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Review Paper

Preparation and Application Progress of Starch-Based Hydrogels

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Abstract. Hydrogels are polymeric materials with a three-dimensional network structure formed via the crosslinking of hydrophilic polymer chains, exhibiting strong water absorption and water retention properties. Starch is a natural, environmentally friendly polysaccharide. Starch-based hydrogels have attracted widespread attention due to their favorable biocompatibility, strong biodegradability, and excellent solvent absorption capacity. This review briefly describes common starch modification methods. Subsequently, the preparation of starch-based hydrogels is summarized from three perspectives: chemically cross-linked starch-based hydrogels, physically cross-linked starch-based hydrogels, and double-cross-linked starch-based hydrogels. Furthermore, the application progress of starch-based hydrogels in biosensors, medical dressings, drug delivery carriers, tissue engineering scaffolds, agricultural soil protection, and other fields is introduced. Finally, in view of the existing challenges, future development directions for starch-based hydrogels are proposed.

Keywords: *Starch modification; Starch-based hydrogels; Biodegradation; Biosensor; Medical dressings; Drug transport carriers; Tissue engineering stents*

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1 Introduction

Hydrogels are hydrophilic three-dimensional network polymers formed through chemical or physical crosslinking of hydrophilic polymer chains, first synthesized by WICHTERLE in 1954[1]. Characterized by a soft texture, tunable mechanical properties, high swellability, high water absorption, and high water retention, hydrogels can also encapsulate diverse materials. They are currently widely applied in agricultural industry, pharmaceuticals, medicine, and food sectors.

Based on their source, hydrogels can be classified into natural and synthetic polymer hydrogels. Starch is an environmentally friendly natural polysaccharide with abundant hydroxyl groups on its molecular chains. Starch consists of amylose and amylopectin: amylose is linked by α-1,4-glycosidic bonds, while the main chain of amylopectin comprises α-1,4-glycosidic bonds with branches connected via α-1,6-glycosidic bonds[2]. Starch is abundant, low-cost, non-toxic, and non-irritating. Hydrogels prepared from starch exhibit good biocompatibility, strong biodegradability, and tunable physicochemical properties, establishing them as one of the most promising bio-based materials.

With increasing environmental awareness, starch hydrogels with excellent biodegradability and biocompatibility have garnered significant attention. This article summarizes starch modification methods, the synthesis of starch-based hydrogels, and their application progress in biosensors, medical dressings, drug delivery carriers, tissue engineering scaffolds, and agricultural soil protection. Future prospects for starch-based hydrogels are also discussed.

2 Starch Modification

Starch is abundant and low-cost, making it highly attractive for developing novel biodegradable materials with promising industrialization prospects. However, starch-based materials often suffer from high water sensitivity and low mechanical strength, necessitating modification to meet specific application requirements. Common starch modification methods include physical modification, chemical modification, enzymatic modification, and composite modification.

2.1 Physical Modification

Physical modification typically improves starch properties without disrupting granular structure and without generating wastewater or by-products. It mainly includes thermophysical modification and non-thermal physical modification. Thermophysical modifications primarily involve dry heat treatment (DHT) and heat-moisture treatment (HMT)[3-4]. Non-thermal physical modifications employ technologies such as ultrasonication, high hydrostatic pressure (HHP), pulsed electric fields (PEF), micronization, cold plasma, and electron beam irradiation (EBI)[5-9]. Beyond these common techniques, pressure-moisture treatment (PMT) alters starch's physicochemical properties and may emerge as a novel physical modification method. KIM et al.[10]modified starch via PMT, experimentally verifying that PMT rearranged starch molecular structure by strengthening interactions between amylose molecules or between amylose and amylopectin. This reduced equilibrium moisture content, solubility, and swelling power, elevated gelatinization temperature, and increased resistant starch (RS) and slowly digestible starch (SDS) contents.

2.2 Chemical Modification

Unlike physical modification, chemical modification utilizes various additives to react with the abundant reactive hydroxyl groups in starch structures via oxidation, esterification, crosslinking, etherification, etc., thereby introducing new functional groups. Chemically modified starch exhibits enhanced functionality and broader application scopes. Octenyl succinic anhydride (OSA) treatment yields octenyl succinic anhydride starch (OSAS). Here, the anhydride ring of OSA opens; one end reacts with starch hydroxyls to form ester bonds, while the other generates a carboxylic acid. OSAS contains both hydrophilic carboxyl groups and hydrophobic alkenyl groups, rendering it amphiphilic with excellent emulsifying properties. Meanwhile, OSA-modified starch exhibits increased viscosity and reduced gelatinization temperature, making it suitable as a thickener[11]. CLASEN et al.[12]modified starch via etherification with maleic acid derivatives (diethyl maleate, dipropyl maleate, dibutyl maleate) to produce etherified starch. Changes in intramolecular and intermolecular hydrogen bonding interactions in etherified starch conferred stronger hydrophobicity compared to native starch.

2.3 Enzymatic Modification

Enzymatic modification is an innovative, eco-friendly approach that selectively targets specific glycosidic bonds or types of glycosidic bonds in starch molecules via enzymes, enabling specific structural and functional modifications. It operates under mild conditions and yields specific products. Enzymes commonly used include amylases, transglycosidases, branching enzymes, and debranching enzymes. 4-α-Glucanotransferase (4αGT) catalyzes intermolecular or intramolecular glycosylation reactions. 4αGT modification alters amylopectin and amylose contents and relative molecular weights, improves freeze-thaw stability, and yields thermally reversible starch gels[13]. Modifying pea starch with Bacillus-derived α-amylase reduced amylose content and particle size; oil absorption capacity and gelatinization enthalpy increased significantly with prolonged enzymatic hydrolysis[14].

2.4 Composite Modification

Composite modification integrates two or more of the aforementioned modification methods, further enhancing starch functionality and utilization efficiency across diverse applications. Compared to single methods, composite modification offers shorter reaction times, higher efficiency, and broader applicability. Pretreating starch with ultrasonication or pulsed electric fields prior to OSA chemical modification yields modified starch with higher degree of substitution (DS) and improved emulsifying capacity and stability[15-16]. ZHENG et al.[17]pretreated high-amylose corn starch via acid hydrolysis before esterification. DS increased progressively with prolonged acid hydrolysis. Ultrasonic-induced molecular motion overcomes internal mass transfer barriers

during enzymatic treatment, effectively enhancing traditional enzymatic modification efficiency. DAI et al.[18]modified starch via composite enzymatic treatment or ultrasound-composite enzymatic treatment. Compared to composite enzymatic modification alone, ultrasound-composite enzymatic modification further reduced amylose content, significantly increased branch density, elevated relative crystallinity, and resulted in more ordered molecular arrangement and stabilized structures. The sequence of modification techniques in composite processes also influences starch properties. WANG et al.[19]modified chestnut starch via ultrasonication, microwave treatment, ultrasonication-microwave (UM), or microwave-ultrasonication (MU). In UM treatment, initial ultrasonication severely disrupted starch crystalline regions, fractured starch chains, and loosened structures; subsequent microwave treatment intensified these changes, yielding UM-modified starch with maximal oil absorption capacity. In MU treatment, prior microwave processing promoted molecular rearrangement, weakening synergistic effects during subsequent ultrasonication; thus, MU-modified starch exhibited maximal water absorption capacity.

3 Preparation of Starch-Based Hydrogels

Starch-based hydrogels can be classified by crosslinking mechanism into chemically cross-linked, physically cross-linked, and double-cross-linked variants. Crosslinking type and extent govern hydrogel swelling ratio, adhesion, mechanical properties, and molecular transport within the network pores.

3.1 Chemically Cross-Linked Starch-Based Hydrogels

Chemical crosslinking involves covalent bond formation to create durable three-dimensional networks, mediated by starch's native functional groups or introduced crosslinkers with reactive end-groups, under mechanical force, ultrasonication, high-energy radiation, light, heat, etc.[20]. Common chemical crosslinking strategies for starch-based hydrogels include free radical polymerization, Michael addition, click chemistry, enzymatic crosslinking, Schiff base reaction, radiation crosslinking, and photopolymerization.

3.1.1 Free Radical Polymerization Crosslinking

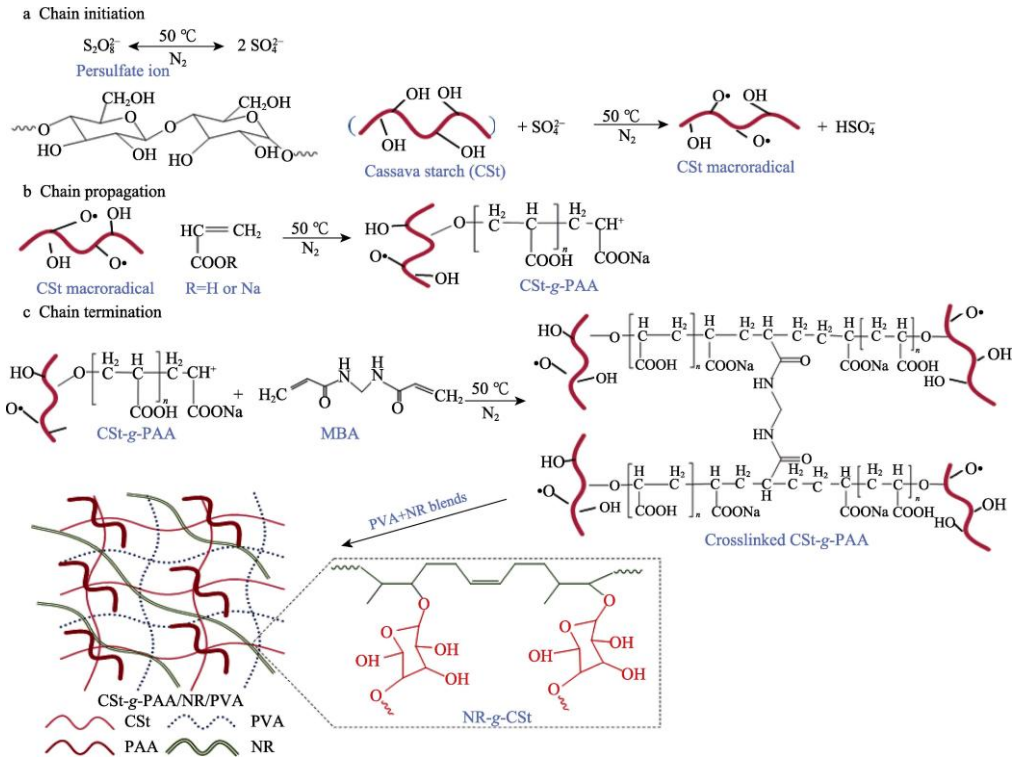

Figure 1 Schematic diagram of reaction mechanism of CSt-g-PAA/NR/PVA hydrogels synthesis[21].

Free radical polymerization is a prevalent method for hydrogel synthesis, primarily via two routes: (1) polymerization of one or more low-molecular-weight vinyl monomers initiated by a crosslinker; (2) derivatization of non-polymerizable water-soluble polymers to bear polymerizable groups, followed by cross-copolymerization. TANAN et al.[21]grafted acrylic acid (AA) onto cassava starch (CSt) using ammonium persulfate (APS) as initiator and N,N'-methylenebisacrylamide (MBA) as crosslinker, obtaining crosslinked CSt-g-PAA solution. Incorporating natural rubber (NR)/polyvinyl alcohol (PVA) blends yielded a low-cost, eco-friendly semi-interpenetrating polymer network hydrogel (CSt-g-PAA/NR/PVA) (Fig. 1). This hydrogel exhibited excellent water retention (63.5% retention after 12 h at 30 °C) and swelling ratios of 794% in distilled water and 244% in 0.9% NaCl aqueous solution. It maintained good swellability over five swelling-drying cycles, demonstrating reusability. ZHAO et al.[22]fabricated starch hydrogel/contact lens composites loaded with epigallocatechin gallate (EGCG) via in situfree radical polymerization. These composites exhibited stronger sustained drug release than conventional hydrogel contact lenses, with EGCG releasing continuously for at least 14 days in deionized water.

3.1.2 Michael Addition Crosslinking

Michael addition involves conjugate addition between an electrophilic conjugated system (electron acceptor) and a nucleophilic carbanion (electron donor), typically between unsaturated carbonyl compounds (aldehydes, ketones, etc.) and nucleophiles (cyanide, halide, thiol, or amine compounds). Starch often requires pre-modification to introduce new groups before Michael addition yields stable hydrogel structures. YAO et al.[23]developed a durable dihydrolipoic acid-modified sulfobetaine-derived starch (SB-ST-D) hydrogel coating for poly(ethylene terephthalate) (PET)-based blood-contacting devices. Polydopamine (PDA) was first deposited onto PET surfaces (PDA/PET). Subsequently, SB-ST-D was covalently immobilized onto PDA/PET via Michael addition between dihydrolipoic acid groups/catechol groups on SB-ST-D and the PDA/PET surface, yielding SSD/PET. Dihydrolipoic acid groups in SB-ST-D served as anchors, forming covalent bonds with the PDA/PET surface while acting as crosslinking sites to form stable SB-ST-D hydrogel coatings via disulfide bonds. These hydrophilic coatings resisted protein adsorption, inhibited cellular and platelet adhesion, alleviated in vivoinflammatory responses, and prevented thrombosis. Functionalizing SB-ST-D hydrogel coatings with endothelial cell-specific peptide REDV (SSDR/PET) not only promoted human umbilical vein endothelial cell (HUVEC) adhesion, proliferation, and migration but also inhibited human aortic smooth muscle cell (HASMC) adhesion and proliferation (Fig. 2).

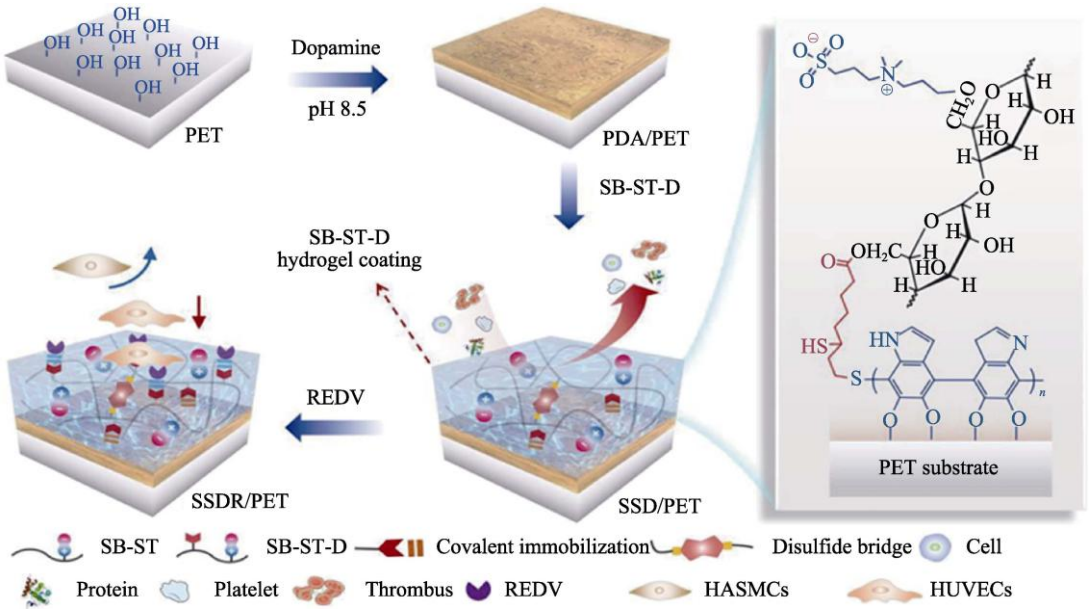

Figure 2 Schematic representation of preparation of SB-ST-D hydrogel coating[23].

LI Yangling et al.[24]synthesized cysteine-based starch and dopamine-based starch derivatives via grafting modification. Michael addition between these derivatives yielded an injectable all-starch-based hydrogel.

Adjusting the molar ratio of the two starch derivatives allowed tuning of gelation time from 3 min to 24 h. DONG et al.[25]prepared amphoteric starch-based "clickable" S/P hydrogels via Michael addition between acylated sulfoxide-derived starch (SB-ST-A) and dithiol-functionalized polyethylene glycol (PEG-SH). These hydrogels served as in vitro3D cell encapsulation systems. Fluorescence imaging revealed >95% viability of encapsulated cells, which maintained high metabolic activity (Fig. 3).

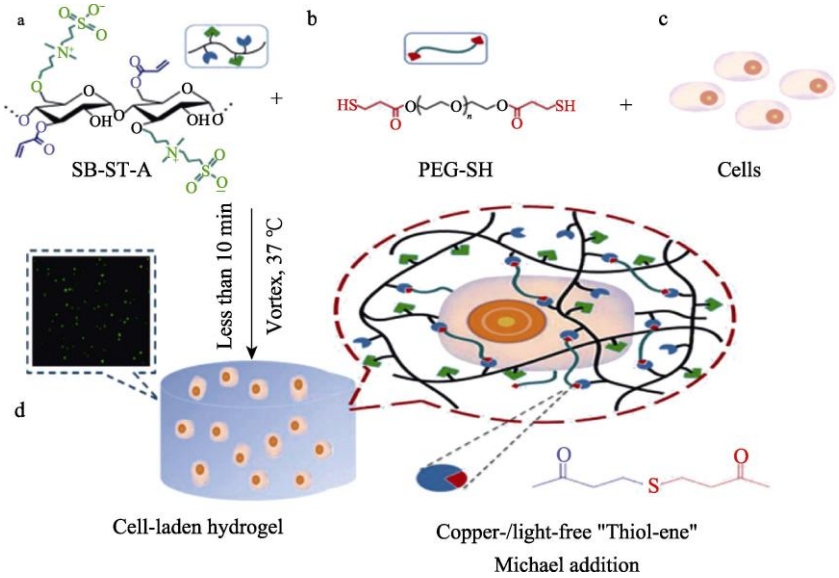

Figure 3 "Thiol-ene" S/P hydrogel for 3D cell encapsulation and culture in vitro[25].

3.1.3 Click Chemistry Crosslinking

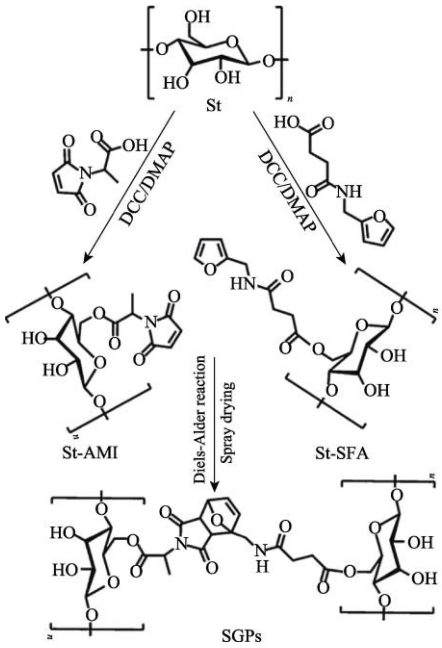

Figure 4 Schematic diagram of synthesis route of esterified starch and SGPs[26].

Click chemistry crosslinking efficiently constructs diverse molecules via splicing of small units. It features simple procedures, rapid reaction rates, minimal by-products, high yields, and tolerance to other functional groups, garnering significant interest for hydrogel fabrication. WEI et al.[26-27]esterified soluble starch (St) to obtain N-maleoylalanine-modified starch (St-AMI) and succinamide-modified starch (St-SFA). Subsequent spray drying combined with Diels-Alder click reactions yielded hydrogel microspheres (SGPs) (Fig. 4). Loading with 5-

fluorouracil (5-Fu) produced drug-loaded starch-based hydrogel microspheres exhibiting sustained release over >180 min—three times longer than unloaded microspheres. Additionally, sequential Diels-Alder click reactions and in situphotopolymerization in water yielded starch-cellulose interpenetrating network hydrogels (IPN-Gel). Their porous network structure and high crosslinking density conferred superior sustained release properties, with drug release sustained for up to 400 min.

3.1.4 Schiff Base Reaction Crosslinking

Schiff base crosslinking forms dynamic imine bonds between amines and aldehydes. Starch-based hydrogels crosslinked via Schiff base linkages are extensively explored due to their high sensitivity, good flexibility, and recyclability. SARMAH et al.[28]incorporated amino-modified chitosan into aldehyde-rich oxidized starch backbones via dynamic Schiff base reactions, fabricating oxidized starch-chitosan-based hydrogels. As drug delivery vehicles, these hydrogels achieved a maximum encapsulation efficiency of 90.66% ± 0.85% and demonstrated potential as pH-dependent drug release systems. RUI et al.[29]prepared CMCS/OPL hydrogels via Schiff base crosslinking between carboxymethyl chitosan (CMCS) and oxidized pullulan (OPL). Biodegradable mesoporous silica nanoparticles loaded with the anticancer drug methotrexate (BMSN-MTX) were encapsulated within this hydrogel. Dynamic imine bonds between OPL and CMCS hydrolyzed readily in acidic media, enabling pH-triggered, controlled delivery of methotrexate (MTX).

3.1.5 Photopolymerization Crosslinking

Photopolymerization employs visible or ultraviolet light interacting with photoinitiators to generate active radicals, which subsequently initiate chain polymerization with visible-light-curable oligomers. Hydrogel fabrication via photopolymerization requires merely minutes or even seconds, drastically 缩短反应时间 compared to thermal curing, representing an economical, efficient, accurate, and rapid preparation method. Photoinitiators are crucial, typically categorized as radical or cationic types. NOE et al.[30]gelatinized amylose and methacrylated it. Using lithium phenyl(2,4,6-trimethylbenzoyl)phosphinate (LAP) as photoinitiator, UV curing successfully yielded methacrylated starch hydrogels with good mechanical properties and biocompatibility. Digital light processing (DLP) 3D printing validated the photo-processability of methacrylated starch. MAJCHER et al.[31]fabricated starch nanoparticle (SNP) network hydrogels via photopolymerization. Esterification with methacrylic anhydride introduced photopolymerizable methacrylate groups onto starch. Photoinitiation induced radical chain-growth polymerization within SNP suspensions, crosslinking SNPs into hydrogels. Compared to linear starch, SNPs formed stiffer, denser hydrogels that resisted cell adhesion while maintaining high cytocompatibility. MOGHADAM et al.[32]polymerized starch-poly(ethylene glycol) acrylate (starch-PEGT), ethylene glycol monoacrylate (EGMA), and modified Fe_3O_4 nanoparticles (NPs) under blue light using camphorquinone (CQ) as photoinitiator, yielding photocurable starch-based hydrogels. As quercetin delivery systems, these hydrogels exhibited high drug loading capacity and enhanced release rates, achieving 56.62% release within 8 h.

3.1.6 Radiation Crosslinking

Radiation crosslinking employs high-energy radiation (γ-rays, electron beams) to irradiate monomer solutions, generating active high-energy particles that initiate polymerization and crosslinking of macromolecules to form covalent networks. This method offers rapid reaction rates and high synthesis efficiency. Hydrogel yield and swelling behavior can be tuned by adjusting radiation dose. SAYED et al.[33]employed γ-ray irradiation-induced crosslinking polymerization to fabricate green nanocomposite hydrogels (ST-PHEMA/GO) reinforced with starch and varying ratios of graphene oxide (GO). GO distribution within the ST-PHEMA matrix became more uniform with increasing irradiation dose. CHEN et al.[34]pre-loaded urea into starch suspensions, then irradiated them to initiate acrylamide (AM) grafting onto corn starch, yielding starch hydrogel-grafted monolithic urea slow-release fertilizer (Fig. 5). Increasing radiation intensity and monomer concentration enhanced grafting efficiency and monomer conversion, elevated hydrogel crosslinking density, and reduced urea release rates. Thus, urea release kinetics from starch hydrogels can be controlled by modulating radiation intensity.

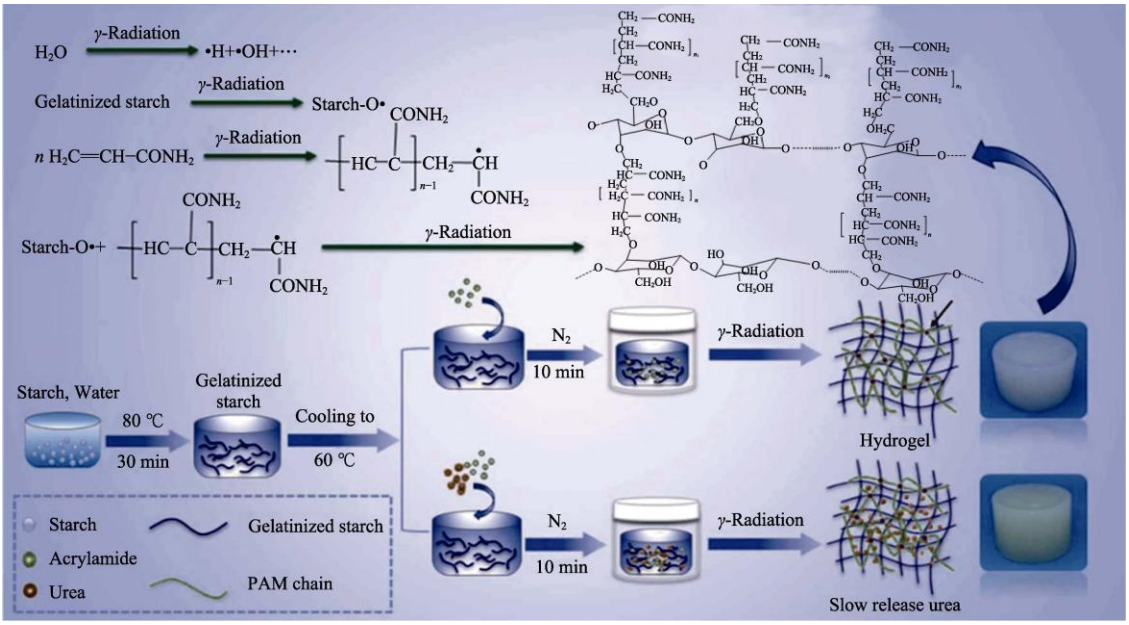

Figure 5 Schematic representation of procedure and principle of polyacrylamide (PAM) grafted starch under γ-ray irradiation[34].

3.1.7 Enzymatic Crosslinking

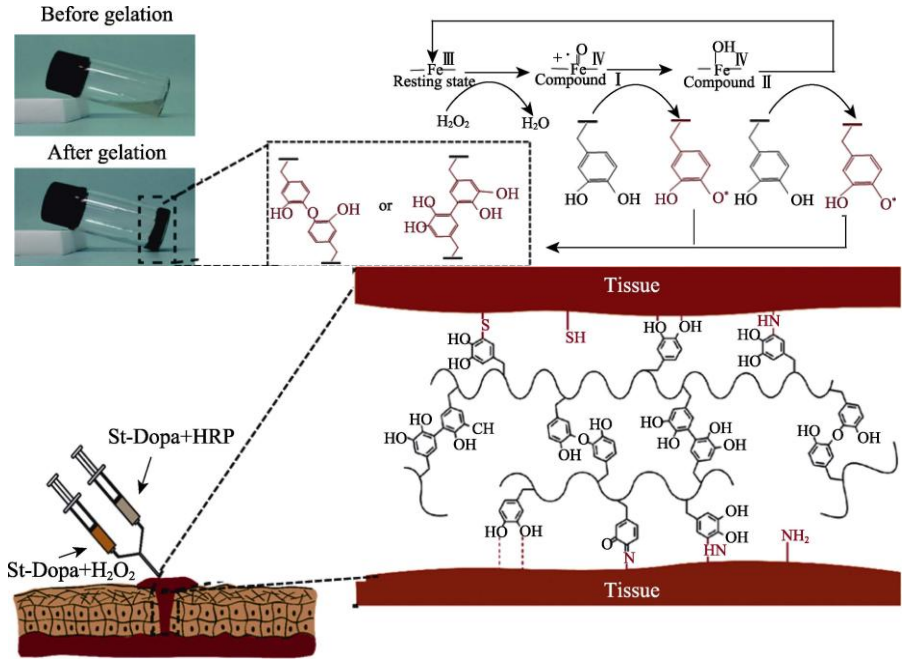

Figure 6 Schematic diagram of enzymatic crosslinking mechanism of St-Dopa hydrogel and its use as a hemostatic material[36].

Enzymatic crosslinking avoids chemical initiators and organic solvents, operating under mild conditions with high catalytic efficiency. Gelation kinetics can be regulated by controlling enzyme concentration, pH, temperature, and other physical parameters, offering immense potential for broadening starch-based hydrogel applications. Tyrosinase- or peroxidase-mediated oxidative crosslinking represents the primary enzymatic approach. Horseradish peroxidase (HRP), a redox enzyme catalyzing diverse oxidation reactions, is widely used to crosslink polymers bearing phenolic groups into 3D hydrogel networks. ESKANDANI et al.[35]developed magnetic hydrogels via HRP-mediated crosslinking, comprising tyramine-functionalized starch, tannic acid, and modified

Fe_3O_4 nanoparticles. These hydrogels exhibited saturation magnetization and porous microstructures (saturation magnetization, δs= 19.2 emu/g; pore size = (2400 ± 200) nm at ~7.4 wt% Fe_3O_4). Loaded with the anticancer drug doxorubicin (Dox), they demonstrated enhanced anticancer activity against MCF-7 breast cancer cells via synergistic chemo-hyperthermia therapy. CUI et al.[36]prepared injectable, tissue-adhesive St-Dopa hydrogels via enzymatic crosslinking, composed of starch, succinic anhydride, and dopamine. Under HRP catalysis, catechol radicals generated intermolecular covalent bonds via C-C coupling between adjacent carbons on aromatic rings or C-O coupling between adjacent carbons and phenolic oxygens (Fig. 6). Catechol groups in dopamine served dual roles as crosslinking segments and interfacial adhesives. Consequently, the hydrogels exhibited excellent tissue adhesion in moist environments, tightly binding to biological tissues to form protective barriers and reduce hemorrhage.

3.2 Physically Cross-Linked Starch-Based Hydrogels

Unlike chemical crosslinking forming covalent bonds, physically cross-linked starch-based hydrogels require no crosslinkers, relying solely on non-covalent interactions between polymers to form networks. Physical crosslinking points are essential and can form via hydrogen bonding, electrostatic interactions, coordination bonds, etc. Physical crosslinking enables rapid, on-demand gelation. While weaker than covalent bonds, these interactions are often reversible under specific conditions, facilitating the design of self-healing and stimuli-responsive materials with potential in life sciences and biomedicine.

3.2.1 Hydrogen Bonding

Hydrogen bonding involves electrostatic attraction between a hydrogen atom and an electronegative atom. It is directional and reversible, serving as a common strategy for constructing 3D hydrogel networks. LU et al.[37]fabricated high-strength, high-modulus, high-toughness SPGN hydrogels using starch, PVA, glycerol (Gly), and sodium citrate (Na_3Cit) via cyclic freeze-thaw cycles and soaking strategies (Fig. 7). SPGN gels exhibited excellent ionic conductivity [(1.47 ± 0.03) S/m] and mechanical properties (tensile strength: 1.45 MPa; elongation at break: 842%; Young's modulus: 8.85 MPa). Gly acted as a crosslinking point, linking starch and PVA chains via hydrogen bonds, enhancing compatibility and imparting good anti-freezing properties. At −15 °C, SPGN gels retained mechanical flexibility (1.33 MPa) and high ionic conductivity (0.5 S/m). DAI et al.[38]prepared conductive PGLA hydrogels with excellent toughness, water retention, anti-freezing properties, and biocompatibility via physical freeze-thaw cycling using PVA, amylopectin, Gly, and LiCl. Assembled into wearable sensors, PGLA hydrogels monitored various bodily strains, from large to subtle movements. ZHANG et al.[39]fabricated physically cross-linked hydrogels with a PAAm/PVA double network reinforced by amylopectin (Amy). Weak hydrogen bonds existed between PAAm and PVA chains; introducing Amy generated strong hydrogen bonds between Amy and PAAm/PVA. Synergy between weak and strong hydrogen bonds endowed Amy/PAAm/PVA hydrogels with high tensile strength (854.1 kPa), high ductility (~8×), high volumetric toughness (4094.8 kJ/m³), good self-recovery (≈92% at room temperature), and strong adhesion to non-porous glass surfaces (~158 kPa).

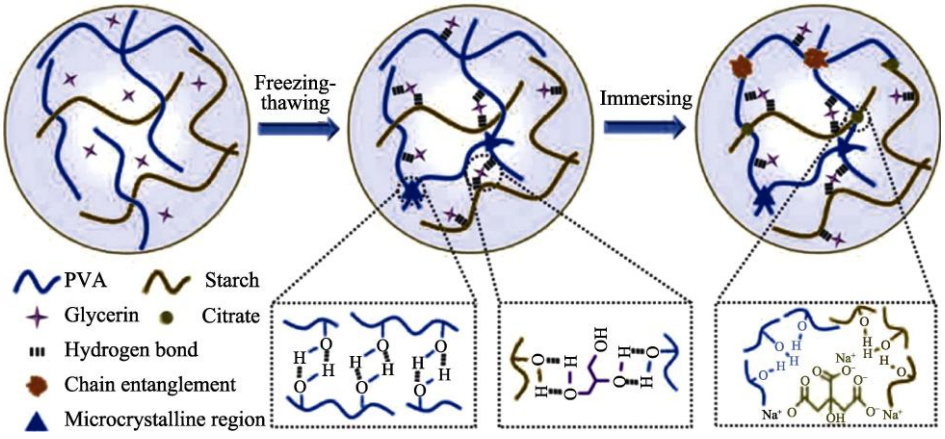

Figure 7 Schematic representation of synthesis mechanism of SPGN hydrogel[37].

3.2.2 Electrostatic Interactions

Electrostatic interactions between oppositely charged polyelectrolytes form polyelectrolyte complex hydrogels. WANG et al.[40]prepared stretchable, conductive, biocompatible GO_3SPNB hydrogels via γ-radiation technology using graphene oxide (GO), soluble starch, sodium 4-vinylbenzenesulfonate (NaSS), and N-[2-(methacryloyloxy)ethyl]-N,N-dimethyl-1-butanaminium bromide (MOBAB) (Fig. 8). Electrostatic interactions between cationic and anion polymer chains during GO_3SPNB formation endowed rapid recovery; repeated use (5 cycles) on aluminum plates caused no significant strength loss. Moreover, the hydrogels achieved complete self-healing at room temperature without external stimuli. HU et al.[41]incorporated MXene nanosheets into networks of amylopectin (AP) and poly-[2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (PDMAPS), fabricating ADM gels. Zwitterionic electrostatic interactions existed within the system. MXene nanosheets bearing reactive groups formed multiple reversible non-covalent bonds with AP and PDMAPS. Dynamic non-covalent interactions and electrostatic forces granted ADM gels high mechanical strength and rapid self-healing capability (elongation at break >2700%). Reversible non-covalent bonds also enabled recyclability; fragmented or dissolved gels could be reconstructed via re-establishing reversible interactions.

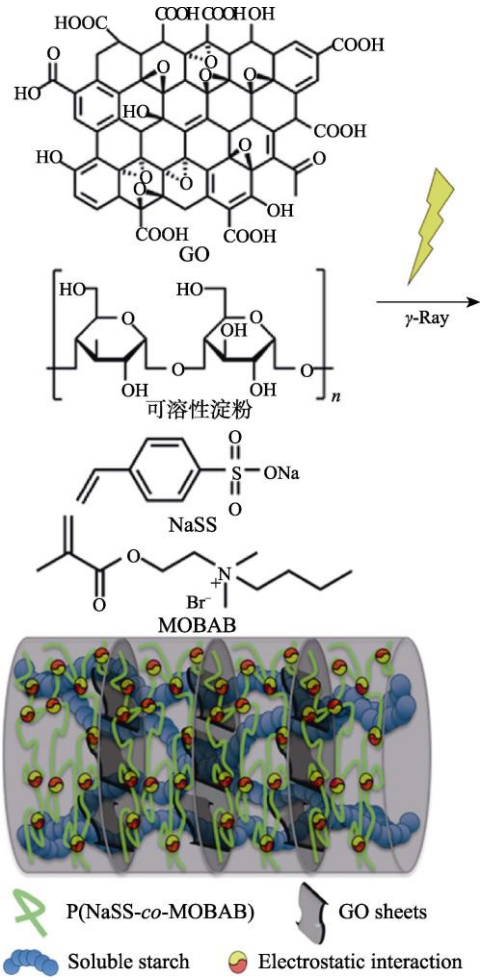

Figure 8 Schematic illustration of preparation of GO_3SPNB hydrogel[40].

3.2.3 Coordination Interactions

Coordination involves reactions between metal elements and inorganic/organic ions or molecules to form coordination compounds. More stable than electrostatic interactions, coordination is frequently employed as supplementary crosslinking to enhance hydrogel mechanics. WANG et al.[42]prepared starch-Fe(III) composite hydrogels. Coordination bonds between Fe(III) and starch hydroxyls strengthened the 3D network and thermal

stability while significantly enhancing the positive electro-response of starch hydrogels. BAI Jie et al.[43]fabricated oxidized starch hydrogel beads via coordination between Fe^{3+} and carboxyl groups on oxidized starch. Optimal stability occurred at a carboxyl:Fe^{3+} molar ratio of 4.58:1, with beads readily releasing encapsulated β-carotene in alkaline intestinal environments.

3.3 Double-Cross-Linked Starch-Based Hydrogels

Single crosslinking methods often confer limited functionality. For instance, chemically cross-linked covalent rigid networks are typically non-recyclable, while physically cross-linked reversible non-covalent networks suffer from suboptimal mechanics. Employing diverse crosslinkers and crosslinking densities enhances mechanical performance. Innovative double-crosslinking strategies, expanding application scopes, have garnered significant interest. Double-crosslinked hydrogels can utilize combinations of covalent/covalent, non-covalent/non-covalent, or covalent/non-covalent networks. Chemical covalent crosslinking substantially improves mechanical properties; reversible physical non-covalent interactions impart dynamic performance and recyclability; chemical/physical double-crosslinking boosts mechanics and adhesion strength without compromising biocompatibility or self-healing capacity.

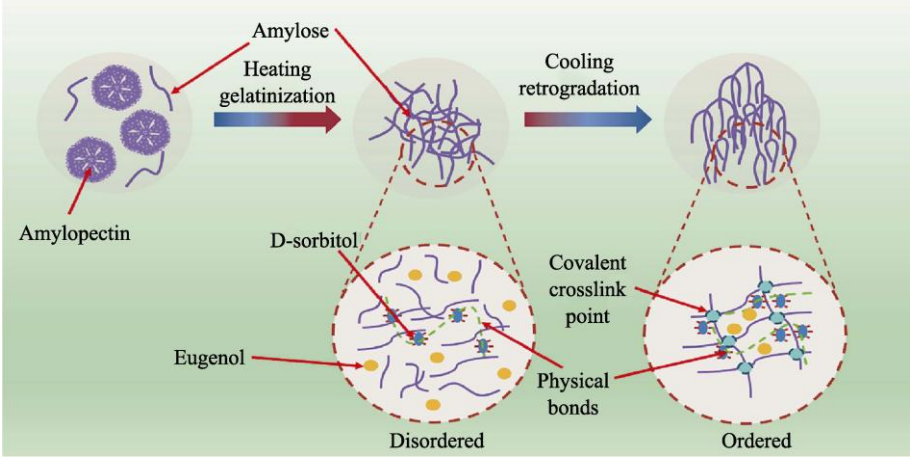

Figure 9 Schematic representation of ESSG hydrogel[45].

SRINGAM et al.[44]first prepared single-network (SN) starch hydrogels using glutaraldehyde (GA) as a crosslinker, forming acetal bridges between GA and starch hydroxyls. Subsequently, PVA and borax served as auxiliary polymer and crosslinker, respectively; complexation between PVA and borate ions formed a secondary physical network, yielding double-network (DN) hydrogels. Compared to SN hydrogels, DN hydrogels possessed denser microstructures, with 30% higher compressive modulus and 39% higher toughness.

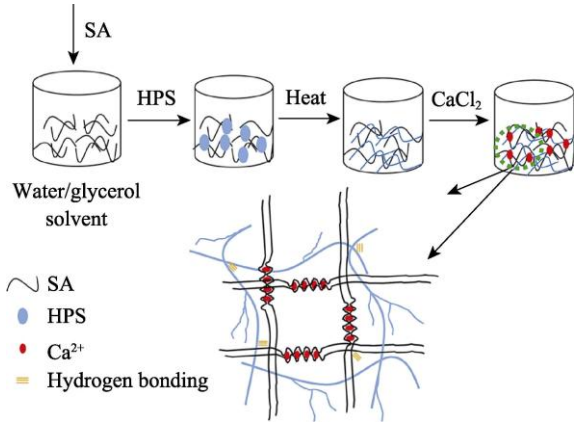

Figure 10 Schematic diagram of synthesis mechanism of HPS/SA DN hydrogel[46].

LIN et al.[45]prepared high-performance eugenol-loaded starch-sorbitol hydrogels (ESSG) via physico-chemical double-crosslinking. Starch formed a crosslinked network via MBA; added sorbitol formed locally ordered polymer networks via covalent bonds and physical interactions, significantly reinforcing the hydrogel skeleton (Fig. 9). At 5 wt% sorbitol, ESSG hydrogels exhibited an internal pore diameter of 10–15 μm and a swelling ratio of 988.8%. LIN et al.[46]fabricated stretchable, compressible, self-healing double-crosslinked hydrogels (HPS/SA DN) based on hydroxypropyl starch (HPS) and sodium alginate (SA) (Fig. 10). HPS formed the first network via hydrogen bonding, providing stretchability and self-healing properties. Chemical crosslinking between SA and Ca^{2+} constituted the second network, conferring high mechanical strength. At 1 wt% SA, the storage modulus increased nearly 80-fold. Prepared in water/Gly binary solvent, the hydrogels retained gel properties even at −15 °C.

3.4 Biodegradability of Starch-Based Hydrogels

From a green sustainability perspective, degradability is crucial for industrial applications. Research confirms that crosslinked starch-based hydrogels exhibit favorable biodegradability. TANAN et al.[21]reported a daily soil degradation rate of 0.63% for their CSt-g-PAA/NR/PVA double-network hydrogel. SARMAH et al.[28]synthesized oxidized starch-chitosan hydrogel drug delivery systems with high biodegradability; dried, drug-free hydrogels degraded completely in soil within 15 days, while drug-loaded variants lost structural integrity within 8 days in pH 7.4 buffer, with decomposition products digestible by endogenous enzymes. SHANG et al.[47]constructed double-network nanocomposite hydrogels from debranched corn starch and PVA, achieving 85.6% mass loss in soil over 180 days. Pure starch hydrogels degrade readily; however, incorporating functional additives can impede this process. ABDUL et al.[48]verified the degradation of starch-based antibacterial hydrogels loaded with patchouli essential oil via in vitroassays. In PBS (pH 7.0, 37 °C), pure starch and waxy starch hydrogels degraded completely within 9 h. Samples containing essential oils and carbopol degraded slower, with waxy starch variants degrading slowest. Thus, maintaining excellent biodegradability while imparting functionality remains a challenge for starch-based hydrogels in functional applications.

4 Applications of Starch-Based Hydrogels

Starch-based hydrogels offer good biocompatibility, biodegradability, low production costs, and scalability, enabling widespread use in biosensors, medical dressings, drug delivery, tissue engineering, and soil protection.

4.1 Biosensors

Wearable electronics (sensors, electronic skin, soft robotics) have attracted immense interest recently. Conventional wearables are often non-recyclable and non-degradable, causing waste and pollution. Hydrogels, with superior mechanics and biocompatibility, are ideal for wearable device development. Incorporating active substances imparts conductivity, stimuli-responsiveness, or self-powering capabilities, representing a current research hotspot[49]. MA et al.[50]tuned hydrogen bonding interactions between high-amylose chains using Gly and $CaCl_2$, enhancing flexibility and strain sensitivity. A one-step method yielded all-starch-based hydrogels, which were further developed into flexible batteries and self-powered (SP) sensors. Flexible batteries maintained accurate current output correlating with deformation even after 1000 compression cycles at 20% strain, demonstrating high-pressure sensitivity and anti-freezing performance (stable output after 7 days at −80 ° C). SP sensors exhibited high strain sensitivity (1.5371 kPa^{-1}), reliably detecting subtle human motions like wrist pulses and throat vibrations with strong, clear, stable signals. WAN et al.[51]fabricated highly stretchable hydrogel wearable patches using lotus root starch with NaCl electrolyte. An electrooculography acquisition system and prototype video game validated immense potential for signal monitoring and human-machine interaction. SI et al.[52]assembled wearable sensors based on starch/PAM/borax/Gly (SPBG) ionohydrogels. These sensors offered excellent resistive response (gauge factor: 1.47) across 0–500% strain, accurately monitoring complex elastic deformations. They also exhibited outstanding conductivity and long-term stability in extreme environments, suitable for real-time human physiological monitoring under harsh conditions. LIANG et al.[53]constructed thermoplastic, regenerative gelatin/oxidized starch/Gly/$ZnCl_2$ organohydrogels (GOGZ). GOGZ possessed excellent thermoplasticity, mechanics, antibacterial properties, and high ionic conductivity (tensile strength: 1.61 MPa; toughness: 2.76 MJ/m^3; elongation at break: 371%). Flexible strain sensors based

on GOGZ showed a linear gauge factor of 1.181 (R^2 = 0.999) across 0–350% strain, with fast response, enduring sensing stability, and reliability for real-time human motion monitoring.

4.2 Medical Dressings

Medical dressings are temporary wound coverings that protect wounds and accelerate healing. Traditional dressings often suffer from poor insulation, breathability, and hemostasis, potentially causing secondary injury. Starch-based hydrogels offer excellent moisture retention, breathability, drug release capability, reduced dressing change frequency, and accelerated healing, making them ideal candidates widely used for infected and refractory wounds. ZHENG et al.[54]constructed oxidized starch hydrogels loaded with coagulation factor Ca^{2+} (CaOMS). CaOMS rapidly absorbed blood fluid components; released Ca^{2+} accelerated hemostasis via cascade coagulation pathways and improved clotting. In vivostudies confirmed CaOMS promoted secretion of epidermal growth factor (EGF) and vascular endothelial growth factor (VEGF), partially restoring weight loss from hemorrhage, while exhibiting excellent hemostatic function (65 s) and wound healing properties. MAO et al.[55]prepared multifunctional wound dressings based on oxidized starch/gelatin shape-memory hydrogels (OSG). Thermally reversible gelatin acted as a shape-memory switch, while Schiff base crosslinks between aldehyde groups in oxidized starch and amine groups in gelatin served as shape-memory nodes. Thermal stimulation prompted the dressing to self-contract from elongated shapes, closing incisions non-invasively. Compared to sutures, OSG-treated wounds yielded smoother skin devoid of visible scars. ALTAF et al.[56]prepared hydrogel films via esterification using PVA, starch, and glutaraldehyde as crosslinker, incorporating essential oils (clove, oregano, tea tree oil) to yield PVA/starch-based hydrogel membranes. Optimal performance (tensile strength: 19.36 MPa; water vapor transmission rate: 36.22 g/(m^2·h); moisture retention: 95.50%; S. aureusinhibition zone: (39.00 ± 0.57) mm; E. coliinhibition zone: (37.00 ± 0.29) mm) was achieved using 0.1 mL clove oil, suitable for burn wound dressings.

4.3 Drug Delivery Carriers

Drug delivery carriers encapsulate active pharmaceuticals and release them at predetermined rates/proportions upon environmental stimuli. Maximizing efficacy while minimizing side effects defines their primary objective. Hydrogels' porous structures enable encapsulation and delivery of bioactive agents, often exhibiting stimuli-responsiveness to pathological microenvironmental changes. Starch-based hydrogels are widely adopted due to favorable patient compliance, biocompatibility, biodegradability, and high drug loading efficiency. GHOLAMALI et al.[57]prepared carboxymethyl cellulose/starch/ZnO nanoparticle composite hydrogel microspheres loaded with doxorubicin to enhance drug release systems. Abundant pores and free volume in ZnO nanoparticles, combined with hydrogen bonding and electrostatic attractions between doxorubicin and ZnO, facilitated deeper drug penetration into hydrogels, elevating encapsulation efficiency. KOEV et al.[58]quantified volumetric and molecular-level structural changes of low- and high-amylose starch hydrogels across stages of in vitrodigestion and colon fermentation models, exploring their potential as oral colon-targeted delivery vehicles. Results confirmed starch hydrogels as viable platforms for colonic drug targeting, offering prolonged release windows and reduced dosing frequency. Drug release was restricted to the large intestine, with minimal or no release in the upper gastrointestinal tract. Release rates (15–56% over 24 h) were several-fold lower than other starch-based nanoparticles or polysaccharide hydrogel platforms, validating feasibility for colon-specific delivery. KANG et al.[59]evaluated protective effects of starch-free emulsion (EM), starch-filled hydrogel (RS-FH), and enzymatically modified starch-filled hydrogel (GS-FH) on curcumin via UV stability tests and simulated gastrointestinal studies. Compared to EM, RS-FH and GS-FH enhanced curcumin stability under UV light and improved retention rates. UV stability of RS-FH improved 2.28-fold over EM; GS-FH prepared after 1 h and 96 h enzymatic modification increased curcumin retention by 2.31-fold and 2.60-fold, respectively. ZHANG et al.[60]prepared water-soluble oxidized high-amylose starch (OHAS) with abundant carboxyl groups. Based on OHAS with 90% oxidation degree, a DO90-Zn^{2+} gel in vitrodelivery system was established. DO90-Zn^{2+} gel encapsulated Lactobacillus paracaseiwith 88.8% efficiency and exhibited excellent controlled-release properties. Combined with chitosan, DO90-Zn^{2+}-chitosan gels effectively protected and sustained release of both hydrophobic (β-carotene) and hydrophilic (tea polyphenols) bioactives, with encapsulation efficiencies of 62.4% and 77.9%, respectively.

4.4 Tissue Engineering Scaffolds

Tissue engineering scaffolds promote tissue repair and regeneration, representing a key research domain in biomedical engineering with broad applications in bone and soft tissue repair. Current research focuses on scaffolds combining biodegradability, biocompatibility, and multifunctionality (drug/bio-signal delivery). LI Peng et al.[61]prepared composite starch hydrogels with calcium silicate exhibiting rheological properties between solids and liquids. These injectable hydrogels were stably extruded through 22G needles under 15 N force, potentially enabling minimally invasive injection into rat cartilage defects and adhesion to osteochondral surfaces. In vivostudies showed single intra-articular injections maintained biological function for up to 6 weeks, promoting osteochondral defect repair. KHANDAN-NASAB et al.[62]fabricated alginate/amylopectin/hyaluronic acid (Alg/Pul/HA) hydrogel scaffolds. These scaffolds possessed excellent swellability and highly porous microstructures (average pore diameter: 100 μm), providing suitable microenvironments for delivering adipose-derived mesenchymal stem cells (ASCs). ASCs attached, survived, and migrated within the scaffolds; cell-seeded hydrogels accelerated wound healing as dressings. XIE et al.[63]prepared nanoporous hydrogels containing cholesterol-bearing pullulan, serving as scaffolds for local bone regeneration. Perforated scaffolds outperformed non-perforated counterparts, exhibiting higher osteoblast activity, cortical bone mineral content, and bone formation rates. Pore size and geometry influenced degradation rates and drug release; notably, 300–400 μm perforations effectively enhanced bone formation.

4.5 Soil Protection

Excessive fertilizer use has raised significant environmental concerns. Developing slow-release fertilizers (SRF) or controlled-release fertilizers mitigates over-application, improves nutrient use efficiency, and prevents leaching pollution. Superabsorbent hydrogels are premier candidates for SRF manufacturing[64]. Starch-based SRF hydrogels are attractive due to biodegradability, low cost, and soil moisture retention. XU et al.[65]blended starch with polyacrylic acid to create hydrogel coating materials, enhancing urea slow release with prolonged nutrient availability and good degradability. Starch-based superabsorbent hydrogels also serve as soil conditioners and nutrient carriers. KOLYA et al.[66]synthesized hydrogels in aqueous media using rice cooking wastewater (starch), acrylamide, and 2-acrylamide-2-methylpropane sulfonic acid. Adding 0.25 wt% (soil basis) to garden soil improved water retention; after 20 days at (30 ± 1) °C, 27 wt% moisture remained. The amended soil supported germination and growth of mung bean, pea, and chili seeds.

4.6 Other Applications

Starch-based hydrogels also find broad utility in electrolytes, textile processing, and wastewater treatment. CRUZ-BALAZ et al.[67]synthesized gel polymer electrolytes (GPE) from chitosan and starch. Electrochemical impedance spectroscopy and cyclic voltammetry confirmed suitability as electrolytes in rechargeable zinc-air batteries (ZABs). YAO et al.[68]treated polyester fiber surfaces with macroporous starch-based gels under alkaline conditions, preparing ultra-light, soft, highly absorbent fabrics via in situpolymerization. Stable chemical bonds and hydrogen bonding integrated starch gels into continuous fiber networks. These superabsorbent fabric-based gels achieved deionized water uptake up to 343 g/g. MOHAMMADZADEH et al.[69]synthesized starch/poly(acrylic acid) hydrogels via free radical polymerization for effective adsorption of methylene blue from wastewater. At pH 10.0 and an acrylic acid:MBA molar ratio of 95:5, the hydrogel achieved maximum adsorption capacity (26.7 mg/g) and efficiency (66.7%) for 20 mg/L dye solutions.

5 Conclusions and Outlook

With societal development and stricter environmental regulations, demand surges for multifunctional degradable materials. Multifunctional starch-based hydrogels boasting high mechanics, excellent self-healing, and recyclability hold significant research value and application potential. Currently, leveraging advantages like good compatibility, biodegradability, and low cost, starch-based hydrogels show broad prospects in biosensors, medical dressings, drug delivery, tissue engineering scaffolds, etc. However, deep research faces persistent challenges. Future studies should focus on:

(1) Optimizing starch modification methods to minimize environmental impact while yielding modified starches with superior properties and broader applicability;

(2) Elucidating crosslinking mechanisms and 3D network formation in starch-based hydrogels. Developing eco-friendly multifunctional crosslinkers/initiators, innovating preparation techniques, and incorporating double networks/nanomaterials to enhance mechanical stability and strength while preserving biocompatibility and degradability;

(3) Combining starch with diverse green functional materials to impart excellent conductivity, thermal conductivity, flame retardancy, antibacterial properties, etc., thereby expanding application scopes.

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