonstrated that a pre-stretching process could promote strong bond (ion complex) formation during the fabrication of a PA gel (Figure 7g).\(^{[140]}\) Because multiple ionic bonds in this gel are mainly formed during dialysis in water, the pre-stretching procedure conducted before the dialysis aligned the polymer chains and made them closer to each other, facilitating the formation of strong bonds. That phenomenon was clearly confirmed by the reduced hydrogel width (Figure 7h, the inset photograph). The resulting hydrogel exhibited a 1.4-fold increase in the tensile fracture strength from \(\approx 1.7\) to 2.5 MPa. However, the pre-stretching caused little changes in the elastic modulus and tensile yield strength despite the considerable reduction in the hydrogel width, because the pre-stretching effect on the alignment of polymer chains and density increase in the PA gel was relatively weak, as indicated by the low degree of its mechanical anisotropy. Therefore, the effective hydrogel strengthening and stiffening require a combination of the (pre-)stretching and fixation processes to hold the aligned polymer chains.

### 4. Potential Methods for Enhancing DN and PA Gels

In this section, we describe some methods that have not been widely applied to DN or PA gel, but which can potentially enhance their mechanical properties, especially strength and stiffness. The first method is a combination of the reinforcement addition and drawing process. The second method includes a solvent exchange for inducing polymer matrix phase separation into sparse and dense (aggregated) regions. Such the formation of the denser and aggregated region often leads to an increase in polymer crystallinity. Because studies on the solvent exchange-induced phase separation in hydrogel matrices and its effect on the hydrogel mechanical properties have been relatively recently initiated, we will add detailed descriptions of the reinforcing and fracture mechanisms of this method that can be useful for improving hydrogel mechanical properties.

#### 4.1. Combining Reinforcement Addition with Drawing Process

Combining the previously described fabrication methods represents a powerful option for the further enhancement of the hydrogel mechanical properties. The reinforcing efficiencies of the various fillers can be ranked as spherical particles < fibers, and fiber reinforcing efficiencies are arranged in the order of totally randomly distributed fibers < randomly distributed fibers on a 2D plane < unidirectionally oriented fibers.\(^{[141,142]}\) Accordingly, applying the drawing process to a fiber-reinforced composite gel can produce a hydrogel consisting of unidirectionally aligned fibers and polymer chains, leading to a significant enhancement of the hydrogel mechanical properties. Because few studies devoted to such combinations for enhancing hydrogel mechanical properties have been published previously, we briefly describe the findings of one such report in the following.

Choi et al. fabricated a highly strengthened stiffened silica/Alg-PAAm DN composite gel, which consisted of unidirectionally aligned mesoporous silica microrods and polymer chains obtained through the drawing process (pre-stretching and fixation) (Figure 8a).\(^{[143]}\) The stretching of the composite gel containing randomly distributed mesoporous silica microrods created silica microrods and polymer chains with anisotropic orientations (Figure 8b). The drawn silica/Alg-PAAm (pre-stretch ratio of 2 and subsequent Al crosslinking) exhibited enhanced mechanical properties corresponding to a tensile strength of 0.52 kPa and an elastic modulus of 2.7 MPa (Figure 8c, blue dotted line). The authors additionally dried the stretched composite gel to increase the degree of orientational anisotropy of its components and ensure their close contact, and further crosslinked the dried gel in an Al\(^{3+}\) solution to fasten the oriented and closely located network components. The final composite gel possessed a superior tensile strength of 1.3 MPa and an elastic modulus of 7.2 MPa.

#### 4.2. Solvent Exchange for the Phase Separation in a Polymer Network

The solvent exchange-induced phase separation in a polymer matrix is an effective way to enhance the hydrogel mechanical properties. Although a few studies report that the solvent...
exchange technique can be used for fabricating homogeneously crosslinked hydrogels or organogels,[144,145] we here introduce the solvent exchange inducing the phase separation of a polymer matrix into sparse and dense (aggregated) regions. In general, a sparse region is formed by the swelling of the polymer network in a good solvent, whereas a dense region is formed by the shrinking of the polymer network in a poor solvent. These two regions in the hydrogel structure are responsible for its unique fracture mechanism. Under loading, while the stretchable polymer network in the sparse region is only slightly stretched, a considerable load amount is transferred to the highly aggregated polymer network in the dense region, drastically increasing the hydrogel strength and stiffness. In the dense region, polymer chains with specific structures or functional groups often form crystalline physically crosslinked by the highly increased number of intra/interchain bonds, which leads to further increase in the mechanical properties compared with those of general hydrogels without crystalline. Despite the multiple phenomenological studies on the phase separation and spatial inhomogeneities in polymer gels at nanoscales,[146–153] the effect of the solvent exchange-induced phase separation on the enhancement of hydrogel mechanical properties was very recently started to be investigated.

Sato et al. induced the phase separation of a PAAm matrix to create dense and sparse regions through the solvent exchange,[154] rather than via natural inhomogeneous structures. The changes of a PAAm gel in a DMF/water solvent with different DMF concentrations. Stress–strain curves of the resulting phase-separated PAAm gel. Fracture mechanism of the phase-separated PAAm gel. From the stress–strain curve of the phase-separated hydrogel (C_{DMF} = 80 wt%, φ = 43%) and illustration of the fracture mechanism (Figure 8e,f), it can be inferred that a substantial load was transferred to the dense region, and the relatively thin parts in that region were fractured first near the yield point. Thereafter, all dense areas were gradually deformed and fractured to undergo strain hardening.

In the case of chitin and cellulose hydrogels, the chitin and cellulose chains could be spontaneously bound together by physical crosslinking (such as hydrogen bonds and hydrophobic interactions) when they are aggregated.[156,157] Xu et al.[156] and Zhao et al.[157] prepared pre-chemically crosslinked chitin and cellulose hydrogels, respectively, and soaked them in aqueous ethanol. The chitin and cellulose networks were supposedly phase separated in the ethanol solution such as the phase separation of PAAm in the DMF solution.[154] The aggregated polymers became crystalline regions containing many physical crosslinking, which allowed

Figure 8. Potential methods for enhancing DN and PA gels. a) Schematic for a pure polymer, silica-reinforced composite, and drawn silica-reinforced composite gels. b) Confocal microscope images of pristine composite and drawn composite gels containing silica microrods labeled with an orange fluorescent dye. c) Stress–strain curves for Alg-PAAm (pure polymer), silica/Alg-PAAm (pristine composite), and drawn silica/Alg-PAAm (drawn composite) gels. Adapted with permission.[143] Copyright 2019, Wiley-VCH. d) The changes of a PAAm gel in a DMF/water solvent with different DMF concentrations. e) Stress–strain curves of the resulting phase-separated PAAm gel. f) Fracture mechanism of the phase-separated PAAm gel. Adapted with permission.[154] Copyright 2015, Wiley-VCH. g,h) Schematic and photographs showing a formation of phase-separated gel through a solvent exchange. i) Stress–strain curves for an initial gel (red line) and the phase-separated gel (blue line). Adapted with permission.[169] Copyright 2020, Elsevier.
the final hydrogel (even obtained after equilibrating in water) to possess significantly enhanced mechanical properties. On the other hand, Yang et al. soaked a chitosan-based hydrogel in an alkaline (NaOH) solution.\textsuperscript{[158]} Because amino groups of chitosan became deprotonated in NaOH solution, the physically cross-linked crystalline was formed in aggregated regions, which contributed to increasing hydrogel strength and stiffness. Such chitosan network could be further enhanced by some anions (e.g., phytate ions) that bind with amines.\textsuperscript{[159]} In addition to such spontaneous crystalline formation, a salt-extracting treatment can be additionally used to the phase-separated polymer matrix to fix the densely aggregated region. Because several anions (dissociated from a salt compound) such as CO$_3^{2-}$ and SO$_4^{2-}$ effectively destabilize hydrogen bonds between the hydrophilic functional groups of the polymer and water and decrease the solubility of nonpolar molecules by increasing solvent surface tension,\textsuperscript{[160–162]} soaking the hydrogel in a specific ionic solution could fix the aggregated region and additionally produce polymer crystalline in the aqueous solution.\textsuperscript{[158,161,163–167]}

Mredha and Tran et al. expanded the principle of the solvent exchange-induced phase separation and successfully fabricated slightly different kinds of hydrogels consisting of hard phase (dense) and soft phase (sparse) regions.\textsuperscript{[168,169]} Using a hydrophobic–hydrophilic copolymer, the authors produced a hydrophobic group-rich dense region with small water content and a hydrophilic group-rich sparse region with high water content (Figure 8g). Specifically, a copolymer P(AAI-co-AAm) organogel consisting of amphiphilic 3-acrylamidoisophthalic acid and hydrophilic acrylamide units was first prepared in a solvent mixture of dimethyl sulfoxide (DMSO) and water.\textsuperscript{[169]} By soaking the as-prepared organogel in pure water, the polymer matrix was separated into the hydrophilic associations and soft phase (hydrophilic associations) regions (Figure 8h). The phase-separated P(AAI-co-AAm) hydrogel equilibrated in water (water content > 70 wt\%) was opaque and had many unconnected small pores. As a result, the phase-separated hydrogel exhibited exceptional mechanical performance as compared with that of the as-prepared organogel (Figure 8i). In particular, its tensile strength and elastic modulus were equal to ≈2.9 and 40 MPa, respectively. The fracture mechanism of this gel was different from that of the abovementioned phase-separated PAAm gel in the DMF solution. In the P(AAI-co-AAm) hydrogel, while polymer networks in the dense region were gradually fractured, polymer networks in the sparse region were stretched. It can be inferred that a combination of the substantial load transfer to the hard dense region and the stretching of the soft sparse region effectively dissipated energy, which led to the high fracture strength and toughness.

5. Conclusion and Outlook

In this review, we summarized several strategies to enhance the mechanical properties of hydrogels, primarily focusing on the strengthening and stiffening aspects. The first strategy involved the addition of strong and stiff reinforcements to a polymer matrix by embedding particles, incorporating biomimetics through mineralization, and impregnating macroscale fibers/fabrics. The second strategy involved the drawing method for aligning polymer chains into the anisotropic densified structure. In addition, we discussed some potential methods for enhancing DN and PA gels, such as the solvent exchange for separating the polymer matrix on the micro- and macroscale.

Several representative hydrogels demonstrated outstanding tensile strengths and elastic moduli. The mineralized CaP/PAAm composite gel possessed a tensile strength of 1.3 MPa and an elastic modulus of 155 MPa.\textsuperscript{[92]} The PLA fiber-mesh/Alg-PAAm composite gel had a tensile strength of 0.75 MPa and an elastic modulus of 6.4 MPa.\textsuperscript{[103]} The glass fiber-fabric/PA composite gel exhibited a tensile strength of 17 MPa and an elastic modulus of 606 MPa.\textsuperscript{[107]} The highly unidirectionally oriented silica microrods/Alg-PAAm composite gel possessed a tensile strength of 1.3 MPa and an elastic modulus of 7.2 MPa.\textsuperscript{[143]} However, there is still a large gap between the existing hydrogels and natural load-bearing tissues with the elastic moduli ranging from 1 MPa to 2 GPa and the high water contents over 50%. Such a gap is expected to be decreased by optimizing and combining the aforementioned methods and elucidating the reinforcing mechanism of each approach.

In the following, we outline several factors that should be considered for achieving the optimal reinforcing effects. First, it is beneficial to select sufficiently long reinforcements with high aspect ratios and strong interfacial adhesion such as continuous fiber fabrics (as opposed to spherical particles or shorter fibers), in which a larger load amount can be transferred to the longer reinforcement.\textsuperscript{[141,142]} The strong dependence of the stiffness reinforcing efficiency on the aspect ratio of reinforcements has been demonstrated elsewhere.\textsuperscript{[84]} Simultaneously, the strong interfacial adhesion between the reinforcement and the matrix is required, because it usually determines the material yield strength and toughness. Because weak reinforcements/matrix interfacial interactions are commonly observed, interfacial bonds, rigid first network in the DN gel (weak bonds in the PA gel), and stretchable second network in the DN gel (strong bonds in the PA gel) are ruptured in the specified order (Figure 3a), which indicates that the reinforcement capability has not been fully exploited. However, in the case of the glass fiber-woven fabric-reinforced PA composite gel, the highly strong interfacial adhesion between the fiber and the matrix (Figure 3b) resulted in the exceptional mechanical properties, which more closely resembled those of the reinforcement and not the properties of the pure polymer gel (Figure 6a,b).\textsuperscript{[107,108]} Therefore, reinforcements with an appropriate aspect ratio and interfacial bonding strength will be able to produce a desirable combination of strength, stiffness, and toughness.

Second, the integration of stretching with the subsequent fixation process provides a method to ensure the formation of aligned and tightly packed polymer networks. If the aligned polymer chains are not firmly fastened through the fixation process after stretching, the drawing process cannot effectively strengthen and stiffen the hydrogel.\textsuperscript{[120,140]} In other words, strong interactions such as multiple hydrogen bonds,\textsuperscript{[121]} ionic bonds,\textsuperscript{[118,120,143]} and even a newly polymerized network\textsuperscript{[117,170]} should be formed in the stretched state.

Third, the increase in the polymer density effectively increases its load-carrying capacity. Because the fracture strength and stiffness of a polymer network are proportional to the number of polymer chains per unit volume (i.e., the polymer density),\textsuperscript{[29,171]}
the polymer aggregation into dense regions considerably increases the strength and stiffness of the hydrogel. In the case of the phase separation of the PAAm gel in the DMF solution, the average polymer volume fraction of the bulk gel was increased to 40%; however, the local polymer volume fraction of the dense region reached a value of 78%. Therefore, increasing the polymer density (even its partial increase through the solvent exchange-induced phase separation) represents an effective way for increasing the load-carrying capacity of the hydrogel.

Hence, by achieving a better understanding of the reinforcing mechanism of each method and the hydrogel fracture mechanism, one can develop an optimal method for fabricating hydrogels with desirable combinations of strength, stiffness, and toughness.

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Conflict of Interest

The authors declare no conflict of interest.

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