Research progress of self-healing intelligent composite materials

P Li[1], G Z Liu and J Y Huang

School of Mechatronics & Vehicle Engineering, East China Jiaotong University, Nanchang, China

[1] E-mail: ecjtulipeng@126.com

Abstract. Self-healing composite material is an important intelligent composite material. In this paper, according to the recent research progress of the self-healing of composite materials, introduced the two kinds of typical extrinsic self-healing methods, which are microcapsule self-healing and hollow fiber self-healing, the paper expounds the repair mechanism of the two methods of self-healing, self-healing system characteristics and research status. This paper introduces some problems existing in the field of self-healing, and looks forward to the application prospect and development direction of self-repairing intelligent composite materials.

1. Introduction

With the rapid development of aviation and aerospace industry, composite materials are widely used in the industry field, but the composites will be damaged to a certain extent in the process of using, the damage is mainly the macroscopic and microscopic damage the crack. Macroscopic damage is usually easier to spot and solve in time, while microscopic damage is not easy to find and cannot be dealt with in a timely manner. The most common failure mode is the formation and propagation of microcracks that reduce the material's structural capabilities. Damage may be fixed through traditional bolted or bonded repair methods, but such repair requires temporary decommission of a part, collection of repair materials, and employee time and effort to enact the repair [1]. Therefore, when people study and solve this problem, the self -healing method is proposed to imitate the biological system, and the development of self-healing materials has also attracted the attention of many scholars [2].

In 1980s, the concept of intelligent biomimetic self-healing composite was proposed and widely studied [3, 4]. Self-healing composite materials can repair itself without the need for external material supplies when it is damaged. The main core of the self-healing technology is the supply of energy and material to the damage. With the development of the intelligent biomimetic composite technology, the self-healing technology of materials has been paid more and more attention and developed rapidly. Self-healing material is a kind of intelligent bionic material. When the material produces tiny cracks, the ability of the intelligent biomimetic self-healing material to repair itself is achieved by mimicking the self-healing features of the organism. Self-healing of composite material means that the material can be repaired without any external damage. Usually these tiny cracks are invisible to the human eyes and it will expand after the formation and with the expansion of the crack, the bearing capacity of the matrix material will decline, and the direct fracture of the material. To prevent the cracks from expanding, the scientists developed a new kind of material; this material will identify the presence of damage and make the appropriate response to self-healing. The self-healing function will greatly improve the use life of the composite material and prolong the service life of the material [5-9].

At present, various methods have been used to restore the mechanical properties of composite materials. In accordance with the need for additional repair agents, the self-healing system can be divided into extrinsic and intrinsic [10, 11]. Among them, the self-healing system of extrinsic can realize self-healing function by adding repair agent into the material system, mainly including microcapsule type and hollow fiber type [12]. The intrinsic self-healing is achieved by the physical or chemical effects of the polymer material itself. It mainly includes reversible covalent self-healing and reversible noncovalent self-healing [11, 13, 14]. Intrinsic self-healing must be performed under specific external conditions, the preparation process is more complicated, and the chemical structure of the resin molecule is strict, the repair effect is poor, and it cannot be applied to commonly used composites. In this paper, two typical extrinsic self-healing methods are summarized for self-healing composites. The repair mechanisms and characteristics are introduced, and analysis its advantages and disadvantages. Finally, the development direction and application prospect of self-repairing composite materials are prospected.

2. Hollow fiber type

The repairing mechanism of hollow fiber self-healing method is to insert hollow fiber into the matrix material. The hollow fiber is equipped with a repair agent fluid, when the material is damaged, the damaged area is repaired by releasing the repair fluid in the hollow fiber and bonding the crack. The method was originally proposed by Dry and Sottos, which was originally used in concrete materials, and then extended to the field of polymer materials. In the process of forming polymer-based composites, hollow glass fibers containing one-component cyanoacrylate or two-component epoxy resin adhesives are embedded in the composite matrix by Dry and others [15]. As shown in figure 1 [11], when the composite material is damaged, the crack propagation force causes the liquid core fiber to burst and the repair agent to bond the crack and restore the mechanical properties of the material. In 1999, Motuku [16] planted liquid core fibers containing vinyl resin or epoxy resin restorers in fiber glass /epoxy composite laminates, through the low speed impact test, they explored the materials of hollow fibers, quantity, spatial distribution, repair agent and other factors on the performance of composite materials. In 2001, Bleay [17] diluted the repairing agent by adding acetone, and filled the repairing agent to a hollow glass fiber (outer diameter is 15 mm, inner diameter is 5 mm) by means of vacuum technology. The experimental results show that the existence of the hollow fiber does not significantly reduce the impact properties of the composite material, but the repair efficiency is low, only about 10%. The utility model has the advantages that not only the material can be self repaired, but also the hollow fiber with small diameter can be embedded into the composite material as an reinforcing body, the disadvantage is that it is difficult to inject the fluid into the fiber. In recent years, a large number of hollow fiber self-healing composite materials have been developed by the Bond IP group in the UK [18~20], they embedded the hollow fiber with two component epoxy resin repair agent and UV dye vertically into the resin matrix composite, and achieved structural enhancement, damage detection and self-healing. The results of four point bending test show that the flexural strength of the material can be restored to about 97% before the impact damage. At the same time, the addition of hollow fibers reduced the initial bending strength of the material by 16%. Kouaourakis [21] discussed the effect of the addition of hollow fibers on the mechanical properties of carbon fiber/epoxy composites. They use a fiber diameter of up to 680μm, the influence of the arrangement and diameter of the hollow fiber on the mechanical properties (modulus of elasticity, tensile strength, etc.) of the base material is discussed. For hollow fiber self-repair system, single component repair agent generally use cyanoacrylate, but its repair reaction speed is fast, the repair agent that has not completely flow into the damage has solidified, so the repair effect is poor, the two-component repair usually using epoxy resin and its curing agent as a repair system, but the epoxy resin viscosity, will also affect the repair effect to a certain extent [22].

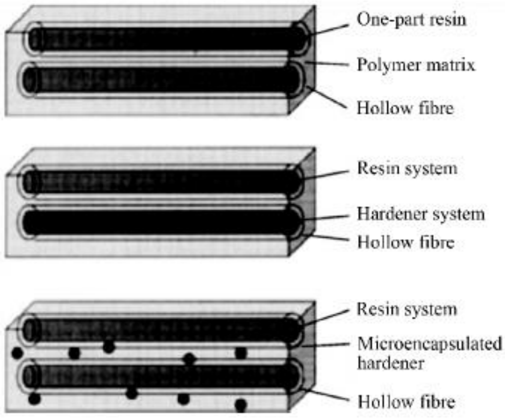

Figure 1. Diagram of hollow-fiber self-healing polymer materials.

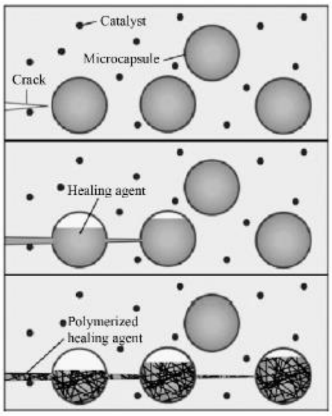

Figure 2. Diagram of microcapsule self-healing mechanism.

For hollow fiber self-repair system, single component repair agent generally use cyanoacrylate, but its repair reaction speed, the repair agent has not completely flow into the damage that occurs at the curing, so the repair effect is poor, two-component repair usually using epoxy resin and its curing agent as a repair system, but the epoxy resin viscosity, will also affect the repair effect to a certain extent. In addition, because the hollow fiber diameter is relatively large, this system is not suitable for self-repair of smooth surface, fiber diameter, fiber arrangement and so on have a great impact on self-repairing composite materials. To make this self-healing system applied to the industry, method need to be further improved. The specific measures include: to explore a better method of filling and sealing hollow fiber; explore other hollow fiber materials such as carbon nanotubes and apply them in practice; effectively filled hollow fiber in large scale application.

3. Microcapsule type

The microcapsule self-healing polymer material was first proposed by White [23] in 2001. It has become the focus of scientific researchers in the following ten years, and has become the most important method of self-healing at present. The self-healing mechanism is shown in figure 2 [23]. The microcapsules containing the repairing agent are embedded in the polymer matrix material while the catalyst is embedded in the matrix. After the material cracks, the crack growth leads to the rupture of microcapsule, and the release of the repair agent spreads to the damage area under the action of siphonage, and the polymerization occurs after the catalyst, and the crack is repaired. In recent years, research has been carried out on the selection of remediation agents, the selection of catalysts and the corresponding microencapsulation technologies.

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3.1. Dicyclopentadiene (DCPD) self-healing agent system

The earliest repair system proposed by White [24] is dicyclopentadiene (DCPD) and metal ruthenium based (Grubbs) catalyst. DCPD can react with Grubbs catalyst to initiate ring opening metathesis polymerization, and play a role in repairing cracks, core material which was prepared by in situ polymerization of DCPD microcapsules, and the microcapsules with catalyst embedded in resin matrix, repair efficiency can reach 90%. Kessler et al. [25, 26] adopted the system to study its repair process of e-glass fiber/epoxy resin composites, the fracture toughness of the system was reduced after the microcapsule was buried in the middle of the 16 laminated plates, the fracture toughness test of the double cantilever beam is used to crack the material. Then manually injected DCPD with the catalyst mixture after the recovery efficiency was 67%, while the manual injection of DCPD after embedded catalyst in the composite material was only 19 percent. This indicates that the good contact between restorer and catalyst is the key to realize self-healing performance. Brown et al. [27, 28] also used the system to study the expansion and self-healing properties of microcapsules on the fatigue crack of materials. The disadvantage of this system is that Grubbs catalyst is expensive, the catalyst is easy to reunite in the matrix and the catalyst is easily lost in contact with the amine curing agent in epoxy resin. To solve the problem of reunion and deactivation of catalyst features, Rule, etc. [29] using paraffin wax formed outside the Grubbs catalyst layer packages, when the catalyst mass fraction is 0.25% and 0.75%, the epoxy resin matrix in the repair efficiency of 75% and 93% respectively. Wilson [30] with epoxy ethyl ester as substrate, Grubbs catalyst DCPD microcapsule and paraffin coated matrix, the epoxy lipid peroxidation agent ethyl amine on the catalyst performance, adding 15% (mass fraction) of DCPD microcapsules and 15% (mass fraction) Grubbs catalyst paraffin-coated, since the repair efficiency is 30%. Jackson et al. [31] encapsulated the Grubbs catalyst with polymethyl methacrylate or polypropylene, and then coated the SiO_2 layer in situ on the surface of the coated DCPD urea-formaldehyde resin microcapsules, which, to a certain extent, allowed the microcapsules and the catalyst in the matrix played a uniform role in the dispersion. Jones and other [32, 33] investigated the effects of the morphology, size and dissolution kinetics of Grubbs catalysts on the self-healing properties and fatigue crack growth. Wilson et al. [34] discussed the repair effect of the second generation Grubbs catalyst, which increased in chemical and thermal stability compared with the first-generation Grubbs, and improved the initial polymerization rate and repair efficiency. Jin et al. [35] added 6.6% (mass fraction) of DCPD microcapsules and 10 mg of Grubbs catalyst to the epoxy resin patch to achieve a maximum repair efficiency of 58%. The initial fracture toughness of the film material was reduced by adding microcapsules with a diameter of 117 μm in the 750 μm thick film material, and the uniform distribution of the microcapsules could alleviate this effect to a certain extent. In order to solve the expensive Grubbs catalyst problem, Kamphaus et al. [36] replaced the Grubbs catalyst with WCl6 catalyst, which also enabled the open-loop metathesis polymerization of DCPD. The self-healing performance of the epoxy resin matrix showed that the catalyst efficiency is lower than Grubbs catalyst.

3.2. Epoxy resin self-healing agent system

At present, most researchers use epoxy resin as self-repairing agent. A large number of studies have been carried out by zhang mingqiu of sun yat-sen university [37-38]. They used melamine-formaldehyde resin as wall materials to prepare microcapsules containing epoxy resin. In the meantime, the microcapsules of the curing agent were prepared by the mixed system of liquid polysulfide pentaerythritol tetramine and benzyl dimethylamine catalyst, the two kinds of microcapsules added to the bisphenol A type epoxy resin matrix, under normal temperature the repair efficiency can reach 82% ~ 88%, under low temperature (-10°C), the repair efficiency can reach 86%. The system has been applied to glass fiber / epoxy resin laminates. After the impact of the laminates, the damage area of the 6 h can be recovered by 85%, and the damage is basically repaired after 12 h. But the system is not suitable for high temperature self-repairing materials, in order to solve this problem, they bisphenol A epoxy resin EPON 828 as the core material preparation of microcapsules, curing agent is still polythiol system, the catalyst using tertiary amine [Tris (dimethylaminomethyl) phenol], the system even at higher than 250℃ ambient temperature, the repair efficiency is still up to 72% to 86% [39].

In order to solve the problem that the self-healing can happen rapidly at room temperature or low temperature to avoid further crack propagation, Zhang et al. [40] also prepared microcapsules of trifluorinated boron ether complex, as the curing agent of epoxy resin restorer. The system can quickly cure adhesive cracks at low temperatures. Experiments show that, by adding the epoxy resin microcapsules with the mass fraction higher than 5% to the epoxy resin matrix and the microcapsules with the boron trifluoride ether complex with the mass fraction higher than 1%, the material repair efficiency can reach 88%. However, because of the large polarity and high activity of three boron fluoride, it is difficult to direct microencapsulation. For this purpose, hollow microcapsules are prepared, and then three fluorinated boron ether complexes are encapsulated by osmosis.

All the above methods belong to the double capsule self-healing system. Zhang also studied the self-healing system of single capsule. Its curing agent USES imidazoles type latent curing agent brominated copper with 2 - methyl imidazole complex [CuBr2 (2 - MeIm) 4], and applied to the epoxy self-healing system, by adding the mass fraction of 10% of epoxy resin microcapsule and 2% [CuBr2 (2 - MeIm) 4], the repair efficiency up to a maximum, repair efficiency up to 111%, this is because the fracture toughness is higher than the fracture toughness of the substrate material after curing.

4. Summary and Prospect

At present, there are still some problems to be solved for the microcapsule self-healing composite materials, for example, how to prepare microcapsules with proper mechanical properties, how to improve the stability of microcapsule and the compatibility of microcapsule and substrate etc. For the hollow fiber type self-healing composite material, it is necessary to solve the problems of how to ensure the arrangement of fibers without changing in the process of processing. The future development trend is as follows: to optimize and develop new self-healing system, improve repair efficiency and self-healing cycle times; the self-healing function does not affect the properties of the matrix material; Self-healing has self-diagnostic function at the same time. It can make self-healing polymer material achieve real bionic material; from laboratory to engineering application.

There is still a gap between China's research on self-healing biomimetic materials and the advanced level of the world, the research of theory and experiment is not carried out deeply and extensively, mostly on the basis of foreign research. Therefore, it is necessary to further intensify the research and strengthen the technology. From raw materials to preparation methods, there should be some breakthroughs. I believe that with the development and improvement of the self-healing composite material technology, self-healing and repair of composite materials will be closer to the organism, its application will be further expanded, the self-healing function will also be more perfect.

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