Advances in Classification and Application of Hydrogel Materials

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Abstract

Hydrogel is a new type of polymer material with a three-dimensional network structure. It has high water content, fast swelling, soft, rubber-like consistency and excellent biocompatibility, and has been widely used and studied. In this paper, the classification, application and current research hotspots of self-repairing hydrogels were studied, and the future development trend was predicted.

Keywords

Hydrogel; Self-Repair; Classification; Application.

1. Introduction

The hydrogel is defined as a general term for some crosslinked polymers that can maintain a large amount of water while water or other biological liquids swell, but cannot be dissolved by the liquids as mentioned above. These polymers are hydrophilic and insoluble in water. They are a class of polymer materials with a three-dimensional network structure in space structure. It is found that these polymers have good physical and chemical properties, and their biological properties also show excellent effects. They can be used for controlled drug release operations, and also have important application prospects in biological adhesion, biocompatibility and biodegradability. At present, it has been used in controlled release, pulse release and trigger release of some new drugs in the human body, so as to improve the efficacy of drugs. Because of its unique water absorption and good biocompatibility, it has attracted the attention of materials science and biomedical workers and has been widely applied and studied.

At present, the most widely studied stimulus-responsive polymer is a hydrogel. The properties of hydrogel polymers are first related to the properties of polymeric monomers and crosslinkers, and secondly to the parameters of polymerization conditions of the raw polymer of a hydrogel, and also to the conditions used in swelling. According to the response of hydrogels to external stimuli, hydrogels can be divided into two categories: one is traditional hydrogel polymer materials, which are relatively insensitive to environmental changes. The other is hydrogel polymer materials which are very sensitive to external conditions. Because of their different response to different environmental conditions, these hydrogel polymer materials can be used as a new type of intelligent materials and have good research and market application prospects [1].

In this paper, the types, properties, applications and practical prospects of hydrogel polymer materials, as well as the research prospects of new intelligent materials in the future, are analyzed and summarized.

2. Classification of Hydrogels

2.1 Intelligent Hydrogel

Intelligent hydrogel is a kind of polymer with a three-dimensional network structure formed by physical or chemical crosslinking of the intelligent polymer. It can absorb a large amount of water and swell to equilibrium volume, but still keep its shape [2]. The smart polymers, which constitute the three-dimensional structure of intelligent hydrogels, can conformate in response to small changes in environmental stimuli, resulting in changes in the volume or other physicochemical properties of gelatin. According to the characteristics of intelligent hydrogels in response to environmental stimuli, intelligent hydrogels can be divided into temperature-responsive [3], pH-responsive [4], specific

ion/molecule-responsive [5-6], glucose concentration-responsive [7], light-responsive [8], electric field-responsive [9], and other different types of hydrogels. Because of the response characteristics of environmental stimuli, environmental responsive intelligent hydrogels have important applications in the fields of sensors [10], artificial muscles [11], software robots [12], chemical reaction switches or microvalves [13], tissue engineering [14], drug controlled release [15], substance separation [16]. Therefore, the research of intelligent hydrogels has attracted much attention.

The properties of intelligent hydrogels include environmental stimulus responsiveness (such as stimulus recognition, response rate and sensitivity) and mechanical properties. In addition to the fast response characteristics [17], the mechanical properties of intelligent hydrogels are also one of the important parameters that directly affect their applications. For example, when smart hydrogels are used as scaffolds for tissue engineering, they need sufficient mechanical strength to withstand stress without being destroyed; when smart hydrogels are used as chemical reaction switches or microvalves, they are required to withstand certain impact and long-term reuse. When intelligent hydrogels are used as artificial muscles, they need to be as tough and strong as possible to be similar to biological tissue muscles [18]. However, conventional smart hydrogels are often brittle because chemical small molecular crosslinking agents form most conventional smart hydrogels. In the formation process of hydrogel network, chemical small molecule crosslinking agents often form cross-linked clusters with the main polymer. The size and distribution of these cross-linked clusters are not uniform, leading to the different length of polymer chains between clusters and clusters during the subsequent gel network construction, and ultimately forming a non-uniform three-dimensional polymer network structure. When external forces deform the hydrogel, the stress is concentrated on the shortest polymer chain, and very short stress can reach the short chain fracture limit of these polymers, which is often destroyed first and then forms a crack. Then, with the increase of external force, the crack is like "breaking the wind" and finally destroys the network of the whole gel [19]. Generally speaking, the basic reason for the poor mechanical properties of conventional intelligent hydrogels is that there is no stress dispersion mechanism in the network structure, which makes it easy to destroy the network structure with less stress. Therefore, it is particularly important to construct a special network structure to dissipate or disperse stress and improve the mechanical properties of intelligent hydrogels.

2.2 Polymer Hydrogel

Polymer gel polymer compounds change in the external environment, such as temperature, pH and so on. When these conditions are changed, the volume will change. This is mainly due to the ionic structure, hydrophobic effect, Fan Dehua force and hydrogen bond.

There are many methods for the preparation and synthesis of hydrogel macromolecule compounds. According to the different initiators, hydrogel macromolecule compounds can be divided into chemical method and radiation method. The chemical method is divided into the emulsion method, inverse emulsion method and so on. Radiation methods can be divided into ultraviolet and gamma-ray radiation methods. Also, the method of monomer grafting initiated by radiation energy is also one of the main methods to synthesize polyelectrolytic hydrogel polymers.

Chen Yongmei et al. [20] Diels-Alder reaction was carried out between 2-fuolevulinic acid-grafted dextran and polyethylene glycol-modified with dichloromaleic acid at both ends to produce dextran hydrogel with self-healing properties. The hydrogel showed that the incision could heal itself about 4 hours.

Deng et al. [21] synthesized hydrogel HG1G2 containing both acylhydrazone bond and disulfide bond. The synthesis mechanism is shown in Fig. 4. When the pH value of the hydrogel is 6, the acylhydrazone bond is reversible, and the hydrogel contacts in the air for 48 hours to achieve self-healing. Under neutral conditions, aniline catalyst was added, the acyl hydrazone bond was activated, and the hydrogel had self-healing property. When pH was 9, the disulfide bond was reversible and the gel could self-repair. The 24h self-repairing efficiency of the gel is over 50%.

The hydrogel with pH value and redox dual response properties can be obtained by using the hydrazone bond and disulfide bond [22]. The addition of acid, alkali or redox material shows a sol-

gel transition, as shown in Figure 1. This reflects the self-adaptability of materials. This self-healing multi-response hydrogel, which combines two dynamic reversible bonds, represents the development of self-healing hydrogels to more abundant cross-linking sites of various types.

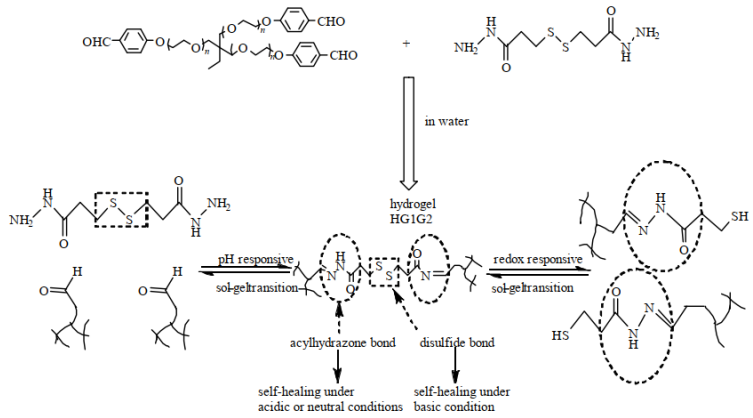

Fig.1 Synthesis of dynamic hydrogel HG1G2 containing both acylhydrazone and disulfide bonds

2.3 Hydrogen Bonded Hydrogel

Self-repairing materials based on weak interaction of hydrogen bonds are a new kind of self-repairing materials developed in recent years. They can achieve self-repairing by breaking and recombining intramolecular or intermolecular hydrogen bonds without implanting repairing agents. They have the advantages of low repair temperature and good repeatability. They have important theoretical and practical significance.

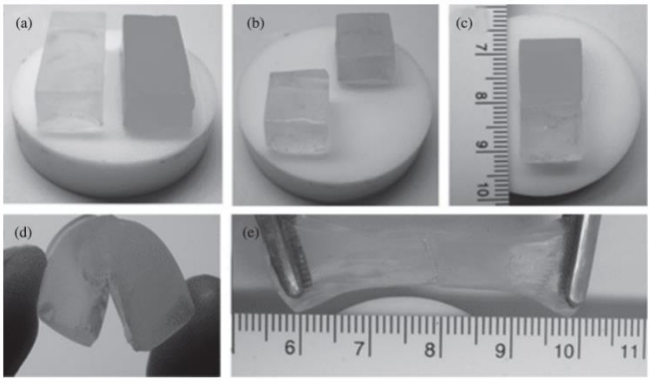

Fig. 2 Self-repairing process of polyvinyl alcohol hydrogel

The Leibler [23] team reported in 2008 that the idea of developing self-healing polymer materials using supramolecular models began to gain popularity when crosslinking of hydrogen-bonded polymer networks was self-healing. After that, many healable or self-healing hydrogen-bonded polymers were successfully prepared. Xia Sheng et al. [24] prepared a self-repairing hydrogel by a freeze-thaw method using polyvinyl alcohol (PVA) at room temperature without any stimulation or repair agent. The broken hydrogels can be repaired by docking them at room temperature for 12 hours. The repairing mechanism is that the diffusion and movement of the fractured molecular chains cause the formation of hydrogen bond interaction between the molecular chains. Figure 2 shows that the two fractured hydrogels are repaired together and have good mechanical properties. Li [25] et al prepared polyurethane hydrogel by using the dynamic four heavy hydrogen bond of 2- urea pyrimidone (UPy) unit. After 5 minutes, the heating efficiency of the gel was 60%, and the equilibrium of 80%~87% reached only within 10min. The healing of scratch gel membrane was also observed under a microscope. The mechanism of the repair was to make use of the multiple hydrogen bond breakage of UPy unit to achieve the repair effect (Fig. 3).

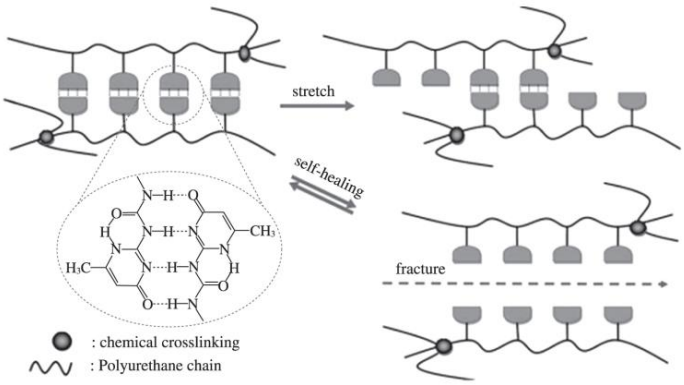

Fig. 3 Self-repairing schematic diagram of hydrogels formed on side chains by PU-oriented UPy units

Although much research has been done on self-repairing materials based on reversible non-covalent bonds such as hydrogen bonds, most of the research focuses on the modification and functionalization of traditional materials, and more in-depth research is needed on the development of new self-repairing systems and materials.

2.4 Graphene Oxide Composite Hydrogel

Graphene oxide (GO) is a kind of two-dimensional nanomaterials with low cost, easy dispersion in water and good photothermal properties. Combining graphene oxide with hydrogels can give hydrogels many excellent properties and greatly expand the potential applications of hydrogels.

Hydroxyl and epoxy groups on the surface of GO sheet can form hydrogen bonds with polymers. Because hydrogen bonding is a reversible physical crosslinking, the cross-section of polymer chains at the fracture site diffuses with GO and polymer chains at the other end of the fracture surface to form a hydrogen-bonded crosslinking network, so GO composite hydrogels have certain self-repairing properties, which can realize the reuse of materials and prolong the service life of materials. In the life system, tissues and organs have self-repairing properties. Hydrogels with self-repairing properties have great potential in the field of biomedicine because of their good biocompatibility and softness [26].

A GO/polyacrylamide (PAM) composite hydrogel was prepared by Liu et al. [27]. The self-repairing properties were attributed to the mutual diffusion of GO and PAM at the cross-section, the elongation of the polymer chain at the cross-section, the hydrogen bond between PAM chains and the hydrogen bond formation between PAM and GO, as shown in Figure 4. The hydrogel has good self-healing ability at room temperature and even at a lower temperature. Extending the repair time, the hydrogel can obtain a very high degree of recovery (up to 88% tensile strength). The self-repairing gel has high tensile strength (0.35MPa) and a very high elongation at break (4900%). Comparative experiments verified the role of GO in the self-healing properties of hydrogels. A traditional PAM hydrogel was prepared by using conventional chemical initiators and crosslinking agents. It was found that PAM hydrogels without GO could only partially heal. GO composite hydrogel and GO free PAM hydrogel were added to deionized water to achieve swelling equilibrium. The PAM hydrogel without GO was split in the swelling process, while the GO composite PAM hydrogel remained intact. This indicates that the strong interaction between PAM chains and GO films is important for self-repairing gel.

Zhong et al. [28] prepared GO-PAA nanocomposite hydrogels with self-repairing properties and super high mechanical strength by one-pot in-situ radical polymerization. The three-dimensional network structure of GO-PAA nanocomposite hydrogels produced double crosslinking by dynamic ion interaction. The first crosslinking point was Fe^{3+}, which was crosslinked between PAA polymer chains by ion interaction. The second crosslinking point is GO, which crosslinks PAA chains through the coordination of Fe^{3+} ions. The mechanical properties of GO-PAA composite hydrogels after self-repairing at different temperatures and repair times are shown in Fig. 5. The GO-PAA nanocomposite hydrogel was self-repairing after 48 hours treatment at 45℃ (495 kPa in tensile strength and 2470%

in elongation at break). The mechanical strength and tensile properties of the self-healing hydrogels are also outstanding and have potential applications in bioengineering materials.

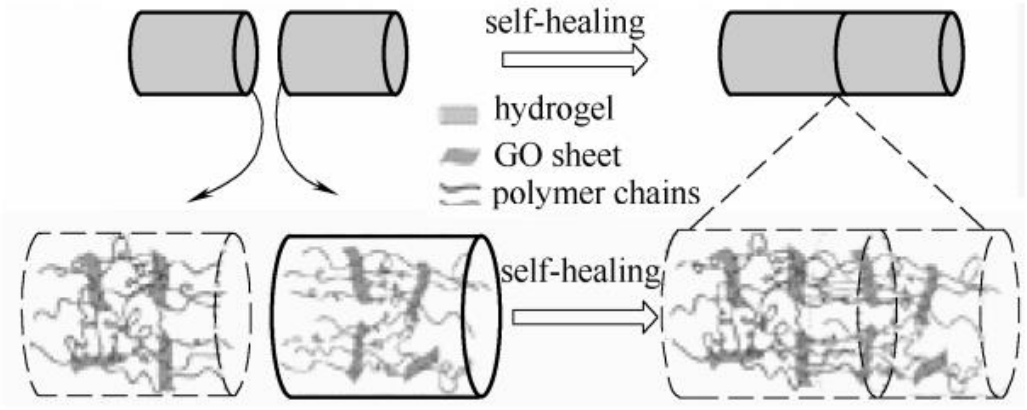

Fig. 4 Proposed self-healing mechanism of GO composite hydrogels

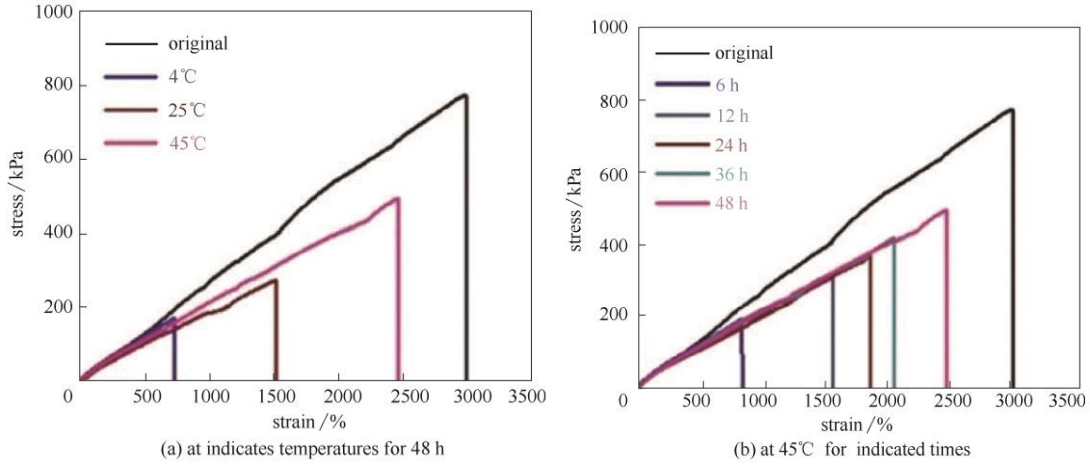

Fig. 5 Stress-strain curves of GO-PAA nanocomposite hydrogels after cutting and self-repairing

3. Application of Hydrogel

3.1 Application of Hydrogel in Medical Field

Hydrogel macromolecule compounds are similar to the structure of living tissues, so they can be used in human body without affecting the metabolic process of living organisms. At the same time, the metabolites in vivo can be excluded by hydrogel, so hydrogels can be used as fillers for some tissues in vivo. Hydrogels can also be used to make contact lenses, medical sensors, artificial skin, etc. [29-30].

Polymer hydrogel materials have a good role in water absorption, and also have a good application in urine and blood suction, so the application in the field of health materials is the earliest and most mature. Therefore, paper diapers, urination bags, physiological towels have a large number of applications.

Polymer hydrogel [31] is currently used in some medicines. Microcapsules are made as carriers of medicines, which can be directionally delivered to the diseased area for controlled sustained release, thereby improving the efficiency of drug use. In the field of biological science, polyacrylamide gel polymer with different pore sizes has been used as a tool for separation of proteins and amino acids with different molecular weights.

3.2 Application of Hydrogel in Industry

Adding hydrogel to coatings can endow them with pseudo plasticity and thixotropy, make them have high viscosity and yield stress, and prevent the flow hanging phenomenon of coatings. Hydrogel can be used as a flocculant to treat wastewater from papermaking, tannery and food processing. Hydrogels can also be used as fresh-keeping packaging materials for cable wrapping materials, drilling

lubricants, food, fruits, vegetables and other high-precision instruments such as humidity sensors, moisture sensors and water leakage detectors used in the electronic industry [32].

3.3 Application of Hydrogel in Tissue Engineering

Many tissues in organisms have the structure of hydrogel macromolecule compounds. The tissues of organisms are composed of cells and extracellular matrix. The components of the extracellular matrix are hydrogel-like substances composed of protein, sugar and water.

The polymer gel currently widely concerned is mainly peptide gel. A series of functional peptide gels were prepared by Masayuki Tomida [33]. Aspartic acid was crosslinked by γ ray irradiation to obtain gel, and the water absorption rate could be as high as 3400 times. Many scientific researchers have also made many useful explorations on the preparation of peptides made from microorganisms. These α-peptides have good biodegradability.

4. Research Trend of Hydrogel Materials

The excellent properties of hydrogels have attracted and are still attracting widespread interest. The research and development of polymer hydrogels with better properties have become an important research hotspot.

Environmental-sensitive polymer hydrogels play an important role in many fields, such as cell separation, immobilization of enzymes, slow-controlled drugs and targeted drugs, and show very good application and market prospects. The important point of environmentally sensitive polymer hydrogels is that they can be used for immobilization of biologically active molecules such as enzymes to achieve effective unification of homogeneous reactions and heterogeneous separation by controlling conditions, while in the field of drug controlled release, they can change with environmental conditions in different occasions. It will play an important role in the research of biologically active molecules and biomedical polymers [34].

It is an important method to improve the mechanical properties of hydrogels by increasing the crosslinking between polymer molecules. There are mainly chemical crosslinking method [35] and physical crosslinking method [36], but the general crosslinking will make the swelling performance of hydrogel polymer compounds very poor, which is very unfavorable to the practical application of hydrogels. Some studies [37] show that adding layered silicates to N, N'-diethylacrylamide hydrogel polymer materials can improve the swelling properties of hydrogels.

According to the development trend of hydrogels in recent years, there are relatively many theoretical studies. Researchers are very interested in the application prospect of hydrogels, especially in the field of biomedicine. Recently, several sensitive behaviors of hot intelligent hydrogels have been studied, which are more outstanding than a series of traditional materials (such as poor mechanical properties and slow response speed of traditional materials). It is expected that new breakthroughs will be made in molecular devices, biomedicine and other fields. At present, a lot of hard work still needs to be done to improve the mechanical properties of hydrogels and to develop new kinds of hydrogels.

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