Development Trends in the Preparation and Application Research of High-Strength Hydrogels

Yilin He[1], Haozhen Huang[1],Yue Xing[1,2], Enbo Wei[1,3], Huiyong An[1,*]

[1]Liaoning Petrochemical University, FuShun, 113001, China
[2]CNOOC Fudao (Hainan) Chemical Co., Ltd., Dongfang, 572600, China
[3]Tianjin Bomesc Offshore Engineering Co., Ltd., Tianjin, 300452, China
[*]Corresponding author：ahy46@sina.com

Abstract: *This article explores the preparation methods and processes of high-strength hydrogels from a novel perspective of different design concepts, detailing their unique properties and characteristics. It also lists the diverse application areas of these hydrogels, including flexible electronics, biomedicine, smart materials, human-computer interaction, and energy. Additionally, the article highlights the challenges faced by current high-strength hydrogels and proposes solutions, while also outlining the future research directions for this material.*

Key words: *Hydrogel; Intensity; Preparation; Application*

Introduction

Hydrogels are a class of soft, wet polymeric materials formed through chemical or physical cross-linking, featuring a three-dimensional network structure. They exhibit high similarity to biological organisms and are one of the materials that most closely resemble the structure of living tissues[1]. However, the high water content characteristic of traditional hydrogels leads to weak interactions between polymer chains and low network cross-linking density, which consequently results in less ideal mechanical properties at the macroscopic level, such as brittleness and limited elongation at break[2]. This greatly restricts the application of hydrogels in high-load fields, including tissue engineering[3], soft robotics[4], and wearable electronic devices[5]. Therefore, how to improve the mechanical strength of hydrogels by adjusting their components and network structure is key to broadening their application domains.

Currently, the design strategies for developing high-mechanical-performance hydrogels mainly include the following four approaches:

a: Introducing "sacrificial bonds" into the hydrogel network structure. Under external force, the sacrificial bonds break first and dissipate energy, thereby enhancing the mechanical properties. A typical design model is the double-network hydrogel.

b: Adding nanoparticles such as clay, graphene oxide, silica, and carbon nanotubes to adsorb the polymer chains of hydrogels, thus forming giant physical cross-linking points. Under external force, these giant cross-linking points can dissipate energy. Additionally, the high specific surface area and high modulus of nanoparticles also contribute to enhancing the mechanical properties of hydrogels.

c: Forming a topologically structured hydrogel network, i.e., replacing fixed covalent cross-linking points with movable cross-linking points to reduce stress concentration caused by uneven distribution of chemical cross-linking points. Typical representatives are slide-ring hydrogels and tetra-arm polyethylene glycol hydrogels.

d: Constructing fully physically cross-linked hydrogels by utilizing non-covalent interactions.

In recent years, researchers have continued to synthesize and integrate the aforementioned concepts by continually optimizing monomer types, network structures, and cross-linking methods, thereby improving and expanding the preparation techniques for high-strength hydrogels and achieving many significant research outcomes. Furthermore, this article will review the research progress on high-strength hydrogels based on the above classifications, including aspects such as synthesis methods and application areas.

1. Double-Network Hydrogels

A double-network refers to a hydrogel network structure formed by the interpenetration of two polymer networks with distinct chemical structures and physical properties[6]. In double-network hydrogels, the first network is rigid and brittle, designed to fracture first under external force to dissipate energy. The second network is relatively soft and tough, serving to maintain the integrity of the hydrogel network under stress, thereby achieving high toughness[7]. Based on different cross-linking methods, researchers have developed various types of double-network hydrogels. The cross-linking methods for hydrogel networks can be categorized as fully chemically cross-linked, fully physically cross-linked, and hybrid cross-linking.

1.1 Fully Chemically Cross-Linked Double-Network Hydrogels

Fully chemically cross-linked double-network hydrogels are interpenetrating network hydrogels obtained through two-step free radical polymerization of two different monomers in the presence of chemical cross-linking agents. Both networks in these hydrogels are interconnected by chemical bonds and remain independent of each other. In 2003, Gong[8] first synthesized covalent double-network hydrogels by employing a dense rigid network as the first network and a loose flexible network as the second network through two-step sequential free radical polymerization. After the first network polymerized, a rigid polyelectrolyte network, poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), was formed. This network was then immersed in an aqueous solution containing a neutral monomer, followed by polymerization within the highly swollen polyelectrolyte network to form the second, loose covalent network of polyacrylamide (PAAm). The resulting PAMPS/PAAm hydrogel featured entangled dense short chains and loose long chains. In subsequent work, inspired by skeletal muscle, T. Matsuda et al.[9] synthesized a self-growing hydrogel. As is well known, the breakage of covalent bonds generates mechanoradicals. The fracture of the first network produces sufficient mechanoradicals, which can initiate the polymerization of remaining monomers in the hydrogel, achieving an effect similar to muscle training-induced strengthening. Although the introduction of covalent cross-linking can effectively improve the mechanical properties of hydrogels, it also has drawbacks. Due to the irreversibility of covalent bonds, covalently cross-linked hydrogels cannot return to their original state after the external force is removed. Additionally, the potential biotoxicity of cross-linking agents significantly limits the application of these hydrogels.

1.2 Hybrid Double-Network Hydrogels

Although the design of traditional double-network structures has achieved enhanced strength and toughness in hydrogels, the first network, which serves as a "sacrificial unit," is chemically cross-linked and irreversible. When subjected to external force, the first network cannot recover after fracture due to its irreversibility. Under the influence of the "Mullins effect," the mechanical properties of the hydrogel deteriorate sharply, which severely restricts the application of double-network hydrogels. Replacing irreversible chemical cross-linking with reversible physical cross-linking to prepare hybrid double-network hydrogels composed of both chemical and physical cross-linking has gradually become a hot research topic. Hybrid cross-linked double-network hydrogels possess reversible cross-linked networks that can dissipate energy during loading, promoting the fatigue resistance and recovery of double-network hydrogels[10]. Simultaneously, the covalently cross-linked network ensures that the hydrogel is sufficiently robust. Additionally, various non-covalent bonds contribute to improving the fracture resistance of the material. Since Suo introduced physically cross-linked networks into double-network hydrogel structures in 2012, many researchers have investigated such hybrid cross-linked double-network hydrogels[11]. Suo[11] combined covalent cross-linking with ionic interactions to prepare a sodium alginate-polyacrylamide hybrid double-network hydrogel. In this system, the two networks can be covalently linked through amide bonds formed between amino and carboxyl groups. The sodium alginate-polyacrylamide hydrogel has a water content of 90%, a fracture strain exceeding 20 times its initial length, and a fracture energy of 87 kJ •m^{-2}. This research not only provides a model for the deformation and energy dissipation mechanisms of hybrid double-network hydrogels but also suggests its potential as a substitute for cartilage materials. Chen[12] combined two types of cross-linked polymer networks to synthesize an ultra-tough double-network hydrogel. This ultra-tough double-network hydrogel uses physically cross-linked agar as the first network and covalently cross-linked polyacrylamide (PAAm) as the second network. The agar/PAAm double-network hydrogel exhibits good mechanical properties, with a fracture energy of 102 to 103 J • m^{-2}. Due to the reversible sacrificial bonds in the first physically cross-linked network, the hybrid cross-linked double-network hydrogel demonstrates excellent mechanical properties, including stable elasticity and toughness, resilience to large deformations, and high compressive strength. However, the polymer chains in hybrid cross-linked double-network hydrogels expand slowly, and the physically cross-linked network contributes minimally to the self-healing effect of the hybrid double-network hydrogel system[12].

1.3 Fully Physically Cross-Linked Double-Network Hydrogels

The methods for preparing ultra-tough double-network hydrogels also include replacing both networks of different cross-linked structures in double-network hydrogels entirely with physically cross-linked networks[13]. Dual physically cross-linked hydrogels based on non-covalent interactions have attracted significant attention due to their excellent mechanical properties and self-healing capabilities. Both the first and second networks are entirely formed through orthogonal types of non-covalent bond interactions. Hydrogels formed via this process can better withstand stress and dissipate energy based on a "reversible chain association-dissociation" mechanism, thereby enhancing the hydrogel's toughness and self-healing properties[14].

The Cheng research group first reported a Hofmeister effect-enhanced sodium polyacrylate and polyvinyl alcohol double-network hydrogel based on polyelectrolytes. The carboxylate ions in sodium polyacrylate can polarize the hydrated molecules surrounding polyvinyl alcohol, inducing their aggregation to form crystals that act as effective cross-linking points within the hydrogel network. This significantly improves the mechanical properties of the double-network hydrogel. Compared to non-polyelectrolyte hydrogels, its tensile strength, compressive strength, Young's modulus, toughness, and fracture energy increased by 73 times, 64 times, 28 times, 135 times, and 19 times, respectively [15]. The Lu research group designed a physically cross-linked double-network hydrogel based on carboxyethyl chitin and polyacrylamide. This hydrogel exhibits outstanding mechanical properties: a tensile strain of up to 1586%, a tensile stress of up to 214 kPa, and a toughness of approximately 1.3 MJ/m^3 . The primary reason for this is the abundant non-covalent interactions, such as hydrogen bonds and hydrophobic interactions, between the rigid backbone of carboxyethyl chitin and polyacrylamide, which provide numerous non-covalent cross-linking sites, greatly enhancing the material's mechanical properties[16]. Yang[17] synthesized a fully physically cross-linked poly(N-hydroxymethylacrylamide)/agar/ethylene glycol (PHA/Agar/EG) ionically conductive double-network hydrogel. The PHA/Agar/EG double-network hydrogel possesses high toughness (25.43 MJ•m^{-3}), high strength (1.75 MPa), high fracture energy (1545 J•m^{-2}), rapid self-recovery, good fatigue resistance, and excellent self-healing properties. The PHA/Agar/EG double-network hydrogel relies on its physically cross-linked network structure and hydrogen bonding with agar for enhancement.

2. Topological Network Hydrogels

Topological gels are characterized by their figure-8 cross-linked loops as a typical structural feature, and this type of cross-linking structure within such gels can slide freely along the polymer chains. Excellent extensibility and superior swelling capacity are the outstanding properties of topological gels[18]. Inspired by interlocked topological structures, the Okumura research group reported the first slide-ring hydrogel based on a freely movable rotaxane-type topological cross-linking structure in 2001[19]. The ingenuity of this gel design lies first in fully mixing amine-terminated polyethylene glycol (PEG) with α-cyclodextrin in an aqueous solution, enabling the long-chain PEG to be threaded through α-cyclodextrin molecules. The PEG ends were then capped with bulky groups to prevent the cyclodextrins from slipping off the PEG chain. Finally, under specific conditions, two cyclodextrin molecules were linked to form a figure-8 cross-link, connecting the long-chain PEG via physical cross-linking. When external stress is applied, this gel can dissipate energy through the sliding of the figure-8 cross-links, thereby preventing the fracture of the long polymer chains. Gels prepared by this design method exhibit excellent flexibility; after optimization of functional groups, their fracture elongation can exceed 20 times, and even after absorbing 400 times their weight in water, the dry gel can maintain its solid shape without breaking. In-depth studies using small-angle neutron scattering on this unique structure confirmed that when the slide-ring hydrogel deforms under external stress, the slide-ring effect avoids stress concentration, as the network structure does not undergo significant deformation and remains uniform. Fleury et al.[20] investigated PEG-α-CD topological gels and concluded that the structure and properties of topological gels are influenced by factors such as cross-linking density, the number of cyclodextrins, and the solvent.

Although topological gels possess excellent properties, their preparation methods are highly specific, and the monomer materials suitable for preparing topological hydrogels are very limited, currently primarily confined to the PEG-α-CD system. These gels enhance the structural regularity of hydrogels at the microscopic level, turning the conceptual model of sliding cross-links into reality, which holds significant importance for the development of chemically cross-linked polymer materials.

3. Non-covalent Interaction Hydrogels

When external force is applied to non-covalently cross-linked hydrogels, the non-covalent bonds with lower bond energy are prone to break, thereby effectively dissipating the external force energy and consequently enhancing the mechanical properties of the hydrogel material. Common non-covalent interactions primarily include hydrogen bonding, hydrophobic association, metal coordination bonding, dipole-dipole interactions, host-guest interactions, and electrostatic interactions[21]. Furthermore, multiple non-covalent interactions can be combined to achieve a synergistic enhancement effect, forming hydrogels with multi-network structures.

3.1 Hydrogen-Bonded Hydrogels

Hydrogen bonding is the most widely utilized force in constructing hydrogels. Formed through interactions between hydrogen atoms and oxygen, nitrogen, or fluorine atoms, hydrogen bonds are characterized by low bond energy, high directionality, and reversible nature. Studies indicate that the bond energy of a single hydrogen bond ranges between 4.2 and 29.4 kJ/mol, which is relatively weak and leads to easy rupture. However, hydrogen bonds rarely exist in isolation; the synergistic effect of multiple consecutive hydrogen bonds can multiplicatively enhance the overall hydrogen bond strength[22]. Furthermore, if hydrogen bonds break, their dynamic and reversible nature allows them to re-associate. This association-dissociation process is highly conducive to energy dissipation within the material. The strategy based on synergistic enhancement through multiple hydrogen bonds is widely applied in constructing high-mechanical-performance hydrogel materials.

The research group of Liu Guangwen at Tianjin University[23] reported a hydrogel with dual hydrogen bonding interactions. The team first synthesized the N-acryloylglycinamide (NAGA) monomer, which contains diamide groups, and then prepared a PNAGA hydrogel with dual hydrogen-bond cross-linking via free radical polymerization of the NAGA monomer. Due to the reversible nature of hydrogen bonding, fragmented hydrogel pieces could completely restore their original structure and mechanical properties after being placed in a 90° C water bath for three hours. Simultaneously, owing to the dual hydrogen bonds within the gel, this hydrogel also exhibits excellent thermoplasticity and mechanical properties, achieving a tensile strength of up to 1.1 MPa. Li et al.[24] reported a fluorescent hydrogel based on multiple hydrogen bonding interactions, prepared from various raw materials including agar, chitosan, polyvinyl alcohol, borax, and glycerol. The first type of hydrogen bonds formed between agar and chitosan, polyvinyl alcohol and chitosan, and agar and polyvinyl alcohol endowed the hydrogel with outstanding mechanical properties, reaching a tensile strength of 6 MPa. Additionally, a third set of hydrogen bonds formed between carbon quantum dots/MXene and other components in the system imparted fluorescent properties to the hydrogel.

3.2 Hydrophobically Associating Hydrogels

Hydrophobically associating hydrogels utilize hydrophobic interactions to form physical cross-links, thereby enhancing the stiffness and toughness of the hydrogel. The hydrophobic segments within the copolymer chains can entangle within micelles, forming physical cross-links. The physically cross-linked structures formed by hydrophobic association effectively hinder crack propagation and absorb substantial deformation energy, significantly improving the mechanical properties of the hydrogel[25].

Gu et al.[26] prepared a dually physically cross-linked P(HMA-co-AAm) hydrogel, which was initiated using cationic latex particles serving as both hydrophobic association and ionic cross-linking centers. The hydrophobic association arises from the interaction between the alkyl chains of HMA and the surface of the cationic latex particles. The maximum tensile strength and toughness of the P(HMA-co-AAm) hydrogel reached 1.32 MPa and 4.53 MJ/m^3, respectively. Surfactants play a significant role in the preparation of hydrophobically associating hydrogels, especially the combined use of different surfactants. Gao et al.[27] employed sodium dodecyl sulfate (SDS) and gum arabic (GA) as surfactants to prepare hydrogels toughened by PBA latex particles. The combined use of surfactants effectively reduced surface tension and formed stable hydrophobic association centers, which stabilized the hydrophobic segments and consequently enhanced the fracture stress and toughness of the hydrogel.

3.3 Metal-Coordinated Self-Healing Hydrogels

Metal coordination bonds are a type of chemical bond formed by metals providing empty orbitals and ligands providing lone pair electrons. The binding equilibrium constant (K_{eq}) of metal coordination bonds is typically influenced by factors such as the type of metal atom and the ligand structure, with K_{eq} values ranging from 10^{3} to 10^{40}. Metal coordination bonds generally exhibit dynamic reversibility, making their introduction an effective strategy for preparing high-strength hydrogels. Li et al.[28] from the California State Polytechnic University, USA, added Fe(III) and polyacrylamide-grafted cellulose nanocrystals (CNC-g-PAM) into an acrylic acid solution and prepared a self-healing nanocomposite hydrogel via in-situ free radical polymerization of the acrylic acid monomer. This nanocomposite hydrogel possesses a dual physically cross-linked network structure. Metal coordination bonds between the carboxyl groups of PAA and Fe(III) ions constitute one physical cross-linked network, while hydrogen bonding between the PAM chains on the CNC-g-PAM surface and the PAA matrix acts as reinforcing nanofillers and physical cross-linkers. This nanocomposite hydrogel achieves a tensile strength of up to 250 kPa and an elongation at break of up to 750%.

3.4 Multiple Non-covalent Cross-linked Hydrogels

A growing body of research demonstrates that constructing high-mechanical-performance hydrogels through multiple non-covalent interactions is an effective strategy. The Gao Guanghui research group utilized a "two-step method" to prepare high-mechanical-performance hydrogels based on hydrogen bonding, hydrophobic association, coordination, and electrostatic interactions[29]. The Sun Junqi research group reported a strategy for constructing high-strength and multifunctional hydrogels utilizing hydrogen bonding and electrostatic interactions[30]. In a collaborative effort, the team of Tian Xingyou/Zhang Xian and the team of Yang Yanyu employed gallium-indium alloy to initiate polymerization, simultaneously using it as a flexible filler, to construct a multifunctional hydrogel with ultra-stretchability and self-healing properties. The synergistic effect between the rigid polyvinyl alcohol microcrystalline network and the tough hydrophobic network, coupled with multiple non-covalent cross-linking interactions within the polymer networks such as ionic coordination and hydrogen bonding, endowed the hydrogel with excellent multifunctionality including ultra-stretchability, toughness, notch-insensitive tear resistance, and self-healing capability[31].

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