Research progress of microcapsule self-healing anticorrosive coatings

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Abstract—During the long-term use of the coating, environmental factors, physical damage or other factors may cause micro-cracks in the coating. The expansion of microcracks will destroy the overall structure of the coating, reduce the protective effect of the coating and degrade its mechanical properties. However, the traditional repair methods need to consume a lot of manpower and material resources, and the micro-cracks in the coating are difficult to be repaired by the traditional external means. Inspired by biological systems, intelligent coatings with certain self-healing ability have attracted wide attention in academia and industry. According to the different remediation agents used in self-healing micro capsules, several common self-healing coating systems of micro capsules were analyzed, including corrosion inhibitor system, capsule drying oil system, capsule reactive repair agent system, etc.

1.Introduction
Polymer materials are widely used in the fields of commodity materials, engineering materials and functional materials. However, for the action of the surrounding environment, the material is vulnerable to macro or micro damage. Cracks and micro cracks are the main forms of micro damage. The propagation of micro cracks will destroy the overall structure of the coating, reduce the protective effect and degrade its mechanical properties[1]. However, the traditional repair methods need to consume a lot of manpower and material resources, and the micro-cracks in the coating are difficult to be repaired by the traditional external means[2]. In view of this, in recent years, many researchers have provided a novel and effective way to repair microcrack damage of coating by imitating the self-repair function of organisms and using self-repair technology[3].

Self-healing technologies are mainly divided into two categories. One type is foreign aid type self-repair, and the other type is intrinsic type self-repair[4]. Due to the intrinsic self-healing has certain requirements on the chemical structure of the material, the synthetic process is complicated and difficult to control, and is limited by external conditions. In contrast, the development of foreign aid self-repair is more mature, especially in the field of coatings. This article will focus on the current common
microcapsule self-healing systems, microcapsule preparation methods, performance evaluation methods of microcapsule self-healing coatings, and application status in various fields, and make an outlook on the application and future development trend of microcapsule-filled self-healing coating.

2. Microcapsule self-healing system

2.1. Corrosion inhibitor system
The corrosion inhibitor is microencapsulated and then applied to the self-healing coating, which are mainly used in the field of metal anti-corrosion coating. This method avoids the disadvantages of adding corrosion inhibitors directly to the coating. Koh et al. prepared microcapsules of polyurethane-encapsulated isosorbide derivative corrosion inhibitor by interfacial polymerization. The salt spray test shows that the coating containing microcapsules has good anti-corrosion and self-repairing functions.

2.2. Capsule drying oil system
In the two-component self-healing system, the presence of catalysts is often needed to accelerate the polymerization reaction of the remediation agent, but the addition of some catalysts will affect the performance and appearance of the coating. The emergence of the single-component self-healing coating system can solve some problems [5]. Due to the presence of unsaturated double bonds in natural drying oils such as tung oil and linseed oil, they are very easy to react with oxygen. Therefore, choosing this kind of drying oil as the inner material to prepare microcapsules has become a direction of the development of self-healing technology.

In 2010, Samadzadeh et al. [6] added the prepared tung oil as the capsule core to the coating, and tested its adhesion and electrochemical impedance. It further verified the repair effect of the microcapsule prepared with tung oil as the repair agent on polymer materials. In 2015, Hasanzadeh et al. [7] and Szabo et al. [8] further modified the self-healing microcapsule system with linseed oil as the core by adding driers and corrosion inhibitors into the linseed oil to improve the repair efficiency of linseed oil.

Single-component microcapsules with dry oil as the repair agent can solve the problems that may cause the coating performance to decrease after the catalyst is added. However, this new type of single-component microcapsule repair coating has relatively low repair efficiency and is rarely used in industrial production.

2.3. Capsule reactive repair agent system
Capsule repair agent such as dicyclopentadiene (DCPD), epoxy resin, organic silicon series reagents and reagent with special functional groups in the microcapsule. These reagents have a certain reactivity, after being released from the microcapsule and contact with the catalyst or triggered by ultraviolet light, heat, oxygen, etc. Then, they will polymerize and form a crosslinked structure to bond the crack and realize self-repair. (1) DCPD self-repair agent system: after DCPD self-repair agent encounter the metal ruthenium-based catalyst (Grubbs), it will occur ring-opening metathesis polymerization to form a cross-linked structure. It is the earliest self-repair system used for microencapsulation. However, the system has some disadvantages such as high price and unstable performance. (2) Epoxy resin self-healing agent system: Yuan et al. [9] used melamine resin as the wall material and epoxy resin as the repairing agent to prepare microcapsules and obtained higher repair strength. Liu et al. [10] prepared self-healing microcapsules with epoxy resin as the repairing agent through interfacial polymerization technology, and applied them to epoxy resin coatings, which used an amide curing agent. The results of electrochemical experiments show that the coating material has good self-healing performance and has good anti-corrosion effect on carbon steel.

2.4. The other system
In addition to the above-mentioned microcapsule self-healing systems, there are other self-healing systems that have emerged and are constantly being improved and developed, such as micro/nano container-filled self-healing coatings, expandable component-filled self-healing coating and shape
memory fiber/polymer repair coating, etc.

For the micro/nano container-filled self-healing coatings, in 2015, Chen et al.[11] reported a kind of mesoporous silica nanocontainer that can be controlled and released by ultraviolet light. The container is filled with benzotriazole, a corrosion inhibitor. The mesoporous structure on the surface of silica can be introduced by azobenzene functional group, which can change its chemical structure under ultraviolet light to realize the opening and closing of mesoporous pores. In this way, not only can the release of preservatives be controlled, but also can realize multiple self-healing coating.

In view of the above-mentioned microcapsule self-healing systems, the current research on self-healing coatings mainly lies in the technological factors in the preparation process. Such as the influence of stirring rate, emulsification time and temperature on the morphology of microcapsules. And the effect of adding microcapsules to coatings on coating performance. At present, a variety of self-repair systems have been excavated and studied, but they will be restricted by various factors. For example, microencapsulation of corrosion inhibitors avoids the interaction between corrosion inhibitors and coating materials, and some corrosion inhibitors are more toxic. However, the activity of corrosives is too different to be coated. DCPD has the advantages of rapid polymerization reaction and rapid curing, but as a repair material, DCPD is easy to volatilize and is toxic. Therefore, it is difficult to be widely used in the actual production of coatings. Dry oil as a one-component repair agent can greatly simplify the microcapsule self-healing system, but it has defects such as low repair efficiency, which makes it difficult to be widely used in the field of coatings. In the current industrial production system, the most commonly used epoxy resin self-healing agent system.

3. Preparation method of self-healing microcapsules

3.1. Interfacial polymerization

In the interfacial polymerization method, two monomers that undergo polymerization reactions are dissolved in two immiscible solutions, and an emulsifier is added to the dissolved solution to emulsify the two liquids. Thereby forming an oil-in-water or water-in-oil emulsion. When the two monomers undergo interfacial polymerization, they move from the inside to the interface respectively. Finally, the inner material is coated with polymer to form microcapsules. The principle is shown in Figure 1[12].

![Fig.1 Schematic diagram of the principle of preparing microcapsules by interfacial polymerization][12]

The process for preparing microcapsules by the interfacial polymerization method is convenient and simple, does not require expensive and complicated equipment, can be carried out at room temperature, has a fast reaction speed, and does not require high purity of reaction monomers. And the raw material ratio of the two reaction monomers is not strict. This method is simple, but the requirement for the coating wall material is high; the reactive monomer must have high reactivity and can undergo polycondensation reaction.

3.2. In-situ polymerization

The in-situ polymerization method is to dissolve the wall material and the mixed stabilizer in water, and
then add the inner material. Disperse the inner material by high-speed stirring to form small droplets. After heating, the wall material is gradually aligned on the surface of the inner material. The wall material and the inner material are cross-linked to form stable microcapsules under continuous heating and stirring. The formation principle is shown in Figure 2\cite{13}.

![Fig.2 Schematic diagram of the preparation of microcapsules by in-situ polymerization.\cite{13}](image1)

The particle size and wall thickness of microcapsules prepared by in-situ polymerization are easy to control, the preparation is simple, the raw material and operation cost is low, and it is easy to industrial production, but the overall reaction time is long, and the catalyst needs to be added in the reaction.

3.3. Solvent evaporation process

The solvent evaporation method mainly dissolves the curing agent and the wall material in the low boiling point solvent which is insoluble in water\cite{14}. Due to the difference of surface tension between the two materials, when the solvent volatiles, the wall material precipitates out the solidifying agent coated droplets to form microcapsules, so as to avoid the loss of the solidifying agent dissolved in water. Therefore, the room temperature solidifying agent microcapsules can be prepared by this method generally.

The preparation principle is shown in Figure 3\cite{15}.

![Fig.3 Schematic diagram of the preparation of microcapsules by solvent volatilization.\cite{15}](image2)

The preparation of microcapsules by this method has the advantages of simple operation, short experiment period, less side reaction, wide source of the inner material, normal temperature reaction, large-scale operation and so on.
4. Performance evaluation of microcapsule self-healing coating

4.1. Evaluation of mechanical properties
The mechanical properties of coatings are one of the most important basic properties of coatings. As for self-repairing coatings, the research on mechanical properties mainly focuses on fracture toughness and bond strength.

Fracture toughness is one of the important indexes to evaluate the mechanical properties of coating materials. The evaluation of fracture toughness is usually carried out by using suspension beam devices. In order to explain the repair mechanism of microcapsules on the fracture toughness of self-repairing coatings, Yuan et al.\[16\] carried out an in-depth study on the dual-arm suspension beam device in 2011. It is found that the rapid release and solidification of the repair agent in the microcapsule can quickly bond to repair the microcrack, and the existence of the microcapsule can play a shielding role on the crack tip, preventing the further expansion of the crack.

The self-repairing effect on the coating can be preliminarily judged by studying the mechanical properties and repair efficiency of the coating. However, this is only the macroscopic performance of the self-repairing properties to the coating, and does not involve the repair process and mechanism. If the performance of the self-healing coating is to be further studied, its corrosion resistance should be combined for the analysis.

4.2. Evaluation of corrosion resistance
The research on the corrosion resistance of self-healing coatings mostly uses electrochemical methods, such as polarization curves and electrochemical impedance spectroscopy (EIS). Among them, the polarization curve technology can judge the corrosion rate (corrosion resistance) of the coating by measuring the polarization current density of the coating, and the corrosion tendency of the coating can be judged by measuring the polarization voltage of the coating. The AC impedance technology can be used to measure the impedance change of the coating to study the repair process and repair mechanism of the self-healing coating.

Liu et al.\[17\] studied the influence of microcapsule addition amount on the corrosion resistance of self-healing coating in 2012. It was found that the corrosion resistance of the self-healing coating increases first and then decreases with the increase of the amount of microcapsules added. When the addition amount is 20% (mass fraction), the corrosion resistance of the coating is the best. The size of corrosion current is an important index to judge the corrosion resistance of the coating.

5. Application of microcapsule self-healing technology in coatings

5.1. Concrete coating
At present, concrete is still the most commonly used building material in the world. However, it is easy to be affected by external conditions to crack and cause corrosion of concrete or reinforced concrete. Therefore, how to effectively prevent or slow down the cracking of concrete has always been a hot and difficult issue of concern in the world today.

In 2013, Song et al.\[18\] developed a self-healing coating for concrete cracking. The coating is to encapsulate the repair material that can fill the cracks in polymer microcapsules, and composite the microcapsules into the cement substrate. When the concrete cracks, the microcapsules will be broken under force, and the internal repair materials will fill the cracks. These repair materials are cured under sunlight, so as to achieve the purpose of repairing cracks. The researchers named this self-healing system the light-triggered self-healing system. Because this process does not require a catalyst, is environmentally friendly, and the cost is not high, it is a practical method for repairing concrete cracks.

5.2. Adhesive coating
Adhesive coatings are usually used to connect different components, which can conduct electricity and heat. In recent years, with the rapid development of high-tech industries and national defense technology,
the application of high-performance adhesive coatings has become more and more extensive, especially the demand for adhesive coatings used in high-precision small devices. Once the bonding coating cracks, it will not only greatly reduce the bonding effect, but also expose the substrate, which will lead to corrosion, so that the service life and safety of the device are greatly affected.

Aiming at the problem that the organic silicon adhesive coating is corroded by oxygen atoms in the aerospace technology field, Xing Ruiying et al. [19] prepared corresponding microcapsules using reactive high-boiling silicone as the core and polyurea-formaldehyde resin as the wall in 2009. When the microcapsules was broken, the released organic silicon molecular reactive with vinyl on the chain. It can be cured under the combined action of catalyst and ultraviolet light, to realize the self-repair of organosilicon adhesive coating. With the development of microcapsule self-healing materials, its application in the field of adhesive coating has become more and more in-depth.

5.3. Decorative coating
Decorative coatings are often affected by the outside world during use, causing various damages to the surface and affecting the appearance of the coating. In severe cases, it may even cause the substrate to rust and affect its service life. The coating needs to be repaired after the damage, and the construction of the repair paint is very troublesome, and the color difference between the repair paint and the original paint has one of the most difficult problems to solve. This problem can be solved by applying microcapsule self-healing materials to decorative coatings.

Aiming at the problem that automobile surface coatings are easily scratched and difficult to repair, Yan Ying et al. [20] proposed a method for preparing automobile coatings with self-repairing function in 2012. The prepared coating is to evenly disperse the microcapsules between the topcoat and the primer. When the surface of the coating is damaged, the repair agent released by the microcapsules can directly undergo cross-linking polymerization with oxygen in the air. So as to fill in the scratches to achieve the purpose of repairing the surface. This can greatly improve the durability of the decorative coating on the surface of the car.

6. Conclusions
In view of the development status of microcapsule self-healing technology, several microcapsule self-healing systems, preparation methods and the application in the field of coating repair were summarized. Future research is suggested to focus on:

(1) The research work should focus on optimizing the existing self-repair system and developing a new self-repair system that is more effective and has a high repair rate; emphasis is put on exploring the repair mechanism of microcapsules, improving the interface bonding force between microcapsules and matrix, improving the timeliness of microcapsule repair, and enhancing its repair effect;

(2) Combine the self-healing properties of the coating with other properties to develop a self-healing coating with a variety of functions at the same time (such as self-healing superhydrophobic coating, self-healing anti-aging coating, self-healing drag reduction coating, etc.);

(3) The self-healing polymer materials can be biomimetic materials in the true sense, that is, they have both self-healing and self-diagnosis functions;

(4) To develop microcapsules that can be applied in large quantities in industrial production and can effectively reduce production costs, and to help various industries to develop and widely apply the self-healing technology of microcapsules.

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References

[1] Cao, K. L., Wu, Y., Yu, C. N., et al. (2016) The influence of CNC and KH560 on the properties of waterborne UV-curable wood coatings. Journal of Forestry Engineering, 1:135-139.

[2] Kessler, M. R., White, S. R. (2001) Self-activated healing of delamination damage in woven composites. Composites Part A-Applied Science and Manufacturing, 32: 683-699.

[3] White, S. R., Caruso, M. M., Moore, J.S. (2008) Autonomic healing of polymers. MRS Bulletin, 33: 766-769.

[4] Guo, Y. K., Zou, D. L., Zhao, P. X., et al. (2017) External self-healing systems and their application in epoxy polymers. Materials Review, 31:72-76.

[5] Zhang, L., Wang, W., Yu, D., et al. (2018) Preparation and coating self-healing properties of UV-initiated self-healing microcapsules. Polymer Materials Science & Engineering, 34:116-120.

[6] Samadzadeh, M., Boura, S. H., Peikari, M., et al. (2010) A review on self-healing coatings based on micro/nanocapsules. Progress in Organic Coatings, 68:159-164.

[7] Hasanzadeh, M., Shahidi, M., Kazemipour. M. (2015) Application of EIS and EN techniques to investigate the self-healing ability of coatings based on microcapsules filled with linseed oil and CeO2 nanoparticles. Progress in Organic Coating, 80:106-119.

[8] Szabo, T., Teleldi, J., Nyikos, L. (2015) Linseed oil-filled microcapsules containing drier and corrosion inhibitor-their effects on self-healing capability of paints. Progress in Organic Coatings, 84:136-142.

[9] Yuan, Y. C., Rong, M. Z., Zhang, M. Q., et al. (2008) Self-healing polymeric materials using epoxy/mercaptan as the healant. Macromolecules, 41:5197-5202.

[10] Xiao, D. S., Yuan, Y. C., Rong, M. Z., et al. (2009) Self-healing epoxy based on cationic chain polymerization. Polymer, 50:2967-2975.

[11] Chen, T., Chen, R., Jin, Z., et al. (2015) Engineering hollow mesoporous silica nanocontainers with molecular switches for continuous self-healing anticorrosion coating. Journal of Materials Chemistry A, 3:9510-9516.

[12] Cui S B, Lu Z Y, Liu D C, et al. (2006) Application of interfacial polymerization technology in material preparation. Materials Guide, 20:91-94.

[13] Dai D Y. (1994) The method and application of in-situ polymerization to prepare microcapsules. Journal of Tianjin Institute of Textile Technology, 1:95-101.

[14] Wang, H. P., Hu, S. Q., Zhang, Y. F. (2012) Preparation of styrene microcapsules by solvent evaporation method. New Chemical Materials, 40:52-53.

[15] Gong X C, Lu Y C, Xiang Z Y, et al. (2007) Preparation of Microcapsules by Solvent Volatilization in Dimethicone. Acta Polymerica Sinica, 8:90-94.

[16] Yuan, Y., Rong, M., Zhang, M. (2011) Self-healing of Fatigue Crack in Epoxy Materials with Epoxy/Mercaptan System. Express Polymer Letters, 5:47-59.

[17] Liu, X. X., Zhang, H. R., Wang, J. X., et al. (2012) Preparation of epoxy microcapsule based self-healing coatings and their Behavior. Surface and Coatings Technology, 206:4976-4980.

[18] Song, Y. K., Jo, Y. H., Lim, Y. J., et al. (2013) Sunlight-induced self-healing of a microcapsule-type protective coating. Acs. Applied Materials&Interfaces, 5:1378-1384.

[19] Xing, R. Y., Zhang, Q. Y., Ai, Q. S., et al. (2009) Preparation and properties research of self-healing microcapsules of reactive ethylene silicone oil/poly (urea-formaldehyde). Materials Review, 23:87-89.

[20] Yan, Y., Mei, Y., Zhang, H. P. (2012) A self-healing function of auto anticorrosive coating and its application: Chinese Patent: CN102390147A.