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Medical Usage of Degradable Shape Memory Polymers

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Abstract. In recent years, with the emergence of a large number of research results on degradable Shape Memory Polymers (dSMPs), some researchers have noticed that this material has a wide range of application scenarios in medicine. This article summarizes the current application status of different types of shape memory materials in various fields of medicine and reflects their application value in medicine. Research has found that dSMPs have already found certain applications in implants. Due to their unique advantages, they are gradually replacing implants made of traditional materials. However, there is less research on them in the field of micro-robots, and they still have broad research prospects. Compared with traditional materials, the special properties of dSMPs enable it to break through the constraints of original thinking in medicine, no longer limited by factors such as shape and volume, and design more complex, advanced and complete medical devices, exerting a profound and extensive influence on the development of medicine.

Keywords: Degradable Shape Memory Polymers; Implants; 4D printing; Micro-robots.

1. Introduction

With the rapid development of the concept of minimally invasive surgery, shape memory materials have received increasing attention in fields such as medical devices and implantable stents. However, implants made of traditional shape memory materials may have uncertain effects if they remain in the body for a long time. To avoid adverse reactions, secondary surgery is often required for removal, which greatly complicates the surgical process and increases the surgical risks. It is precisely under this background that dSMPs have become a research hotspot.

In recent years, research based on degradable shape memory materials has achieved remarkable results in multiple aspects. From the perspective of material design, researchers have successfully developed a degradable shape memory material system with a recovery temperature close to human body temperature through means such as composite materials, copolymerization, and chemical modification. For instance, the poly(glycerol dodecanoate) acrylate (PGDA) 4D printing technology has a transition temperature range of 20°C to 37°C, making it suitable for shape programming at room temperature and shape unfolding in the human body [1]. Research that combines dSMPs with drug sustained-release technology is also one of the popular directions. By embedding drugs within implants with degradation capabilities, complex multiple surgical procedures can be simplified into a single operation. For instance, Mahmoud et al. utilized dSMPs in combination with drug sustained-release technology to prepare an intelligent gastric retention system based on 4D printing. The material is endowed with controllable deformation and timing response characteristics, achieving the functions of delayed release and precise delivery of drugs in the body [2].

At present, medical dSMPs also face many challenges. Biocompatibility and the toxicity of degradation products remain unresolved issues. Although some materials such as PLA have been proven to have very low toxicity of degradation products to the human body [3], more clinical trials are still needed to support the impact of more dSMPs on the human body. Maintaining the degradation rate and structural integrity is also one of the key issues. At present complete model of the in vivo environment and implant degradation in the human body still needs to be established to improve the predictability of the implant degradation process. In addition, the manufacturing process and response regulation still need to be further optimized to meet the complex medical application requirements.

Despite facing various challenges, the application of medical dSMPs can still have an impact that cannot be ignored. This article will systematically review the current development status and future trends of medical dSMPs. First, introduce the basic theory, classification and commonly used polymer systems of dSMPs; Secondly, introduce the application directions of different materials respectively according to their characteristics. Subsequently, the key issues affecting its medical application were analyzed, including biocompatibility, degradation kinetics, shape memory mechanism and preparation process; Finally, let's look forward to the development directions of dSMPs and 4D printing, bioactive modification and multi-functional integration.

2. The Characteristics of Degradable Shape Memory Polymers

2.1. Shape Memory Ability

The shape memory ability of dSMPs enables implants made of dSMPs material to enter specific positions in the human body through minimally invasive surgery. Compared with the traditional medical procedures that require large-scale incisions for implant surgery, the implants made by dSMPs only need to make a small incision on the human skin, simplifying the complex-shaped implants into simple shapes such as spherical or filamentous ones, and then the implant devices are injected into the predetermined positions through tiny pipes. This operation simplifies the surgical process, significantly reduces the difficulty of incision, not only shortens the wound healing time, but also minimizes the occurrence of wound infection as much as possible.

2.2. Remote Operation Capability

The remote operation capability of dSMPs also enables complex control that traditional implants cannot perform. If traditional implants need to be operated remotely, they often require an internal energy source similar to a battery to assist in signal transmission between the implant and the outside world. The size of the battery is unacceptable for micro implants. Implants made of dSMPs materials have multiple control methods. They can not only be directly heated to control the implants to perform specified actions but also be remotely controlled by indirectly heating the implants through methods such as external infrared and magnetic fields. The implants do not require external power supply. Simply changing the physical environment of the implants can achieve signal transmission across the inner and outer layers of the human body. The alteration of the chemical environment is also one of the means to operate implants, and it can even enable implants to automatically respond to changes in the human body's environment.

2.3. Degradation Ability

Compared with ordinary SMP materials, dSMPs materials have the characteristic of being degradable in the human body. Under normal circumstances, except for a few implants that need to coexist permanently with the human body, most implants that enter the human body need to be removed after achieving the set goals. For patients, one operation has already caused certain harm. And when the implant needs to be removed, the wound from the first operation often has just healed, and a second operation is required to remove the implant. This is detrimental to both the physical and mental health of the patients. Previously, many degradable materials in the body have been used to make implants. The implants in the patient's body gradually degrade over time, eliminating the need for a second operation and reducing the harm to the human body. Moreover, the implants will not remain in the body for a long time and cause unpredictable effects. dSMPs combine the features of degradable materials and shape memory materials. It not only does not require large-scale surgical implantation of the implant but also does not need a second operation to remove the implant. It only needs to wait for the implant to be metabolized and degraded by the human body over time, minimizing the patient's pain and the difficulty of the surgery.

3. Degradable Shape Memory Polymers Applied in Medicine

At present, the most widely used medical dSMPs mainly consist of PLA or PU as the main components.

3.1. Poly Lactic Acid (PLA)

PLA materials are among the earliest implant materials applied by humans. According to different polymerization methods and copolymerization modification techniques, PLA materials can be classified into three categories: poly L-lactic acid (PLLA), poly D-lactic acid (PDLA), poly DL-lactic acid (PDLLA), and their mixed polymers.

3.1.1. Poly L-lactic Acid (PLLA)

Poly-l-lactic acid (PLLA) is a high-molecular material formed by the ring-opening polymerization of L-lactic acid monomers, featuring highly helical molecular chains, which enables the crystallinity of PLLA to reach 60%. The high cleanliness also endows PLLA with high rigidity and strength, with tensile strength reaching 60-70 MPa and elastic modulus reaching 2-4 GPa [4]. This feature enables PLLA to be used as a structural material in scenarios such as human bones that provide support. As a dSMPs, PLLA also has the ability to convert crystal phases between stationary and non-stationary phases. The activity ability of amorphous segments in SMP PLLA materials based on temperature control is enhanced during the heating process, causing deformation of the materials. When the temperature drops, the crystal phase restricts the activity of molecular chains, thereby fixing the shape. The glass transition temperature (Tg) of PLLA is approximately 55 ° C -65 ° C [5]. When the temperature exceeds Tg, the material can return to its original state. The degradation ability of dSMPs material is also possessed by PLLA material. The degradation of PLLA is achieved through the enzymatic catalysis of ester bonds in the body, converting it into non-toxic compounds. Its degradation cycle can last up to two years, providing sufficient time to support the human body.

3.1.2. Poly D-lactic Acid (PDLA)

Poly D-lactic acid (PDLA) is polymerized from D-lactic acid and has a similar structure to PLLA. The two are called enantiomer relationships. Compared with PLLA, PDLA has a higher melting point, better thermal stability than PLLA, and other properties are similar to those of PLLA. In recent years, PDLA has begun to be applied in the production of degradable shape memory vascular stents and occluders. These implants, which are prepared by combining dSMPs and PDLA with 4D printing technology, can provide support during the process of human tissue repair and create a suitable environment for cell adhesion and proliferation. This type of stent gradually degrades over time, so there is no need to worry about rejection reactions that may occur due to long-term implantation, nor does it require surgical removal. It perfectly avoids the problems that exist in traditional vascular stents.

3.1.3. Poly DL-lactic Acid (PDLLA)

Poly DL-lactic acid (PDLLA) is an amorphous polymer formed by the copolymerization of L-lactic acid and D-lactic acid. The irregular characteristics of its molecules endow PDLLA with unique physicochemical properties. The amorphous nature at the molecular level makes it easier for water molecules to be catalytically hydrolyzed under the action of enzymes, resulting in a shorter degradation cycle (6-12 months). Compared with PLLA and PDLA, PDLLA also has a higher elongation at break (8%-12%) and a lower Tg(50 ° C -60 ° C)[6]. In recent years, composite materials composed of PDLLA, and other materials have achieved relatively complete development. Among them, the composite material composed of PDLLA(PLLA) and polylactic acyl-glycolic acid copolymer (PLGA) can be used to fabricate special vascular tissues. Through thermally induced self-curling, vascular tissue engineering materials can achieve self-curling at specific temperatures and effectively wrap injured blood vessels. Compared with traditional artificial blood vessels, the materials prepared by this method have better adhesion. The composite material composed of PDLLA and hydroxyapatite (HA) is superior to pure PDLLA material in terms of shape memory effect. HA

particles can enhance shape memory ability. PDLLA/HA composite materials have application potential in the biomedical field. This type of material can be implanted into the body in a minimally invasive temporary form and then triggered to adhere to the tissue defect site. In the field of sustained-release drugs, PDLLA also demonstrates unique advantages. By encapsulating drugs in microspheres, nanoparticles or other carriers made of PDLLA, the slow release of drugs can be achieved by taking advantage of their degradation properties. For instance, in some sustained-release preparations of anti-cancer drugs, the PDLLA carrier can stably release the drug around the tumor tissue for a long time, maintain an effective drug concentration, enhance the therapeutic effect of the drug, and simultaneously reduce the systemic side effects of the drug [7].

3.2. Polyurethane (PU)

At present, in the field of medical dSMPs, polyurethane (PU) materials occupy an important position due to their unique performance combination. This type of material typically uses degradable polyesters such as polycaprolactone (PCL) and polylactic acid (PLA) as soft segments, which react with diisocyanate and chain extenders to form a cross-linked network. Through chemical structure design, the shape memory effect and biodegradability can be synergistically regulated. Based on the differences in soft segment composition and crosslinking density, degradable shape memory PU materials can be classified into PCL-based PU, PLA-based PU, and multi-component blend PU.

3.2.1. PCL-based PU

PCL-based PU uses polycaprolactone diol (PCL-diol) as a soft segment, featuring excellent flexibility and crystallinity. Its shape memory fixation rate can reach over 95%, and the recovery rate exceeds 90%[8], making it suitable for implantation scenarios triggered by body temperature. For instance, by introducing oligomers (glycolic acid) as chain extenders, the tensile toughness of PCL-based PU can be significantly enhanced. Meanwhile, the enzymatic degradation rate increases with the increase in the proportion of oligoGA, and it exhibits an excellent thermos-temperature-responsive shape memory effect at 37 ° C [9]. It is an ideal candidate material for interventional devices such as vascular stents. In terms of degradation mechanism, degradable shape memory PU mainly degrades gradually through the hydrolysis reaction of ester bonds, with the products being carbon dioxide and water, and no toxic residue [10]. Its degradation rate is significantly influenced by the chemical structure: the higher the crystallinity of the soft segment (such as high-molecular-weight PCL), the slower the degradation. Introducing hydrophilic groups or reducing crosslinking density will accelerate degradation [11].

3.2.2. PLA-based PU

PLA-based PU is prepared through the reaction of polylactic acid diol with isocyanate, and its mechanical properties and degradation rate can be regulated by the length of PLA chain segments. Studies have shown that when the ratio of PLA to PCL is 2:1, the mechanical properties and degradation characteristics of the scaffold are the best, and it can completely restore its original shape within 15 seconds at 37℃. In bone tissue engineering scaffolds, it can provide a suitable mechanical microenvironment for cell adhesion and proliferation [12]. In the field of soft tissue regeneration, PLA-based PU frames have become a research hotspot due to their excellent biocompatibility, degradability and adjustable mechanical properties.

3.2.3. Multi-component Blend PU

Materials prepared by compounding various components with PU possess a wide range of different functions. For instance, PU with polyglyceryl sebacate (PGS) as the soft segment can complete degradation within three months under physiological conditions due to the high density of ester bonds in its molecular chain, making it suitable for short-term hemostatic materials [13]. The composite material of PU foam and iodine-doped hydrogel has a fluid absorption capacity 19 times that of pure PU foam. After shape recovery, its volume can expand by more than 15 times, and it can achieve a bacterial killing rate of 80%. In non-compressive wound hemostasis, it can quickly seal the wound

surface and reduce the risk of infection [14]. In vascular interventional therapy, after the PU-based shape memory stent is implanted through minimally invasive methods, it can return to the preset shape under the trigger of body temperature, with a radial support force of 6.12kPa, and gradually degrade as the blood vessel heals, avoiding the long-term complications of traditional metal stents [15]. In addition, the PU porous scaffold prepared by 3D printing technology has a porosity of over 90%. It can not only guide tissue regeneration, but also its shape memory property enables the scaffold to adaptively match the bone defect area after implantation, significantly improving the repair effect.

4. Challenges and Prospects

4.1. Challenges

4.1.1. Biocompatibility and Toxicity

Biocompatibility and toxicity are the primary constraints on the use of dSMPs. Although the toxicity of the degradation products of the shape memory materials mentioned earlier are mostly within the tolerance range of the human body (such as CO2, lactic acid, etc.), the degradation process of this material itself is a sustained-release process of the degradation products. For implants with a longer degradation cycle, long-term stimulation of fixed positions by degradation products may lead to lesions in the corresponding areas, causing adverse reactions such as vascular proliferation and changes in tissue structure. For implants with a relatively short degradation cycle, the short-term and large-scale production of degradation products can strongly stimulate cells and lead to inflammation, which is unacceptable for implants implanted at critical organs. Based on these issues, early intervention measures can be implemented to prevent the occurrence of adverse reactions. The decomposition products that may cause adverse reactions can be neutralized in advance by attaching degradable drugs to the implanted body in advance. These drugs are gradually released as the implant degradates, and their release rate is directly related to the decomposition rate of the implant. Through this approach, the neutralization of decomposition products without external intervention is achieved. In addition, for scenarios where short-term and rapid degradation of implants is required, drug administration or injection is also an optional approach.

4.1.2. Response Controllability

How to stably predict the deformation and degradation process of dSMPs in vivo is also one of the important reasons restricting the application of this material in medicine. As a complex environment, the human body is prone to changes in indicators such as temperature and pressure. This may cause implants based on temperature changes to be triggered earlier or later due to sudden temperature variations in the local microenvironment. The instability of the chemical environment not only leads to the instability of the shape memory effect but also makes the degradation process of the implant difficult to control. Both too fast and too slow degradation will affect the treatment cycle and the treatment effect. To address these issues, a more comprehensive data model needs to be established for analyzing the usage strategies of implants, evaluating which type of material-made implants are more suitable for patients, and forming a complete risk assessment strategy to control the negative impact of implants on patients as much as possible.

4.2. Prospects

4.2.1. Combined with 4D Printing

At present, the combination of medical dSMPs and 4D printing is a popular research direction. Nowadays, most 4D printing technologies are combined with degradable shape memory polymer materials. Degradable shape memory alloys have high strength and fast response speed, but 4D printing technology based on degradable shape memory alloys still lacks research. Using 4D printing technology to directly wrap degradable shape memory alloys inside the printed components can enhance the strength of the components and achieve a faster response speed. Similarly, 4D printing with degradable materials that do not have shape memory properties on the outside of shape memory

alloy materials is also a method worth trying. In this case, the implant only uses the internal shape memory alloy as the driving force for deformation. This not only broadens the types of materials that can be used but also provides a relatively fixed reaction time for the material response. For example, temperature-corresponding shape memory materials can adjust the thickness of the outer layer material wrapped in the shape memory alloy, accordingly, delaying the time for heat to reach the alloy or extending the time required for heat dissipation. Then, after reaching the specified temperature, the shape memory alloy responds rapidly and deforms. Through this strategy, the accuracy of controlling the deformation of shape memory alloy materials can be significantly increased.

4.2.2. Combined with Sustained-Release Drugs

The combination of dSMPs and sustained-release drugs is also a research direction with extensive application scenarios. There are already precedents for the use of sustained-release drugs in vivo. As mentioned earlier, chemical substances that neutralize and decompose products can be implanted inside the implant to inhibit lesions and slow down validation reactions. Similarly, the drug can be placed inside the implant and gradually released along with the decomposition of the implant. In this way, a single implant surgery can achieve multiple therapeutic effects and simplify the surgical process. Implants can also carry drugs that induce or inhibit the growth of cells and blood vessels, thereby enabling more detailed environmental adjustments to the surgical site. This approach can also be a solution to the premature failure of the structural strength of the implant. For complex implants, due to their varying thicknesses, at the same degradation rate, implants at thinner positions may degrade prematurely, leading to premature structural failure. The implants may break, shift, or even enter the circulatory system, resulting in extremely serious consequences. To prevent this situation from happening, on the one hand, more substances that induce cell growth can be introduced at the weak position to enable the tissue at the weak position to replace the implant more quickly, so that the tissue can effectively replace the position of the original structure before the structure fails. On the other hand, sustained-release agents that inhibit decomposition can be added at the weak position to delay the decomposition of the weak position. In conclusion, embedding sustained-release drugs in dSMPs is an effective regulatory and therapeutic approach.

5. Conclusion

Degradable shape memory materials (dSMPs), as a material with great potential for development in the medical field, possess shape memory capabilities, remote response capabilities, and degradability, enabling them to achieve many functions that traditional materials are completely unable to fulfill. The dSMPs materials are composed of various components and the composite materials formed by them with other materials vary in degradation rate, strength, toughness and other aspects, which can cover a wide range of application scenarios and lay the foundation for the extensive use of dSMPs in medicine. At present, the large-scale application of dSMPs materials in medicine still faces many problems. This article also puts forward some ideas for researchers to solve these problems. The research significance of dSMPs materials in medicine cannot be ignored. In the future, this material will be able to form a simplified surgical procedure, not only enabling surgeries that traditional methods cannot complete, but also integrating complex functions that require multiple steps in traditional surgery in the form of a single minimally invasive operation, which is of great significance to the development of medicine.

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