

Self-healing polymer materials: Basic concepts and applications

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ABSTRACT

Since the past few decades, the trend of researching self-healing materials such as ceramic, concrete, and self-healing polymer has always been a very hot topic in materials science. Considering polymer self-healing materials (and their composites), several hundred new articles are published yearly. What is the self-healing feature? This is the ability of materials, thanks to some special mechanisms, to self-recover from damage (scratches, cuts...) returning to an almost intact state. This ability is achieved by adding external healing agents (the specialized term is "healing agent"), or based on dynamic interactions between internal components in the material. If in the past, self-healing polymer materials thanks to the addition of foreign materials (extrinsic self-healing) were of interest in development, in recent times, intrinsic self-healing polymer materials (intrinsic self-healing) have been developed and received more attention. Whether self-healing internally or externally, self-healing polymer materials have many applications such as raw materials for manufacturing sensors, electronic components, surface protection layers, and medical implants... With the ability of application, self-healing polymer materials are an area that attracts a large number of research facilities and technology companies around the world.

Keywords: Polymer; Self-healing material; Medical application; Composite; Mechanism; Sensor; Surface protection; Biomaterial; Implant.

1. Overview of polymer materials

Polymers are macromolecular compounds (compounds with high molecular weight) and in their structure, basic links are repeated many times [1]. Polymer materials today are widely used in many fields such as biomedicine; electronics, information technology; transportation, and aerospace. In biomedicine, polymers have been commonly used in the medical industry with many different applications (Figure 1). Biodegradable and biocompatible biopolymers are used for medical implants, sutures, drug delivery, and wound healing applications. For example, chitosan is a polymer derived from chitin that has antibacterial and anti-inflammatory properties, making it ideal for wound healing applications.



Figure 1. Applications of polymers in Biomedicine [1]

In electronics and information technology: because silicon materials are brittle and break easily, they cannot be used to produce chips used in flexible objects such as clothes (Figure 2). This is the reason why organic polymers are used. The engine is used as a chip. For example, printing plastic chips on consumer items such as T-shirts, beverage cartons, and food boxes to display relevant information.

In transportation and aerospace: many types of polymers are commonly used to make car and spacecraft shells, as well as complex details in their engines (Figure 3).



Figure 2. Applications of polymers in electronics and information technology [1]



Figure 3. Applications of polymers in transportation and aerospace [1]

1.1. Study Objectives

This article introduces an overview of polymer materials emphasizing self-healing polymers. The basic concepts of self-healing polymer materials are introduced, followed by applications of the materials in different fields.

2. Self-healing polymer materials

During operation and use, the polymer material is damaged, and small cracks appear (Figure 4) [2]. Crack propagation can lead to serious material damage affecting the entire product. Unlike biological materials, repair and recovery of cracks with artificial polymers is impossible, unless they can heal themselves.

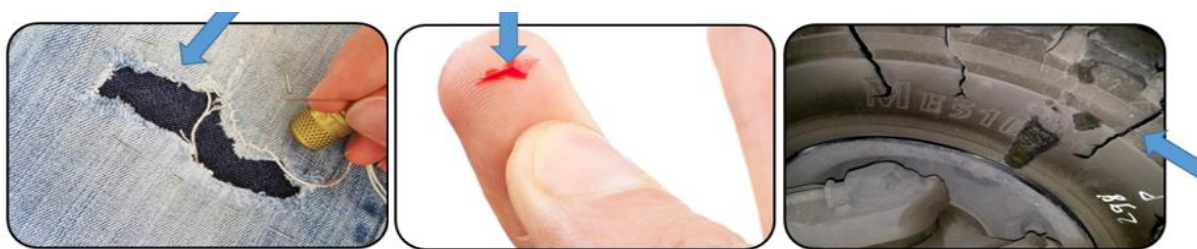


Figure 4. Illustration of the material's self-healing ability [2]

Self-healing materials include polymers, metals, ceramics, and synthetic materials that, after being damaged, by heat, force, or otherwise, can heal and restore to reestablish their original properties of materials. This is an important feature, highly effective in expanding and enhancing the product life cycle and meeting economic and safety issues for users. Material damage often starts with small cracks (microcracks). In most self-healing material systems, these small cracks are where the self-healing and material recovery process takes place, which creates the effect of eliminating or inhibiting crack propagation, helping the self-healing process. When crack surfaces are close together, specific agents or functional groups create a self-healing effect that bridges the gap created by the crack, helping to partially or completely restore the properties of the material. Based on this self-healing theory, for

polymer materials, people often incorporate functional groups or self-healing agents into the network connections, which has given very positive results.

The concept of “self-healing polymers” is the best known and widely studied, initiated by author Scott White and colleagues and published in the journal Nature in 2001 [3], based on a system in which microcapsules (micro-tablets) containing active ingredients combined in a polymer matrix that breaks under the impact of a crack, then the active ingredient is released, a network reaction takes place to heal the crack (Figure 5).

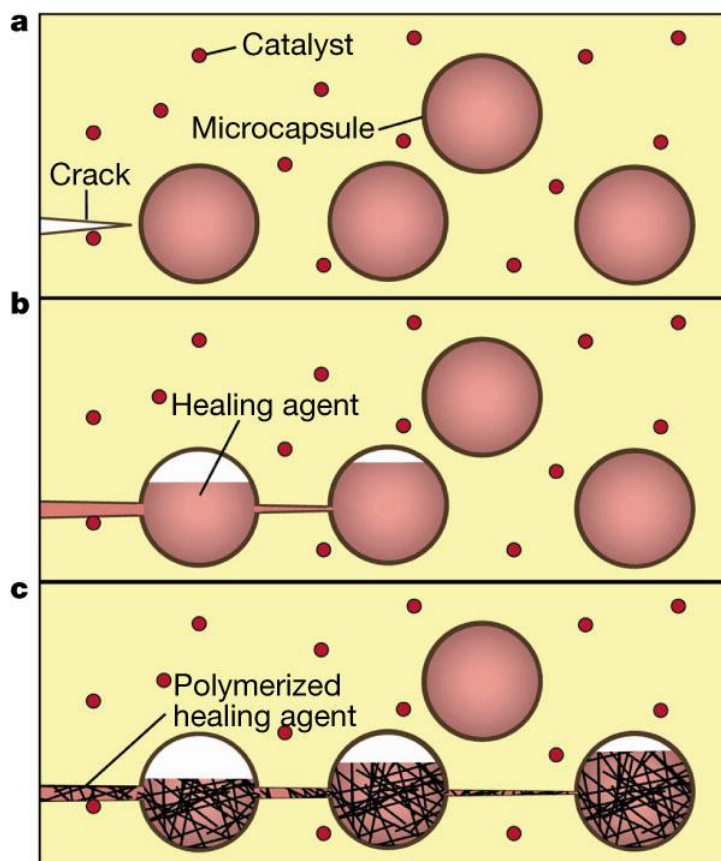


Figure 5. Illustration of the study by S.R. White et al. [3]

Applying this concept, many networked chemical mechanisms have been studied to induce self-healing properties in many polymers. However, research into the production of self-healing materials poses many challenges for scientists, and it is still a new field, that the potential level of self-healing materials is extremely high, so this field is attracting a lot of attention from the scientific community.

3. Some examples of self-healing polymers

Self-healing polymers are potential materials for use in equipment with a high risk of damage, especially in harsh working conditions, to prolong the life of the material, and slow down the remanufacturing and installation process. Replace the parts [4]. In addition, progress in applied research in self-healing polymers has expanded to other materials such as electronic skin, supercapacitors, wearable devices, biomedical devices, bio-concrete, and other materials. Self-healing epoxy can be incorporated into metals to prevent corrosion. One metal surface showed extensive corrosion and rust after 72 hours of exposure, but after being coated with self-healing epoxy there was no visible damage when scanned by SEM after 72 hours of exposure (Figure 6).

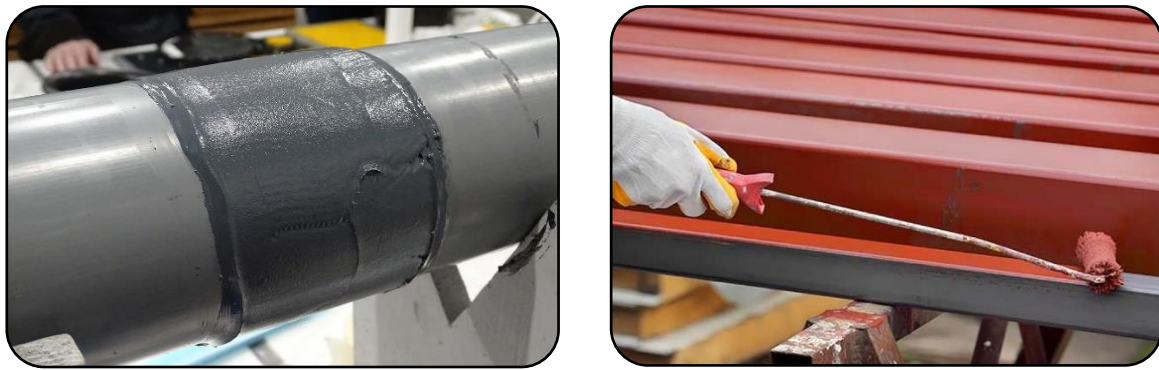


Figure 6. Illustration of anti-rust Epoxy paint [4]

Self-healing materials are being researched and applied in manufacturing aircraft skins. British scientists are researching to create a new type of aircraft shell that self-heals cracks. To create this type, microcapsules carrying healing agents were inserted into the carbon fiber composite matrix.

The Korean Chemical Engineering Research Institute has successfully developed a new protective coating for cars [2, 5]. A notable point of this product is its self-healing ability, helping scratches on the car to completely disappear within 30 minutes. Scientists used a layer of artificial plastic to cover a polymer network made from acryl polyol, then photothermally dyed the surface. This dye layer will absorb infrared light from the sun and convert it into heat energy. The chemical connections between the polymer structures will react to heat, disintegrate, and then recombine, gradually restoring damaged polymer structures (in this case, scratches) until they return to their original state (Figures 7–8).

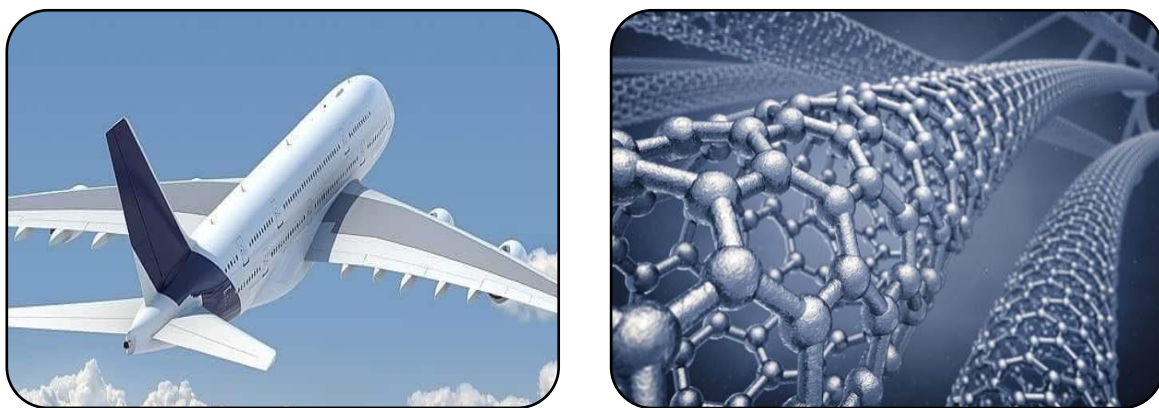


Figure 7. Illustration of self-healing carbon fiber material [5]

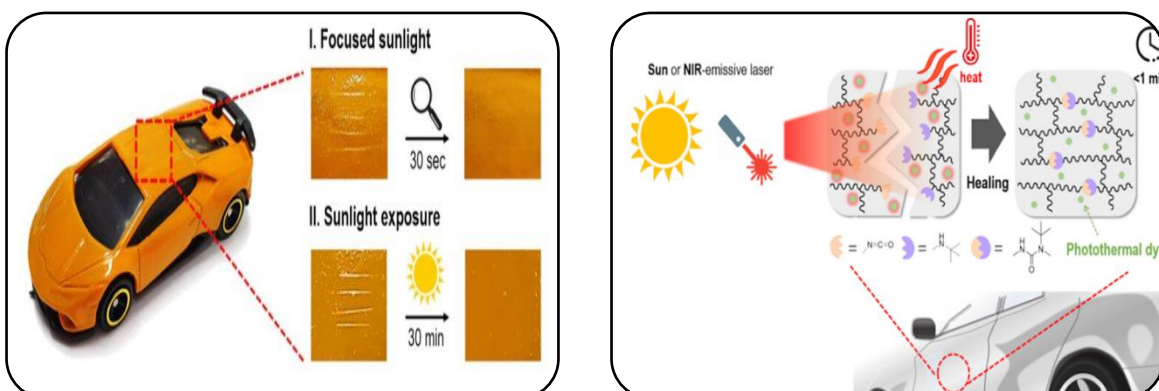


Figure 8. Illustration of anti-scratch paint for vehicles [5]

4. Self-healing mechanism of polymer

Self-healing polymers can be divided into two main groups: self-healing polymers based on the mechanism of foreign agents into the polymer matrix and self-healing polymers based on the mechanism of reversible binding.

4.1. Self-healing materials rely on the mechanism of introducing external agents into the polymer matrix

This type of self-healing material is also called automatic self-healing material or external self-healing material (the self-healing mechanism is not based on the existing bonds of the base material structure) [5-6]. In this group of materials, self-healing agents (or catalysts) are contained in microcapsules or capillaries. In this case, it is common to use liquid self-healing agents to achieve good flow. When damage occurs, small cracks are created in the material, and they will break capillaries or break microcapsules. These self-healing agents flow out, and spread and a healing reaction takes place.

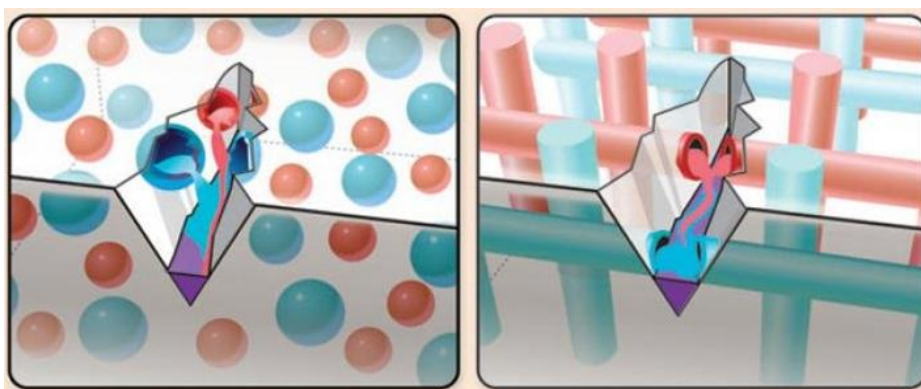


Figure 9. Self-healing material based on the mechanism of introducing external agents into the polymer matrix [6]

For the capillary method, introducing hollow tubes into the polymer matrix can affect the material's load-bearing capacity. In addition, capillary diameter, degree of branching, location of branch points, and orientation are points to note when building capillary networks in materials. Materials that are not subjected to as much deformation can build more microcircuit networks than materials that are subjected to a lot of impact during use. On the other hand, for interconnected microvascular networks, interconnected circuits have a higher self-healing efficiency than discrete circuits but are more difficult and expensive to create. As for the method of using microcapsules, it is similar to the microvascular network method. Microcapsules containing monomers are mixed into a thermosetting polymer matrix. When the crack reaches the microcapsule, it breaks and the agent in the microcapsule flows into the crack, where it can polymerize and repair the crack. If the wall of the capsules is too thick, it cannot be broken by crack contact, but if it is too thin, it will break prematurely.

Typically, for the polymerization of a self-healing agent to occur at room temperature, in addition to the reactants being maintained in the monomer state in the capsule, a catalyst is also mixed into the material matrix. The catalyst lowers the energy barrier of the reaction and allows the monomers to undergo polymerization without additional heat. The monomer and catalyst are maintained separately until cracks facilitate the reaction.

For the use of microencapsulation, the “automatic” self-healing system can only perform the healing process once at the same location due to the full use of the self-healing agent. Conversely, capillaries can allow for additional

healing agents to be loaded from an external source or an undamaged adjacent area and thus will result in more self-healing effects. The interest in studying polymer materials containing self-healing agents, as well as the self-healing process, has attracted attention over the past decade.

4.2. Self-healing materials rely on the reversible mechanism of network connection

This type of self-healing material is classified as conditionally self-healing material or intrinsically self-healing material [6]. In this group of self-healing materials, the molecular structure of the material contains chemical bonds that can regenerate after being broken. This regenerative ability is activated by an external stimulus such as temperature, light, oxygen, electricity, and magnetism. The self-healing process involves breaking and creating new chemical bonds that can be activated (Figures 9-11).

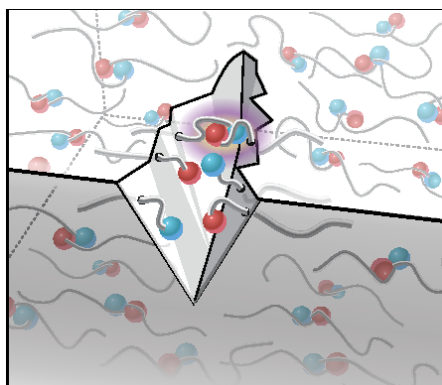


Figure 10. Self-healing material based on reversible mechanism of network connection [6]

The self-healing process is based on the recovery reaction of a reversible component in the circuit that can convert from an unconnected state to a networked state by adding external energy. Generally, the fractured polymer is heated or subjected to strong photo-intensification to increase mobility in the crack area, stimulating bond regeneration and healing the crack.

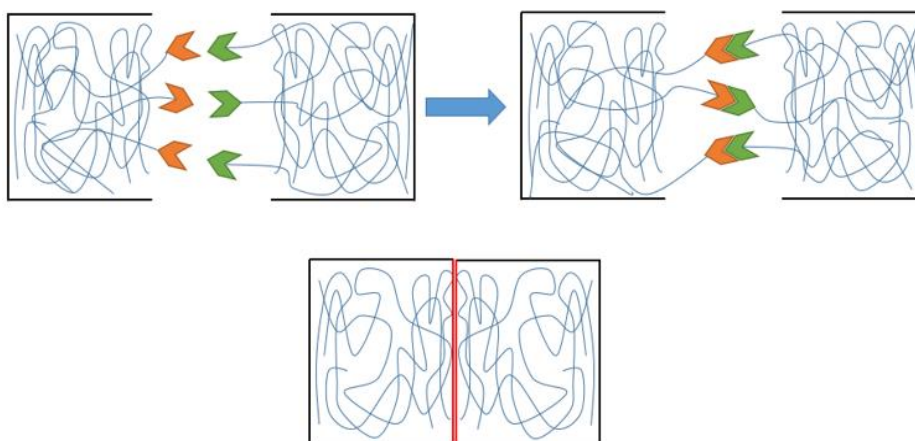


Figure 11. Self-healing mechanism based on the reversible mechanism of network connection [6]

By designing a reasonable molecular structure, the reversible bonds in the polymer chain network can act as weak bonds that are preferentially broken when subjected to deformation and cracking. This has great implications for self-healing applications: the material is damaged on a large scale, the weak bonds are broken, and then the molecular structure can be completely recovered after use.

5. Conclusion

Although there are still many challenges in developing manufacturing technology, self-healing materials in general and self-healing polymers, in particular, are attracting attention from the technology world and businesses because of their rich application potential. It is expected to be an important contribution to the new wave of technology, making everything smarter, with a huge impact on industries and social life. The future of self-healing materials technology is expected to grow beyond current methods, with the ability to develop a continuously circulating biological system that can help heal a variety of materials. Thus, self-healing polymers have many practical applications in life and industry. This is a promising material in research and application development.

Declarations

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Competing Interests Statement

The author declares having no competing interest with any party concerned during this publication.

Consent for Publication

The author declares that he consented to the publication of this study.

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