

Study on the properties of self-healing epoxy coating based on Pickering emulsion system

Xiaolin Liao, Wei Li, Baichen Wang*, Yu Gao

Shenyang Aerospace University Shenyang, China

* Corresponding Author Email: wang_baichen@126.com

Abstract. In this study, Pickering emulsion template method and interfacial polymerization method are used to prepare microcapsules containing tung oil with Polyvinyl alcohol (PVA) as stabilizer, PUA as wall material and tung oil as core material. Microcapsules are structured and spherical, with uniform size distribution. The prepared microcapsules were dispersed in epoxy resin to form a self-healing epoxy coating. The effect of brine soaking time on the corrosion resistance of the self-healing epoxy coating was studied. EIS results showed that the self-healing epoxy coating with microcapsules had better corrosion resistance than pure epoxy resin. The mechanical properties of the self-healing epoxy coating with microcapsule content were studied by measuring the tensile strength, tensile shear strength and coating hardness. When the microcapsule content was 3%, the tensile strength increased to 84.71 MPa, which was 35.53% higher than that of pure epoxy resin. The hardness of self-healing epoxy coating is 22.46 HV, which is 0.18% lower than that of pure epoxy coating. The experimental results show that a small amount of microcapsules can improve the mechanical properties of the self-healing coating.

Keywords: Microcapsule; self-healing epoxy coating; corrosion resistance; mechanical property.

1. Introduction

Metal materials are very prone to corrosion, which has brought huge economic losses to the world, so it is of vital significance to study the corrosion and protection of metal. Currently, one of the most cost-effective ways to prevent corrosion is to coat the surface of a metal with an anticorrosive coating. However, the anticorrosive coating will inevitably suffer from external force or mechanical damage and produce cracks, through which the corrosive medium will gradually penetrate to the interface between the coating and the metal matrix, causing corrosion to the metal matrix [1-5]. Therefore, it is of vital significance to study intelligent anticorrosive coating with bionic self-healing function. Once the coating is damaged, it can realize self-healing without manual intervention [6-9].

One of the self-healing mechanisms of the intelligent anticorrosive coating is that the repair agent is coated in the microcapsule, and then dispersed in the coating substrate. When the coating is damaged and cracks occur, the microcapsule breaks and releases the repair agent to repair the coating defect, thus preventing further corrosion of the metal. The repair mechanism is shown in Fig. 1. Microcapsules are widely used in the field of self-healing materials. After the material is microencapsulated, the physical properties of the coating material are improved, the stability of the coated substance is enhanced, the odor is blocked, the toxicity of the substance is greatly reduced, and the pollution of toxic substances to the environment is reduced [10].

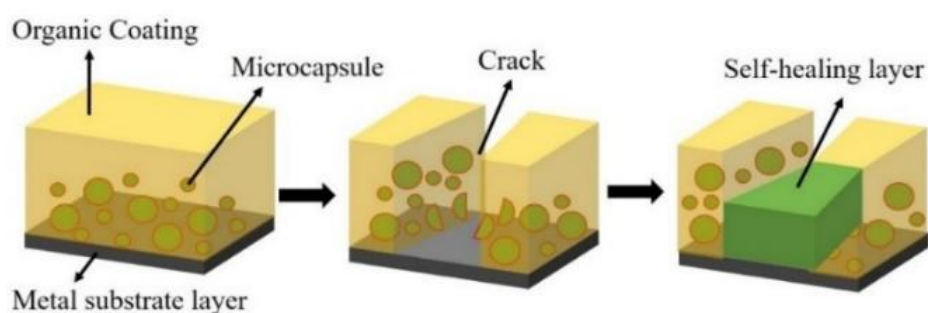


Fig 1. Self-healing mechanism of intelligent anticorrosive coating.

At present, the commonly used repair agents include dicyclopentadiene [11, 12], active epoxy resin [13, 14], dry oil [15] and isocyanate [16, 17], etc. Yin[18] et al. synthesized a two-component repair agent system consisting of polyurea microcapsules containing epoxy resin and $\text{CuBr}_2(2\text{-MeIm})_4$ (complex of CuBr_2 and 2-methylimidazole) latent curing agent. The experimental results showed that the repair efficiency of this microcapsule reached 68%. Li [19] et al. synthesized microcapsules with the hybrid of IPDI and terminal isocyanate prepolymer (CPU) as the active repair agent to prepare the anti-corrosion coating. Experimental results show that the coating containing 10% microcapsule scratches place have obvious healing effect, the $|Z|_{f=0.01\text{Hz}}$ value is about $1.9 \times 10^6 \Omega \cdot \text{cm}^2$, almost three orders of magnitude higher than the pure epoxy coating and shows strong corrosion resistance. Li [20] et al. synthesized urea-formaldehyde microcapsules with tung oil as core material through in situ polymerization. EIS test results show that the impedance of the self-healing coating exceeds $10^6 \Omega \cdot \text{cm}^2$, much higher than that of the pure epoxy coating $10^3 \Omega \cdot \text{cm}^2$, which confirms the excellent corrosion resistance of the prepared self-healing coating.

For dicyclopentadiene and active epoxy resin repair agents, it is necessary to add a catalyst to trigger the polymerization of repair agents in the coating, and isocyanate esters have certain toxicity. Therefore, self-healing materials without catalyst, non-toxic and environmental protection have attracted great attention from researchers [21-23]. Tung oil is a kind of dry plant oil natural film forming material, it contains 80% tung acid, the rest is linolenic acid, linoleic acid and oleic acid, these substances contain unsaturated double bonds, can be oxidized into film in air [24, 25]. The structural formula of tung oil is shown in Fig. 2. Due to the good biodegradability of tung oil, the self-healing coating prepared by tung oil as restorer not only meets the requirements of environmental protection, but also reduces the cost.

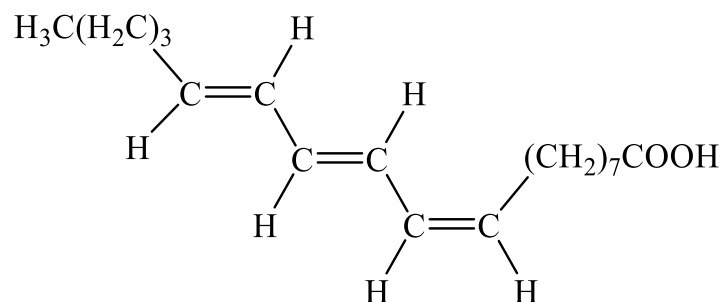


Fig 2. Structural formula of tung oil.

2. Experiment

2.1. Preparation of microcapsules containing tung oil

Microcapsules containing tung oil were prepared by Pickering emulsion template method and interfacial polymerization method. Weighing 9g tung oil and 4.5g toluene diisocyanate (TDI) evenly mixed as oil phase, and taking 5wt% PVA aqueous solution 150mL as water phase. The oil droplets were added to the water phase and homogenized for 5min at 11000rpm by digital display high speed dispersing homogenizer to form O/W emulsion. Then the O/W emulsion was transferred to a three-port flask containing 300mL deionized water, and mechanical stirring at a constant speed for 3h was performed in a water bath at 60°C until the reaction was completed to obtain microcapsule suspension. The microcapsule suspension was centrifuged, washed, frozen overnight, and then dried in freeze vacuum for 24h. The white powder was PVA/PUA microcapsules.

2.2. Performance characterization of microcapsules containing tung oil

Optical microscopy (OM) and scanning electron microscopy (SEM) were used to observe the morphology and particle size distribution of emulsion and microcapsules.

2.3. Preparation of self-healing epoxy coating

A3 steel plate (50mm×40mm×1mm) was selected as the metal matrix material. 120 and 400 mesh sandpaper were used to polish the steel plate, remove the oxide film on the surface, and the surface was cleaned, decontamination and oil removal with an aqueous ethanol. PVA/PUA microcapsules were weighed and added into the preheated epoxy resin, the content of microcapsules was 3%, 5%, 8%, and ultrasonic dispersion was 1h. The curing agent 2-ethyl-4-methylimidazole (EMI-2, 4) with the mass of 3% epoxy resin was added, stirred evenly, and coated on the previously prepared and preheated metal matrix surface with the coating rod. The curing mechanism was 60°C for 2h and 70°C for 4h. The control sample was pure epoxy coated (without microcapsules) and was prepared by the same method as above.

2.4. Performance characterization of self-healing epoxy coatings

2.4.1. Brine immersion experiment

Use a scalpel to make an "X" shape scratch on the surface of the coating with even force to ensure that the scratch depth is enough to reach the metal matrix. Leave it at room temperature for 72h to fully repair the scratch area. The working area was 1cm², and the coating was immersed in 3.5wt% NaCl solution at room temperature for 1d, 5d and 10d. The corrosion of the coating was photographed with the camera.

2.4.2. EIS Test

Electrochemical workstation was used to test AC impedance spectroscopy (EIS) of the self-healing epoxy coating to study the corrosion resistance of the coating. The test used a three-electrode system. The working electrode was coated with A3 steel plate with self-healing epoxy coating. The reference electrode was saturated calomel electrode and the auxiliary electrode was platinum wire electrode, and the working area was 1cm². After the stable open-circuit potential was measured, the EIS was tested in the frequency range of 10⁻²-10⁵Hz.

2.4.3. Tensile performance test

Standard tensile specimens were prepared according to GB/T2567-2021. The epoxy resin dispersed with different microcapsule contents (0%, 3%, 5%, 8%) was poured into the drawing mold, vacuumed for 30min, and the curing temperature was 60°C for 2h and 70°C for 4h. After curing, it was taken out and tested by an electronic universal testing machine with a tensile rate of 2mm/min. There are 5 samples in each group, and the average value is taken after measurement. The calculation formula of tensile strength is shown in Equation (1):

$$\sigma = \frac{F}{b \times h} \quad (1)$$

Where, σ is the tensile strength (MPa), F is the maximum load borne by the specimen at fracture (N), b is the width of the specimen (mm), and h is the thickness of the specimen (mm).

2.4.4. Tensile shear strength test

The sample was prepared according to the method specified in GB/T7124-2008, and the thickness of the adhesive layer was 0.2mm. The tensile rate was 1mm/min using an electronic universal testing machine. There are 5 samples in each group, and the average value is taken after measurement. The calculation formula of tensile shear strength is shown in Equation (2):

$$\tau = \frac{F}{L \times b} \quad (2)$$

Among them, τ is tensile shear strength (MPa), F is the maximum load borne by the specimen when it is broken (N), L is the adhesive width of the specimen (mm), b is the adhesive thickness of the specimen (mm).

2.4.5. Coating hardness test

In this experiment, Vickers hardness was used to characterize the experimental force of 300g and the experimental retention time of 15s. Select 5 points on each coating surface for experiment, and take average value after test.

3. Results and analysis

3.1. Morphology and particle size of microcapsules

As shown in Fig. 3, under the conditions of 5% stabilizer concentration, 11000rpm emulsification speed and 2:1 core-shell ratio, the prepared microcapsules were spherical in shape, uniform in size distribution, and no agglomeration phenomenon.

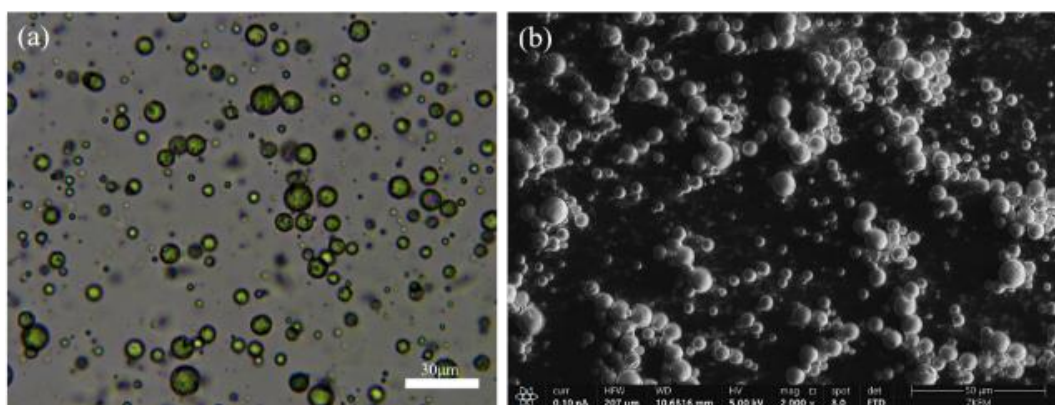


Fig 3. Microcapsules: (a) OM diagram; (b) SEM diagram.

3.2. Observation of macroscopic corrosion resistance of self-healing epoxy coating

As can be seen from Fig. 4, the scratch area of the self-healing epoxy coating sample soaked in 3.5% NaCl solution began to rust after a period of time and worsened with the increase of time. When the epoxy coating with 0% microcapsule content was soaked for 5 days, slight corrosion occurred in the scratches. The corrosion products increase gradually with the increase of time. This is because the metal iron matrix at the scratch has lost the protective effect of the coating, and is directly exposed to the corrosive environment to corrosion and generate rust. When the microcapsule content is 5%, the scratches of the self-healing epoxy coating do not appear obvious corrosion phenomenon during the soaking cycle, and the corrosion resistance is good. The experimental results show that the overall corrosion of epoxy coating with tung oil microcapsules is better than that of pure epoxy coating.

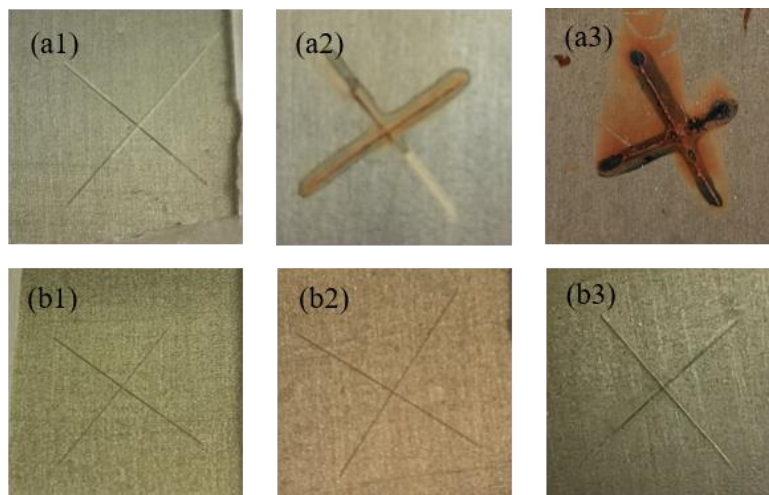


Fig 4. Macroscopic corrosion diagram of self-healing epoxy coatings with different microcapsule contents as a function of soaking time:(a) 0%; (b) 5%; (1-3): 0d; 5d; 10d.

3.3. Analysis of EIS

As shown in Fig. 5, the Nyquist plots of the self-healing epoxy coatings all show a capacitive reactance arc. The arc radius of capacitive reactance of the epoxy coating containing microcapsules is significantly larger than that of the pure epoxy coating, because the microcapsules are broken and the repair agent is released to the scratch to generate a new polymer film, which hinders the penetration of corrosive media and improves the corrosion resistance of the coating. With the same microcapsule content, the arc radius of the capacious reactance of the self-healing epoxy coating gradually decreases with the increase of soaking time, which means that the corrosion resistance of the coating decreases with the increase of soaking time and the gradual penetration of electrolyte solution. This is because the self-healing epoxy coating itself has pores, and there is a certain gap between the microcapsules and the epoxy matrix. With the increase of soaking time, the corrosive medium will slowly penetrate through these pores to the surface of the metal matrix, resulting in a continuous decrease in the impedance of the coating at the later stage of soaking.

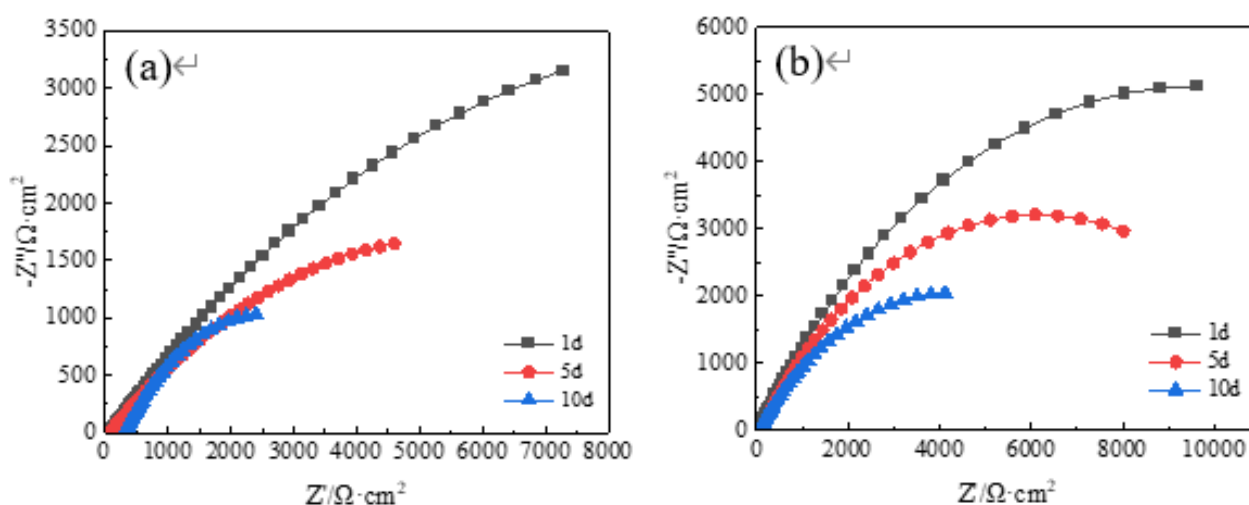


Fig 5. Nyquist diagram of self-healing epoxy coatings with different microcapsule contents as a function of soaking time: (a) 0%; (b) 5%.

3.4. Tensile property analysis

As shown in Fig. 6(a, b), with the increase of microcapsule content, the tensile strength of the self-healing epoxy resin first increased and then decreased. The tensile strength of pure epoxy resin is 62.50 MPa. When the microcapsule content was 3%, the tensile strength of self-healing epoxy resin was 84.71 MPa, which was 35.53% higher than that of pure epoxy resin. This is because when the microcapsule content is low, the microcapsules can be evenly dispersed in the epoxy resin without causing stress concentration, thus improving the toughness of the resin and the tensile strength of the resin. The tensile strength of the self-healing epoxy resin decreased gradually when the microcapsule content was increased. When the microcapsule content was 5%, the tensile strength of self-healing epoxy resin was reduced to 42.53 MPa, which was 31.95% lower than that of pure epoxy resin. When the microcapsule content was 8%, the tensile strength of the self-healing epoxy resin was reduced to 35.91 MPa, which was 42.56% lower than that of the pure epoxy resin. On the one hand, as the content of microcapsules increases, their dispersion in epoxy resin becomes worse, resulting in agglomeration phenomenon, resulting in stress concentration in the use process of resin, which leads to the reduction of the tensile strength of resin. On the other hand, under the action of external tension, the microcapsule is broken, and the inside is liquid. After the rupture, there will be holes, resulting in the increase of pores and stress concentration points in the resin, which speeds up the failure rate of the resin and leads to the great reduction of the tensile strength of the self-healing epoxy resin.

As shown in Fig. 6(c), elongation at break of pure epoxy resin is 6.53%, and elongation at break of self-healing epoxy resin with 3% microcapsule content is 9.54%, 46.09% higher than that of pure

epoxy resin. The elongation at break of the self-healing epoxy resin decreased when the microcapsule content was increased. When the microcapsule content was 8%, the elongation at break of self-healing epoxy resin decreased by 3.50%, which was 46.40% lower than that of pure epoxy resin. The experimental results show that a small number of microcapsules can improve the tensile properties of the self-healing epoxy resin.

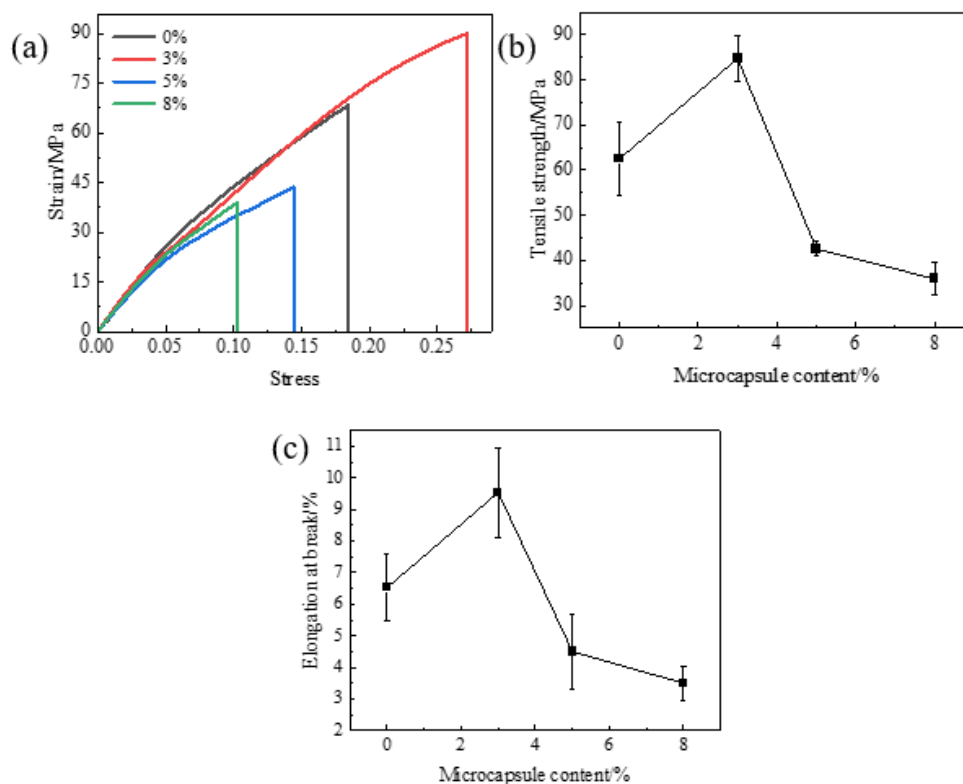


Fig 6. Tensile properties of epoxy resins with different microcapsule contents: (a) stress-strain; (b) tensile strength; (c) elongation at break.

3.5. Analysis of tensile shear strength

Since the bonding mechanism between epoxy resin and metal matrix is the joint action of mechanical, chemical and adsorption, the bonding property between epoxy resin and metal matrix is analyzed by using tensile shear strength. As shown in Fig. 7(a, b), the tensile shear strength of the pure epoxy resin coating is 5.44 MPa. With the increase of microcapsule content, the tensile shear strength of the self-healing epoxy coating gradually decreases. When the microcapsule content is 3%, the tensile shear strength of the coating is 3.08 MPa, which is 43.38% lower than that of the pure epoxy resin coating. When the microcapsule content continued to increase to 8%, the tensile shear strength of the self-healing epoxy coating decreased to 2.38 MPa, which was 56.25% lower than that of the pure epoxy coating. On the one hand, the addition of microcapsules occupies the inner space of the resin matrix, reducing the contact probability between resin molecules, making it difficult for polycondensation reaction to occur between resin molecules and cross-linking, and thus greatly reducing the force between resin molecules. At the same time, there are microcapsules as spacers between resin molecules. The force between microcapsules and resin molecules is the intermolecular force, which belongs to the physical interaction. This interaction is weak. On the other hand, the increased content of microcapsules reduces the dispersion degree of microcapsules in epoxy resin, resulting in agglomeration, defects in the epoxy resin matrix, stress concentration, and ultimately the reduction of tensile shear strength of self-healing epoxy coating. The experimental results show that the addition of microcapsules reduces the tensile shear strength of the self-healing epoxy coating, and gradually decreases with the increase of the content of microcapsules, that is to say, the adhesion of the coating decreases.

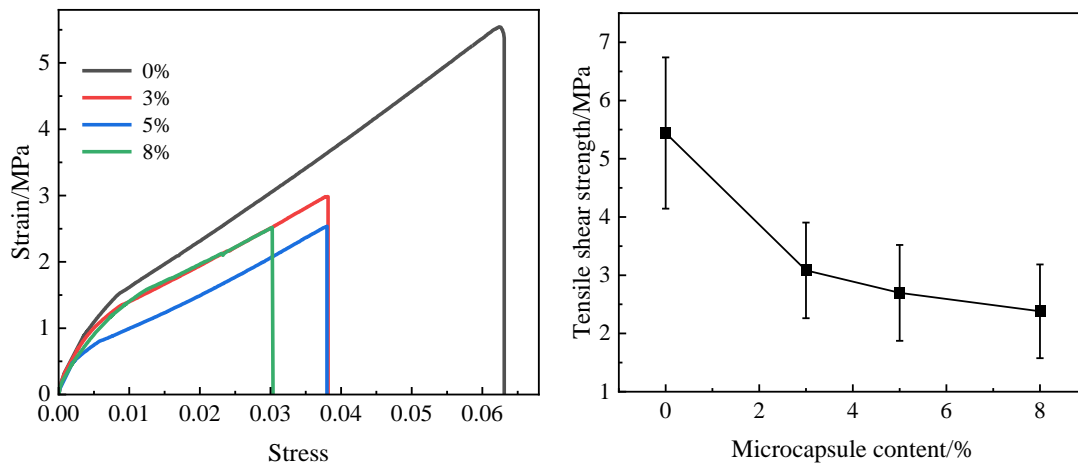


Fig 7. Tensile shear strength of self-healing epoxy coatings with different microcapsule contents: (a) stress-strain; (b) tensile shear strength.

3.6. Coating hardness analysis

As shown in Fig. 8, the hardness of the self-healing epoxy coating gradually decreases with the increase of microcapsule content. The hardness of the pure epoxy coating is 22.5 HV. When the microcapsule content was 3%, the hardness of the self-healing epoxy coating was 22.46 HV, which decreased by 0.18% compared with that of the pure epoxy coating. This is because the small content of microcapsules improves the local flexibility of the coating, but the microcapsules themselves have certain compressive strength, so they have little influence on the hardness of the coating. When the microcapsule content continued to increase to 8%, the hardness of the self-healing epoxy coating decreased to 21.48 HV, 4.53% lower than that of the pure epoxy coating. This is because with the increase of microcapsule content, agglomeration phenomenon will inevitably occur, resulting in defects inside the coating, and ultimately resulting in the reduction of coating hardness.

As shown in Fig. 9, under the same pressure and pressure time, with the increase of microcapsule content, coating damage is gradually serious. The pure epoxy coating has no obvious damage. When the microcapsule content was 3%, a small number of cracks appeared at the indentation edge of the coating. When the microcapsule content is 5%, a small amount of damage occurs on the surface of the coating. When the microcapsule content is 8%, the damage around the coating indentation is serious, and a large area of coating damage or even fall off. The experimental results show that adding a small amount of microcapsules to the self-healing epoxy coating can reduce the hardness of the self-healing coating, but the overall effect is not significant.

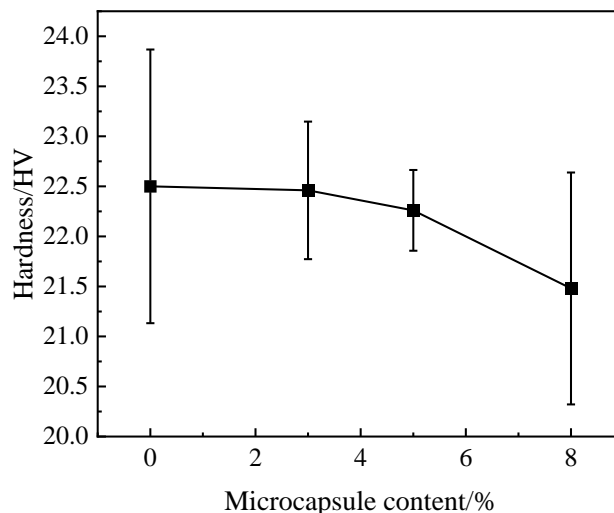


Fig 8. Hardness maps of self-healing epoxy coatings with different microcapsule contents

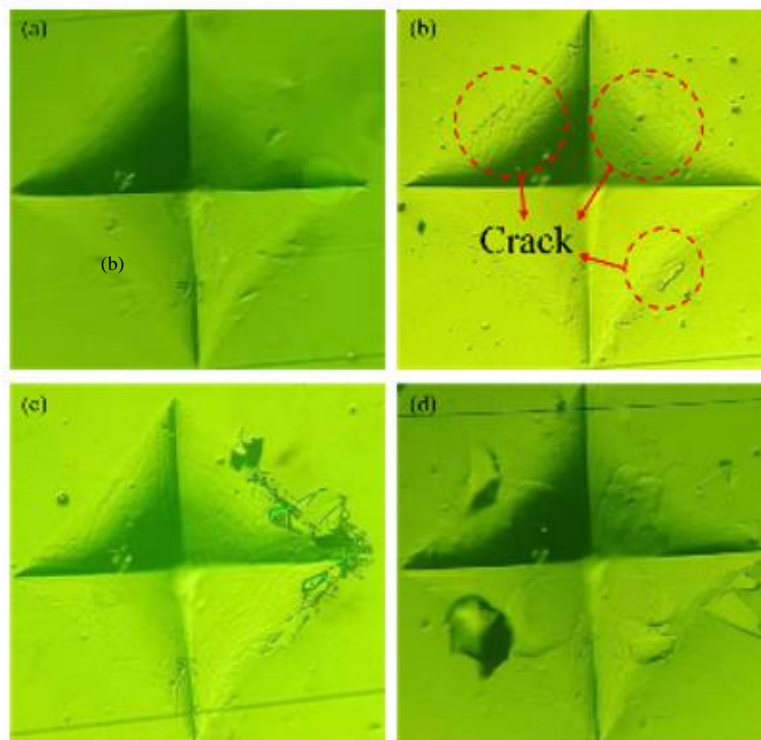


Fig 9. Surface topography of self-healing epoxy coatings with different microcapsule contents after hardness test: (a) 0%; (b) 3%; (c) 5%; (d) 8%.

4. Conclusion

(1) Using Pickering emulsion template method and interfacial polymerization method, using PVA as stabilizer, PUA as wall material and Tung oil as core material, the prepared microcapsules were structured and spherical with uniform size distribution.

(2) The results of scratch brine immersion experiment and EIS test show that the overall corrosion of self-healing epoxy coating with microcapsules is significantly better than that of pure epoxy coating.

(3) The mechanical properties test results show that with the increase of microcapsule content, the tensile strength and elongation at break of the composite material increase first and then decrease. The tensile shear strength of the self-healing epoxy coating decreases gradually, the adhesion decreases greatly, and the hardness weakens gradually. When the microcapsule content was 3%, the tensile strength increased to 84.71 MPa, which was 35.53% higher than that of pure epoxy resin. The hardness of self-healing epoxy coating is 22.46 HV, which is 0.18% lower than that of pure epoxy coating.

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