Recent Progress of Self-healing Nanomaterials and their Applications

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Abstract. In this paper, the importance and research degree of self-healing nanomaterials are first introduced, and some methods of self-healing nanomaterials are briefly described, and then some advantages of self-healing technology in nanomaterials compared with traditional nanomaterials are listed. The internal and external factors of self-healing nanomaterials are mainly elaborated. External factors include light-induced self-healing, heat-induced self-healing, and chemical self-healing. Internal factors include dynamic chemical bonding, built-in microcapsules, and nanoparticle migration. By studying the specific reaction processes and mechanisms of each remediation, as well as giving examples of specific materials, the differences between external and internal causes are compared, and the advantages and disadvantages of each are listed. Finally, several applications of self-healing nanomaterials are described, including the application of self-healing pressure sensors and self-healing temperature sensors in smart textiles. It also describes the prospect of the application of self-healing nanomaterials in medical self-healing wearable biosensors and self-healing flexible electronic skin.

Keywords: Self-healing, Internal and external driven, Nanomaterials.

1. Introduction

From a variety of assembly materials to tech suits, self-healing nanomaterials are becoming more and more common in science fiction works, this material has received a lot of attention in the past few years, and it can be used in many fields, for example, aerospace, medical protective clothing, firefighting clothing, etc. Self-healing nanomaterials can reduce the material loss rate, prolong the life of items, and reduce maintenance costs. Nowadays, there is more and more material waste, a large amount of plastic waste is generated, and the pollution to the environment is getting heavier and heavier. Self-healing nanomaterials can extend their service life, reduces the environmental stress associated with changing materials. With the increasing attention of circular economy, self-healing nanomaterials are becoming more efficient and energy-saving. Now, with the strong support of the government, there is more and more research on self-healing nanomaterial technology. In the process of research, it has been found that self-healing nanomaterials have important scientific significance and application value, these materials imitate the self-healing phenomenon in nature and automatically repair themselves after damage [1]. Therefore, in recent years, there have been more and more studies on self-healing nanomaterials, and there are more and more methods [2]. For example, the coating method involves applying a self-healing coating to the surface of a material, which usually contains self-healing microcapsules or polymers that heal self-healing under certain conditions. When the coating is scratched or damaged, the self-healing mechanism is activated to fill in the damaged area. Dynamic covalent bonds introduce chemical bonds in materials that are capable of breaking and reforming, such as disulfide, hydrogen, or ester bonds. When the material is damaged, these dynamic bonds are re-formed to repair the damage. Dispersion nanoparticles: Nanoparticles with specific functions are introduced into the material, such as metal nanoparticles, carbon nanotubes, or graphene. When a material is damaged, nanoparticles can fill the damaged area through diffusion, migration, or interfacial reactions. The advantages of self-healing nanomaterials are as follows self-healing technology extends the life of the material. Self-healing nanomaterials can be repaired at an early stage, preventing them from becoming major failures and improving safety. The reliability of the product is improved while reducing waste, enhancing sustainability and greatly improving the protection of the environment.

2. Self-healing nanomaterials

2.1. Extrinsically driven self-healing

Externally-driven self-healing mechanisms rely on changes in the external environment or external stimuli to trigger the self-healing process of materials. Common external factors include light, heat, humidity, chemicals, mechanical forces, etc.

2.1.1. Light-induced self-healing

Light-responsive polymers refer to the chemical reaction of light-sensitive components in certain materials under specific wavelengths of light. For example, broken molecular bonds are recombined to repair damage to the material. This mechanism is commonly used in light-sensitive polymers. For example, polymer-based nanocomposites (containing photoactive molecules) contain photosensitizers or light-responsive nanoparticles, such as barium titanate (BaTiO3) or gold nanoparticles [3]. These nanomaterials are exposed to ultraviolet or visible light and are subject to local chemical reactions or deformations. Its working principle is that under the irradiation of light, photosensitizers or nanoparticles will excite electrons or initiate thermal effects, resulting in the rearrangement of polymer segments in the material or the release of repair agents, so as to achieve the self-healing function of the material. For example, photosensitizers absorb light and produce free radicals that can trigger cross-linking reactions between polymer chains to fill cracks. The mechanism of photoinduced repair is that photosensitizers absorb light energy, produce free radicals, and induce cross-linking reactions in polymers, thereby repairing cracks or damage in materials. The reaction mechanism is a light-initiated polymerization reaction. Light-initiated polymerization refers to the formation of free radicals by the action of light, which can initiate polymerization reactions to form new polymer chains. After absorbing light energy, the photosensitizer in the material excites and produces free radicals, which trigger the polymerization of the surrounding monomer or polymer chains, and finally form a cross-linking network to repair cracks. Based on light-induced research, researchers at the Institute of Chemistry of the Chinese Academy of Sciences have developed a light-induced self-healing material using titanium dioxide (TiO2) nanoparticles [4]. The material generates free radicals when exposed to UV light, which can repair broken or damaged structures in the material, especially for coatings and textiles that are resistant to UV aging, it is particularly suitable for coatings and textiles that are resistant to UV aging.

2.1.2. Heat-induced self-healing

When the temperature of a thermoplastic material rises, the thermoplastic components in the material become soft or molten, and the damaged area can be filled with a flow to fill the cracks, which can then be re-cured when cooled, restoring the integrity of the material. Common heat-induced self-healing nanomaterials include polymer-based self-healing nanocomposites, metal-nanoparticle composites with carbon nanotube-reinforced self-healing materials, graphene-based self-healing nanomaterials, and microencapsulated heat-induced self-healing materials. Among them, the thermoplastic polyurethane material has good elasticity and flexibility, and can be softened and reshaped at a certain temperature. The principle of operation is that when a TPU material is heated, the molecular chains in the material are able to reflow and rearrange to fill the cracks [5]. The physical form of the material changes from a solid state to a soft molten state when heated, and the damaged area gradually heals under the action of heat, and the material returns to its original state when cooled. In thermoplastic polyurethane (TPU), for example, the polymer segments are softened and flowed under heated conditions, filled with cracks, cooled and re-cured, and repaired, after cooling, the material returns to its original state. In thermoplastic polyurethane (TPU), for example, the polymer segments are softened and flowed under heated conditions, filled with cracks, cooled and re-cured, and repaired.

2.1.3. Chemically induced self-healing

Certain components of a material react chemically when they come into contact with external chemicals such as oxygen, forming new chemical bonds or fillers that repair the damage. A microencapsulated self-healing material is a polymer composite material embedded in a microscopic capsule. The capsule is usually filled with a repair agent, and when the material is damaged, the capsule ruptures, and the repair agent is released, and a chemical reaction is carried out to repair the crack. The working principle is that the microcapsules in the material break under the action of external forces, releasing internal repair agents (such as unsaturated resins or curing agents) [6]. The restorative diffuses into the crack and reacts with oxygen in the air or a catalyst in the material to create a new polymer structure that fills the crack. The microcapsules inside the material during the reaction contain a repair agent, and when the material is damaged, the capsule ruptures and the repair agent spreads into the cracks. The restorative reacts with oxygen in the air or a catalyst in the material to polymerize or crosslink to form a new polymer network and repair the cracks. For example, when the repair agent (epoxy resin) in the microcapsule comes into contact with the catalyst, it undergoes a polymerization reaction to form a new solid polymer structure and repair the damage.

2.2. Intrinsically driven self-healing

Intrinsically driven self-healing mechanisms rely on spontaneous processes within the material and usually do not require external stimuli to occur. This mechanism depends on the properties of the material itself and the structural design of the interior.

2.2.1. Dynamic chemical bonding

Reversible covalent bonds, which introduce reversible chemical bonds into the material, such as disulfide bonds, hydrogen bonds, ester bonds, etc. These bonds are able to break and re-form after mechanical damage, repairing the damage to the material. The Diels-Alder reaction is a chemical reaction in which conjugated dienes and dienomers form reversible covalent bonds. At high temperatures, this reaction can be reversed, while at low temperatures, the reaction regenerates. Thus, the polymers of the Diels-Alder reactants can achieve dynamic self-healing under temperature changes [7]. It works on the principle that when the material is heated, the covalent bonds (usually C-C bonds) in the Diels-Alder reaction break and the molecular chains can be rearranged. As the material cools, the reaction reverses and new covalent bonds are formed, repairing the damage.

2.2.2. Built-in microcapsules

(Microcapsule Repair Agent Release) A microcapsule containing a repair agent is embedded inside the material, and when the material is damaged, the microcapsule ruptures, releasing the repair agent. These restorative agents react with the base material to fill cracks or repair damage. Epoxy-based microencapsulated self-healing materials are polymers commonly used in structural materials with good mechanical properties and corrosion resistance. Self-healing functions can be achieved by embedding microcapsules containing restorative agents in an epoxy matrix [8].When the material is damaged, the microcapsules rupture, releasing the internal repair agents (such as liquid epoxy resin), which diffuse into the cracks and react chemically with the matrix or components in the air (such as the curing agent), and the repair agent polymerizes with the curing agent to generate new chemical bonds, re-form the cross-linked solid structure, repair the cracks and restore the mechanical properties of the material. For example, styrene monomers form new cross-linked structures through free radical polymerization to fill cracks in the material.

2.2.3. Nanoparticle migration

Functional nanoparticles are introduced into the material matrix that are able to move to the crack location in the damaged area through diffusion or self-organizing behavior, filling the damage. Silica (SiO_2) nanoparticle-reinforced coating materials are commonly used in self-healing coatings due to their excellent heat resistance, chemical stability, and anti-wear properties. Silica nanoparticles are able to migrate when the coating is damaged and repair the coating cracks by filling [9]. When the coating is subjected to abrasion or scratches, the embedded silica nanoparticles migrate along the cracks and repair the surface of the coating by physical filling and rearrangement. The high hardness of the nanoparticles also helps to restore the wear resistance of the coating. For example, silica nanoparticles migrate to cracks under the action of external forces, and fill the cracks through self-organizing effects to achieve repair.

3. Applications of self-healing nanomaterials

3.1. Smart Textile Applications

3.1.1. Self-healing pressure sensor

Self-healing pressure sensors, conductive polymer nanofibers can be woven into flexible pressure sensors in smart textiles. Such sensors can monitor human movement, pressure changes, or posture [10]. When the sensor material is mechanically damaged (e.g., stretched, torn), the self-healing mechanism in the conductive nanofibers can repair the circuit through rearrangement or chemical used in health monitoring garments, monitoring the wearer's physiological parameters in real time, such as heart rate, respiratory rate, or gait analysis.

3.1.2. Self-healing temperature sensor

Self-healing temperature sensor conductive polymer nanofibers can be used as temperature sensors in smart textiles to monitor temperature changes in the environment or the human body. When the fibers of the temperature sensor are damaged, the conductivity and temperature sensing functions of the sensor can be automatically restored through the self-healing mechanism in the nanofibers. This self-healing temperature sensor can be applied to baby wear, elderly care clothing, or outdoor adventure clothing to monitor the wearer's body temperature changes in real time and provide timely warnings.

3.2. Medical Applications

3.2.1. Self-healing wearable biosensors

Self-healing wearable biosensors, conductive polymer nanofibers can be used to create wearable biosensors that can continuously monitor a patient's physiological indicators, such as electrocardiograms, oxygen saturation, or blood glucose levels. During long-term use, the sensor may be damaged due to friction, tensile or other mechanical stress. Self-healing, conductive nanofibers are able to automatically repair circuitry after damage, ensuring that the sensor continues to record physiological data accurately. For patients who need continuous monitoring of their health status, such as heart disease or diabetes, real-time health monitoring through wearable devices.

3.2.2. Self-healing flexible e-skin

A self-healing flexible e-skin is a biomimetic electronic device that attaches to the surface of the human body and is able to sense pressure, temperature, or other environmental changes. Conductive polymer nanofibers are key materials for this e-skin. Electronic skin is susceptible to damage during attachment or use, and self-healing nanofibers are able to automatically repair the material when it is damaged, thus maintaining its sensing function and flexibility. It is used in rehabilitation therapy or prosthetic devices to help patients perceive the external environment or restore sensory function through electronic skin.

4. Conclusion

In summary, there are many ways to self-heal nanomaterials, among which the advantage of internal factors is that the material can be automatically repaired after damage without external stimuli, and does not require any additional energy input or external conditions. Because it does not depend on external conditions, intrinsic self-healing materials can maintain their repair ability for a long time, making them suitable for long-term applications. Since the material is repaired automatically, the frequency of maintenance and replacement is greatly reduced. Disadvantages, intrinsic self-repair often relies on specific material structure design and molecular chemistry, and cannot cope with all forms of damage, especially deep or large-scale damage. The rate of repair is slower, and the process of self-healing by internal causes may be slower than that of self-healing by external causes, especially in the case of larger cracks or more severe damage. There are relatively few types of materials that can achieve intrinsic self-healing, and the development and manufacturing costs of such materials are high. The advantages of external factors are that external self-healing materials can cope with various forms of damage (such as large-scale cracks, surface scratches, etc.), and the materials can be repaired in different environments by selecting different external stimulation methods. External stimuli can significantly speed up the repair process, especially heat, light, electricity, etc., which can quickly trigger reactions inside the material. Extrinsic self-healing materials can be realized through various means and material design, and different material types can be developed for specific application scenarios. Due to external shortcomings, the process of self-healing requires external stimuli to be triggered, and depends on specific environmental conditions (such as light, heat source, power supply, etc.), which limits the application scenarios. Some extrinsic self-healing materials require additional equipment or operations (e.g., heating equipment, light sources, etc.), which adds complexity and cost. Durability is not as good as intrinsic materials, and because the repair mechanisms in the materials rely on external stimuli, prolonged exposure to harsh environments may result in attenuation or loss of repair capabilities. All in all, self-healing nanomaterials are getting more and more attention and are becoming more and more widely used. From the laboratory to practical application, it has shown broad prospects in medicine and other fields. At present, the hot spots are self-healing sensors, self-healing coatings, etc. Although there has been significant progress so far, there are still many challenges, such as the rate of repair, efficiency, etc. Research is currently underway to continuously optimize the composition and structure of the material to improve the performance. Future self-healing nanomaterials focus on speed and efficiency. And it will further improve intelligence, such as self-adjusting hardness, flexibility, and conductivity in different environments. With the deepening of research, the cost of self-healing nanomaterials will become lower and lower, and they will gradually enter daily life from high-end aerospace. In the future, we will pay more attention to environmental protection and sustainability, develop recyclable self-healing nanomaterials, and reduce environmental pollution.

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