Analysis on Self-healing Properties of Membrane

Shixi Wang
Chemical Engineering, Hebei University of Technology Tianjin, China
*Corresponding author’s e-mail: 308033373@qq.com

Abstract—Due to special compositions and structures, polymer membrane materials usually show a variety of excellent functions. However, the hardness of polymer materials are much lower than inorganic materials, so they are easy to suffer external damage in the process of use. The damaged polymer material will lose its original function and become unable to continue to use, which will have a serious impact on our production and life. Therefore, it is one of the most effective methods to extend the service life and improve the functional reliability of polymer functional materials to endue them with self-healing properties. In this paper, the principle, classification and research results of self-healing membrane are introduced. In particular, this paper explores the application of microcapsule self-healing technology in membrane field, conclude the influence of various components of microcapsule self-healing technology on membrane properties, and discuss the self-healing technology of cellulose membrane and polyethersulfone membrane. In addition, the author also pointed out the development direction of self-healing technique in membrane field.

1. Introduction
With the rapid development of modern science and technology, polymer-based composites are increasingly appearing in various fields of people’s life, such as in aerospace, vehicle production, packaging materials[1]. When the external environment changes, the polymer material will be subjected to load, which will have different degrees of impact on its own structure. Generally, the micro-cracks generated in the material are the initial cause of degradation of various properties of the material, and eventually lead to material damage and loss. Due to the existing conditions, the artificial detection of microcracks has certain limitations, such as ultrasonic, radiography and other technologies can not repair the deep microcracks. Therefore, in response to the increasing demand of people, intelligent self-healing materials, as emerging materials, have also obtained rapid development in recent years. It is particularly important to explore self-healing polymer-based composites to improve their service life and performance. Self-healing technology can detect the damage in materials by itself, and repair the damage under certain conditions, which can prolong the service life of polymers, and has a broad development prospect.

2. Literature Review
White et al. first studied the new polymer materials that can repair themselves in 2001, and researchers have applied the self-healing technology to different polymer composites, such as metal anticorrosive coating[2, 3], multifunctional transparent polymer film[4], cement-based materials[5]. Traditional self-healing materials are mostly used in protective coatings and cement, but their exploration in membrane industry is still limited. In 2010, Mary M. Caruso et al. [1] made a microcapsule of (PU/UF), and the microcapsules are high stability, which solves the problem of instability when polymer matrix is formed at high temperature while maintaining the good interface bonding force. In
2014, Dong Zhao et al. [2] made a self-healing anticorrosive coating for metal. In 2015, Lei Gao et al. [3] made use of TiO2’s light absorption characteristics to make a photosensitive self-healing coating containing light-absorbable microcapsules. After the capsules were broken, the leaking core material could cure and repair the substrate under UV light. Wang Yan et al. [4] made a transparent self-healing PAA membrane with anti-fog function by means of layer by layer assembly. Sang-Ryoung Kim et al. [5] prepared an example of self-healing membrane applied to water treatment.

![Figure 1. The theory of self-healing water treatment membrane](image)

By embedding microcapsules in polyethersulfone membrane, when the membrane was damaged, the capsule core was released and polymerized in contact with water, so that the membrane could achieve self-healing effect.

3. **Analysis on Self-healing Properties**

3.1. **Classification of self-healing techniques**

3.1.1. **External aid self-healing.** The healing agent of the repairable material is first loaded by microcapsule package or microvascular tube, and then embedded into other material. In the case of cracks, self-healing material and catalyst are released and mixed, and polymerization reaction occurs to achieve the repair effect. Common external aid self-healing methods include hollow fiber self-healing, micro-capsule self-healing, nanoparticle self-healing, microvascular network self-healing and so on.

The advantage is that there are a wide range of suitable substrates, which are integrated into the materials in a simple way, and even the macroscopic damage can be repaired. The disadvantage is that the packaging technology of the repair agent is usually complex, and can only be repaired once, and the packaging material no longer has the ability to repair after release.
3.1.2. Intrinsic self-healing. The main ways to repair materials are chain segment motion repair of polymer internal molecules, and reversible reactions between molecules in materials. The intrinsic self-healing methods include reversible covalent self-healing (e.g. Disulfide bond) and reversible non-covalent self-healing [6] (e.g. Electrostatic interaction, hydrogen bond, etc.).

The advantage is that it can repair the damage inside the substrate for many times and not required anything else, while the disadvantage is that it has strict requirements on the matrix structure and only applies to the special matrix, so its application scope is limited. Moreover, the introduction of these two valence bonds will correspondingly weaken the mechanical properties of the material.

3.2. Microcapsule self-healing

3.2.1. Microcapsule self-healing technology. Microcapsules usually refer to particles with a “core-shell” structure, “shell” refers to the outer wall of the particle, and “core” refers to the covered substances, such as gas, liquid droplets, solid particles, etc. [7] The material covered by the capsule wall of the microcapsule is the capsule core. Under the protection of the capsule wall, the capsule core is released slowly under certain conditions to achieve the desired effect.
3.2.2. **Microcapsule self-healing system.** Common microcapsule self-healing systems can be divided into the following categories:

(a) single-component microcapsule self-healing systems, in which reactive chemicals, suspensions or solvents can be encapsulated and react with potential functional groups in the polymer matrix after release;

(b) healing agent capsule/catalyst system, based on the microcapsule supporting monomer and the catalyst dispersed in the polymer matrix, the monomer contacts the catalyst after the microcapsule breaks;

(c) two-capsule self-healing system, which is usually adopted when the required reactants are two kinds of chemical substances requiring isolation and encapsulation;

(d) integrated microcapsule system, and this kind of system is a completely self-contained self-healing system. The healing agent and catalyst are in the microcapsule[8].

![Figure 5. Schematic drawing of different self-healing system: (a) single-component microcapsule self-healing systems (b) healing agent capsule/catalyst system (c) two-capsule self-healing system (d) integrated microcapsule system](image)

3.3. **Effects of Two Main Components on Membrane Properties**

3.3.1. **Microcapsule wall.** Microcapsule wall material is the key factors to microcapsule performance. Generally speaking, the main requirements for wall are non-toxic, stable performance, good film-forming, has a certain intensity and plasticity, etc. If the microcapsule wall instable, it will affected by the external environment core is easy reveal and it will influence the original performance such as light, air permeability, hydrophilic effect. There are considerable amount of inorganic material and organic material can be used as shell material, but the most commonly used polymer materials. At present, can be a lot of polymeric materials as the microcapsule shell material. It is mainly divided into natural polymer materials and synthetic polymer materials.

3.3.2. **Core material.** If the core material has a high viscosity or is solid, it is difficult for the core material to flow to the crack after release, which will affect the repair effect of the membrane. If the core material reacts with the membrane, it will also affect the performance of the membrane itself. The core materials must meet the following conditions: the repair agent is a low-viscosity liquid that can be coated in microcapsules; The catalyst (curing agent) of the polymerization reaction does not react with the substrate, and the repair agent performs polymerization reaction at room temperature under the action of the catalyst.
4. Discussion

We should put more attention to the self-healing materials combined with membrane technology field, because the membrane technology has developed rapidly in recent years, membrane technology is widely used in various fields, and many of the membrane are disposable products which caused a lot of membrane costs increase, so the research about self-healing membrane has great potential. In self-healing technology, microcapsule self-healing technology has been relatively mature, so considering the combination of microcapsule self-healing technology and membrane technology, the membrane production not only has excellent performance but also can self-healing.

4.1. Application

4.1.1. Self-healing technology of cellulose membrane. As the world’s largest natural macromolecular material, cellulose membrane is made of cellulose has high strength, good transparency and excellent gas barrier performance, and has a wide application prospect in packaging, drug release, dialysis, ultrafiltration and other aspects.

![Figure 6. SEM photos of (a) pristine cellulose membrane and (b) self-healing cellulose membrane](image)

Zhang Lu et al. first made a microcapsule of ultraviolet curing agent and photoinitiator, and embedded it in cellulose membrane. When the cellulose membrane microcapsule was damaged, the inner core material of the microcapsule would overflow, which could quickly cross-link the cellulose membrane under UV light.

![Figure 7. Confocal laser scanning microscope images of (a) pristine cellulose membrane (b) damaged cellulose membrane (c) self-healed cellulose membrane and sectional images of (d) pristine cellulose membrane (e) damaged cellulose membrane (f) self-healed cellulose membrane (scale bar is 50um).](image)
After fluorescence treatment of cellulose membrane, confocal laser scanning microscope (CLSM) was used to image and analyze the self-healing technology of microcapsules on the surface and cross section of procellulose membrane and cellulose membrane before and after uv light repair. The test results are shown in figure 7. It can be seen that the original cellulose membrane surface is flat gully, the crack caused by using a thin blade of cellulose membrane, cellulose membrane was completely truncation (figure 7 (b), (e)), by the UV light after repair of surface and cross section image can be seen that there was no significant alteration of the surface morphology of cellulose membrane. Cross section morphology showed two sections are linked by core material, this is due to the limited core material content cannot fill the cracks therefore it can't repair the whole crack repair agent.

4.1.2. Self-healing technology of polyethersulfone membrane. Polyethersulfone has excellent heat resistance, physical and mechanical properties, insulation properties, etc., especially has outstanding advantages such as continuous use at high temperature and stable performance in the environment of rapid temperature change. It has been widely used in many fields[9]. The self-healing water treatment membrane can restore its water flux properties autonomously.

![Figure 8. The effect of self-healing membrane](image)

The self-healing membrane is fabricated by embedding microcapsules within a conventional poly(ether sulfone) membrane. When the membrane structure is physically damaged, the microcapsules release a reactive healing agent that reacts with the surrounding water to form a material that plugs the damage. The self-healing was found to recover the water flux of the membrane to 103% of the original membrane’s performance. The results of this study show that microcapsule-embedded membranes[10] are a promising approach to fabricating versatile membranes that can self-healing.

4.2. Existing problems

The self-healing technology of microcapsules provides a new and effective way for the bonding repair of microcracks in polymer matrix composites and a new method to prevent the potential harm of composites. Self-healing composite materials can be applied in more and more fields, and microcapsule self-healing technology will have a wide application prospect. However, there are still many problems in the application of microcapsule self-healing technology in composite materials. First, microcapsules may block the pores of the membrane and have certain effects on the hydrophilicity of the membrane. The second microcapsule self-healing technology cannot achieve multiple repairs.

4.3. Suggestions

Firstly, about the hydrophilicity problem, make microcapsules as small as possible so they do not clog holes easily. Secondly, it can solve the multiple repairs problems of healing material not easy to flow all of the body by replacing the microcapsule structure with a tiny mesh tube, and when the area that is broken is broken again, the material from the other area can flow in and restore it.
5. Conclusion
Microcapsule self-healing technology develops rapidly and is widely used in many aspects such as metal corrosion prevention and building materials. The new field of combining self-healing technology with membrane science has a broad prospect. The membrane with self-healing function has great potential. Many people have explored this field and made great progress, discovering more and more self-healing materials and self-healing principles. Of course, there are many problems that need to be studied, such as the influence of using environment on microcapsules, the repair efficiency of microcapsules and so on. However, these problems are worth further investigation to improve the stability and repair efficiency of microcapsules make membrane materials with better repair performance.

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