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3D Printing with Self-Healing Materials and Applications

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Abstract:

3D printing also called as the additive manufacturing. It is revolutionizing various industries by enabling the production of complex objects directly from digital models. This technology offers significant advantages over traditional manufacturing methods. Especially in reducing material waste and increased design flexibility. The range of 3D printing application contains healthcare to aerospace, reflecting its growing importance in modern society. Recently, 3D printing advancements have introduced in self-healing (SH) materials, it saved limitations related to the durability and repairability of printed objects. SH materials are categorized into external and internal systems. External SH materials use embedded healing agents that repair damage through chemical reactions, while internal systems rely on dynamic bonding within the material itself. This innovation not only extends the functional life of 3D printed items but also supports trends in mass customization and sustainability. This paper explores the mechanisms, types, and applications of SH materials in 3D printing, and mainly focus on their potential to enhance product longevity and functionality across medical, construction, and consumer goods sectors.

Keywords: 3D Printing; Self-Healing Materials; Applications.

1. Introduction

3D printing also called as the additive manufacturing or digital fabrication technology [1]. It can produce complex objects directly from digital models. By continuedly adding the printing materials to made the final product. This process of 3D printing is to building objects layer by layer. Therefore, it has several advantages over traditional manufacturing methods, such as reducing waste and increasing design flexibility. With the development of technology, 3D printing technology can even be used for mass customization. Based on these special properties, 3D printing is widely used. Demand for 3D printing has surged in recent years due to its application in a wide range of industries, including healthcare, automotive, aerospace, and consumer goods. For example, it solved the time-consuming subtraction process that traditional manufacturing often involves wasting materials [2]. Faster production speed and fewer production materials can greatly reduce the cost of products. Besides, 3D printing allows for rapid prototyping, enabling designers and engineers to test and refine their ideas faster and more efficiently. This ability is particularly important in industries where innovation and time to market are critical. What's more, 3D printing supports the trend of mass customization, where products are tailored to the specific needs and preferences of individual customers, thereby increasing user satisfaction, and creating new business opportunities. Especially in the medical field, medical devices such as artificial limbs can be customized with the patient's personal data. 3D printing is the technology of printing a digital model layer by layer to create a physical object. Computer-aided design (CAD) software is often used to design digital models. In slicing software (Slicer) processing, the 3D model is broken down into a series of horizontal slices. Then select the appropriate materials and manufacturing methods to make the final product. Common 3D printing technologies are fused deposition moulding (FDM), light curing stereo plat printing (SLA), selective laser sintering (SLS), and electron beam melting (EBM) [2]. Through different materials and product characteristics, different production methods. Common traditional materials are polymers, metals, composite materials, and so on. Among them, the SH material is a very special 3D printing material [3]. It's a major advance in material science.

Although 3D printing can consume less material to make products. However, for every part 3D printed out, the 3D printed object will also fail due to the deterioration of mechanical properties caused by the use and aging of the material, thus limiting the service life. In addition, 3d printed parts tend to have complex structures and are difficult to repair by hand due to the difficulty of obtaining them [3]. Therefore, automatically restoring initial properties and item properties after damage, also known as self-healing (SH) materials, seems to be an attractive method for 3D printing [4]. These materials are designed to repair themselves after suffering damage, thus extending their functional life and preserving their structural integrity. The concept of SH materials is inspired by biological systems, which have the inherent ability to repair wounds and regenerate tissue. Current research on SH materials is focused on understanding the mechanisms that enable SH and developing new materials with enhanced SH capabilities. These materials can be divided into two main categories: external and internal SH materials.

2. Mechanism of SH-Materials

SH-material is a kind of materials that could be repaired autonomously without external human intervention [5]. It can partially or completely recover its integrity and mechanical properties after damage and recover from cracks on a macro or micro scale [5]. SH processes can be divided into two main categories: exogenous and endogenous, healing agent release (in the external system), or bond recombination (in the internal system). Both of these methods can effectively restore the properties of the material.

2.1 External Repair: Healing Agents

In extrinsic SH systems, healing agents (such as unreacted monomers, solvents, or low-glass-transition-temperature polymers) are encapsulated in reservoirs embedded within the polymer matrix. The healing agents can be configured in either capsule or vascular forms [6]. When the material undergoes mechanical damage, it leads to chain scission and molecular chain disentanglement, ultimately triggering the formation and propagation of cracks. As the crack propagates to the reservoir, the healing agent is released and fills the crack, acting as a sealant to repair it. Through mechanisms such as in situ polymerization, solvent welding, macromolecular diffusion, and re-entanglement with the matrix, the material's primary properties can be effectively restored.

Extrinsic SH materials repair damage through embedded healing agents. These agents are typically encapsulated in microcapsules or contained within a vascular network resembling a biological circulatory system. When the material is damaged, the capsules or vessels rupture, releasing the healing agent into the damaged area. The healing agent usually consists of a monomer and a catalyst, which polymerizes upon contact with the catalyst, forming new chemical bonds and restoring the material's integrity. The advantage of this approach lies in its ability to perform targeted repair at the site of damage. However, a major limitation of this method is that the healing agent is consumed during the repair process, meaning the material can only self-heal once. In recent years, research on extrinsic SH materials has focused on improving the efficiency and reliability of the SH process. For example, researchers have developed multi-component healing systems capable of undergoing multiple healing cycles. These systems achieve the possibility of multiple repairs through the sequential release of different combinations of healing agents. NASA is studying composites containing microencapsulated polymers for use in spacecraft components. This is a microcapsule containing a restorative, such as epoxy resin, or polyurethane [7].

2.2 Intrinsic Repair: Dynamic Bonding

Intrinsic SH materials do not rely on external healing agents. Instead, they are composed of polymers with dynamic bonds that can break and reform in response to external stimuli. This property allows the material to heal itself multiple times without the need for additional resources.

2.2.1 Thermal activation

One common approach to intrinsic SH is thermal activation. When the material is heated, the polymer chains within the material gain mobility, allowing the dynamic bonds to break and reform. This process can close cracks and restore the material's mechanical properties. Thermal activation is particularly useful in applications where the material is subjected to repeated mechanical stress, as it allows for continuous repair over the material's lifetime. However, thermal activation has its challenges. The temperature required to activate the healing process may be too high for certain applications, leading to potential degradation of the material or surrounding components. Additionally, the repair process can be slow, depending on the size and complexity of the damage.

Take Poly(vinyl alcohol) (PVA) self-healing gel. It has dynamic bonding properties that enable it to restore its integrity after damage. Especially when heated, the internal cross-linked structure can be reorganized, so as to achieve self-repair. For example, heating can re-form cross-linked networks in the gel to repair cracks or damage. It is often used in flexible electronics and smart packaging materials, such as self-healing electronic skin and smart packaging film [8].

2.2.2 Vat photopolymerization

With the rapid development of electronic skin, soft robots, wearable devices and other segments, related products have put forward higher requirements for the mechanical properties, flame retardancy, reliability, detection range, sensitivity and so on. Research on SH has focused on capsule-based systems, as vascular systems are not compatible with this technology due to inherent limitations. Autonomous, self-healing silicone materials triggered by sunlight have been prepared through a photoactivated methylene click reaction between multifunctional merohedry siloxanes (MS) and bifunctional vinyl siloxanes (VS) [8]. During the printing process, capsules containing a low viscosity unreacted prepolymer resin are added to the composite. When fracture occurs, these monomers are released, providing fast SH, as polymerization takes less than 30 seconds under ambient sunlight. This is especially useful for outdoor applications. The material is also 3D printable, enabling the manufacture of different objects such as antagonist muscle actuators and Kagome towers.

Poly(glycidyl methacrylate) (PGMA) is a self-healing photopolymer resin. This photosensitive resin contains a photocurable resin with dynamic covalent bonds, which can cure under light and form a stable network structure. It is generally used for 3D printed parts with high precision and complex shapes, such as medical implants or dental restorations. Light activates a chemical reaction during the curing process, causing the material to form a high-strength cross-linked network. The light in the subsequent repair process can trigger the repair mechanism inside the material to restore the micro-damaged area [9].

2.3 Dual-network Systems

Dual-network systems represent an innovative approach to intrinsic SH materials. These systems combine two polymer networks with complementary properties: one provides mechanical strength, while the other enables self-healing. When damage occurs, the flexible network can flow into the damaged area and re-bond, restoring the material's integrity. This approach offers several advantages, including improved mechanical properties and the ability to heal large-scale damage. Dual-network systems have been successfully applied in various applications, such as soft robotics, where the material's flexibility and durability are critical. Recent studies have explored the use of dual-network systems in 3D printing, enabling the creation of complex structures that can self-heal after sustaining damage. This technology has the potential to revolutionize industries where durability and reliability are paramount.

Polydimethylsiloxane (PDMS)/Polyurethane (PU) is a double network elastomer. This system combines a cross-linked PDMS network with a dynamic cross-linked PU network [10]. The PDMS network provides elasticity and structural stability, while the PU network has dynamic crosslinking capabilities, allowing materials to regain shape and function after damage through the self-healing mechanism of the PU network. It is commonly used for high-durability and elastic components such as automotive seals, flexible robotic parts and wearable devices. PDMS/PU dual network elastomers can recover elasticity and integrity after damage through dynamic crosslinking of PU network and support of PDMS network [11].

3. SH Materials

Different SH Materials will have different effects in different healing environments. According to their self-healing mechanism, these materials can be divided into several categories, such as thermoplastic polyurethane (TPU), Diels-Alder reaction based composite materials and ionic gel materials. TPU is self-healing through reversible cross-linked bonds in its molecular structure, and is suitable for scenarios that require frequent bending or stretching; Diels-alder composites rely on reversible chemical reactions for repair and are suitable for high-strength applications such as aerospace; Ionic gels rely on the electrostatic action of ionic liquids for self-healing, and are widely used in wearable devices and flexible electronic components. Different types of self-healing materials show their advantages in different fields.

3.1 TPU

Thermoplastic polyurethane (TPU) is an elastomeric material with excellent flexibility and wear resistance. The self-healing ability of TPU stems from reversible cross-linked bonds in its molecular structure. When the material is damaged, by external heating or applying pressure, these cross-linked bonds can rearrange and restore the integrity of the material. TPUs are widely used in 3D printing elastic parts, protective housings and footwear products, especially for scenarios that require frequent bending or stretching. Its self-healing properties not only extend the service life of the product, but also reduce the cost of replacement and repair.

3.2 Diels-Alder composites

Polymer composites based on the Diels-Alder reaction are a class of materials that achieve self-healing through chemical reactions. The Diels-Alder reaction is a reversible chemical reaction that can be triggered when a material is damaged by the application of a certain amount of heat, reconnecting the molecular chains of the material and thus repairing cracks or breaks. This type of material has high strength and good self-healing ability, making it ideal for 3D printing structural parts in the aerospace and automotive industries. Their application not only reduces material weight but also improves safety and reliability.

3.3 Ionic Gel

Self-healing gel materials based on ionic liquids, such as a gel material consisting of a polymer network and an ionic liquid, have significant self-healing properties. Ionic liquids act as mobile ions in the gel network, and when the material is damaged, these ions can rearrange and repair the damage through intermolecular electrostatic interactions. Due to its softness and elasticity, this material has a wide range of applications in the 3D printing of wearable devices, biomedical devices, and flexible electronic components. Its self-healing properties are critical to improving the durability and safety of these devices.

4. Application of SH Materials in Different Areas

Because of the SH properties of SH Materials, they have applications in various industries, from medical devices to consumer products. The following sections will delve into how SH materials can be used in various industries.

4.1 Medical Applications

In the medical field, 3D printing has already made a significant contribution by creating custom implants, prosthetics, and surgical tools. Introducing SH materials into this field offers even greater possibilities. For example, SH materials can be used to create implants that can repair themselves after experiencing wear or damage. This can reduce the need for revision surgery, thereby reducing surgical risks for patients. In addition, SH materials can be SH stents that can automatically repair small cracks or damage caused by natural movement of the human body, ensuring the continuous and reliable support of blood vessels. Another promising application is the development of wearable medical devices. These devices are often subjected to mechanical stress, which can lead to damage and failure. By incorporating SH materials, these devices can maintain their function over a longer period of time, improving patient outcomes and reducing healthcare costs.

And 3D printing technology can replicate the natural structure of the skin. The 3D-printed skin could be used to test drugs, cosmetics, and chemical products, reducing the reliance on animal skin. If it is made of self-healing materials, it can simulate the immunity of humans themselves. To improve the authenticity of the results of the research products.

4.2 Construction Applications

The construction industry will benefit greatly from the combination of SH materials with 3D printing. One of the main challenges in construction is the maintenance and repair of the infrastructure, which can be costly and time-consuming. SH materials provide a solution that enables building components to self-repair when damaged. By adding SH agents to the concrete mixture, it is possible to create structures that can automatically repair cracks and other forms of damage. This can greatly reduce the need for maintenance and extend the useful life of buildings and infrastructure.

3D printing with SH materials also has the potential to revolutionize the construction of modular buildings. Modular construction involves manufacturing building parts off-site and then assembling them on site. By using SH materials in the manufacturing process, more durable and damage resistant parts can be made, thereby improving the overall quality and longevity of the final structure.

4.3 Consumer Products Applications

The consumer goods industry is another area where 3D printing using self-healing materials could have a significant impact. By incorporating self-healing materials, these products can self-repair minor damage such as scratches or dents, extending their service life and reducing the need for replacement. For example, auto parts made from self-healing materials can automatically repair minor damage caused by accidents or environmental factors, reducing maintenance costs and improving vehicle safety. Similarly, self-healing materials can be used to create durable, long-lasting shoes that can be adapted to the wearer’s foot type over time, improving comfort and performance.

The integration of self-healing materials into consumer products is also in line with the growing demand for sustainable and environmentally friendly products. By extending the life of the product, self-healing materials reduce the need for frequent replacement, thereby reducing the environmental impact of manufacturing and disposal. When producers independently make 3D printing products at home, there may be some slight cracking. SH materials can also help producers reduce the number of reproductions, thereby reducing wear and tear and costs.

5. Conclusion

The integration of self-healing (SH) materials into 3D printing technology represents a significant advancement in both material science and manufacturing processes. By incorporating SH capabilities, 3D printing can overcome some of its inherent limitations, particularly regarding the durability and repairability of printed objects. SH materials, which can autonomously repair themselves after damage, offer promising solutions to extend the lifespan and functionality of products created through additive manufacturing.

The development of SH materials can be broadly categorized into external and internal systems. External SH materials utilize healing agents embedded within the material that activates upon damage, filling cracks and restoring integrity. Although effective, this approach often allows for only a limited number of repairs due to the consumption of healing agents. Conversely, internal SH systems rely on dynamic bonds within the material that can reform without additional resources, enabling repeated self-healing over time. Innovations such as dual-network systems, which combine two polymer networks to enhance both mechanical strength and self-healing capabilities, further advance this field.

The applications of SH materials in 3D printing are vast and varied. In healthcare, they can lead to more durable and reliable medical implants, prosthetics, and wearable devices, reducing the need for revision surgeries and enhancing patient outcomes. In construction, SH materials can transform infrastructure maintenance by allowing buildings and structures to self-repair, potentially reducing costs, and extending their useful life. The consumer goods industry also stands to benefit, with products made from SH materials offering increased durability and sustainability, aligning with growing environmental and economic concerns.

Overall, the integration of SH materials into 3D printing technology promises to revolutionize multiple industries by improving product durability, reducing maintenance costs, and supporting the trend toward sustainable manufacturing practices. As research and development continue, the potential for these materials to impact various sectors will only grow, highlighting their importance in the future of advanced manufacturing.

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