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Review article

Research progress of environment-responsive hydrogel applications in agriculture

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Abstract. Environment-responsive hydrogels are environmentally friendly polymeric materials that rapidly respond to their environment by changing their volume or strength when the external environment, such as temperature, pH, light, and magnetism, changes. As environment-responsive hydrogels, they are uniquely flexible and sensitive, enabling them to be used in various applications, and are now at the forefront of polymer science research. Scholars have reviewed more environment-responsive hydrogels in biomedicine, detection sensors, and drug release. We present a detailed description of the reaction mechanism and preparation process of environment-responsive hydrogels, taking temperature-responsive, pH-responsive, and light-responsive hydrogels as examples. Finally, a summary is given at the end: 1) the application of environmentally responsive hydrogels in agriculture, and 2) the problems and future trends of their application in agriculture.

Keywords: *intelligent hydrogel, preparation method, temperature sensitivity, pH sensitivity, agricultural application*

1. Introduction

The outline of the 14th five-year plan of the national economic and social development of the people's republic of China and vision 2035 includes ecosystem protection and restoration as a priority task. Ecological issues are relevant to all of us, and desertification and drought are currently severe threats to sustainable and healthy ecological development. Northwest and north China, which account for 52.2% of China's land area and about 30% of the country's arable land, are regions with low annual precipitation, with average annual precipitation and evaporation of about 100 mm and >1600 mm [1, 2]. Rainfall is the primary groundwater source, and the geological deficit has led to sparse vegetation, severe soil erosion, and low soil water storage, which does not effectively promote plant growth. Hydrogel, a new type of water storage material, is used in agriculture to solve the lack of groundwater resources and severe water loss. Hydrogels are a class of polymers with a three-dimensional network structure that can hold large amounts of aqueous solvents and biological fluids, which can absorb water and swell to tens of thousands of times their volume [3]. Due to its excellent properties, such as deformability, flexibility, and viscoelasticity [4], it has emerging applications in slow drug release [5], wastewater treatment [6], and water conservation in agriculture and forestry [6, 7].

Hydrogels play the role of small reservoirs in agriculture and forestry, combining water absorption and water control functions, which can effectively utilize water resources and promote seed germination and growth. Although traditional hydrogels have a strong capacity to absorb water, they release water relatively slowly, even under tremendous pressure [8, 9], and lack timeliness in supplying water to vegetation

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at higher natural temperatures. While environment-responsive hydrogels can effectively improve water supply efficiency and release capacity, significantly reducing water and nutrient wastage, improving application efficiency, and promoting vegetation growth. At present, most reviews of environment-responsive hydrogels have described their applications in drug delivery [10], bone repair [11], environmental pollution treatment [12], *etc*. Fewer mentions are made of their applications in agriculture; for example, Pushpamalar *et al*. [13] transformed biomass waste sago pulp into a slow-releasing fertilizer carrier and a biodegradable water-retaining material. The hydrogel can also be used as a valve to regulate water flow according to soil moisture by using its ability to swell and shrink [14]. The preparation of light-responsive, controlled-release herbicide hydrogels with a core-shell structure can improve weed control [15]. Currently, many researchers are less aware of the advantages and problems of environmental-responsive hydrogels in agricultural applications.

Therefore, to better summarize the application examples of environment-responsive hydrogels in agriculture, we have outlined the preparation methods and advantages of different functional hydrogels, as well as the different roles they play in different soil environments, introduced the mechanism of action of various intelligent materials and provided an overview of specific application methods. At the same time, the latest progress in applying environment-responsive hydrogels in agriculture, the current ways to improve the performance of intelligent hydrogels, and the future development trends in agriculture are reviewed.

2. Environment-responsive hydrogel physical and chemical response

Hydrogels can be classified according to the synthesis method into physically cross-linked hydrogels and chemically cross-linked hydrogels. Physically cross-linked hydrogels are usually formed by physical interactions between polymers, *e.g.*, hydrophobic, electrostatic, and hydrogen-bonding interactions. It is relatively simple to synthesize but has low mechanical strength and tends to change to solution at elevated temperatures. This hydrogel requires more reagents to synthesize than a physically cross-linked hydrogel, and the resulting hydrogel is not homogeneous, with agglomerates that reduce water swelling capacity and enhance cross-linking properties [16]. It is stable, less susceptible to hydrolysis, and has excellent mechanical properties. The other is chemically cross-linked hydrogels, which are formed by the polymerization of monomers through an initiator and crosslinker. It has good physical stability and biocompatibility, can control the release of water, and is widely used in medicine, agriculture, environment, and other fields. However, the preparation of chemical cross-linked hydrogels requires certain technology and conditions and has particular pollution and influence on the environment.

Hydrogels can be divided into conventional hydrogels and environmental-responsive hydrogels according to their stimulatory response to the external environment. Conventional hydrogels only produce simple shrinkage and swelling, and the water absorption does not change with the external environment. Environmental-responsive hydrogels [17], also known as stimulus-responsive hydrogels, can respond stimulatively to temperature, pH and light, magnetism [18]. Its polymeric main or side chains contain a large number of hydrophilic groups and have an appropriate cross-linked network structure, allowing it to change its volume and strength more intelligently, rapidly, and significantly than conventional hydrogels, releasing water or other solvents, drugs, *etc*. to meet different needs. Environmental-responsive hydrogel materials are popular with researchers because of their flexibility.

Environment-responsive hydrogels can be divided into two types according to their physical and chemical responses: one can respond to physical stimuli such as light [19], temperature [20], electric fields [21], sound, *etc*., and the other can respond to chemical stimuli such as pH [22], ionic strength [23], solvent composition [24], *etc*. In addition to hydrogels that respond to a single physical and chemical stimulus, multi-sensitive hydrogels can respond to both types synergistically or sequentially. Typical multifunctional responsive hydrogels include temperature/pH-responsive hydrogels [25], thermal/ionic strength responsive hydrogels [26], and ionic strength/pH-responsive hydrogels [27]. The following section of this paper will detail several common environment-responsive hydrogels that respond to physical and chemical stimuli.

2.1. Temperature-responsive hydrogels

Temperature-responsive hydrogels have two types: thermal expansion and thermal contraction. The

thermal expansion type means the hydrogel has low water absorption at low temperatures. When the temperature reaches the upper critical solution temperature (UCST), the hydrogel's swelling degree becomes more significant due to the intermolecular hydration, making the hydrogel expand rapidly; the thermal shrinkage type of hydrogel is opposite to the thermal expansion type; the swelling degree is higher at low temperature, and the water absorption rate changes abruptly when the temperature rises to a specific value, and the swelling degree decreases as the temperature increases. The temperature at which the hydrogel's water absorption rate changes abruptly is the lowest critical temperature (LCST), which is above and below the hydrophilic and hydrophobic temperatures, respectively, due to the presence of hydrophilic groups (–$CONH_2$) and hydrophobic groups (–CH_3, –CH_2CH_3) in the molecules of temperature-sensitive hydrogels. When the temperature is higher than LCST, the thermal movement of molecules is intense, the hydrogen bonds between hydrophilic groups and water molecules are destroyed, and the hydrophobic groups in the structure play a dominant role. The hydrogel becomes hydrophobic and recedes from the swelling [28], and the mechanism of action is shown in Figure 1.

Temperature-responsive monomers generally contain unsaturated –C=C– to open the double bond in an aqueous solution for polymerization, as well as –COOH, –NH_2, and other groups that can form hydrogen bonds with water molecules after the formation of hydrogen bonds, the hydrogel's hydrophilicity, is enhanced, the phenomenon of swelling occurs. As the temperature rises, the intermolecular forces are broken, the hydrogen bond is damaged or destroyed, the hydrogel collapses, and the water absorption decreases. Table 1 shows several typical temperature-responsive monomers with their LCST. One of the most common and studied is PNIPAAm hydrogels, a class of temperature-sensitive polymers with a low critical solubility temperature with a transition temperature of around 32 °C [29]. When the temperature increases, the hydrophilic amide group will form a hydrogen bond with the water molecule, thereby enhancing the water absorption capacity of the hydrogel. When hydrophobicity predominates, the hydrogel's ability to absorb water is significantly weakened. The minimum critical temperature of the PNIPAAm hydrogel is easy to be adjusted. For example, Mariani *et al*. [30] successfully synthesized the semi-interpenetrating network of PNIPAAm and methylcellulose. The hydrogel with an LCST of 30.8 °C was prepared, and the addition of methylcellulose reduced the LCST of the hydrogel.

Another typical temperature-responsive monomer is dimethylaminoethyl methacrylate (DMAEMA), a colorless or pale yellow transparent liquid with an LCST of 40–50 °C. At temperatures above 40 °C, tertiary amino group interactions become dominant, PDMAEMA side chains tend to shrink or collapse, and polymer opacity increases, making the polymer

Table 1. Several common temperature-responsive materials.

Material	Abbreviation	LCST [°C]	References
Chitosan and its derivatives	CTS	200	[31]
Polyethylene glycol polymer	PEG	120	[32]
Polyvinyl alcohol	PVA	125	[33]
Polydimethylaminoethyl methacrylate	DMAEMA	42	[34]
Hydroxypropyl cellulose	HPC	55	[35]
Methylcellulose	MC	80	[30]
Poly *N*-isopropyl acrylamide	PNIPAAM	32	[29]

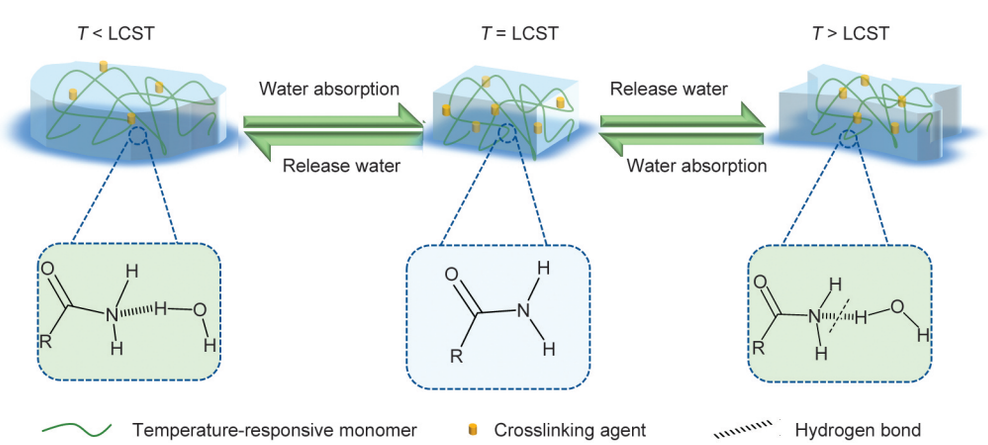

Figure 1. Sensitivity mechanism of thermally shrinkable hydrogels to temperature.

exhibit temperature sensitivity [36, 37]. Geyik *et al*. [36] synthesized *k*-carrageenan grafted DMAEMA using a microwave radiation radical copolymerization method and measured the LCST of the polymer to be 47 °C in distilled water. Dinari *et al*. [34] synthesized lignin-*g*-P(NIPAM-*co*-DMAEMA) hydrogels using fully brominated lignin as an ATRP macromolecular initiator and prepared four nanogel systems with different LCSTs were ready, which are 32, 34, 37, and 42 °C.

2.2. pH-responsive hydrogels

pH-responsive hydrogels refer to the dramatic changes in the volume of the hydrogel molecules when the pH in the environment changes so that water is absorbed or released [22]. The network structure of pH-responsive hydrogels usually contains acidic groups or primary groups, and they can be dissociated into ions; the primary groups are –COOH and $–NH_2$. Figure 2 shows the sensitivity mechanism of pH-responsive hydrogels.

Table 2 shows the classification of several typical pH-responsive monomers. AA is the simplest unsaturated carboxylic acid, with a highly reactive alkenyl group at the end that provides the possibility of reactive graft polymerization, and also has a –COOH group, which can make the synthesized polymers pH-responsive [38]. Under acidic conditions, –COO–, $–NH_2$ are easily protonated to form –COOH, $–NH_3^+$, reducing electrostatic repulsion between groups. Under alkaline conditions, –COO– increases the electrostatic repulsion inside the hydrogel, while the hydrogen bonds formed between –COO–, $–NH_2$, and H_2O will increase the water absorption of the hydrogel [24, 28]. DMAEMA is also a common pH-responsive monomer, and its molecule contains unsaturated double bonds, which can be polymerized with other monomers to form long polymer chains. Protonation occurs under acidic conditions to generate quaternary ammonium cations, enhancing the polymer's hydrophilicity and swelling ability.

Table 2. Several common pH-responsive materials.

Classification	Material	Abbreviation	References
Synthetic material	Polyacrylic acid	PAA	[28]
	Methacrylate	MMA	[36]
	Polyamines	PEA	[34]
Natural ingredients	Xylan	HRE	[38]
	Chitosan	CTS	[39]

2.3. Light-responsive hydrogels

Light is the most common natural resource in life. Light-responsive hydrogels can be prepared by introducing light-responsive groups. As shown in Figure 3, a standard class of light-responsive molecules is based on azobenzene (AB) derivatives. This type of molecule can occur under illumination cis-trans isomerization. Due to the –C=C– double bond, AB has two configurations: trans and cis. Under the irradiation of ultraviolet light, the AB molecule can rapidly change from the trans configuration to the cis configuration. Format, the photoisomerization speed is fast, and the photoisomerization efficiency is high; under the thermal effect or the irradiation of visible light, it can be converted from the cis configuration to the trans structure. This photoinduced cis-trans isomerization has excellent reversibility [17]. In addition to AB derivatives, gelatin can also be applied to prepare photosensitive materials, such as films made of gelatin, which respond to relative humidity by changing the refractive index and thickness. The thickness of the film is the smallest when it is dry,

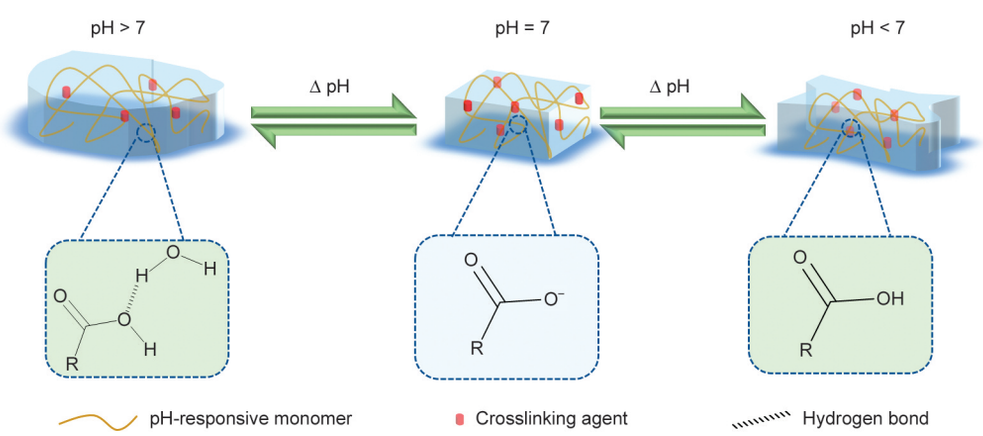

Figure 2. Mechanism of pH sensitivity of pH-responsive hydrogels.

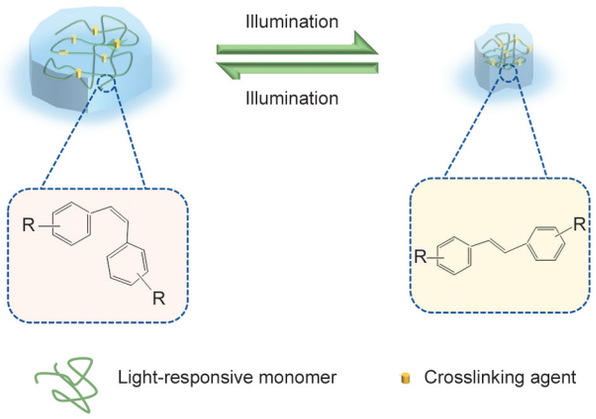

Figure 3. Sensitivity mechanism of light-responsive hydrogel prepared by photosensitive group.

and its refractive index is higher. However, when the water vapor is absorbed by the film, its refractive index decreases, and the thickness becomes larger [40].

In addition to the introduction of photosensitive groups to prepare light-responsive hydrogels, temperature-responsive monomers can also be combined with graphene to make hydrogels light-responsive. As shown in Figure 4, the near-infrared responsive PNIPAAm/graphene oxide nanocomposite hydrogel with ultra-high tensile properties utilizes graphene nanosheets in the polymer network to absorb near-infrared light and convert it into heat [41], resulting in a local temperature increase in the hydrogel, PNIPAAm followed by a temperature response, when the hydrogel temperature increased to 32 °C, the interaction between the hydrophobic groups dominated, and the hydrogel underwent volume shrinkage.

2.4. Enzyme-responsive hydrogels

The enzyme is a protein that rapidly converts many copies of a substrate molecule into a product with fine specificity [42]. The enzyme-catalyzed reaction is particular and selective for the substrate. The enzyme-regulated hydrogels have a targeted release function, which enables the delivery of substances such as drugs and fertilizers to exactly where they are needed, enhancing the utilization of substances such as drugs and fertilizers. These hydrogels can also inhibit the degradation of meanings and can be used in biomedicine, agriculture, and other fields. Enzyme-responsive hydrogels are divided into two standard modes of action. One is that enzyme-responsive hydrogels use enzymes as triggering drugs. As shown in Figure 5, the enzymes destroy the corresponding liposomes to convert lipids the drug encapsulated in the body hydrogel is released. Li *et al.* [43] prepared a new liposomal hydrogel. The drug is encapsulated in the liposome as a core material. The hydrogel acts as a shell material to encase the liposomes, and the enzymes in the wound exudate destroy the liposomes to release the drug.

The other refers to the enzyme as an additive stably immobilized in the 3D network structure of the hydrogel synthesized by monomers and polymers for regulating the synthesis and self-repair of the hydrogel [44]. In Figure 6a, the left panel shows a single network polymeric hydrogel formed by combining a monomer and a cross-linking agent. The hydrogel contains many primary amines, which are partially oxidized to aldehydes after enzyme catalysis and combine with amines to form imines, including secondary cross-linked networks, which is the mechanism used by the enzyme to synthesize the hydrogel. Conventional hydrogels can also undergo partial healing, but enzyme-induced water synthesis by reversible covalent bonds (R2C=NR′, R3C=O–NH–N=CR1R2). The hydrogel has a good self-healing function, and the self-healing speed is breakneck. As shown in Figure 6b, Zhang *et al.* [45] prepared an enzyme-mediated rapid self-healing

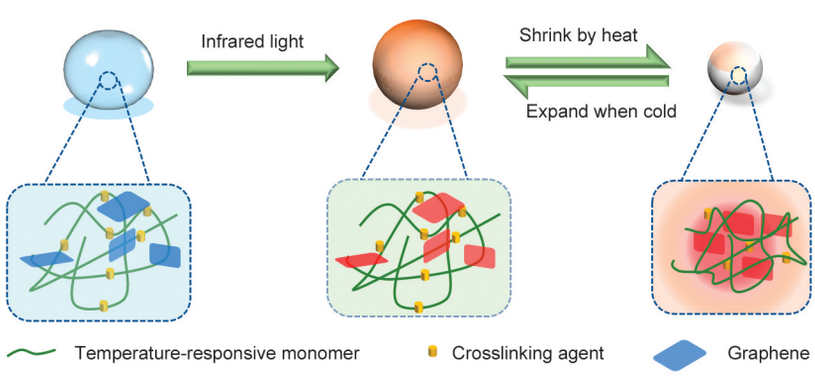

Figure 4. Sensitivity mechanism of light-responsive hydrogel prepared from temperature-responsive monomer and graphene.

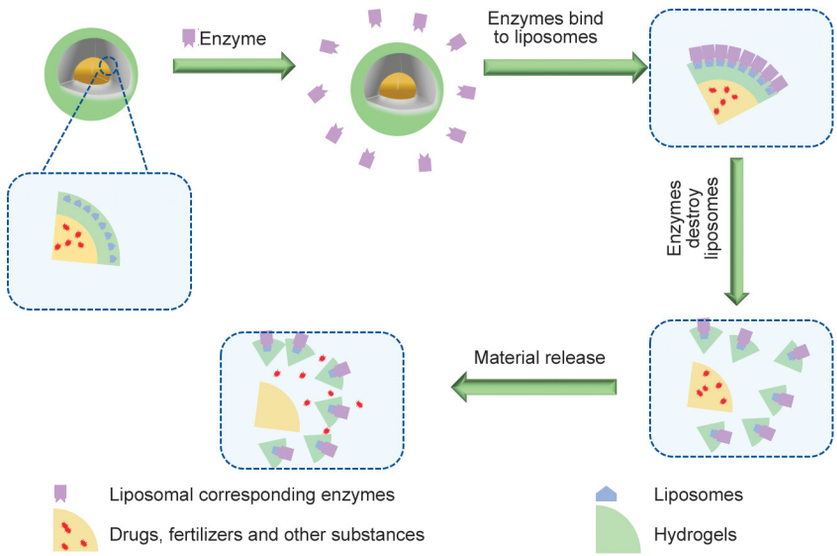

Figure 5. Sensitivity mechanism of enzymes as trigger drugs for enzyme-responsive hydrogels.

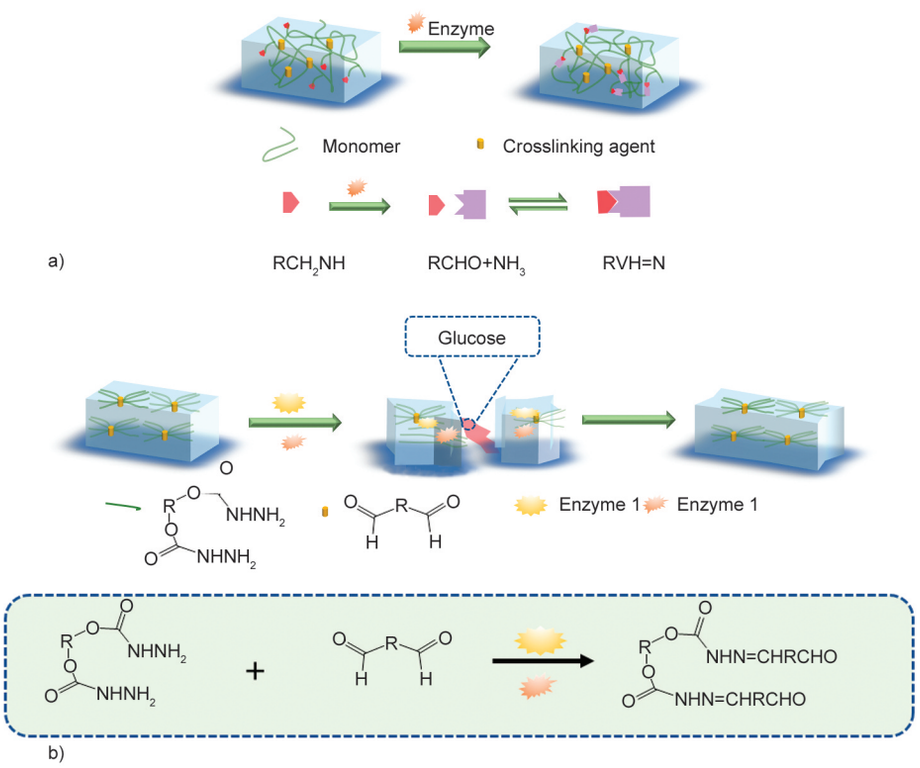

Figure 6. a) Enzymes are used as additives to synthesize hydrogels, b) enzymes are used as additives to regulate the self-repair process of hydrogels.

hydrogel. During gelation, the enzymes in the hydrogel reduce the system's pH by consuming glucose to generate gluconic acid, which is conducive to the reformation of the dynamic aldimine bond and further accelerates the self-healing behavior of the hydrogel. At the same time, the by-product hydrogen peroxide can be decomposed into water and oxygen by another enzyme.

2.5. Temperature/pH-responsive hydrogels

Temperature and pH are the most studied and concerning types of intelligent hydrogels, and the combination of the two has excellent application prospects in biomedicine, water purification, and other fields [25, 46]. Based on microwave irradiation, Işıklan and Polat [37] synthesized the heat-responsive and pH-responsive pectin-grafted PDMAEMA

with PDMAEMA side chains. Incorporation enables pectin to generate LCST at 41 °C, and the ionization of carboxylic acid groups makes the copolymer pH-responsive.

2.6. Thermal/ionic strength responsive hydrogels

Thermal/ionic strength responsive hydrogel is a relatively common type of dual hydrogel. The hydrogel has two layers: one layer can sense ion concentration and change shape according to ion concentration; one layer is temperature/thermal responsive. It can shrink or expand depending on the temperature. Zhou *et al*. [26] have designed a new bilayer hollow spherical hydrogel with ionic strength and temperature responsiveness. The inner layer of the hydrogel is ionic strength responsive. The alginate layer, the inner hydrogel layer, swells when transferred from a highly concentrated ionic solution to deionized water. The outer layer is a thermo-responsive alginate-poly(2-(dimethylamino) ethyl methacrylate) (Alg-PDMAEMA) layer. When the temperature changes from low to high, the external hydrogel shrinks, and the hydrogel is in a curved state.

3. Preparation of environment-responsive hydrogels

3.1. Radical polymerization method

The free-radical polymerization includes chain initiation, chain growth, and chain termination stages. The chain initiation refers to the decomposition of the initiator to form free radicals, which act on the hydroxyl group of the main chain to produce oxygen radicals [47]. Chain growth refers to the action of oxygen radicals on double bonds to form chain segments with free radicals, which undergo several repeated addition reactions with monomers to form long polymer chains. Chain termination is the formation of a stable polymer molecule mainly by the interaction between two free radical chains.

This method of preparation is relatively simple and can usually also be used to increase the pore space and enhance the water absorption by adding a pore-making agent, but the initiator, cross-linking agent, and pore-making agent added during the reaction process can be challenging to remove and can have an impact on the quality of the hydrogel. Radical polymerization includes bulk, solution, suspension, and emulsion polymerization. Table 3 shows the specific comparisons: Chiu *et al*. [48] used free radical polymerization to prepare NIPAAm, Nt-butylacrylamide (BA), acrylic acid, and *N*-methacryloylglycine *p*-nitrophenyl ester (the polymer precursor composed of MAGlyGlyONp) was cross-linked with cysteamine to prepare temperature/pH-sensitive hydrogels

3.2. Network aggregation

Network aggregation includes interpenetrating network (IPN) and semi-interpenetrating network aggregation (semi-IPN) [52, 53]. The difference between the two methods lies in the combination and arrangement. Linked network structure, semi-interpenetrating network polymerization is a cross-linked network structure, and the other is a chain structure. Both cross-linking methods increase the mechanical strength of the hydrogel and enable the polymer chains to act synergistically.

3.2.1. Interpenetrating network aggregation

Interpenetrating network hydrogels are different from graft or block copolymers and distinct from general polymer blends or polymer composites. They mainly use two additional components to form separate

Table 3. Comparison of several typical free radical polymerization reactions.

Method	Main ingredients	Aggregation site	Advantage	Shortcoming	References
Bulk polymerization	Monomer, initiator	In the body	High product purity	Reaction heat is not easy to remove	[49]
Solution polymerization	Monomer, initiator, solvent, cross-linking agent	In solution	Conducive to heat loss	Low reaction rate	[50]
Suspension polymerization	Monomer, initiator, water, dispersant	Inside the monomer drop	Easy to dissipate heat	The composition of the system is complex, resulting in low product purity	[19]
Emulsion polymerization	Monomer, initiator, water, emulsifier	Latex particles	Can increase molecular weight and polymerization rate at the same time	If drying requires demulsification, the process is difficult to control	[51]

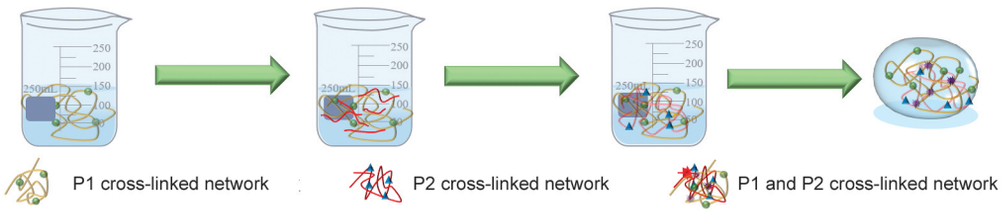

Figure 7. Schematic diagram of interpenetrating network synthesis.

polymer networks. Various polymers have their phases, and there is no chemical combination. The two polymer networks are entangled to create a whole, which cannot be detached and then form an interpenetrating network. The network cross-linking and interpenetration can significantly improve the mechanical strength of the water-absorbing and water-retaining materials and produce special synergistic effects. Figure 7 is a schematic diagram of the interpenetrating network polymer. Multi-sensitive hydrogels such as temperature and pH can be polymerized using interpenetrating networks. The hydrogels synthesized in this way maintain the temperature and pH-responsiveness of the hydrogels. The interpenetrating entanglement cross-linking enhances the mechanical properties of the hydrogels, and the IPN hydrogels shrink more slowly than traditional cross-linked hydrogels, allowing longer release times for substances such as water, urea, or pesticides. Barbieri *et al*. [54] synthesized PNIPAAm/alginate-loaded Nile red (NR) fluorescent dye using IPN technology and developed beads for simultaneous non-contact temperature sensing and fluid flow tracking.

3.2.2. Semi-interpenetrating network aggregation

The semi-interpenetrating polymer network means that among the two polymers that constitute the IPN, only one is a cross-linked network structure, and the other is a linear non-cross-linked chain structure [55, 56]. Figure 8 is a schematic diagram of the synthesis of the semi-interpenetrating network.

Ahmad *et al*. [57] investigated the preparation of cyclic ether epoxies with three-atom rings consisting of temperature-sensitive P(NIPAM-MBAAm) and P(NIPAM-glyceryl methacrylate) (P(NIPAM-GMA)) functionalities semi-interpenetrating polymer network hydrogel microspheres. The microspheres exhibit a temperature-responsive bulk phase transition in the range of 33–35 °C.

3.3. Block copolymerization

Block copolymer is a special polymer that connects several polymer segments with different properties. Block polymers with a specific structure will behave differently from simple linear polymers. For most random polymers, the various properties of the mixture of copolymers and homopolymers are shown in Figure 9 to synthesize simple linear triblock copolymers and nonlinear block copolymers.

Mukae *et al*. [58] synthesized interpenetrating polymer networks of poly(ethylene oxide)-dimethylsiloxane-ethylene oxide (PEO-PDMS-PEO) triblock copolymers and PNIPAAm as temperature-responsive hydrogels. Cui *et al*. [59] prepared a series of polycaprolactone-polyethylene glycol-polycaprolactone (PCL-PEG-PCL) triblock polymers. The polycaprolactone block has strong crystallinity, which improves the ink's printing performance and mechanical properties.

The advantages of free radical polymerization are mild reaction conditions, a wide range of applications, fast reaction rates, and ease of operational control. Disadvantages include a wide molecular weight distribution, uneven polymerization degree distribution, difficulty in controlling the molecular structure and properties of the polymer, and a less friendly environment. The advantages of network polymerization

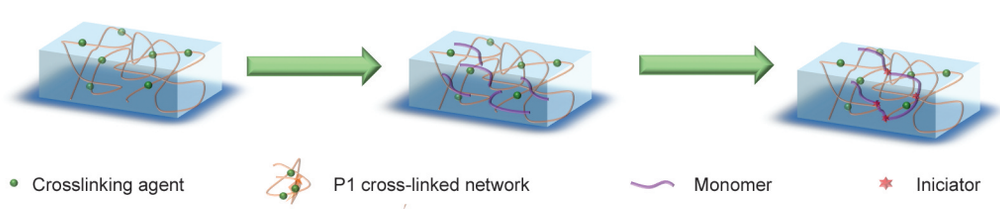

Figure 8. Schematic diagram of semi-interpenetrating network synthesis.

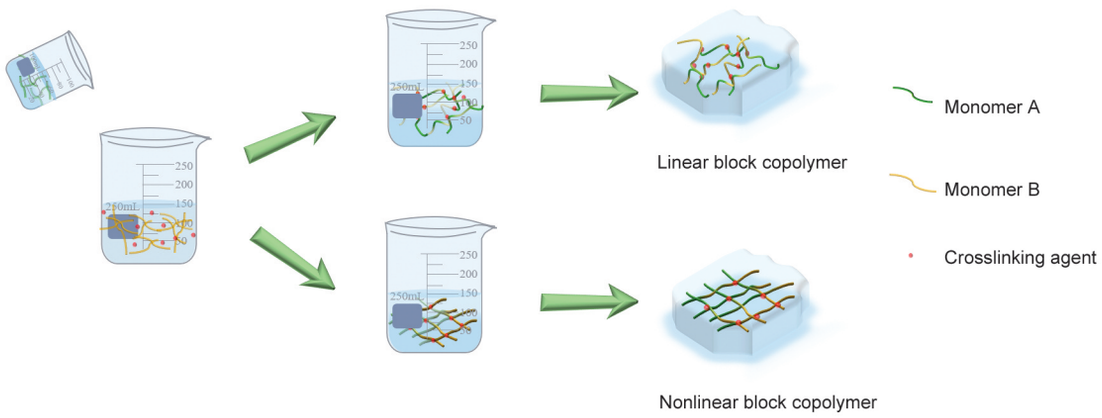

Figure 9. Schematic diagram of the synthesis of simple linear triblock copolymers and nonlinear block copolymers.

are the formation of a 3D network structure after polymerization, better mechanical strength and chemical resistance, higher degree of polymerization, and ease of preparation into thin films and coating materials. The disadvantages are that the polymerization process is prone to side reactions and requires certain synthesis techniques and high costs. The advantages of block copolymerization are the ability to precisely control the structure and properties of the polymer, the production of polymeric materials with specific functions, and a narrow molecular weight distribution. Disadvantages include the need for certain synthesis techniques, high costs, and the tendency for side reactions to occur during the polymerization process. Free radical polymerization is suitable for the preparation of simpler polymers, block copolymerization for the preparation of polymers with specific functions, and network polymerization for the preparation of polymers with excellent chemical and physical properties.

4. Applications of environment-responsive hydrogels in agriculture

To ensure the quality and yield of agricultural products, many researchers have designed and prepared environmentally responsive hydrogels and their applications in agriculture. Their main applications include soil drought and water retention agents, drug and nutrient enrichment, plant growth promoters, soil remediation, adsorption of heavy metals in soil, agricultural sensors, *etc*. Table 4 shows the latest applications of environmental-responsive hydrogels in agriculture in recent years.

4.1. Soil drought-resistant water-retaining agent

When water retention in the soil is reduced, water loss and evapotranspiration are high, plant and crop growth is reduced, and sometimes permanent damage is caused to the soil biota, so water is critical for soils. Importantly, hydrogels have been used as soil

Table 4. Comparison of several typical free radical polymerization reactions.

Material	Smart Responsiveness	Performance	Year	References
Cellulose/MOFs hydrogels	pH-responsive urea release, the urea release rate at pH 11 is much lower than that at pH 3	The highest water absorption at pH 11 reaches 101 g/g	2021	[60]
Polyphosphazene nanocarriers	pH-controlled release of diosgenin and two brassinosteroids	Sustained release of about 30% of pesticides after four days	2019	[61]
Sodium carboxymethyl cellulose (CMC-Na) /AA/AMPS hydrogel	Nitrogen adsorption to slow the loss of soil nutrients, and high salt tolerance	The maximum adsorption capacity of ammonia nitrogen is 30 mg/g, and the water absorption in distilled water and brine reaches 604 g/g and 119 g/g, respectively	2022	[62]
Carboxymethyl cellulose (CMC)-*g*-carboxymethyl polyvinyl alcohol (CMPVA) hydrogel	pH-responsive	pH 1, 7, and 11, swelling ratios were 360, 1440, and 2277%, respectively	2018	[63]

drought-resistant and water-retaining agents, improving soil structure and water-holding capacity and assisting plant growth [64]. For example, hydrogels prepared from biological waste can be used to alleviate the problem of soil drought stress [65].

(1) Improving soil structure: in the process of absorbing and releasing water, hydrogels can make the soil softer, making it easier for groundwater to leak into the ground, and can also improve the uniformity of water distribution in the soil [66].
(2) Improving soil water holding capacity: hydrogel has a hydrophilic three-dimensional network with a high water absorption rate, which can increase soil water retention, reduce water loss, reduce water infiltration channels, and hinder water infiltration downwards so that a large amount of water stays in the upper layer of the water retention agent; in addition to reusability, in water or other media, its volume can constantly be through shrinkage or swelling, to achieve the purpose of providing plants with the required water and nutrients and reduce the frequency of irrigation.
(3) Assisting plant growth: hydrogels can also assist plant germination and development, improve plant survival rate, and improve plant growth performance. It can promote plant growth by providing plants with a nutrient-rich environment, maximum water absorption, and slow release of nutrients. Slow-release nutrients can make plants utilize these nutrients over a more extended period [67].

The traditional hydrogel has a fast water absorption rate. It can reach the swelling equilibrium quickly, but its water release rate is slow and cannot provide the required water to the plant according to the temperature or pH change of the soil around the plant. This problem can be better solved by applying flexible hydrogels to farmland. The existence of environment-responsive hydrogels can effectively reduce the consumption of irrigation water, reduce the loss of water, and at the same time, it can be released into the soil in a more targeted manner moisture. For example, the maximum temperature of the soil surface in the desert can reach 40–50 °C, and the minimum temperature is –30 °C [68]. The crops planted on the ground under high-temperature conditions are difficult to survive because the surface temperature is too high and there is not enough water. The application of temperature-responsive hydrogel to the desert surface can absorb the excess water on the surface when the rainwater is lost in the rainy season and respond to the temperature when the surface temperature reaches 30–50 °C, releasing more water more quickly. Generally speaking, the pH in the soil is 8.8, and in sandy soils, the pH = 9.0. In contrast, traditional hydrogels have a high absorption rate in distilled water with a neutral pH and a much lower absorption rate in alkaline aqueous solutions. For this reason, the preparation of pH-responsive or alkali-responsive hydrogels for application in the soil can improve efficiency.

The distribution range of saline-alkali land in my country is enormous. Due to the slight precipitation and extensive evaporation in arid and semi-arid areas, the salt dissolved in water quickly accumulates on the soil surface. The soil salinization is serious, and the soil contains carbonate or diphosphoric acid. Salt can cause an increase in the osmotic pressure of the soil solution, hinder the normal water absorption of the roots, and lead to the physiological dehydration of plants [69]. In contrast, conventional hydrogels have a low water absorption rate in saline environments. pH-responsive hydrogels remove water according to the pH of the ground, delaying water loss from saline soils and reducing water deficiency. It can ensure the growth and germination of plants and improve the viability of plants in saline-alkali soil. Nanocomposites consisting of alabaster (ATP), phosphogypsum (PG), sodium polyacrylate (SP), and weathered coal (WC) can effectively reduce salinity in saline sites through ion exchange, deactivation and pH adjustment [70].

4.2. Rich in drugs and nutrients

Hydrogels can also be combined with chemical fertilizers, pesticides, herbicides, *etc*. They can slow the release of chemical fertilizers, pesticides, and herbicides, reduce the application and waste of chemical fertilizers and pesticides, improve their utilization efficiency, and keep crops more prolonged. They deserved fertilizer efficiency. The hydrogels release pesticides have many significant advantages, including reducing phytotoxicity, leaching, volatilization, drift, and soil degradation, as well as improving safety during application [71], such as pesticides within a certain period. It can be released at any location to be more targeted to the crop's own needs and can reduce environmental pollution.

The use of intelligent hydrogels for the loading of fertilizers, pesticides, and herbicides is more favorable

for the release of pesticides. For example, temperature-responsive hydrogels are used to load drugs. When the temperature is lower than the minimum critical temperature, the hydrogel shrinks, and the surface of the hydrogel is in a reserved condition. A dense protective layer is formed, and it is challenging to release pesticides. When the temperature is higher than the minimum critical temperature, the hydrogel absorbs water. It expands, the protective layer is damaged, or holes are formed, and pesticides begin to be released, allowing the crop to receive the nutrients it needs to promote better root, stem, and leaf growth in produce.

In addition, the use of the pH-responsive properties of the hydrogel can also release the pesticides needed by plants, which can achieve the purpose of killing pests on specific leaves. Chen *et al*. [71] synthesized leaf glue abamectin nanocapsules with pH-responsive controlled release properties. The capsules adhere to the surface of the crop leaves through hydrogen bonding and can be disrupted at low pH, releasing the avermectin and significantly increasing its insecticidal effect.

In addition to typical temperature/pH-responsive hydrogels that can release pesticides and other substances, light-responsive hydrogels are also often used in agriculture. The drug in the hydrogel is released. Chen *et al*. [15] developed light-responsive controlled-release herbicide particles with a core-shell structure. Under light irradiation, AB molecules undergo trans-to-cis and cis-to-trans transformations, which play a role in light of vigorous stirring to promote the release of glyphosate (Gly) from the hydrogel through nanopores for weeding was verified in pot experiments.

In addition to releasing fertilizer, environmental-responsive hydrogels can also release substances that are beneficial to plants or remove harmful substances from soil or water. For example, Lopez-Velazquez *et al*. [72] prepared biodegradable hydrogels releasing inulin isolated from Dahlia tubers to induce protection in chili plants against *Phytophthora capsici*. The pH-sensitive polymer hydrogels prepared by Ramirez *et al*. [73] can remove lead from aqueous solutions. Generally, there are three ways to combine hydrogels with fertilizers and pesticides:

(1) *In-situ* compounding. Figure 10 shows the preparation and slow-release mechanism of *in-situ* compound hydrogels of pesticides and fertilizers. *In-situ* compounding refers to the process of hydrogel processing. During the period, urea, *etc*., were dissolved in water to form a urea solution, and monomers were radically polymerized in the aqueous urea solution. Shen *et al*. [74] cross-linked with sodium alginate (SA) and $CaCl_2$ Dextrin (MAH-CD), AA, AM as monomers, polyethylene glycol methacrylic acid (PEGDA) as a cross-linking agent, and halloysite nanotubes (HNTs) as additives for radical polymerization in aqueous urea solution, a new type of double-network water-retaining slow-release fertilizer (WSF) was prepared. Experiments

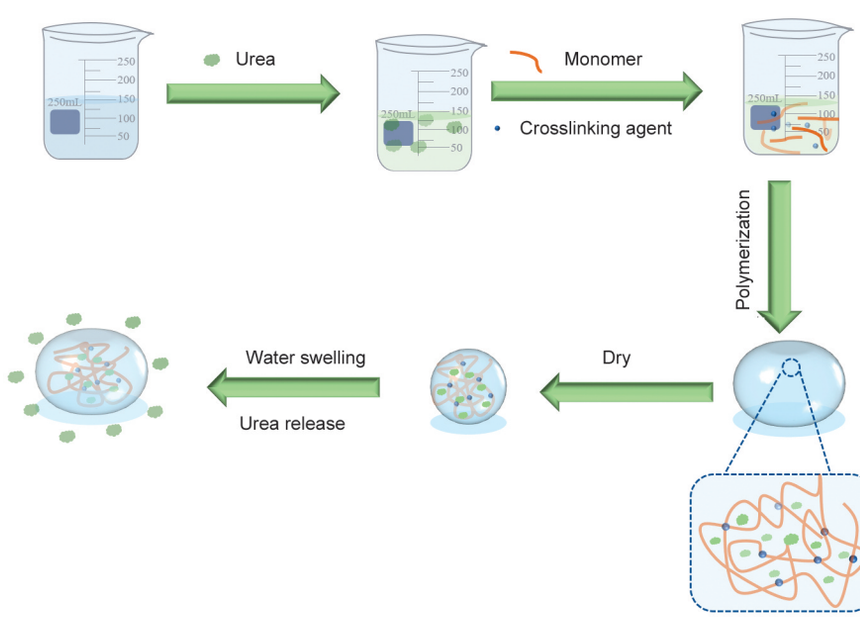

Figure 10. Study on preparation and slow release mechanism of pesticide and fertilizer in-situ composite hydrogel.

show that the presence of halloysite can improve the water-retention capacity of the soil. The surface of the WSF sample is smooth and dense, which hinders the rapid entry of water into the interior of the WSF beads, which helps Slow down the release rate of urea and prolong the release time of urea so that the soil provides a fertilizer effect for a longer time.

(2) Coating, coating refers to the hydrogel coating on the surface of urea to synthesize urea beads. Figure 11 is a schematic diagram of the preparation of hydrogel-coated urea. de Gao *et al*. [75] A low-cost, environmentally friendly WB-*g*-PAA/LA superabsorbent composite was prepared by free radical graft copolymerization of wheat bran (WB), AA, and laterite (LA) in an aqueous solution. Urea, laterite, and distilled water were then mixed to form a homogeneous mixture. The mixture was cross-linked with $CaCl_2$ solution to form urea beads (UB); the obtained UB was filtered and put into a rotating disk to coat WB-*g*-PAA/LA superabsorbent composites. In this way, urea bead-coated superabsorbent composites (UBCSCs) with WB-*g*-PAA/LA adhered to the outer surface of UBS were obtained.

(3) Leaching: leaching means that the prepared hydrogel is placed in a solution of a certain percentage of urea, *etc*. After some time, substances such as urea will enter the hydrogel through osmotic pressure. Then, the hydrogel is dried and sprinkled into the soil or surface to release the nutrients within the hydrogel. The mixture of biochar and N–P–K nutrient solution was kept at 25±0.5 °C and then dried in an oven and applied to the soil. After 45 days of research, the N–P–K in the soil Release rate was 35.46–90.83% [76].

4.3. Adsorption of heavy metal ions in the soil

The distribution of saline land in China is significant. In arid and semi-arid areas, due to low precipitation and high evaporation, the salts dissolved in water tend to accumulate in the surface layer of soil, and soil salinization is serious. The soil contains carbonate or heavy phosphate, which will cause an increase in the osmotic pressure of the soil solution, hindering the normal absorption of water by the roots and leading to physiological dehydration of plants. The pH value is high, resulting in alkaline soil [77]. After using this water for farmland irrigation, the content of heavy metal ions in the soil will exceed the standard. The crops are rich in metal ions and seriously damage human health. Adsorption of heavy metal ions in the ground is a significant task, and commonly used wastewater Treatment methods include the chemical precipitation method [78], ion exchange resin method [79], adsorption method [80], *etc*. The most economical and widely used way to treat heavy metal ions in wastewater is to use natural adsorbent materials (*e.g.*, peat, diatom-based soil, vermiculite). In addition to this, superabsorbent resins can also be used to immobilize mobile heavy metal ions. Raw adsorption materials have the defects of single adsorption performance, poor adsorption effect, slow adsorption rate, and slow absorption rate. It isn't easy to reduce the concentration of heavy metals to a safe level. Hydrogels can chelate with various metal ions, have a three-dimensional network structure, and adsorb ions or undergo an ion exchange for more targeted adsorption of heavy metal ions. For example, Zhou *et al*. [81] prepared a new soil remediation agent. Namely, a composite hydrogel (residual *m*-*g*-polyacrylic acid/montmorillonite/urea) by radical polymerization was applied to heavy metal-contaminated soil. It shows that the addition of hydrogel weakens the toxic effect of heavy metals on

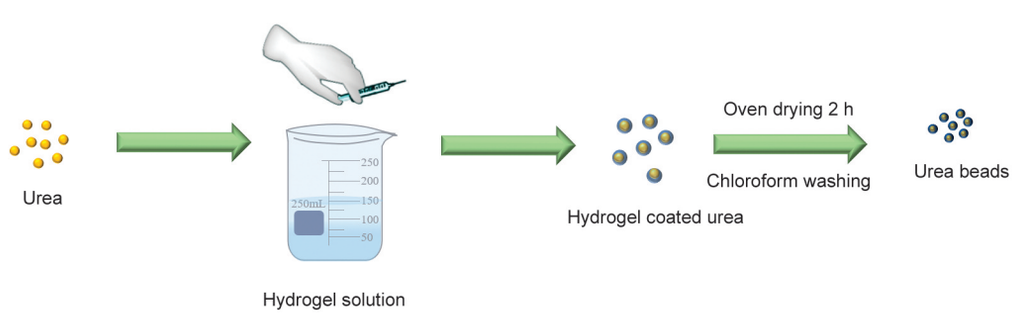

Figure 11. Schematic diagram of the preparation of hydrogel-coated urea.

cotton seeds, and with the increase in the amount of hydrogel, the product becomes more and more apparent. The hydrogel can also improve soil organic matter content, cation exchange capacity, and N, P content. Also, Perumal *et al*. [51] used inverse emulsion polymerization to prepare graphene oxide-embedded chitosan/gelatin hydrogel particles. In a single metal system, the hydrogel could remove 55% of the mercury because of the high binding affinity of the $–NH_2$ and –CN groups present in the hydrogel particles for mercury ions. The new double-net amino-functionalized starch/PAA hydrogel adsorbent can also be used to remove heavy metals from wastewater [80]. The adsorption process can rapidly reach equilibrium and effectively treat wastewater with high metal concentrations.

4.4. Environment-responsive hydrogel agricultural sensors

The development of intelligent, responsive materials is becoming more and more perfect. With the rapid growth of polymer materials, 'intelligent' biomaterials that are highly responsive to small changes in the environment have been upgraded. It is widely used in aviation, power grid, home furnishing, clothing [82], *etc*. In agriculture, the emergence of intelligent agricultural sensor applications can solve the problems of poor plant growth conditions and soil water shortage. In addition, it can also detect pesticide content and adjust water irrigation. For example, tris[(hydroxymethyl)methyl]acrylamide-*g*-methyl methacrylate hydrogels were used to regulate water flow according to soil moisture, develop and operate valves, and effectively control soil irrigation for white horseradish lily plants [14]. Through the electrochemical copolymerization of polyaniline (PANI) and hyaluronic acid (HA), PANI/HA hydrogels with porous microstructure and highly active specific areas were prepared. The linear response of 0.01–1 $ng \cdot ml^{-1}$, with a detection limit of 0.0034 $ng \cdot ml^{-1}$, can determine carbamide in fruit samples, showing efficient sensing ability [10]. Moreover, integrating long-period fiber gratings (LPFGs) with ionic strength-responsive hydrogels produces a refractive index-based, high-sensitivity, fast-response salinity fiber-optic sensor because the refractive index (RI) of seawater varies with seawater. Changes in salinity and accurate salinity can be measured indirectly through the refractive index [83].

5. Future perspectives

At present, the application of intelligent hydrogels in agriculture is not perfect. We focus on the development trend of environmentally responsive hydrogels in the field of agriculture and put forward some prospects for the future, as follows:

5.1. Preparation of environment-responsive hydrogels with good practical performance and environmental coordination performance based on biomass waste

Agricultural and forestry production produces many biomass wastes, such as straw, tailing vegetables, fallen leaves, and fruit peels, which are rarely used. Accumulation will cause environmental pollution and waste of resources, which does not meet our current strategic energy conservation and emission reduction requirements. Maximizing the utilization of biomass waste resources has become the most urgent problem we need to solve at present. Biomass waste is divided into urban biomass waste, Crop waste, animal manure, *etc*. Among them, crop waste accounts for a large proportion. A large number of wastes, such as watermelon peel (WMP), cabbage (CB), walnut peel (WP), *etc*., are discarded in the fields, which not only pollutes the environment but also is not beautiful. These crop wastes contain many sugars, cellulose, proteins, *etc*., and groups such as hydroxyl, carboxyl, and double bonds, which can cross-link and graft polymers. The treated waste can be used to prepare non-toxic and harmless, biodegradable, eco-environmental materials hydrogels that will not cause secondary pollution. For example, Zhang *et al*. [84] prepared waste CB and 2-acrylamide-2-methyl-1-propanesulfonic acid (AMPS). The super absorbent polymer has high water absorption capacity, salt resistance, water retention, and thermal stability. At present, biomass waste to prepare environment-responsive hydrogels mainly focuses on straws, *etc*., and waste resources such as vegetable tailings are not familiar, so this is also a development direction of environment-responsive hydrogels in the future.

5.2. Improving water absorption, salt resistance, and rapid response in environment-responsive hydrogels

Water absorption is an essential criterion for judging quality. Table 5 compares the water absorption of

Table 5. Comparison of water absorption between traditional hydrogel materials and environment-responsive hydrogel materials.

Traditional hydrogel	Water absorption [g/g]	References	Environment-responsive hydrogel	Water absorption [g/g]	References
CB-p(AA-*co*-AMPS)	1 914	[84]	SA-*g*-(PAA-*co*-PDMC)	277	[6]
Sodium hydroxymethyl cellulose-*g*-P(AA-*co*-AMPS)/red clay	1 329	[85]	Xylan-based temperature/pH-sensitive hydrogel	25	[38]
PAA/PAMPS/nanoparticles	13 600	[86]	SA-p(AA)/PVP/montmorillonite	619	[87]

traditional hydrogel materials and innovative hydrogel materials in distilled water. The water absorption rate of hydrogels is getting higher and higher, and the water absorption rate of environment-responsive hydrogels is generally too low.

The water absorption capacity of environment-responsive hydrogels mainly depends on their composition and structure [88]. Hydrogels typically contain more active –C=C– and hydrophilic groups that can form hydrogen bonds with water molecules; the hydrophilic order of common hydrophilic groups is $–SO_3^-$ > –COO– > –OH > $–NH_2$. The stronger the hydrophilic group, the more the content, the more the number of hydrogen bonds formed with water, and the greater the hydrogel absorption rate. The hydrogel must also have a three-dimensional network structure with a low degree of cross-linking to obtain high water absorption. The higher the degree of cross-linking, the more serious the accumulation of the hydrogel, the stronger the rigidity, and the lower the water absorption. It can also improve the porosity of hydrogels, which can play multiple roles in enhancing the total water absorption capacity and response rate by reducing the migration resistance [89]. Adding a pore-forming agent to the polymer can generate air bubbles during the hydrogel formation process, which helps to form a porous structure inside the hydrogel to increase porosity [47]. Pore-forming agents are divided into physical and chemical pore formers. Biological pore-forming agents do not participate in the polymerization reaction and act as solutes. Low boiling point substances such as anhydrous ethanol can be added to the solution as a pore-making agent. As the temperature rises, along with the volatilization of water molecules from the hydrogel, the water loss hardness of the absorbent resin hydrogel gradually increases, thus leaving a porous structure in the absorbent resin. The chemical pore-forming agent refers to the chemical change in the reaction, resulting in the formation of new substances and polymer pore structure. Such as NH_4HCO_3, in the process of aqueous polymerization, NH_4HCO_3 is dissolved in the solution. After polymerization, the temperature is raised to decompose H_2O, CO_2, and NH_3 to form uniform pores inside the hydrogel [90].

Salt tolerance is also significant for the application of hydrogels in agriculture. The primary soluble salts in soil are Na_2SO_4, $CaSO_4$, $MgSO_4$, *etc*. The presence of soluble salts will increase the concentration of water ions around the ground. When the hydrogel absorbs water, the hydrophilic groups will combine with water molecules, and the hydrophilic groups in the polymer network begin to ionize. The electrostatic repulsion generated between the ions in the network will expand the polymer chain, and the ions inside and outside the network will grow. The concentration difference is caused, and the osmotic pressure difference is formed inside and outside the network structure. Water molecules can penetrate the network through osmotic pressure, and the concentration of water ions in the soil is large, which reduces the osmotic pressure inside the hydrogel. The water absorption of the hydrogel rate decreased. When there is sufficient moisture in the rainy season, the water absorption of the hydrogel decreases. When the farmland needs adequate humidity, it cannot meet the needs, limited in farmland applications. Improving the salt resistance of smart hydrogel can introduce non-ionic hydrophilic groups and ionic hydrophilic groups ionization when absorbing water to produce ions, ions between the charge shielding effect, which will reduce the electrostatic repulsion, thus affecting the polymer chain expansion. In contrast, non-ionic hydrophilic groups are not affected by the external salt solution, can use hydrogen bonding with water molecules, not only can not improve the water absorption rate of hydrogel but can also improve Salt resistance performance [47]. The preparation and development of an intelligent and responsive hydrogel with high water absorption and high salt resistance is essential.

The response rate is also significant for environment-responsive hydrogels. When the environment changes, the hydrogel with a fast response rate can expand or contract in a short time to adapt to the changes in the background. Traditional environment-responsive hydrogels can reach equilibrium in hours or days, while fast hydrogels can increase stability in seconds or minutes. Quick response rates can be achieved by changing the hydrogel size morphology or increasing the hydrogel porosity. Generally speaking, the smaller the hydrogel or the film-like shape, the easier it is for the hydrogel to absorb water quickly. Emulsion polymerization and precipitation polymerization to increase hydrogel porosity, highly interconnected porous hydrogels can be prepared. Emulsion polymerization can achieve the dynamic stability of synthetic materials by selecting appropriate emulsifiers and polymerizing the continuous phase containing monomers. Afterward, the internal dispersed phase is removed, and the monolithic, highly porous polymer material with a specific structure can be obtained [91]. In addition, super porous hydrogels can also be synthesized, whose pores are interconnected to form open capillary channels, through which water molecules are rapidly absorbed or excluded and have a rapid response to changes in ambient temperature, *etc*. The PNIPAAm/chondroitin sulfate (ChS) hydrogel prepared by Varghese *et al*. [92] showed rapid swelling for 2 min. The introduction of ChS increased the water absorption of the PNIPAAm hydrogel. It used the method of precipitation polymerization to control the internal microstructure of PNIPAAm hydrogel, inducing porous network morphology to enhance the thermal response of the hydrogel. Using virgin coconut oil as raw material, Dharmasiri *et al*. [91] prepared highly permeable and fast-response PNIPAAM hydrogels by emulsion template polymerization, which reached an equilibrium swelling state within 15 s.

5.3. Increase the application of environment-responsive hydrogels

The use of environment-responsive hydrogels in agriculture is not yet well established. There is an urgent need to increase their use in agriculture, such as sludge curing, preparation of agricultural land films, *etc*. The sludge formed after sewage treatment is often high in water, not easily dewatered, and perishable, odorous, and fine-grained. Due to its low density, it cannot be sent directly to a landfill and needs to be solidified to a specific strength before it can be landfilled [93]. The most widely used is cement solidification, an efficient but time-consuming method for waste disposal. It is essential to discover and prepare a simple, efficient, and time-saving way; Ye *et al*. [94] incorporated polyacrylamide hydrogels in Portland cement pastes. It only takes a few minutes to solidify the waste. However, some particular wastewater, such as the sludge generated in chemical wastewater treatment, is hazardous waste, and it needs to be treated in advance before being landfilled. The hydrogel has a three-dimensional network structure, which can treat dangerous waste Adsorption can reduce toxicity, and most hydrogels are easily degradable. They will not cause too much damage to the environment, so there is still a long way to use hydrogels to solidify sludge.

Mulch film usually improves crop yield by inhibiting weeds, maintaining soil moisture, and increasing soil temperature [95]. Polyethylene film is the most used, which is not easy to degrade and pollute the environment. There are many reports on the preparation, performance, and application of degradable polymer materials, but few words on the agricultural application of degradable mulch films [96]. The currently prepared phosphorylated starch films are degradable with phosphorus introduced into the polymer [97]. The cross-linked polymer film has stable mechanical properties and good water resistance, is not easy to hydrolyze, and provides phosphorus to the soil after biodegradation. Light-responsive hydrogels can be used for the preparation of mulch films. Photo-responsive hydrogels prepared using the cis-trans isomerism of photo-responsive monomers can promote plant growth by varying the water within the membrane through changes in thickness. Hydrogels can also be used as agrarian mulch due to their network structure, insolubility in water, degradability, and deformability.

5.4. Strengthen the research on integrated cultivation technology of environment-responsive hydrogels application in the field

At present, the agricultural applications of environment-responsive hydrogels are small-scale pilot studies or laboratory-scale studies. For example, Song *et al*. [98] prepared a lignin/SA hydrogel with degradable, non-toxic, water-absorbing, and soil nutrient-retentive properties. The results of drought

stress experiments using the hydrogel on potted tobacco plants showed that the hydrogel could affect proline and reduce the concentration of intracellular sugars and other regulators, improving the drought resistance of tobacco plants. Although small-scale pilot studies and laboratory-scale studies are more convenient and can draw relevant conclusions quickly, there are some problems:

(1) The environment and climate are different from the field. Taking the Gymnocarpos przewalskii growing in the Guazhou Extremely Dry Desert National Nature Reserve as an example, the annual average temperature in Guazhou is 8.8 °C, the extreme maximum temperature is 42.8 °C, and the extreme minimum temperature is –29.1 °C, with little rainfall, significant evaporation, long sunshine time, and fast water evaporation, while the temperature in the laboratory is generally 20 °C and lack of sunlight;

(2) The short test period does not give a good indication of the performance of the hydrogel, which is fast in absorbing water but slow in releasing it, and the ability of the hydrogel to act is not reflected in a short study. In addition, hydrogel plays a vital role in the growth and germination of plants. It can reduce soil water evaporation, promote the growth and development of plant roots, and improve soil structure, which profoundly impacts the future growth of plants. Short-term experiments cannot observe changes in plants;

(3) The relationship between environmental-responsive hydrogels application and field climate, environment, and other conditions is inconsistent, which leads to the lack of the evaluation and summary of ecological environment coordination. Based on the above analysis, promoting the large-scale application of environment-responsive hydrogels is imminent.

6. Conclusions

In summary, this paper reviews several types of environmental-responsive hydrogels, which react very quickly to external stimuli, can achieve volume change in a few seconds, and are highly sensitive. The response of the environment to the volume change of the hydrogel is reversible; that is, when the external stimuli are eliminated, the hydrogel will return to its initial state. In addition, the mechanism of their response is elaborated, and by adjusting the composition and structure of the hydrogel, its response characteristics can be precisely controlled so that it has different responses to different stimuli. Three methods for preparing environment-responsive hydrogels, including free radical polymerization, network polymerization, and block polymerization, were summarized, and the advantages and disadvantages of each method were discussed and compared. Environmental-responsive hydrogels are very common in various fields, such as smart sensors, biomedicines, mechanical actuators, *etc*., while applications in agriculture are relatively scarce.
Finally, their application in agriculture is introduced and prospected. More application of environmental-responsive hydrogels in agriculture is conducive to alleviating the problems of low vegetation survival rate caused by high temperature, water shortage, and severe saline-alkali phenomenon in desert areas, which is of great significance to realize the protection and restoration of ecosystems.

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