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Study on 4D Printing Shape Memory Polymers in the Field of Biomedical Progress

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ABSTRACT

Shape memory polymers are intelligent materials that produce shape changes under external stimulus conditions, and 4D printing is based on deformable materials and 3D printing. A comprehensive technology, shape memory polymer in deformable materials is the most widely used, and the current 4D printing shape memory polymer is in various collars. The domain has applications, especially in the biomedical field, which has excellent application value. 4D printing technology breaks through the personalized technology in traditional medicine. The bottleneck provides a new opportunity for the further development of the biomedical field. This article first reviews shape-memory polymers, 3D printing technology, and 4D printing. We will review the research progress of shape memory polymers at home and abroad and introduce examples of 4D printed shape memory polymers in biomedicine. Finally, the application prospects, existing problems, and future development directions of 4D printed shape memory polymers in the biomedical field are summarized.

KEYWORDS:*Shape memory polymers, Composites, Biomedical, Intelligent structures, 4D printing.*

INTRODUCTION

Shape memory polymer (SMP) is a stimulus-responsive material that can be temporarily removed under external stimulus conditions. The shape changes to the initial shape, completing a shape memory loop and, simultaneously, the root. The memory effect and reversible shape memory effect can realize the memory of multiple shapes and reversible deformation (Figure 1). SMP has better quality and better recovery performance. Biodegradable, biotoxicity, or even low non-toxic and other characteristics [1-5]. SMP was originally developed by the French company CDF Chime. An excellent SMP has been developed and has shown remarkable results in many fields. The potential application value of SMP has been applied to various areas, such as aviation aerospace [6,7], additive manufacturing [8], clothing materials, and biomedical [9-11] research. The structure of the SMPs is almost always a simple linear junction structure, similar to cardiac, bone, tracheal stents, and other structures opposite complex, individualized, precision-demanding structures, traditional preparation. Technology is challenging to achieve, and the advent of 4D printing complements this shortcoming.

On February 20, 2013, Ti-from the Massachusetts Institute of Technology in the United States berts [12,13] 4D printing technology was first proposed at the TED conference, where he showed his 4D printing research results. The combination of technology and the use of SMP as a "smart material" with shape memory function material "3D printing" formed 4D printing technology. SMP energy interacts with stimulus conditions, so SMP printing by 4D printing in the absence of the structure in the aftermath of external stimuli (e.g., temperature, humidity, through electrical, pH, etc.) after [14], which produces a corresponding shape change (Figure 2) [15]. 4D printing SMP can be carried out by pre-setting its deformation scheme (package including target shapes, attributes, functions, etc.) to achieve self-deformation, self-grouping installation, self-healing, and other functions [16-21]. Currently, 4D-printed SMP is used in tissue engineering, medical devices, and pharmaceuticals. Applications in the biomedical field, such as conveyor carriers, have been made significant in many ways. The result is the personalized implantation of devices and high-precision medical devices with complex structures. The requirements of machinery are getting higher and higher. The materials and structures in the field of biomedical has become the future of each other.

In this study mainly reviews four-dimension printing SMP and its composites in the biomedical field, such as tissue engineering, applications in medical devices, drug delivery carriers, etc. Further analysis of 4D printing SMP in biomedical problems and the future development of domain applications. Currently, in 4D printing SMP square, the main methods are fused deposition modeling (FDM), stereo lithography apparatus (SLA), polymer jetting technology (PolyJet), straight writing technology (direct-writing, DIW), etc.

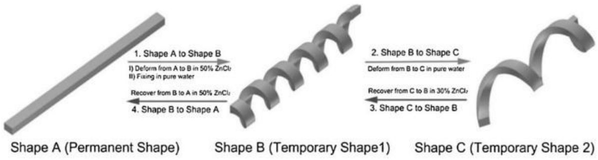

Figure 1: Schematic diagram of SMP self-folding deformation process [3].

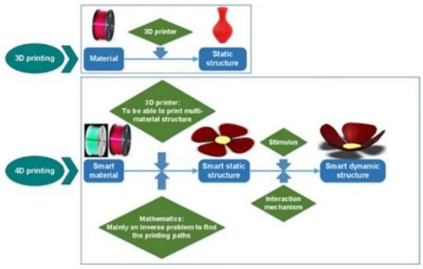

Figure 2: Schematic diagram of 4D printing [15]

2. Application of 4D printing SMP in biomedicine

A. Bone scaffold

Senatov et al. [22] PLA with hydroxyapatite (HA) at 20:3, the mass ratio is mixed, and FDM prints a kind of work with shape memory. It can be used for porous stents for bone defects, and mechanical properties and structure are carried out by testing characteristics and shape memory effects. HA particles are ordered over stage dispersions to form a rigid stationary phase in PLA molecular chains, which reduces the fraction. The fluidity of the sub results in the T_g of the material rising from 53 °C to 57.1 °C, resulting in the shape. Memory tests show an increase in the recovery stress of the scaffold, PLA/HA, and more. The hole bracket undergoes a cycle of 3 compression-heating-compression processes and is not divided. The highest shape recovery rate in the PLA/HA porous bracket is 98%. The memory effect can be used as an autologous implant to repair bone defects. Figure 3 shows a change in the shape memory effect of the porous scaffold for the bone defect process.

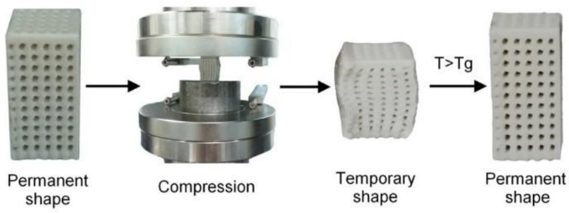

Figure 3: Fixes the temporary shape of the PLA/HAP porous bracket by compression, which is restored to the original shape after heating [22]

Subsequently, in related biological experiments, *Senatov et al.* [23] conducted the PLA/HA porous bracket. Cell culture experiments have shown that MSCs can be found on the scaffold. Attach quickly and observe HE staining by light microscope (Figures 4(a) and (b)). The MSC exhibits excellent cell adhesion and forms a cellular network with no use of determination of CD105-FITC-stained cells by epidemic fluorescence analysis (Figure 4(c)(e)). The MSC diffuses widely on the scaffold and forms strongly on the scaffold's surface. The interaction of 3D-printed porous PLA/HA brackets with the MSC has excellent adhesion properties that support cell survival while stimulating cell proliferation, which is a key prerequisite for its medical application in the bracket. The presence of MSC facilitates the formation of blood vessels at the implantation site, which can be supported. MSC growth proliferates shape memory scaffolds, with adaptive implantation in bone replacement. The application of things has excellent prospects.

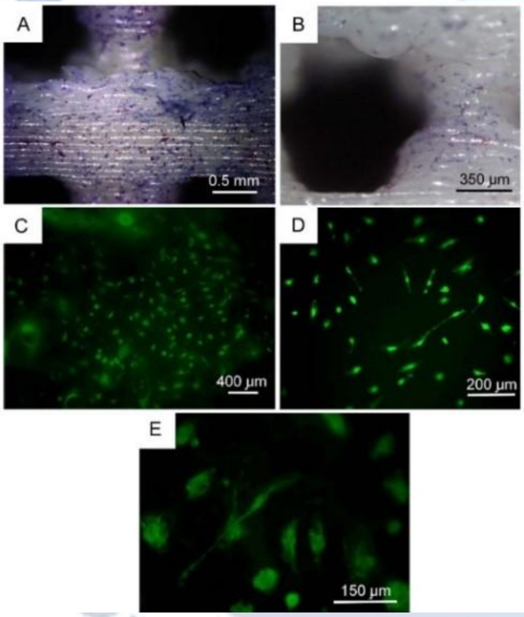

Figure 4: MSC on the surface of PLA/HA bracket, Optical microscope (a) 0.5 mm;(b) 350 μm. Immunofluorescence assay: (c) 400 μm; 200μm;(e)150μm[23]

B. Vascular stents

Wei et al. [24] As magnetic Fe3O4 nanoparticles are added to polylactic acid (PLA), a SMP that the magnetic drive can deform is prepared. Shape memory experiments have shown figure 5 that unfolding within 10s, based on this material, the straight spiral bracket structure of the writing print can be autonomously under the action of a magnetic field. PLA has magnetically driven properties, and you can apply this material. DIW designs personalized blood for patients that perfectly suits them.

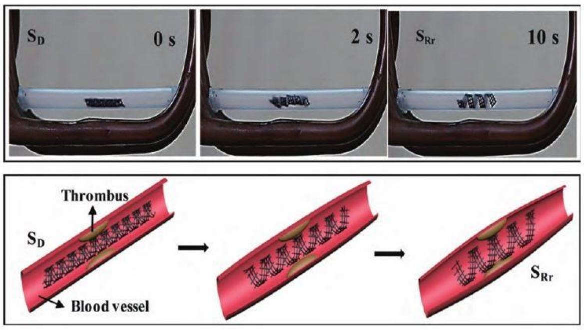

Figure 5: Schematic diagram of deformation of a 4D printed shape memory vascular stent under the action of an applied magnetic field [24]

Self-unfolding vascular stents can treat blood vessels caused by thrombosis and other cardiovascular diseases when self-unfolding vascular stents reach vascular stenosis. At this time, the stent is unfolded by adjusting the strength of the external magnetic field, and the vascular stent is expanded. The diameter becomes larger to prop up the narrowed blood vessels so the blood can flow normally.

Kuang et al. [25] polyurethane diacrylate and semi-crystalline synthesis of a new ink material with high elasticity and flexibility (photocurable ink) by UV light assisted curing printing technology (UV assisted DIW 3D printing) manufactured with shape memory performance (SM) and self-healing performance (SH) intelligent functional elastomers. Figure 6 shows shape memory experiments after raising the glass transition temperature (Tg). Regarding the application value of 4D printing and SMP technology for soft robots and intelligent creatures, the development of medical devices provides the basis for research.

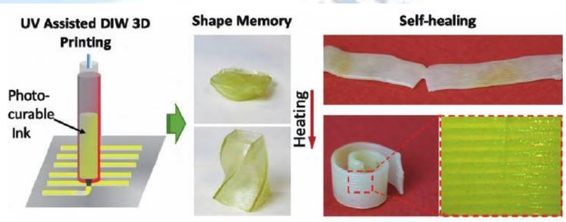

Figure 6: Printing process and heat deformation process of elastomer [25]

C. Tracheal stent

Morrison et al. [26] Apply SLA 3D printing technology to gather strength within yourself. The ester (PCL) prepared a tracheal stent for the printing material and successfully applied it. Depending on the patient's CT scan, images and Medical Digital Imaging (DICOM) were built for the 3D gas Tube model (Figure 7(a)), design stereoscopic graphics in STL format (Figure 7(b)), and Simulated combination of tracheal and stent models on a computer (Figure 7(c)). It was surgically implanted into the patient's body (Figure 7(d)) and cured three patients. Plant In vivo testing of the tracheal stent after entry has shown that the tracheal stent may accompany the patient. The continuous growth is biodegraded by the human body and is also mentioned for patients under one year of age. Personalized design not only meets patients' individual requirements but, after three years, the material can also be used when the patient's trachea grows soundly. Body biodegradation eliminates the pain of requiring multiple surgeries. This is based on 3D printing SMP materials prepared with shape memory. The effect of the tracheal stent came into being.

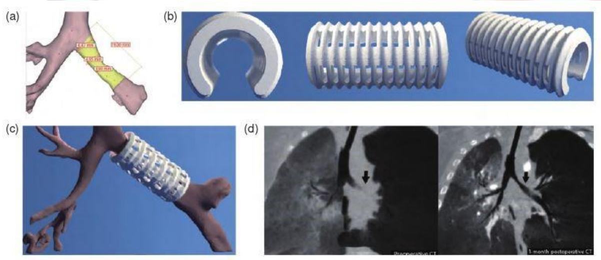

Figure 7: (a) 3D tracheal model constructed using DICOM; (b) STL stereo graphics; (c) virtual evaluation of fit with tracheal model on computer; (d) CT image of tracheal stent in the patient [26]

Zarek et al. [27] applied UV-LED stereo printers to 10000 g/mol methacrylate polycaprolactone as printing material, printed a shape-memory tracheal branch that can be deformed in the case of heat shelves (Figure 8A), and performed relevant in vivo tests. No longer changed (Figure 8B) and prepared by 4D printing shape memory polymers. Tracheal stents can be prepared according to the individual condition of the patient's trachea. "Stent making" solves the problem that the traditional tracheal stent cannot be completed due to individual differences. The issue of entirely fitting the patient's tracheal wall does not need to be passed. Relative to Morrison et al., people [36] prepared tracheal scaffolds, *Zarek et al*. [27] Although not carried out in related in vivo experiments, the tracheal scaffold has changed its shape—the purpose of propping up the trachea.

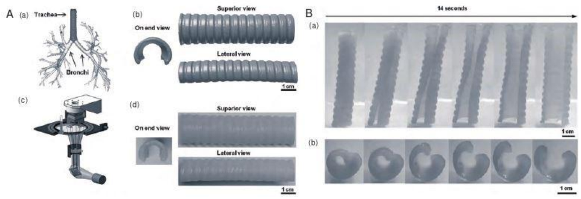

Figure 8, A: Shape memory tracheal scaffolding production process: (a) digital model of tracheal and bronchial trees established by MRI scanning; (b) 3D model of trachea; (c) SLA hit Printing machine; (d) shape memory tracheal bracket. B, shape memory The deformation process from the temporary shape to the final shape within 14s of the tracheal scaffold: (a) side view of the deformation of the scaffold; (b) scaffolding Distorted top view. [27]

D. Cardiac stent

Cabrera et al. [28] prepared by FDM in combination with medical technology. A stent can be applied for in vivo remodeling surgery of heart valves. The stent can be implanted into the heart by minimally invasive implantation surgery, where the stent is placed before implantation within the curling device (Figure 9(a)), reducing its diameter to 10 mm (Figure 9(b)). The holder is then transferred from the curling device to the implantation tool with a diameter of 12mm inside (Figure 9(c)); place the curled bracket in a water bath at 37 °C to simulate the transfusion. Send the stent to the heart environment and gradually push the stent out of the implantation tool. The stent will automatically expand into a designed shape (Figures 15(d) and 15(h)). A reticular structure can be narrowed down to a certain extent after implantation. The swelling thus automatically reverts to its original shape and is suitable for pediatric patients. Mechanical properties have shown that their mechanical properties can be used in animal testing. The conventional stent for heart valve implantation is comparable. In vitro degradation characterization experiments have demonstrated that the scaffold can biodegrade. 4D printing technology prepares the reticular structure of the shape memory cardiac stent in biomedicine. The field has broad application prospects.

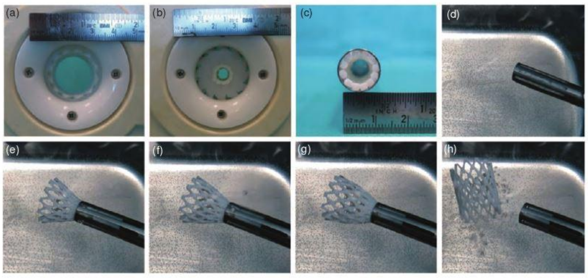

Figure 9: In vitro simulation of the implantation process of remodeling surgical stents in vivo of heart valves. (a) the bracket is placed in a compression device; (b) the bracket is curled to the diameter ~10 mm; (c) transfer the stent to a trans cardiac tip conveyor with an inner diameter of 12 mm; (d) ~(h) In a 37°C water bath, the stent is pushed out of the implantation tool as the self-expansion process. [28].

E. Cell scaffold

Miao et al. [29] Utilize 3D light-curing printers and new renewable soya bean oil epoxy acrylate material (Figure 8), printed out to be able to support people. Bone marrow mesenchymal stem cells (hMSCs) grow in the shape memory scaffold. The branching frame has shape memory and is highly biocompatible. Shape Memory experimental analysis showed that the scaffold could be fixed at -18°C. The temporary shape, at the human temperature (37 °C), will fully restore its original experimental cytotoxicity analysis, showing a novel type of shape memory.

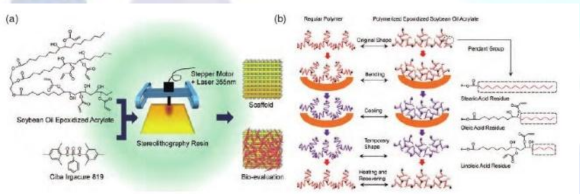

Figure 10: (a) 3D light-curing printer printing soybean oil epoxy acrylate material preparation principle; (b) polymerized soybean oil epoxy acrylate and conventional poly Schematic diagram of differences in shape memory mechanisms of complexes. [29]

Hendrikson et al. [30] polyurethane using biomaterial shape memory (TPU) and 4D printing technology successfully printed two fiber alignment directions (0/90° and 0/45°) into shape memory scaffolds, stimulating cell hair growth. Morphological changes and mechanical strength experiments on shape memory tables were conducted. Detection of signs and study of cell activity thermomechanical strength analysis characterizes the display. The temperature at which both brackets activate the shape memory effect is 32 °C. The Ming Tg is not affected by the direction of fiber arrangement. Place the stand as shown in Figure 10 at 65 °C; an external force is applied to obtain a temporary shape, and at 4 °C Cool fixations and seeding of the cells onto a scaffold at 30 °C culture to allow the cells to adhere on the stent and multiply, raise the temperature to 37 °C stents gradually return to the beginning start shape. Determination of shape memory characterization shows that there are two types of branches. The permanent shape has good resilience due to the fibers of the two brackets. The alignment direction is different, and the 0/45° bracket exhibits higher shape recovery ability.

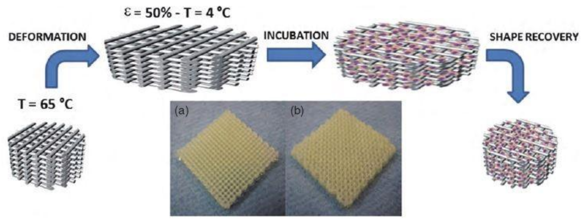

Figure 11: (a) 0/90° bracket; (b) 0/45° bracket shape change process schematic. [30]

Cell viability studies experiments after 14 days of culture show that, as shown in Figure 12(c) and (f), the cell activity conducted on both scaffolds is entirely normal. Depending on the cell, the tensile direction grows, presenting an elongated state. The deformation parameters calculate the elongation of 0.36 and 0.23, respectively (the sphere is 1), illustrating that 4D printed SMP cell scaffolds can be restored to cells by shape. Mechanical stimulation is produced, which leads to the directed growth of cells and nuclei. The scaffold's cell compatibility is good, and a single mechanical stimulus is sufficient to induce changes in the morphology of adhesion cells.

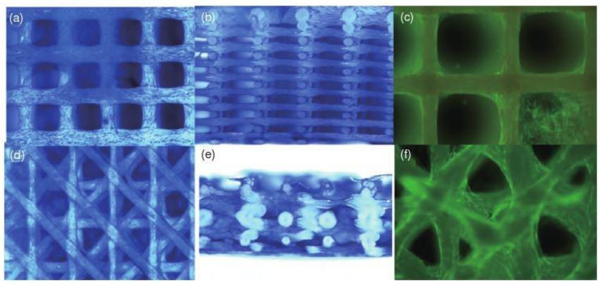

Figure 12: Stent of seeded cells: (a) 0/90° scaffold top view; (b) 0/90° scaffold side view; (d) 0/45° scaffold top view; (e) 0/45° scaffold side view. Cell growth after 14d of cell culture: (c) 0/90° scaffold; (f) 0/45° scaffold [30]

Cell scaffolds prepared by 4D printed SMP can induce cells *Miao et al.* [29]. A new type of raw material can be synthesized. Recycled soybean oil epoxy acrylate material, in contrast with conventional PEGDA, enhances the adhesion and proliferation of cells; *Hendrikson et al*. [30] From change Starting from the fiber arrangement direction of the stent, two fiber arrangement squares were prepared. On the cell scaffold, it is confirmed that the deformation of the cell scaffold is produced on the cell. Mechanical stimulation can lead to the directed growth of cells and nuclei; *Miao et al.* [31] the internal structure of the scaffold, a bionic gradient is prepared. Stent of the void structure, the cell can extend the void to grow inward, and the void can also be used. These three examples never play a role in transporting nutritional and metabolic waste. Some advantages of 4D-printed SMP cell scaffolds were developed and tested at the same angle. Currently, it is suitable for 4D printing and has high biocompatibility. SMP species are still very few, through 4D printing technology, and are highly biocompatible. The research and development of sexual intelligence biomaterials will guide new functional life in the future.

F. Other Applications

Yang et al. [32] Use improved FDM to print PLA or polyether ketone (PEEK) and continuous carbon fiber (CF) as a 4D printing material (Figure 13). Printed and manufactured two (CF/PLA and CF/PEEK) can be passed by temperature straight. Connect or electrically activate the intelligent structural member to achieve the deformation effect (Figure 14). Thermo-mechanical strength analysis shows the internal continuity of the intelligent structure after heating or energization. The thermal loss between the surface of CF and the PLA/PEEK substratum is different, causing it to bend; the electric deformation force test shows that when the ambient temperature reaches Tg, the two intelligent structural parts can achieve maximum deformation. These 4D-printed smart composites that can be driven by heat or electricity to produce shape changes can be applied to manufacture bionic sensors and artificial muscles.

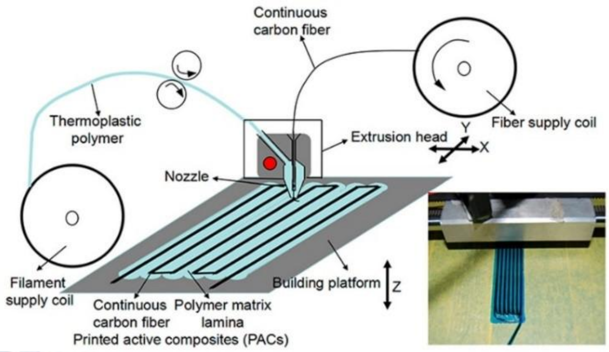

Figure 13: Schematic diagram of improved FDM preparation process for CF and PLA/PEEK co extrusion. [32]

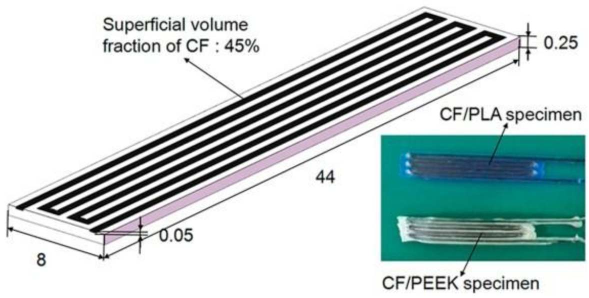

Figure 14: CF/PLA intelligent component and CF/PEEK intelligent component [32]

MIT researchers use 4D printing technology to manufacture a miniature drug capsule driven by temperature to phase such capsules. The shape of the body should change when the body is symptomatic of fever caused by certain diseases. The capsule will deform when the temperature is too high, and the drug inside will be released. The body temperature of the release of the drug is further controlled; when humans are not sensitive to the rise in body temperature, the drug is released for the first time.

A biodegradable material has been developed and printed using 4D printing technology based on this material. Biodegradable prosthetic milk was successfully implanted into the patient. Breast reconstruction is performed on the body. Patients with breast cancer require a breast group before the total resection of breast tissue, the diseased breast, and MRI laminar scans and MRI scans of diseased breast tissue. It traces and collects a computer's stereoscopic image information of breasts and breast tumors. The software performs three-dimensional modeling and simulated excision and designs the model of the prosthetic tooth in parallel with 4D printing. The 4D will be made at the same time as the removal of the breast tumor will be performed. Prosthetic milk is implanted in the tumor resection site to complete the breast reconstruction. Postoperatively Long-term follow-up examination found that prosthetic milk has good compatibility with tissue and is autologous. Vitamin vascular tissue begins to grow and gradually grows into prosthetic milk. Within the next two years, the human body completely degrades it, and the fibrous tissue of the body begins to self-degrade. In the end, it will completely replace prosthetic milk, and this 4D-printed SMP prosthetic milk is not only avoided. It eliminates residue in the body and ensures the shape of the breast, improving the patient's quality of life.

3. Application Prospect of 4D Printing SMP in the Field of Biomedicine

It is proposed to exchange ions for poly ion-exchange polymer metal composite, IPMC), dielectric elastomer (DE), SMP, and other intelligent materials combined with 4D printing technology to create a multi-degree of freedom operation. It can be used in minimally invasive surgical instruments. There are also corresponding examples abroad. Son, from Georgia Technical College Qi and Singapore University of Technology Ge[33], co-developed a temperature-sensitive SMP based on this SMP is 4D printed with a mixture of other materials, and the printed structure is warped. After that, the over-temperature drive can change from a temporary shape to a designed one. The state is restored to its initial form, embraced in medical devices and human organ stents. There is excellent potential for use; the University of Texas at Dallas, *Shaf-for et al*. [34] The PLA is crosslinked after radiation to form FDM4D printed knots. The components have excellent application prospects in the research and development of medical devices, coming from Gladman et al. of the Massachusetts Institute of Technology. [35] Apply 4D printing technology to copolymer cellulose hydrogels and acrylamide as printing materials, depending on the person. The organ morphology of the body is then programmed by a computer and printed.

A bionic organ model can be medically implanted with this bionic organ model. The human body degrades some components, and some components are not. The tissue will grow inward, forming new tissues or organs that will give life to the original. The research team continues to use this material and, through 4D printing technology, made a new heart stent, this heart. The dirty stent is injected into a vein farther from the heart and circulates through the bloodstream. The system can reach a designated heart location and assemble itself for vascular stents. 4D printing combines materials science and medicine more closely. Together, they are a perfect body for the "combination of medicine and engineering" in modern scientific research. They will play a more critical role in the future development of the biomedical field.

4. 4D Printing SMP Problems in the Biomedical Field and the Direction of Development

What is clear is that 4D-printed SMP has broad application prospects in the biomedical field for medical devices and related junctions. The structure requirements are very high, and there are many questions between the scientific research stage and the practical application. The problem needs to be solved. Therefore, the production and clinical production of 4D printed SMPs makes several problems that need to be solved.

4D printing technology is not mature enough. The concept of 4D printing technology is still there. However, it is relatively new; problems include excessive printing time, material type and printer are not matched, the printer's accuracy is not high enough, and the related technology is still to be done. Further improvement to research and develops more high-precision medical devices. Research and development apply to the field of 4D printing technology, which must solve the above problems. 4D printing technology in the biomedical field is the development direction of 4D printing.

The material performance is not good enough. At present, there are many kinds of SMPs at home and abroad. Many, but very few, shape-memory materials are suitable for the biomedical field. There are very few main problems, which are:

- The T_g of SMP is too high, and it is difficult for the body to bear.
- The mechanical strength of some SMPs cannot meet the needs of medical devices of the degree of emphasis required.
- The implantation of medical devices requires SMP to have Biodegradable and biocompatible.

Currently, it is suitable for biomedical treatment. There are fewer types of SMPs used, and there are T_g

comparisons for research and development in the biomedical field. New materials with low biocompatibility and good biocompatibility match 4D printing technology, which is undoubtedly one of the next directions for its development.

As we all know, SMP drives like thermal, electric, light, magnetic, pH, ion drives, enzyme drives, etc., and the driving method is suitable for the biomedical field. Most are also limited to thermal movements, so developing multi-incentive response SMP composites is necessary. The remote drive is achieved using a magnetic drive and a pH drive. SMPs that will be driven in the future will inevitably be found in these two areas. More breakthroughs to meet the requirements of biomedical applications.

Functional application verification of 4D printing components Currently, almost all the structural parts of a 4D printed SMP are still stuck in the finished product that has been printed and not carried out. It is proven non-toxic if the 4D-printed structural parts are applied safely and effectively in the body. Inside, it is indispensable to the comprehensive study of clinical trials and 4D printing knots at home and abroad. The research of components in the field of biomedicine is still in the preliminary stages of the laboratory. There are still many challenges in moving out of the laboratory toward clinical application.

5. Conclusions and Outlook

This article describes the development of SMP and 4D printing technology. The application of 4D SMP printing research in biomedical advancements, including vascular stents, tracheal stents, cell growth stents, bone stents, cardiac stents, drug releases, fake milk, biomedical components, etc., and its research possibilities have finally pointed to the problem of 4D printing in biomedicine. The trend of future development 4D the application of printed SMP in the biomedical field changes the traditional medical device. Technical bottlenecks for clinical minimally invasive surgery reduce the number of surgeries and drugs. Controlled release of substances, tissue, and organ transplants offers more significant potential for 4D printed SMP to quickly and accurately target medical care to patients, including personalized treatment, reducing patient pain, and improving quality of life. The further development of medical care provides an entirely new direction. Polymer materials with shape memory can improve bioprinting capabilities. 4D printers continue to evolve into more intelligent, more personalized medical devices. In the future, it will be used in biomedicine, 4D SMP printing, and biology. The organic combination of the medical field is a new trend in the development of the medical field in the future.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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