Research Progress of Conductive Hydrogel Materials and Their Biomedical Applications

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Abstract: Hydrogel is a new functional polymer material, which has hydrophilic groups, can be swollen by water but is insoluble in water and has a three-dimensional network structure. Hydrogels have been widely used in the past decades because of their inherent characteristics, such as dynamics and versatility. Conductive adhesive has the advantages of no environmental pollution, fine pitch and ultra-fine pitch interconnection, low cost, good environmental compatibility, low bonding temperature, high resolution and simple use steps. Conductive hydrogel organically combines hydrophilic matrix and conductive medium, which is a new type of composite hydrogel with good processability, high flexibility and excellent electrochemical performance. In the biomedical field, the surface of hydrogel is not easy to adhere to cells and protein, so it shows good biological description when it comes into contact with human tissues. In this paper, the research frontier and trends of conductive hydrogel are introduced, and its application in biomedicine is discussed, which provides new research ideas for the construction and design of conductive hydrogel functional electronic materials.

1. Introduction

Hydrogel is a kind of soft material with three-dimensional network structure, which is formed by crosslinking hydrophilic polymers through covalent bonds, hydrogen bonds or coordination bonds. It can sense the small changes of external stimuli and make corresponding sensitive responses to the small changes, often by swelling or shrinking the volume [1]. In the biomedical field, the surface of hydrogel is not easy to adhere to cells and protein, so it shows good biological description when it contacts with human tissues [2]. Its unique tissue structure, after absorbing water, the internal structure contains a lot of water to make the gel soft, similar to the biological tissue, and it can have good mechanical properties through special preparation methods [3]. Because of its unique porous structure and good flexibility, hydrogels show excellent application prospects in flexible wearable electronic products, batteries and biosensors, and these applications require hydrogels to have good conductivity [4]. Conductive adhesive is a kind of adhesive that integrates cohesiveness and conductivity, and has certain conductivity after curing or drying. It usually consists of matrix resin and conductive filler. Through the bonding effect of matrix resin, the conductive particles are combined to form a conductive path, and the conductive connection of the adhered materials is realized [5]. Hydrogel nanoparticles not only have the characteristics of environmental responsiveness of hydrogels, but also have unique nano-characteristics such as interface effect, surface effect, volume effect, size effect, seepage effect and so on [6]. Conductive adhesive has the advantages of no environmental pollution, fine pitch and ultra-fine pitch interconnection, low cost, good environmental compatibility, low bonding temperature, high resolution and simple use steps [7]. Hydrogel is a kind of polymer material with hydrophilic three-dimensional network structure formed by chemical crosslinking or physical crosslinking, which can absorb and keep a lot of water in water and swell without dissolving [8]. In addition to stimulus responsiveness, hydrogels are also used in drug delivery systems, catalysis, pollutant degradation and energy storage. In the process of catalysis, hydrogel is used as a carrier by immobilizing substrate molecules/particles [9]. At present, the preparation and application of conductive hydrogels have become a research hotspot, and many preparation methods of hydrogels have been reported, which are widely used in pharmacy,

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biomedicine and other fields. In this paper, the research frontier and trends of conductive hydrogel are introduced, and its application in biomedicine is discussed, which provides new research ideas for the construction and design of conductive hydrogel functional electronic materials.

2. Composition and classification of conductive adhesives

Prepolymer is the main component of the matrix, which provides adhesive properties for conductive adhesives, mainly various organic adhesives, such as epoxy resin, polyurethane, phenolic resin and so on. After curing, the prepolymer forms a molecular skeleton structure, which is the source of mechanical properties and bonding properties of conductive adhesives [10]. Structural conductive adhesive and composite filled conductive adhesive. Structural conductive adhesive is mainly a polymer matrix, which has conductivity itself and does not need to add other inorganic fillers. The preparation of structural conductive polymers is very complicated, and the conductivity can only reach the level of semiconductors, and the conductivity stability and repeatability are poor, so it is difficult to play the role of conductive connection.

In the preparation of conductive adhesive, the viscosity of conductive filler is greatly increased. In order to reduce the viscosity and facilitate the use, some diluents, such as acetone and ether, are often added. Conductive filler of conductive adhesive is the main source of conductivity, which can be generally divided into metal filler, inorganic filler and mixed filler [11]. Composite filled conductive adhesive is generally composed of polymer resin matrix, inorganic conductive filler, curing agent, dispersant and other additives, in which the resin matrix provides mechanical and mechanical properties for conductive adhesive, while inorganic conductive particles provide the required conductivity for conductive adhesive. Now most conductive adhesives are composite filled [12]. Tunneling effect refers to some conductive particles that are not in contact with each other. Due to electron transition, electrons cross the barrier to participate in conduction, resulting in conductivity. According to the field emission theory, the probability of contact between conductive particles is very small when the diameter is nanometer, and the tunneling effect and thermionic emission are the main reasons for the conductivity of the system. Figure 1 shows the microstructure of conductive hydrogel.

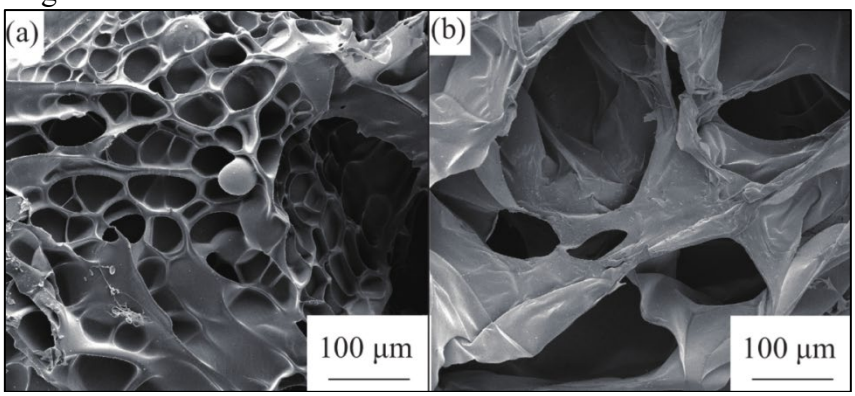

Figure 1 Microstructure of conductive hydrogel

Thermosetting composite filled conductive adhesive is generally composed of prepolymer, curing agent, conductive filler, plasticizer, coupling agent and other additives. Resin polymerization occurs during curing. Curing temperature has a certain influence on curing time, among which the curing time of medium temperature curing is ideal and suitable for production application [13]. According to the matrix, there are two kinds: thermoplastic and thermosetting. At high temperature, the matrix molecules of thermoplastic conductive adhesive have fluidity, while the matrix molecules of thermosetting conductive adhesive are not easy to flow. Curing agent is a kind of substance or mixture that can promote or control the curing reaction. Its main function is to react with polymer resin matrix to shrink the volume of resin and form three-dimensional network of insoluble and insoluble polymers. Conductive filler is the source of conductivity of conductive adhesive, so it is a very important component.

Conductive hydrogel, as a conductive polymer with porous structure, is widely used in energy conversion devices. Conductive polymer-based biomass-based conductive hydrogels mainly transfer electrons based on the unique π conjugate structure of polymers. The three-dimensional continuous porous network of polymer is very effective to improve the adsorption capacity and ion migration capacity of polymer for liquid electrolyte. Due to the bridging effect of polar group $-NH_2$ in phenylenediamine molecule, the conductive polymer formed by aniline during oxidative polymerization was grafted onto PAAm chain, which significantly improved the compatibility of PANI with water. Conductive hydrogel is formed by in-situ polymerization in preformed hydrogel, so that the hydrogel matrix network and the conductive polymer network form an interpenetrating or semi-interpenetrating network, and the conductivity of hydrogel can be adjusted by controlling the polymer content. In addition, the introduction of p-phenylenediamine improves the nucleation conditions of PANI monomer, makes the anisotropic distribution of polymer uniform, and makes the contact between PANI network and electrolyte more complete, thus improving the electrochemical properties of materials.

3. Application of conductive hydrogel materials in biomedicine

Hydrogels have both liquid and solid properties. In low concentration gel, water molecules and drug molecules can pass freely, and the diffusion speed is equivalent to that in solution. When the gel concentration increases or the crosslinking degree increases, the diffusion speed of drug molecules decreases relatively. At present, as an environmentally responsive and nano-controlled release drug delivery system, the application of hydrogel nanoparticles in biomedicine has been widely concerned [14]. As a drug carrier, polymer intelligent hydrogel nanoparticles have the advantages of reducing the times of taking drugs, shielding the pungent smell of drugs, artificially controlling the drug dosage through external conditions, improving the curative effect of drugs and reducing the cost of drugs [15]. Drug release can be controlled by the blocking effect of hydrogel on solute diffusion, which is also one of the applications of hydrogel in pharmacy. The hydrogel with pH sensitivity can also be used as a carrier to protect protein and polypeptide drugs, so that these drugs can be released in a relatively mild position, and the effectiveness of drug administration through the gastrointestinal tract can be realized.

The high volume resistivity of conductive adhesive has always been a limiting factor in its application, so how to effectively reduce the resistivity of conductive adhesive naturally becomes the focus of modification research. Due to the enhancement of cross-cell delivery path, the delivery rate of oligonucleotides that have interacted with hydrogel nanoparticles is obviously faster than that of unmodified oligonucleotides when passing through the monolayer of Caco-2 cells, and the drug properties of oligonucleotides fixed in gel nanoparticles have not deteriorated when passing through the monolayer of intestinal cells, which shows that this method is expected to be applied in oral administration [16]. Protein on the surface of hydrogel has little adhesion to cells, and when it comes into contact with blood, body fluids and human tissues, it shows good biocompatibility. Because it contains a lot of water, the hydrogel is soft and similar to biological tissues, and it can be used as human implants to reduce adverse reactions, so it is regarded as an excellent biomedical material [17]. In the process of storage and use of metal conductive fillers, there will inevitably be oxidation, thus forming an oxide film on the surface to affect the conductivity, so reducing the metal oxide film on the surface of conductive fillers is also a way to improve the conductivity of conductive adhesives [18].

Peptides and protein used for treatment have sensitive biochemical characteristics, and at present they can only be administered by intramuscular or intravenous injection to achieve better efficacy [19]. However, protease in biological fluid will degrade their receptors, and long-term and multi-dose drug injection also brings pain to patients. There are many injectable hydrogel scaffold materials, among which natural hydrogel scaffold materials have excellent characteristics such as extracellular matrix components similar to chondrocytes, which can simulate the microenvironment of tissues and maintain cell phenotype, so they become important materials for cartilage defect repair scaffolds. Figure 2 shows the application of conductive hydrogel in biomedicine.

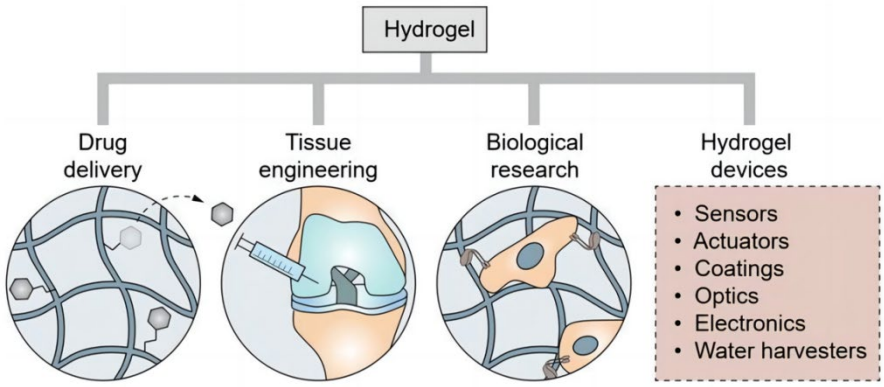

Figure 2 Application of conductive hydrogel in biomedicine

In some inflammations, the natural polymer of synovial fluid, hyaluronan, will degenerate and no longer provide normal viscoelasticity. When injected with hyaluronan, it is expensive and the effect is not long [20]. Hydrogel nanoparticles, as intelligent nano-drug carriers, have good targeting, environmental self-regulation and suitable half-life of drug release, and have good aging resistance, so they can provide long-term satisfactory results. The conductivity of conductive adhesive is mainly provided by conductive filler. Changing the shape, size and composition of conductive filler properly can improve the conductivity, thus improving the conductivity.

4. Conclusions

Compared with traditional hydrogels, conductive hydrogels combine high elasticity, flexibility and good biocompatibility of hydrogels with unique conductivity, which makes them have excellent application prospects in flexible wearable electronic products. According to the required product performance requirements, using the flexibility and diversity of sustainable biomass materials, the application performance of hydrogels is improved by physical/chemical means or adding or subtracting related materials, and even the hydrogels are endowed with multi-functions, making them a leader in the field of green chemistry. Different drugs are loaded to achieve different therapeutic effects, which reflects the important role of responsive hydrogels in biomedicine. Facing the shortage of traditional materials in the medical field, hydrogel, as a rare new functional polymer material, has some outstanding properties that traditional materials do not have, which makes it more and more widely involved in the biomedical high-tech field. Controlling the precise release of drugs, controlling the hydrogel system to respond to stimulation conditions more sensitively and accurately to achieve better therapeutic effects, and truly applying responsive hydrogels in the biomedical field to realize its therapeutic value and generate economic and social benefits are important scientific research transformation problems that need the cooperation of scientists and clinicians.

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