

Progress in Self Repairing Polymer

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Abstract: In recent years, self-healing materials have attracted more and more attention due to their ability to repair small cracks and scratches in a small range, and the wide range of applications of polymers, including military equipment, electronic products, aircraft, automobile, building materials, etc. The self-healing polymer is mainly based on microcapsule technology. This paper focuses on the self-healing mechanism of self-healing polymers and the chemical methods and chemical essence involved in the process of self-healing, focusing on the latest research progress of self-healing polymers. At the same time, the development prospect of self-healing polymers is prospected..

1. Introduction

Because of its many other metal and nonmetal materials do not have the characteristics (such as high temperature resistance, corrosion resistance, good toughness, high strength), these excellent properties make it widely used in military equipment, electronic products, aircraft, automobile, building materials and so on. However, in the process of processing and long-term application, microcracks will appear on the internal and external surfaces. If the microcracks are not repaired in time, the performance of the material will decline. Moreover, too many microcracks in a certain scale will lead to the fracture of the whole material, thus affecting the service life of the whole material, and may cause significant damage to the whole material in the process of application hidden danger. In order to solve this problem, in the 1980s and 1990s, scholars proposed to make materials self repair, that is, self repair The principle of healing technology is that when the material is damaged by external factors (such as pressure, high temperature, low temperature, etc.), it can self repair, so as to restore to the original state and maintain the original properties. At the same time, scholars have also carried out a large amount of research on the process and mechanism of self-healing.

In 2001, the concept of making microcapsules to realize self-healing of materials was put forward by the WHTI Research Group [1]. Once the concept was put forward, it has aroused widespread concern, and more and more researchers have participated in this research. In 2007, Trask Research Group [2-4] conducted in-depth research on hollow fiber self-healing. Both microcapsule technology and hollow fiber self-healing technology are micro cracks caused by the rupture of microcapsule or hollow fiber in the material when the material is subjected to external force, which makes the internal repair material flow out to the damaged part. However, both microcapsule self-healing technology and hollow fiber self-healing technology can only be repaired once. In order to solve this problem, Toohey research group proposed microvascular technology

based on hollow fiber technology [5-7]. This new self-healing technology can be repaired many times. In this paper, microcapsule, hollow fiber and microvascular are introduced in detail.

2. Self Repairing Technology

2.1 Self Healing of Microcapsules

2.1.1 Principle

The self-healing of microcapsules is mainly realized by the repair materials dispersed in the microcapsules of the material. When the material itself is subjected to external force, the material itself produces microcracks and the inner microcapsules are broken. The repair materials wrapped in the microcapsules flow to the place where the microcracks are generated. Due to the effect of the catalyst dispersed in the material, the cracks are adhered to the surface .

2.1.2 Development of Microencapsulation Technology

White et al. [1] first proposed the ring opening translocation polymerization of dicyclopentadiene (DCPD) to realize the self-healing of materials. In the process of preparation, polyurea formaldehyde resin was used as the outer capsule of DCPD, and the Gibbs catalyst for the polymerization of DCPD was uniformly dispersed in the material. After that, Jackson et al. [8] coated a layer of polypropylene (PP) or polymethylmethacrylate (PMMA) on the surface of Gibbs catalyst, and then coated a layer of SiO₂ on the surface of the coated catalyst and DCPD microcapsules. In this way, Gibbs catalyst and DCPD can be well dispersed in the polymer matrix.

In recent years, many researchers have carried out the research on the preparation of microcapsules using isocyanate as a repair agent. Isocyanates can be polymerized only by water molecules in the air, and self-healing can be achieved without additional catalyst in the polymer matrix. Liang Fengshou [9] prepared a new self repairing microcapsule with isophorone diisocyanate (IPDI) as repairing material and polysulfide network resin as encapsulated capsule, and added the microcapsule into epoxy resin matrix to prepare self repairing material in humid environment. Yang et al. [10] prepared self-healing materials with IPDI as repair material and polyurethane (PU) as encapsulation capsule by interfacial polymerization. The properties of the microencapsulated material are very stable. The loss rate of IPDI is only 10% after storage at room temperature for 6 months.

Credico et al. [11] deeply studied how to prepare a kind of microcapsule with strong stability. They prepared a kind of microcapsule with neat outer surface, using double-layer polyurethane (PU) / polyurea formaldehyde polyurethane (PUF) as the coating repair material and isopoisson diisocyanate (IPDI) as the internal self repair material. The mechanical and physical properties of microcapsules can be adjusted by increasing the amount of monomers and prepolymers on the surface of microcapsules. The thickness of microcapsule wall can be adjusted by coating thickness and chemical reaction.

Microencapsulated self-healing system based on epoxy resin (EP) as repair material is also the focus of research in recent years. In this system, the polymerization of EP monomer is catalyzed by catalyst to make it crosslink and solidify. Yuan et al. [12] found a new self-healing capsule through in-depth research in order to make EP have enough high heat resistance. They prepared EPON 828 microcapsules and DMP-30 microcapsules by encapsulating them with bisphenol A epoxy resin (EPON 828) as repair material and 2,4,6-tris (Dimethylaminomethyl) phenol (DMP-30) as catalyst. Due to the strong thermal stability of EPON 828 and the weak volatility of DMP-30, the repairing agent can not only achieve high temperature curing, but also make the self repairing material have

good self repairing performance, mechanical properties and fatigue resistance. After testing, the self-healing efficiency of the material can still reach more than 72% at 250 °C [13].

Li et al. [14] developed a new self-healing microcapsule with polyether amine (PEA) as the repair material and polymethylmethacrylate as the outer surface. The microcapsules have good thermal stability and the catalyst is chemically stable and not easy to decompose.

Self repairing microcapsules based on maleimide group are also a major category of self repairing microcapsules. Maleimide can react with furan by Diels alder ring opening addition reaction. The reaction has the advantages of mild reaction process and no by-products. So we can make maleimide group as the internal repair material of microcapsule, and let the furan group evenly disperse in the polymer matrix to prepare the polymer material with self repair ability. Peterson et al. [15] studied a kind of epoxy thermosetting resin containing furan group. The system used bismaleimide solution as repair material to react with furan group to repair cracks. After many experiments, the average repair rate reached 70%.

2.2 Hollow Fiber Self Repairing Technology

2.2.1 Principle

The self-healing mechanism of hollow fiber is similar to the self-healing process of animal capillary injury. The damaged part can be self repaired by the repair materials provided by other places.

Compared with hollow fiber self-healing technology, microcapsule self-healing technology has the following advantages: firstly, an efficient production method can be obtained through spinning process; secondly, adding fiber into the matrix material can improve the strength of the material; thirdly, the most important thing is that the repair agent can be transported to the damaged position more quickly and efficiently [16].

Hollow fiber is divided into hollow glass tube, hollow glass fiber and hollow polymer fiber. They are embedded in the fabric layer of the material in a certain order, and embedded in the composite to form a repair layer.

2.2.2 Development of Hollow Fiber Self Repairing

The earliest use of hollow fiber is hollow glass tube. Dry et al. [17,18] used cyanoacrylate and ethyl cyanoacrylate as repair materials and embedded them in hollow glass tubes. Their research results have proved that it is feasible to use insulating glass tube as the container of decoration materials. After that, insulating glass tube has been used in the self-healing of epoxy resin materials. Motuku et al. [19] carried out relevant experiments on hollow glass tubes in fiber reinforced composites. The results show that hollow glass tubes not only have the structural properties of reinforced materials, but also achieve the original self-healing effect.

For some materials, the diameter of hollow glass tube is too large to meet the demand. Researchers have designed hollow glass fiber for self-healing. Bleay et al. [20] made hollow glass fiber with an outer diameter of 15 μm and an inner diameter of 5 μm, and used it as a container for repairing micro cracks in epoxy resin matrix. Some researchers also use experiments to prove that hollow glass fiber can effectively repair itself. Pang et al. [21,22] increased the diameter of hollow glass fiber to 60 μm to improve its internal fluidity. The research team vertically crossed the hollow fiber containing the repair material and the hollow glass fiber containing the catalyst and embedded them in the resin matrix composite. The experimental results show that the strength of the self repairing material can be restored to 97% of the original strength.

Due to the limitation of its mechanical properties, the application range of hollow glass fiber is greatly limited, so the latest hollow polymer fiber has attracted more attention. Some research results show that the diameter and arrangement of hollow fibers have great influence on the self-healing efficiency and the strength after repair. In order to solve these problems, Williams et al. [23, 24] proposed to use hollow polymer fiber to improve the situation after research. In 2010, Jeong ho et al. [25] prepared hollow fiber with polyvinylpyrrolidone (PVP) as the outer skin and polydimethylsiloxane as the inner skin. The self-healing material was completely wrapped in the inner skin. Subsequent experiments show that the material can effectively repair the polymer. Shangzhi et al. [26] used epoxy resin and catalyst as repair materials, polystyrene as hollow polymer materials, and embedded in the matrix resin to realize the self repair of microcracks.

2.3 Microvascular Self Repair Technology

2.3.1 Principle

Either microcapsule self-healing technology or hollow fiber self-healing technology can not be repaired many times, and the material parts after single repair are prone to crack again. The principle of microvascular self-healing technology is that the microvascular used to transport the repair agent is embedded in the composite material in advance. When the material is damaged, the repair agent is released to the damaged area through the microvascular, and the repair agent is solidified to repair the damage. [27]

2.3.2 Development of Microvascular Self Repair Technology

On the basis of hollow fiber technology, Toohey et al. [5] proposed for the first time that microvascular was embedded in the material to transport repair material to the damaged position to realize self repair of the material. They used a single vessel technique. In the experiment, they found that when the repair material was injected into the same place many times, the activity of the catalyst decreased and the repair effect decreased. In order to solve this problem, Toohey et al. [7] proposed the double vessel technology, in which two vessels were embedded in the material matrix, one was used to transport the repair material, and the other was used to transport the catalyst. Through experiments, it was found that this technology can make self repair at the same position up to 16 times, which is obviously better than the single vessel technology.

Hansen et al. [28] developed a new epoxy resin and epoxy curing agent system, changed the improvement of repair agent and microvascular system, improved the fatigue strength of materials, and provided a new idea for the latecomers.

3. Expectation

As a new type of intelligent material, self repairing polymer undoubtedly has a vast space for development. After 20 years of development, there are not only many theories, but also a large number of successful examples. However, the design steps of composite materials are complex, the technical theory is too scattered, and there is no system. Some problems still restrict the development of this new type of intelligent material. But the broad application prospects of self repairing materials in military equipment, electronic products, aircraft, automobile, building materials and so on all tell us the bright future of this road.

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